

# Competitive Adsorption Between an AMPS<sup>®</sup>-Based Fluid Loss Polymer and Welan Gum Biopolymer in Oil Well Cement

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Received 28 May 2009; accepted 27 November 2009

DOI 10.1002/app.31865

Published online 28 January 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Water-soluble 2-acrylamido-2-methylpropane sulfonic acid (AMPS<sup>®</sup>)-based copolymers are commonly used to provide water retention (fluid loss control) for oil well cement slurries. Here, the fluid loss performance of a CaAMPS<sup>®</sup>-*N,N*-dimethylacrylamide copolymer (CaAMPS<sup>®</sup>-*co*-NNDMA) in the presence of Welan gum, an anionic microbial biopolymer produced by anaerobic fermentation using *Alcaligenes* ATCC 31555 bacteria was investigated at 80°C. Welan gum is used to control unwanted free water development at the surface of the cement slurry. The effectiveness of CaAMPS<sup>®</sup>-*co*-NNDMA fluid loss additive (FLA) solely relies on its high adsorption onto the positively charged surfaces of cement hydrates. Adsorption of the FLA is, however, perturbed by Welan gum. This anionic polysaccharide competes with CaAMPS<sup>®</sup>-*co*-NNDMA for adsorption sites on the cement surface. This effect is surprising because in cement pore solution, Welan gum exhibits a much lower specific anionic charge amount than CaAMPS<sup>®</sup>-*co*-NNDMA. The reason is that Welan gum possesses carboxylate function-

alities, which are much stronger anchor groups than the sulfonate groups present in CaAMPS<sup>®</sup>-*co*-NNDMA. The superiority of the carboxylate groups regarding their affinity to the mineral surface, which possesses insufficiently coordinated Ca atoms is confirmed by a higher calcium binding capability for Welan gum than for the FLA. Thus, Welan gum can reduce effectiveness of CaAMPS<sup>®</sup>-*co*-NNDMA as fluid loss agent by preventing its adsorption or through displacement of already adsorbed FLA molecules from the surface of cement. In multiadmixture systems, which are commonly used in oil well cement, concrete or mortars, competitive adsorption between different additives for surface sites can negatively impact the performance of these additives. Understanding the reasons behind can help to develop more effective admixture systems. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2913–2919, 2010

**Key words:** oil well cement; fluid loss additive; AMPS<sup>®</sup> copolymer; Welan gum

## INTRODUCTION

Zonal isolation is the main purpose of primary cementing. To achieve cement slurries which meet the demanding borehole conditions, such as high temperature, pressure, and salinity, different additives are combined for optimum performance.<sup>1,2</sup> Among the admixtures, which are applied to prevent the loss of water from the cement slurry while being pumped along a porous formation are copolymers of 2-acrylamido-2-methylpropane sulfonic acid and *N,N*-dimethylacrylamide. These synthetic anionic polyelectrolytes achieve fluid loss control by reducing filter cake permeability through polymer adsorption onto the positively charged surfaces of cement hydrates (adsorptive working mechanism).<sup>3,4</sup> It has been shown that while this fluid loss additive

(FLA) works excellent when being the sole admixture, its effectiveness may be impeded when other polymers possessing higher anionic character are present in the cement slurry.<sup>5</sup> As a result of this competitive adsorption, increased fluid loss was observed. An example for an admixture, which perturbs effectiveness of CaAMPS<sup>®</sup>-*co*-NNDMA is acetone-formaldehyde-sulfite (AFS) dispersant. Its molar anionic charge density is approx. 20 times higher than that of the FLA.<sup>6</sup> Consequently, its affinity to the positively charged surface of cement hydrates is much stronger than that of CaAMPS<sup>®</sup>-*co*-NNDMA.

