

Polyelectrolyte Complexes from Polyethylene Imine/Acetone Formaldehyde Sulfite Polycondensates: A Novel Reagent for Effective Fluid Loss Control of Oil Well Cement Slurries

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Received 6 May 2010; accepted 20 August 2010

DOI 10.1002/app.33228

Published online 2 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: When used by itself, polyethylene imine (PEI) does not perform well as cement fluid loss additive. Its combination with acetone formaldehyde sulfite (AFS) polycondensate, however, exhibits excellent filtration control. The mechanism underlying this synergistic effect was studied and the conditions producing best results were determined. For optimum performance, PEI and AFS must be reacted with each other to yield a polyelectrolyte complex (PEC) ($d \sim 5\text{--}10 \mu\text{m}$), which effectively plugs the pores of the cement filter cake. Composition, size, and effectiveness of the PEC are strongly influenced by the anionic charge amount of the AFS dispersant. Ionic interactions between cationic imine functionalities of PEI and anionic sulfonate groups existing in AFS were confirmed by conductivity, infrared, zeta potential, and particle size measurements. For

AFS samples possessing different degrees of sulfonation, the largest particle size and hence best fluid loss performance of the PEC was found to occur at a PEI:AFS molar ratio, which corresponds to neutral charge. Occurrence of large PEC particles ($d \sim 5 \mu\text{m}$) within the cement filter cake pores was visualized by scanning electron microscopy, and their stability in highly alkaline cement pore solution was confirmed by particle size measurement. Other anionic polyelectrolytes may be used to yield such PECs with PEI to provide effective fluid loss control for cement slurries. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1262–1275, 2011

Key words: polyethylene imine; acetone formaldehyde sulfite polycondensate; polyelectrolytes; fluid loss additive; oil well cement

INTRODUCTION

Polyethylene imine (PEI) is a synthetic polymer, which is used in various industrial applications including food preparations, coatings, paint and glue systems, and, in particular, the paper industry.^{1–3} There, it is applied to provide water retention and as a flocculant for the negatively charged fibers and CaCO_3 particles.^{4,5} Industrially, PEI is made by catalytic polymerization of ethylene imine monomer. Depending on the specific process conditions, either low molecular weight PEI possessing a linear structure or high molecular weight (HMW) PEI exhibiting a branched or hyperbranched structure are obtained. Commercial HMW PEI typically possesses primary, secondary, and tertiary amino groups.^{6,7} Its approximated chemical structure is displayed in Figure 1. The main chain of HMW PEI shows branch points at about every 3 to 3.5 monomer units and contains secondary and tertiary amino groups. Whereas, the

side chain consists of ethylene imine units with secondary and terminating primary amino groups.^{7,8} In HMW PEI, the ratio of primary-to-secondary-to-tertiary amino groups typically is $\sim 1 : 2 : 1$.

Generally, PEI represents a polybase, which exhibits a weak polyelectrolyte character in unbuffered water but behaves as a strong polyelectrolyte in acidic environment.⁹ The latter effect is owed to protonation of the amino functionalities. The degree of protonation of the PEI amino groups (α) varies with pH of the solution. It can be calculated based on the principle of electroneutrality valid for all charge-bearing species existing in solution. For example, when HCl was added to a PEI solution, α is attainable as follows (Equation 1):⁷

$$\alpha = [(c_{\text{H}^+}^+)_{\text{added}} - (c_{\text{H}^+}^+)_{\text{free}} + (c_{\text{OH}^-}^-)_{\text{free}}]/[\text{EI}] \quad (1)$$

where $(c_{\text{H}^+}^+)_{\text{added}}$ is the concentration of HCl added (in mol/L), whereas $(c_{\text{H}^+}^+)_{\text{free}}$ and $(c_{\text{OH}^-}^-)_{\text{free}}$ are the concentrations of free protons and hydroxyl ions existing in this solution. They can be determined from pH measurement of the solution by using the relationship $(c_{\text{H}^+}^+)_{\text{free}} \cdot (c_{\text{OH}^-}^-)_{\text{free}} = 1.0 \cdot 10^{-14} \text{ mol}^2/\text{L}^2$. Whereas, [EI] represents the PEI concentration expressed as monomeric equivalents of ethylene imine present in the

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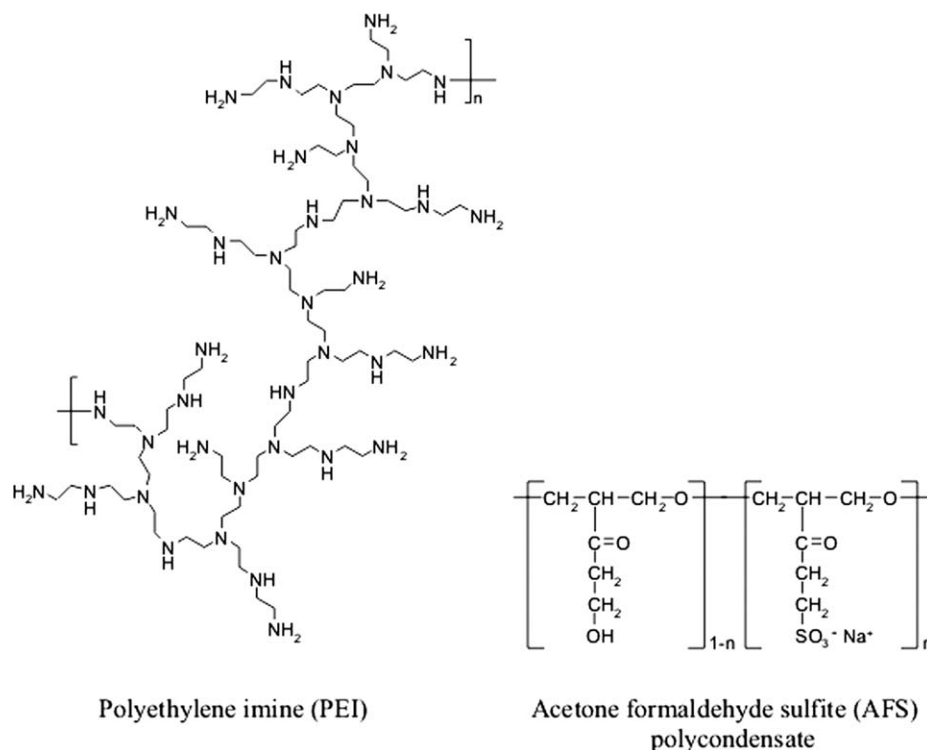


Figure 1 Chemical structures of PEI and AFS polycondensate samples.

sample. For branched PEI at pH values of 3, 7, and 10, the values of α were reported as 0.71, 0.22, and 0.01, respectively.⁷ Thus, at pH 3, 71% of all amine groups present are protonated, whereas at pH 10, the molecule exists practically in its deprotonated form. Lindquist and Stratton⁶ studied the influence of pH on the molecular size of PEI. They found that a fully protonated PEI macromolecule attains a more stretched conformation, compared with its uncharged counterpart, which is more coiled. Consequently, the steric size of protonated PEI was found to exceed that of the deprotonated molecule by 65%.

Polyelectrolyte complexes (PECs) are a large family of associative compounds which, in an ideal case, result from electrostatic interaction between cationic and anionic oligomeric or polymeric species.¹⁰ Additionally, PECs can form through ion mediation, or by hydrophobic (micelle type) cooperative interaction between polyelectrolytes and surfactants. In recent years, polymer-surfactant systems have found increased attention, owed to their widespread use in industries as diverse as cosmetics, detergents, paints, coating fluids, inks, and drug delivery systems. For example, a number of studies was performed to investigate the interaction between PEI and sodium dodecyl sulfate (SDS), an anionic surfactant.^{9,11,12} They revealed that association between PEI and SDS not only relied on electrostatic attraction. For example, Winnik et al.⁹ presented evidence for occurrence of both electrostatic and micelle-like collective inter-

actions, with the latter dominating at high pH. From calorimetric data, Li et al.¹³ confirmed a nonelectrostatic contribution to PEI/SDS interaction. The role of nonelectrostatic interaction also was presented for combinations of PEI with cationic surfactants such as cetyl trimethyl ammonium bromide.¹⁴

Interestingly, in another work Winnik et al.¹⁵ observed an increase in pH when PEI was combined with SDS. This effect was attributed to the consumption of protons by PEI and subsequent PEC formation, as presented by equation 2. Accordingly, PEI can exist in its protonated form even at high pH.



