Role of Colloidal Polymer Associates for the Effectiveness of Hydroxyethyl Cellulose as a Fluid Loss Control Additive in Oil Well Cement

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ABSTRACT: The working mechanism of hydroxyethyl cellulose (HEC) as a fluid loss additive in oil well cement was investigated. The specific anionic charge amount, intrinsic viscosity, and associative behavior in a cement pore solution were determined. The fluid loss performance was probed through the static filtration of cement slurries. HEC achieves fluid loss control by reducing cement filtercake permeability. No influence on the filtercake microstructure was observed. ζ Potential measurements and a special filtration test indicated that no adsorption on cement occurred. Environmental scanning electron microscopy images revealed that in a wet environment, HEC swelled to a multiple of its size and possessed an enormous water-sorption capacity. Concentration-dependent measurements of the hydrodynamic diameter of HEC dissolved in a cement pore solution showed that large associates were formed. These colloidal associates physically obstructed the filtercake pores. Finally, the addition of sulfonated melamine formaldehyde dispersant to the cement slurries containing HEC greatly improved the fluid loss control. A specific interaction was responsible for this synergistic effect. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: hydroxyethyl cellulose; fluid loss additive; working mechanism; dispersant; oil well cement

INTRODUCTION

Oil well cementing is considered one of the most important operations performed in the construction of a well bore.[1,2] The placement of the cement slurry under pressure across a permeable formation, however, may lead to rapid dehydration and result in poor pumpability and incomplete cement hydration. To control the properties of oil well cement slurries, admixtures are included in the formulation.[3] Fluid loss additives (FLAs) are applied to reduce uncontrolled water loss from the slurry while it is pumped along porous formations in the bore hole.[4,5] Because of their environmental compatibility and good performance at temperatures up to 150°C, cellulose ethers are popular FLAs. Hydroxyethyl cellulose (HEC) is among the most widely used cellulosic fluid loss control agents, whereas carboxymethyl hydroxyethyl cellulose is less common.[6,7] Here, the working mechanism of HEC as an FLA in oil well cement was investigated.

According to previous studies by Desbrières,[8,9] three fundamental working mechanisms for polymeric FLAs are known: First, an increased dynamic viscosity (η_{dyn}) of the cement filtrate stemming from polymer addition can decelerate the filtration rate. Second, anionic FLAs may adsorb onto hydrating cement particles and obstruct the cement filtercake pores by polymer segments, which either freely protrude into the pore space or even bridge cement particles. Through this adsorptive mechanism, filtercake permeability is reduced, and a low fluid loss is achieved. Third, once a certain polymer dosage is exceeded, FLAs may plug cement filtercake pores through the formation of a polymer film or through associates, which can bind an enormous amount of water molecules in their inner sphere and hydrate shells. This way, a large portion of the mixing water is physically bound and will not be released during the filtration process.

In recent studies, we investigated the fluid loss behaviors of 2-acrylamido-2-methylpropanesulfonic acid-*co*-N,N-dimethylacrylamide (CaAMPS®-*co*-NNDMA)[10] and poly(vinyl alcohol).[11] We found that these FLAs worked either by adsorption onto the surface of the hydrating cement (CaAMPS®-*co*-NNDMA) or by physical plugging as a result of polymer film formation [poly(vinyl alcohol)]. Recent publications have discussed the influence of cellulose ethers on water transport in the porous structure of cement-based materials and investigated their effect on cement hydration.[12,13] However, the fundamental processes underlying the mechanism for water retention have yet not been investigated

TABLE I
Phase Composition (quantitative X-ray diffraction, Rietveld), Specific Density, Specific Surface Area (Blaine), and d_{50} Value of API Class G Oil Well Cement Sample

C_3S (wt %)	C_2S (wt %)	C_3A_c (wt %)	C_4AF (wt %)	CaO (wt %)	$CaSO_4 \cdot 2H_2O$ (wt %)	$CaSO_4 \cdot 0.5\ H_2O$ (wt %)	$CaSO_4$ (wt %)	Specific density (kg/L)	Specific surface area (cm^2/g)	d_{50} value (μm)
59.6	22.8	1.2	13.0	<0.3	2.7[a]	0.0[a]	0.7	3.18	3,058	11

C_3S, tricalcium silicate [$Ca_3(SiO_4)O$]; C_2S, dicalcium silicate (Ca_2SiO_4); C_3A_c, cubic modification of tricalcium aluminate ($Ca_9Al_6O_{18}$); C_4AF, tetra calcium aluminate ferrite ($Ca_4Al_2Fe_2O_{10}$).
[a] Measured by thermogravimetry.

thoroughly. For that reason, the filtercake permeability and dynamic filtrate viscosity of high-pressure (HP)/high-temperature (HT) filtrates from American Petroleum Institute (API) class G oil well cement slurries incorporating HEC were measured here. Furthermore, HEC adsorption on cement was probed via ζ potential and adsorption measurements. Finally, the concentration-dependent hydrodynamic diameters of the HEC particles present in the cement pore solution were determined.

In addition to FLAs, oil well cement slurries often contain dispersants. It has been shown before that different additives can interact with each other. This can lead to either severe incompatibility or a positive synergistic effect.[11,14] Surprisingly, it was found that sulfonated melamine formaldehyde (SMF) addition to cement slurries containing HEC greatly improved the fluid loss control. This effect was unexpected because when used individually, dispersants such as SMF typically increase fluid loss. To understand the mechanism of interaction between HEC and SMF, the η_{dyn} value of the cement filtrates and the ζ potential of the cement slurries containing both admixtures were measured. Moreover, the synergistic effect of the combination was investigated by quantification of the hydrodynamic diameters of the polymers present in the cement pore solution.

