Effect of Different Anchor Groups on Adsorption Behavior and Effectiveness of Poly(*N,N*-dimethylacrylamide-*co*-Ca 2-acrylamido-2-methylpropanesulfonate) as Cement Fluid Loss Additive in Presence of Acetone–Formaldehyde–Sulfite Dispersant

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ABSTRACT: The impact of various anchor groups on adsorption behavior of AMPS® copolymers was studied. The anchor groups differ in anionic charge density. Copolymer adsorption and water retention of oil well cement slurries achieved from CaAMPS®-*co*-NNDMA in the presence of an acetone–formaldehyde–sulfite (AFS) dispersant were improved by incorporation of minor amounts (~ 1% by weight of polymer) of acrylic acid (CaAMPS®-*co*-NNDMA-*co*-AA), maleic acid anhydride (CaAMPS®-*co*-NNDMA-*co*-MAA), or vinyl phosphonic acid (CaAMPS®-*co*-NNDMA-*co*-VPA), respectively. Performance of these terpolymers was studied by measuring static filtration properties of oil well cement slurries at 27°C and 70 bar pressure. All fluid loss additives possess comparable molar masses and show the same adsorption behavior and effectiveness when no other admixture is present. In the presence of AFS dispersant, however, adsorption of CaAMPS®-*co*-NNDMA and hence fluid loss control is dramatically reduced, whereas effectiveness of CaAMPS®-*co*-NNDMA-*co*-AA is less influenced because of acrylic acid incorporated as additional anchor group. Even more, CaAMPS®-*co*-NNDMA-*co*-MAA combined with AFS allows simultaneous adsorption of both polymers and thus produces good fluid loss control. CaAMPS®-*co*-NNDMA-*co*-VPA no longer allows adsorption of AFS dispersant. This was also confirmed by rheological measurements. The results show that, in a binary admixture system, adsorption of the anionic polymer with anchor groups possessing higher charge density is preferred. Surface affinity of the anchor groups studied increase in the order $-SO_3^- \rightarrow -COO^- \rightarrow$ vic-$(-COO^-)_2 \rightarrow -PO_3^{2-}$. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3889–3894, 2007

Key words: water-soluble polymer; polyelectrolytes; fluid loss additive; oil well cement; adsorption

INTRODUCTION

Cementing casing into the borehole is one of the most important operations performed in the construction of an oil, gas, or geothermal well.[1] Primary objectives of cementing are to provide a stable borehole, keep the casings in place, prevent corrosion from formation water, and, most important, to avoid migration of fluids and gases up or down the borehole to other formations (''zonal isolation''). Nowadays, combinations of admixtures are frequently used in oil well cementing to adjust the complex properties of cement slurries under harsh borehole conditions such as high temperature, pressure, and salinity. High temperature stable fluid loss additives (FLAs), e.g., copolymers of Ca 2-acrylamido-2-methylpropane sulfonic acid and *N,N*-dimethylacrylamide (CaAMPS®-co-NNDMA), are added to the cement to prevent water loss from the slurry to the porous formation.[2–6] An acetone–formaldehyde–sulfite (AFS) based dispersant is commonly used to reduce the viscosity of the cement slurry during mixing and pumping over a distance of several kilometers. In previous work, incompatibility between CaAMPS®-*co*-NNDMA and AFS was found, resulting in a dramatic increase of cement fluid loss in the binary admixture system.[7] The reason being that AFS reduces CaAMPS®-*co*-NNDMA adsorption. FLA effectiveness is impeded because of competition between these two admixtures for limited adsorption area on the positively charged surface of cement hydrates.[8] It was also found that CaAMPS®-*co*-NNDMA achieves fluid loss control by reducing filter cake permeability.

