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Working mechanism of methyl hydroxyethyl cellulose (MHEC) as water retention agent

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ABSTRACT

The working mechanism of methyl hydroxyethyl cellulose, MHEC ($M_w = 2.5 \cdot 10^5$ g/mol, $DS_{methyl} = 1.81$, $MS_{hydroxyethyl} = 0.15$) as water retention agent in cement was investigated. First, the hydrocolloid was characterized and its performance as non-ionic water retention agent was determined employing the filter paper test. Also, water sorption and swelling of individual MHEC fibers under conditions of different humidities were monitored by ESEM imaging. Second, its working mechanism was established. It was found that at low dosages, MHEC achieves water retention by intramolecular sorption of water and concomitant swelling while at higher dosages, MHEC molecules agglomerate into large hydrocolloidal microgel particles ($d > 1$ μm) which effectively plug the pores in the mortar matrix. MHEC association was evidenced by an exponential increase in solution viscosity as concentration rises, a strong increase in the hydrodynamic diameter of solved MHEC molecules, and a noticeable reduction of surface tension.

1. Introduction

Water retention additives play an important role in modern building products, particularly in dry-mix mortars [1]. Their function is to prevent uncontrolled water loss into porous substrates such as brick, lime stone, and aerated concrete. In industrial products, cellulose ethers dominate this market because of their favorable cost effectiveness and their good environmental compatibility [2]. The first reports on the preparation of methyl cellulose and its derivates originate from Lilienfeld [3], Leuchs [4] and Dreyfus [5]. Based on their pioneering work in cellulose ether synthesis, production started in Germany in the 1920s and in the United States in 1938. Major current applications of cellulose ethers include wall renders and plasters, joint compounds for gypsum board paneling, cementitious tile adhesives (CTAs), floor screeds, self-leveling underlayments (SLUs) and water-proofing membranes [6]. In dry mortars, cellulose ethers serve to provide water retention and viscosity. Some types retard Portland cement hydration severely [7,8]. The effect depends on the specific composition (e.g. degree and type of substitution) of the cellulose ether. Application dosages may range between 0.1 and 1.5% by weight of binder, depending on the desired properties. Among the most frequently used cellulose ethers are methyl hydroxyethyl cellulose (MHEC, also referred to as HEMC) and methyl hydroxypropyl cellulose (MHPC) [9–11]. MHEC is predominantly applied in self-leveling flooring compounds and cementitious tile adhesives (CTAs) while MHPC, because of its air-entraining effect stemming from the hydrophobic hydroxypropyl groups, is the product of choice for wall renders and plasters.

In previous publications, the impact of molecular weight of cellulose ethers on both water retention and rheological properties of mortars has been investigated. The authors conclude that consistency was increased and water retention was improved by higher molecular weight ethers. The mortar rheology is highlighted as one of the key properties relative to water retention [12]. Other studies discussed the influence of cellulose ethers on water transport in the porous structure of cement-based materials and investigated their effect on cement hydration [13,14]. They found that the type of substituents attached to the anhydro glucose ring of the cellulose ether is critical for water transport and development of the microstructure of fresh and hardened cement. Furthermore, the degree of substitution represents the key parameter relative to cement hydration, as was evidenced by different time periods at which portlandite precipitation occurs.

In the past, attempts have been made to clarify the working mechanism of methyl cellulose (MC). Early works from Schweizer et al. present the effect of cellulose ethers on water retention and rheology of cementitious mortars and gypsum-based machinery plasters [15,16]. They demonstrate that adsorption of methyl cellulose is clearly dependent on the degree of substitution (DS). At DS values of >1.6 which are typical for MC products used in the

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building industry, only a minor amount (~20%) of the MC powder adsorbs. In a very skillful experiment the authors show that during the drying process of a gypsum-based render, MC migrates with the water to the surface of the render and is not retained by adsorption. Thus, they conclude that MC does not adsorb on the binder or its hydrates. Similar observations have been made by Yammamuro et al. [17].

In another study, Jenni et al. stained MHEC with a fluorescent dye and visualized and quantified the migration of MHEC through the capillaries of mortars. They found that MHEC accumulates at system interfaces exhibiting a reduced porosity. From this, they conclude that the cellulose ethers can migrate through the pore system and are therefore not or only partly adsorbed on cement particles under wet conditions [18]. In a later publication from this group they state that the dissolved CE is transported downwards through the capillary pores, but accumulates at the contact layer and substrate surface, which act as micro-filters [19].

Thus, there seems to be agreement that methyl cellulose does not adsorb. None of these works, however, offers an alternative model which clearly can describe the mechanism behind water retention capability of MC. Accordingly, there is still a need for clarification.