Since many years, PEI is being used as an effective cement fluid loss additive when combined with an anionic dispersant. For example, in a patent Brothers and Burkhalter¹⁶ describe a cement slurry possessing low fluid loss, which is based on PEI and a naphthalene sulfonic acid-formaldehyde polycondensate. According to them, PEI needs to be combined with an anionic additive to achieve its performance. Whereas, the mechanism by which such combinations exercise their effect was not presented.

Thus, the goal of our investigation was to identify the fundamental mechanism underlying the fluid loss performance of PEI in cement slurries. The mechanism was probed for individual PEI and a combination of PEI with a variety of acetone

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

C_3S^a (wt%)	C_2S^b (wt%)	$C_3A_c^c$ (wt%)	C_4AF^d (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 (cm ² /g)	d_{50} value (μm)
59.6	22.8	1.2	13.0	<0.3	2.7 ^e	0.0 ^e	0.7	3.18	3058	9.8

^a C_3S : tricalcium silicate, $Ca_3(SiO_4)O$.

^b C_2S : dicalcium silicate, $Ca_2(SiO_4)$.

^c C_3A_c : cubic modification of tricalcium aluminate, $Ca_9Al_6O_{18}$.

^d C_4AF : tetra calcium aluminate ferrite, $Ca_4Al_2Fe_2O_{10}$.

^e Measured by thermogravimetry.

formaldehyde sulfite (AFS) polycondensates possessing different degrees of sulfonation (DS).

First, cement fluid loss provided in absence and presence of AFS was measured. Next, impact of the polymer mixing method, the reaction time, the weight ratio between PEI and AFS as well as the influence of the anionic charge amount present in the AFS sample on fluid loss control were examined.

In the second part, the nature of the PEI/AFS interaction was investigated. Here, insight into electrostatic contributions to the formation of PEI/AFS PEC was obtained via conductivity and pH measurements. Furthermore, the impact of variations in the anionic charge amount of AFS on charge neutralization between PEI and AFS and the particle size of the resulting PEC were probed. Based on those results, an optimum preparation method for the PEC to be used in cement, and a model describing the individual steps leading to its formation are presented.

EXPERIMENTAL

Materials

Oil well cement

An API Class G oil well cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) according to American Petroleum Institute (API) Specification 10 A was used.¹⁷ Phase composition, specific density, average particle size (d_{50} value), and specific surface area of the sample are presented in Table I.

PEI

Branched PEI (Epomin[®]-1000) was purchased from Nippon Shokubai, Osaka, Japan in the form of a 30 wt% aqueous solution. According to the manufacturer's specification, this sample contains primary, secondary, and tertiary amine groups at a molar ratio of 1 : 2 : 1.

AFS polycondensate

Four AFS polycondensate samples were synthesized from acetone, formaldehyde, and sodium sulfite in a base-catalyzed aldol reaction following a previously

published method.¹⁸ In all AFS samples prepared, the molar ratio of acetone:formaldehyde was kept constant at 1 : 3, whereas the sulfite content varied and was set at 0.5; 0.4; 0.3; and 0.2, respectively. Thus, the AFS samples mainly differ in the DS and in the resulting specific anionic charge amount. Like most polycondensates, the AFS samples studied here exhibit broad molecular weight distributions (Polydispersity index of 3.6–5.6) and Burchard parameters of 1.1–1.4. This indicates a star-shaped, branched structure for the dispersant molecules. Table II lists the characteristic properties of all synthesized AFS samples.

PES-Na

In charge titration experiments, a 0.001N solution of anionic sodium polyethylene sulfonate (PES-Na) obtained from BTG Mütek GmbH (Herrsching, Germany) was used as anionic polyelectrolyte.

Poly(Dadmac)

In charge titration experiments, a 0.001N solution of poly(diallyl dimethyl ammonium chloride) obtained from BTG Mütek GmbH (Herrsching, Germany) was used as cationic polyelectrolyte.

Welan gum

Biozan[®], a commercial biogum sample obtained from CP Kelco (Houston, TX) was used. Welan gum is a microbial polymer produced by fermentation using a bacterial strain of the species *Alcaligenes ATCC 31555*. It yields an anionic polysaccharide with carboxylate groups directly attached to anhydro glucose rings.¹⁹ According to supplier information, this sample possesses a molecular weight (M_w) of $\sim 1.0 \times 10^6$ g/mol.

Instruments

Adsorption

A high TOC II instrument from Elementar (Hanau, Germany) with CO₂ detector was used.

TABLE II
Characteristic Properties of Polyethylene Imine and Acetone Formaldehyde Sulfite Polycondensate Samples

Designation of polymer	Molar ratio acetone: formaldehyde:sulfite	Molecular weight		Polydispersity index M_w/M_n	Radius of gyration R_g (nm)	Burchard parameter $\rho R_g/R_h$	Specific charge amount ϵ (C/g)	
		M_w (g/mol)	M_n (g/mol)				In water	In cement pore solution
PEI	–	230,000	74,000	3.1	41	2.0	+260	+21
0.2 AFS	1 : 3 : 0.2	56,000	15,000	3.6	6	1.1	–90	–110
0.3 AFS	1 : 3 : 0.3	74,000	14,000	5.3	7	1.1	–170	–180
0.4 AFS	1 : 3 : 0.4	63,000	12,000	5.6	14	1.4	–205	–210
0.5 AFS	1 : 3 : 0.5	66,000	17,000	3.7	9	1.4	–260	–270

API filtration cell

A 500 mL OFITE high temperature high pressure filter press (Part No. 171-00-C, OFI Testing Equipment Inc., Houston, Texas) was used.

Cement testing

Quantitative phase composition of the cement sample was established using an X-ray diffraction instrument (D8 Advance, Bruker AXS, Karlsruhe, Germany) with Bragg-Bretano geometry and Topas 3.0 software for Rietveld refinement. The diffractometer is equipped with a scintillation detector using CuK_α ($\lambda = 1.5406 \text{ \AA}$) radiation with a scanning range between 5 and $80^\circ 2\theta$ at a scanning speed of 0.5 s/step (with $0.008^\circ/\text{step}$). Specific density of the cement was determined on an Ultracycrometer[®] 1000 (Quantachrome Instruments, Boynton Beach, FL). Average particle size (d_{50}) was measured using a laser-based particle size analyser (Cilas 1064, Marseille, France). Specific surface area was analyzed using a Blaine instrument (Toni Technik, Berlin, Germany). A blade type laboratory blender manufactured by Waring Commercial (Torrington, CT) was used to prepare the cement slurry. The slurry was homogenized in an atmospheric consistometer (Model 1250, Chandler Engineering, Tulsa, OK).

Charge titration

A PCD 03 pH instrument from BTG Müttek GmbH (Herrsching, Germany) and a blue ribbon filter paper obtained from Whatman[®] (Dassel, Germany) were used.

Conductivity measurements

Tests were carried out with a conductivity meter Qcond 2200 (Merck, Darmstadt, Germany).

Particle size measurements

The average particle sizes of solved PEI and of the PEI/AFS PEC were measured using a Zetasizer

Nano-ZS instrument from Malvern Instruments, Herrenberg, Germany. A 4 mW He-Ne laser operating at 633 nm was used. A constant temperature of 25°C was maintained and the particle sizes obtained were reported as averages of 13 measurements.

pH measurement

The pH values were measured at 25°C with a SCHOTT pH mV meter equipped with a SCHOTT A161 pH electrode (Schott Geräte GmbH, Mainz, Germany). The meter was standardized by a two-point calibration method.

Infrared spectroscopy

Fourier Transform Infrared Spectrometer FT/IR-460 Plus from JASCO Corporation (Gross-Umstadt, Germany) was used.

Zeta potential measurements

Zeta potentials of PEI and of the PEI/AFS PEC were determined by a Zetasizer Nano-ZS apparatus (Malvern Instruments). A constant temperature of 25°C was maintained and zeta potential values were reported as averages of 13 measurements.