Free water developed at the top of a cement column in the borehole can pose a serious problem for zonal isolation. Free water control agents such as Welan gum are commonly added to the slurry to prevent this undesired effect.<sup>1</sup> Because of the anionic character of this microbial biopolymer, the question arises whether this additive may reduce effectiveness of the AMPS<sup>®</sup>-based FLA through a competitive adsorption mechanism in a similar way as has been described before for anionic AFS dispersant.<sup>4–6</sup>

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TABLE I  
Phase Composition (XRD, Rietveld), Specific Density, Specific Surface Area (Blaine), and  $d_{50}$  Value of API Class G Oil Well Cement Sample

C <sub>3</sub> S (wt %)	C <sub>2</sub> S (wt %)	C <sub>3</sub> A <sub>c</sub> (wt %)	C <sub>4</sub> AF (wt %)	Free CaO (wt %)	CaSO <sub>4</sub> ·2H <sub>2</sub> O (wt %)	CaSO <sub>4</sub> ·1/2 H <sub>2</sub> O (wt %)	CaSO <sub>4</sub> (wt %)	Specific density (kg/L)	Specific surface area (cm <sup>2</sup> /g)	$d_{50}$ value (μm)
59.6	22.8	1.2	13.0	<0.3	2.7 <sup>a</sup>	0.0 <sup>a</sup>	0.7	3.18	3,058	9.8

C<sub>3</sub>S: tricalcium silicate (Ca<sub>3</sub>(SiO<sub>4</sub>)O); C<sub>2</sub>S: dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>); C<sub>3</sub>A<sub>c</sub>: cubic modification of tricalcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>7</sub>); C<sub>4</sub>AF: tetra calcium aluminate ferrite (Ca<sub>4</sub>Al<sub>2</sub>Fe<sub>2</sub>O<sub>10</sub>).

<sup>a</sup> Measured by thermogravimetry.

The goal of this investigation was to clarify the interactions between CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum in cement slurries with respect to the performance of these polymers. For this purpose, fluid loss, rheology and free water content of cement slurries containing FLA and Welan gum were measured at 80°C. To understand the mechanism of interaction, adsorption of CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum when used as a single additive and of combinations of both admixtures on cement was measured. Additionally, the calcium binding capability of the AMPS<sup>®</sup>-based copolymer and Welan gum, resp. was determined.

## EXPERIMENTAL

### Materials

#### Oil well cement

An API Class G oil well cement ("black label", from Dyckerhoff AG, Wiesbaden, Germany) according to the American Petroleum Institute (API) Spec. 10A was used.<sup>7</sup> Phase composition, specific density, specific surface area (Blaine) and particle size ( $d_{50}$  value) of the cement are listed in Table I.

#### CaAMPS<sup>®</sup>-*co*-NNDMA fluid loss polymer

The copolymer of *N,N*-dimethylacrylamide and 2-acrylamido-2-methylpropane sulfonic acid was synthesized by aqueous free radical polymerization according to a method described in the literature.<sup>4,5</sup>

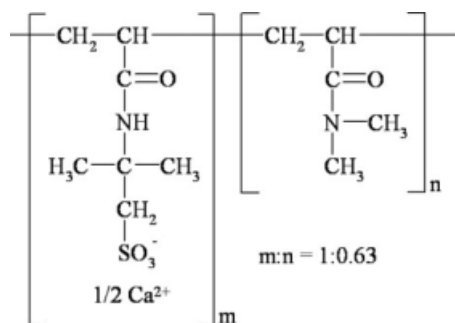


Figure 1 Chemical structure of CaAMPS<sup>®</sup>-*co*-NNDMA fluid loss polymer.

The liquid polymer was drum dried at 150°C, yielding a white powder. Laboratory grade AMPS<sup>®</sup> (Merck-Schuchardt, Darmstadt, Germany) and NNDMA (Sigma-Aldrich Chemical, München, Germany) were used. The chemical structure of CaAMPS<sup>®</sup>-*co*-NNDMA is shown in Figure 1. GPC analysis produced molecular weights for the FLA of approx.  $1.8 \times 10^6$  g/mol ( $M_w$ ) and  $1.2 \times 10^6$  g/mol ( $M_n$ ). Table II lists other characteristic properties (specific anionic charge amount and intrinsic viscosity) of the synthesized FLA, measured in cement pore solution.

#### Welan gum

A commercial sample (Biozan<sup>®</sup>; Kelco Oil Field Group, Houston, TX) was used as obtained. The chemical structure of this anionic polysaccharide is shown in Figure 2. Its molecular weight ( $M_w$ ) was approx.  $1.0 \times 10^6$  g/mol as determined by photometric analysis.<sup>8</sup> Further characteristic properties (specific anionic charge amount and intrinsic viscosity) of Welan gum in cement pore solution are shown in Table II.

