

Working Mechanism of Poly(vinyl alcohol) Cement Fluid Loss Additive

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ABSTRACT: The working mechanism of poly(vinyl alcohol) (PVA, $M_w \sim 200,000 \text{ g mol}^{-1}$), a fluid loss control additive (FLA) applied in oil well cementing, was investigated. First, characteristic properties of PVA such as solubility and particle size in cold and hot water, minimum film forming temperature, adsorption on cement, viscosity of cement pore solution and static filtration properties of cement slurries treated with PVA were determined. It was found that the working mechanism of PVA relies on hydrated, but water-insoluble PVA particles ($d_{50} \sim 2.4 \mu\text{m}$). During cement slurry filtration, they coalesce into a polymer film. This film effectively plugs the pores of the cement filter cake. The sample studied here becomes water-soluble at temperatures $> 40^\circ\text{C}$ (d_{50} decreases to

$\sim 50 \text{ nm}$) and loses its effectiveness. Addition of highly anionic dispersants such as β -naphthalenesulfonate formaldehyde (BNS) or acetone formaldehyde sulfite (AFS) polycondensate extends the temperature range at which PVA works from 40°C to $\sim 60^\circ\text{C}$. This effect is ascribed to lower solubility of PVA in the presence of these dispersants. The study reveals that decreased performance of PVA caused by higher temperatures is not the result of thermal degradation of the polymer, but is owed to its increasing water-solubility. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2290–2298, 2010

Key words: poly(vinyl alcohol); polymer film; oil well cement; dispersant; fluid loss additive

INTRODUCTION

Oil well cementing is often considered as one of the most important operations performed in the construction of a well bore.^{1,2} Placement of the cement slurry under pressure across a permeable formation, however, may lead to rapid dehydration, resulting in poor pumpability and incomplete cement hydration. To control the properties of oil well cement slurries, additives are included into the formulation.³ Dispersants such as β -naphthalenesulfonate-formaldehyde (BNS), sulfonated melamine-formaldehyde and acetone formaldehyde sulfite (AFS) polycondensates are employed to reduce friction while pumping the slurry.⁴ These anionic polyelectrolytes adsorb on positively charged surfaces of cement hydrates, thus rendering them overall negatively charged. The resulting electrostatic repulsion between the cement particles leads to disagglomeration of the solids and produces a cement slurry with lower viscosity.⁴

Fluid loss additives (FLAs) are added to oil well cement to reduce uncontrolled water loss from the slurry while being pumped along porous formations

in the bore hole.^{4,5} For polymeric FLAs, three types of working mechanisms are known.^{4,6} First, long chain anionic FLAs may adsorb onto hydrating cement particles and obstruct filter cake pores either by polymer segments which freely protrude into the pore space or even bridge cement particles. Through this adsorptive mechanism, filter cake permeability is reduced and low fluid loss is achieved. Second, FLAs may plug the pores of the cement filter cake through formation of a polymer film or micelles. Third, when exceeding a certain threshold concentration, some FLA polymers such as cellulose ethers form associates which can bind an enormous amount of water molecules in their inner sphere and their hydrate shells. This way, a large portion of the mixing water is physically bound and is not released during the filtration process. Besides, the uptake of water results in swelling of the hydrocolloid which then, because of its large size, can obstruct the pores of the cement filter cake.

Common fluid loss polymers for oil well cementing include poly(vinyl alcohol) (PVA), hydroxyethyl cellulose (HEC), carboxymethyl hydroxyethyl cellulose (CMHEC), polyethyleneimine (PEI) and various synthetic sulfonated copolymers such as e.g., CaAMPS[®]-co-NNDMA. These products differ with respect to temperature and salt tolerance, viscosity imparted to the cement slurry, cost and environmental effects.

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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_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_2SiO_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.

Performance characteristics of PVA present in oil well cement slurries has been presented before. For example, Nelson describes that PVA provides fluid loss control only at low temperatures.⁴ He reports a temperature limitation for this FLA of 38°C. To extend the temperature range for PVA, Audebert crosslinked PVA with boric acid.⁷ Through this intermolecular crosslinking, PVA is presented to provide fluid loss control at temperatures up to 121°C. A disadvantage of this method is the time-dependent de-crosslinking which occurs under highly alkaline conditions and becomes apparent when extended pumping times (6–8 h) are required. Still, little is known about the interaction of PVA with cement and the reason behind its strongly temperature dependant fluid loss control performance.