Environmental scanning electron microscopy and energy dispersive X-ray analysis

Environmental scanning electron microscopy (ESEM) images of the fresh, wet cement filter cake were obtained on an XL 30 ESEM—FEG instrument from Philips (now FEI Company), Eindhoven, The Netherlands. Samples were studied under a water vapor pressure of 1.5 mbar using a Gaseous Secondary Electron Detector. Acceleration voltage was 10 kV. Images were recorded $\sim 30 \text{ min}$ after completion of the high temperature–high pressure (HTHP) filtration test. Energy dispersive X-ray (EDX) analysis was used to determine elemental composition in the cross section of the cement filter cake. For preparation, the solid cement filter cake produced in the HTHP filtration

test was broken into two parts in such a way where a vertical cross section is exhibited. From the center of the filter cake, a $\sim 5 \times 5 \times 5$ mm large piece was carefully removed and the cross section of the filter cake was studied under the ESEM instrument.

Procedures

Cement slurry preparation

Cement slurries were prepared in accordance with the test procedures set forth in Recommended Practice for Testing Well Cements, API Recommended Practice 10 B, issued by the API, using API Class G oil well cement and deionized water.²⁰ The cement slurry was mixed at a water-to-cement ratio of 0.44 using a Waring blender. Depending on the preparation method, 700 g of cement either were added as such to an aqueous PEI/AFS polymer blend dissolved in 308 g of deionised (DI) water yielding a total volume of 350 mL, or as a dry blend of cement with the respective additive(s). Within 15 s, the cement or the cement/additive blend was added to the mixing water or PEI/AFS solution and was mixed for 35 s at 12,000 rpm. To ensure homogeneity, all slurries were stirred for 20 min in an atmospheric consistometer at the respective temperature.

API static fluid loss

Static fluid loss was determined at 27°C following API RP 10B procedure using a 500 mL HTHP filter press.²⁰ After pouring the homogenized cement slurry into the filter cell, a differential pressure of 70 bar (N_2) was applied to the top of the cell. Filtration proceeded through a 3.5 sq. in. mesh metal sieve placed at the bottom of the cell. The filtrate produced by the differential pressure was collected for 30 min (V_{30}). As described by API RP 10B, the collected filtrate volume was doubled and designated as API fluid loss of the corresponding cement slurry.

Adsorption

Generally, the depletion method was applied, i.e., it was assumed that a decrease in the polymer concentration before and after contact with water was solely due to adsorption/retention on the mineral surface. Achievement of adsorption equilibrium was checked by comparing polymer adsorption in cement slurry stirred for 20 min in the atmospheric consistometer against a slurry, which was not stirred. In both cases, the same amount of polymer retained was found. The amount of admixture adsorbed on cement was determined from the filtrate of the cement slurry collected in the fluid loss test. Adsorbed amount was calculated from the difference between the equilibrium concentrations of the polymer present in the liquid phase before and after mixing with cement. PEI

concentration present in the filtrate was determined by total organic carbon analysis.

Charge titration

A total of 0.2 g/L of cationic PEI and 0.2 g/L of anionic AFS were titrated in DI water and in cement pore solution against 0.001N solutions of anionic sodium polyethylene sulfonate (PES-Na) and cationic polydiallyl dimethyl ammonium chloride (Poly-Dadmac), respectively. Cement pore solution was obtained by vacuum filtration of the cement slurry as prepared above without additives using a blue ribbon filter paper obtained from Whatman[®] GmbH. From the volume of titrant required to neutralize the oppositely charged polymer, the specific charge amount of the polymer was calculated. Charge titrations were performed using 1 mL of 0.2 g/L aqueous solutions of fluid loss additive (FLA) and dispersant samples, respectively, which were then diluted with either 9 mL cement pore solution or with DI water.

Conductivity and pH measurement

A total of 0.2 wt% aqueous solutions of each AFS sample (DS = 0.5, 0.4, 0.3, and 0.2) were titrated with 500 mL of a 1 wt% PEI solution whereby the first 100 mL of the PEI solution were added in 1 mL steps, followed by 50 mL steps. Total time of titration was 30 min. Measurements were carried out at 25°C under constant stirring, and conductivity as well as pH of the solutions were recorded.

Infrared spectroscopy

Infrared (IR) spectra of a 1 wt% aqueous PEI solution, of a 0.2 wt% aqueous AFS solution (DS = 0.5), and of a combined solution containing 1 mL of each polymer solution mixed for 5 min were recorded at 25°C in the range of 400–4000 cm^{-1} .

Zeta potential and particle size measurement

Electrical charge and particle size of PEI and the PEI/AFS PEC were measured by stepwise titration of a 0.002 wt% aqueous AFS solution to 10 mL of a 0.01 wt% PEI solution. Before measurement, the solutions were stirred for 10 min with a magnetic stirrer at 200 rpm to ensure homogeneity. Particle size measurements of the PEC were conducted in cement pore solution. There, 1 mL of the combined PEI/AFS solutions holding specific PEI:AFS ratios which correspond to the isoelectric point of each AFS sample were homogenized for 30 min with 2 mL of cement pore solution.

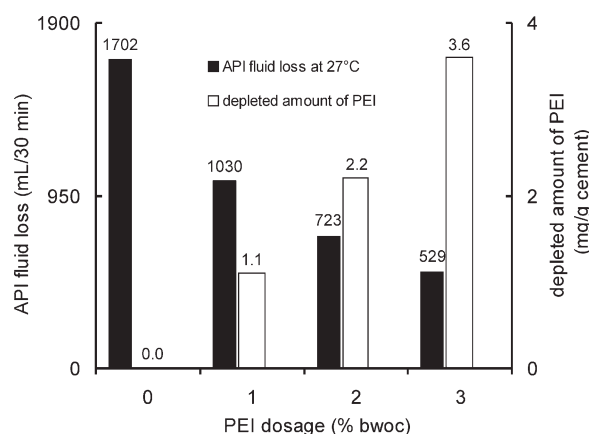


Figure 2 API fluid loss of Class G cement slurries ($w/c = 0.44$) containing increasing dosages of PEI, measured at 27°C.

RESULTS AND DISCUSSION

Properties of the PEI sample

The PEI sample used in this study exhibited a weight average molecular weight (M_w) of 230,000 g/mol (GPC measurement, eluent 0.2 mol/L NaNO_3). The polydispersity index M_w/M_n of the sample was found to be ~ 3 . Calculation of the Burchard parameter $\rho = R_g/R_h$ from GPC data confirmed the existence of a three-dimensional, randomly coiled structure for this branched PEI in aqueous solution ($\rho = 2$). When diluted to a concentration of 1 wt%, the PEI sample exhibited a pH of 10.7. The main properties of the PEI sample are listed in Table II.

Fluid loss performance of individual PEI

The API fluid loss of cement slurries treated with increasing dosages of PEI is shown in Figure 2. When used by itself, PEI does not provide satisfactory fluid loss. Even at dosages as high as 3% by weight of cement (BWOC) of PEI, the filtrate volume collected was 529 mL. This exceeds by far the commonly accepted value of ~ 50 mL/30 min, which is thought to be necessary when porous rock formations are being cemented. Additionally, at such high PEI dosage, the cement slurry is too viscous to allow easy pumping in the field.

Analysis of the cement filtrate revealed that while some depletion of PEI through adsorption/retention on cement had occurred (1.1 and 3.6 mg of PEI/g cement at dosages of 1 and 3% BWOC, resp.), no direct correlation exists between the adsorbed amount of PEI and cement fluid loss (Fig. 2). Instead, the amount of PEI retained seems to be merely proportional to the dosage of PEI added. Thus, adsorption can be excluded as working mechanism for PEI. Obviously, this polymer achieves fluid loss by strongly increasing the viscosity of the cement filtrate,

as was evidenced by measurement of the dynamic viscosity of PEI dissolved in cement pore solution using an Ubbelohde apparatus. At PEI concentrations of 1 and 3 wt%, respectively, the dynamic viscosity increased from 1.39 mPa s to 2.99 mPa s.

