Complexation and precipitation of scale-forming cations in oilfield produced water with polyelectrolytes

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Abstract: Divalent cations such as Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+}, commonly found in oil/gas produced water at high concentrations, adversely affect oil and gas production by forming scales in pipes, tanks, process equipment such as oil-water separators, and treatment equipment such as filters and reverse osmosis membranes. If the water is reinjected, e.g., for water flooding, scales may also form on the well screens and in the producing formation. Water soluble polyelectrolytes have been used to inhibit scale formation in oil and gas production and to eliminate cationic metals from water via membrane separation. However, the underlying interactions between scale-forming cations and various polyelectrolytes are not well understood. To this end, two commercially available anionic polyelectrolytes with different repeating functional groups, poly(acrylic acid) (PAA) and poly(sodium 4-styrenesulfonate) (PSS), were used to evaluate complexation and precipitation of Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+} in binary systems, multi-ion mixtures, and produced water. The apparent dissociation constant (*pKa*) of PAA was determined by titration to be 6.7, indicating a high affinity of PAA for H^+. The strength of the complexes formed between PAA and scale-forming cations (binding strength) decreased in the order $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$ at pH 5. Higher pH values led to a higher affinity of PAA for divalent cations, which is attributable to the increase in binding sites for cations as the PAA more completely ionizes. By contrast, the affinity of PSS decreases in the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$, with no significant pH effect. The formation and precipitation behavior of polyelectrolyte complexes (PECs) was investigated by reacting cations with the sodium salt of PAA (sodium polyacrylate) or with PSS. Only Ba^{2+} formed precipitates with PSS in single-cation solutions, although small amounts of Sr^{2+} were also removed by PSS from a mixed cation solution. However, all of the scale-forming cations formed PEC precipitates with PAA in both binary and mixed-ion solutions, depending on the cation concentration and molar ratio of PAA to divalent cations. The maximum amount of precipitation occurred at a molar ratio of PAA to M^{2+} of 1.5 to 1.7, while overdosing of PAA caused dispersion of the precipitates. High concentrations of monovalent cations inhibited precipitation of divalent cations with PAA. Up to 73% of scale-forming cations were removed from field-collected produced water samples through repeated (4 times) addition of PAA at a molar concentration ratio of 1. The release of scale-forming cations from PAA-M^{2+} precipitates, thereby regenerating PAA, was achieved by adding HCl.

Keywords: Scale-forming cations; Produced water; Polyelectrolytes; Precipitation; Poly(acrylic acid); Poly(sodium 4-styrenesulfonate)

1. Introduction

Produced water is water drawn from the ground during oil and gas production, which typically has very high salinity and contains numerous organic and inorganic contaminants [1-3] . The disposal of produced water has become an increasingly burdensome task in the United States because of its potential adverse impacts on terrestrial and aquatic ecosystems if released into the environment [4, 5]. The standard industry practice in many areas has been to dispose of the water by injecting it into Class II Underground Injection Control (UIC) wells [6]. However, this practice has come under scrutiny because of suspected links with seismic events, and restrictions on disposal by deep well injection have recently been put in place in a number of locations, including Kansas and Oklahoma [7]. By comparison, only 0.61% of the total managed produced water generated in the United States was treated for beneficial reuse as of 2012 [8]. In addition, much of the oil and gas production in the U.S. takes place in regions where freshwater resources are limited, resulting in competition with other uses (primarily agriculture) for existing supplies. Considering these factors, increased reuse of produced water could provide important freshwater conservation benefits on a localized scale while also decreasing the need for disposal by deep well injection.

One significant barrier to produced water treatment and reuse is the presence of high concentrations of divalent cations, which can form scales that adversely affect the performance of both membrane and thermal desalination technologies. Membrane desalination technologies are becoming increasingly popular for producing freshwater from saline waters [3, 9-12]; but their successful application can be greatly limited by membrane fouling [13, 14], which increases operation and maintenance costs and reduces both membrane performance and membrane life. Mineral scaling is a common cause of membrane fouling; and calcium, magnesium, barium and strontium cations are prone to forming scales with carbonate and sulfate anions [15]. Scale formation in thermal desalination systems, typically considered when treating waters too saline for a reverse osmosis system, reduces heat transfer efficiency and increases operation and maintenance costs. For example, scaling problems limit inland desalination applications, such as brackish water RO processes [11] and desalination of oil/gas produced water [3]. Scale formation can also clog pipes and well screens; reduce the permeability of the formation if injected (e.g., for water flooding); and cause any radium present to accumulate (via co-precipitation) perhaps to the extent that pipes and process equipment must be handled as a low-level radioactive waste. Therefore, removal of scale-forming cations (e.g., Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+}) is a critical step in preparing produced water for desalination and reuse.

Water soluble polyelectrolytes, polymers that have a positive or negative charge due to the presence of repeating ionizable groups [16, 17], have been used as scale inhibitors in oil production [18, 19], nanoparticle templates in material synthesis [20-22], flocculants in water treatment [23, 24], and nano-sized ion exchangers or adsorbents for removing contaminants from water and wastewater [25-29]. Polyelectrolyte complexes (PECs) form when polyelectrolytes associate with other species of opposite charge (e.g., multivalent cations). Under some conditions, the polyelectrolytes may be “salted out”, forming solid phase PECs (precipitates) that can be separated from solution by sedimentation, centrifugation, or membrane filtration [30-33]. In this process, multivalent cations effectively serve as cross-linking agents for the polyelectrolytes, and are thereby trapped in the PECs and can be separated from aqueous solution [20, 27].This provides a mechanism for selectively removing scale-forming cations from solutions with very high concentrations of monovalent ions, as is typically the case for produced waters.

The extent to which PECs precipitated depends on counter-ion valence and binding strength, and on the properties of the polyelectrolytes including their molecular weight and functional groups [31]. In this study, two commercially available anionic polyelectrolytes with different functional groups, poly(acrylic acid) (PAA) and poly(sodium 4-styrenesulfonate) (PSS), were used to evaluate complexation and precipitation of Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+} in binary systems, multi-ion mixtures, and produced water. The objectives of this study were (1) to compare the complexation of scale-forming cations by two different polyelectrolytes; (2) to investigate the precipitation of PECs as a means of removing scale-forming cations; (3) to examine the release of divalent cations from precipitated PECs, as a preliminary step in assessing the possibility of regenerating and reusing polyelectrolytes for cation removal; and (4) to study the removal of scale-forming cations from produced water by precipitating PECs.

2. Materials and Methods

2.1 Materials

Poly(sodium 4-styrenesulfonate) (PSS) with a manufacturer-supplied average molecular weight of ~200 kDa (as 20 wt% in H_2O) and polyacrylic acid (PAA) with a manufacturer-supplied average molecular weight of ~250 kDa (as 35 wt% in H_2O) were both purchased from Sigma Aldrich, USA, and used directly without further purification. Sodium polyacrylate (also abbreviated as PAA) was generated by mixing PAA and NaOH in reagent water in equimolar concentrations (polymer molar concentrations are reported as monomer units throughout this paper). HCl, NaOH, and NaCl used to prepare solutions and adjust their pH were all analytical grade. Solutions of Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} were all prepared from their respective analytical grade chloride salts. Reagent water (18.2 MΩ/cm water prepared using a Milli-Q Direct 8 system) was used in all experiments.

