# Removing Scale-Forming Cations from Produced Waters

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This work examines the removal of scale-forming cations from oil and gas wastewater (produced water) using polyelectrolyte-enhanced ultrafiltration, a novel technology. Polyelectrolytes were more selective than chemical precipitation for removing Ba and Sr, the most common scale-forming elements. Improved cation removal will reduce one of the major barriers to increased reuse of produced water as a substitute for fresh water.

**Removing Scale-Forming Cations from Produced Waters**

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Abstract

The formation of precipitates (scales) during reinjection limits the reuse of oil and gas

production water (produced water) for additional oil recovery. Selective removal strategies that target

Ba and Sr, the primary scale-forming cations, would limit produced water treatment costs, reduce waste

generation, and increase produced water reuse. A novel treatment technique for targeted Ba and Sr

removal, complexation with polyelectrolyte polymers, is compared with chemical precipitation (sulfate

addition and precipitative softening) for the removal of Ba and Sr from Kansas oil field brines. Four

polymers were examined for cation removal, both with and without ultrafiltration: poly-vinyl sulfonate

(PVS), poly(4-styrenesulfonate) (PSS), polyacrylic acid (PAA), and poly(4-styrenesulfonic acid-co-maleic

acid) (PSSM).  PSSM and PSS were effective for Ba and Sr removal from the lower salinity brine (TDS of

31,000 mg/L), but exhibited limited Sr removal in the absence of Ba in the high salinity brine (TDS of

92,000 mg/l). Similar results were achieved in both brines using sulfate addition.   PSSM used in

conjunction with ultrafiltration removed > 99% of initial Sr and Ba from the lower salinity brine, while

removing only 65% and 78% of Mg and Ca, respectively. These results compare favorably to precipitative

softening, which removed >90% of all divalent cations from the same brine but was less selective for Ba

and Sr. PAA plus ultrafiltration removed 58% of Sr (and 68% of Ca) from the high-salinity brine at pH 9.

While increased Sr removal can be achieved by polymer-assisted ultrafiltration, further development of

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this process, including methods for polymer recovery and regeneration, will be needed to improve its

performance compared to precipitative softening.

Keywords

Produced water treatment, scale inhibition, divalent cation removal, polymer complexes, ultrafiltration

1.  Introduction

Global oil and gas (O&G) production was approximately 98 million barrels (16 billion liters) per

day in 2017 [1]. O&G production is very water-intensive, both in its requirements for freshwater and in the

production of formation water (or produced water) extracted from subsurface reservoirs [2]. Overall,

more than 20 billion barrels (3.2 trillion liters) of produced water are generated in the US each year,

with a national average of > 9 barrels of water generated per barrel of oil produced [3]. The volume of

produced water can be more than 10 times the volume of oil produced over the life of an oil field,

increasing as a field matures. Disposal of this produced water has the potential for signficant

environmental impacts [4-6].  Underground injection control wells have been connected to increased

seismic activity in the United States [7], while surface disposal can have secondary impacts on water and

sediment quality [8, 9]  At the same time, oil and gas production often requires large volumes of water.

Increasing reuse of produced water for oil production could thus provide important economic and

conservation benefits by reducing disposal volumes while also reducing industry demands for fresh

water [10-13].

A major issue limiting water reuse is the formation of precipitates (scales) during re-injection. These

scales can plug injection and production wells, and coat production tubing and surface equipment,

increasing costs and even shutting down operations [12, 14-16]. The most common cause of scale formation

in oil and gas production activities is supersaturation with respect to sulfate (and to a lesser extent

carbonate) salts of Ca, Sr, and Ba [16-19]. Scale precursors can originate from the injection water, from

dissolution of formation materials as water flows through the formation, or both, as when sulfate-

containing waters are injected into a reservoir containing barium. Changes in temperature, pressure,

and acidity can also contribute to scale buildup. While carbonate and hydroxide scales can easily be

dissolved in acid [17, 19, 20], $BaSO_4$ (barite), $SrSO_4$ (celestite), and $(Ba,Sr)SO4$ (co-precipitates), once formed,

are very difficult to remove. Selective removal of Ba and Sr from produced waters could thus reduce

treatment requirements and waste disposal costs while also reducing the potential for sulfate scale

formation during reuse.

Precipitation processes that rely on the insolubility of sulfate and carbonate scales to pre-emptively

remove divalent cations during a controlled treatment process are relatively simple and inexpensive to

implement. In single cation systems (no competing ions, organic material, or other interferents) the

solubility of relevant salts is as follows: $MgSO_4 \gg CaSO_4 > SrSO_4 > MgCO_3 > SrCO_3 > CaCO_3 > BaCO_3 \gg$

$BaSO_4$ [17, 18]. $Mg(OH)_2$ is also formed at high pH and is highly insoluble under those conditions.

Precipitative softening with either lime or caustic soda has been widely used in produced water

treatment for control of water hardness [4, 21-23]. Few studies, however, have directly addressed Ba and Sr

removal by precipitative softening processes. As shown in Table 1, there is a wide range in the

effectiveness of these different procedures, particularly for Sr removal. This variation is likely related to

the wide variation in additives and in final pH during the treatment process. In fresh waters, however,

lime softening has been effective at Ba and Sr removal [24, 25]. Sodium sulfate ($Na_2SO_4$) addition is also an

industry-accepted method for removing alkaline earth metals from water to prevent scale formation [17].

Studies using acid-mine drainage as a sulfate source have achieved good removal of Ba from Marcellus

shale produced water (Table 1). Sr is removed in these processes primarily through substitution into

barite, raising questions about the effectiveness of this process for Sr removal in waters containing lower Ba concentrations [26, 27].

