Mechanistic Study on Carboxymethyl Hydroxyethyl Cellulose as Fluid Loss Control Additive in Oil Well Cement

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ABSTRACT: The working mechanism of carboxymethyl hydroxyethyl cellulose (CMHEC, M_w 2.6 × 10^5 g/mol) as fluid loss control additive (FLA) for oil well cement was investigated. First, characteristic properties of CMHEC such as anionic charge amount, intrinsic viscosity in cement pore solution, and static filtration properties of cement slurries containing CMHEC were determined at 27°C and 70 bar. Effectiveness of the FLA was found to rely on reduction of cement filter cake permeability. Consequently, the working mechanism is ascribed to constriction of cement filter cake pores. Zeta potential measurements confirm that at low CMHEC dosages (0–0.3% by weight of cement, bwoc), adsorption of the polymer onto the surface of hydrating cement occurs. However, at dosages of 0.4% bwoc and higher, an associated polymer network is formed. This was evidenced by a strong increase in hydrodynamic diameter of solved CMHEC molecules, an exponential increase in viscosity and a noticeable reduction of surface tension.

Thus, the working mechanism of CMHEC changes with dosage. At low dosages, adsorption presents the predominant mode of action, whereas above a threshold concentration of ∼ 10 g/L (the "overlapping concentration"), formation of associated polymer networks is responsible for effectiveness of CMHEC. Addition of anionic polyelectrolytes (e.g., sulfonated melamine formaldehyde polycondensate, M_w 2.0 × 10^5 g/mol) to cement slurries containing CMHEC greatly improves fluid loss control. Apparently, the presence of such polyelectrolytes causes the formation of colloidal associates from CMHEC to occur at lower dosages. Through this mechanism, effectiveness of CMHEC as cement fluid loss additive is enhanced. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2340–2347, 2012

Key words: carboxymethyl hydroxyethyl cellulose; fluid loss additive; hydrocolloid; polymer associates; oil well cement

INTRODUCTION

Oil well cementing is often considered as one of the most important operations performed in the construction of a well bore. Placement of the cement slurry under pressure across a permeable formation, however, may lead to rapid dehydration, resulting in poor pumpability and incomplete cement hydration.[1,2] To control the properties of oil well cement slurries, additives are included into the formulation.[3] 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.[4,5] Because of their environmental compatibility, cellulose ethers are popular FLAs. In the late 1950s, carboxymethyl hydroxyethyl cellulose (CMHEC) was introduced for fluid loss control first in water-based drilling fluids and later also in oil well cement slurries.[6] In spite of this long history of

successful application, the working mechanism of CMHEC as cement fluid loss polymer has never been investigated before.

According to Desbrières,[7,8] three fundamental working mechanisms for polymeric FLAs are known. First, increased dynamic viscosity of the cement filtrate can decelerate the rate of filtration. Second, anionic FLAs may adsorb onto hydrating cement particles and obstruct filter cake pores either by polymer segments which freely protrude into the pore space or even bridge adjacent cement particles. Through this adsorptive mechanism, filter cake permeability is reduced and low fluid loss can be achieved. And third, some FLAs may plug the pores of the cement filter cake either through formation of polymer films, of polyelectrolyte complexes or through polymer associates, which can bind an enormous amount of water molecules in their inner sphere and hydrate shells. In the latter case, performance of the fluid loss polymer is further enhanced because a significant portion of the mixing water is physically bound and will not be released during the filtration process.

In recent studies, we have investigated the fluid loss behavior of poly(Ca 2-acrylamido-2-methylpropane-sulfonate-*co*-N,N-dimethylacryamide) (CaAMPS®-*co*-

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TABLE I
Phase Composition (QXRD, 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 %)	Free 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 Blaine (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	3058	11 ± 1.1

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.

NNDMA),[9] polyvinyl alcohol (PVA),[10] polyethylene imine (PEI),[11] and hydroxyethyl cellulose (HEC).[12] We found that these FLAs work either by adsorption onto the surface of hydrating cement (CaAMPS®-co-NNDMA) or through a plugging mechanism instigated by the formation of a polymer film (PVA), of polyelectrolyte complexes (PEI in combination with anionic dispersants), and of associated polymer networks (HEC), respectively.