2.2 Determination of PAA Dissociation

The dissociation of PAA was determined by the pH titration method. An aqueous solution of PAA (10 mM monomer units) was titrated with 10 mM NaOH at room temperature. Solution pH was measured using a pH meter (Fisher Accumet AB15) with a glass pH electrode (Fisher Accumet, Cat. #13-620-223A). The volume of NaOH solution added into the PAA solution and the corresponding solution pH value were recorded to make a titration curve.

2.3 Affinity of Polyelectrolytes for Scale-Forming Cations

The complex formation affinities of Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} with PAA were determined through an ultrafiltration separation experiment. Solutions with 5 mM PAA and varying concentrations of divalent cations (1-3 mM) were prepared as experimental samples. The total volume of each experimental sample was 100 mL, and pH was adjusted to 5 by dropwise addition of 10 mM NaOH. A dead-end ultrafiltration cell (Amicon, USA, model 8200), with a stirrer and cellulose membranes (Diaflo, USA) with a diameter of 62 mm and effective area of 28.7 cm^2, was used to separate the aqueous phase cations from those associated with the polyelectrolyte. Membranes used in these experiments had a molecular weight cut-off (MWCO) of 10 kDa. All experiments were conducted at room temperature and 30 psi, using nitrogen gas as the pressure source. Following separation, the concentration of each cation in the permeate was determined through inductively coupled plasma - optical emission spectrometry (ICP-OES, PerkinElmer, Optima 2000 DV), and the concentration in the polyelectrolyte phase was calculated based on the difference between the initial added cation concentration and the aqueous (permeate) concentration.

A PAA solution (sodium polyacrylate) was used to investigate the effect of pH and background ion concentration on divalent cation affinity for PAA. HCl was added into a solution containing PAA (as sodium polyacrylate) and Ca^{2+} to produce pHs ranging from 3 to 5. NaCl concentrations from 0.01 to 0.1 M were added into a PAA and Ca^{2+} solution maintained at pH 5 to evaluate the influence of the background concentration of monovalent cations (i.e., Na^+).

2.4 Precipitation of Scale-Forming Cations with Polyelectrolytes

Varying concentrations of PAA (as sodium polyacrylate) were added into a series of solutions, each containing 5 mM of a single scale-forming cation, to investigate the potential for precipitate formation. The solution pH in each case was 7-7.5 after PAA addition. Following PAA addition, each 10 mL sample was vortexed and allowed to sit for 24 hour. Subsamples (2 mL) were then taken and centrifuged in either a plain centrifuge tube or a centrifuge tube with a 3 kDa filter (Vivaspin, PN VS0192, 2 mL) for 15 min at 14000 rpm. Following centrifugation, the cation concentrations were measured in both the supernatant and the filtrate by ICP-OES. Dynamic light scattering (DLS) experiments employing a NanoBrook Omni particle sizer (Brookhaven Instruments Corp.) were used to determine the effective PEC particle size. Three consecutive 1 min measurements were obtained by detecting light scattering at a 90° angle. The mean effective diameter was determined by the method of cumulants [21, 34]. A similar process was performed using PSS instead of PAA. For these experiments, samples were allowed to stand for 24 hours, and then centrifuged for 15 min at 14000 rpm. The divalent cation concentration in each supernatant was then determined using ICP-OES.

2.5 Cation Release and PAA Regeneration

Two mL of a multiple scale-forming cation solution (12.5 mM each of Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+}) were reacted with 50 mM PAA (as sodium polyacrylate) for 30 min to form cation-polyelectrolyte precipitates. Following centrifugation at 14,000 rpm for 15 min, the supernatant was removed. HCl was then added to the precipitate at concentrations from 50 - 100 mM, and the sample was sonicated for 30 min before being filtered using a 3 kDa filter and then analyzed to determine the extent of cation release under acidic conditions.

Based on the results of initial studies, PAA regeneration was performed by adding 75 mM HCl to centrifuged precipitates (50 mM PAA monomer in a 50 mL sample), followed by sonication for 30 min. After sonication, the solution was filtered through a 10 kDa UF membrane at 30 psi (applied with N_2 gas) and room temperature, until concentrated 10 fold (to 5 mL); and NaOH was then added to adjust pH to 8.5 to regenerate the PAA.

2.6 Scale-Forming Cation Removal from Produced Water

Produced water collected from Reno County, Kansas was used as a real-world water sample to test precipitative removal of scale-forming cations through the addition of PAA. The water sample had a TDS concentration of 128,000 mg/L and pH of 6.2; and the concentrations of selected cation were as shown in **Table 1**. PAA stock solution (~2114 mM, as sodium polyacrylate monomer) was added into 50 mL produced water samples at a PAA (monomer) to total scale-forming cation concentration ratio of 1, and the sample was vortex mixed for 30 s. Then the sample stood for 15 min before the supernatant was collected to measure cation concentrations by ICP-OES. This process was repeated four times to maximize removal of the scale-forming cations.

Table 1. Concentrations of selected ions in produced water from Reno County, Kansas

Cation	Concentration (mM)
Na^+	1355
Ca^{2+}	133.8
Sr^{2+}	19.7
Mg^{2+}	64.7
Ba^{2+}	0.042
Cl^-	1718
HCO_3^-	3.61
SO_4^{2-}	1.15

3. Results and Discussion

3.1 Dissociation of PAA and PSS

Figure 1a shows the pH change when adding 10 mM NaOH into a PAA solution (10 mM PAA monomer). The slope of the curve is lower between pH values 6 and 8 as compared to pHs outside that range, as this is where PAA has the highest buffer capacity. Using the manufacturer-supplied average molecular weight of PAA, the apparent pK_a was calculated as 6.7, where the slope of the curve is smallest. This is close to the value of 6.5 measured by Tomida *et al.* [35] for 10 kDa PAA and the value of 6.45 determined by Roman *et al*. [36] for PAA modified polypropylene. However, this value is higher than the value of 6.17 obtained by Gregor *et al.* [37] for 30 – 100 kDa PAA.