Generally, three principle working mechanisms for water retention can come into place whenever a cement paste is subject to filtration on a substrate. These potential mechanisms have been proposed in earlier works by Desbrières and are as follows [20,21]: (a) Water retention as a result of increased viscosity: increased dynamic filtrate viscosity can decelerate the filtration rate. (b) Water retention as a result of adsorption: anionic polymers 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 cement particles. Through this mechanism, filter cake permeability is reduced. (c) Water retention as a result of physical pore plugging: polymers may plug pores in the cementitious matrix through formation of polymer films (e.g. latexes), or through large polymer associates which form a 3D network, or through simple swelling and expansion caused by the uptake of an enormous amount of water into the inner sphere and hydrate shells of polymers. This process leads to the formation of large microgel particles. Through this mechanism, a large portion of the mixing water is physically bound and cannot leak-off into a porous substrate. The enormous water-binding capacity of polysaccharides has been described in an earlier study. By using a sorption balance and a microcalorimeter it was found that at the saturation level, neutral polysaccharides (amylose and amylopectin) can bind up to four water molecules per anhydroglucose unit [22].

In recent studies we have investigated the water retention behavior of hydroxyethyl cellulose (HEC) and carboxymethyl hydroxyethyl cellulose (CMHEC) in oil well cement, respectively. We found that the working mechanism of HEC relies on a dual effect, namely its enormous intramolecular water sorption (binding) capacity and a concentration dependent formation of hydrocolloidal associated polymer networks [23]. Contrary to this, the working mechanism of CMHEC changes with dosage. At low dosages (up to ~0.3% by weight of cement), adsorption presents the predominant mode of action, whereas above a certain threshold concentration (the “overlapping” concentration), formation of associated polymer networks is responsible for its effectiveness [24].

Here, an attempt was made to establish the working mechanism of MHEC. For this purpose, its water retention effectiveness in cement paste and its dynamic viscosity in cement pore solution were measured. Furthermore, its potential adsorption on cement was probed via a specifically designed static filtration test. Finally, concentration-dependent hydrodynamic diameters of solved MHEC molecules, and their surface tension in cement pore solution were measured to establish the mechanism underlying the effectiveness of MHEC as water retention agent.

2. Materials and methods

2.1. Cement

This study was conducted using a CEM I 52.5N sample (“*Milke*®” from HeidelbergCement AG, Heidelberg, Germany). Its properties are presented in Table 1. Composition of the cement was obtained by Q-XRD using a Bruker axs D8 Advance instrument (Bruker, Karlsruhe, Germany) with Bragg–Brentano geometry. Topas 4.0 software was employed to quantify the amounts of individual phases present in the sample by following *Rietveld's* method of refinement. The amounts of gypsum ($CaSO_4 \cdot 2H_2O$) and hemi-hydrate ($CaSO_4 \cdot 0.5H_2O$) were measured by thermogravimetry. Free lime (CaO) was 3.0 wt.% as quantified following the extraction method established by Franke [25]. Using a *Blaine* instrument (Toni Technik, Berlin, Germany), the specific surface area was found at 3316 cm^2/g. The specific density of this sample was 3.16 kg/L, as measured by Helium pycnometry (Ultrapycnometer® 1000 from Quantachrome Instruments, Boynton Beach, FL, USA). Particle size distribution of this cement was determined employing a laser-based particle size analyzer (CILAS 1064 instrument from Cilas, Marseille, France). Average particle size (d_{50} value) was 10 µm (see Table 1).

2.2. MHEC

A commercial sample of methyl hydroxyethyl cellulose (Tylose® MHB 10000 P2, supplied by SE Tylose GmbH & Co KG, Wiesbaden, Germany) exhibiting a degree of substitution (DS methyl) of 1.81 and a molar degree of substitution (MS hydroxyethyl) of 0.15 was used (DS and MS terminology and values are supplier information). Its characteristic properties are shown in Table 2. Particle size measurement produced a d_{50} value of 116 µm for the dry MHEC powder.

For determination of molar masses (M_w and M_n), polydispersity index and molecular size in solution ($R_{h(z)}$), size exclusion chromatography (Waters Alliance 2695 instrument) equipped with RI detector 2414 from Waters, Eschborn, Germany and an 18 angle dynamic light scattering detector (Dawn EOS from Wyatt Technology, Santa Barbara, CA/USA) was utilized. Prior to application on the columns, the 2 g/L MHEC solution was filtered through a 5 µm filter and separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). Eluent was 0.2 M aqueous $NaNO_3$ solution (adjusted to pH 9.0 with NaOH) pumped at a flow rate of 1.0 mL/min. The value of dn/dc used to calculate M_w and M_n was 0.159 mL/g (value for hydroxyethyl cellulose) [26].

The specific anionic charge amount of the polymer in cement pore solution was determined at room temperature using a PCD 03 pH apparatus (BTG Mütek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature description employing a 0.001 N solution of laboratory grade poly(diallyl dimethylammonium chloride) from BTG Mütek GmbH, Herrsching, Germany as cationic polyelectrolyte [27]. The value presented is the average obtained from three different measurements. Deviation of this method was found to be ±3 C/g.