EXPERIMENTAL

Materials

Oil well cement

An API class G oil well cement (black label from Dyckerhoff AG, Wiesbaden, Germany) corresponding to API specification 10A was used.[15] Its clinker composition was determined through powder quantitative X-ray diffraction (QXRD) technique with Rietveld refinement. The amounts of gypsum ($CaSO_4 \cdot 2H_2O$) and hemihydrate ($CaSO_4 \cdot 0.5H_2O$) present in the cement sample were measured by thermogravimetry. Free lime (CaO) was quantified by the extraction method established by Franke.[16] Using a Blaine instrument, we determined the specific surface area to be 3,058 cm^2/g. The specific density of this sample was 3.18 kg/L, as

measured by helium pycnometry. The particle size distribution of the cement sample was determined by a laser-based particle size analyzer. Its average particle size distribution (d_{50}) value was 11 μm (see Table I).

HEC

A commercial sample of HEC (HEC-59, Cellosize®, Dow Chemical Co., Midland, MI) was used. The Brookfield viscosity of an aqueous solution containing 2 wt % of this FLA was 185 mPa·s, as measured at 27°C. The chemical structure of the HEC sample is presented in Figure 1. Its characteristic properties are shown in Table II. Size exclusion chromatography (SEC) analysis (HEC concentration = 0.2 wt % in $0.2M$ $NaNO_3$ at pH 9 adjusted with NaOH) produced molar masses for the FLA of about 2.1×10^5 g/mol [weight-average molecular weight (M_w)] and 1.2×10^5 g/mol [number-average molecular weight (M_n)]. With SEC analysis, a hydrodynamic radius [$R_{h(z)}$] of 20.5 nm and a gyration radius [$R_{g(z)}$] of 27.1 nm were found for this polymer. In an alkaline cement pore solution, HEC exhibited a specific anionic charge amount of −28 C/g, as measured by charge titration with poly(diallyl dimethylammonium chloride (polyDADMAC) as a cationic polymer.[17] This negative charge was due to partial deprotonation of the hydroxyl groups present in the anhydroglucose rings of HEC.

SMF polycondensate

A commercial sample of SMF (Melment® F10, BASF Construction Polymers GmbH, Trostberg, Germany) was used. The chemical structure of the SMF polycondensate is presented in Figure 1. SEC analysis (eluent = 0.1M $NaNO_3$ at pH 10 adjusted with NaOH) produced molecular weights for the FLA of about 2.0×10^5 g/mol (M_w) and 1.4×10^5 g/mol (M_n). $R_{h(z)}$ of this polymer was found to be 1.6 ± 0.08 nm. In a cement pore solution, SMF provided a specific anionic charge amount of −269 C/g.

Instruments

Cement characterization

The phase composition of the cement sample was obtained by X-ray powder diffraction with a Bruker

hydroxyethyl cellulose

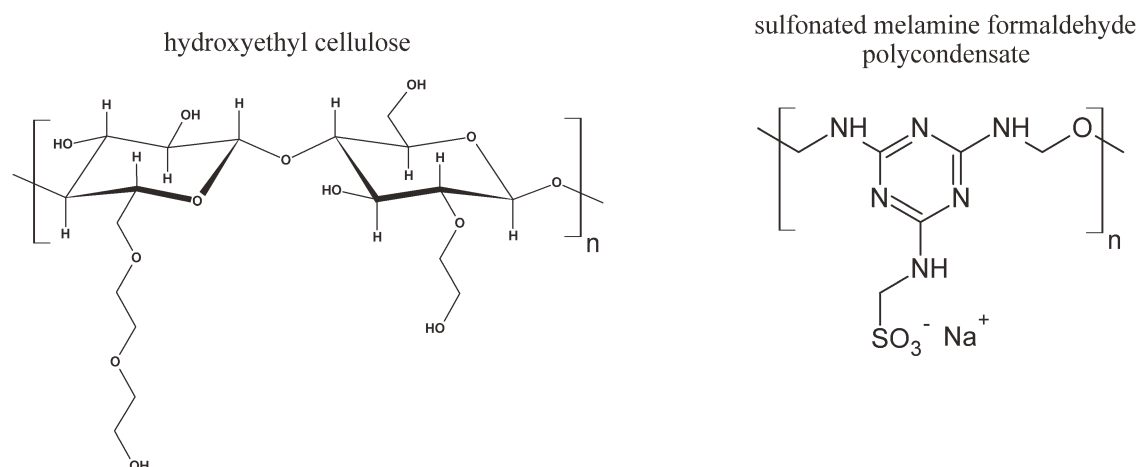sulfonated melamine formaldehyde polycondensate

Figure 1 Chemical structures of the HEC fluid loss polymer possessing a degree of substitution of 1.0 and a molar degree of substitution of 1.5 and the SMF polycondensate dispersant.

AXS D8 Advance instrument from Bruker (Karlsruhe, Germany) with Bragg–Bretano geometry. Topas 3.0 software from Bruker (Karlsruhe, Germany) was used to quantify the amounts of individual phases present in the sample according to Rietveld's method of refinement.[18] The instrument was equipped with a scintillation detector with Cu Kα radiation ($\lambda = 1.5406$ Å) with a scanning range between 2θ values of 5 and 80°. $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$ present in the cement sample were quantified by thermogravimetry with an STA 409 CD instrument (Netzsch Gerätebau GmbH, Selb, Germany). Measurement was conducted under a nitrogen atmosphere at a heating rate of 10°C/min. The specific density of the cement sample was measured on an Ultrapycnometer 1000 (Quantachrome Instruments, Boynton Beach, FL). The specific surface area of the sample was determined with a Blaine instrument (Toni Technik, Berlin, Germany). The d_{50} value was obtained from a laser-based particle size analyzer (1064 instrument from Cilas, Marseille, France).