In the absence of other salts, the dissociation of 10 mM PAA in the absence of added salt can be defined by **equation 1** [37],

$$K_a = [H^+]\left(\frac{[A^-]}{[HA]}\right)^2 \tag{1}$$

where A refers to the monomer of the polymer acid. Based on **equation 1**, the relation between pH and the degree of PAA deprotonation (ionization), α, can be determined using the modified Henderson-Hasselbach equation (**eq 2**) [35],

$$pH = pK_a - 2log\left(\frac{1-\alpha}{\alpha}\right) \tag{2}$$

Using **equation 2** and the titration results, the degree of deprotonation of PAA was calculated as a function of pH, as shown in **Figure 1b**. The measured values of α were determined from the molar ratio of NaOH added to PAA carboxylic monomers. When the pH is lower than 4, around 5% of the PAA functional groups in solution are ionized, and the degree of ionization increases as pH increases. When the pH reaches 8, ionization of PAA is above 80%. The degree of ionization of PAA was close to the results determined via FTIR spectra by Qi *et al.* [38]. The curve of pH – log[(1-α)/α] is almost straight in the pH range 6-8. The concentration of deprotonated PAA equals the concentration of protonated PAA (PAA acid) at pH 6.7, i.e., where pK_a = 6.7, α = 0.5, and log[(1-α)/α] = 0.

Unlike the weak acid carboxylic groups of PAA, the sulfonic acid groups of PSS can be treated as strong acids. The pK_a for PSS was estimated at 1.6 by measuring pH while adding a known concentration of HCl (data not shown), close to the previous reported value (1.95) reported by Yoo *et al.* [39], indicating the PSS has a much lower affinity for H^+ than does PAA.

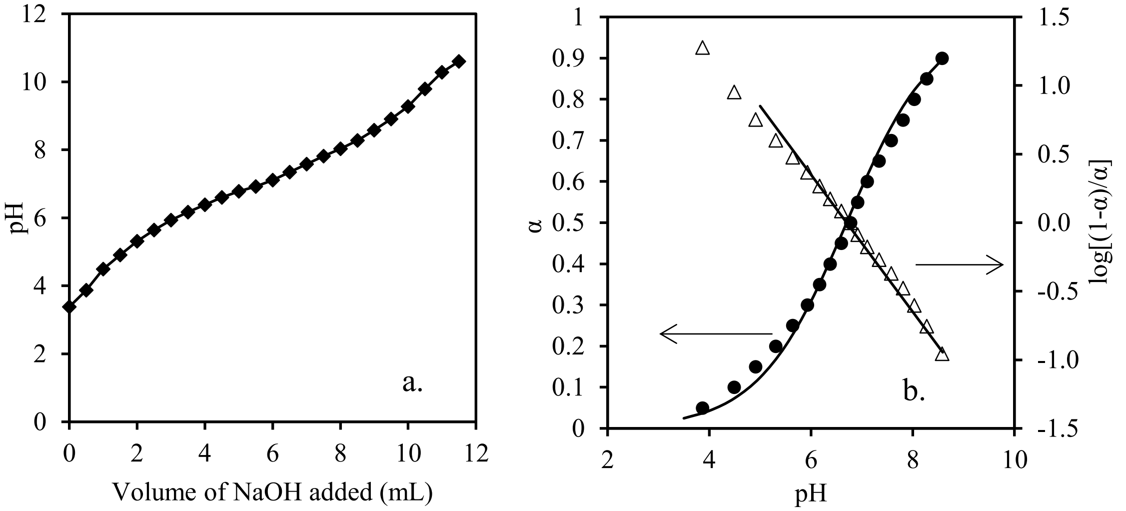


Figure 1. PAA titration curves. (a) 10 mM PAA solution titrated by 10 mM NaOH solution; (b) Degree of deprotonation of PAA versus pH in the absence of salts (black circle for α and open triangle for log[(1-α)/α], lines show model values calculated based on experimental *pKa*).

3.2 Affinity of Polyelectrolytes for Cations

Figure 2a shows the distribution of Ba^{2+}, Ca^{2+}, Sr^{2+}, and Mg^{2+} between the aqueous phase and PAA complexes at pH 5. (The pH was adjusted by dropwise addition of 10 mM NaOH to the PAA solution.) The affinity of PAA for the cations tested decreased in the order $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$. The order of Sr^{2+} and Ca^{2+} is different than their affinity for PSS, which was previously determined to be $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ [40]. In addition, higher concentrations of aqueous scale-forming cations required more NaOH to adjust the solution to pH 5, because more protons were released from the PAA as increasing amounts of scale-forming cations were bound.

Figure 2b shows the binding of Ca^{2+} by 5 mM PAA^- at different solution pH values (pH was adjusted by dropwise addition of HCl to the sodium polyacrylate solution). As pH increased, more Ca^{2+} associated with the polyelectrolyte phase, showing that more Ca^{2+} binding sites were available within the polyelectrolyte phase. This occurs both because more carboxylate groups (which strongly bind calcium) are formed as the PAA dissociates, and because there are fewer protons present to compete for these binding sites. **Equations 3** and **4** [41] describe the dissociation of PAA and the formation of a cation-PAA complex.

$$PAA \overset{K_a}{\leftrightarrow} H^+ + PAA^- \tag{3}$$

$$nPAA^- + M^{m+} \overset{K}{\leftrightarrow} MPAA_n^{(m-n)+} \tag{4}$$

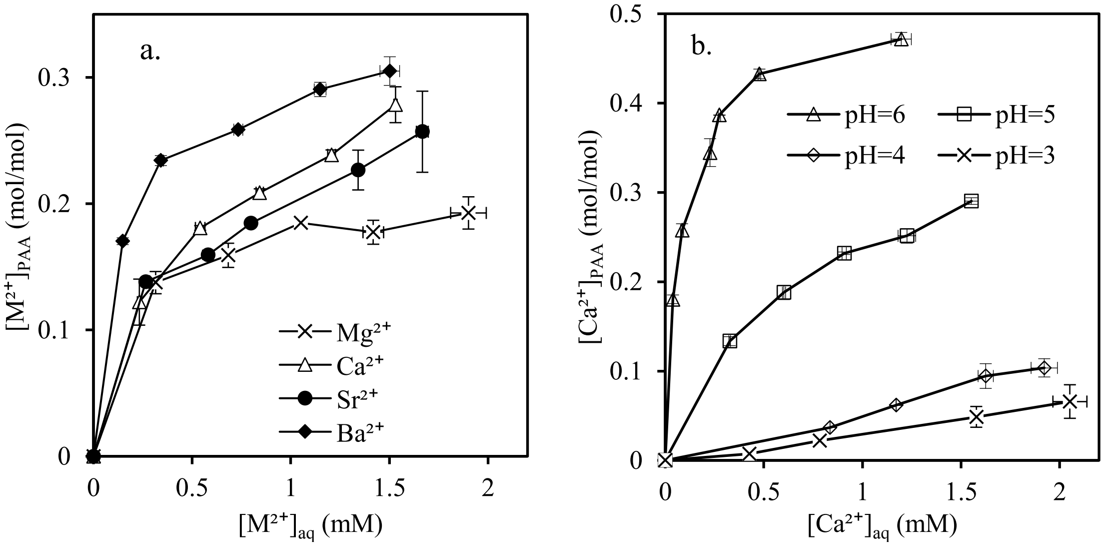
where *M* refers to a given cation in solution; m represents the charge of the cation; *n* is the average coordination number of PAA ligands bound to one cation.