Dynamic viscosities of cement pore solutions containing dissolved MHEC polymer and of filtrates obtained from static filtration tests were determined on an *Ubbelohde* viscometer using 501 10/I, 501 20/II, 501 30/III, and 501 40/IV capillaries supplied by Schott Instruments, Mainz, Germany. 15 mL of individual solutions was filled into the reservoir of the viscometer and the flow time was measured. From this, the kinematic viscosity of the filtrate 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 dependent *Hagenbach–Couette* correction

Table 1
Phase composition (Q-XRD, *Rietveld*), specific density, specific surface area (*Blaine*) and d_{50} value of cement sample CEM I 52.5N.

C_3S (wt.%)	C_2S (wt.%)	C_3A_c (wt.%)	C_3A_o (wt.%)	C_4AF (wt.%)	free CaO (wt.%)	$CaSO_4 \cdot 2H_2O$ (wt.%)	$CaSO_4 \cdot 0.5H_2O$ (wt.%)	$CaSO_4$ (wt.%)	Specific density (kg/L)	Specific surface area Blaine (cm^2/g)	d_{50} value (μm)
62.9	20.4	3.9	3.3	2.3	0.1	3.5 [a]	2.0 [a]	2.1	3.16	3316	10 ± 1.0

[a] Measured by thermogravimetry.

term which is provided in the instrument instruction sheet. Multiplying the value for the kinematic viscosity with the specific density of the filtrate produced the value for the dynamic viscosity η_{dyn}, as is expressed by Eq. (2).

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

Water sorption (swelling) of MHEC powder in moist atmosphere was investigated by exposing the cellulose ether to relative humidities of 10%, 50% and 60%, respectively, under an environmental scanning electron microscope (XL 30 ESEM FEG from FEI Company, Eindhoven, The Netherlands). These humidities correspond to water vapor pressures of 0.6, 2.0 and 3.3 mbar, respectively, in the ESEM chamber.

Hydrodynamic diameter (d_{50} value) of the MHEC polymer associates were measured in cement pore solution using a dynamic light scattering particle size analyzer (LB-550 from Horiba, Irvine, CA, USA).

Surface tension of cement pore solution containing dissolved MHEC was quantified on a Processor Tensiometer K100 (Krüss GmbH, Hamburg, Germany) employing the *Wilhelmy* plate method using a platinum plate. First, the surface tension of deionized water was established using a Drop Shape Analyzer DSA 100 (Krüss GmbH, Hamburg, Germany) whereby a value of 71.7 mN/m was attained. Next, the surface tension of MHEC solutions was recorded as a function of concentration (10 steps from 10 to 1 g/L, with decreasing intervals of 2 to 0.4 g/L). Furthermore, the surface tension of solutions holding 15 and 20 g/L MHEC was determined using the pendant drop method. All experiments were performed at room temperature.

2.3. Preparation of cement paste

For water retention and static filtration tests, cement pastes were prepared using *Milke*® cement CEM I 52.5 N and deionized water. The cement paste was mixed at a water-to-cement ratio of 0.53 using a blade type laboratory Waring blender (Torrington/CT, USA). 700 g of cement and the respective amount of MHEC powder (0.1–0.8% bwoc) were dry-blended and homogenized. Within 15 s, the cement/polymer blend was added to 371 g of DI water placed in the cup of the Waring blender and was mixed for 35 s at “low” speed (4000 rpm). To ensure homogeneous consistency, all pastes were stirred for 20 min and homogenized in an atmospheric consistometer (Model 1250, Chandler Engineering, Broken Arrow/OK, USA) at 25 °C.

2.4. Water retention test

Water retention effectiveness was determined using a modified version of the filter paper method which is specified in EN 495-2 (former DIN-18555-7) [28,29]. Here, in a typical experiment 15 half-folded filter papers (size 240 mm × 105 mm from Einzinger, Munich, Germany) were covered with a tissue (Delicarta S.p.A., Porcari, Italy) and a Vicat cone (70 × 80 × 40 mm) was placed on top of the stack, with the smaller diameter facing the bottom (see Fig. 1). To establish the value for water retention, a cement paste was prepared at a water-to-cement ratio of 0.53 using the procedure from Section 2.3, filled into the Vicat cone exactly to the brim and leveled with a spatula. After a test period of 7.5 min during which water is sucked from the paste by the filter papers, both the Vicat cone holding the cement paste and the tissue were removed carefully from the stack of filter papers. The amount of water absorbed (w_{abs}) was determined from the difference in weight between the stack of paper after and before exposure to the cement paste. From this, the value for water retention in % was calculated relative to the amount of mixing water contained in the paste placed in the Vicat cone (w_0; here: 113.6 g), as presented in Eq. (3).

$$water\,retention(\%) = \left(1 - \frac{w_{abs}}{w_0}\right) \cdot 100 \tag{3}$$

Static filtration tests of cement pastes were conducted using a 500 mL HTHP filter press (Part No. 171-00-C, OFI Testing Equipment Inc., Houston/TX, USA). The test procedure followed the recommended practice for testing oil well cements established by the American Petroleum Institute (API RP 10B-2) [30]. After pouring the homogenized cement paste into the filter cell, a differential pressure of 7 bar (N_2) was applied at the top of the cell. Filtration proceeded through a 3.5 $in.^2$ mesh metal sieve placed at the bottom of the cell. The filtrate produced by the differential pressure was collected for 15 min.