The use of polymers, both sulfonates and carboxylates, to bind metals, followed by removal through ultrafiltration has been proposed previously for the removal from aqueous solution of a long list of metal cations, including Ag, As, Cu, Co, Ni, Cd, Zn, Pb, Ca, Mg, Sr, Cr, and Al [28-30]. In previous studies, members of this project team explored divalent and monovalent cation affinity for two polyelectrolytes, poly(4-styrenesulfonate) (PSS) and polyacrylic acid (PAA) in both low and high salinity brine solutions [31, 32]. Both polyelectrolytes have a strong preference for $Ba^{2+}$ complexation over other common produced water divalent cations ($Ca^{2+}$, $Sr^{2+}$, $Mg^{2+}$), while PSS also prefers $Sr^{2+}$ to $Ca^{2+}$ and $Mg^{2+}$. PAA formed polyelectrolyte complex precipitates with all scale-forming compounds, but this precipitation was inhibited by high concentrations of monovalent cations. An initial experiment was conducted using PAA to remove Ba and Sr from a field-collected high-salinity produced water (TDS = 92,000 mg/l) containing 3.6 mg/l B and 1,800 mg/l Sr. After 4 sequential addition and separation steps, this experiment achieved 73% and 67% removal of Ba and Sr, respectively, while also removing > 60% of $Ca^{2+}$ and $Mg^{2+}$ [32].

*Table 1: Previous studies of Ba and Sr removal from produced water by chemical precipitation.*

| Additive | Water | pH* | Ba | Sr | Other | Reference |
|---|---|---|---|---|---|---|
| Lime + alum | Illinois Basin Oilfield PW | 7.3-7.6 | 21% | No removal | No removal for Ca or Mg | [33] |
| NaOH | Oilfield PW, Kern County CA | 9.3 | 98% | 97% | 91% removal of total hardness | [34] |
| NaOH + alum | Marcellus shale PW | 10 | 48% | 20% | 46% and 19% removal of Ca and Mg | [35] |
| $Na_2SO_4$ | Synthetic flowback water | NA | 55-100% | 4-37% | Removal increased with sulfate concentration | [36] |
| Acid mine drainage | Marcellus shale flowback fluid | NA | > 99% | 70% | Sr co-precipitated with barite | [26] |
| PAA | Reno County, KS PW | NA | 73% | 66% | 4 sequential additions of PAA | [32] |

*- Adjusted pH used for softening processes.

The current study investigates the removal of divalent cations ($Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$, and $Mg^{2+}$) from produced water as a stand-alone treatment strategy to reduce scale-formation potential of the treated waters. The goal of this treatment strategy is to decrease scale-formation potential and thereby increase produced water reuse for further oil production with minimal additional treatment, such as reverse osmosis or nanofiltration, which are costly and not ideal for treating high salinity brines [20, 37]. Chemical precipitation using sulfate addition and precipitative softening was used to treat two different field-collected oil-field brines.  The results were compared to cation removal through complexation with four polyelectrolytes (PSS, PAA, poly-vinyl sulfonate (PVS), and poly(4-styrenesulfonic acid-co-maleic acid) (PSSM)) commonly used as scale inhibitors in the oil industry. Removal of precipitated or complexed cations was accomplished by either settling / centrifugation or ultrafiltration.

2.   Experimental

2.1.  Produced water collection

Produced water samples were collected from two locations in Kansas, one in Douglas County (DC) and one in Reno County (RC). Both waters were collected at the pump, with pH, conductivity, and temperature measured immediately in the field. The waters were then filtered in the field using a 0.2 micron cellulose-acetate filter, stored on ice during transport, and later stored in a laboratory refrigerator at 4 °C. At no point during transport did the samples freeze. No other sample pretreatment occurred. The initial characteristics of the two produced waters are shown in Table 2.

*Table 2. Major cation and anion concentrations and other water quality data for two Kansas produced waters.*

|  | Douglas County (DC) | Reno County (RC) |
|---|---|---|
| Temperature, °C | 18.6 | 34.5 |
| pH | 6.6 | 6.2 |
| Specific conductivity ($\mu$S/cm) | 52,000 | 170,000 |
| Total Organic Carbon, mg/L | 3.9 | 48 |
| Total Dissolved Solids, mg/L | 31,000 | 92,000 |
| Total Alkalinity, mg/l as $CaCO_3$ | 700 | 180 |
| Sodium, mg/L | 9,000 | 21,000 |
| Calcium, mg/L | 600 | 5,600 |
| Strontium, mg/L | 80 | 1,800 |
| Magnesium, mg/L | 260 | 1,600 |
| Barium, mg/L | 430 | 3.6 |
| Chloride, mg/L | 19,000 | 61,000 |
| Bromide, mg/L | 46 | 300 |
| Bicarbonate, mg/L | 850 | 220 |
| Sulfate, mg/L | 3.0 | 110 |

Note: Concentrations are reported to 2 significant figures to reflect an overall CV of 10%.

Despite being collected from wells geographically located within 200 miles of each other, the two brines are quite different. The DC brine has a TDS concentration of 31,000 mg/L with both barium and strontium present, whereas the RC brine has a TDS concentration of 92,000 mg/L, a Sr concentration of 1,800 mg/L, and very little Ba. The RC brine does, however, have a significant sulfate concentration (110 mg/L) that the DC brine does not have, while the DC brine has a higher bicarbonate concentration.  In general, produced waters can also contain dispersed oils, production chemicals such as polymers and surfactants, and other organic components [19, 38-40]. The TOC concentrations for these two brines, however, were relatively small, (3.9 mg/L in the DC brine and 48 mg/L in the RC brine), indicating little presence of organic constituents. This is probably due to the extent to which the selected fields have previously been waterflooded.