Polymer characterization

The viscosity of the polymer solution was quantified with a Brookfield viscometer (model HAT from Brookfield Engineering Labs., Inc., Middleboro, MA) equipped with a #H2 spindle. The measurement was carried out at 50 rpm and at room temperature. By multiplying the dimensionless reading with the

correspondent factor, we obtained the viscosity in millipascal seconds.

The kinematic viscosities of the cement pore solutions containing HEC and the solutions containing HEC and SMF, respectively, were determined on an Ubbelohde viscometer with 501 10/I, 501 20/II, and 501 30/III capillaries supplied by Schott Instruments (Mainz, Germany). The kinematic viscosities of the cement slurry filtrates containing dosages between 0 and 1% (by weight of cement, bwoc) of HEC (incremental steps of 0.22% bwoc) and of aqueous HEC/SMF solutions were determined at 27°C with the Ubbelohde viscometer. The filtrate (15 mL) was filled into the reservoir of the viscometer, and the flow time (t) was measured. From this, the kinematic viscosity of the filtrate (υ) was calculated according to eq. (1):

$$\upsilon = K(t - \zeta) \tag{1}$$

where K is the viscometer constant (0.1004 mm^2/s^2) and ζ is the flow-time-dependent Hagenbach–Couette correction term, which was provided in the instrument instruction sheet. Multiplying the value for the kinematic viscosity with the specific density of the filtrate produced the value for η_{dyn}, as expressed by eq. (2):

$$\eta_{dyn} = \upsilon \cdot \rho \tag{2}$$

TABLE II
Characteristic Properties of the HEC Sample

Molar mass (g/mol)		Polydispersity index (M_w/M_n)	$R_{h(z)}$ (nm)	Specific anionic charge (C/g)[a]	Intrinsic viscosity at 27°C (L/g)[a]	Degree of substitution	Molar degree of substitution
M_w	M_n						
210,000	120,000	1.7	20.5	28	0.28	~ 1.0	~ 1.5

[a] In cement pore solution.

where ρ is the specific density of the filtrate at 27°C (0.9965 g/mL). From this, the reduced viscosity of the filtrate (η_{red}) was calculated according to eq. (3). η_0 is the dynamic viscosity of the cement filtrate containing the polymer, and c represents the respective concentration of HEC in the filtrate:

$$\eta_{\text{red}} = \frac{\eta_{\text{dyn}} - \eta_0}{\eta_0 \cdot c} \qquad (3)$$

An SEC instrument (Waters Alliance 2695, Waters, Eschborn, Germany) equipped with a refractive-index detector (Waters 2414) and an 18-angle dynamic light-scattering detector (Dawn EOS, Wyatt Technologies, Clinton, SC) was used. HEC was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). The molecular weights (M_w and M_n) and radii [$R_{h(z)}$ and $R_{g(z)}$] of the FLA were determined with a $0.2M$ aqueous $NaNO_3$ solution (adjusted to pH 9.0 with NaOH) as an eluent at a flow rate of 1.0 mL/min. The value of dn/dc (differential index of refraction) used to calculate M_w, and the M_n values for HEC were 0.159 mL/g (HEC)[19] and 0.135 mL/g [poly(ethylene oxide)][20] for SMF, respectively.

The specific anionic charge amounts of the polymers used in this study were determined in a cement pore solution at room temperature with a PCD 03 pH apparatus (BTG Mütek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature description with a $0.001N$ solution of laboratory-grade poly(diallyl dimethylammonium chloride) from BTG Mütek GmbH as a cationic polyelectrolyte.[17] The values presented in this study are the averages obtained from three different measurements. The standard deviation of this method was found to be ±5 C/g.

The d_{50} values of the associates were measured in a cement pore solution with a dynamic light-scattering particle size analyzer (LB-550, Horiba, Irvine, CA).

The surface tension was quantified on a drop shape analyzer (DSA 100, Krüss GmbH, Hamburg, Germany) with the pendant drop method. Before the measurement of the HEC solution, the surface tension of the deionized water was measured to calibrate the system. In accordance with the literature, this water exhibited a surface tension of 71.7 mN/m at 27°C.[21] The surface tension was recorded continuously as a function of the HEC concentration (from 1 to 20 g/L).

Cement slurry preparation

Cement slurries were prepared in accordance with the procedures set forth in the Recommended Practice for Testing Well Cements, API Recommended Practice 10B-2, issued by API.[22] The slurries were mixed at a water-to-cement (w/c) ratio of 0.44 with a blade-type laboratory blender manufactured by Waring Products, Inc. (Torrington, CT). The admixture dosages are stated in percentages by weight of cement (bwoc). Before cement addition, the powdered HEC was dry-blended with the cement. The homogenized mixture was added within 15 s to the water placed in a Waring blender cup and mixed for 35 s at 12,000 rpm. To ensure a homogeneous consistency, all slurries were stirred in an atmospheric consistometer (model 1250, Chandler Engineering, Tulsa, OK) for 20 min at 27°C. The pore solution of the cement slurry prepared without polymer addition was produced by vacuum filtration (12 mbar) with a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany).

