Effects of Divalent Cations, Seawater, and Formation Brine on Positively Charged Polyethylenimine/Dextran Sulfate/Chromium(III) Polyelectrolyte Complexes and Partially Hydrolyzed Polyacrylamide/Chromium(III) Gelation

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ABSTRACT: Polyacrylamide crosslinked with Cr(III) is a common blocking agent that is injected into oil reservoirs to shut off the water flow to features such as fractures and high-permeability rock to improve the volumetric sweep efficiency during water flooding. This technique is limited to situations where enough gelant can be injected to fill the high-permeability zones before gelation occurs. Cr(III) may be encapsulated with a high entrapment efficiency in self-assembling polyelectrolyte complex nanoparticles with effective diameters of about 100–200 nm and formed by the mixture of polyethylenimine and dextran sulfate in nonstoichiometric amounts. The electrostatic interaction between the polyelectrolytes and the Cr(III) is reversible, but diffusion out of the nanoparticles is retarded, and this results in a delay in gelation from minutes or hours to several days in deionized water. Produced and injection waters often contain salts at concentrations comparable to seawater. The effects of these salts were investigated, and we found that the delay in gelation was further extended to as much as 35 days at 40°C and 35 h at 80°C in the presence of divalent ions at seawater concentrations, either alone or in a field brine or seawater; this greatly increases their potential utility. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1008–1014, 2010

Key words: gels; nanotechnology; polyelectrolytes

INTRODUCTION

Water flooding of oil reservoirs is a common method of producing oil when the energy stored in the reservoir (e.g., due to pressure from dissolved gas or an underlying aquifer) has been depleted. Oil reservoirs are complex structures consisting of both oil and water phases in a porous medium, and the heterogeneity of the reservoir can lead to an inefficient process. Injected water flows preferentially through high-permeability (high-hydraulic-conductivity) zones, bypassing large volumes of oil-bearing rock. In an effort to maximize the volume of an oil reservoir that is contacted by the injected water (volumetric sweep efficiency), it is common to try and block these high-permeability zones.[1,2] Historically, the most common blocking agent used for water shutoff and sweep improvement is partially hydrolyzed polyacrylamide (HPAM), in which a fraction of the amide groups are hydrolyzed to form negatively charged carboxyl groups and which can be crosslinked with a polyvalent cation, most often Cr(III), to form a gel.[3–10] A solution of HPAM is mixed with Cr(III) [typically, 5000-ppm HPAM and 100-ppm Cr(III)] and injected into the formation, where it invades the highest permeability spaces and sets in place.[8–11] To maximize the depth of placement of the gelant, it is desirable to have a long gelation time because, once set, the pressure required to continue propagation into the formation may not be attained because of limitations imposed by the hydraulic conductivity, parting pressure of the rock (the pressure at which the rock fractures, which further increases the hydraulic conductivity), and available pumping capacity.[12] Because of the large volumes involved, an ideal system would have a gelation time measured in days, weeks, or even months. Cr(III) is often used in association with ligands such as acetate and propionate to delay gelation,[13–16] but even so, the typical gelation time is on the order of a few hours;[10,17] this potentially limits the use of this system to the near-wellbore region or to reservoirs with fractures close to or intersecting the wells.[9,10,18]

The gelation of HPAM exhibits three stages: induction, gelation (or acceleration), and pseudo-equilibrium (or terminal equilibrium).[19] The induction stage is characterized by the nucleation and

growth of pregel aggregates. In the gelation stage, the mean molecular weight increases abruptly with an attendant increase in viscosity. Eventually, most of the polymer is immobilized in a more or less rigid network, and the remaining polymer in solution becomes aggregated with the bulk gel during the pseudo-equilibrium stage. This sequence was studied experimentally and modeled by Cheng et al.[20] A similar pattern was also seen in agarose, a polysaccharide derived from seaweed,[21] although unlike agarose, which forms gels spontaneously under the right temperature regime, the gelation in HPAM was dependent on an external crosslinker, in this case Cr(III). Free polyethylenimine (PEI) is also capable of crosslinking HPAM.[22,23]

There is a need for a controlled-release delivery system to delay gelation and promote the in-depth treatment of high-permeability intervals to reduce the flow of water. We previously reported a novel system in which Cr(III) was entrapped in charged, nonstoichiometric PEI/dextran sulfate (DS) polyelectrolyte complexes (PECs) with good colloidal stability. When this mixture was added to HPAM, this resulted in delayed gel formation.[24]