The DC brine was chosen for method optimization as it is representative of Kansas brines that contain both barium and strontium; however, four of the polymers were tested against the RC brine as well to evaluate performance in the absence of barium and corresponding presence of sulfate.

2.2. Produced water characterization

Alkaline earth metals were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) immediately upon receipt in the lab, and then re-measured each time a sample was treated to establish the appropriate control value for a particular experiment. A Perkin Elmer Optima 2000 ICP-OES was used to measure Na, Ca, Sr, Mg, and Ba in the initial brines. All samples were diluted 200-fold in 2% nitric acid (Fisher Scientific PN A509) in deionized water (DI, 18.2 MΩ·cm Type 1 water prepared using a Milli-Q Direct 8 system) prior to analysis to achieve a sample pH of less than 2 as required by EPA method 200.7 [41]. Additional dilutions with 2% nitric acid were made as necessary to bring sample concentrations within the instrument's range.

Temperature, pH, and total dissolved solids (TDS) were measured in the field using an Accumet AP85 portable meter. Total alkalinity and anion concentrations were measured immediately upon return of the sample to the laboratory, for characterization purposes only. Alkalinity was measured using a standard titration method. Reported bicarbonate values were calculated using the pH and alkalinity results. All other anion measurements were made using ion chromatography (Dionex ICS-2000, Ion Pac AS18 analytical column). Total organic carbon was measured using a Teledyne TORCH TOC analyzer.

2.3. Sulfate addition

A 0.2 M $Na_2SO_4$ solution, prepared by dissolving sodium sulfate ($Na_2SO_4$, Fisher Scientific PN S429) in DI water (Type 1), was added to the oil-field brine in increasing amounts to induce sulfate precipitation. DI water was also added as appropriate to maintain a constant final solution volume. Samples were mixed using a vortex mixer and then allowed to sit for 24 hours (unless otherwise noted). These solutions were then centrifuged to separate out the precipitate. (Centrifugation was later found to have no impact on

cation removal using this method.) Mg, Ca, Sr, and Ba concentrations in the supernatant were measured by ICP after acidification and dilution.

## 2.4. Precipitative softening

Precipitative softening [18] was accomplished through additions of sodium hydroxide (NaOH 50% solution, Fisher Science PN SS254-1) and sodium carbonate ($Na_2CO_3$, Fisher Science PN S263). NaOH, rather than lime ($Ca(OH)_2$), was used to adjust the pH to avoid adding additional calcium to the samples. As calcium was the most common divalent cation in both brines, the lack of additional calcium should not substantially alter the softening mechanism. Furthermore, nearly all of the calcium in the brines was non-carbonate hardness, so lime addition would initially have resulted in little or no removal of calcium and would in fact have simply increased the calcium concentration, in proportion to the lime dosage, once any carbonate alkalinity present had been consumed.
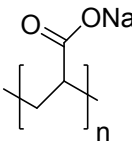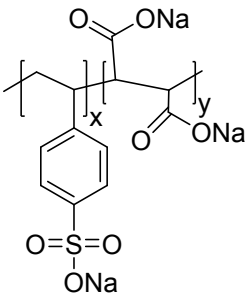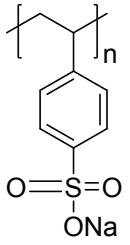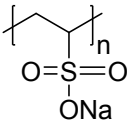
The brine pH was first adjusted using the NaOH solution until a pH greater than 11 was achieved. Increasing quantities of a 0.2M solution of $Na_2CO_3$ were then added to achieve final solution concentrations up to 0.1 M in the final solution. For higher dosages of $Na_2CO_3$, powdered $Na_2CO_3$ was added directly to the brine. Finally, additional DI water was added to maintain a constant solution volume constant. These solutions were vortexed and then allowed to settle for 24 hours.

Initially, samples were centrifuged to separate out the precipitates. As with the sulfate experiments, this step was subsequently determined to have no impact on final dissolved cation concentration. At 24 hours, settling was complete, and the treated supernatant solution could be easily collected from the top of the centrifuge tube. Mg, Ca, Sr, and Ba in the treated solutions were measured by ICP after acidification and dilution.

## 2.5. Polymer addition

The polymers used in these experiments (Table 3) included one carboxylate-containing polymer, polyacrylic acid (PAA); two formulations of poly(4-styrenesulfonic acid-co-maleic acid) (PSSM), a co-block polymer containing sulfate and carboxylate moieties in 1:1 and 3:1 ratios, respectively; and two sulfonate-containing polymers, poly-vinyl sulfonate (PVS) and poly(4-styrenesulfonate) (PSS). The average molecular weights were 100 kD for PAA, 20 kD for both of the PSSM formulations, 70 kD for PSS, and 4-6 kD for PVS.

*Table 3. Structures of polymers used in this study.*

| | Poly(acrylic acid) sodium salt | Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt | Poly(4-styrenesolfunate) sodium salt | Poly(vinylsulfonic acid) sodium salt |
|---|---|---|---|---|
| Abbreviation | PAA | PSSM | PSS | PVS |
| Structure |  |  |  |  |
| Avg. MW, Aldrich Part # | 100kD, 523925 250kD, 416002 | x=1, y=1: 20kD, 434558 X=3, y=1: 20kD, 561215 | 70kD, 527483 200kD, 561967 | 4-6kD, 278424 |

Cation removal using these polymers was tested in the manner depicted in Figure 1.  The polymer, diluted in DI water, was added directly to brine held in a tightly capped centrifuge tube. The sample was vortexed briefly and then allowed to sit for a specified period of time (24 hours unless stated otherwise).