Performance of PEI/AFS combination

In field applications, FLAs are often combined with dispersants to lower slurry rheology. In our study, excessive viscosity of the cement slurry containing PEI was reduced by addition of an AFS polycondensate dispersant which was dry-blended into cement and was mixed with water holding dissolved PEI. Surprisingly, it was found that such combination of PEI with AFS ($DS = 0.5$) greatly improves fluid loss control of the cement slurry. For example, a mixture of 2.5% BWOC PEI and 0.4% BWOC AFS produced an API fluid loss of only 47 mL/30 min (Table III). This is a remarkable improvement over individual PEI which produced an API fluid loss of 529 mL at a dosage of 3% BWOC PEI (Fig. 2).

Influence of mixing procedure

Further improvement of cement fluid loss was observed when before cement addition, AFS was predissolved together with PEI in the mixing water by constant stirring using a magnetic stirrer at 200 rpm. For example, predissolving 0.4% BWOC of AFS possessing a DS of 0.5 with only 1% BWOC PEI and stirring for 60 min produces a fluid loss of 38 mL/30 min only (Table III). This compares with an API filtrate of 47 mL/30 min when as much as 2.5% BWOC of PEI, applied with the same dosage of AFS, were dry blended into cement. Thus, it is demonstrated that dissolving both polymers in the mixing water is highly advantageous.

Influence of reaction time

The huge impact of the mixing procedure observed indicates that during the dissolution process, a reaction between PEI and AFS might occur. To investigate, the mixing time for the two polymers in aqueous solution was varied. Thus, 1% BWOC of PEI and 0.4% BWOC of AFS ($DS = 0.5$) were predissolved in 350 mL DI water at room temperature. After stirring for 1, 10, and 60 min, respectively, 700 g of cement were added, a cement slurry was prepared according to API RP 10 B and its fluid loss was probed. It was found that when the reaction time was prolonged from 1 to 10 min, the API fluid loss dropped significantly from 425 mL to 49 mL (Table III). Further extension of the reaction time produced an API filtrate volume which was even less (38 mL/30 min, see Table III). This result instigates that along with

TABLE III
API Fluid Loss of Class G Cement Slurries (w/c = 0.44) as a Function of a) Mixing Procedure for the Cement Slurry, b) Reaction Time Between PEI and AFS, c) PEI:AFS Weight Ratio, and d) Anionic Charge Amount of the AFS Samples, Respectively

Parameter	Preparation	PEI dosage (% BWOC)	AFS dosage (% BWOC)	DS of AFS sample	API fluid loss (mL/30 min)
–	PEI solved in mixing water	3	–	–	528
Mixing procedure	PEI and AFS predissolved in mixing water, stirred for 60 min	1	0.4	0.5 AFS	38
	AFS dry-blended into cement; PEI predissolved in mixing water	2.5	0.4	0.5 AFS	47
Reaction time	PEI and AFS predissolved in mixing water, stirred for 1 min	1	0.4	0.5 AFS	425
	PEI and AFS predissolved in mixing water, stirred for 10 min	1	0.4	0.5 AFS	49
	PEI and AFS predissolved in mixing water, stirred for 60 min	1	0.4	0.5 AFS	38
PEI:AFS weight ratio	PEI and AFS predissolved in mixing water, stirred 10 min	1	0.2	0.5 AFS	208
		1	0.3	0.5 AFS	46
		1	0.4	0.5 AFS	49
Anionic charge amount of AFS	PEI and AFS predissolved in mixing water, stirred 10 min	1	0.25	0.5 AFS	46
		1	0.35	0.4 AFS	48
		1	0.45	0.3 AFS	44
		1	0.65	0.2 AFS	46

the mixing procedure, the mixing time is also critical for the effectiveness of the PEI/AFS combination.

Influence of PEI/AFS ratio

Next, the question arises whether the fluid loss performance is also dependent upon the PEI:AFS ratio. For clarification, cement slurry filtration tests at constant PEI dosage (1% BWOC) but at different AFS concentrations were performed. In all experiments, PEI and AFS were predissolved in the mixing water for 10 min. At 1% BWOC PEI, the minimum dosage of AFS (DS = 0.5) required to obtain a fluid loss of less than 50 mL/30 min lies at 0.30% BWOC. Lowering the dispersant dosage below this threshold concentration, e.g., to 0.2% BWOC, results in a higher fluid loss (208 mL/30 min, Table III). Hence, it becomes apparent that for the weight ratio between PEI and AFS, a specific range is required to achieve optimum performance.

All results described earlier instigate that some sort of associative interaction between the PEI and AFS polymers occurs. One such possibility is the formation of a large PEC which exercises a plugging effect in the cement filter cake. Typically, formation of PECs is based on ion pairing between cationic (here: protonated amino) and anionic (here: sulfonate) groups. To investigate, the effect of the anionic charge amount present in AFS on the fluid loss performance of the PEI/AFS combination was probed.

Effect of anionic charge amount of AFS

AFS samples possessing different DS (DS = 0.2; 0.3; 0.4; and 0.5) were prepared and studied with respect

to their interaction with PEI. Thus, in the presence of 1% BWOC PEI dissolved in the mixing water, the dosage of each AFS sample was determined at which a fluid loss of <50 mL/30 min was achieved. Because the high dosages needed for AFS samples possessing lower DS can produce low fluid loss values owed to excessive dispersion and sedimentation of cement (so called “faked” fluid loss), an antisetling agent (0.05% BWOC of welan gum) was dry blended into the cement before mixing all slurries.

The minimum dosages required for each AFS sample to obtain a fluid loss <50 mL/30 min are shown in Table III. With increased DS, the minimum AFS dosages were found to decrease. From this experiment, it was concluded that apparently, a certain amount of anionic charge provided by AFS is necessary to achieve complete charge neutralization of the PEI polymer. This finding strongly supports the hypothesis that performance of the PEI/AFS combination relies on the formation of a PEC. To confirm, a series of mechanistic experiments was conducted next.

PEI/AFS PEC

Formation of a PEC between PEI and AFS was first probed by conductivity and pH measurements.

Conductivity and pH measurements

Conductivity was measured by titrating 0.2 wt% aqueous solutions of AFS samples possessing different DS values with 1 wt% aqueous PEI solution. As

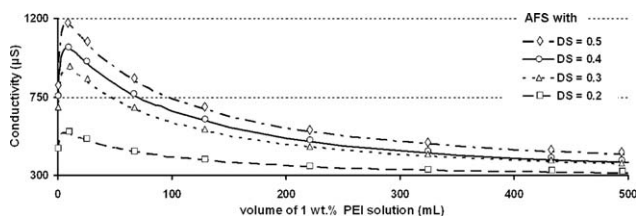


Figure 3 Conductivity of 0.2 wt% aqueous solutions of AFS samples possessing DS values of 0.2; 0.3; 0.4; and 0.5, respectively, titrated at 27°C with 1 wt% PEI solution.

evidenced in Figure 3, the conductivity of solutions containing the individual AFS samples (with no PEI present) rises with increasing DS (from 437 μS for the AFS sample possessing a DS of 0.2 to 797 μS for 0.5 AFS sample with DS = 0.5). Obviously, a higher DS increases the ionic character of the polyelectrolyte. Addition of minor amounts (~ 10 mL) of PEI to these AFS solutions at first produces an increase in conductivity until a maximum value is reached. Apparently, charge neutralization between AFS and PEI does not occur in this range of PEI addition. Thereafter, however, conductivity decreases strongly as a consequence of progressive charge neutralization between PEI and the polycondensate. Obviously, formation of the PEI/AFS PEC only starts after exceeding a certain PEI threshold concentration. For all AFS samples, conductivity levels out at PEI additions of ≥ 500 mL and attains a final value of ~ 300 μS , which corresponds to the conductivity of the individual PEI solution.

The experiments demonstrate that intermolecular attraction between these two polymers is dependent upon the anionic charge amount present in AFS. Accordingly, the highest decline in conductivity occurs for the most anionic AFS sample possessing a DS of 0.5 (from 1169 μS to 420 μS after addition of 500 mL PEI solution) while the AFS showing a DS of 0.2 exhibits a relatively minor decrease in conductivity (from 545 μS to 312 μS after addition of 500 mL PEI solution). There, a much smaller amount of PEI is sufficient to achieve charge neutralization.