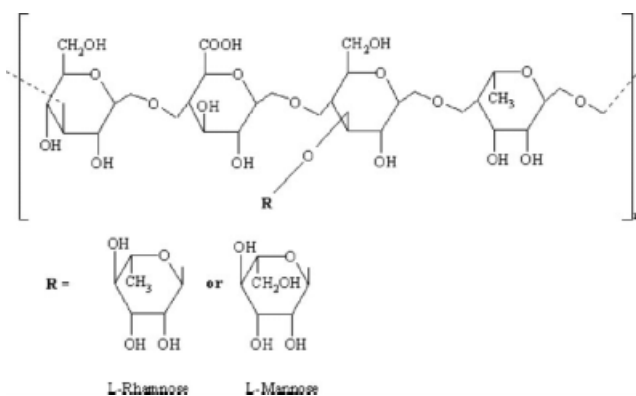
### Instruments and procedures

#### Cement characterization

Phase composition of the cement sample was obtained by X-ray powder diffraction using a diffractometer (Bruker axs D8 Advance; Bruker, Karlsruhe, Germany) with Bragg-Bretano geometry. The instrument is equipped with a scintillation detector using Cu K<sub>α</sub> ( $\lambda = 1.5406$  Å) radiation with a scanning range between 5° and 80° 2 $\theta$ . Specific density of the cement sample was measured on an Ultracycrometer<sup>®</sup>1000 (Quantachrome Instruments,

TABLE II  
Characteristic Properties of CaAMPS<sup>®</sup>-*co*-NNDMA and Welan Gum, Measured in Cement Pore Solution

Polymer	Specific anionic charge amount (C/g)	Intrinsic viscosity at 80°C (L/g)
CaAMPS <sup>®</sup> - <i>co</i> -NNDMA	337	0.32
Welan gum	121	0.65



**Figure 2** Chemical structure of Welan gum biopolymer.

Boynton Beach, FL). The specific surface area of the samples was determined with a Blaine instrument (Toni Technik, Berlin, Germany). The average particle size ( $d_{50}$ ) measurement was carried out using a laser-based particle size analyzer (Cilas 1064, Marseille, France).

#### Polymer characterization

Size exclusion chromatography (Waters Alliance 2695; Waters, Eschborn, Germany) equipped with RI detector 2414 (Waters, Eschborn, Germany) and an 18 angle dynamic light scattering detector (Dawn EOS; Wyatt Technologies, Clinton, IA) was used. CaAMPS<sup>®</sup>-*co*-NNDMA was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany).  $M_w$  and  $M_n$  of the FLA were determined using a 0.2 M NaNO<sub>3</sub> aqueous solution (adjusted with NaOH to pH 9) as an eluant at a flow rate of 1.0 mL/min. The value of  $dn/dc$  used to calculate  $M_w$  and  $M_n$  was 0.156 mL/g (value for polyacrylamide).<sup>9</sup> Thus, the molecular weights of the FLA measured are relative to polyacrylamide.

The specific anionic charge amounts of CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum, resp. were determined in cement pore solution and in 0.1 M NaOH (pH 12.6) with and without calcium ions (0.6 g/L Ca<sup>2+</sup>, added as CaCl<sub>2</sub> 2H<sub>2</sub>O) at room temperature using a PCD 03 pH apparatus (Mütek Analytic, Herrsching, Germany). Charge titration was carried out with 0.001 N solution of poly(diallyl-dimethyl-ammoniumchloride) laboratory grade (BTG Mütek GmbH, Herrsching, Germany) as cationic polyelectrolyte.<sup>10</sup> Kinematic viscosities of polymers dissolved in cement pore solution were measured by an Ubbelohde viscometer (50110/I, Schott, Mainz, Germany) at 80°C.

#### 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, issued by the American Petroleum Institute.<sup>11</sup> The slurries were mixed at a water-to-cement (w/c) ratio of 0.44 and 0.70, resp. using a blade-type laboratory blender manufactured by Waring ( Torrington, CT). Here, cement and the respective polymers were dry blended, added within 15s to the water placed in the Waring blender cup and mixed for 35s at 12,000 rpm. To ensure homogeneous consistency, all slurries were stirred in an atmospheric consistometer (model 1250; Chandler Engineering, Tulsa, OK) for 20 min at 80°C before measurements were taken. Pore solution of cement slurries prepared without polymer addition at 80°C was produced by vacuum filtration (12mbar) using a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany). Testing of cement slurries was generally carried out according to API Specification 10B, issued by the American Petroleum Institute.<sup>11</sup>