Goal of this investigation was to study the impact of different anchor groups in FLA with respect to admixture compatibility between FLA and AFS and effective fluid loss control. Higher adsorption and better effectiveness of CaAMPS®-*co*-NNDMA in the presence of AFS was to be achieved by introducing

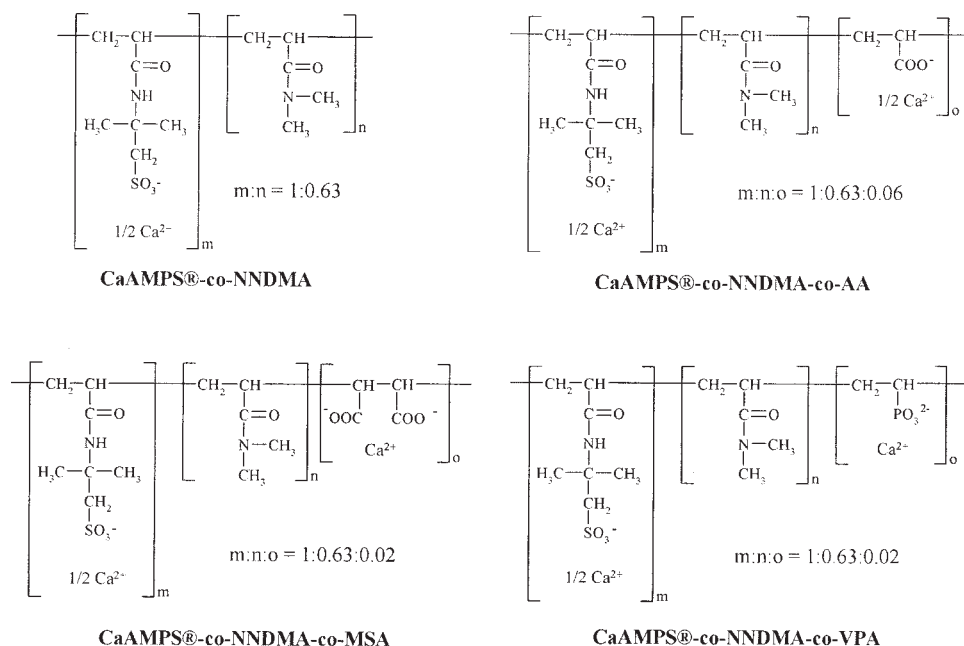*Correspondence to:* J. Plank (johann.plank@bauchemie.ch. tum.de).

Figure 1 Chemical structures of synthesized CaAMPS®-*co*-NNDMA and CaAMPS®-*co*-NNDMA-*co*-X terpolymers (X = AA, MSA, VPA).

additional, stronger anchor groups, namely —COO⁻, vic-(—COO⁻)₂, and —PO₃²⁻, respectively, into CaAMPS®-*co*-NNDMA. Fluid loss control and rheology of cement slurries containing such modified CaAMPS®-*co*-NNDMA terpolymers in combination with AFS were measured. To understand the mechanism of interaction, adsorption of each admixture by itself and in the combination were determined. The impact of the negative charge density in anchor groups and their influence on the adsorption of anionic polymers on cement surface is discussed.

EXPERIMENTAL

Synthesis and characterization of FLAs

First, a binary copolymer of *N*,*N*-dimethylacrylamide (NNDMA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS®) was prepared as reference material and designated CaAMPS®-*co*-NNDMA. Then ternary copolymers of NNDMA and AMPS® with acrylic acid (AA), maleic acid anhydride (MAA), and vinyl phosphonic acid (VPA), respectively, were synthesized. NNDMA was obtained from ç-Aldrich Chemical Co. (Munich, Germany). AMPS®, AA, MAA, and VPA were obtained from Merck-Schuchardt (Darmstadt, Germany). CaAMPS®-*co*-NNDMA, CaAMPS®-*co*-NNDMA-*co*-AA, CaAMPS®-*co*-NNDMA-*co*-MAA, and CaAMPS®-*co*-NNDMA-*co*-VPA were prepared by the same aqueous solution polymerization technique described in a previous work.[7] Monomers (molar ratio AMPS® : NNDMA = 1 : 0.63; AMPS® : NNDMA : AA = 1 : 0.63 : 0.06;