Along with conductivity, the pH of each AFS solution was measured. In general, AFS samples exhibiting lower DS values show lower pH (DS = 0.2: pH 6.5; DS = 0.3: pH 8.6; DS = 0.4: pH 9.3; and DS = 0.5: pH 9.9) (Fig. 4). Addition of alkaline 1 wt% PEI solution (pH 10.7) first increases the pH of all AFS solutions to reach a maximum value while further PEI addition causes a drop of pH to a final value of approximately 10.7, which is identical for all AFS samples. The maximum value of pH generally occurs at volumes of PEI solution added which coincide with those observed at maximum conductivity, as was shown in Figure 3. This result can be interpreted such that in a first step, the polybase PEI abstracts a proton from water, and thus becomes a cationic poly-

electrolyte (equation 3). Existence of protonated PEI species was evidenced from previous charge titration experiments where a positive charge was attained for this PEI sample even in highly alkaline cement pore solution of pH 12.6 (Table II). Through this mechanism, the initial increase in pH observed after addition of PEI solution is explained by a release of OH^- ions as a result of protonation of PEI.



The protonated PEI species can now associate itself with anionic AFS and thus form a PEC, $\text{PEI} - \text{H}^+ \text{AFS}^-$, as expressed by equation 4. Once $\text{PEI} - \text{H}^+$ is progressively consumed by this reaction, more amino groups present in PEI will be protonated, according to the equilibrium shown in equation 3, which in turn increases the pH. Similar observations were reported by Mészáros et al.¹¹ for PEI titrated with an aqueous solution of SDS. Owing to this mechanism, the contribution of OH^- ions to the total conductivity of the AFS solution titrated with PEI is significant and explains the observed initial rise of both conductivity and pH. Apparently, after addition of ~ 10 mL PEI solution, hydrogen abstraction by PEI ceases and subsequently, conductivity drops because of PEC formation.

To investigate the ionic interaction between PEI and AFS further, infrared spectra of the aqueous 0.2 wt% AFS solution (DS = 0.5); of the 1 wt% PEI solution; and of a combine of 1 mL of each polymer solution mixed for 10 min were recorded (Fig. 5). The functional groups contained in PEI produce characteristic signals at the wave numbers as follows: 3253 cm^{-1} ($-\text{NH}-$), 3037 cm^{-1} ($-\text{NH}_3^+$), 2920, and 2856 ($-\text{CH}_2-$), 2357 cm^{-1} ($-\text{NH}_2^+$ and $-\text{NH}_2^+-$), 1583 cm^{-1} ($-\text{NH}_2$), and 1452 cm^{-1} ($-\text{CH}_2-$).²¹ Analysis of the AFS sample (DS = 0.5) exhibits characteristic functionalities at these wave numbers: 2922 and 2796 cm^{-1} ($-\text{OH}$, intramolecular H bridging), 1587 cm^{-1} ($\text{C} = \text{O}$), 1354 cm^{-1} ($-\text{OH}$), 1171 cm^{-1} (SO_3^-), and 1041 cm^{-1} ($\text{C}-\text{O}$). Interestingly,

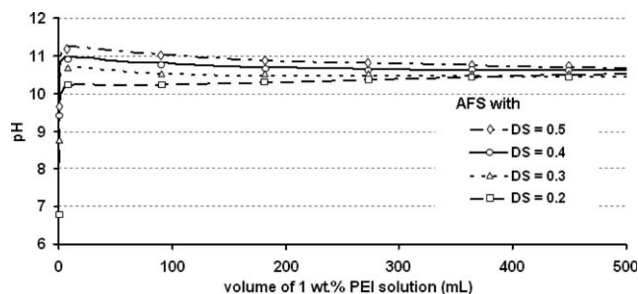


Figure 4 pH of 0.2 wt% aqueous solutions of AFS samples possessing different DS as a function of PEI addition to this solution.

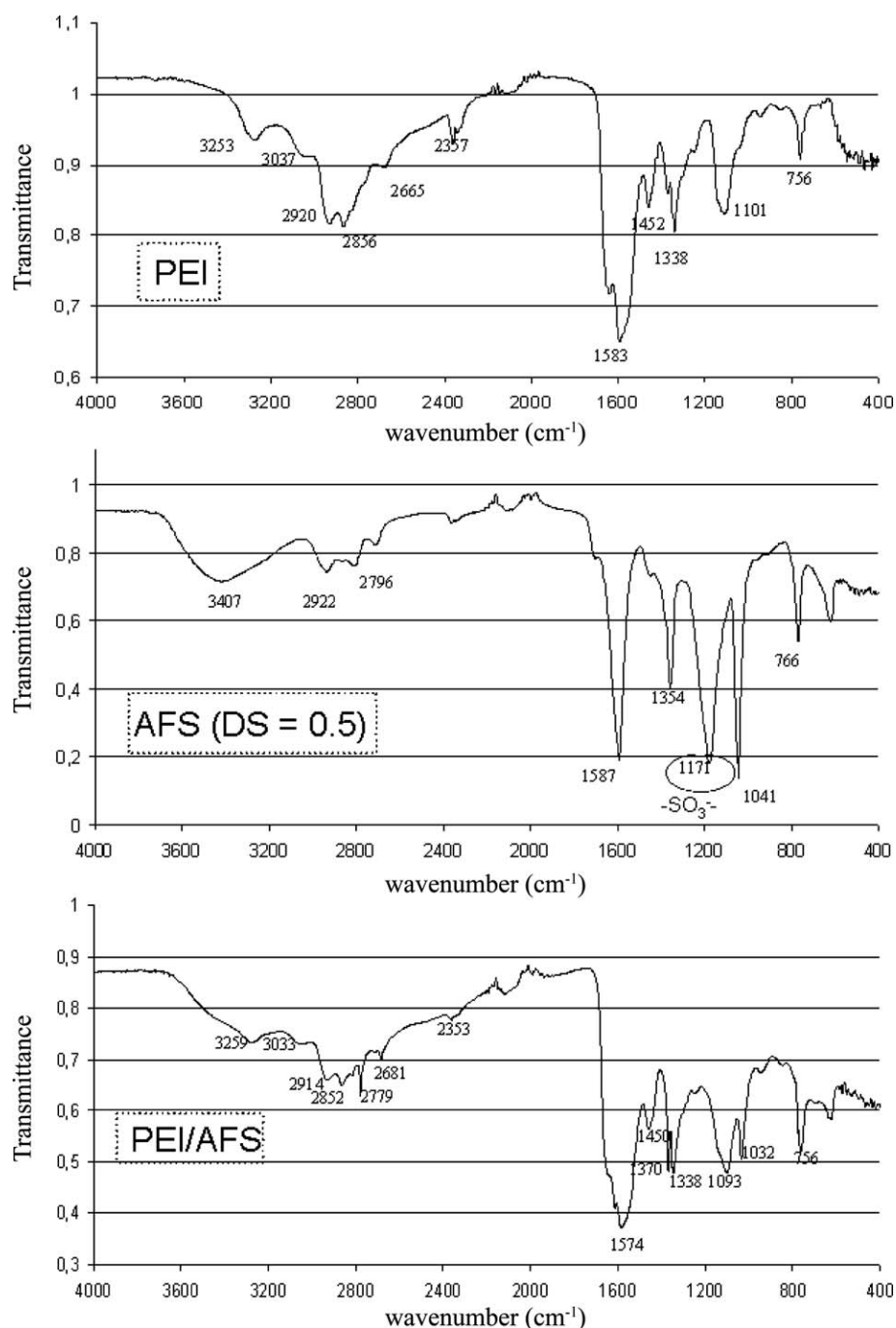


Figure 5 Infrared (IR) spectra of aqueous 1 wt% PEI solution, 0.2 wt% AFS solution (DS = 0.5), and of a combine prepared by mixing 1 mL of each polymer solution, measured at 25°C.

in the IR spectrum of PEI/AFS combined, the absorbance for $-\text{SO}_3^-$, which occurs at 1171 cm^{-1} and is characteristic for AFS has disappeared. It suggests strong participation of this functional group in the interaction between PEI and AFS. Obviously, no more free $-\text{SO}_3^-$ functionalities are present in the PEI/AFS combine. Whereas, the signals representing cationic amine functionalities in PEI occurring ~ 3035 , 2680 , and 2355 cm^{-1} still appear in the spectrum of the PEI/AFS combine. Obviously, all $-\text{SO}_3^-$ groups are involved in the interaction with PEI, but owed to the

large amount of PEI added and the branched character of this PEI sample, an excess of cationic amine groups not participating in the interaction is present in the mixture. This way, the IR study confirms that ionic interaction occurs between PEI and AFS.