Fluid loss test

The static fluid loss was measured at 27°C with a 500-mL HP/HT stainless steel filter press cell manufactured by OFI Testing Equipment, Inc. (Houston, TX). The design of this HP/HT filter cell and its operation were described in detail in a norm issued by API.[22] After pouring the homogenized slurry obtained from the atmospheric consistometer into the HT/HP cell, we used a heating jacket (OFI Testing Equipment) to adjust the test temperature. Then, a differential pressure of 70 bar of N_2 was applied at the top of the cell. Filtration proceeded through a 22.6-cm^2 (3.5-$in.^2$) mesh metal sieve placed at the bottom of the cell. The fluid volume collected within 30 min was doubled, as described by API RP 10B-2, and regarded as the API fluid loss of the corresponding slurry. The value reported for the respective API fluid loss test represents the average obtained from three separate measurements. The maximum deviation of the fluid loss value was ±10 mL/30 min.

Retention of HEC in the cement filtercake

The retained amount of the HEC FLA was determined from the filtrate collected in the respective fluid loss test. Generally, the depletion method was applied; that is, it was assumed that the decrease in the polymer concentration before and after contact with cement solely resulted from interaction with cement and not from insolubility of the polymer. This assumption was confirmed through a solubility test. For this purpose, 11.36 g/L HEC (this concentration correlated to a polymer dosage of 0.5% bwoc) was dissolved in a cement pore solution and stored for 1 day. No precipitation of HEC was observed. The retained amount was calculated from the difference in the equilibrium concentration of the polymer present in the liquid phase before and after contact

with cement (depletion method). A High total organic carbon (TOC) II apparatus (Elementar, Hanau, Germany) equipped with a CO_2 detector was used to quantify polymer retention. Before conducting the TOC analysis, we adjusted the alkaline cement filtrate containing the nonretained, dissolved HEC polymer to pH 1.0 by adding 0.1M HCl. Here, the maximum deviation of the measurement was found to be ±0.1 mg of polymer/g of cement.

ζ Potential measurement

The ζ potential values of the cement slurries were measured at room temperature on an electro-acoustic spectrometer (DT-1200, Dispersion Technology, Inc., Bedford Hills, NY).[17] Because the ζ potential was determined as a function of time (here, 30 min), the cement slurries were poured immediately after they were mixed into the cup of the spectrometer and measured without homogenization in the atmospheric consistometer. The accuracy of this method was ±1 mV.

Environmental scanning electron microscopy (ESEM) and mercury intrusion porosimetry

The surface of the cement filtercake was analyzed with an environmental scanning electron microscope (XL 30 ESEM FEG from FEI Co., Eindhoven, The Netherlands) at 1.0 mbar pressure in the sample chamber. The water sorption (swelling) of the HEC powder in a wet environment was investigated by exposure of the cellulose ether to relative humidities between 47.5 and 100%. These humidities corresponded to water vapor pressures of 3.5 and 7.1 mbar, respectively, in the ESEM chamber.

The hardened cement filtercake (curing time = 2 days) was analyzed by mercury intrusion porosimetry (Poremaster 60 from Quantachrome, Odelzhausen, Germany). A small piece of the cement filtercake (∼ 0.5 g) was exposed to HP mercury intrusion.

RESULTS AND DISCUSSION

Fluid loss performance of HEC

The filtrate volumes of the cement slurries containing increased dosages of HEC were measured at 27°C. As shown in Figure 2, higher concentrations of HEC produced lower API fluid loss values. For example, the API fluid loss decreased from 318 mL at 0.4% bwoc of HEC to 36 mL at 1.0% bwoc of HEC. The concentration of HEC needed to achieve an API fluid loss of below 100 mL/30 min at 27°C was found to lie at 0.7% bwoc. HEC dosages higher than 1.0% bwoc produced enormously viscous cement slurries and, thus, were not investigated.
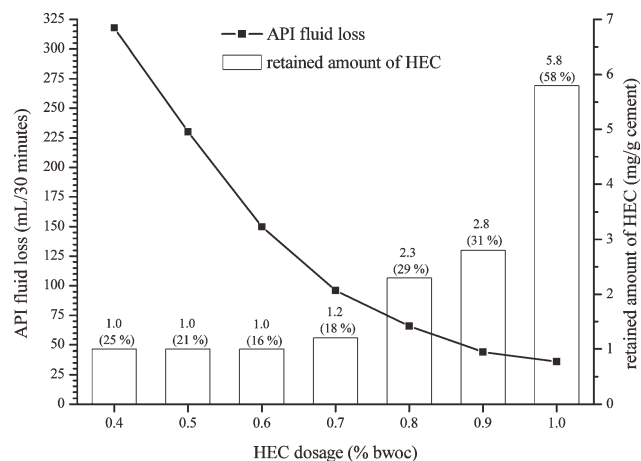

Figure 2 API fluid loss (line) of the API class G oil well cement slurries (w/c = 0.44) and retained amount of HEC (white bars) as a function of dosage.

Mechanistic study

To uncover the working mechanism of HEC and to understand its fluid loss performance, a series of experiments was devised. Following the procedure described by Desbrières,[8,9] we found that HEC significantly reduced the filtercake permeability (see Table III). A low filtercake permeability was always observed when an effective fluid loss control was achieved. For example, at 27°C, the filtercake permeability dropped from 1,711 μD for 0.4% bwoc of HEC to 36 μD at 1.0% bwoc of HEC. At the same time, the API fluid loss decreased from 318 mL/30 min to 24 mL/30 min.