One desirable feature of such a system is the small size of the entrapping particles to allow ready penetration of suspended particles into reservoir rock without loss due to settling or filtration[12,25] Particles of less than a few hundred nanometers generally demonstrate good colloidal stability because of Brownian motion, and the agglomeration of particles may be prevented by control of the surface charge to maximize electrostatic repulsion. The short diffusive path lengths in such small particles may result in early release and, hence, unacceptably short delays in gelation times, but this may be addressed by the formulation of particles in such a way that release is impeded by electrostatic binding events within the particles. PECs, formed by self-assembly upon the mixing of selected polycations and polyanions, can be produced with a variety of properties by the control of the composition and conditions[26,27] and have been used to entrap and deliver molecules of biomedical interest.[28,29]

In field applications, gelant systems are exposed to a variety of salts at concentrations up to and beyond those found in sea water; this may affect the stability and gelation times relative to the model system so far described. In this study, we examined the effects of divalent cations (Ca^{2+} and Mg^{2+}), synthetic brines representing sea water, and a formation brine representative of an oil field in Alaska on the particle size and charge of PEI/DS/Cr PECs and the gelation time of Cr(III)/HPAM gelants made with Cr(III)-loaded PECs at different temperatures.

TABLE I
Synthetic Formation Brine and Seawater Compositions

Component	Formation brine (g/kg)[a]	Seawater (g/kg)[b]
NaCl	22.982	26.518
KCl	0.151	0.725
$CaCl_2 \cdot 2H_2O$	0.253	1.141
$MgCl_2 \cdot 6H_2O$	1.071	2.447
$NaHCO_3$	2.706	0.202
NaBr	0.000	0.083
Na_2SO_4	0.145	0.000
$MgSO_4$	0.000	3.305
H_2O	To 1000 g	To 1000 g

[a] pH 8.17.
[b] pH 8.00.

EXPERIMENTAL

Cr(III)-loaded PEC nanoparticles were prepared and characterized with the following procedures.

Materials

DS (molecular weight = 500 kDa, Fisher Scientific, Pittsburg, PA) and PEI (molecular weight = 25 kDa, Aldrich, St. Louis, MO) were used as obtained without further purification. HPAM (molecular weight = 6000 kDa, AlcoFlood 935, lot A2247BOV) was obtained from Ciba Specialty Chemicals (Suffolk, VA). Chromium chloride ($CrCl_3 \cdot 6H_2O$; molecular weight = 266.45, Fisher Scientific) was used as a gelation crosslinker. Magnesium chloride ($MgCl_2 \cdot 6H_2O$), calcium chloride ($CaCl_2 \cdot 2H_2O$), sodium bromide (NaBr), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrogen peroxide (H_2O_2), sodium azide (NaN_3), and hydrochloric acid (HCl) were obtained from Fisher Scientific and were used as received. Synthetic formation brine and seawater[30] were prepared according to the compositions shown in Table I.

Preparation of PEC nanoparticles

A typical method was used to prepare the Cr(III)-loaded PEC nanoparticles as follows: a 10,000-mg/kg aqueous solution of DS (15.32 g) was added rapidly by hand from a syringe fitted with a 16-gauge needle to 34.26 g of a 10,000-mg/kg aqueous solution of PEI with stirring at 600 rpm. Once the foam from this addition subsided, 1.0 mL of a Cr stock solution was injected, and the mixture was stirred for an additional 30 min. The Cr stock solution (~ 19,500 mg/kg Cr(III) as ~ 100,000 mg/kg $CrCl_3 \cdot 6H_2O$) was made immediately before use by the dissolution of $CrCl_3 \cdot 6H_2O$ in 18-MΩ water. The particle suspension was used as prepared.