Here, it was attempted to establish the working mechanism of CMHEC. For CMHEC which is an anionic, high molecular weight hydrocolloid, adsorption on cement, high filtrate viscosity, and/or polymer association appear to be likely candidates for the mechanism. To probe, cement filter cake permeability and dynamic viscosity of filtrates collected from static filtration tests of cement slurries containing CMHEC were determined. Furthermore, adsorption of CMHEC on cement was probed via measurement of zeta potential and dissolved total organic carbon content of cement filtrates. Finally, the concentration-dependant hydrodynamic diameter of dissolved CMHEC molecules in cement pore solution and the surface tension of aqueous CMHEC solutions were investigated. From this data, a model for the working mechanism of CMHEC cement FLA was developed.

EXPERIMENTAL

Materials

Oil well cement

An API Class G oil well cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) corresponding to American Petroleum Institute (API) Specification 10A was used.[13] Its clinker composition was determined through powder QXRD technique using Rietveld refinement. The amounts of gypsum ($CaSO_4 \cdot 2$ H_2O) and hemi-hydrate ($CaSO_4 \cdot 0.5$ H_2O) present in the cement sample were measured by thermogravimetry. Free lime (CaO) was quantified following the extraction method established by Franke.[14] Using a Blaine instrument, the specific surface area was found at 3058 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 using a laser-based particle size analyzer. Its d_{50} value was 11 µm (see Table I).

Carboxymethyl hydroxyethyl cellulose

A commercial sample of CMHEC (®Tylose HC 50 NP2, a white powder supplied by SE Tylose GmbH and Co. KG, Wiesbaden, Germany) exhibiting a degree of substitution (DS carboxymethyl) of 0.43 and a molar degree of substitution (MS hydroxyethyl) of 1.01 was used (DS and MS terminology and values are supplier information); according to this, DS carboxymethyl represents the average number of carboxyl groups substituting hydroxyl groups per anhydro glucose unit, whereas MS hydroxyethyl expresses the average number of hydroxyethyl groups per anhydro glucose ring. The statistical chemical structure of the CMHEC sample is presented in Figure 1. GPC analysis (CMHEC concentration: 0.2 wt % in 0.2M NaNO$_3$ at pH of 9 adjusted with 50 wt % NaOH) produced molar masses for the FLA of 2.6×10^5 g/mol (M_w, ± 0.6%) and of 1.5×10^5 g/mol (M_n, ± 0.5%), respectively. Additional characteristic properties of the CMHEC sample are shown in Table II. In alkaline cement pore solution, CMHEC exhibited a specific anionic charge amount of −236 C/g, as measured by charge
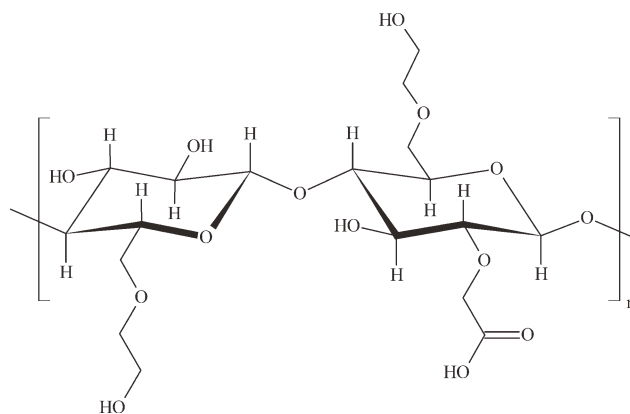

Figure 1 Chemical structure of carboxymethyl hydroxyethyl cellulose exhibiting a DS (carboxymethyl) of 0.5 and an MS (hydroxyethyl) of 1.0.

Polymer	Molar masses (g/mol)		Polydispersity index (M_w/M_n)	Hydrodynamic radius $R_{h(z)}$ (nm)	Specific anionic charge amount ε (C/g)[a]	Intrinsic viscosity η at 27°C (L/g)
	M_w	M_n				
CMHEC	260,000	150,000	1.8	4.6 ± 0.14	236 ± 18	0.24 ± 0.065
SMF	200,000	140,000	1.5	1.6 ± 0.08	269 ± 10	–

[a] Measured in cement pore solution.

titration using polyDADMAC as a cationic polymer.[15] The negative charge is primarily owed to deprotonation of the carboxymethyl groups. It is comparable to that of other common oil well cement additives such as lignosulfonate retarder (-210 C/g) but lower than CaAMPS®-co-NNDMA fluid loss polymer (-370 C/g) or NaAMPS®-co-itaconic acid retarder (-528 C/g).