Zeta potential and particle size

To clarify the electrical charge of the PEI/AFS combine, the zeta potential of 0.01 wt% PEI solution titrated with 0.002 wt% AFS solution was measured.

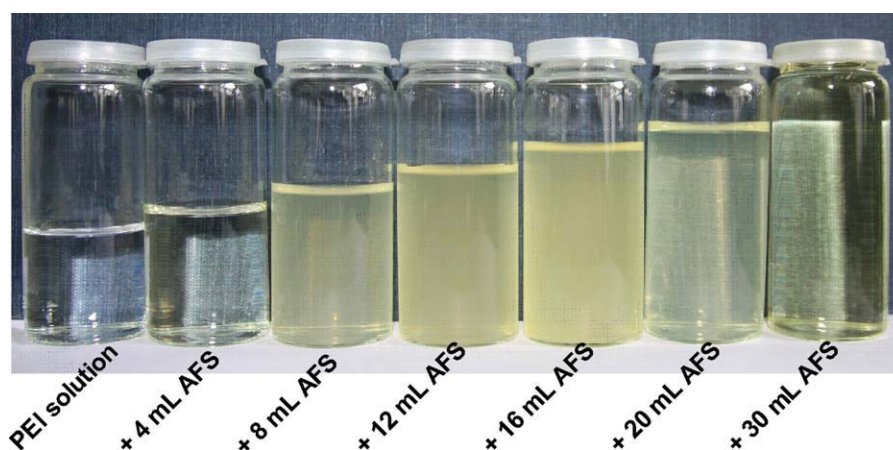


Figure 6 Titration of 0.01 wt% aqueous PEI solution with increased volumes of 0.002 wt% aqueous AFS solution (DS = 0.5); precipitation of a PEI/AFS PEC is observed at additions of 8–16 mL of AFS solution while at higher dosages, resolubilization occurs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

After addition of 1 mL of AFS solution each, stirring proceeded for 10 min to allow establishment of equilibrium conditions before the zeta potential measurement was taken.

During titration, a general occurrence was observed for all AFS samples. At low dispersant concentrations, the PEI/AFS combine is transparent while at increased AFS dosage, the solution turns first turbid and shows a yellowish precipitate until it becomes transparent again when an excess amount of AFS is present (Fig. 6). For AFS samples possessing lower DS, precipitation requires a higher AFS dosage to commence. For example, for the AFS sample exhibiting a DS of 0.5, precipitation occurs at 6 mL of PEI solution added, whereas the AFS sample possessing a DS of 0.2 requires 25 mL of volume added to reach the precipitation regime. These observations indicate that a process involving association, charge neutralization and subsequent dissociation of macromolecules is taking place. The higher the amount of sulfite groups present in the polycondensate, the lower is the quantity of AFS required for charge neutralization of the given amount of protonated amino groups present in PEI. Such behavior has been observed previously for polyelectrolyte/surfactant complexes made from oppositely charged components. There, initial precipitation of the polymer/surfactant complex is followed by dissolution as a consequence of repulsive interaction of the surfactant with the polymer.¹¹

The principle process of ion pairing, which underlies the formation of the PEC was confirmed via zeta potential measurement. With decreasing DS, the dispersant dosage necessary for achieving the isoelectric point of 0 mV increases (for the AFS sample possessing DS = 0.5: 6 mL of 0.002 wt% AFS solution; for AFS with DS = 0.4: 9 mL; for AFS with DS = 0.3: 12 mL; for AFS with DS = 0.2: 25 mL). As is shown

in Figure 7, the original PEI solution exhibits a positive zeta potential +3.5 mV. This is owed to the protonated amino groups, as presented earlier.⁷ At low AFS addition (in the preprecipitation regime), this positive zeta potential increases further until a maximum value is reached. Thereafter, it decreases to the isoelectric point and beyond, where it attains a final negative value. Obviously, the initial rise of the positive charge is due to an increase of the number of positively charged particles.

The reason behind this effect became evident from particle size measurements. For all AFS samples, the initial rise of the zeta potential at very low dispersant concentrations is accompanied by a decrease in particle size (d_{50} value), as is evidenced by dynamic light scattering measurements (Table IV). Apparently, AFS addition induces separation of initially formed PEI agglomerates into smaller particles or even single macromolecules. Through this mechanism, abstraction of protons from water molecules

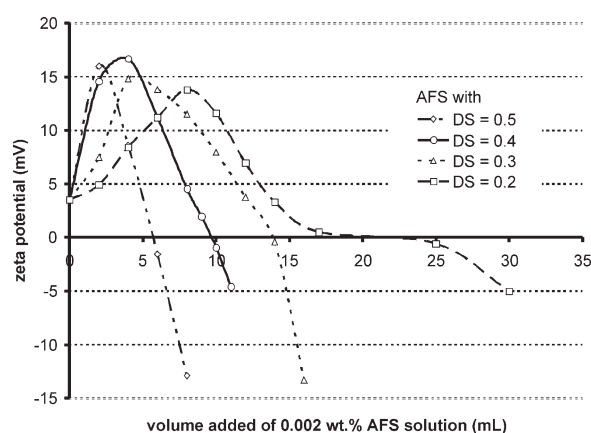


Figure 7 Zeta potential of 0.01 wt% aqueous PEI solution as a function of volume added of 0.002 wt% aqueous AFS solutions; AFS samples possess different DS.

TABLE IV
Average Size of Particles (d_{50} Value) Present in 0.01 wt% Aqueous PEI Solution After Titration with 0–4 mL of 0.002 wt% AFS Solution, Measured by Dynamic Light Scattering

Volume added of AFS solution (mL)	Average particle size (d_{50} value) (nm)			
	AFS DS = 0.2	AFS DS = 0.3	AFS DS = 0.4	AFS DS = 0.5
0	91	91	91	91
1	89	77	80	58
2	63	78	66	51
3	66	87	61	410
4	68	134	178	1,752

by PEI is facilitated better and occurs more extensively. As a result, the number of positively charged particles increases and a more positive zeta potential results. Thus, when 2 mL of AFS solution (DS = 0.5) are added to the PEI solution, the size of the PEI aggregates decreases from 91 nm to 51 nm (Table IV). This value is comparable with the radius of gyration (R_g) of single molecules ($R_g = 41$ nm) present in our PEI sample (Table II). Further AFS addition strongly increases particle size and reduces the zeta potential continuously until negative values are obtained for all AFS samples. There, dispersant molecules bind to PEI via electrostatic interactions to produce an uncharged complex. This PEC possess such large particle size (several μm , Table IV) that it can effectively obstruct the pores of a cement filter cake. When addition of AFS is continued, particle size decreases as a result of disintegration and resolubilization of the PEC.

Furthermore, the average particle diameter of the PEI/AFS PEC were determined using a Zetasizer instrument. In Figure 8, the particle size of PEI is plotted against the volume added of the AFS samples possessing different DS values. For all samples,