Characterization of PEC nanoparticles

PECs were characterized by the determination of the mean particle size and the ζ potential. The mean PEC particle size was estimated from dynamic light scattering by a ZetaPALS zeta potential analyzer (Brookhaven Instruments Corp., Huntsville, NY). Typically, two drops of nanoparticle suspension from a transfer pipette was diluted with deionized water in a 1-cm^2 polystyrene cuvette, and three consecutive 1-min measurements were obtained by the detection of light scattering at a 90° angle. The mean effective diameter and polydispersity were determined by the method of cumulants.[31] The ζ potential of the particles was investigated by phase analysis light scattering with the same instrument. Four-drop samples were diluted to 1.4 mL with a 1×10^{-3} mol/kg KCl solution. The ζ potential was calculated from the electrophoretic mobility with the Smoluchowski approximation. Three measurements were taken for each sample.

Determination of the Cr concentrations

Cr concentrations were determined by oxidation of Cr(III) to Cr(VI) and measurement of the UV–vis absorbance at a wavelength of 373 nm according to reported procedures.[16] The oxidation of Cr was accomplished by the mixture of 0.5–1.0 mL Cr(III) samples with 1.0 mL of 3% H_2O_2 and 1.0 mL of $1N$ KOH and the heating of the mixture for 1 h at 87°C. The oxidized samples were then diluted to a Cr(VI) concentration between 1 and 10 mg/kg by the addition of deionized water. A PerkinElmer (Waltham, MA) Lambda-20 UV–vis spectrometer was used to measure the UV absorbance of Cr(VI) at ambient temperature. The Cr(III) concentration in the sample was determined with a Cr(VI) concentration versus UV absorbance standard curve at 373 nm. Relative standard deviations of less than 0.1% were typical for 11 absorbance measurements on a given sample. The concentration in the original solution was calculated by multiplication by the appropriate dilution factor.

Cr entrapment efficiency

The entrapment efficiency of Cr into polyelectrolyte nanoparticles was calculated by an indirect method where the Cr concentration was determined in the supernatant after the centrifugation of a sample and subtracted from the initial amount added to the nanoparticle suspension. Freshly made nanoparticles were centrifuged at 13,000 rpm for at least 20 min. The supernatant was collected for the Cr concentration measurement. The entrapment of Cr was calculated as follows:

$$\text{Entrapment efficiency} = \frac{[Cr^{3+}]_0 - [Cr^{3+}]_s}{[Cr^{3+}]_0} \times 100\%,$$

where $[Cr^{3+}]_0$ and $[Cr^{3+}]_s$ are the Cr(III) concentrations entered into the experiment and measured in the supernatant after mixing with particles, respectively.

Preparation of gelants

An HPAM stock solution (20,000 ppm) was prepared by the dissolution of solid HPAM in 4% (w/w) NaCl/400-mg/kg NaN_3 solution. A container with a known amount of cold 18-MΩ water or brine was vigorously stirred to create a deep vortex. The polymer was slowly added to the shoulder of the vortex to effectively wet the polymer beads. The container was sealed to minimize evaporation and was stirred continuously for 48 h to ensure the complete dissolution of polymer. The stock solution was optionally filtered through a 1-μm cellulose filter under a driving pressure of 15 psi. The HPAM stock solution was mixed with either 18-MΩ water or brine/seawater and finally the nanoparticles. The amounts of the three components were tuned so that the final gelant contained 5000-ppm HPAM and 100-ppm Cr(III) in a 1% (w/w) NaCl/100-ppm NaN_3 solution. The gelant was stirred for a few minutes until a visually homogeneous solution was obtained and was then kept at constant temperature and allowed to gel.

Measurement of the gel time under various conditions

A Brookfield (Brookfield Engineering, Middleboro, MA) digital cone-and-plate viscometer (model DV-II + Pro) fitted with a 0.8° cone (model C-40) was used periodically to monitor the viscosity of the subsamples of the gelants and thus to determine the gel time. The *gel time* was defined as the time when the viscosity of the gelant increased abruptly to a value greater than 1028 cP (the upper range of the instrument) at a shear rate of 2.25 s^{-1}. The temperature of the viscometer was controlled at 25°C.