Next, at different HEC dosages, the influence of the dynamic filtrate viscosity on the API fluid loss performance was probed (Table III). Up to a dosage of 0.7% bwoc of HEC, the dynamic filtrate viscosity increased, and a correlation, albeit a poor correlation, with the API fluid loss control was found. However, when this threshold concentration was exceeded, a decrease in the dynamic filtrate viscosity values was observed. Accordingly, between 0.7 and 1.0% bwoc of HEC, a drop in viscosity from 11 to 7.9 mPa·s was measured. Opposite to this trend in the viscosity development, the filtercake permeability decreased steadily with increasing HEC dosage (from 6,366 μD for the neat cement slurry to 36 μD for the cement slurry containing 1.0% bwoc of HEC). Thus, a direct relationship between the filtercake permeability and the cement fluid loss control became obvious. The results confirmed that the reduction in filtercake permeability and not the increased filtrate viscosity was the predominant reason for the low fluid loss achieved by HEC.

To determine the mechanism behind this reduction in filtercake permeability, the effects as follows were considered: (1) modification of the filtercake

TABLE III
API Fluid Loss, Reduced Filter Cake Volume, Dynamic Filtrate Viscosity, and Filter
Cake Permeability of the Cement Slurries as a Function of FLA Dosage

FLA dosage (% bwoc)	API fluid loss at 27°C (mL/30 min)	Filter cake permeability (K; μD)	Dynamic filtrate viscosity (η; mPa·s)	Reduced filter cake volume
0	1,270 (calculated)	6,366	1.0	2.0
0.4	318 (calculated)	1,711	4.8	2.7
0.5	230 (calculated)	1,566	6.9	2.6
0.6	150	1,016	9.8	2.4
0.7	96	587	11.9	2.7
0.8	60	207	10.5	2.8
0.9	44	80	8.9	2.4
1.0	34	36	7.9	2.0

structure, (2) adsorption of HEC on the cement particles, and (3) physical plugging and obstruction of the filtercake pores by retained polymer particles. First, fresh filtercakes of cement slurries without and holding 0.8% bwoc of HEC were comparable with ESEM imaging (Fig. 3). After the addition of HEC, no modification of the filtercake structure was observed. The packing and size of the hydrating cement particles and the pore sizes in the filtercake were comparable. Fresh filtercakes prepared from cement slurries without and holding 0.8% bwoc of HEC exhibited similar pore sizes of about 1 μm, as measured by mercury intrusion porosimetry.

Because HEC did not modify the microstructure of the filtercake with respect to the packing and size of hydrating cement particles, the constriction of filtercake pores through adsorption or physical plugging was studied next.

For this purpose, the amounts of HEC adsorbed on cement or otherwise retained were measured. If the working mechanism of HEC was based on physical adsorption, the retained amount should have increased with dosage until a plateau was reached. At this saturation point, the cement surface was covered with the maximum possible amount of polymer. This behavior was represented by a Langmuir adsorption isotherm. As shown in Figure 2, at dosages up to 0.7% bwoc, the depleted amount of HEC did not change much, whereas the API fluid loss values decreased significantly. However, starting at a dosage of 0.8% bwoc HEC, the retained amount increased significantly from 2.3 mg of polymer/g of cement (at 0.8% bwoc HEC) to 5.8 mg of polymer/g of cement (at 1.0% bwoc). The occurrence of polymer adsorption could be confirmed experimentally by the increased negative ζ potential values of the cement slurries when polymer was added to the cement slurry.[10] Thus, to clarify whether the adsorption of HEC took place, the ζ potentials of the cement pastes without and with increased dosages of HEC were measured. After the addition of HEC, no change in the charge of the cement particles was

observed (−6 mV for the neat cement slurry vs −5 mV for the cement slurry containing 0.8% bwoc of HEC). Thus, it was confirmed that no adsorption of HEC took place and that the adsorption played no role in its working mechanism.
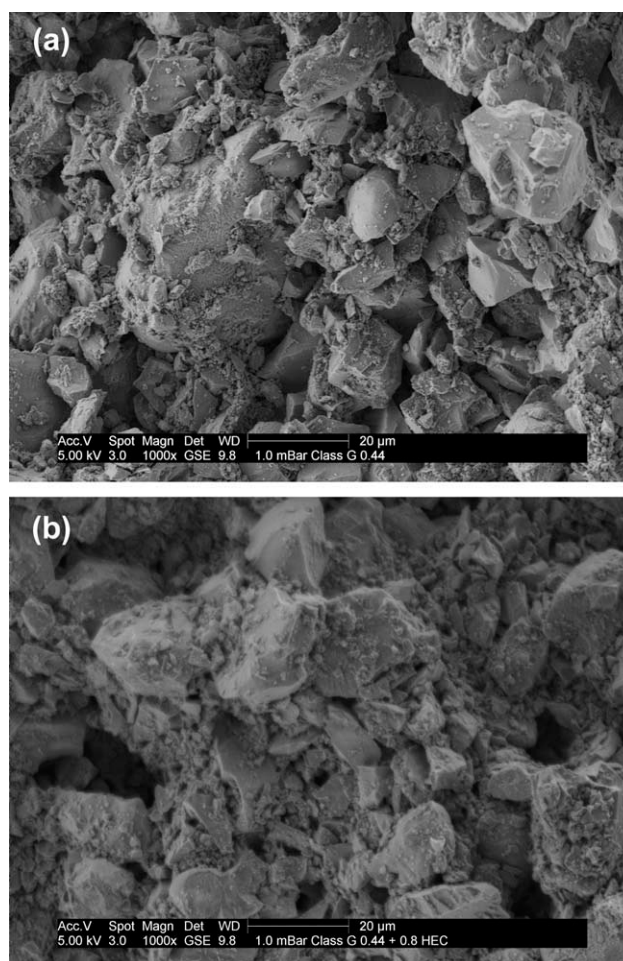