2.5. Retention on cement

The amount of MHEC retained by cement was determined from the filtrate collected in the static filtration experiment described above. Generally, the depletion method was applied, i.e. it was assumed that the decrease in 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, 20 g/L of MHEC (this concentration correlates to a polymer dosage of 1.06% bwoc) was dissolved in cement pore solution and stored for one day. No precipitation of MHEC was observed. Note that the calculated amounts of MHEC retained include all polymers present. Thus, all further statements on retained amount of MHEC refer to MHEC plus any minor constituent or by-product. The retained amount was calculated from the difference in the equilibrium concentrations of the polymer present in the liquid phase before and after contact with cement. A High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO_2 detector was used to quantify polymer concentration. Before conducting the TOC analysis, the alkaline

Table 2
Characteristic properties of the MHEC sample.

Molar masses (g/mol)		Polydispersity index (M_w/M_n)	Hydrodynamic radius $R_{h(z)}$ (nm)	Radius of gyration $R_{g(z)}$ (nm)	Specific anionic charge amount ε (C/g)*	Intrinsic viscosity η at 25 °C (L/g)*
M_w	M_n					
248,000	174,000	1.4	31.0	39.7	6 ± 3	0.32 ± 0.058

* Measured in cement pore solution.

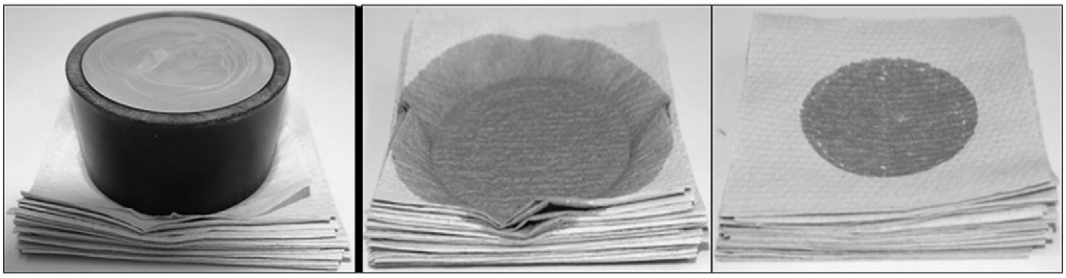

Fig. 1. “Filter paper test” to determine water retention by cement paste; left: placement of Vicat cone on the paper stack at beginning of test; middle: paper stack showing large quantity of sorbed water at end of test from a cement paste without and (right) after addition of 0.8% bwoc of MHEC.

cement filtrate containing the non-retained polymer was diluted with 0.1 M HCl at a ratio of 1:10 (v./v.). Final pH of the solution was 1.0. Maximum deviation of the measurement was found to be ±0.1 mg polymer/g cement.

3. Results and discussion

3.1. Characteristics properties of MHEC sample

The general chemical structure of MHEC is presented in Fig. 2. According to supplier information, the sample employed in the study exhibited a degree of substitution relative to methylation (DS value) of 1.81, and a molar degree of substitution relative to hydroxyethylation (MS) of 0.15. Gel permeation chromatography (GPC) analysis produced molar masses of $2.48\cdot10^5$ g/mol (M_w) and of $1.74\cdot10^5$ g/mol (M_n), respectively (Table 2). Using the GPC method, a hydrodynamic radius $R_{h(z)}$ of 31.0 nm and a radius of gyration $R_{g(z)}$ of 39.7 nm were found for this polymer. From this data, the *Burchard* parameter $\rho = R_{g(z)}/R_{h(z)}$ which describes the solved conformation of macromolecules can be calculated [31,32]. According to this model, a value of 1.3 which corresponds to a polymer architecture close to that of a linear statistic coil was established [33].

In alkaline cement pore solution (pH ~ 12.8), the MHEC sample exhibited an almost negligible specific anionic charge amount of -6 ± 3 C/g, as measured by charge titration employing polyDADMAC as cationic counter polymer [27]. According to this result, MHEC is practically non-ionic in cement pore solution.