RESULTS AND DISCUSSION

Effects of various Mg^{2+} and Ca^{2+} concentrations on the PEI/DS/Cr PECs and the HPAM/Cr(III) gelation times

The PEC formulations exhibited immediate precipitation when prepared with PEI and DS stock solutions made with brine-containing divalent ions. However, PECs assembled with polyelectrolyte stock solutions made with 18-MΩ water remained stable after the addition of calcium or magnesium
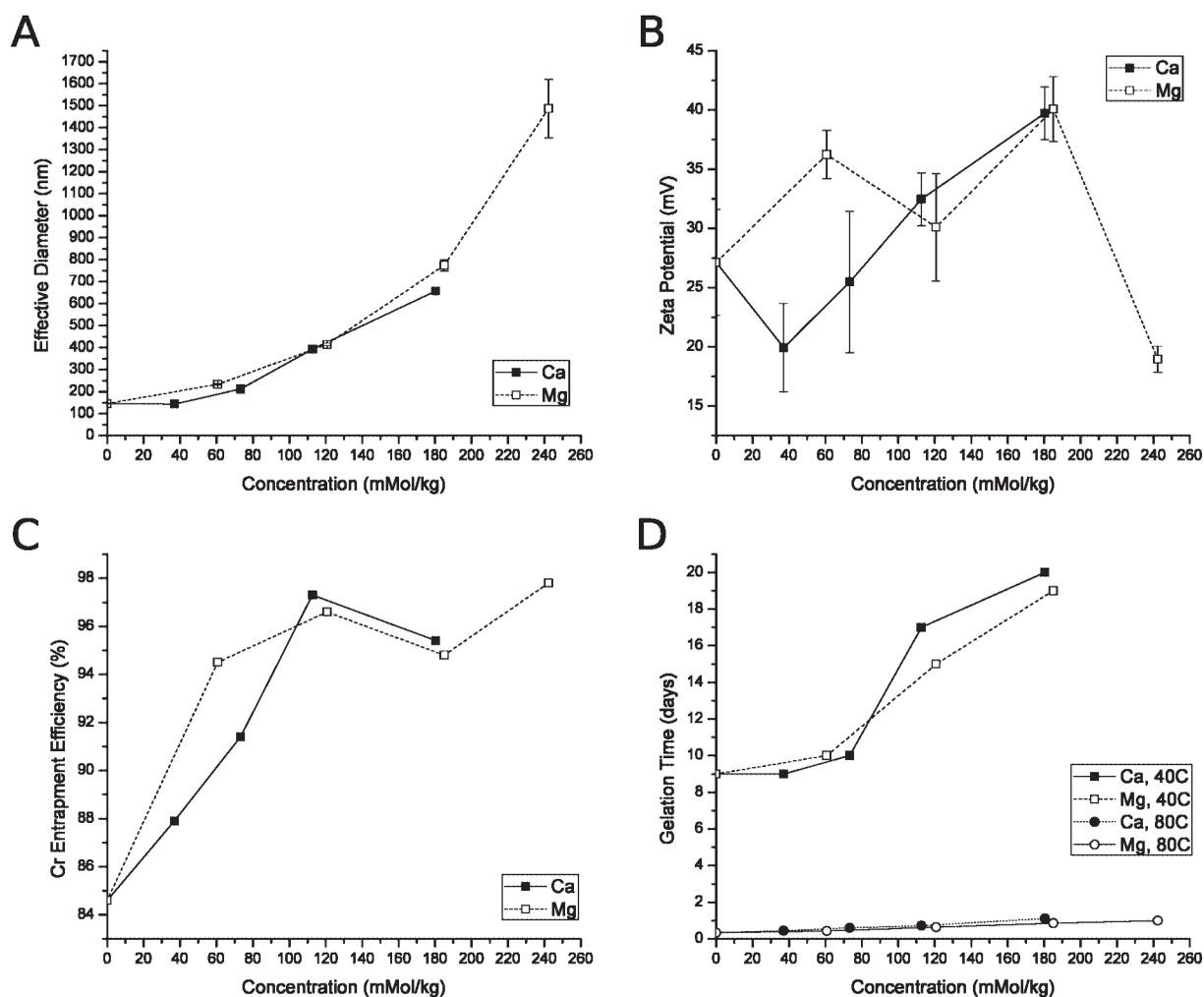
Figure 1 Effect of increasing concentrations of Ca^{2+} and Mg^{2+} on positively charged PEI/DS/Cr(III) PEC nanoparticle suspensions: (A) the effective diameter of the nanoparticles, (B) the ζ potential, (C) the chromium entrapment efficiency, and (D) the gelation times for 5000-ppm HPAM/100-ppm Cr gelants (error bars = standard error).

chloride. For example, 4.15 g of Mg^{2+} (as $MgCl_2 \cdot 6H_2O$) or Ca^{2+} (as $CaCl_2 \cdot 2H_2O$) solutions were added to the PEI/DS stock complex made in 18-MΩ water to give a final concentration in the PEC suspension in the range $0\text{–}240 \times 10^{-3}$ mol/kg. The effective diameter, ζ potential, and Cr entrapment efficiency of the PECs were determined and plotted against the molar concentration [Fig. 1(A–C)]. In all cases, the nanoparticle suspension retained colloidal stability for at least 48 h after synthesis before it was added to the gelant system.