Sulfonated melamine formaldehyde polycondensate

A commercial sample of sulfonated melamine formaldehyde (SMF) resin (Melment® F10, BASF Construction Polymers GmbH, Trostberg, Germany) was used. Its chemical structure is shown in Figure 2. This product is manufactured from melamine, formaldehyde, and sodium pyrosulfite at molar ratios of 1 : 3 : 0.5 through a polycondensation reaction carried out at pH 5–6. The resulting 40% liquid is spray-dried to yield a white powder. GPC analysis (eluent: 0.1M NaNO$_3$ at pH 10 adjusted with 50 wt % NaOH) produced molecular weights for SMF of 2.0×10^5 g/mol (M_w, ± 1.0%) and 1.4×10^5 g/mol (M_n, ± 1.2%), respectively. Further characteristic properties of the polymer are shown in Table II.

Instruments and procedures

Cement characterization

Phase composition of the cement sample was obtained by X-ray powder diffraction using a Bruker axs D8 Advance instrument from Bruker, Karlsruhe, Germany with Bragg-Bretano geometry. Topas 3.0 software was used to quantify the amounts of individual phases present in the sample by following Rietveld's method of refinement.[16] The instrument was equipped with a scintillation detector using Cu K$_\alpha$ (λ = 1.5406 E) radiation with a scanning range between 5° and 80° 2θ. Specific density of the cement sample was measured on an Ultrapycnometer® 1000 (Quantachrome Instruments, Boynton Beach, FL/USA). The specific surface area of the sample was determined using a Blaine instrument (Toni Technik, Berlin, Germany). The average particle size (d_{50} value) was obtained from a laser-based particle size analyzer (Cilas 1064 instrument, Marseille, France).

Polymer characterization

Size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn, Germany) equipped with RI detector 2414 (Waters, Eschborn, Germany) and an 18 angle dynamic light scattering detector (Dawn EOS from Wyatt Technologies, Santa Barbara, CA/USA) was used. Before application on the columns, the solution was filtered through a 5 μm filter. CMHEC was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). Molecular weights (M_w and M_n) and hydrodynamic radius ($R_{h(z)}$) of the FLA were determined using a 0.2M aqueous NaNO$_3$ solution (adjusted to pH 9.0 with NaOH) as an eluant at a flow rate of 1.0 mL/min. The value of dn/dc used to calculate M_w and M_n for CMHEC was 0.159 mL/g (value for hydroxyethyl cellulose)[17] and 0.135 mL/g (value for polyethylene oxide)[18] for SMF, respectively.

Kinematic viscosities of cement pore solutions containing CMHEC were measured at 27°C, 50°C, and 80°C on an Ubbelohde viscometer using 501 10/I, 501 20/II, and 501 30/III capillaries supplied by Schott Instruments, Mainz, Germany. The kinematic viscosities of cement slurry filtrates containing dosages between 0 and 0.5% by weight of cement (bwoc) of CMHEC (incremental steps of 0.1% bwoc) were determined at 27°C using the Ubbelohde viscometer. A total of 15 mL of solution were filled into the reservoir of the viscometer and the flow time
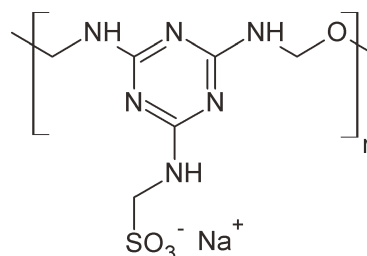

Figure 2 Chemical structure of sulfonated melamine formaldehyde (SMF) polycondensate sample used in the study.

was measured. From this, the kinematic viscosity of the solution was calculated according to eq. (1).