Combining **equations 3** and **4**, **equation 5** is obtained,

$$nPAA + M^{m+} \leftrightarrow nH^+ + MPAA_n^{(m-n)+} \tag{5}$$

According to **eq 5**, a lower pH leads to a higher degree of neutralization of PAA, and more -COOH groups inhibit the interaction between cations and PAA; increasing pH enhances the formation of the polyelectrolyte complexes (PECs). Qi *et al.* [38] also reported that complexation between lanthanide ions and PAA strengthens as pH increased, because cations are much more strongly bound by carboxylate groups (-COO$^-$) than by carboxylic acids (-COOH). In the current experiments, "salting out" also occurred at pH 5 and 6 when aqueous phase Ca^{2+} concentrations were higher than 1 mM, but the solution remained clear at pH 3 and 4 over the full experimental range of PAA concentrations.

Figure 2c shows the competition between Na$^+$ and Ca^{2+} for PAA. Although the interaction between PAA and divalent cations was reported as chelating binding [36, 41, 42], monovalent cations, e.g., Na$^+$, are still competitive with scale-forming cations over the experimental concentration range. In contrast, previous studies have shown that divalent cations have a much higher affinity for PSS than does any monovalent cation, including H$^+$, even at low pH [40] .



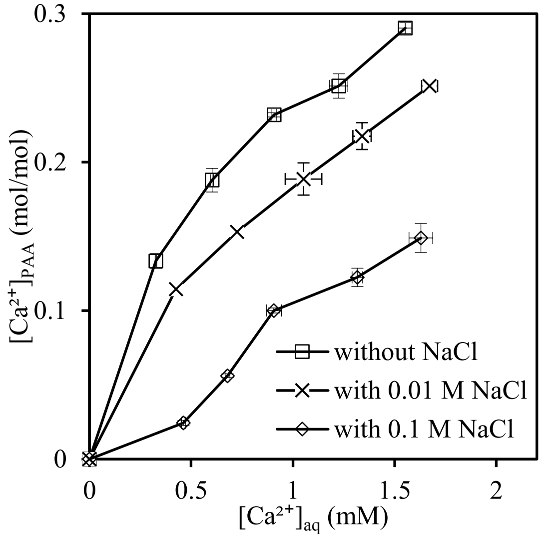


Figure 2. Binding of scale-forming cations to PAA in 5 mM solutions of PAA (based on monomeric units). (a) Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} at pH 5; (b) Ca^{2+} at different pH values; (c) Ca^{2+} with competition from Na^+ at pH 5.

3.3 Precipitation of Scale-forming Cations by Anionic Polyelectrolytes

3.3.1 Precipitation of Scale-forming Cations Using PAA

Figure 3 shows the effect of PAA addition on PEC and aggregate formation in the presence of 5 mM divalent cations. For all cations, PAA addition initially resulted in divalent cation removal after centrifugation or membrane filtration. Below 5 mM polymer addition, only Mg^{2+} showed a difference in aqueous concentration between these two separation methods. As polymer addition continued, however, centrifugation became less effective than membrane filtration at removing all cations. The highest removals of cations using centrifugation were achieved at PAA dosages of about 7.0 to 8.5 mM, corresponding to polymer to cation molar ratios of about 1.5 to 1.7, with a maximum of 80% removal of Ba^{2+}, 70% of Ca^{2+} and Sr^{2+}, and 60% of Mg^{2+}.

Cation removal by filtration through the 3 kDa membrane, however, continued to increase as more PAA was added. Removal following membrane filtration was nearly complete at a PAA concentration of 10 mM (PAA to cation equivalent ratio of 1:1), and at PAA dosages lower than 10 mM, the slope of the cation concentration versus PAA addition is approximately 1:1 on an equivalent basis for each cation (**Figure 3**). Thus each divalent cation is almost completely bound by PAA at a polymer to cation equivalent ratio less than 1. However, this does not necessarily indicate that every functional group was bound to a divalent cation; some may have been bound to Na^+ or H^+ ions, and some divalent cations may have been bound to a single carboxylate group. At a polymer concentration of 15 mM or greater, corresponding to a polymer to divalent cation molar ratio of 3, aqueous divalent cation concentrations in the filtrate were below detection, indicating complete removal.

The initial removal of scale-forming cations following addition of low dosages of PAA is consistent with their known complexation with PAA. The fact that similar removal was achieved by both centrifugation and filtration at low dosages of PAA demonstrates that the complexes are aggregating to form particles large enough to settle under the centrifugal force applied, and even to some extent by gravity (sedimentation) in the case of Ba^{+2} and Mg^{+2}. This presumably occurs because multivalent cations are able to bridge carboxylate groups on two neighboring polyelectrolyte molecules, effectively acting as cross-linking agents and increasing the molecular size of the PECs. The fact that similar removals were observed following centrifugation and filtration (**Figure 3**) indicates that virtually all of the PAA molecules are cross-linked at PAA to cation molar ratios of 1 or less, including very low ratios. If this were not so, centrifugation would not have been able to remove PECs (and their associated metal ions) to the same extent as membrane filtration.

Increasing the PAA dosage beyond about 8.5 mM (a PAA to divalent cation molar ratio greater than 1.7) caused disaggregation of the PECs, as evidenced by the complete loss of cation removal by centrifugation (and by sedimentation in the cases of Ba^{+2} and Mg^{+2}). This disaggregation is presumably caused by the increasing negative charge of the PECs as the PAA concentration increases, resulting in electrostatic repulsion between polyelectrolyte molecules. Since cation removal by membrane filtration continues to increase, there is no indication that this process adversely affects the formation of polyelectrolyte-metal complexes, though it clearly affects their physical aggregation.

It also can be seen in **Figure 3** that aggregation of Ba and, to a lesser extent, Mg, PECs proceeded further than for Sr and Ca, allowing for cation removal by gravity settling. For both cations, maximum removal through settling alone was achieved at polymer to divalent cation molar ratios near 1. As the PAA concentration increased, these larger aggregates were destabilized. Navarro *et al.* [27] also reported on a similar precipitation and redispersion of heavy metal complexes formed by adding phosphonomethylated polyethyleneimine.