Above about 40×10^{-3} mol/kg of either cation, the effective diameter of the PECs increased from an initial value of about 145 nm and reached about 1500 nm at a concentration of about 240×10^{-3} mol/kg. There was no clear effect of changing Mg^{2+} concentration on the ζ potential but the increase of Ca^{2+} over the range studied seemed to increase the ζ potential. The chromium entrapment efficiency

improved with increasing concentration of both Mg^{2+} and Ca^{2+} and reached a maximum of 95–98%.

HPAM/Cr(III) gelants were prepared with the divalent-ion-containing PECs, and the gelation times for different concentrations of Mg^{2+} and Ca^{2+} at 40 and 80°C were determined [Fig. 1(D)]. The gelation time of gelants made with PECs with no divalent cations was about 9 days at 40°C, and the gelation time at this temperature increased to about 18 days when the divalent ions increased from 80 to 180×10^{-3} mol/kg. Gelation occurred in a matter of hours at 80°C, but nevertheless, a similar doubling in gelation time with increasing divalent ion concentration was seen.

Effect of Mg^{2+} and Ca^{2+} in seawater and formation brine on the PEI/DS/Cr PECs and the associated HPAM/Cr(III) gelation times

PECs were made with 18-MΩ water as described. The gelants were prepared by the mixture of 10 g of

TABLE II
Effects of Ca²⁺ and Mg²⁺, Separately and Together in Synthetic Formation Brine and Seawater, on the PEI/DS/Cr PEC Nanoparticles

Diluent	Effective diameter (nm)	Polydispersity	ζ potential (mV)
Control	160.6 ± 2.7	0.084 ± 0.021	15.53 ± 1.4
Ca²⁺ (420 ppm)	168.4 ± 4.5	0.043 ± 0.033	16.68 ± 1.61
Mg²⁺ (1298 ppm)	1638.5 ± 35.6	0.395 ± 0.014	18.05 ± 0.63
Formation brine	3245.8 ± 2860.5	0.509 ± 0.433	6.92 ± 6.34
Seawater	1487.7 ± 754.5	0.201 ± 0.157	18.66 ± 0.94