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

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

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

The specific anionic charge amounts of the polymers used in this study were determined in cement pore solution at room temperature using a PCD 03 pH apparatus (BTG Mütek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature description using a $0.001N$ solution of laboratory grade poly(diallyl dimethylammonium chloride) from BTG Mütek GmbH, Herrsching, Germany as cationic polyelectrolyte.[15] The values presented in this study are the average obtained from three different measurements.

Hydrodynamic particle size (d_{50} value) of the associates was measured in cement pore solution using a dynamic light scattering particle size analyzer (LB-550 from Horiba, Irvine, CA/USA). This property of CMHEC was determined by dissolving, e.g., 1 g of the polymer in 1 L cement pore solution. The CMHEC solution was then filtered through 1.2 μm filter to eliminate undesired dust particles. For our instrumentation, a viscosity below 3 mPa.s was required.

Surface tension at room temperature was quantified on a Processor Tensiometer K100 (Krüss GmbH, Hamburg, Germany) applying the Wilhelmy plate method using a platinum plate. Before the measurement of the CMHEC solutions, the surface tension of deionized water was measured. In accordance with literature, this water exhibited a surface tension of 71.7 mN/m at 27°C. Surface tension was recorded continuously as a function of concentration (10 steps from 20 to 1 g/L, with decreasing intervals from 5 to 0.3 g/L). Further concentrations were determined on a Drop Shape Analyzer DSA 100 (Krüss GmbH, Hamburg, Germany) using the pendant drop method.

Cement slurry preparation

Cement slurries were prepared in accordance with the procedures set forth in Recommended Practice for Testing Well Cements, API Recommended Practice 10B-2, issued by the American Petroleum Institute.[19] The slurries were mixed at a water-to-cement (w/c) ratio of 0.44 using a blade-type laboratory blender manufactured by Waring Products Inc. (Torrington, CT/USA). Admixture dosages are stated in % by weight of cement (bwoc). Before cement addition, the powdered CMHEC was dry blended with the cement. The homogenized mixture was added within 15 s to the deionized water placed in a Waring blender cup and mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, all slurries were stirred in an atmospheric consistometer (model 1250 from Chandler Engineering, Tulsa, OK/USA) for 20 min at 27°C. The pore solution of the cement slurry prepared without polymer addition was produced by vacuum filtration (12 mbar) using a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany).

Fluid loss test

Static fluid loss was measured at 27°C using a 500 mL high pressure, high temperature (HP/HT) stainless steel filter press cell manufactured by OFI Testing Equipment Inc. (Houston, Texas/USA). Design of this HP/HT filter cell and its operation are described in detail in a norm issued by the American Petroleum Institute (API).[19] After pouring the homogenized slurry obtained from the atmospheric consistometer into the HT/HP cell, a heating jacket (OFI Testing Equipment Inc., Houston, Texas/USA) was used to adjust the test temperature. Then, a differential pressure of 70 bar 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 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.

Adsorption/retention of CMHEC in cement filter cake

Adsorbed/retained amount of the CMHEC FLA was determined from the filtrate collected in the respective fluid loss test. Generally, the depletion method was applied, i.e., it was assumed that the decrease in the polymer concentration before and after contact with cement solely resulted from interaction with cement or pore plugging, and not from insolubility of the polymer. This assumption was confirmed through a solubility test. For this purpose, 20 g/L of CMHEC (this concentration correlates to a polymer dosage of 0.88% bwoc) was dissolved in cement pore solution and stored for one day. No precipitation of CMHEC was observed. The retained amount was calculated from the difference in the equilibrium concentration of the polymer present in the
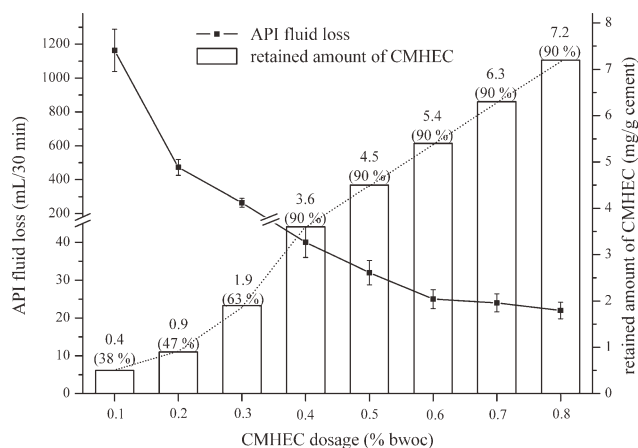
Figure 3 API fluid loss and retained amount of CMHEC as a function of polymer dosage.