AMPS® : NNDMA : MAA = 1:0.63:0.02; AMPS® : NNDMA : VPA = 1 : 0.63 : 0.02) were dissolved in degassed, distilled water to give a 12.0 wt % solution. Nitrogen gas was bubbled through the reaction mixture for 30 min at 25°C with slow stirring. After heating to 60°C, 0.15% (by weight of monomer) ammonium persulfate in aqueous solution was added drop wise to the reaction mixture to initiate polymerization. The reaction flask was kept at 60°C for 2 h with constant stirring of the solution. During polymerization, the reaction mixture became viscous. The solution was diluted with water thrice its volume and neutralized with 2% Ca(OH)₂ solution. The polymer solutions had a solids content of 4.1 wt %, determined by infrared balance (Sartorius, Germany). Chemical structures of the synthesized FLAs are presented in Figure 1.

Molecular weights (M_w, M_n) of synthesized FLAs were determined by gel permeation chromatography (GPC) using $0.2M$ NaNO₃ aqueous solution (adjusted with NaOH to pH = 9) as an eluant at a flow rate of 1.0 mL/min. FLA solution was filtered through a 5 μm filter. GPC spectrum was measured on Waters Alliance 2695 using Aquagel precolumn and two Aquagel-OH 60 columns from (Polymer Laboratories) with RI-detector 2414 (Waters) using an 18 angle dynamic light scattering detector (Wyatt Dawn EOS) and dn/dc = 0.156 mL/g (value for polyacrylamides).[9]

The anionic charge amounts of FLAs in cement pore solution were determined by charge titration with a PCD 03 pH (Mütek Analytic, Germany) using poly(diallyl-dimethyl-ammonium-chloride) as cationic polyelectrolyte. The properties of FLAs are listed in Table I.

TABLE I
Characteristic Properties of Co- and Terpolymers (FLAs) and Anionic Dispersant (AFS)

| Polymer | Molecular weight | | Poly-dispersity index M_w/M_n | Radius of gyration Rg_w (nm) | Anionic charge density ϵ of polymer in cement filtrate (C/g) |
	M_w (g/mol)	M_n (g/mol)			
CaAMPS®-co-NNDMA	1,672,000	1,054,000	1.6	68.4	361
CaAMPS®-co-NNDMA-co-AA	1,403,000	1,050,000	1.4	58.8	389
CaAMPS®-co-NNDMA-co-MSA	1,455,000	1,040,000	1.4	62.0	384
CaAMPS®-co-NNDMA-co-VPA	1,728,000	1,170,000	1.5	69.5	381
AFS	112,500	19,730	5.7	10.5[a]	321

[a] Values < 12 nm are not accurate.

Synthesis and characterization of AFS

Sythesis of AFS polycondensate was carried out according to Aignesberger and Plank, which is also reported in previous work.[7,10,11] A possible chemical structure of AFS derived from IR and ^{1}H NMR data is presented in Figure 2.

Molecular weight (M_w, M_n) of AFS was determined with GPC measurement (Table I). The polymer was analyzed in $0.1M$ NaNO$_3$ aqueous solution (adjusted with NaOH to pH = 12) as an eluant at a flow rate of 1.0 mL/min. The AFS solution was filtered through a 0.2 μm filter and measured on Alliance 2695 (Waters) using Ultrahydrogel 500, 250, 120 columns (Waters) with RI-detector 2414 (Waters) and a 3 angle dynamic light scattering detector (Dawn EOS, Wyatt Technologies). A dn/dc of 0.135 mL/g (value for poly(ethylene oxide))[12] was applied.

The anionic charge amount of AFS in cement pore solution was determined by charge titration with a PCD 03 pH (Mütek Analytic, Germany) and poly (diallyl-dimethyl-ammonium-chloride) as cationic polyelectrolyte. The properties of AFS are listed in Table I.