a solution of 20,000-ppm HPAM, 4% NaCl, and 0.04% NaN₃ with a mixture consisting of 11.45 g of nanoparticle suspension (pH 9.2) and 18.55 g of either a solution of divalent ions at a concentration similar to that found in seawater [1298-ppm Mg²⁺ (as MgCl₂·6H₂O) or 420-ppm Ca²⁺ (as CaCl₂·2H₂O)], synthetic formation brine, or synthetic sea water (Table I). The particles were analyzed immediately after being mixed with brine, and the effective diameter, polydispersity, and ζ potentials are shown in Table II. In all cases, the pH of the final gelant was in the range 9.3–9.5. Particles mixed with formation brine, seawater, and Mg²⁺ exhibited an increase in the effective diameter of an order of magnitude, along with a significant increase in polydispersity, which was indicative of a bimodal distribution of particle sizes. Ca²⁺ by itself at a concentration comparable to that seen in seawater did not have a significant effect on either the size or polydispersity, probably because of its lower concentration when compared with Mg²⁺. At these concentrations, the ζ potential was not affected by the presence of divalent ions either alone or in seawater, but a reduction
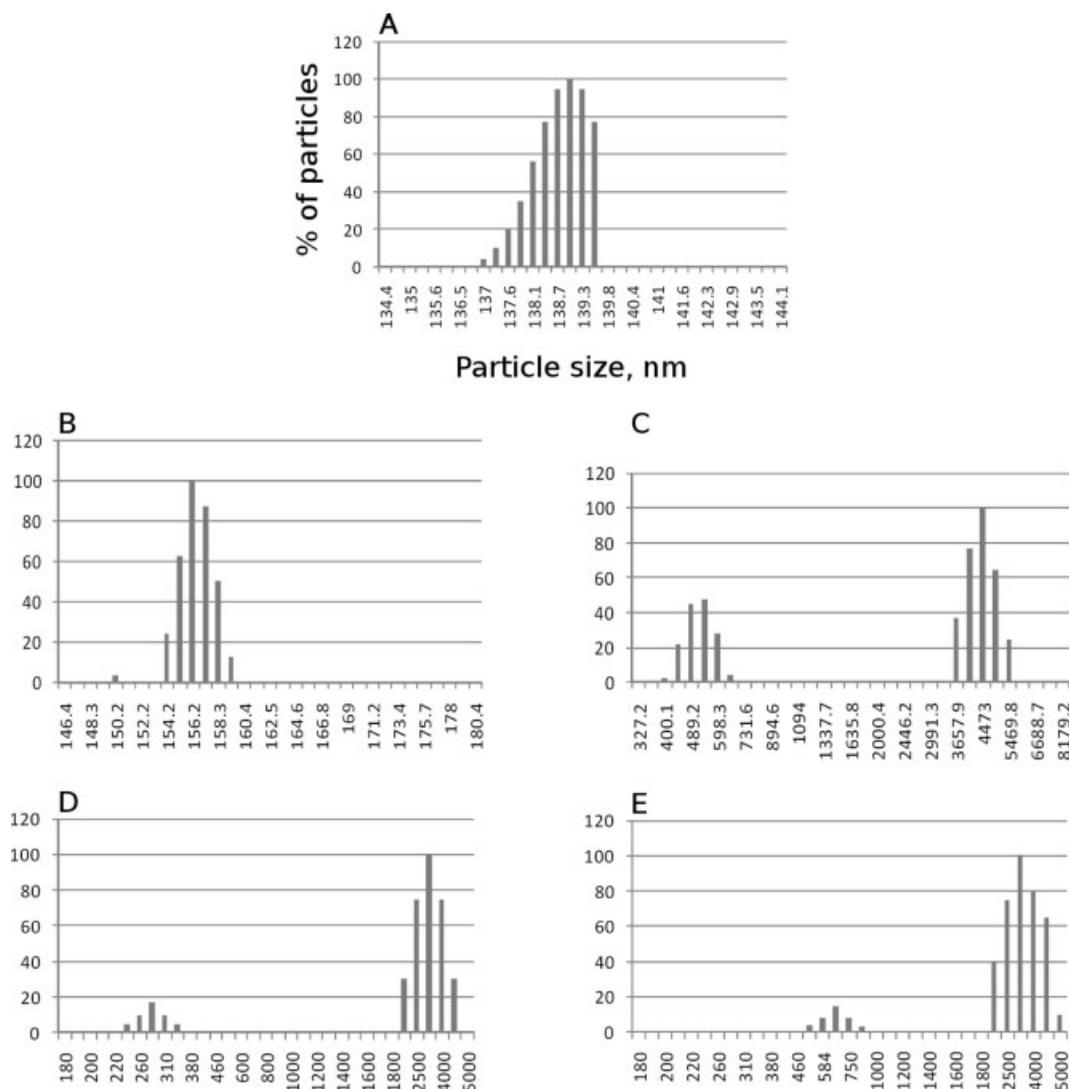
Figure 2 Size distributions of PEC nanoparticles exposed to different salt solutions: (A) control, (B) 420-ppm Ca²⁺, (C) 1298-ppm Mg²⁺, (D) field brine, and (E) seawater.
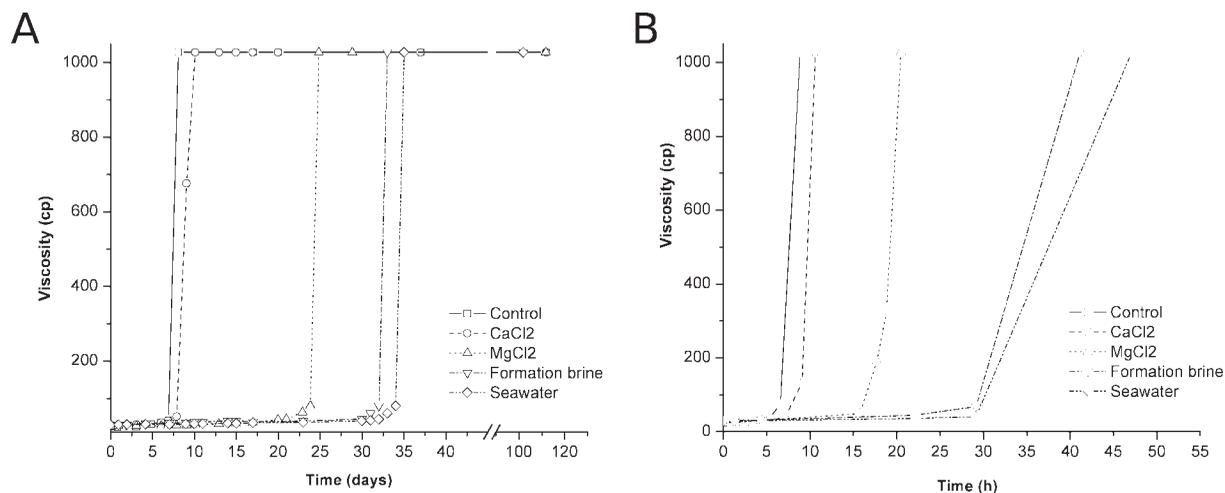
Figure 3 Viscosity at 25°C versus time for 5000-ppm HPAM/100-ppm Cr gelants made with positively charged PEI/DS/Cr(III) PEC nanoparticles with the addition of divalent cations, seawater, or formation brine and stored at (A) 40 or (B) 80°C. The control system had no divalent ions added. The gelation time of HPAM with 100-ppm free Cr(III) without divalent ions was approximately 30 min.