#### Rheology

For rheological measurements of the cement slurries, a Couette-type coaxial cylinder rotational viscometer, FANN 35SA (Fann Instruments Company, Houston, TX) equipped with R1 rotor sleeve (rotor radius: 18.415 mm), B1 bob (bob radius: 17.245 mm, bob height: 3.80 cm), and F1 torsion spring was used. The values of viscometer reading are recorded for six speeds of the rotor (3, 6, 100, 200, 300, 600). The value of shear stress  $\tau$  (Pa) is calculated by including the torsion spring factor ( $N$ , cm/degree), the shear stress constant for the effective bob surface (cm<sup>-3</sup>), and the shear rate constant (s<sup>-1</sup>/rpm).<sup>12</sup> The values of yield point (YP) and plastic viscosity (PV) are obtained according to eq. (1), which describes the behavior of a Bingham fluid.

$$\tau = \tau_0 + \mu_p \times \gamma \quad (1)$$

where  $\tau_0$  is the yield point (Pa),  $\mu_p$  is the plastic viscosity (Pa s), and  $\gamma$  is the shear rate (s<sup>-1</sup>).<sup>11</sup>

#### Free water content

Stability of the cement slurries (separation of so-called "bleeding" or free water) was determined at 80°C. For this purpose, the cement slurry was placed in a 250 mL glass cylinder ( $\varnothing$  2.8 cm). The volume of water, which separates at the top of the cement slurry after 2 h was declared free water content.

#### Fluid loss

Static fluid loss was measured at 80°C using a 500 mL high temperature high pressure (HTHP) filter press cell manufactured by OFI Testing Equipment

(Houston, TX). After pouring the homogenized cement slurry into the HTHP cell, a differential pressure of 70bar N<sub>2</sub> was applied at the top of the cell. Filtration proceeded through a 3.5 sq. inch mesh metal sieve placed at the bottom of the cell. The fluid volume collected within 30 min ( $V_{30}$ ) was doubled as described by API RP 10B and regarded as API fluid loss of the corresponding slurry. When dehydration of the cement slurry occurred previous to the test ending, API fluid loss was calculated according to eq. (2).

$$\text{API fluid loss} = 2 \cdot V_t \times \sqrt{\frac{30}{t}} \quad (2)$$

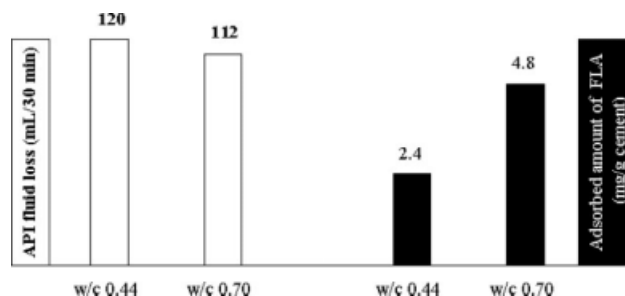
where  $V_t$  (mL) is the filtrate volume collected until dehydration of cement slurry occurred at the time  $t$  (min).<sup>11</sup>

### Adsorption

The adsorbed amounts of admixtures were determined from the filtrate collected in the fluid loss test. Achievement of adsorption equilibrium was confirmed by  $\zeta$ -potential values, which were constant at the time of collecting the filtrate for adsorption measurement. The adsorbed amount was calculated from the difference in the equilibrium concentrations of the polymers present in the liquid phase before and after adsorption (depletion method). When CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum was the sole polymer present in the cement filtrate, its concentration was measured by TOC analysis (High TOC II; Elementar, Hanau, Germany; equipped with CO<sub>2</sub>-detector). When both admixtures were present, CaAMPS<sup>®</sup>-*co*-NNDMA concentration was determined by TN analysis (High TOC II; Elementar, Hanau, Germany; equipped with NO<sub>x</sub>-detector). Adsorbed amount of Welan gum was calculated by subtracting CaAMPS<sup>®</sup>-*co*-NNDMA concentration from the sum of adsorbed CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum measured by TOC analysis. For TOC analysis, the alkaline cement filtrate containing the unadsorbed polymers was adjusted to neutral pH by adding 0.01 M phosphoric acid. Adsorption was confirmed to be the sole reason for FLA depletion through a solubility test. For this purpose, 7.14 g/L of CaAMPS<sup>®</sup>-*co*-NNDMA were dissolved in cement pore solution and stored for 1 day. No precipitation of CaAMPS<sup>®</sup>-*co*-NNDMA was observed. Following this method, 0.86 g/L Welan gum were dissolved in cement pore solution. Again, no precipitation occurred.