Figure 3 ESEM images of the microstructures of the cement filtercakes prepared without FLA (a) magnification, 1,000× and in the presence of 0.8% bwoc HEC (b) magnification, 1,000×
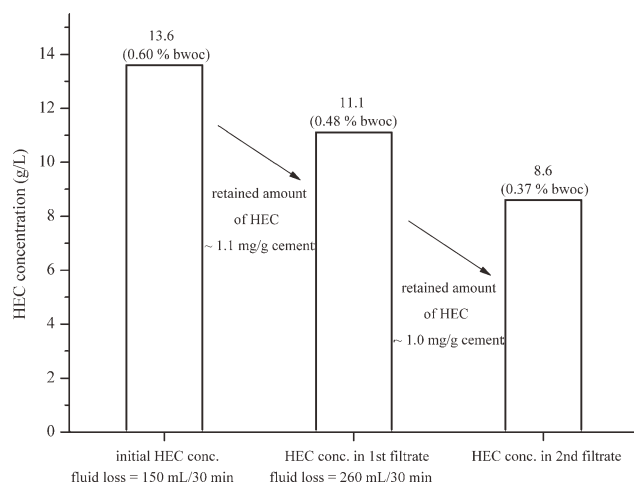
Figure 4 Initial HEC concentration present in the cement pore solution before static filtration and HEC concentrations present after two static filtration tests.

To probe further into the working mechanism, the following experiment was conducted: the filtrate obtained from an HT/HP filtration test was used for the preparation of the cement slurry, which was subjected to a subsequent second static filtration test. The results presented in Figure 4 clearly exclude an adsorptive working mechanism. There, the concentration of HEC in the filtrate as added (13.6 g/L, corresponding to 0.6% bwoc) decreased to 11.1 g/L (corresponding to 0.45% bwoc) after the first filtration test. This indicated that about 25% of the total HEC dosage added was retained. Repeating the static filtration test by using this filtrate containing about 0.45% bwoc of HEC as mixing water, we observed that the same amount (and not percentage) of HEC was lost during filtration (the HEC concentration dropped from 11.1 to 8.6 g/L in the second filtrate). Thus, it became obvious that in every filtration test, a certain constant amount of HEC ($\sim$ 2.5 g/L) was retained in the filtercake through a mechanism that was independent of adsorption.

Role of hydrocolloidal polymeric associates for HEC performance

Because the fluid loss control achieved by HEC was not caused by filtercake modification or adsorption on cement, a physical plugging effect was considered next for the working mechanism. Generally, HEC is a hydrocolloid that in a moist atmosphere sorbs significant amounts of water, as was revealed by ESEM imaging (Fig. 5). At relative humidities ranging from 47.5 to 100%, the polymer increased its volume considerably as a result of the uptake of water. Massive swelling of the polymer to a multiple of its particle size was observed. When the humidity was reduced back to 47.5%, the polymer did not

release much of the water sorbed. Thus, a strong binding capacity of water by HEC was confirmed. The existence of large hydrated hydrocolloidal particles also became evident from dynamic light-scattering measurements performed in the cement pore solution at 27°C. At 1 g/L of HEC dissolved in the cement pore solution, a d_{50} value of 5.2 nm for the HEC particles was found, with no particles less than 3 nm or greater than 8 nm being present. The particle size remained constant up to a concentration of 3.5 g/L HEC. There, sharply increased particle sizes ($\sim$ 100 nm) were measured; this indicated that from this concentration onward, the association of the HEC molecules occurred. Unfortunately, higher HEC concentrations could not be measured because of the rapid increase of viscosity of the solution containing greater than 4 g/L HEC.

Another important observation was the exponential increase in the viscosity of cement pore solutions containing HEC at concentrations above 15 g/L (this corresponded to 0.66% bwoc HEC). At concentrations below 15 g/L, the viscosities of the solutions were nearly constant (Fig. 6). The exponential
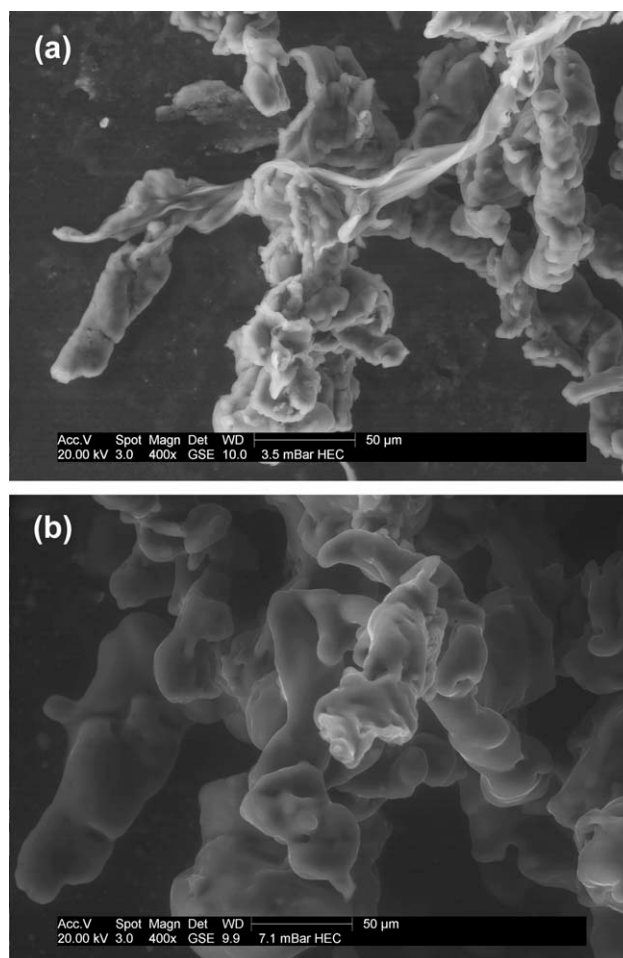