After sitting, the sample was either centrifuged directly in the same tube or transferred to a 3kD molecular weight cut-off (MWCO) combination filter/centrifuge tube (Vivaspin® 500, PN VS0192, 1.5mL). Tubes were centrifuged between 15 and 90 minutes at 17.0 G for ultrafiltration. Although no significant differences in cation removal were observed between centrifuged and uncentrifuged samples when testing sulfate addition and precipitative softening, the centrifugation step was retained for polymer

processing because no visible precipitate was formed. Once centrifugation was complete, the supernatant

or filtered portion was removed from the tube, acidified, and diluted for ICP analysis.

In some cases (indicated where applicable), the pH of the polymer solution was adjusted using

either sodium hydroxide (50% NaOH, Fisher Science PN SS254-1) or hydrochloric acid (6N HCl, Ricca PN

375032) prior to addition to the brine. Polymer concentration was controlled through the addition of DI

water to a constant volume. The pH values of the unadjusted polymer solutions (12.5% w/v) were as

follows: 7.5 for both PSSM(1:1) and PSSM(3:1), 8.4 for PVS, 2.8 for PSS, and 1.7 for PAA.
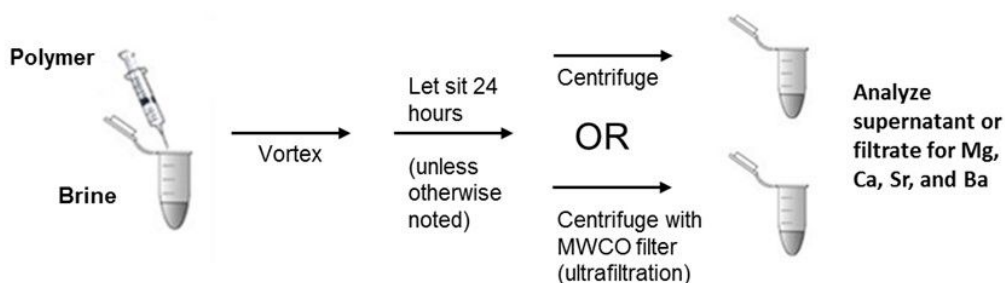


*Figure 1. Experimental approach for polymer addition.*

### 2.6. Variance in the data

Each data point on a graph or in a table represents a single measurement (including repeated

measurements on some samples, which were plotted as separate points). In cases where trends were

being measured (e.g., addition of increasing concentrations of a chemical) single measurements were

taken at each concentration to allow multiple concentrations to be tested. Where trends were less clear,

more data points were collected (either at additional concentrations or at a specific concentration) and

all data points were included in the figure.

Control samples of the brine were analyzed with every experiment. To obtain an estimate of

variance in the data measurement itself, the coefficients of variance ($\%CV = \frac{Mean}{StdDev} * 100$) for two data

sets (one with 6 samples, the other with 7) were calculated. The data in these sets were collected over a

period of weeks and thus included run-to-run instrument variability as well as method variability. Both

sets yielded %CVs of less than 10% (6% for one and 9% for the other).  Based on the instrument

variability and the run-to-run variability given by the coefficients of variance, differences between data

points of less than 10% should not be considered significant. Differences greater than 10% may be

considered significant within the context of the experiment. All reported error bars reflect this

measurement variability.

3.   Results

3.1.  Sulfate addition

Adding $Na_2SO_4$ to oil-field brine is an effective barium removal technique [42], and addition of  as

little as 0.020 moles of $Na_2SO_4$ per liter of brine achieved complete Ba removal from the DC brine after

48 hours (Figure 2A). At this same dosage, only about 40% of the Sr was removed.  As more $Na_2SO_4$ was

added, Sr removal initially increased, but further additions had minimal effect, with removal plateauing

at approximately 65%. No consistent removal of Ca or Mg was observed due to sulfate addition, and

total divalent cation removal therefore did not increase significantly after this point (corresponding to

the addition of approximately 0.045 moles $Na_2SO_4$/L brine). Precipitation was clearly observable within

the first five minutes, and further testing showed no changes in cation removal at different mixing times

(5, 15 and 30 minutes) or standing times (2, 4, 24 and 48 hours) prior to separation.

Strontium removal from the RC brine ranged from 8-12% with $Na_2SO_4$ addition, but there was no

direct relationship between Sr removal and the amount of sulfate added (Figure 2B).  Ca and Mg were

removed in similar proportion, and their removal was similarly unaffected by changes in sulfate

addition. Equilibrium calculations using the geochemical speciation program PHREEQC [43] indicate that

the RC brine system was oversaturated with respect to celestite ($SrSO_4$) formation (SI > 1) at all levels of

$Na_2SO_4$ addition. However, the formation of strontium sulfate can be kinetically limited in produced

waters[36]. Additionally, the RC brine had a higher concentration of dissolved organic matter than the DC brine. Other studies have shown that organic acids, particularly carboxylic acids, can have an inhibitory effect on formation of sulfate precipitates [44].