3.2. Water retention capability of MHEC

Water retention of cement pastes containing increasing dosages of MHEC was measured at 25 °C. As is shown in Fig. 3, increased amounts of MHEC produce improved water retention. For example, water retention increases from 84% at 0% bwoc dosage to 97% at 0.3% bwoc MHEC. At 25 °C, the minimum concentration needed to achieve a water retention capability of >98% which is common in high performance dry-mortar products was found to lie at 0.4% bwoc. Obviously, effectiveness of MHEC first increases rapidly with dosage and then asymptotically approaches a value of 100%. MHEC dosages higher than 1% bwoc produce extremely viscous cement pastes and thus were not investigated.

3.3. Viscosifying property

Generally, most cellulose ethers viscosify aqueous or cement pore solutions. Apart from concentration, this effect is dependent on the molecular weight (chain length) of the sample. The MHEC sample selected for this study was a type which develops medium viscosity. Here, the dynamic viscosities of cement pore solutions holding 0–0.8% bwoc of MHEC were measured at 25, 40, and 60 °C, respectively. The results are presented in Fig. 4. At 25 °C and for concentrations below 6 g/L (0.32% bwoc) only a minor increase of viscosity appears. Above this threshold (“overlapping”) concentration [34], an exponential rise in viscosity was found, indicating that beginning at this concentration, MHEC molecules start to associate and form a 3D network which is the reason behind the steep increase in viscosity.

At 40 °C, “overlapping” of MHEC molecules occurs at a higher concentration (~8 g/L), and viscosity increases less than at 25 °C. This explains the reduced water retention performance of MHEC at elevated temperatures. When temperature was further increased to 60 °C, the sample did not viscosify anymore due to its insolubility at higher temperatures. The effect of a steep viscosity increase as well as the “overlapping” at higher concentrations was no longer observed at high temperatures.

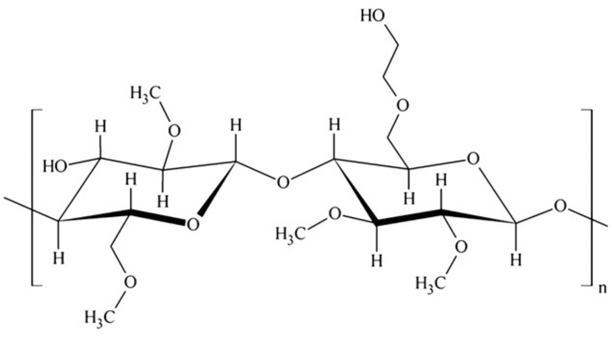

Fig. 2. Chemical structure of methyl hydroxyethyl cellulose exhibiting a DS (methyl) of 2.0 and an MS (hydroxyethyl) of 0.5.

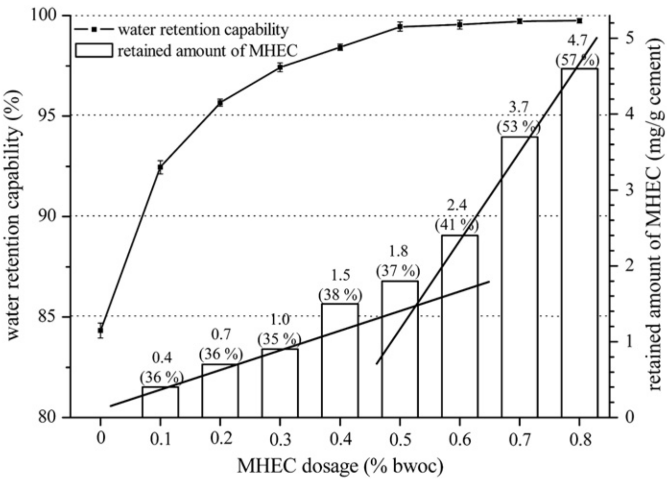

Fig. 3. Water retention capability and retained amount of MHEC as a function of polymer dosage.

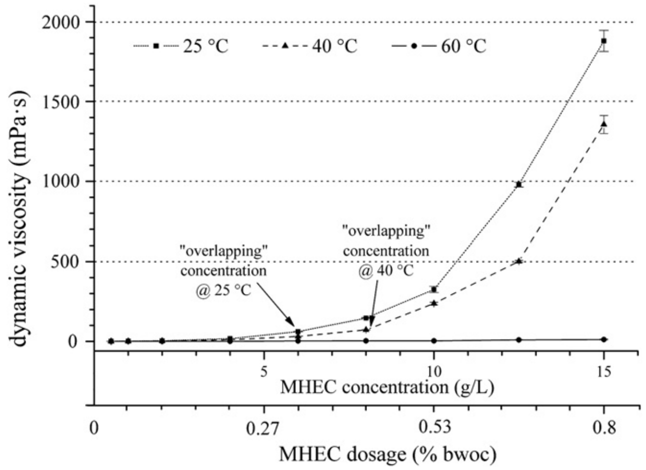

Fig. 4. Dynamic viscosity of cement pore solutions containing MHEC as a function of polymer concentration/dosage and temperature.