The fundamental processes underlying the working mechanism of PVA as fluid loss additive have not yet been investigated thoroughly. For example, the reason behind its abrupt loss of effectiveness at elevated temperatures is still not understood. Owing to this lack of knowledge, PVA repeatedly has failed in certain formulations, and thus has gained the reputation of being an unreliable FLA in practical applications.

Thus, the goal of this study was to investigate the working mechanism of PVA by determining its effect on cement filtrate viscosity and filter cake permeability, its potential adsorption on cement and its film-forming properties in cement pore solution. Special attention was given to its temperature-dependant solubility behavior by monitoring its particle size in water at temperatures between 27 and 90°C, respectively. These results were correlated

with its temperature-dependant fluid loss control behavior and an attempt was made to develop a mechanistic model which explains its performance in cement. Another goal was to uncover the mechanism behind the significant improvement of fluid loss control achieved by PVA when cement dispersants such as AFS or BNS are present.

EXPERIMENTAL

Materials

Oil well cement

An American Petroleum Institute (API) Class G cement ("black label" from Dyckerhoff AG, Wiesbaden/Germany) according to API specification 10A was used.⁸ Phase composition, specific density, particle size (d_{50} value) and specific surface area of the sample are presented in Table I.

PVA

A commercial sample of 88% hydrolyzed PVA (Mowiol 47–88, G2 grade), supplied by Kuraray Specialities Europe GmbH (Frankfurt am Main/Germany) with M_w 150,000–200,000 $g\ mol^{-1}$ was used. The chemical composition of the PVA is presented in Figure 1.

Dispersants

Acetone formaldehyde sulfite (AFS) polycondensate was synthesized from acetone, formaldehyde and sodium sulfite at molar ratio of 1 : 3 : 0.5 following a

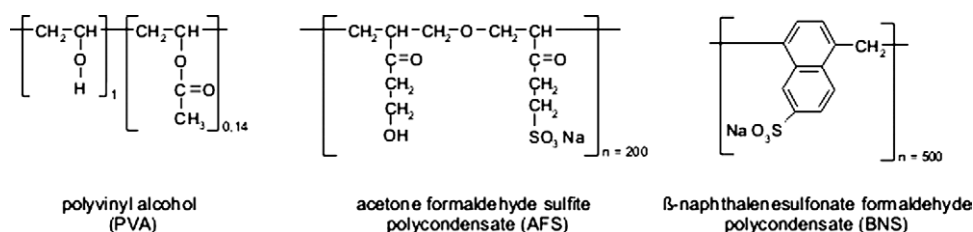


Figure 1 Chemical structures of PVA, AFS polycondensate, and BNS polycondensate samples studied.

modified version of the procedure described by Aignesberger and Plank.⁹ The modification included that sodium sulfite was completely dissolved in water at 50°C. After cooling to 40°C, acetone was added and the reaction flask was then kept at 40°C for 1 h at constant stirring. Owing to the highly exothermic character of the aldol reaction, aqueous formaldehyde at 30 wt % concentration was added dropwise over a period of 1 h, while the increasing temperature was maintained at 60–65°C by cooling with cold water. The molecular weight (M_w) of the synthesized AFS was found to be $\sim 64,000 \text{ g mol}^{-1}$.¹⁰

A commercial β -naphthalenesulfonate formaldehyde (BNS) polycondensate (Melcret[®] 500F supplied by BASF SE, Ludwigshafen/Germany) was used. Its molecular weight (M_w) was determined by GPC to be $\sim 119,000 \text{ g mol}^{-1}$. This suggests that the polymer consists of ~ 500 monomer units. The chemical structures of the dispersants are presented in Figure 1.

Poly(DADMAC)

A 0.001 N solution of poly(diallyl dimethyl ammonium chloride) obtained from BTG Mytek GmbH (Herrsching/Germany) was used as cationic polyelectrolyte.

Instruments

Charge titration

PCD 03 pH (Mütek Analytic, Herrsching/Germany) and a blue ribbon filter paper obtained from Whatman[®] (Dassel/Germany) were used.