Overall, Sr removal from the DC brine accounts for ~ 10-15% of total divalent cation removal on a molar basis. This ratio is consistent with previous reports of Sr removal through co-precipitation with barium sulfate [26, 27, 42, 45], although the Sr substitution ratio here is near the low end of reported values. However, there is little evidence for direct precipitation of strontium sulfate in the absence of Ba. This is also consistent with previous reports that celestite formation is very slow when sulfate is added to produced waters[36].  Ca and Mg sulfates are relatively soluble under most conditions in water and therefore sulfate addition has little effect on removal of these elements.
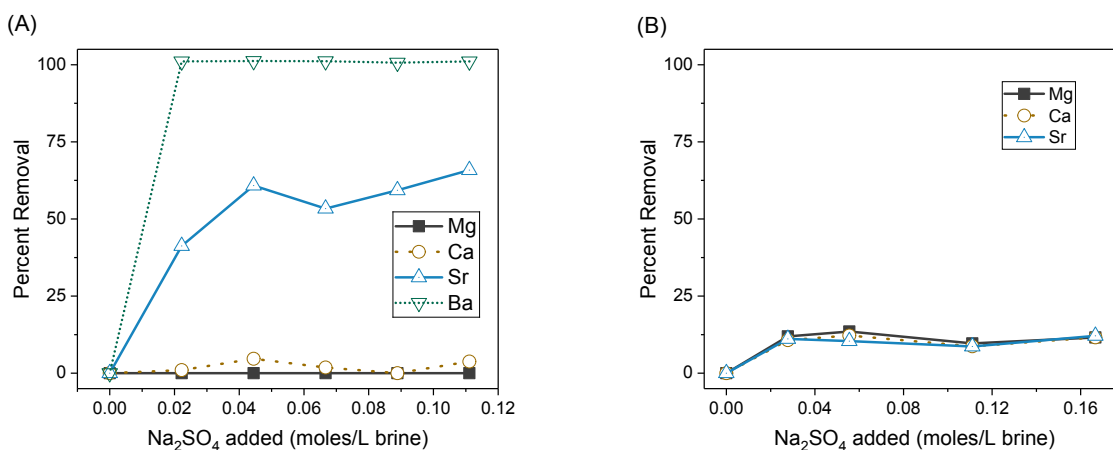


Figure 2. Removal of divalent cations through sodium sulfate addition to (A) DC brine and (B) RC brine.

3.2. Precipitative softening

Adjustment of the brine to pH 11 using NaOH effectively removed all Mg from solution through formation of $Mg(OH)_2$ (Figure 3), while carbonate salts of other cations were formed with increasing dosages of $Na_2CO_3$ in the order Ca first, then Sr, and finally Ba. In the DC brine, NaOH addition (and its reaction with the brine alkalinity to form carbonate) removed 72%, 55% and 36% of the Ca, Ba and Sr

ions. The RC brine required significantly more $Na_2CO_3$ to achieve complete removal (0.27 moles/L versus 0.029 moles/L for the DC brine) due to its much higher total divalent cation concentration. This approach to precipitative softening achieved significantly higher levels of Ba and Sr removal than previous softening processes that were targeted at general hardness removal [33, 35]. However, Ba and Sr removal can only be achieved after first removing calcium, which will require significant additional carbonate addition in many produced waters.
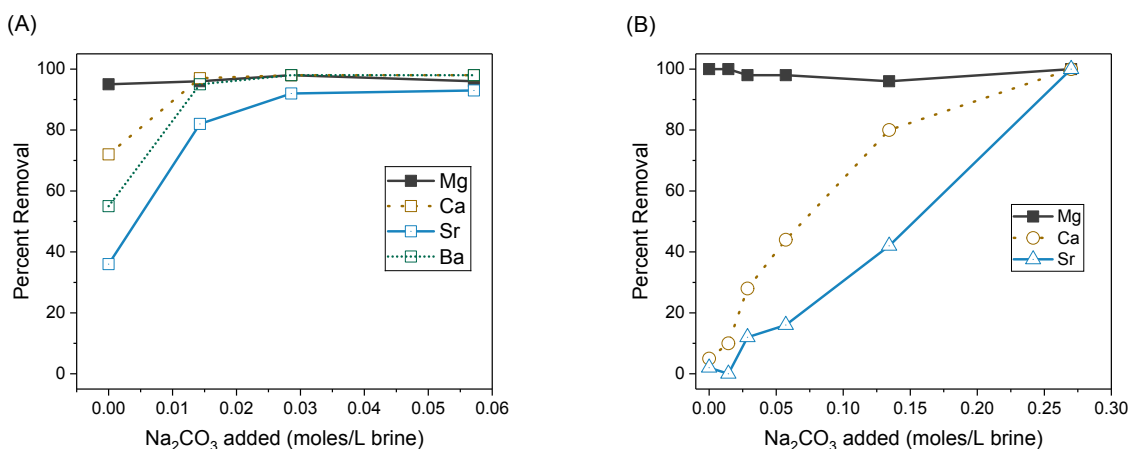


*Figure 3. Removal of divalent cations through precipitative softening of (A) DC brine and (B) RC brine.*