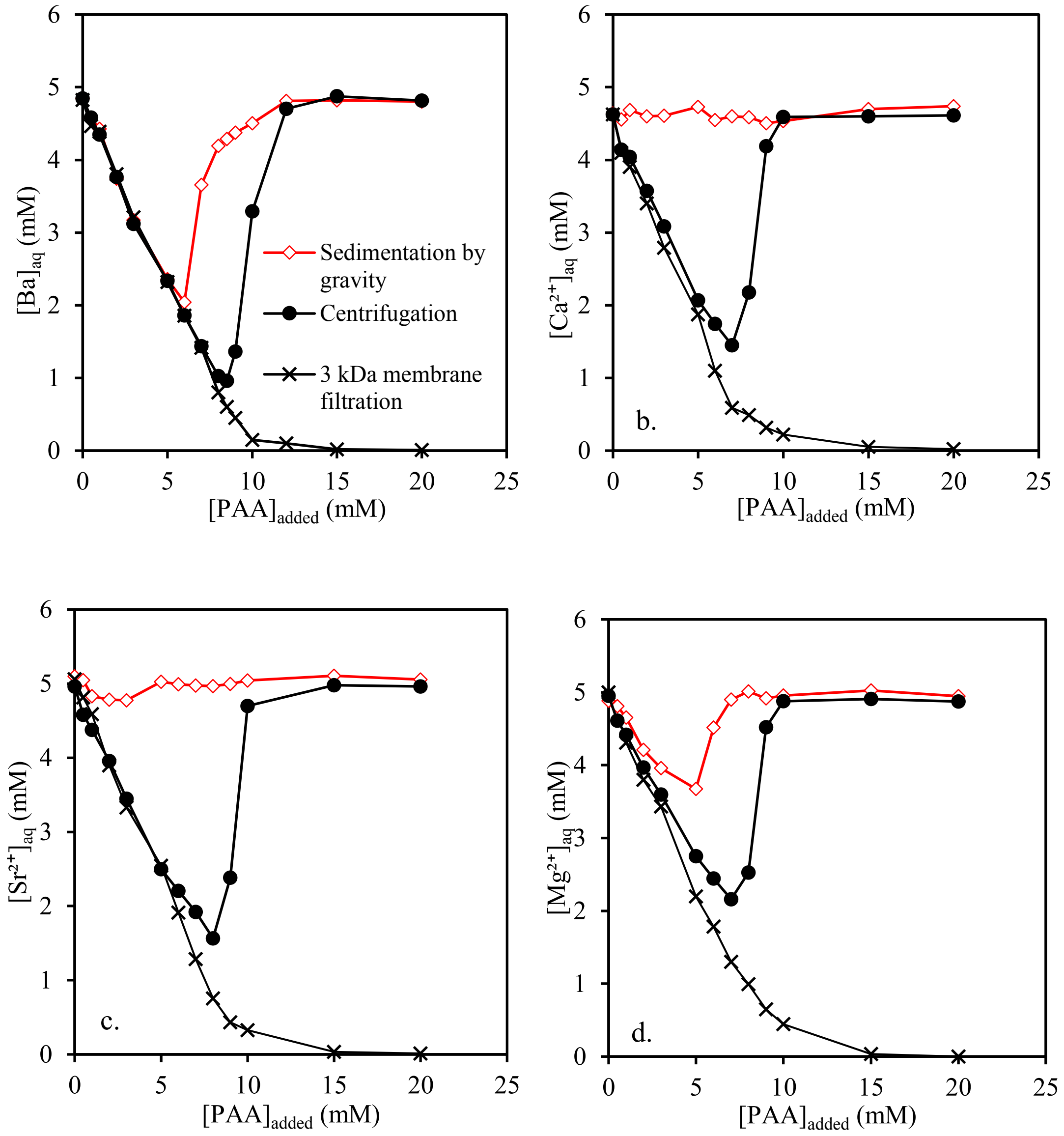


Figure 3. Removal of scale-forming cations *versus* PAA concentration at ~pH 7-7.5. (a) Ba^{2+}; (b) Ca^{2+}; (c) Sr^{2+}; (d) Mg^{2+}.

Figure 4a shows the mean effective particle size (based on lognormal distribution) of PECs formed by PAA and individual scale-forming cations, each at 5 mM concentration (polymer to M^{2+} ratio of 1). After 24 hours, the Ba-PECs precipitated and settled out easily (**Figure 4a**) while the other PECs exhibited precipitation (as indicated by the cloudy solutions) but little to no settling, suggesting that the Ba-PECs had a larger effective particle size than the other three types of PECs. The particle size distribution results (**Figure 4a**) show that cation-PEC particle size decreased in the order of Ba >> Mg > Sr > Ca, consistent with their settlement performance shown in **Figure 3**. The effective sizes of the Ca-PECs and Sr-PECs were smaller than that of the Mg-PECs, such that they were not removed by sedimentation. However, Ca^{2+} and Sr^{2+} still exhibited greater affinity for complexation with PAA than Mg, as shown by the greater removal of Ca and Sr by centrifugation after adding 5 mM PAA.

Figure 4b shows the mean effective particle sizes of Ca-PECs formed at varying molar concentration ratios of PAA to Ca^{2+} , with $[Ca^{2+}]$ = 5 mM. Mean particle size decreased as the molar concentration ratio increased, but more Ca^{2+} was complexed by PECs at higher PAA to Ca^{2+} concentration ratios, forming increasingly larger numbers of smaller PECs and resulting in greater removal of Ca^{2+}, up to a polymer/cation concentration ratio of 1.75. As the polymer/cation molar concentration ratio increased above 2, the particle size distribution approached that of pure PAA (not shown in the figure), indicating redispersion of PEC aggregates. **Figure 4c** shows the mean effective particle size of Ca-PECs at varying initial Ca concentrations, all at a polymer/Ca molar ratio of 1. Particle size increased as the concentration of Ca^{2+} increased, indicating that a higher concentration of scale-forming cations forms larger PEC aggregates. Ca concentrations $\geq$ 10 mM resulted in direct sedimentation by gravity of the Ca-PECs, similar to the effect observed for Ba at an initial concentration of 5 mM.