3.4. Water sorption by MHEC

Uptake of water by an individual MHEC fiber at different relative humidities (10, 50, and 60%) was monitored using an ESEM instrument (see Fig. 5). It was observed that as a result of water sorption, the polymer swells and its volume increases considerably. For example, at 60% relative humidity, the diameter of the MHEC fiber was increased by a factor of ~3, thus confirming huge uptake of water. It is interesting to note that when the humidity in the ESEM chamber was reduced to 10%, the swollen polymer did not release all of the sorbed water. Instead, formation of polymer films and of cross-linked network structures was observed. This confirms the strong water-binding capacity of the hydrated hydrocolloidal molecule. Additionally, it instigates that films of MHEC polymer are present in the cementitious matrix. This way, MHEC provides a dual effect for mortar: In the fresh, wet paste (within the first ~60 min), MHEC solely acts as a water retention agent while later, when the water has been consumed by hydration and desiccation, MHEC modifies the mechanical properties of mortar through polymer film formation in the cementitious matrix. It should be noted here that Jenni et al. reported instantaneous film formation in the fresh matrix [19]. According to them, particle coalescence occurs at specific locations in the microstructure, namely in the water films present between air voids. Such immediate film formation was not observed here.

3.5. Mechanistic study

To uncover the working mechanism of MHEC and to understand its water retention performance, a series of experiments was devised. Theoretically, the filtration rate of mortar can be reduced either by a lower filter cake permeability or a higher filtrate viscosity. The dynamic viscosity values of cement pore solutions presented before in Section 3.3. imply that increased filtrate viscosity may play a role in the working mechanism of MHEC. And indeed, the dynamic filtrate viscosities measured in cement pore solution (see Table 3) rise from 2.1 mPa·s for 0.1% bwoc of MHEC to 64.8 mPa·s for a dosage of 0.8% bwoc. Nevertheless, a value of ~65 mPa·s is by far not high enough to explain the enormous water retention capability of MHEC.

In his earlier study Desbrières found that in most cases, a reduction in filter cake permeability is the predominant mechanism for effective water retention achieved by polymers. This concept was adopted and the following possibilities were considered: (a) adsorption of MHEC on cement and (b) physical plugging of pore spaces existing in the cement paste by associated 3D polymer networks. Both mechanisms would lead to a reduced permeability of the mortar matrix. Model (b) coincides well with the findings of Jenni et al. [11,18,19]. In their study, utilizing laser-scanning microscopy, MHEC was found to be trapped in micro cracks of the concrete substrate. The hydrated, swollen MHEC aggregates could possibly plug pores, micro cracks or an entire interface to a porous substrate.

3.5.1. Retention of MHEC on cement

The amount of MHEC retained in the cement paste was determined from filtrates collected from a static filtration test

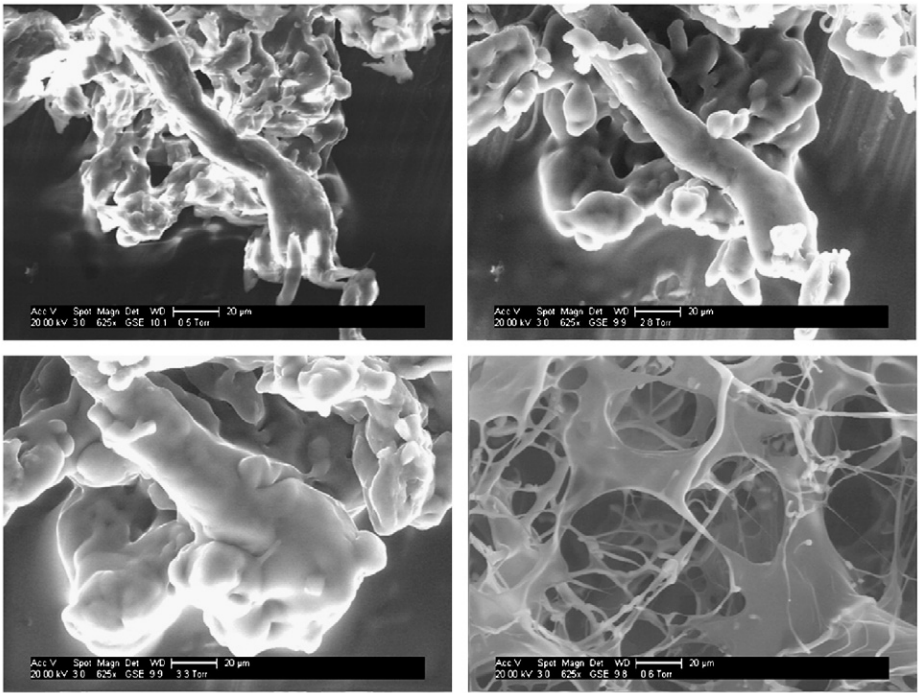

Fig. 5. ESEM images of dry MHEC sample before water sorption (top left); after exposure for 5 min to rel. humidities of 50 and 60% (top right and bottom left); and of MHEC polymer films after reduction of rel. humidity to 10% (bottom right).