### 3.3. Polymer-assisted removal

Results for Ba and Sr removal in the DC brine as a function of added polymer concentration are shown in Figure 4. The PSS and PSSM polymers removed almost all of the barium and up to 60% of the strontium, although Sr removal required higher polymer doses. The PSSM co-block polymers and PSS performed much better than PAA and PVS for both Ba and Sr removal. PAA was able to achieve complete Ba removal at 3% polymer by weight (compared to 1% for the PSSM and PSS compounds), but no better than 40% Sr removal, while PVS showed little removal of either cation. No appreciable removal of calcium or magnesium was observed using any of the polymers (at dosages up to 10% by weight) in the absence of filtration. Thus, the PSSM and PSS polymers are selective for Ba and Sr removal under these conditions.
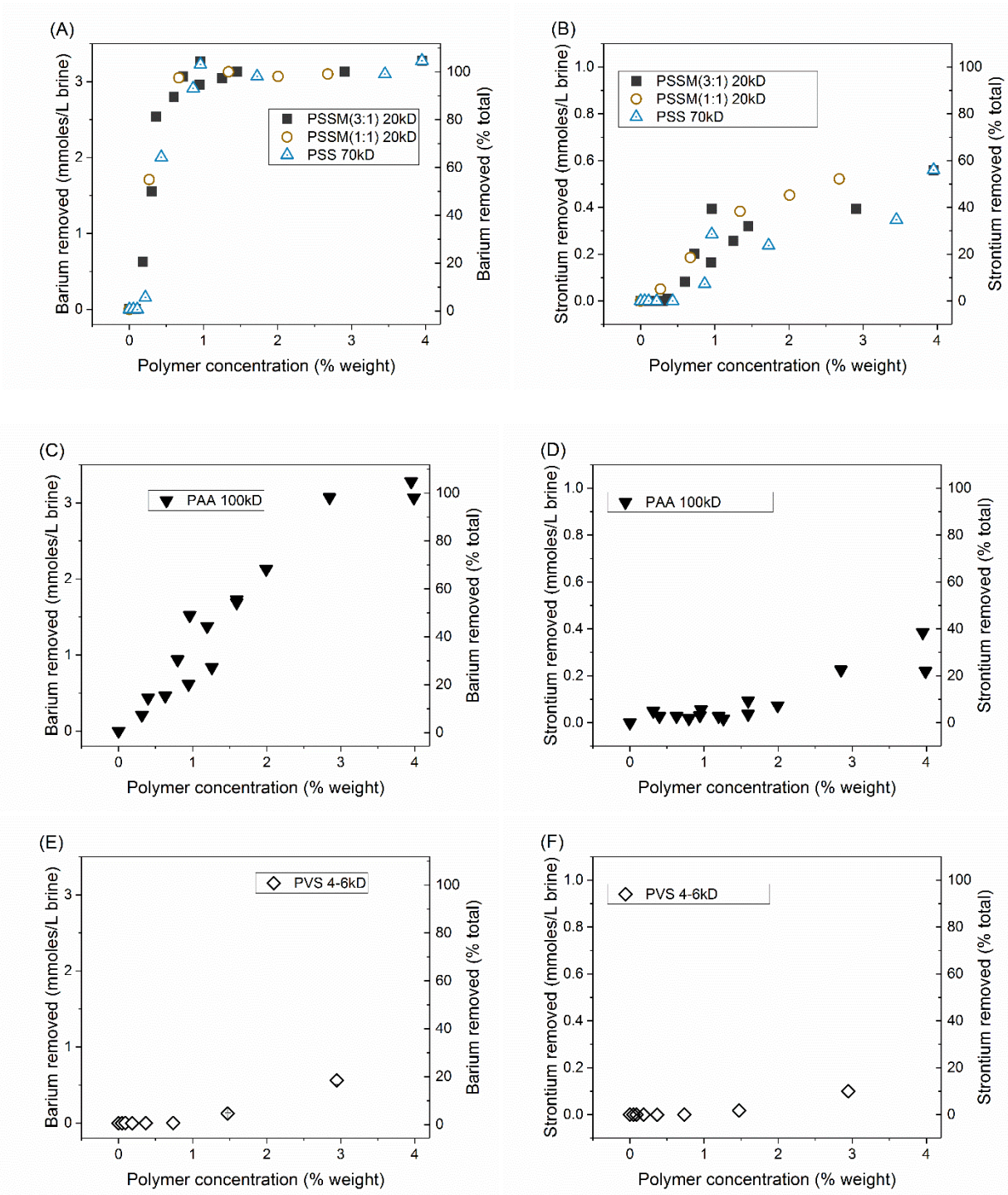
*Figure 4. Ba and Sr removal from DC brine using different polymers. No appreciable magnesium or calcium removal was observed using these polymers at concentrations up to 10% by weight (not shown).*

Figure 5 shows cation removal after ultrafiltration from both DC and RC brines with four of the five tested polymers (all except PVS).  The use of a 3kD MWCO filter substantially increased Sr removal for all four of these polymers. PVS, by contrast, did not show increased Sr removal with ultrafiltration, presumably because the PVS molecule has a similar median size (4-6 kD) to the MWCO.  Without pH adjustment, PSS had the highest Sr removal percentage from the DC brine, with the PSSM and PAA compounds showing 60-75% removal. Sr removal was lower (as a percentage of initial concentration) from the RC brine, and there was less difference between polymers. For the DC brine, the use of ultrafiltration resulted in significant removal of both Ca and Mg, although at lower percentages than Sr or Ba.  For the RC brine, all cations were removed at similar percentages in most cases.  Increasing solution pH improved the effectiveness of PAA for cation removal, consistent with previously reported trends for PAA complexation with divalent cations[32] . When the pH of the PAA solution was raised to 9 prior to adding it to the brine, all four divalent cations had >90% removal from the DC brine (Figure 5A). Cation removal from the RC brine was incomplete, but substantially higher than for the other polymers or for the non-pH adjusted PAA at the same 4 wt% addition (Figure 5B).
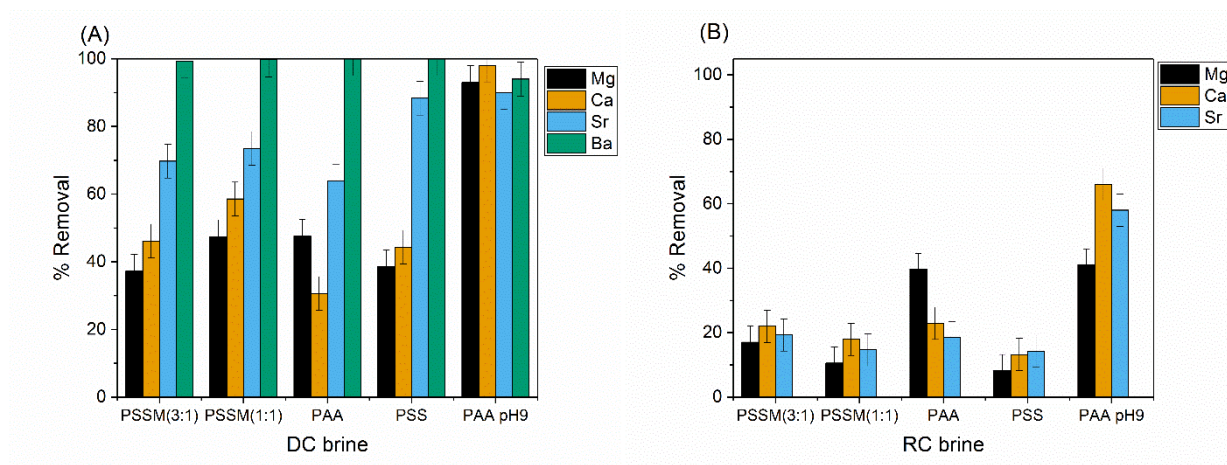