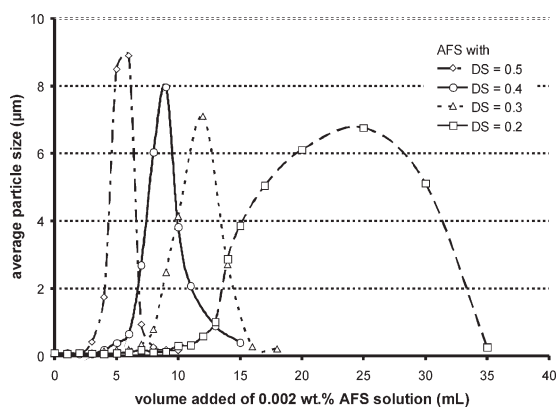


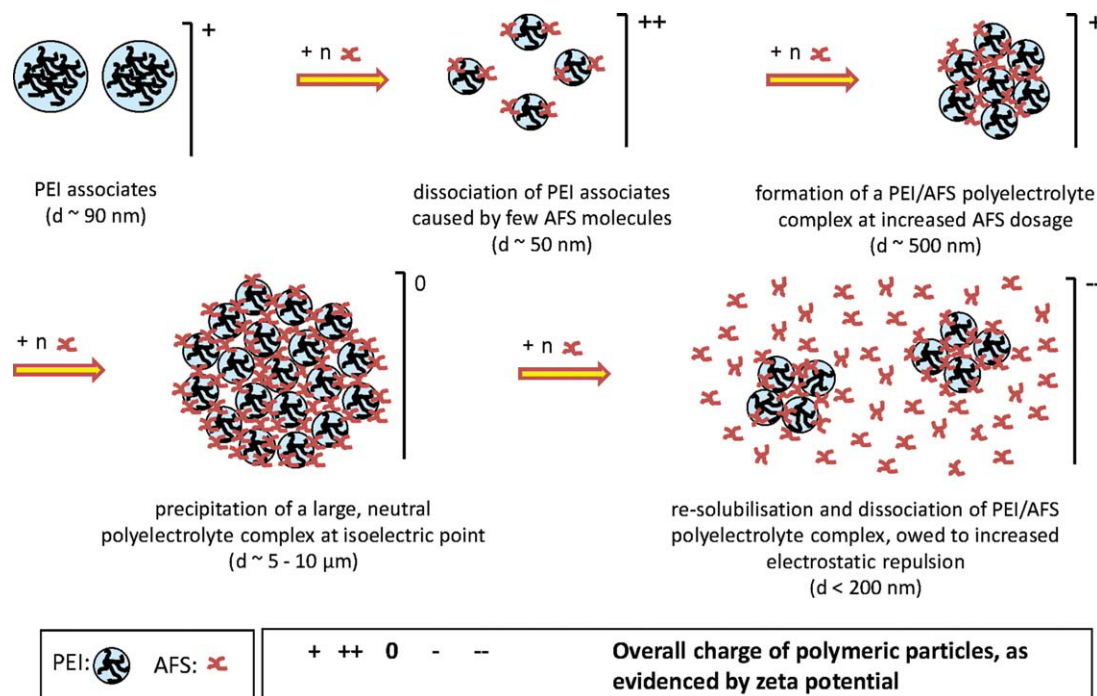
Figure 8 Hydrodynamic radius (R_h) of particles present in 0.01 wt% aqueous PEI solution as a function of volume added of 0.002 wt% aqueous AFS solution; AFS samples showing different DS.

TABLE V
Molar Ratio of AFS:PEI and Ratio of $-\text{SO}_3^-$ to $-\text{NR}_3^+$ Groups Present in the Polyelectrolyte Complex Existing at the Isoelectric Point

DS of AFS sample	Molar ratio of AFS:PEI at isoelectric point	Molar ratio between protonated amino:sulfonate groups at isoelectric point
0.2	2.05 : 1	14
0.3	0.87 : 1	14
0.4	0.73 : 1	13
0.5	0.52 : 1	13

maximum particle sizes were found to occur around the isoelectric point, as was evidenced by the zeta potential measurements displayed in Figure 7. As described earlier, turbidity of the combines generally was observed in the region where the electrokinetic properties of the system lie around the isoelectric point. This regime is characterized by the occurrence of very large particles produced by ion pairing and charge neutralization. Later on, progressive binding of AFS molecules to the PEC results in negatively charged PEI/AFS complexes.

During PEC formation, the isoelectric point (IEP) is transgressed. The question arises whether a certain ratio between the protonated amino groups present in PEI and the sulfonate groups occurring in AFS exist at the isoelectric point. To probe, the weight ratios between PEI and AFS existing for each AFS sample at the isoelectric point as evidenced from the zeta potential measurements shown in Figure 7 were converted into molar ratios of PEI:AFS. Those values were then used to calculate the molar ratios between ethylene imine monomer (assuming that one mole of PEI contains 423 ethylene imine units, as derived from M_w of PEI), and the AFS building block holding one sulfonate group. The result is exhibited in Table V. There, it is clearly shown that with increasing DS of AFS, less moles of AFS are required to achieve a PEC which is neutral in charge. Furthermore, at pH 7 (this value of pH was measured for all AFS samples at the isoelectric point), 22% of amino groups present in PEI are protonated.⁷ Applying this factor to the different amounts of PEI present in the PECs formed from AFS molecules possessing variable DS produces the molar ratio between protonated amino groups and sulfonate functionalities occurring at the isoelectric point in the PECs. Interestingly, it was found that this molar ratio is comparable for all AFS samples and lies ~ 13 –14 (Table V). This indicates that AFS molecules can interact only with protonated amino groups present on the surface of the spherical PEI macromolecules, whereas those inside are inaccessible for the AFS polyelectrolyte. Consequently, it appears that the PEC possesses a core-shell structure, with the core made up of associated PEI molecules, whereas



Scheme 1 Schematic illustration of individual steps leading to PEC formation and subsequent disintegration during titration of anionic AFS polyelectrolyte to an aqueous PEI solution (pH ~ 8); particle sizes shown are not to scale. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

comparatively small AFS molecules are attached to its cationic surface and form an anionic shell.

The various interactions occurring between PEI and AFS at different regimes of the combine are summarized in Scheme 1. In aqueous solution, pure PEI exists in the form of an associative molecule colloid. There, individual macromolecules are bound together via hydrogen bridges involving nitrogen donor atoms and =N—H functionalities. When AFS is added, disintegration of the PEI associates occurs. AFS attaches to several PEI macromolecules and crosslinks them. This way, a large, precipitated multipolymer complex (d ~ 7–8 μ m) producing maximum turbidity around the isoelectric point is formed. Once this point is transgressed, then addition of more dispersant leads to an increasingly negative charge of the polymeric associates. Consequently, electrostatic repulsion between molecules present in the PEC increases. This effect results in gradual disintegration of the PECs and finally, particle sizes of <200 nm are attained. A comparable decrease in particle size at higher surfactant concentrations was reported by Li et al. for a PEI/surfactant combination. It was ascribed to repulsive micellar interaction.²² Whereas here, dissociation of the PEC can be attributed mainly to electrostatic repulsive forces. The final result of AFS addition is resolubilization of the precipitated PEC. This is owed to an excess of AFS molecules which instigate an increasingly negative charge to the PEI/AFS colloid

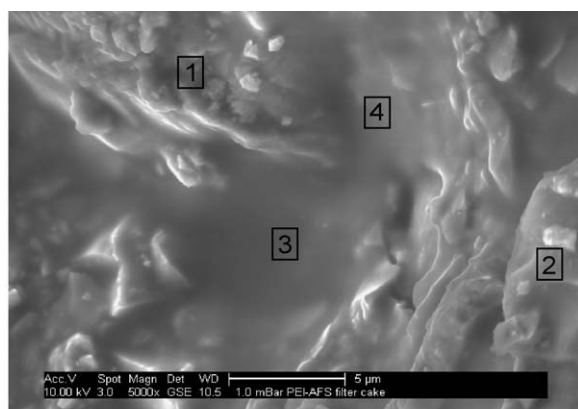
and thus enhance its hydrophilic character. At very high-AFS dosages, mainly small AFS molecules are present, with few of them coating PEI molecules, as is shown in Scheme 1.

The same principle behavior can be ascribed to all AFS dispersant samples. The only difference being that for AFS samples possessing a low degree of sulfonation, the amount of AFS required to form the PEC and to disintegrate it is higher than for AFS samples exhibiting a high DS.

Behavior of PEC in cement

The mechanistic study instigates that for AFS samples possessing lower DS, the dosage needed to form the PEC is higher than for AFS with high DS. This assumption is in agreement with the fluid loss experiments exhibited in Table III. There, with decreased DS of AFS samples, the dosage needed to achieve an API fluid loss of <50 mL/30 min increases. For example, the AFS sample possessing a DS of 0.5 required only a dosage of 0.25% BWOC, whereas for AFS of DS = 0.2, a dosage of 0.65% BWOC is needed to reduce cement fluid loss <50 mL/30 min.