Table 3
Dynamic filtrate viscosity of the MHEC sample in cement pore solution as a function of dosage.

MHEC dosage (% bwoc)	Dynamic filtrate viscosity η (mPa·s)
0	1.0
0.1	2.1
0.2	5.1
0.3	10.8
0.4	22.3
0.5	49.9
0.6	59.8
0.7	61.8
0.8	64.8

Table 4
Dosage-dependent development of MHEC concentration in cement filtrate and after two subsequent static filtration steps.

Initial concentration added to cement paste		MHEC concentration in 1st filtrate		MHEC concentration in 2nd filtrate	
(g/L)	(% bwoc)	(g/L)	(% bwoc)	(g/L)	(% bwoc)
5.0	0.27	4.4	0.23	4.2	0.22
13.0	0.69	6.2	0.33	3.3	0.17

conducted on a filter press at 7 bar differential pressure. If the working mechanism was indeed relying on adsorption, then the depleted amount of MHEC should increase linearly with dosage until it reaches a plateau which indicates that the cement surface has been covered with the maximum possible amount of polymer (= saturation equilibrium). This behavior is presented by a *Langmuir* isotherm. As is shown in Fig. 3, below a dosage of up to 0.3% bwoc, the amount of MHEC retained increases nearly linear. Due to its very low charge amount, adsorption of MHEC seems highly unlikely. This indicates that another effect may come into play here. Industrial MHEC samples normally contain certain amounts of auxiliaries or by-products which can adsorb on cement. For example, cellulose ethers often contain impurities such as glycolates, thickeners (~15%) such as e.g. anionic polyacrylamides, or rheology modifiers (e.g.: hydroxypropyl starch). Some of these by-products are highly anionic and therefore can lead to this adsorbed amount. Beyond an MHEC dosage of 0.5% bwoc, the retained amount again increases linearly, but steeper than at the lower dosages, thus indicating that a second regime comes into play here. These results perfectly agree with the concentration-dependent values for dynamic viscosities of MHEC solutions (see Fig. 4). There, also two linear regimes were observed, one at a MHEC dosage ≤0.3% bwoc ($R^2 = 0.98$) and one at >0.5% dosage ($R^2 = 0.99$). The combined findings can be interpreted as such that at low MHEC dosages, minor parts (presumably impurities and auxiliary admixtures) adsorb on cement while at higher dosages, MHEC agglomerates formed by the "overlapping" mechanism are retained within the pores of the cementitious matrix because of their large size. In this second regime, adsorption on cement can be excluded because no direct correlation between the retained amount of MHEC and its water-retention capability exists and no equilibrium state (point of saturated adsorption) is reached (see Fig. 3).

To confirm the existence of two different regimes for the working mechanism of MHEC, the experiments as follows were devised: First, two different concentrations of MHEC were selected, one representing the adsorptive regime (5.0 g/L, corr. to a dosage of 0.27% bwoc) and the second the associative/agglomerated regime (13.0 g/L or 0.69% bwoc). For both cement pastes, water-retention as well as the retained amount of MHEC was measured using a static filtration test. In both cases, the filtrate collected from this first static filtration test was used as mixing water for the preparation of a second cement paste which was then subjected to another static filtration test. The results are shown in Table 4. In the cement paste containing the lower dosage of the cellulose ether, MHEC concentration drops by 12% only from initially 5.0 g/L to 4.4 g/L in the first filtration test and nearly stabilizes at 4.2 g/L after the second filtration. This result indicates that the MHEC sample contains some constituents (by-products etc.) which are screened off by cement through adsorption, but are irrelevant for achieving water-retention. Whereas, a completely different behavior is observed for the paste containing a high concentration of MHEC. Therefore, after the first filtration the MHEC concentration is halved (from 13.0 g/L to 6.2 g/L) and drops by another 50% after the second filtration (to 3.3 g/L only). Such behavior is well explained by the mechanism of overlapping cellulose ether molecules. They are so voluminous that in every filtration step, a large amount is retained in the pores of the filter-cake. As a result of this considerable MHEC depletion, water-retention is significantly reduced.

These results further support our mechanistic model whereby at low additions (<0.3% bwoc), MHEC attains its water-retention capability from uptake of water through hydration and swelling while at higher dosages (≥0.6% bwoc), water-retention mainly results from physical plugging of the cement pores achieved by large agglomerates of MHEC molecules.

3.5.2. Formation of polymer associates

To confirm occurrence of MHEC agglomerates at concentrations beyond the "overlapping" point, dosage dependent diameters of MHEC molecules solved in cement pore solution were determined at 25 °C using dynamic light scattering technique.