*Figure 5. Removal of divalent cations using 4% polymer and ultrafiltration to treat (A) DC brine and (B) RC brine.*

Figure 6 shows cation removal, both with and without ultrafiltration, from the DC brine using PAA (250kD), PSS (70kD), and PSSM(3:1) solutions adjusted to a range of pH values between 2 and 9 prior to addition to the brine. PVS was not used in these additional studies due to poor performance in the initial tests. The impact of pH on cation removal by centrifugation only can be seen in Figure 6. For the PSSM(3:1), removal of Mg, Ca, and Ba was independent of pH in the absence of filtration, with Ba completely removed under all conditions. Sr removal, however, was strongly affected by pH, with best performance between pH 3 and 5. Sr removal by PSS and PAA was not significantly impacted by pH.

Adding ultrafiltration to the removal process increased removal of Sr, Mg, and Ca with the PSSM(3:1) across the pH range (Figure 6B). Ultrafiltration also increased Sr removal with PSS and PAA, although significant removal with PAA was only observed at pH $\geq$ 7 (Figure 6D and 6F). Ca and Mg removal also increased above pH 7, decreasing the selectivity of the removal process. PSS, the only compound without a carboxylate functional group, showed the smallest increase in Ca and Mg removal.

Figure 7 compares the impact of pH adjustment on Sr removal using both the PSSM(3:1) and the PSSM (1:1) polymers. From pH 2-5, more than 50% of the initial strontium can be removed by centrifugation alone, while ultrafiltration increases Sr removal by approximately 15%. As the pH increases above 5, Sr removal becomes less effective in the absence of ultrafiltration. This may indicate that the polymer aggregates less under neutral to basic conditions. Unlike the 3:1 polymer, the 1:1 polymer shows greater Sr removal at high pH using the 3 kD MWCO filter. These results suggest that optimization of the PSSM polymer could result in higher levels of Sr removal than those reported in our initial tests. Additional parameters, such as polymer molecular weight and reaction timing, were also tested and found to have no effect on cation removal beyond the first few hours.
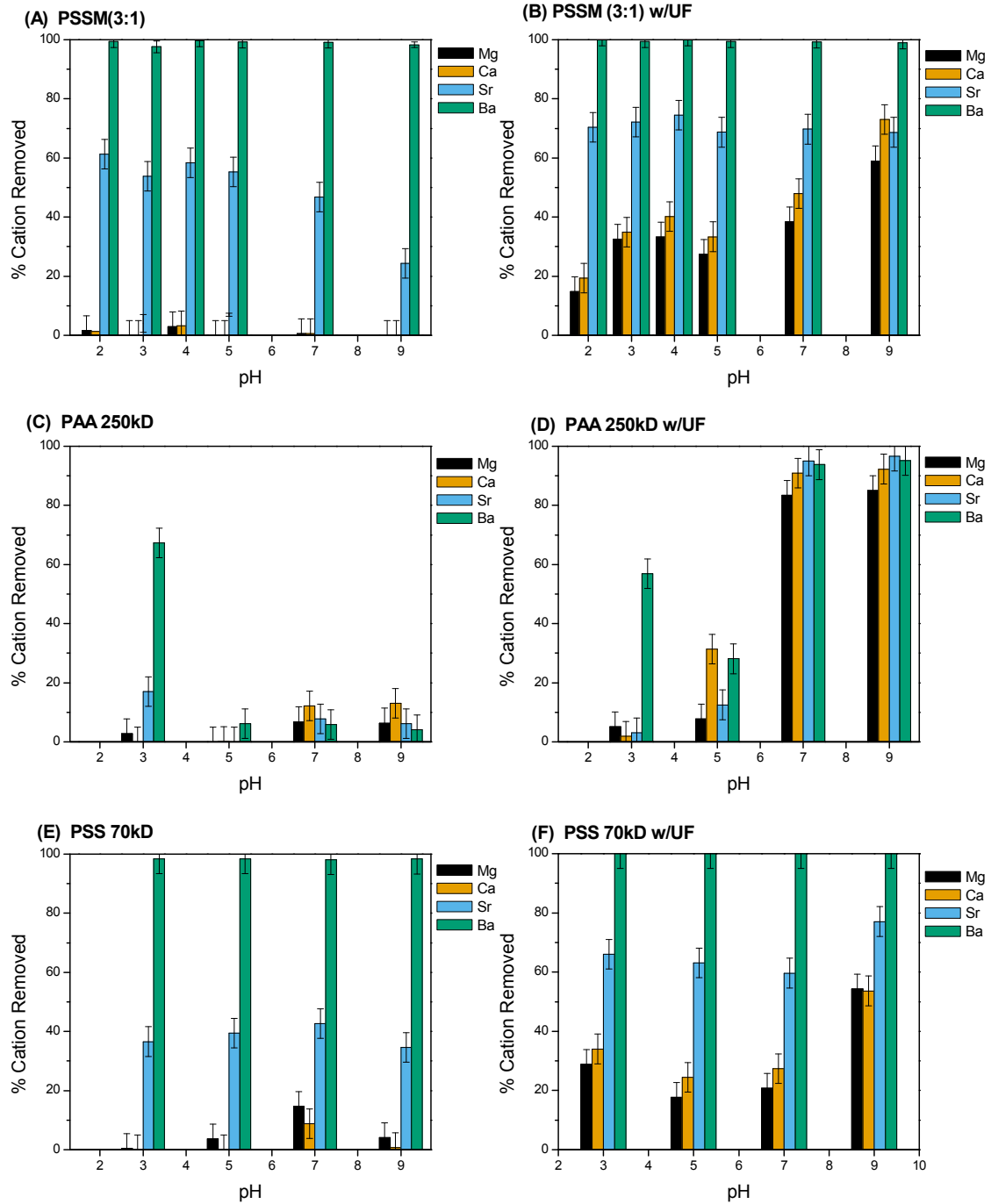
Figure 6. pH dependence of divalent cation removal from DC brine using 4% PSSM(3:1), PAA 250kD, and PSS 70kD with and without ultrafiltration.
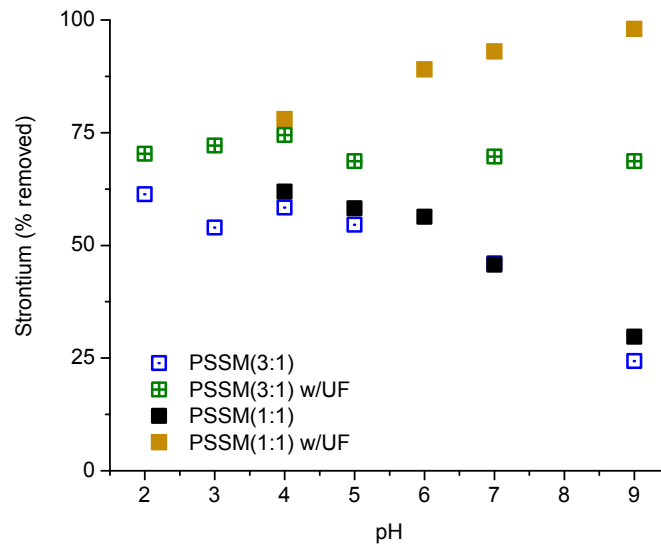
*Figure 7. pH dependence of Sr removal from DC brine using 4% PSSM (1:1 or 3:1) with and without ultrafiltration.*