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

Zeta potential measurement

Zeta potential of cement slurries was measured at room temperature on an electro acoustic spectrometer (DT-1200 from Dispersion Technology Inc., Bedford Hills, NY/USA).[15] As zeta potential was determined as a function of time (here 30 min), cement slurries were poured immediately after mixing into the cup of the spectrometer and measured without homogenization in the atmospheric consistometer. The accuracy of this method is $\sim \pm 1$ mV.

RESULTS AND DISCUSSION

Fluid loss performance of CMHEC

Filtrate volumes of cement slurries containing increased dosages of CMHEC were measured at 27°C. As is shown in Figure 3, higher amounts of CMHEC produce lower API fluid loss. For example, API fluid loss decreases from 1163 mL at 0.1% bwoc of CMHEC to 32 mL at a dosage of 0.5% bwoc. At 27°C, the minimum CMHEC concentration needed to achieve an API fluid loss below 100 mL/30 min was $\sim 0.4\%$ bwoc. This API fluid loss value is generally considered to provide adequate filtration control for successful placement of the cement slurry behind the casing. Small increases of CMHEC dosage result in an enormous improvement of fluid loss control. Compared to HEC,[12] which is another cellulose ether

commonly applied for fluid loss control in oil well cement, CMHEC requires lower dosage for comparable fluid loss control.

Dynamic viscosity of CMHEC in cement pore solution

Most cellulose ethers exhibit high viscosity in aqueous and cement pore solution, respectively. The results obtained at 27°C, 50°C, and 80°C for the dynamic viscosity of CMHEC in cement pore solution are presented in Figure 4. At 27°C and for CMHEC concentrations below 10 g/L (this corresponds to a dosage of 0.44% bwoc), only a minor and almost linear increase in viscosity appears. Above this concentration, an exponential increase of viscosity was found. This effect has been described before for other hydrocolloids, and the threshold concentration, which presents the on-set point for the steep viscosity increase, is generally designated as "overlapping concentration."[20] Beyond this concentration, the molecules of the hydrocolloid can entangle with each other and thus form a 3D network which is responsible for the drastic increase in viscosity. For the CMHEC sample tested here, the "overlapping concentration" was found to lie between 10 to 15 g/L. At temperatures of 50°C and 80°C, respectively, the on-set of the exponential viscosity increase (and thus the "overlapping concentration") shifts to higher concentrations. This effect explains the decreased fluid loss control performance of CMHEC at higher temperatures.

Mechanistic study

To probe into the working mechanism of CMHEC, a series of experiments were devised. First, following the procedure of Desbrières, it was found that
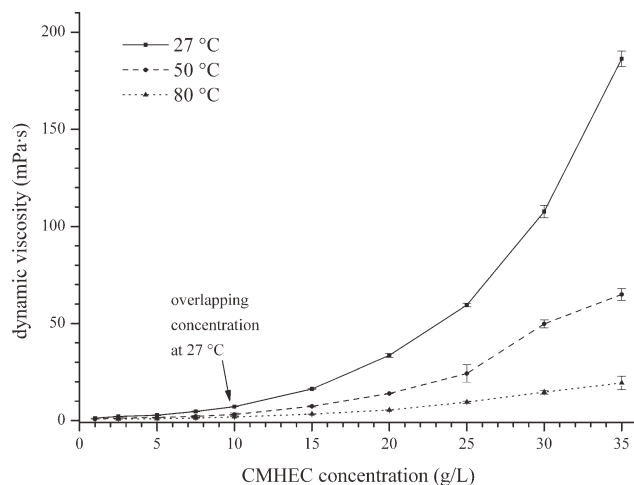

Figure 4 Dynamic viscosity of cement pore solutions containing CMHEC as a function of polymer concentration and temperature.