Cement slurry preparation

Cement slurries were prepared according to API Specification 10 B using API Class G oil well cement and deionized water.[13] The cement slurry was mixed at a water-to-cement ratio of 0.44 using a Waring Blender. To ensure homogeneous consistency, all slurries were prepared at ambient temperature and then stirred in an atmospheric consistometer at 27°C for 20 min. Phase composition, specific density, particle size (d_{50}), and specific surface area of the oil well cement sample (Dyckerhoff Class G, black label) are presented in Table II.

API static fluid loss

Static fluid loss was determined following API RP 10B procedure using a high temperature high pressure filter press at 70 bar differential pressure and 27°C. The fluid volume collected within 30 min (V_{30}) was doubled as described by API RP 10B and designated API fluid loss of the corresponding cement slurry. It represents the effectiveness of the FLA. The lower the fluid loss, the more effective is the FLA.

Rheological measurements

Rheology of cement slurry was determined following API RP 10A procedure using a FANN 35SA viscometer. Shear stress (lbs/100 ft^2) was measured for shear rates of 600, 300, 200, 100, 6, and 3 rpm.[14] It represents the effectiveness of the AFS. The lower the shear stress at a given shear rate, the more effective is the AFS dispersant.

Adsorption measurements

The adsorbed amount of admixture was determined from the filtrate collected in the fluid loss test. Achievement of adsorption equilibrium was checked by comparing polymer adsorption in cement slurry stirred for 20 min in the atmospheric consistometer with slurry which was not stirred and measured immediately after mixing. In both cases, the same values for adsorbed amount of polymers were found. Equilibrium was also confirmed by ζ-potential numbers which are 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 in the liquid phase before and after adsorption. When only FLA was present in the cement filtrate, its concentration was measured by TOC analysis (Elementar High TOC II with CO$_2$-detector). When both admix-
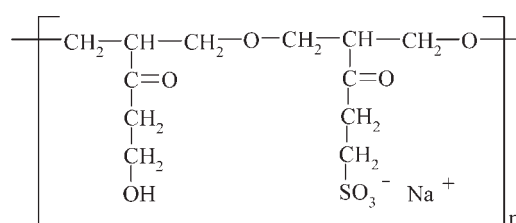

Figure 2 Proposed chemical structure of AFS dispersant.

TABLE II
Phase Composition (XRD, 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 %)	$CaSO_4 \cdot 1/2\ H_2O$ (wt %)	$CaSO_4$ (wt %)	Specific density (kg/L)	Specific surface area (m²/kg)	d_{50}-value (μm)
64.5	16.0	1.0	14.5	0.1	3.0[a]	0.0[a]	0.0	3.18	305.8	9.8

[a] Measured by TG.

tures were present, FLA concentration was determined by TN analysis (Elementar High TOC II with NO-detector). Adsorbed AFS was determined by subtracting FLA concentration from the sum of adsorbed FLA and AFS measured by TOC analysis. For TOC analysis, the alkaline cement filtrate containing the unadsorbed polymers obtained from the fluid loss test was adjusted to neutral pH by adding 0.01M phosphoric acid.

RESULTS AND DISCUSSION

Molecular weight and polymer architecture of FLA terpolymers

All modified FLAs have molecular weights and gyration radii similar to those of CaAMPS®-co-NNDMA. Obviously, the addition of minor amounts of AA, MAA, and VPA does not change the polymerization process. Thus the only major difference between all FLAs lies in type, number, and steric arrangement of the anchor groups.