Cement testing

Phase composition of the cement sample was determined using an XRD instrument (D8 Advance, Bruker AXS, Karlsruhe/Germany) with Bragg-Brentano geometry. 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° 2 θ at a scanning speed of 0.5 s/step (with 0.008°/step). Specific density of the cement was measured on an Ultrapycometer[®]1000 (Quantachrome Instruments, FL). The average particle size (d_{50}) measurement was carried out using a laser-based particle size analyser (Cilas 1064, Marseille/France). The specific surface area was determined with a Blaine instrument (Toni Technik, Berlin/Germany). A blade type laboratory blender manufactured by Waring (Torrington/USA) was used to prepare the cement slurry. The slurry was homogenized in an atmospheric consistometer (Model 1250, Chandler Engineering, Oklahoma/USA).

API filtration cell

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

Rheology

A Couette type coaxial cylinder rotational viscometer, FANN 35SA (Fann Instruments Company, Houston/USA) equipped with R1 rotor sleeve (rotor radius: 1.84 cm), B1 bob (bob radius: 1.73 cm, bob height: 3.8 cm) and F1 torsion spring was used.

Adsorption

High TOC II (Elementar, Hanau/Germany) with CO₂ detector was used.

Nanoparticle size analyzer

Particle sizes were measured with Horiba LB 550 dynamic light scattering particle size analyzer (Retsch Technology GmbH, Haan/Germany).

Viscometer

Kinematic viscosity of cement pore solutions containing PVA was determined with an Ubbelohde viscometer (50110/I, Schott Instruments, Mainz/Germany).

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 10B, issued by the American Petroleum Institute, using API Class G oil well cement and deionised water.¹¹ The cement slurry was mixed at a water-to-cement ratio of 0.44 using the Waring blender. 700 g of cement and the respective amount of FLA powder were dry-blended and added to 308 g water. In experiments using dispersants, AFS and BNS, respectively were dissolved in the mixing water before cement was added. Within 15 s, the cement/FLA blend was added to the mixing water holding the dispersant and was mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, 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.¹¹ After pouring the homogenised cement slurry into the filter cell, a differential pressure of 70 bar (N₂) was applied at the top of the cell. Filtration proceeded through a 3.5 square inch mesh metal sieve placed at the bottom of the cell. The filtrate produced by the differential pressure was collected for 30 min (V₃₀). As described by API RP 10B, the collected filtrate volume was doubled and designated as API fluid loss of the corresponding cement slurry.

Rheology

Rheology of the cement slurry was determined following API RP 10B procedure using the FANN 35SA rotational viscometer.¹¹ The homogenised cement slurry obtained after stirring in the atmospheric consistometer was poured into the 300 mL cup of the FANN rheometer. Shear stress (lbs/100 ft²) was measured at shear rates of 600, 300, 200, 100, 6, and 3 rpm. The initial instrument dial reading was taken 1 min after continuous rotation at 300 rpm. The following readings were taken in ascending order after continuous rotation of 20 s at each speed. Finally, the reading at 600 rpm was taken.

Charge titration

The specific anionic charge amounts of dispersant and FLA, respectively in cement pore solution were determined by charge titration using poly(diallyl dimethyl ammonium chloride) as cationic polyelectrolyte. Cement pore solution was prepared by vacuum filtration of the cement slurry without additives using a blue ribbon filter paper. Charge titration was performed with a solution prepared from 9 mL cement pore solution and 1 mL of a 0.2 g/L aqueous solution of either dispersant or FLA.

Adsorption

The amount of admixture adsorbed on cement 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 a slurry which was not stirred. In both cases, the same values for adsorbed amounts of polymers were found. The adsorbed amount was calculated from the difference in the equilibrium concentrations of the polymers in the liquid phase before and after adsorption. FLA concentration in the filtrate was determined by TOC analysis. The adsorbed amount of PVA was calculated by subtracting the concentration of unadsorbed polymer contained in the filtrate from the initial concentration of PVA.

Particle size measurement

Particle sizes of PVA in cold water and at 38°C were determined by dissolving 11.36 g of PVA in 1 L deionised water (this corresponds to a concentration of 0.5% bwoc PVA) under stirring in a Waring blender. Particle size measurement was carried out after mixing for 10 minutes. Particle size in hot water was measured by dissolving 11.36 g/L PVA in 1 L deionised water at 90°C. Particle size of PVA in presence of dispersants was determined as follows: PVA (22.72 g/L, this corresponds to a dosage of 1% bwoc FLA) were completely dissolved in deionised water at 70°C and 4.54 g/L dispersant (this corresponds to a concentration of 0.2% bwoc BNS and AFS, respectively) were added. After the dispersant was completely solved (stirring for 5 minutes), the size of particles present in solution was determined. Additionally, solutions containing 4.54 g/L dispersant were stirred for 5 min at 70°C and the particle sizes were measured.