CMHEC dosage (% bwoc)	API fluid loss at 27°C (mL/30 min)	Filter cake permeability K (μD)	Dynamic filtrate viscosity η (mPa.s)
0	1270 (calculated)[a]	6366	1.0
0.1	1163 (calculated)[a]	2645	1.0
0.2	473 (calculated)[a]	1556	1.1
0.3	264	824	1.4
0.4	40	33	0.9
0.5	32	18	0.8

[a] Dehydration of slurry occurred in less than 30 min.

CMHEC strongly reduces filter cake permeability (see Table III).[8] Low filter cake permeability was always observed when effective fluid loss control was achieved. For example, filter cake permeability dropped from 2645 μD (at 0.1% bwoc of CMHEC) to 33 μD (at 0.4% bwoc dosage). At the same time, the API fluid loss decreased from 1163 mL/30 min to 40 mL/30 min.

Next, the influence of dynamic filtrate viscosity on API fluid loss performance at different CMHEC dosages was studied (Table III). There, no correlation with API fluid loss control was found. At first, a slight increase in dynamic filtrate viscosity (from 1 to 1.4 mPa.s) up to a dosage of 0.3% bwoc was observed, but at higher CMHEC concentrations, this effect was reversed. This result indicates that the filtrate viscosity virtually has no influence on the fluid loss performance of CMHEC. Contrary to this, filter cake permeability was reduced dramatically by increased dosages. Accordingly, the results instigate that the reduction in filter cake permeability is the predominant reason for low fluid loss achieved by CMHEC.

To clarify the reason behind this reduction in filter cake permeability, the points as follows were considered and probed: (a) modification of the filter cake microstructure, (b) adsorption of CMHEC on cement particles, and (c) physical plugging of the pores. Here, in presence of CMHEC, no modification of the filter cake microstructure was observed on SEM images (not shown here). Packing and size of the hydrating cement particles as well as the pore sizes present in the filter cake were comparable for all investigated samples, whether or not they contained CMHEC. Consequently, constriction of the filter cake pores through adsorption or physical plugging was studied next as a potential mechanism for fluid loss control achieved by CMHEC.

Adsorption of CMHEC

Thus, the adsorbed amount of CMHEC on cement was measured. If the working mechanism of CMHEC was in fact owed to adsorption, then the adsorbed amount should linearly increase with dosage up to a plateau (the saturation point) at which the cement surface has been covered with the maximum possible amount of polymer. This behavior is presented by a Langmuir isotherm. CMHEC adsorption onto positively charged cement hydrates seemed to present a plausible mechanism because of the significant anionic charge of the polymer, which in cement pore solution was found to lie at 236 C/g (see Table II). As is shown in Figure 3, no adsorption maximum was attained. Instead, the amount of CMHEC retained at first increases gradually (dosage range 0–0.3% bwoc CMHEC) until a stable retention of 90% of dosage added is obtained. This behavior clearly indicates that at low dosages (0–0.3%), increased amounts of CMHEC are retained by cement, possibly through a combination of physical adsorption and obstruction by associated polymer molecules. Beyond a dosage of 0.4% bwoc of CMHEC, the retained amount always presents 90% of polymer dosage added. Consequently, practically the entire quantity of CMHEC polymer added is retained. The remaining nonretained 10% are water-soluble impurities such as glycolates and salts present in the industrial CMHEC sample.

The fact that no saturated adsorption is achieved although cement fluid loss levels off at CMHEC dosages of ≥ 0.6% bwoc contradicts polymer adsorption. Instead, depletion of CMHEC might be attributable to retention of polymer associates within the pores of the cement filter cake. An adsorptive mechanism generally can be confirmed by zeta potential measurement which increases with polymer dosage to more negative values if adsorption occurs. Thus, zeta potentials of cement pastes in absence and presence of increased amounts of this anionic FLA were measured (Fig. 5). They indicate that adsorption takes place at low (0–0.4% bwoc) CMHEC dosages (zeta potential −5.0 mV for the neat cement slurry versus −10.5 mV for the slurry containing 0.4% bwoc of CMHEC). At a dosage of 0.4% bwoc, the
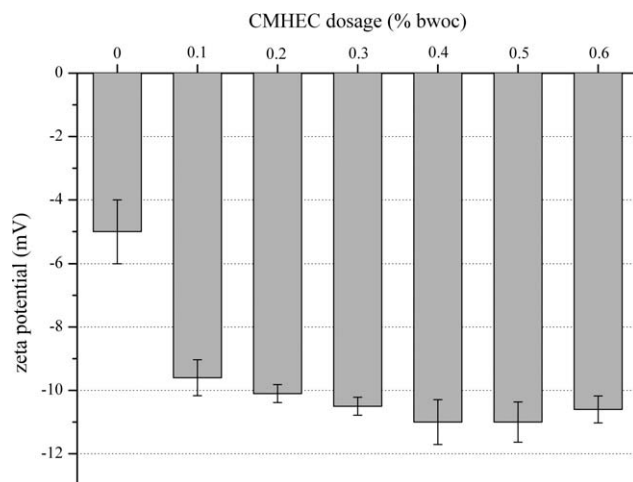
Figure 5 Zeta potential of cement slurries (w/c = 0.44) containing increased dosages of CMHEC, measured at 27°C.