Distribution of the monomers holding the new anchor groups (AA, MAA, and VPA) along the backbone of CaAMPS®-co-NNDMA are important for the adsorbed conformation of modified FLAs. Acrylic acid, for example will prefer homopolymerization because Q and e values for AA and AMPS® are completely different (see Table III).[15] Therefore, AA will form blocks within CaAMPS®-co-NNDMA-co-AA. In this copolymer, AMPS® and NNDMA show an alternating arrangement along the trunk of the molecule, because of their inverse e values (see Table III). The same as for AA can be expected for MAA in CaAMPS®-co-NNDMA-co-MAA, since Q and e values for MAA and AMPS® are completely different. Vinyl phosphonic acid, however, polymerizes ideally with AMPS® since Q values for VPA and

AMPS® are similar and e values have different signs (see Table III). This behavior also explains the higher molecular weight for CaAMPS®-co-NNDMA-co-VPA, when compared with the other FLAs. The result is a statistical terpolymer with phosphonic anchor groups distributed statistically along the polymer trunk. For such terpolymer, a "train" type adsorbed conformation on cement surface is more likely than for the block-type copolymers containing AA or MAA.

Fluid loss control and adsorption of FLAs

From cement slurries containing the FLA polymers, static fluid loss volumes and the adsorbed amount of FLA polymer was determined. Figure 3 shows that, at a dosage of 0.5 by wt % of cement (bwoc), all FLAs have practically the same API fluid loss (38–42 mL/30 min). Also, adsorbed amounts of FLA polymers are the same (4.6 mg/g). This is in line with previous work in which a direct relationship between the volume of fluid loss and adsorbed amount of FLA polymer was found.[7]

FLA behavior in the presence of AFS

For combinations of 0.5% bwoc FLA with 0.2% bwoc AFS, fluid loss volumes, adsorbed amount of each admixture, and cement slurry rheology were measured. The relationship between API fluid loss volumes and adsorbed amounts of FLA and AFS are shown in Figure 4. CaAMPS®-co-NNDMA produces

TABLE III
Q and e Values of the Monomers Used for Preparation of FLAs[15]

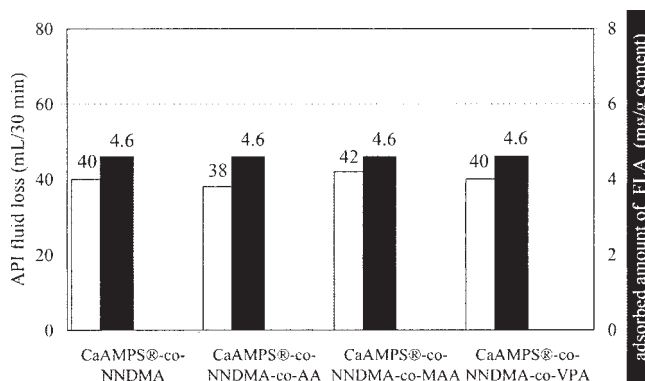| Monomer	Q	e
AMPS®	0.39	0.22
NNDMA	0.41	−0.26
AA	0.83	0.88
MAA	0.86	3.69
VPA	0.24	−0.25

Figure 3 API fluid loss (white bars) and adsorbed amount (black bars) of synthesized FLA polymers (FLA dosage: 0.5% bwoc).
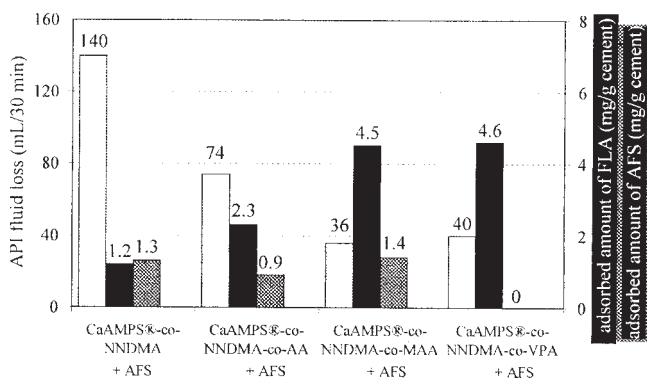
Figure 4 API fluid loss (white bars) and adsorbed amount of FLA (black bars) and AFS (dotted bars) for different FLA polymers (dosages: FLA 0.5% bwoc, AFS 0.2% bwoc).
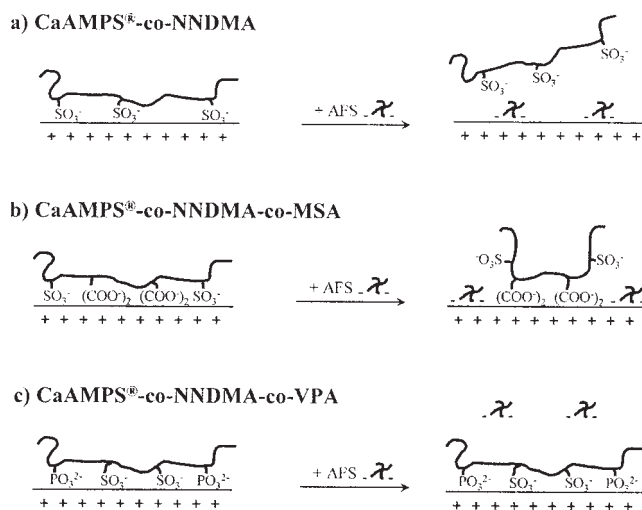