Viscosity

Potential association of PVA particles in cement pore solution was assessed by determination of Huggins' constant K_H, derived from viscosity data. First, kinematic viscosities of cement slurry filtrates with dosages ranging between 0 and 1% bwoc PVA (incremental steps of 0.2% bwoc) were determined at 27°C using an Ubbelohde type capillary viscometer. Fifteen milliliter of 15 mL of filtrate were filled into the reservoir of the viscometer and the flow time was measured. From this, the kinematic viscosity of the filtrate was calculated according to eq. (1).

$$v = K(t - \zeta) \quad (1)$$

where K is the viscometer constant (0.1004 mm²/s²), t is the flow time and ζ is the flow time dependant Hagenbach-Couette correction term which is provided in the instrument instruction sheet. Multiplying the value for the kinematic viscosity with the specific density of the filtrate produced the value for the dynamic viscosity η_{dyn} as is expressed by eq. (2).

$$\eta_{\text{dyn}} = v \cdot \rho \quad (2)$$

From this, the reduced viscosity of the filtrate η_{red} was calculated according to eq. (3).

$$\eta_{\text{red}} = \frac{\eta_{\text{dyn}} - \eta_0}{\eta_0 \cdot c} \quad (3)$$

where η₀ is the dynamic viscosity of the cement filtrate with polymer and c represents the respective

concentration of PVA in the filtrate. Finally, Huggins constant was calculated based on eq. (4).

$$\eta_{\text{red}} = \eta_{\text{intr}} + K_H \cdot \eta_{\text{intr}}^2 \cdot c \quad (4)$$

There, the product of $K_H \cdot \eta_{\text{intr}}^2$ represents the slope of the linear function $\eta_{\text{red}} = f(c)$ and the intrinsic viscosity η_{intr} is obtained from the intercept point of $\eta_{\text{red}} = f(c)$ with the y-axis when c is extrapolated to 0.

RESULTS AND DISCUSSION

PVA is generally prepared by hydrolysis of poly(vinyl acetate) into PVA. The PVA sample used in this study contained 12% residual acetyl groups. This corresponds to a degree of hydrolysis of 88%. It is insoluble in cold water. Partial dissolution starts at $\sim 40^\circ\text{C}$ and at temperatures $>60^\circ\text{C}$, the sample is completely dissolved. A high degree of hydrolysis generally increases the crystalline portion in PVA through formation of hydrogen bridges between $-\text{OH}$ groups located on adjacent strains of the polymer.¹² Through these hydrogen bridges, the polymer strains become highly ordered and form lamellas, as is shown in Figure 2. Large crystalline domains are produced which render PVA water-insoluble. Contrary to this, polymer segments which still show vinyl acetate functionalities represent amorphous domains and are water-accessible.

Fluid loss performance of PVA

Filtrate volumes of cement slurries containing increasing dosages of PVA were measured at different temperatures. The results are shown in Figure 3. The minimum PVA concentration needed to achieve an API fluid loss of below 100 mL/30 minutes at 27°C was found to be 0.4% bwoc. At 37°C , this concentration increases to 0.8% bwoc, and at 49°C , more than 2.0% bwoc PVA are needed to obtain low fluid loss. From this data, one can conclude that the temperature limitation for this PVA sample is at $\sim 40^\circ\text{C}$. At temperatures higher than this, even excessive dosages cannot achieve low fluid loss volumes.



Figure 2 Structural model of semicrystalline PVA.

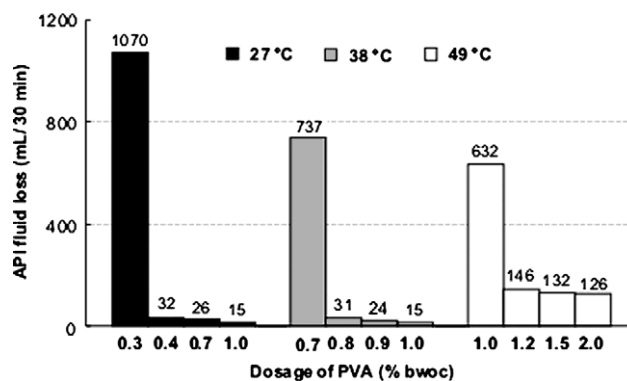


Figure 3 API fluid loss of cement slurries containing increasing dosages of PVA, measured at different temperatures (27°C , 38°C , and 49°C , respectively).