### Zeta potential

Zeta potentials of cement slurries were measured at room temperature on an electro acoustic spectrome-



**Figure 3** API fluid loss (white bars) of cement slurries and adsorbed amounts of CaAMPS<sup>®</sup>-*co*-NNDMA (black bars) dosed at 0.5% bwoc as a function of w/c ratio, measured at 80°C.

ter (DT-1200; Dispersion Technology, Bedford Hills, NY) over a period of 30 min.<sup>10</sup> The test systems included the neat cement paste and pastes containing 0.5% bwoc of FLA and 0.06% bwoc of Welan gum. The cement slurries (preparation as described earlier at w/c ratio 0.70) were poured into the 250 mL cup of the spectrometer immediately after mixing in the Waring blender without further homogenization in the atmospheric consistometer.

## RESULTS AND DISCUSSION

### Interaction of CaAMPS<sup>®</sup>-*co*-NNDMA with cement

The relationship between HTHP fluid loss and the amount of CaAMPS<sup>®</sup>-*co*-NNDMA adsorbed on cement was determined at different w/c ratios (0.44 and 0.70, resp.) and 80°C. The results are presented in Figure 3. As can be seen there, the adsorbed amount of the FLA increases with increased w/c ratio (2.4 mg FLA/g cement at w/c 0.44 vs. 4.8 mg FLA/g cement at w/c 0.70). Nevertheless, the resulting fluid loss control of the slurry remains almost constant (120 mL/30 min at w/c 0.44 vs. 112 mL/30 min at w/c 0.70). At higher w/c ratios, additional mixing water is present in the cement slurry. Thus, more capillary pores are formed in the matrix of hydrating cement.<sup>13</sup> To achieve a comparable reduction of filter cake permeability through FLA adsorption, a higher adsorbed amount of CaAMPS<sup>®</sup>-*co*-NNDMA is necessary.

Polymer adsorption was confirmed by zeta potential measurements. Neat cement slurry possesses a zeta potential of approx. -5 mV. When CaAMPS<sup>®</sup>-*co*-NNDMA at 0.5% bwoc dosage was added, the zeta potential decreased to a value of -20 mV. The reason for this effect is the loading of negative charges onto the cement surface caused by adsorption of the anionic polymer. Rheological data of the cement slurry prepared with 0.5% bwoc CaAMPS<sup>®</sup>-*co*-NNDMA shown in Table III demonstrate that at a w/c ratio of 0.70, the cement slurry possesses practically no yield point (YP), leading to sedimentation

**TABLE III**  
**Rheology (Shear Stress) and Free Water Content of Cement Slurries Containing 0.5% bwoc CaAMPS<sup>®</sup>-co-NNDMA and Increasing Dosages of Welan Gum, Measured at 80°C**

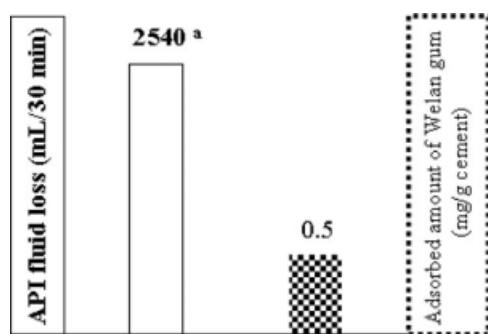
w/c Ratio	Welan gum dosage (% bwoc)	Free water content (mL)	Shear stress (Pa) at different shear rates (s <sup>-1</sup> )						Plastic viscosity $\mu_p$ (mPa·s)	Yield point $\tau_0$ (Pa)
			1022	511	340	170	10.2	5.1		
0.44	0	0	109	75	57	38	7	6	67	6.1
0.70	0	3	16	10	7	4	1	0	12	0.2
0.70	0.06	0	35	21	16	10	3	3	27	2.5

and development of free water. Therefore, such slurry requires stabilization by Welan gum for free water control.