in the ζ potential was seen in the formation brine. At higher divalent ion concentrations (e.g., Mg at seawater concentrations, brine, and seawater), the particle size distribution (Fig. 2) became bimodal, and this suggested that growth was by the agglomeration of particles rather than by a simple expansion of individual nanoparticles. This was consistent with the known affinity of primary amines (which account for about 25% of the amines in PEI for divalent cations).[32]

The viscosity was monitored over time in the gelants stored at 40°C [Fig. 3(A)] and 80°C [Fig. 3(B)]. In all cases, a strong stable gel was formed, although there was degradation of the gel at 80°C under aerobic conditions. This degradation did not occur under anaerobic conditions, which are more representative of the field.

The encapsulation of Cr(III) in PEC nanoparticles was already shown to delay gelation in the HPAM/Cr(III) system ($\sim$ 7 days at 40°C and $\sim$ 6 h at 80°C compared to <30 min at 40°C with unencapsulated CrCl$_3$).[24] Gelation was further delayed by all of the treatments containing divalent cations: Ca^{2+} at seawater concentrations had the least effect, followed by Mg^{2+}, formation brine, and seawater, in that order, at both temperatures. The delay with brine and seawater was greater than the individual delays due to Ca^{2+} and Mg^{2+} alone, which suggested either a synergistic effect or that monovalent cations and anions may have also contributed to the delay. The delay in gelation time with formation brine and seawater was highly significant, with an increase over the base case with PEC-encapsulated Cr(III) of approximately sixfold.

Presumably, this improvement was a result of the improved entrapment efficiency (and, hence, a corre-

spondingly lower concentration of free Cr in the PEC suspension) and the larger particle size. The release of Cr(III) from the PECs was a function of particle size because of a combination of longer diffusive path lengths and reduced surface area to volume ratios.

CONCLUSIONS

The PEI/DS/Cr(III) PEC nanoparticles prepared in 18-MΩ water and exposed to calcium and magnesium ions, either alone or in field brine or seawater, exhibit increased effective diameters but retained colloidal stability (although calcium ions alone at seawater concentration did not significantly affect the particle size). A delay in the gelation of HPAM/Cr(III), with the chromium encapsulated in nanoparticles, was extended in the presence of divalent cations, either alone or in field brine or seawater; this greatly increases the potential utility of the system and offers the potential for in-depth treatment of the high-permeability zones, which cannot be treated with current gel systems. The improvement in the gelation delay was associated with an increase in the effective particle diameter, which we hypothesize might hinder the penetration of the Cr-bearing particles into the rock matrix in especially tight formations.

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