most negative zeta potential (supposedly representing saturation adsorption) is reached. However, at this dosage, cement fluid loss is still high. The results allow to conclude that while some adsorption of anionic CMHEC on cement seems to occur at low dosages, it cannot explain the excellent fluid loss control achieved at higher CMHEC dosages. There, another mechanism seems to come into place.

Formation of associated polymer network

To probe into this, physical plugging of the cement filter cake owed to polymer associates was investigated. Occurrence of large hydrocolloidal particles at higher CMHEC concentrations was confirmed by dynamic light scattering measurement in cement pore solution. At CMHEC concentrations of 1–2 g/L only, a constant d_{50} value of $\sim 6 \pm 1$ nm was found for the hydrodynamic diameter, with no particles
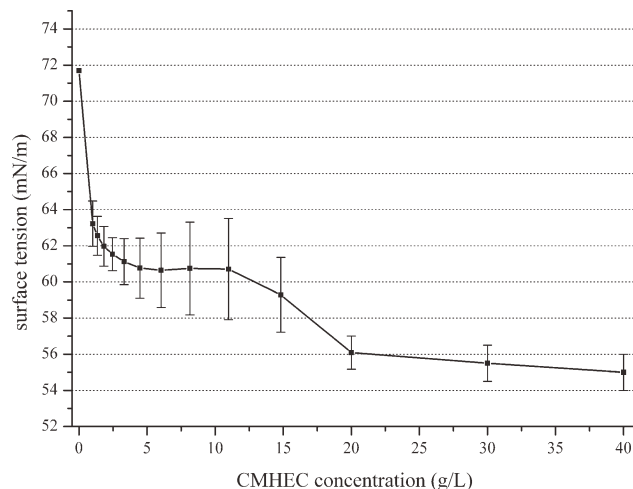

Figure 6 Surface tension of aqueous solutions in dependence of CMHEC concentration, measured at 27°C.

< 5 nm and > 10 nm present, whereas at 5 g/L of CMHEC, a significantly higher diameter was obtained for the solved molecules (d_{50} value = 380 $\pm$ 20 nm), thus indicating beginning association of CMHEC molecules. Unfortunately, concentrations > 5 g/L could not be measured, due to the rapid increase of viscosity of such CMHEC solutions. This exponential increase in solution viscosity observed at higher CMHEC concentrations (see Fig. 4) also supports the concept of a plugging mechanism for CMHEC originating from the formation of associated polymer networks. To conclude, at first no interaction takes place in a system of soluted and separated polymer molecules. At higher concentrations, however, associated polymer networks with increasing particle size are formed. This association occurs at a specific concentration which is called the "overlapping concentration."[20]

To finally prove the association of CMHEC, surface tension measurements were conducted in aqueous solution at 27°C and at different concentrations. Because of instrumental limitations, surface tension had to be measured in aqueous solution. Nevertheless, the general behavior of CMHEC here can be expected to be similar to that in cement pore solution. Polymer association would clearly reduce surface tension. The surface activity of cellulose ethers is influenced by their anionic charge amount. The higher the anionic charge, the lower the surface activity. As is shown in Figure 6, surface tension decreases rapidly with dosage to 61 mN/m and remains constant till a CMHEC concentration of ~ 10 g/L is attained. This behavior can be explained by the simultaneous presence of hydrophobic and hydrophilic charged functional groups which render the CMHEC molecule an anionic surfactant. Beginning at the "overlapping concentration" of ~ 10 g/L CMHEC, surface tension is reduced further to 56 mN/m. Even at concentrations as high as 40 g/L, no further reduction was obtained. This behavior can be ascribed to association of polymer molecules.