### Interaction of Welan gum with cement

Welan gum is a microbial polysaccharide, which is commonly used in oil well cements and concrete to prevent the formation of free water. It is produced from D-glucose using bacteria from the *Alcaligenes* ATCC 31555 species. Welan gum contains repeating units with randomly distributed L-mannosyl and L-rhamnosyl terminal groups substituted on C3 of every (1→4)-linked glucose unit (Fig. 2).<sup>14</sup> In aqueous solution, this molecule forms a double helix where the side chains fold back on the main chain to form hydrogen bonds with the carboxylate groups.<sup>15</sup> This steric shielding effect provides stability of the double helix against the high Ca<sup>2+</sup> concentrations existing in cement pore solution (~ 0.6 g/L at w/c 0.44, as determined by AAS). Welan gum controls free water formation of cement slurries by increasing their yield point. This way, segregation and sedimentation are prevented.

First, we quantified the adsorption of Welan gum on cement by TOC analysis. The results are shown in Figure 4. There, it becomes obvious that most of the Welan gum added adsorbs (~ 90% adsorption at a dosage of 0.06% bwoc), indicating a very strong



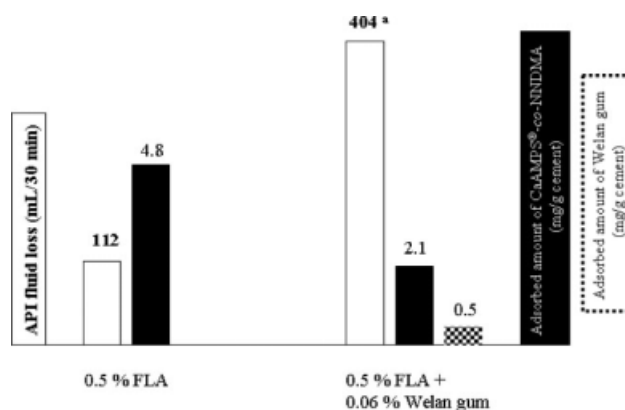
**Figure 4** API fluid loss (white bars) of cement slurries and adsorbed amounts of Welan gum (dotted bars), measured at 0.06% bwoc Welan gum and 80°C (w/c 0.70).<sup>a</sup>Dehydration of cement slurry within less than 30 min.

interaction with cement, in spite of the low anionic charge amount found for this biopolymer (Table II). Adsorption of anionic Welan gum was confirmed by zeta potential measurements. The zeta potential of the cement slurry (-5 mV) becomes more negative when 0.06% bwoc of Welan gum are added (-9.8 mV). This way, it is demonstrated that the higher negative charge of the cement particles is caused by adsorption of this anionic polysaccharide.

Addition of this polysaccharide, however, does not provide any fluid loss control to the cement slurry (API fluid loss (calc.) ~ 2500 mL/30 min at 0.06% bwoc Welan gum; Fig. 4). This result confirms that Welan gum solely acts as viscosity modifier and free water control agent.

### Combination of CaAMPS<sup>®</sup>-co-NNDMA and Welan gum

At first, effectiveness of Welan gum with respect to free water control of cement slurries possessing w/c 0.70 and containing 0.5% bwoc FLA was tested. The results are shown in Table III. There, it becomes obvious that a dosage of only 0.06% bwoc Welan gum is sufficient to prevent any free water. The rheological data indicates that the biopolymer



**Figure 5** API fluid loss (white bars) of cement slurries and adsorbed amounts of CaAMPS<sup>®</sup>-co-NNDMA (black bars) and Welan gum (dotted bars) measured at 80°C (w/c 0.70).<sup>a</sup>Dehydration of cement slurry within less than 30 min.

**TABLE IV**  
**Specific Anionic Charge Amount of CaAMPS<sup>®</sup>-*co*-NNDMA and Welan Gum, respectively Measured in 0.1 M NaOH (pH 12.6) in Presence and Absence of 0.6g/L Ca<sup>2+</sup> (Polymer Concentration: 0.02g/L)**

Polymer	Specific anionic charge amount (C/g)		Reduction of anionic charge of the respective polymer by Ca <sup>2+</sup>
	Water @ pH 12.6	Water @ pH 12.6 plus 0.6g/L Ca <sup>2+</sup>	
CaAMPS <sup>®</sup> - <i>co</i> -NNDMA	368	352	4%
Welan gum	117	87	26%

stabilizes the cement slurry without destroying its pumpability by imparting excessive viscosity. The effect is attributed to the shear-thinning type of rheology provided by Welan gum. It establishes a high yield point (YP) in the cement slurry, which prevents sag of solid particles, whereas the plastic viscosity (PV) is not much increased (Table III).<sup>16</sup>