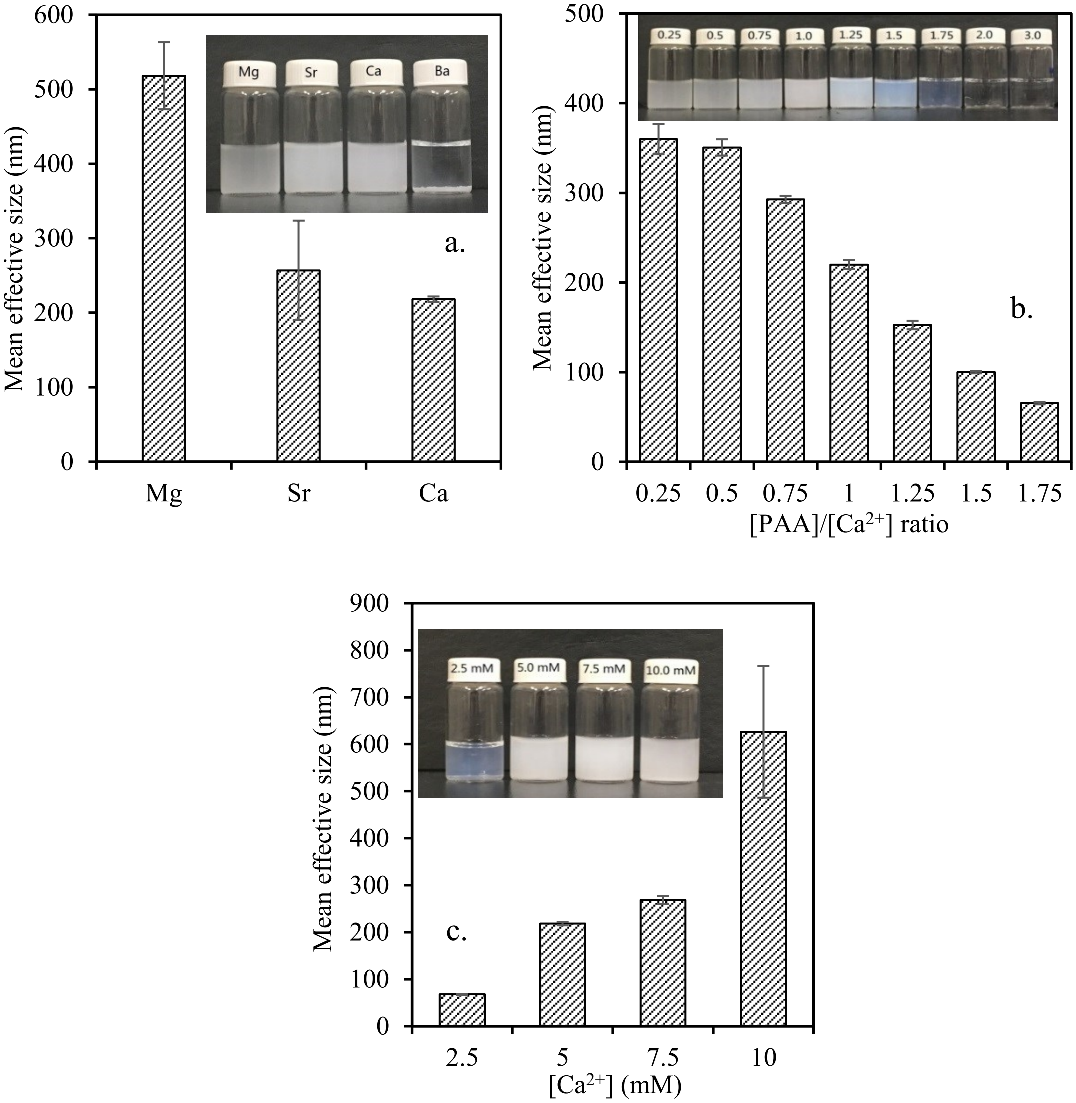


Figure 4. Mean effective size of PECs by DLS: (a) For different cations, each at 5 mM with 5 mM PAA added (molar concentration ratio = 1); (b) Ca-PEC sizes at different PAA/Ca^{2+} molar concentration ratios ([Ca^{2+}] = 5 mM); (c) Particle size of Ca-PECs formed at varying initial Ca^{2+} concentrations (PAA to Ca^{+2} molar ratio = 1).

Figure 5 demonstrates the impact of initial Ba^{2+} concentration on Ba-PEC removal by sedimentation. The basic pattern is the same at all initial barium concentrations, with maximum

Ba removal at a polymer/Ba molar ratio of approximately 1.7, and increased polymer addition beyond that point causing disaggregation. However, a higher initial concentration of Ba^{2+} led to a higher overall removal of Ba^{2+} from solution, presumably due to formation of larger sized particles, as occurred with Ca^{2+} (**Figure 4c**). The results indicate that the extent of precipitate aggregation of PEC complexes is related both to the polymer/cation ratio and the initial concentration of scale-forming cations.

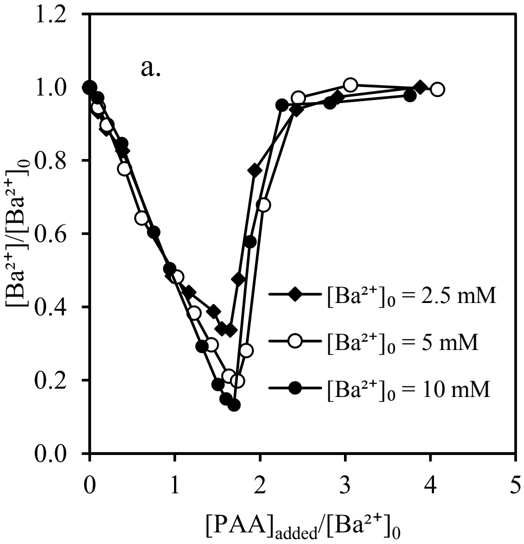


Figure 5. Ba^{2+} removal by precipitation with PAA, with varying initial Ba^{2+} concentrations.

3.3.2 Precipitation of Scale-forming Cations Using PSS

Individual solutions of each scale-forming cation were also reacted with PSS and centrifuged (**Figure 6)**. Unlike PAA, PSS formed larger aggregates only with Ba^{2+}, likely because of the high affinity of the sulfonate groups for Ba^{2+} [40], while Sr^{2+}, Ca^{2+}, and Mg^{2+} solutions stayed clear throughout the experimental PSS concentration range. Ba-PSS removal increased with increasing PSS concentration, with no indication of redispersion effects at higher polymer/Ba ratios, as was observed with PAA.

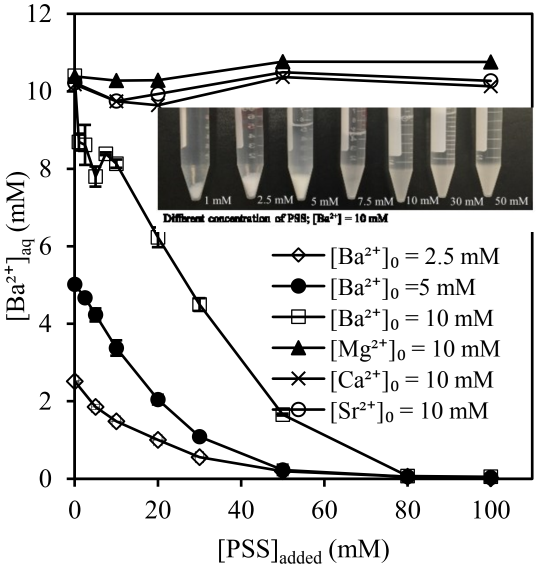


Figure 6. Precipitation of divalent cations by PSS addition and centrifugation

3.4 Precipitation of Scale-Forming Cations in Mixed-Ion Solutions

The effect of PAA or PSS addition on the removal of scale-forming cations in mixed-ion solutions following centrifugation is shown in **Figure 7**. For each solution, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} were each present at 2.5 mM, for an overall divalent cation concentration of 10 mM. Cation removal with PAA (**Figure 7a)** follows the same pattern as centrifugation-based removal for the single-cation solutions (**Figure 3**). The highest removal of each of the four cations occurred at polymer concentrations of 15-17 mM, corresponding to a molar ratio of polymer to total divalent cations of 1.5-1.7. When the concentration of PAA reached 20 mM (ratio of 2), the PECs formed by all four cations were redispersed. Although Ba has a higher affinity for PAA than Ca, the removals of Ba and Ca were similar in the mixed solution, such that Ca removal was enhanced in the mixed solution compared to its removal from a single-ion solution. Overall, the removal order from the mixed ionic solution was $Ba^{2+} \approx Ca^{2+} > Sr^{2+} > Mg^{2+}$. These results indicate that the total concentration of divalent ions is a more important indicator of mixed-solution behavior than the individual ion concentrations.