Mechanistic study

To understand this behavior, we devised a series of experiments to uncover the underlying mechanism. First, by following the procedure described by Desbrieres, we found that PVA significantly reduces filter cake permeability (see Table II).⁶ Lower filter cake permeability was always observed when effective fluid loss control was achieved. For example, at 27°C filter cake permeability dropped from 3653 mD when 0.3% bwoc PVA were applied and the API fluid loss was 1070 mL/30 min to 15 mD and an API filtrate of 32 mL/30 min when PVA dosage was increased to 0.4% bwoc. The same abrupt effect was found at 38°C where filter cake permeability decreases from 3427 mD at 0.7% bwoc PVA to 18 mD at 0.8% bwoc PVA. At the same time, API fluid loss drops from 737 mL/30 min to 31 mL/30 min. Next, we studied whether the reason behind this reduction in filter cake permeability was owed to any of the phenomena as follows: (a) increased viscosity of the cement pore solution caused by higher PVA dosages, (b) adsorption of PVA on cement particles or (c) another mechanism.

At first, the dynamic viscosity of cement filtrates obtained using different PVA dosages was studied. The results presented in Table II clearly demonstrate that the viscosity increase imparted by PVA is relatively minor. For example, the increase in filtrate viscosity at 27°C from 1.5 to 3.2 mPa s caused by PVA addition cannot explain the dramatic decrease in API fluid loss from 1060 mL at 0.3% bwoc PVA to 15 mL achieved with 1.0% bwoc PVA. Thus, this relatively minor effect of PVA on cement filtrate viscosity is not critical for its performance as fluid loss additive.

Next, an adsorptive working mechanism was considered for PVA and its adsorption on cement (depleted amount after contact with cement) was measured. If the working mechanism of this FLA was based on adsorption, then at a certain PVA

TABLE II
Filter Cake Permeability, Dynamic Filtrate Viscosity and API Fluid Loss of Cement Pastes Containing Different Dosages of PVA, Measured at 27 and 38°C, Respectively

Temperature (°C)	PVA dosage (% bwoc)	Filter cake permeability (mD)	Dynamic filtrate viscosity (mPa s)	Reduced filtrate viscosity (L/g)	API fluid loss (mL/30 min)
27	0.3	3653	1.5	0.4	1070
	0.4	15	1.5	0.4	32
	0.7	13	2.2	0.6	26
	1.0	8	3.2	0.8	15
38	0.7	3427	2.2	0.6	737
	0.8	18	2.1	0.7	31
	0.9	15	2.6	0.8	24
	1.0	4	2.1	0.8	15

dosage, the adsorbed amount should reach a plateau, indicating that the cement surface has been covered with the maximum possible amount of polymer. This behavior is represented by a LANGMUIR isotherm. The adsorption data measured at 27 and 38°C are presented in Figure 4. There, the depleted amount of PVA increases with increasing dosage, especially at 38°C. Obviously, no sufficient correlation between the trend in the API fluid loss and the adsorbed amount exists. For example, at 27°C and a PVA dosage of 0.4% bwoc, the depleted amount of PVA is only 0.9 mg/g cement whereas the API fluid loss is excellent (32 mL/30 minutes; see Fig. 3). Whereas at 0.7% bwoc PVA, practically the same API fluid loss is obtained, but the depleted amount of PVA is much higher (2.5 mg/g cement). Such result makes it doubtful whether the depleted amount of PVA can in fact be ascribed to adsorption on cement. Instead, it points to another mechanism which underlies the fluid loss behavior of PVA.

When the filtration cell was disassembled after conducting the fluid loss test, an important observation was made: a coherent polymer film situated between the sieve and the cement filter cake was

always present when effective fluid loss control was achieved. A picture of such PVA film found between the sieve and the cement filter cake is shown in Figure 5. This film is formed as a result of spurt loss and pressure applied. Under these conditions, the swollen and hydrated but undissolved PVA particles are pressed together and coalesce into a polymer film. Existence of large undissolved PVA particles in cold water (27°C) was confirmed by dynamic light scattering measurements. When 11.36 g/L of PVA were suspended in deionised water, a d_{50} value for the PVA particles of 2.4 μm was found, with no particles being $<2 \mu\text{m}$ and $>3 \mu\text{m}$ in size (Fig. 6). This value remained stable even after stirring for 1 day. Whereas, when heating the PVA solution up to only 38°C, a significant decrease of the size of PVA particles was noticed (d_{50} value $\sim 37 \text{ nm}$). This observation confirms the known hot water solubility of PVA.