Figure 5 Schematic illustration of proposed adsorbed conformation of synthesized FLA polymers on cement surface in absence and presence of AFS dispersant.

an insufficient fluid loss of 140 mL/30 min since its adsorbed amount is only 1.2 mg/g. Note that in absence of AFS, adsorbed amount of FLA was 4.6 mg/g. In presence of CaAMPS®-co-NNDMA, adsorbed amount of AFS is 1.3 mg/g and 1.4 mg/g in absence of FLA. Obviously, AFS shows higher affinity to cement surface. Hence, its adsorption is preferred over CaAMPS®-co-NNDMA adsorption. AFS adsorption was also confirmed by rheological mesurements of the cement slurry. Upon addition of 0.2% bwoc AFS to a cement slurry holding 0.5% bwoc CaAMPS®-co-NNDMA, shear stresses determined at different shear rates are reduced significantly, indicating better flowability of the cement paste (Table IV).

CaAMPS®-co-NNDMA-co-AA, however, adsorbs in higher amount (2.3 mg/g) than CaAMPS®-co-NNDMA (1.2 mg/g) when AFS is present. Corre-

TABLE IV
Rheology (Shear Stress) of Cement Slurries Containing Combinations of Synthesized FLAs at 0.5% bwoc Dosage with 0.2% bwoc AFS Dispersant at Different Shear Rates

Admixture combination	Shear stress (lbs/100 ft^2)[a] shear rate (rpm) 600-300-200-100- 6- 3
Without Additive	122- 83- 69- 54-23-17
AFS	55- 30- 22- 18- 6- 5
CaAMPS®-co-NNDMA	286-170-126- 75- 8- 6
CaAMPS®-co-NNDMA+AFS	257-151-109- 62- 6- 4
CaAMPS®-co-NNDMA-co-AA	300-190-138- 81- 8- 5
CaAMPS®-co-NNDMA-co-AA +AFS	287-169-122- 70- 7- 4
CaAMPS®-co-NNDMA-co-MAA	276-169-124- 73- 8- 6
CaAMPS®-co-NNDMA-co-MAA +AFS	291-173-126- 74- 9- 6
CaAMPS®-co-NNDMA-co-VPA	>300-212-159- 98-20-18
CaAMPS®-co-NNDMA-co-VPA +AFS	>300-225-176-106-25-25

[a] Measured on FANN 35SA rheometer (FANN Instruments, Houston/TX).

spondingly, in the binary admixture system the adsorbed amount of AFS decreases (0.9 mg/g). Higher adsorption of CaAMPS®-co-NNDMA-co-AA in presence of AFS is due to the additional carboxylate groups introduced by AA. They possess higher anionic charge density than sulfonate groups. Therefore, they provide stronger anchor groups for the FLA. Because of increased FLA adsorption, API fluid loss of CaAMPS®-co-NNDMA-co-AA is better than for CaAMPS®-co-NNDMA (74 mL/30 min vs. 140 mL/30 min) (see Fig. 4). Rheological measurements of the cement slurry with CaAMPS®-co-NNDMA-co-AA and AFS confirm AFS adsorption and dispersing effectiveness (Table IV).