In a binary additive system containing both CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum, because of its strong interaction with cement the anionic biopolymer may compete with the FLA for adsorption sites and thus negatively impact its fluid loss performance. To investigate, we compared the API fluid loss of cement slurries containing both CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum with the adsorbed amount of each admixture. The results are shown in Figure 5. When used as the sole admixture, CaAMPS<sup>®</sup>-*co*-NNDMA adsorbs in high amount (4.8 mg/g cement) and provides good fluid loss control (112 mL/30 min). When Welan gum is added, however, fluid loss control is decreased substantially. At the same time, the adsorbed amount of CaAMPS<sup>®</sup>-*co*-NNDMA drops (from 4.8 mg/g cement in absence of Welan gum to 2.4 mg/g cement in the presence of 0.06% Welan gum) while Welan gum adsorbs in considerable amount (0.5 mg/g cement). Thus, it becomes clear that Welan gum occupies surface sites on cement hydrates, which then no longer are available for the FLA to adsorb. Consequently, the fluid loss control of the slurries decreases.

The reason behind this effect are the carboxylate functionalities present in Welan gum. They are much stronger anchor groups for adsorption than the sulfonate groups in CaAMPS<sup>®</sup>-*co*-NNDMA, because they possess much stronger complexation ability for calcium.<sup>17</sup> To confirm, we compared the specific anionic charge amount of CaAMPS<sup>®</sup>-*co*-NNDMA and Welan gum in alkaline solution with and without 0.6 g/L calcium ions. The results listed in Table IV show that calcium ions chelate the carboxylate functionalities of Welan gum much more than the sulfonate groups contained in the FLA

polymer. In the presence of Ca<sup>2+</sup>, the anionic charge of Welan gum decreases by 26% vs. only 4% for CaAMPS<sup>®</sup>-*co*-NNDMA. This way, it is confirmed that Welan gum possesses a much stronger calcium binding capability than the AMPS<sup>®</sup>-based FLA. This property explains its more pronounced interaction with calcium atoms present at the surface of cement and hence its high adsorption.

The negative effect of Welan gum on FLA performance can be overcome by a much increased dosage of CaAMPS<sup>®</sup>-*co*-NNDMA. While in the absence of Welan gum only 0.5% bwoc FLA are required to achieve an API fluid loss of 120 mL/30 min at 80°C, the FLA dosage necessary to achieve the same fluid loss increases to 1.1% bwoc when 0.06% bwoc Welan gum are present. The disadvantage of this increased dosage is high cost.

## CONCLUSIONS

CaAMPS<sup>®</sup>-*co*-NNDMA achieves fluid loss control solely by adsorption onto the surfaces of cement particles. When it is hindered or even entirely prevented from adsorption, poor or no fluid loss control is observed.

Adsorption of CaAMPS<sup>®</sup>-*co*-NNDMA may be perturbed by other anionic admixture molecules possessing a stronger affinity to the cement surface than the FLA. Through a competitive mechanism, FLA adsorption may be reduced and hence its performance as FLA decreases. The interaction between competing additives depends on their anionic charge density, the quality of their anchor groups to the binder surface (calcium chelating ability), and their concentrations. When additives possessing the same anchor group are combined, then their molar anionic charge density determines their adsorption behavior. In this case, the additive showing a higher anionic charge density will adsorb more. When additives with chemically different anchor groups are combined, then the calcium binding capability of the anchor groups relative to each other becomes important. Here, we have shown that because of its carboxylate functionalities, which possess high calcium chelating capability, Welan gum can successfully reduce adsorption of CaAMPS<sup>®</sup>-*co*-NNDMA, in spite of Welan gum possessing a much lower anionic charge amount than the FLA. The results clearly demonstrate that the calcium binding capability of an admixture is a key factor, which strongly impacts its interaction with cement and hence its adsorption behavior.

Competitive adsorption between additives and resulting admixture incompatibilities can be addressed by fine-tuning the molecular structures of the polymers with respect to their anionic charge density and the type of their anchor group. This

way, multi-admixture systems with superior performance can be built. Understanding the interactions and working mechanisms provides the key to optimize the performance of these molecules.

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