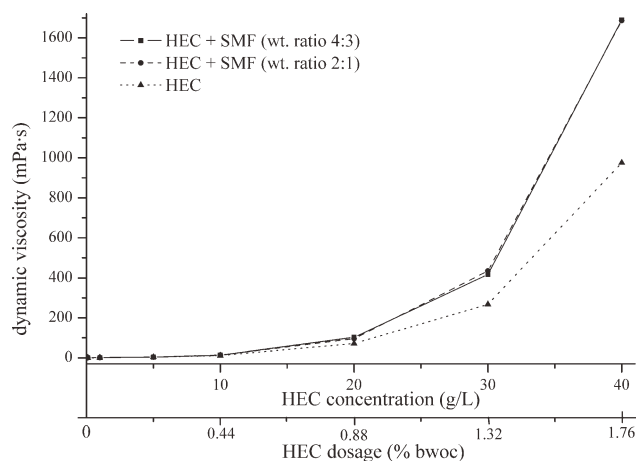**Figure 5** ESEM images of HEC at relative humidities of 47.5% (a) and 100% (b).

Figure 6 η_{dyn} values of the cement pore solutions containing individual HEC and HEC/SMF combinations.

increase in viscosity that occurred when this threshold concentration of 15 g/L HEC was transgressed indicated that above this concentration, HEC might have formed associated polymer networks, as has been described for hydrocolloids in general.[23] A schematic illustration of the concentration-dependent HEC polymer association is shown in Figure 7. According to the viscosity measurements, at low dosages of hydrocolloid (here, <15 g/L HEC), no interaction took place between individual hydrated polymer molecules, which remained separated. However, beginning at about 15 g/L HEC, individual polymer particles entangled and associated to form larger hydrocolloids with defined hydrodynamic diameters. The specific concentration at which such association commences is generally called the *overlapping concentration*. Here, it was about 15 g/L HEC. At further increased HEC dosages, the polymer associates formed a dense network. As a result, increasing amounts of water were retained, and consequently, the cement fluid loss was improved further.

To evidence the association of HEC further, surface tension measurements were conducted at 27°C

for cement pore solutions holding different concentrations of HEC. Normally, cellulose ethers exhibit surface activity, depending on their anionic charge amount. The higher the anionic charge is, the lower the surface activity will be. Thus, the occurrence of association will clearly result in an altered surface tension. As is shown in Figure 8, upon HEC addition, the surface tension rapidly decreased to about 65 mN/m and remained constant at HEC dosages of up to 10 g/L. Beyond this concentration, however, the surface tension decreased further to about 61 mN/m. This effect could be ascribed to the beginning association of HEC molecules. Thus, the results indicate that the working mechanism of HEC was based on the obstruction of filtercake pores by large hydrocolloidal polymeric associates, which formed a three-dimensional network.

Synergistic interaction between HEC and SMF

The second part of this study dealt with the interaction between HEC and the SMF dispersant. When 0.4% bwoc of HEC was used in combination with increasing amounts (0–0.4% bwoc) of SMF, at up to 0.2% bwoc of SMF, no effect on the cement fluid loss was observed (Fig. 9). However, at further increased SMF dosages, a synergistic effect between HEC and SMF occurred. The improvement generally began at a specific ratio between the two polymers of 2 : 1 (w/w) and reached its maximum when the HEC/SMF ratio attained a value of 1.3 or lower. For example, in a combined system containing 0.4% bwoc of HEC and 0.4% bwoc of SMF, the API fluid loss decreased from 318 mL/30 min (at 0.4% bwoc of individual HEC) to 36 mL/30 min for the combination. To understand the reason behind this effect, first, η_{dyn} of the cement pore solution containing both polymers was investigated (Fig. 6). It revealed that in the presence of SMF, the increase in the viscosity of the HEC solution was much more pronounced than in the absence of SMF.
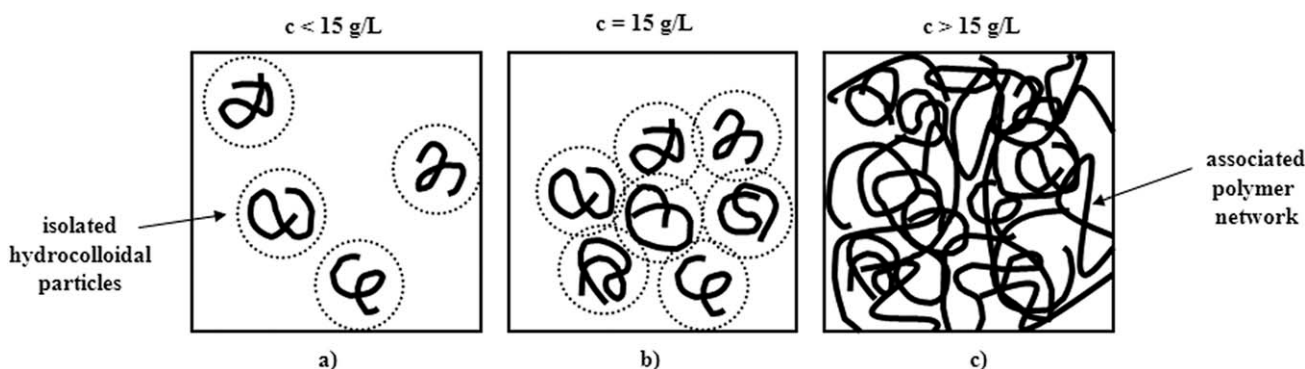