For the combination CaAMPS®-co-NNDMA-co-MAA and AFS, no change in adsorbed amounts of each polymer versus the single admixture system is observed (Fig. 4). Hence, CaAMPS®-co-NNDMA-co-MAA and AFS can adsorb simultaneously on the cement surface in the presence of each other. The dicarboxylate groups of MAA in CaAMPS®-co-NNDMA-co-MAA provide stronger anchor groups than single carboxylate groups in CaAMPS®-co-NNDMA-co-AA, thus it can compete with AFS for adsorption sites. At the same time, the adsorbed amount of AFS is still high (1.4 mg/g; see Fig. 4). This higher surface coverage with polymer can be explained by a change of the adsorbed conformation of CaAMPS®-co-NNDMA-co-MAA from "train" to "loop" or "tail" type when AFS is present. Also, fluid loss control slightly improves from 42 mL/30 min without AFS (see Fig. 3) to 36 mL/30 min (see Fig. 4) in the binary admixture system, even though adsorption of CaAMPS®-co-NNDMA-co-MAA does not increase. It is thought that the change from "train" to a less rigid adsorbed conformation ("loop" or "tail") of CaAMPS®-co-NNDMA-co-MAA reduces

cement filter cake permeability more effectively and thus produces lower filtrate volumes (see Fig. 5).

By incorporation of VPA, CaAMPS®-*co*-NNDMA-*co*-VPA possesses anchor groups with the highest anionic charge density. As expected, adsorption of CaAMPS®-*co*-NNDMA-*co*-VPA is not influenced by AFS and fluid loss of the cement slurry is also retained. Even more, CaAMPS®-*co*-NNDMA-*co*-VPA shows such a high affinity to the cement surface that AFS adsorption is now prevented. Thus, the CaAMPS®-*co*-NNDMA-*co*-VPA/AFS binary system represents the inversion of the original combination of CaAMPS®-*co*-NNDMA with AFS, where AFS was displacing CaAMPS®-*co*-NNDMA on the surface. Obviously, the phosphonate groups in CaAMPS®-*co*-NNDMA-*co*-VPA provide such a strong interaction with the positively charged cement surface that the FLA now can successfully compete with AFS. It can be assumed that CaAMPS®-*co*-NNDMA-*co*-VPA is adsorbed in a ''train'' type conformation. Thus, it achieves complete coverage of cement surface and prevents additional adsorption of AFS molecules (see Fig. 5).

CONCLUSIONS

Adsorption and fluid loss control of poly(*N,N*-dimethylacrylamide-*co*-Ca 2-acrylamido-2-methylpropanesulfonate) in cement paste containing an AFS dispersant was dramatically improved by introducing into the FLA polymer minor amounts of additional anchor groups possessing higher anionic charge density. The following order of surface affinity for different anchor groups was established: $-SO_3^-$ < $-COO^-$ < $-$vic$-$ $(COO^-)_2$ < $-PO_3^{2-}$. Stronger anchor groups may not only result in higher adsorbed amount, but also may change the adsorbed conformation of the FLA. Measurement of cement fluid loss achieved with different synthesized FLAs confirms the adsorptive working mechanism established in previous work. The adsorption of anionic polymers on the positive cement surface or cement hydrate phases is electrostatic in nature.[16,17] In situations of competitive adsorption between two anionic polymers, adsorption of the polymer possessing stronger anchor groups is favored. Thus, ''incompatibility'' problems between admixtures can be addressed by fine-tuning their molecular structure with respect to the quality of their anchor groups. Relatively minor changes in type, number, and anionic charge density of the anchor group can result in significantly different adsorption behavior, adsorbed conformation and effectiveness of a polyelectrolyte. The overall specific anionic charge density of AMPS® copolymers is less important for their adsorption behavior than the type of anchor groups contained in the macromolecule.

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