To conclude, the results instigate that at low dosages, the working mechanism of CMHEC mainly

TABLE IV
API Fluid Loss of Class G Cement Slurries as a Function of CMHEC and SMF Dosages

CMHEC dosage (% bwoc)	SMF dosage (% bwoc)	API fluid loss at 27°C (mL/30 min)
0.2	0	473 (calculated)[a]
0.2	0.1	295 (calculated)[a]
0.2	0.2	160
0.2	0.3	90
0.2	0.4	50
0.2	0.5	52

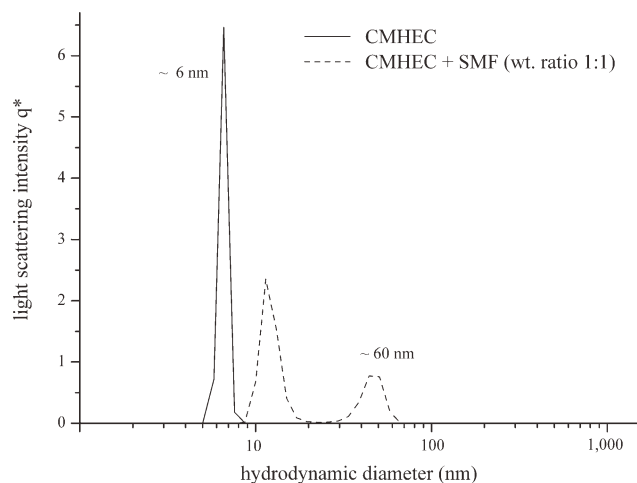[a] Dehydration of slurry occurred in less than 30 min.

Figure 7 Hydrodynamic diameter of CMHEC molecule (2 g/L) and a mixture of CMHEC (2 g/L) and SMF (2 g/L) in cement pore solution.

results from physical adsorption onto cement, whereas at higher dosages (0.4–0.8% bwoc), large associated polymer networks of CMHEC plug the pores of the cement filter cake.

Interaction between CMHEC and SMF

To further prove this concept, combinations of CMHEC with SMF dispersant were probed for API fluid loss and hydrodynamic diameter of solved molecules in cement pore solution. Such combination is frequently used in actual field application. First, it was found that SMF significantly improves fluid loss performance of CMHEC (Table IV). Furthermore, the hydrodynamic diameter of CMHEC (2 g/L) solved in combination with SMF (2 g/L) was obtained (Fig. 7). Individual CMHEC and SMF molecules possess hydrodynamic sizes of 6 nm and of less than 1 nm, respectively. For the combination, a bimodal particle size distribution exhibiting significantly higher polymer diameters were observed. Two species possessing hydrodynamic diameters of $\sim$ 12 nm and $\sim$ 60 nm (d_{50} values) were detected. Apparently, anionic SMF molecules promote the formation of larger colloidal associates from CMHEC which exhibit an increased plugging effect in the cement filter cake.

CONCLUSIONS

The working mechanism of CMHEC as cement FLA is concentration dependant. Below 10 g/L of CMHEC (this corresponds to a dosage of $\sim$ 0.4%

bwoc), adsorption on cement presents the predominant reason for fluid loss control. Above 10 to 15 g/L, the working mechanism changes completely and is henceforth governed by the formation of highly associated polymer networks, which physically plug cement filter cake pores. Formation of polymer associates from CMHEC is much enhanced by the presence of anionic polyelectrolytes such as SMF. This effect explains the synergistic action of SMF and other common cement dispersants on CMHEC relative to fluid loss, an observation which is frequently made by applicators in the field.

Further studies are underway to investigate the associative behavior of CMHEC with other hydrocolloids used in oil well cementing. Among them are welan and diutan gum, two microbially produced biopolymers that are used in cement slurries as free water agents and viscosifiers.

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