Figure 7 Schematic illustration of the formation of associated polymer networks by HEC in solution: (a) below, (b) at, and (c) above the overlapping concentration (after de Gennes[23]).
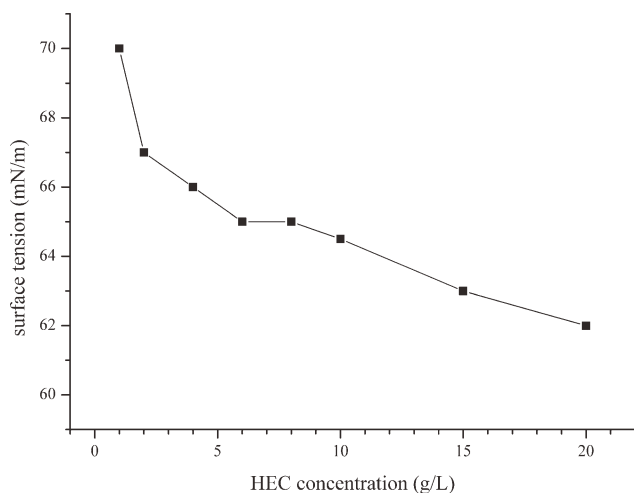
Figure 8 Surface tension of the cement pore solutions and its dependence on HEC concentration at 27°C.

Obviously, SMF instigates the formation of large polymer networks from HEC to occur at lower HEC dosages. Furthermore, a comparison of the ζ potentials of the cement slurries containing 0.3% bwoc of individual SMF (-27 mV) with that of a cement slurry containing 0.3% bwoc of SMF and 0.4% bwoc of HEC (-18 mV) showed that both molecules interacted. Obviously, the anionic charge amount of SMF was partially shielded. Because competitive adsorption between the two polymers was excluded, on the basis of HEC's low anionic charge amount, apparently, an intermolecular interaction between HEC and SMF took place. Finally, dynamic light-scattering measurements with cement pore solution confirmed that in the presence of SMF, the increased formation of large associated polymer particles incorporating both HEC and SMF occurred. Already, at a dosage of 0.1 wt % of HEC and SMF each (HEC/SMF weight ratio $= 1$), an average particle size (R_h) of 80 nm was found. This was significantly higher than that for individual HEC. In the cement pore solution, an R_h of about 5 nm was found for HEC. Hence, it became obvious that SMF significantly reduced the threshold dosage at which HEC formed associated networks. Moreover, a threshold amount of SMF had to be exceeded to produce the strong synergistic effect with HEC with regard to fluid loss control.

CONCLUSIONS

The working mechanism of HEC as a cement FLA relied on a dual effect, which stemmed from its enormous water-binding capacity and a concentration-dependent formation of hydrocolloidal associated polymer networks. At concentrations below 15 g/L of HEC (this corresponded to 0.66% bwoc), fluid loss control was mainly achieved through the water-binding capacity of hydrocolloidal HEC. Above 15 g/L HEC, this working mechanism was supplemented by the formation of highly associated polymer networks.

From a previous work, it was already known that nonionic cellulose ethers work by reducing the filtercake permeability of oil well cement.[9] Here, we investigated the reason behind this effect. First, a direct correlation between the HP/HT filtrate viscosity and the API fluid loss could not be established. Second, ESEM images revealed that HEC did not change the filtercake structure. Additionally, adsorption was excluded by ζ potential measurement and consecutive static filtration tests. The only potential mechanism left was physical plugging of the filtercake pores. It was found that at low HEC concentrations, the obstruction of filtercake pores was due to water sorption and swelling of the HEC molecules, whereas at higher concentrations, the formation of large hydrocolloidal particles consisting of associated HEC molecules further contributed to reduced cement fluid loss.

Additionally, it was found that HEC and SMF could act synergistically with respect to fluid loss control. The effect occurred only at specific HEC/SMF ratios. Dynamic light-scattering measurements revealed that in the presence of SMF, the association of HEC molecules was greatly enhanced. Those larger hydrocolloidal polymer associates plugged the filtercake pores more effectively.

Further studies are underway to determine HEC compatibility with other common oil well cement additives. The goal was to obtain a fundamental understanding of the parameters impacting admixture compatibility and to establish guidelines for the avoidance of undesired interactions. This should allow a more economical use of those expensive admixtures and result in safer applications.
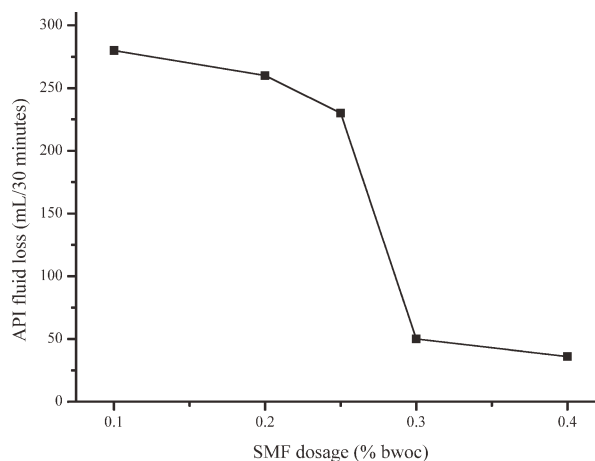

Figure 9 API fluid loss of API class G oil well cement slurries (w/c $= 0.44$) containing 0.4% bwoc HEC as a function of increasing SMF dosage (0.1–0.4% bwoc).

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