Next, steric size and stability of the PEI/AFS complex in cement pore solution was investigated. For this purpose, PEI and AFS (DS = 0.5) solutions were combined at the ratio corresponding to the isoelectric point (Fig. 7), stirred for 10 min and 2 mL of the combine were added to 2 mL of cement pore solution.



position	relative intensity				
	C	N	S	Ca	Si
1	11.7	3.0	0	65.6	19.5
2	7.2	3.4	0	79.6	8.9
3	43.1	12.2	4.5	36.7	3.5
4	36.8	11.3	4.5	36.0	13.2

Figure 9 ESEM image of a fresh cement filter cake obtained from HTHP filtration test of a Class G cement slurry containing 1% BWOC of PEI and 0.25% BWOC of AFS (DS = 0.5); elemental mapping (rel. intensities) by EDX analysis; positions no. 1–2: cement matrix; positions no. 3–4: pores filled with particles of PEI/AFS PEC.

After stirring for 30 min, the hydrodynamic radii of the PEI/AFS PEC were measured using a Zetasizer instrument.

It was found that in cement pore solution, the size of the PEI/AFS complexes generally are smaller than in DI water. Compared with DI water, the shrinkage observed in cement pore solution is 37%, 33%, 10 and 12% for the AFS samples possessing DS values of 0.2, 0.3, 0.4, and 0.5, respectively. Owing to the presence of K^+ , Na^+ , Ca^{2+} , Al^{3+} , SO_4^{2-} , and OH^- ions in cement pore solution (total electrolyte content ~ 13 g/L), the charged polymers attain a more coiled conformation.²³ Consequently, the steric size of the PEC diminishes. Owing to this effect, in cement slurry a higher dosage of AFS is required than in water to form sufficiently large and plenty PECs required for effective physical pore plugging. Nevertheless, the findings confirm that once formed, PEI/AFS PEC are stable in the highly alkaline and electrolyte loaded cement pore solution.

The presence of PEI/AFS PEC exercising a plugging effect in the fresh cement filter cake was visualized by ESEM images. Probing a filter cake obtained from an HTHP filtration test as described above utilizing 1% BWOC of PEI and 0.25% BWOC of AFS (DS = 0.5) revealed that in the top section of the filter cake, pores typically contained a very high concentration of organic polymer, as was evidenced via EDX analysis by high carbon (35–45% rel. int.), nitrogen (9–13%) and sulfur contents ($\sim 4.5\%$) (Fig. 9). Whereas, in the solid matrix surrounding the pores in the filter cake, calcium and silicon were the predominant elements, as is to be expected for hydrat-

ing Portland cement. When probing deeper into the filter cake in vertical direction, the number of pores filled with organic matter decreased rapidly. This indicates that during formation of the cement filter cake, initially a spurt loss of water is released and concomitant deposition of cement particles occurs. Once some gel-like or solid filter cake has formed, the large PEI/AFS PEC particles begin to infiltrate into the filter cake and, owing to their large size, start to plug the pores of the cake. Through this mechanism, the top layer of the cake now is sealed off, any further water loss is effectively prevented and no more deposition of cement particles occurs. The final result is a cement filter cake possessing very low permeability against water.

CONCLUSIONS

PEI works as an effective cement fluid loss additive only if combined with an anionic polyelectrolyte such as AFS which allows the formation of a large and partly insoluble PEC. These particles physically plug the pores of the cement filter cake. Successful formation of the PEI/AFS complex depends on many parameters such as mixing procedure, mixing time, pH, molar ratio between the polymers and the anionic charge amount present in PEI and AFS. All of these factors strongly influence the fluid loss performance of the PEI/AFS combination.

Apparently, PEC formation from PEI and AFS solely relies on ionic interaction between these two species. This result differs significantly from observations made for the PEI/SDS and PEI/cetyl trimethyl ammonium bromide systems where non-electrostatic, micelle-like cooperative interactions contribute as well.

In aqueous solution, a pH-dependant equilibrium between protonated cationic PEI and nonprotonated neutral PEI exists. Addition of AFS consumes the protonated PEI species via formation of a PEC formed by ion-pairing between the cationic and anionic polyelectrolytes. As a result of the equilibrium, continuous production of the protonated PEI occurs until all AFS is bound by cooperative interaction. At this point, the PEC is neutral, it partly precipitates from solution and has a large diameter of ~ 5 – 10 μm . Kinetics of the PEC formation is governed by the protonation and association steps and seems to be relatively slow, as was evidenced by reaction times of at least 10 min. for PEI and AFS.

In highly alkaline cement pore solution, the cationic character of PEI is reduced, due to the high pH which disfavors protonation of PEI. Consequently, and because of the high ionic strength existing in cement pore solution, the hydrodynamic radius of the PEC particles is less than in DI water. Still, PEI/AFS complexes can be used successfully to provide

fluid loss control to oil well cement slurries. For optimum effectiveness, successful and quantitative formation of the PEC in the mixing water prior to cement addition appears to be critical. The PEC particles enter the filter cake, lodge between the cement grains, and prevent the water loss by physically plugging the pores. This mechanism resembles the effect of finely ground and sized particulate materials used for cement fluid loss control such as bentonite, microsilica, asphaltenes, and latex polymers.

Similar PECs and fluid loss reagents were obtained when instead of AFS we used other anionic dispersants, namely melamine formaldehyde sulfite polycondensate, β -naphthalene sulfonate formaldehyde polycondensate, and polycarboxylate copolymers made from methacrylic acid and ω -methoxy poly(ethylene glycol) methacrylate ester were used. This demonstrates the general applicability of our findings. According to them, PEC exhibiting a particle size of $>1 \mu\text{m}$ can be used successfully for cement fluid loss control. This presents a new method to achieve fluid loss control for cement slurries.

References

1. Thünemann, A. F.; General, S. *Langmuir* 2000, 16, 9634.
2. Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC Press: Boca Raton, FL, 1983.
3. Madkour, T. M. *Polymer Data Handbook*; Mark, J. E., Ed.; Oxford University Press: New York, 1999.
4. Gane, P. A. C.; Schölkopf, J.; Gantenbein, D.; Gerard, D. E. US patent 0,086,987, 2010.
5. Horn, D.; Linhart, F. In *Paper Chemistry*; Roberts, J., Ed.; Blackie Academic & Professional: London, 1996.
6. Lindquist, G. M.; Stratton, R. A. *J Colloid Interface Sci* 1976, 55, 45.
7. Wang, H.; Wang, Y.; Yan, H.; Zhang, J.; Thomas, R. K. *Langmuir* 2006, 22, 1526.
8. Rivas, B. L.; Geckeler, K. E. *Adv Polym Sci* 1992, 102, 171.
9. Winnik, M. A.; Bystryak, S. M.; Chassenieux, C.; Strashko, V.; Macdonald, P. M.; Siddiqui, J. *Langmuir* 2000, 16, 4495.
10. Nylander, T.; Samoshina, Y.; Lindman, B. *Adv Colloid Interface Sci* 2006, 105, 123.
11. Mészáros, R.; Thompson, L.; Bos, M.; Varga, I.; Gilanyi, T. *Langmuir* 2003, 19, 609.
12. Bystryak, S. M.; Winnik, M. A.; Siddiqui, J. *Langmuir* 1999, 15, 3748.
13. Li, Y.; Xu, R.; Couderc, S.; Bloor, D. M.; Warr, J.; Penfold, J.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* 2001, 17, 5657.
14. O'Driscoll, B. M. D.; Milsom, E.; Fernandez-Martin, C.; White, L.; Roser, S. J.; Edler, K. J. *Macromolecules* 2005, 38, 8785.
15. Winnik, M. A.; Bystryak, S. M.; Siddiqui, J. *Macromolecules* 1999, 32, 624.
16. Brothers, L. E.; Burkhalter, J. F. US patent 4,791,989, 1988.
17. American Petroleum Institute. *API Specification 10A*, 23rd ed.; American Petroleum Institute: Washington, 2002.
18. Plank, J.; Dugonjic-Bilic, F.; Lummer, N. R. *J Appl Polym Sci* 2009, 111, 2018.
19. Plank, J. In *Biopolymers, General Aspects and Special Applications* Steinbüchel, A., Ed.; Wiley-VCH: Weinheim, 2003.
20. American Petroleum Institute. *API Recommended Practice 10B*, 22nd ed.; American Petroleum Institute: Washington, 1997.
21. Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, New York, 1991.
22. Li, Y.; Ghoreishi, S. M.; Warr, J.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* 2000, 16, 3093.
23. Rothstein, D.; Thomas, J. J.; Christensen, B. J.; Jennings, H. M. *J Cem Concr Res* 2002, 32, 1663.