Figure 7b demonstrates the centrifuge-assisted removal of scale-forming cations from mixed-ion solutions following addition of PSS. Cation removal was very similar to that observed with solutions of the individual ions under similar conditions (**Figure 6**). Only Ba^{2+} was precipitated, and the presence of Mg^{2+}, Ca^{2+}, and Sr^{2+} did not influence the precipitation of Ba. Increased concentrations of PSS did not cause precipitation of Mg and Ca in the mixed solution. However, a small fraction of Sr^{2+} was removed when the concentration of PSS was higher than 50 mM, and Sr^{2+} removal increased to 12.6% as the PSS concentration increased to 100 mM. This increase in Sr removal results from higher levels of PSS aggregation (relative to the Sr-only solution) due to the presence of Ba.

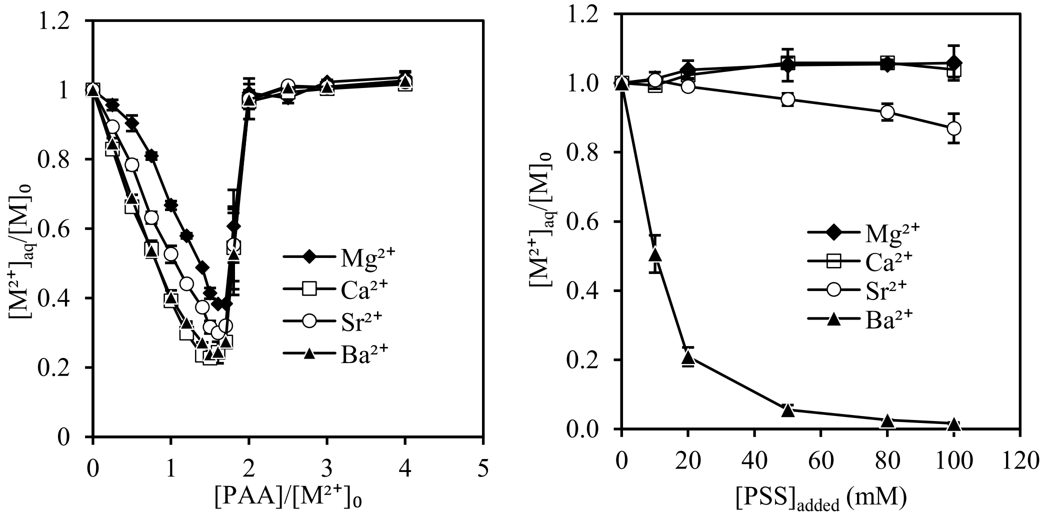


Figure 7. Removal of scale-forming cations from mixed-ion solutions by centrifugation after adding (a) PAA and (b) PSS

Figure 8 shows the influence of a monovalent cation (Na^+) on centrifuge-assisted removal of scale-forming cations with PAA in mixed-ion solutions at the same divalent cation concentrations as before (2.5 mM for each cation, total divalent ion concentration of 10 mM). Without competition from additional Na^+, removal of scale-forming cations by precipitation increased as the ratio of polymer to total concentration of scale-forming cations increased, up to the highest ratio tested (1.5). With a background NaCl concentration of 100 mM, less divalent cation precipitation occurred at each ratio tested, and the precipitates redispersed as the polymer/divalent cation ratio increased to 1.5. (More detailed results on the influence of added NaCl at concentrations ranging from 0 to 100 mM are shown in the Supporting Information.) Based on these results, competition from Na^+ is reducing binding of divalent cations, hindering aggregation of the PECs, reducing their charge, and causing them to redisperse at lower ratios of PAA to divalent cations. It is difficult to separate out any effects on polymer-cation complexation due to higher ionic strength from the increased competition for PAA from Na^+, but these results definitely show that higher salt concentrations will reduce the effectiveness of PAA for precipitating divalent cations.

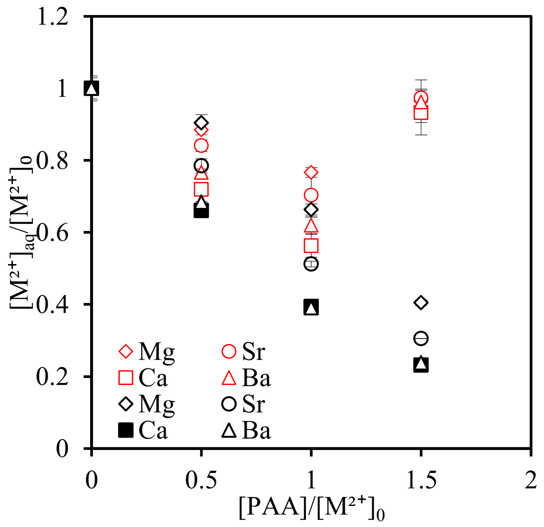


Figure 8. Na^+ influence on precipitation of scale-forming cations from mixed-ion solution by PAA addition and centrifugation. Black points show the results without adding NaCl; red points show the results with 100 mM NaCl added.

3.5 Release of Cations from Precipitated PECs and Regeneration of PAA

Figure 9 shows the effects of acidification on release of divalent cations from aggregated PECs formed using PAA. Adding 50 mM of PAA to multiple samples of a solution containing 50 mM total cations (12.5 mM each of Ba^{2+}, Ca^{2+}, Sr^{2+}, and Mg^{2+}) resulted in the removal, after centrifugation, of 25.3 ± 0.4 mM total cations. Cation removal followed the same trends observed in **Figure 7**, with better removal of Ba and Ca from the mixed solution. Cation removal patterns are addressed further in Section 3.6. Redispersion of the aggregated solids in the first sample with 50 mM HCl resulted in only ~88% of the cations being released from the PEC aggregates. Cations release was in the opposite order of cation affinity for PAA, i.e., more Ca and Ba remained on the regenerated PAA, but less Sr and almost no Mg. When the HCl concentration was increased to 60 mM or higher, all of the scale-forming cations were released from the PECs into the aqueous solution phase. Using an acid concentration exceeding the total PAA concentration reduces the pH of the solution to less than 2, with lower pH leading to lower ionization of PAA (less than 0.4% according to **Figure 2b**) and greater dissolution of the cation-PAA complexes.