To investigate whether association of PVA particles into a cohesive film really occurs, the Huggins constant (K_H) was determined according to the procedure described by Elias.¹³ A value of 0.6 was found. According to Huggins' theory, association

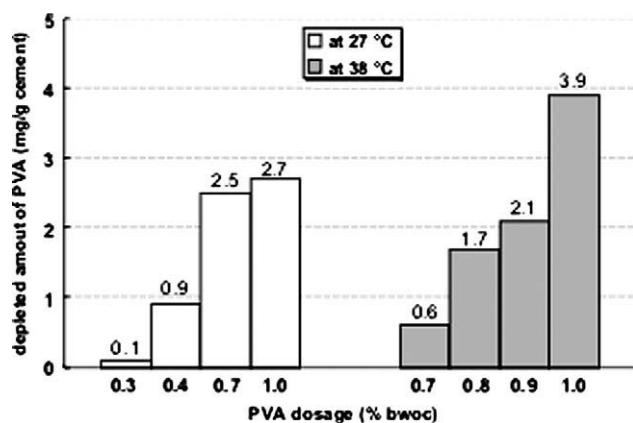


Figure 4 Depleted amounts of PVA found for cement pastes containing increasing dosages of FLA, measured at 27 and 38°C, respectively.



Figure 5 Image of the polymer film observed between the cement filter cake and the sieve after performing the HTHP filtration test using 0.5% bwoc PVA at 27°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

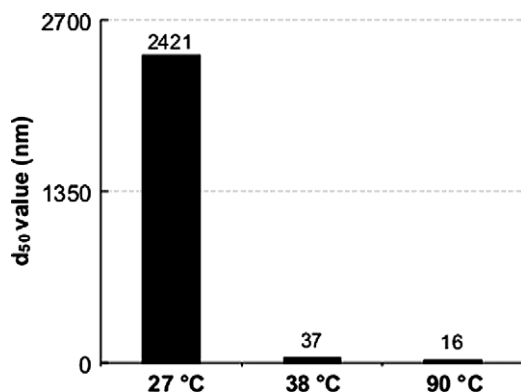


Figure 6 Particle size (d_{50} value) of PVA dispersed in deionized water (concentration: 11.36 g/L), measured at 27, 38, and 90°C, respectively.

takes place if K_H exceeds a threshold value of 0.5. Thus, it was confirmed that PVA particles form some kind of associates which effectively plug the pores of the cement filter cake. To confirm the film forming mechanism further, the minimum film forming temperature (MFFT) of this PVA sample was determined on a Kofler bench. For 1 wt % PVA suspended in cement pore solution, an MFFT of $<7^\circ\text{C}$ was found. This demonstrates that at the temperatures investigated here and when water is removed from the PVA suspension and even no pressure is applied, PVA particles can coalesce into a polymer film. As was shown before, the PVA sample studied here loses its effectiveness at temperatures above 40°C, apparently because increased temperature results in higher solubility of the FLA. Consequently, the concentration of PVA particles which is necessary to form a film drops below the critical threshold value. This model for the working mechanism based on film formation was supported by the observation that above 40°C, the amount of polymer film observed rapidly decreased, indicating gradual dissolution of PVA. At 49°C, for example, no more PVA film was found within the cement filter cake.

Effectiveness of dissolved PVA

If film formation was the critical mechanism to achieve fluid loss control with PVA, then completely dissolved PVA should not provide any fluid loss control. To investigate, PVA was completely dissolved in water by heating up to 90°C while stirring at 300 rpm. A clear solution was obtained which was tested for fluid loss control in the same way as the PVA powder before. The results obtained at 27°C are shown in Figure 7. Obviously, when PVA is dissolved in the mixing water, no fluid loss control is achieved. At normal dosages (e.g., 0.4% bwoc of dissolved PVA), the cement slurries dehydrate in

less than 30 min. Even at the addition of 2.0% bwoc PVA, an API fluid loss of 228 mL/30 min only is observed. The PVA film which was always formed when FLA powder was used and low fluid loss was accomplished, was not found when PVA was dissolved in water. The minor improvement in fluid loss with increasing dosage is due to the higher amount of dissolved PVA present in the pore solution and the increased dynamic filtrate viscosity (from 7 to 49 mPa·s). Obviously, heating reduces intra and inter molecular attraction between the PVA strains and makes it completely water soluble, as has been shown by previous authors.^{14,15} The consequence of this effect is that film formation is no longer possible. Thus, fluid loss control is lost.