Therefore, when 0.5 g/L of MHEC were dissolved, a d_{50} value for the hydrodynamic diameter of 6.9 ± 1.1 nm was found; with no particles being <4 nm and >10 nm (see Fig. 6). At higher MHEC concentrations (4.0 g/L and 16.0 g/L, respectively), however, increased formation of large associates possessing diameters up to 1.3 μm and 4 μm was observed. For example, at a dosage of 4.0 g/L additional particle diameters at ~60 nm, ~450 nm and ~1.3 μm were recorded while at 16 g/L, even associates as large as ~4 μm were found. Consequently, this experiment allows to conclude that in cement pore solution already at remarkably low dosages (~0.2% bwoc), MHEC molecules begin to form large associates. They are responsible for the viscosity increase and water retention effectiveness. Thus, at low MHEC concentrations no intermolecular interaction takes place in a system of soluted and separated polymer molecules. As concentration increases, however, association into polymer

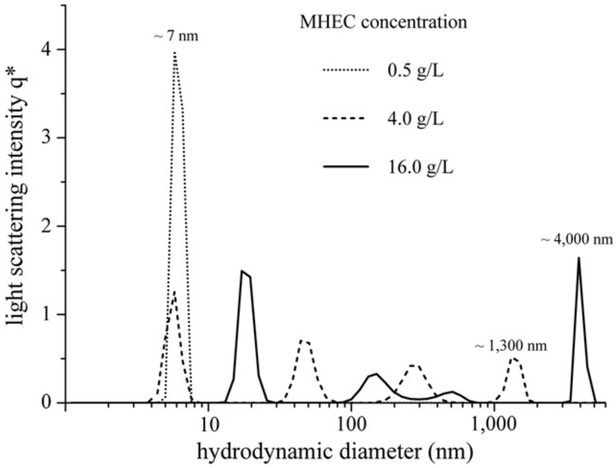

Fig. 6. Hydrodynamic diameter of MHEC molecules dissolved in cement pore solution, as measured by dynamic light scattering.

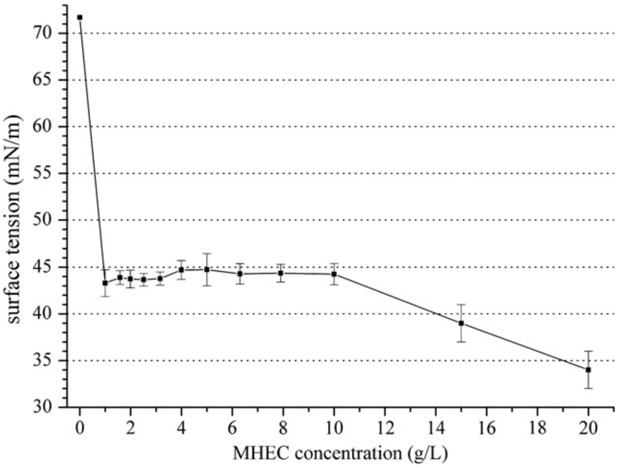

Fig. 7. Surface tension of cement pore solution in dependence of MHEC concentration, measured at 25 °C.

networks starts to occur and progresses rapidly once a specific concentration (the so-called "overlapping" concentration) is exceeded [34].

To further prove the concept of association of MHEC molecules, the surface tension of aqueous MHEC solutions was measured. Generally, cellulose ethers are macrotensides which always exhibit surface activity. The reduction in surface tension of water depends on their anionic charge amount. The higher the anionic charge, the lower the surface activity. The MHEC sample tested here is practically non-ionic (see Section 3.1). Therefore, it can be expected to show strong surface activity. This behavior was confirmed, as shown in Fig. 7. According to this data, at only 1 g/L of MHEC dissolved in cement pore solution, surface tension decreases to ~44 mN/m and remains constant until an MHEC concentration of ~10 g/L is reached. Beyond this value which is in the region of the "overlapping" concentration, a further decrease of the surface tension begins (e.g. to 34 mN/m at 20 g/L). This effect can be ascribed to progressing association of polymer molecules. Such process is commonly known to result in lower surface tension [35].

4. Conclusions

The working mechanism of MHEC as water retention agent in cement relies on two separate effects: first, its water sorption capacity and second the formation of hydrocolloidal associated 3D polymer networks. At low MHEC concentrations (≤6 g/L which corresponds to a dosage of 0.32% bwoc), water sorption presents the main mechanism for water retention while above this concentration, the first mechanism is supplemented by the formation of associated polymer networks which are highly effective in retaining water within the cementitious matrix.

The experiments also demonstrate that potential adsorption of MHEC on cement plays no role with respect to its water-retention capability. This way, the working mechanism of MHEC at low dosages differs from those established for HEC and CMHEC, but is consistent with them at higher dosages.

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