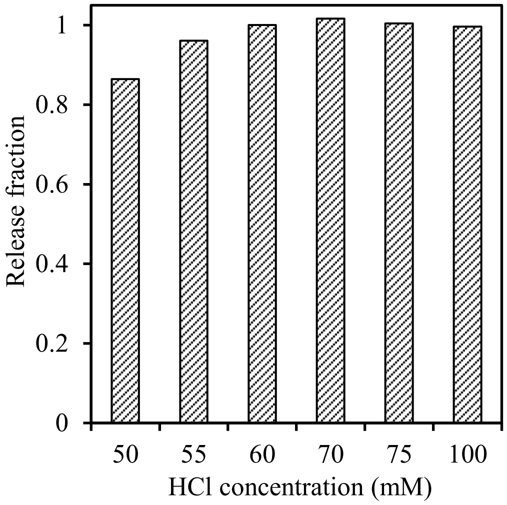


Figure 9. Release of cations from PEC aggregates after acidification

Regenerated PAA produced by reaction with 75 mM HCl to release all complexed cations was collected for reuse in conjunction with ultrafiltration. Approximately 74% of the PAA was retained for a second use cycle following this process (**Figure 10).** Based on previous studies [40] using PSS, where around 20% of 'nominally' 200 kDa PSS passed through a 10 kDa UF membrane, this reduction in concentration was likely due to the loss of smaller PAA molecules able to pass through the UF membrane. In the second contact with a 50 mM multi-cation solution, the regenerated PAA removed 18.6 mM of scale-forming cations, as compared to an initial removal of 25 mM. After a second regeneration cycle, 67% of the initial PAA was retained. Significantly less active PAA was lost in this second cycle as compared to the first, as fewer small molecules capable of passing through the UF membrane were present. After the second regeneration, the recovered PAA removed 16.8 mM of scale-forming cations from solution. In general, the polydispersity of polymers would affect polymer recovery, with a higher dispersity (more small fragments) likely resulting in greater loss of polymer during cation complexation, separation and polymer recovery.

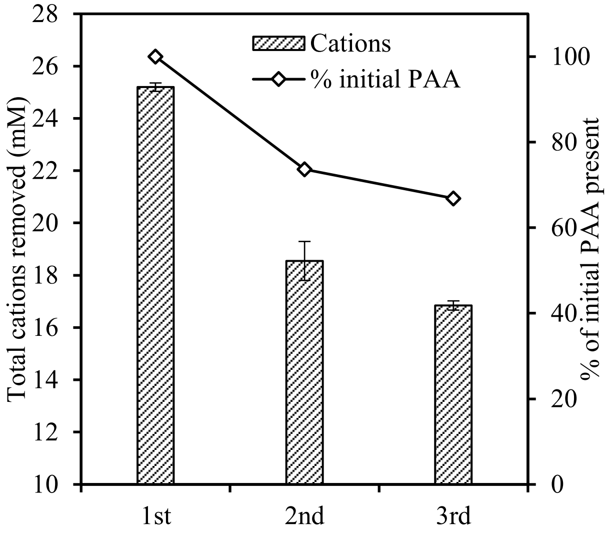


Figure 10. Cation removal after successive PAA regenerations with HCl

3.6 Removal of Scale-Forming Cations from Produced Water by Precipitation with PAA

A multi-stage experiment was performed to examine divalent cation removal from produced water obtained from an active oil production well in Reno County, KS (**Table 1**). **Figure 11** shows the divalent cation removal due to the formation of cation-PAA aggregates for four successive additions of polymer. Aggregates were separated out by precipitation after each PAA addition, and PAA addition in each stage was adjusted to maintain a polymer/divalent cation ratio of 1 based on the remaining cation concentration in the supernatant. After four polymer addition and separation stages, 73% of the divalent cations present in the initial oil produced water had been removed from solution. Individual cation removal ranged from 60.6% to 79.9% with the order $Ca^{2+} > Sr^{2+} > Mg^{2+}$. (Total Ba removal was 73.2 %, but the initial Ba concentration was much lower than that of the other divalent cations. Ba^{2+} in this water is limited by barium sulfate solubility in the presence of dissolved sulfate.) In the first stage, 28.1% of total divalent cations were precipitated, 23% in the second stage, 14.3% in the third stage and only 7.5% in the last stage. As the scale-forming cations were removed from the water, the remaining concentration of each cation decreased, and the concentration ratio of Na to remaining divalent cations increased from 6 to 20. Both of these changes contributed to the decreasing effectiveness of cation removal with successive additions of PAA.

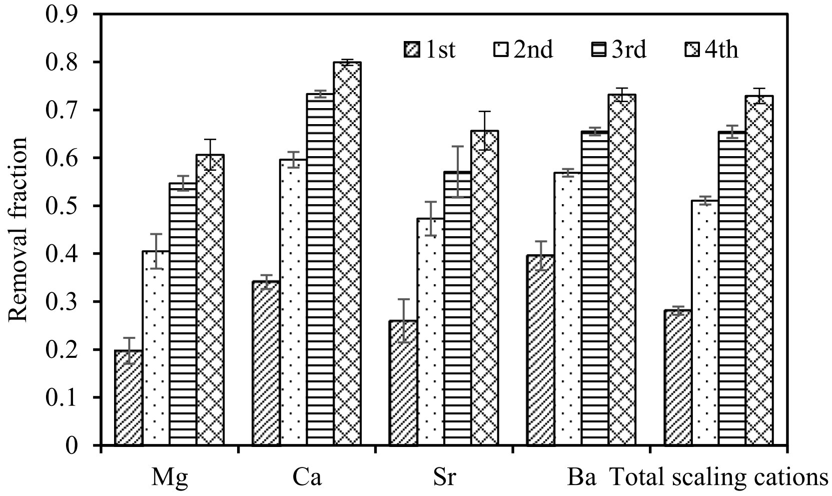


Figure 11. Removal of scale-forming cations from an oilfield produced water with successive additions of PAA

Conclusions

The complexation and precipitation behavior of the scale-forming cations Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+} with two commercially available anionic polyelectrolytes, poly (acrylic acid) (PAA) and poly (sodium 4-styrenesulfonate) (PSS), was investigated. The apparent dissociation constant (*pKa*) of PAA, which contains carboxylic acid functional groups, was determined as 6.7 by titration; in contrast, H^+ shows low affinity for PSS (*pKa* = 1.6). Complexation affinity between scale-forming cations and polyelectrolytes decreases in the order $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$ for PAA at pH 5, while the selectivity order was $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ for PSS with no significant pH effect. Higher pH leads to a higher distribution of cations on PAA, which is attributable to the increased number of available binding sites as the PAA dissociates, as well as reduced competition from H^+ ions. Ba formed precipitates with PSS under all conditions, and did not exhibit redispersion even at high polymer/cation ratios. In mixed-solution, a small amount of Sr removal by PSS was also observed, but no removal occurred in the absence of Ba. All four scale-forming cations can form PEC aggregates with PAA in single and mixed-ion solutions, depending on both the cation concentration and the molar ratio of PAA to cations. The greatest amount of precipitation was found to occur at a polymer to total divalent cation ratio between 1.5 and 1.7, while higher ratios cause redispersion of the precipitates. Higher initial cation concentrations result in larger PEC particles, which facilitated removal by both sedimentation and centrifugation. However, high concentrations of sodium inhibited the precipitation of scale-forming cations with PAA. In a real oilfield produced water sample collected from central Kansas, up to 73% of scale-forming cations were precipitated when treated by using sequential additions of PAA. These results show potential for targeted removal of scale-forming cations through PAA addition to high-salinity waters.

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