To confirm this mechanism further, particle sizes of PVA powder added to cold water (27°C) and of a sample dissolved at 90°C were compared using a dynamic light scattering particle size analyzer. As is shown in Figure 6, the cold water preparation obtained by agitating 11.36 g/L PVA in deionised water (this concentration corresponds to a dosage of 0.5% bwoc PVA) using a Waring blender and measured at 27°C produced a d_{50} value of 2.4 μm . In contrast to this, PVA dissolved at 90°C resulted in a d_{50} value of only 16 nm. This way, a direct relationship between the particle size of PVA and its film forming capability was established. Small particle size indicates dissolution of PVA and subsequent impossibility of controlling fluid loss by film formation.

Performance of PVA in presence of AFS and BNS dispersant, respectively

AFS polycondensate and BNS polycondensate dispersants are commonly used to lower the viscosity of oil well cement slurries.^{3,4,16} Here, we tested combinations of 1% bwoc PVA with 0.2% bwoc of these dispersants at 49 and 60°C, respectively. The results

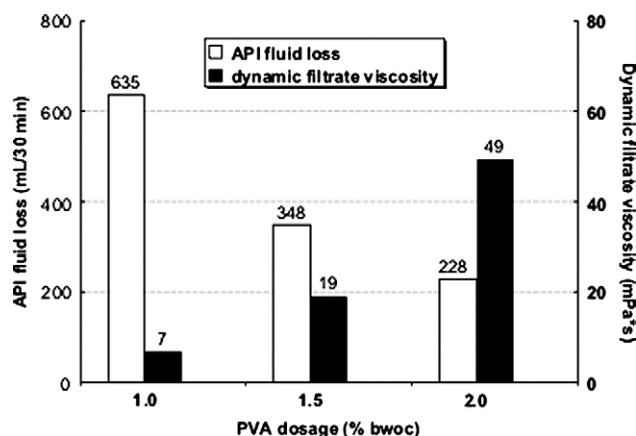


Figure 7 Dynamic filtrate viscosity and API fluid loss of cement slurries containing fully dissolved PVA, measured at 27°C.

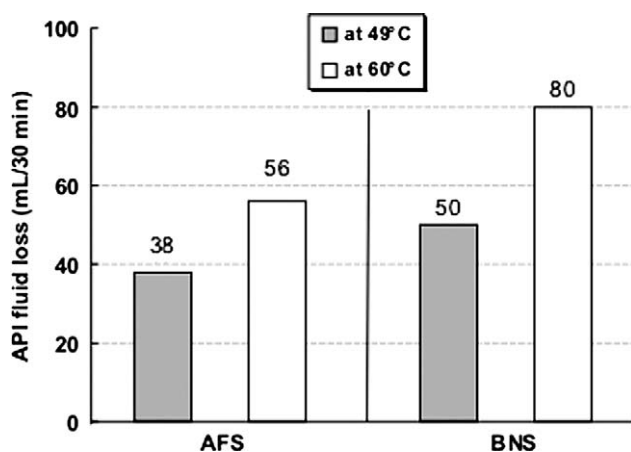


Figure 8 API fluid loss of cement slurries containing 1.0% bwoc PVA and 0.2% bwoc of AFS or BNS dispersant, measured at 49 and 60°C, respectively.

are presented in Figure 8 and Table III. Addition of a dispersant to the slurry containing PVA provides a significant reduction in API fluid loss. For example, at 40°C the API fluid loss of 632 mL/30 min found for the cement slurry containing 1% bwoc PVA drops to 38 mL/30 min after addition of AFS and to 50 mL/30 min when BNS is added. Thus, by using such combination the temperature range at which PVA works effectively as FLA can be extended up to at least 60°C. A comparison of the two dispersants shows that AFS is slightly more effective than BNS.

To understand the mechanism behind this synergistic effect, the specific anionic charge amounts of PVA, AFS and BNS were determined in cement pore solution. They were found to be 59 C/g for PVA, 243 C/g for AFS and 220 C/g for BNS. This clearly shows that the dispersants are much more hydrophilic than PVA, and thus possess a higher solubility in water. Their presence in the filtrate prevents the less anionic PVA from going into solution. This way, undissolved PVA particles which can form a polymer film are preserved even at higher temperatures. Particle size measurements confirmed this mechanism. At 70°C, the sizes of particles present in 4.54

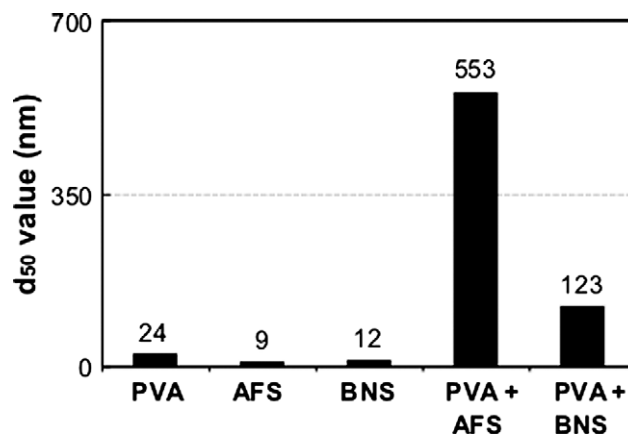


Figure 9 Particle size (d_{50} value) of PVA (concentration: 22.72 g/L), AFS and BNS (concentrations: 4.54 g/L), and of combinations between PVA and AFS or BNS, dispersed in deionised water, measured at 70°C.

g/L AFS and BNS solutions respectively (corresponding to a dosage of 0.2% bwoc dispersant) were found to be less than 15 nm (Fig. 9). In contrast, a suspension holding admixture dosages of 1% bwoc PVA and 0.2% bwoc dispersant, prepared at 70°C, showed an average particle size of 553 nm (in presence of AFS) and 123 nm (in presence of BNS). It indicates that large PVA microgel particles are still present in these suspensions. For comparison, at 70°C the same PVA solution without dispersant shows a particle size of 24 nm only, indicating that PVA was mostly dissolved. This way, dispersant addition to PVA increases the temperature range at which PVA works from 40 to ~60°C, depending on dosage.

CONCLUSIONS

The working mechanism of PVA as cement fluid loss additive depends on its water-insolubility and is based on the formation of a polymer film. This way, PVA behaves similar to latex dispersions (e.g., styrene-butadiene rubber) which are applied to prevent gas migration in hardened oil well cement.⁴ Film

TABLE III
Rheology (Shear Stress) of Cement Slurries Containing 1% bwoc of Pure PVA Without and with 0.2% bwoc BNS and AFS, Respectively, Measured at Different Shear Rates and Temperatures

Temperature (°C)	Dispersant (0.2% bwoc)	Shear stress (lbs/100 ft ²) at shear rate (rpm)					
		600	300	200	100	6	3
49	–	>300	193	155	113	50	32
	BNS	208	104	71	36	4	3
	AFS	180	90	62	33	4	3
60	–	>300	187	138	103	45	30
	BNS	177	104	70	38	6	5
	AFS	151	84	57	32	6	5

formation occurs by coalescence of insoluble PVA microgels existing between hydrating cement particles. At elevated temperatures where PVA becomes water-soluble (40°C), this FLA loses its effectiveness because film formation is no longer possible. According to this mechanism, several options exist to extend the performance of PVA at higher temperatures. The first option comprises addition of additives with higher water-solubility, e.g., sulfonated polycondensates with higher anionic charge amount than PVA. They can prevent PVA from going into solution at higher temperatures. Another option is the addition of fine inorganic particles such as e.g., microsilica which reduce the effective filter cake pore diameter to less than 1 μm . There, even partially dissolved PVA microgel particles are large enough to provide sufficient fluid loss control simply through a plugging mechanism. The third option is application of PVA with higher molecular weight and almost 100% degree of hydrolysis. Such large PVA macromolecules which do not possess any amorphous domains can be expected to be water-insoluble even at much higher temperatures than the sample tested here. Its particles will coalesce easily and can provide effective fluid loss control even at temperatures which may reach 100°C.

Our study demonstrates that the decreased performance of PVA cement fluid loss additive at elevated temperatures is not the result of temperature induced degradation of the polymer, as was often speculated by applicators. Instead, its water-solubility is the key parameter which determines its effective-

ness as cement fluid loss polymer. Insight into the working mechanism of PVA and the physico-chemical processes occurring in cement pore solution provides the basis for more reliable performance in its application. This way, it contributes to seal off oil and gas wells more safely.

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