4. Discussion

Table 4 shows the best results achieved for alkaline earth cation removal using the different methods from this study. These results show that the most effective treatment for Ba and Sr removal will likely vary substantially with the composition of the produced water. In waters with high concentrations of both Ba and Sr and moderate TDS, such as the DC brine, sulfate precipitation is an effective method of removing both elements. While complete Sr removal was not achieved, the sulfate precipitation process leaves Ca and Mg in solution, which limits the mass of solids generated. However, the RC brine results confirm, as others have reported, that sulfate precipitation cannot achieve Sr removal in produced waters where Ba is not already present. The same limitations would presumably apply in waters where Sr concentrations are much higher than Ba, since the major Sr removal pathway

appears to be co-precipitation with barite[26, 27].  Under these conditions, sulfate precipitation will not be

effective for controlling Sr concentrations.

Precipitative softening achieved nearly complete removal of both Ba and Sr from both brines,

but at very high sodium carbonate dosages, particularly for the RC brine. As Sr removal occurred only

after the formation of calcium carbonate, complete removal of Ca is also required. (Mg was also

completely removed in these experiments, but that could be minimized by reducing the NaOH addition

to maintain a lower pH.)  In produced waters containing high concentrations of both Ca and Sr, softening

will therefore produce large amounts of precipitated sludge that will need to be disposed of as solid

waste. This disposal will further add to the costs of this treatment process. Solids disposal could be a

particular problem for produced waters containing Ra.  While Ra was not included in this study, it is

usually assumed to behave similarly to Ba due to their similar chemical properties. Thus, it is likely that

Ra would co-precipitate with the other divalent cations when precipitative softening is carried out,

which could result in the solid materials requiring disposal as hazardous waste [42].

*Table 4. Maximum divalent cation removal by different methods.*

| | % Removal Douglas County Brine | | | | % Removal Reno County Brine | | |
|---|---|---|---|---|---|---|---|
| | Mg | Ca | Sr | Ba | Mg | Ca | Sr |
| Sulfate Addition* | 0 | 4 | 66 | 100 | 12 | 11 | 11 |
| Precipitative Softening** | 96 | 98 | 93 | 98 | 100 | 100 | 100 |
| 4% PSSM(1:1) pH 8 w/UF | 65 | 78 | 100 | 100 | 11 | 18 | 15 |
| 4% PAA pH 9 w/UF | 93 | 98 | 90 | 94 | 41 | 66 | 58 |

*Sulfate addition of 0.11 moles $SO_4$/L brine
** Addition of 0.057 moles $CO_3$/L for DC brine and  0.27 moles $CO_3$/L for RC brine at pH 11

Without the use of ultrafiltration, maximum strontium removal from the DC brine using

sulfonated polymers (PSS or PSSM) was similar to that achieved by sulfate precipitation. Polymer

aggregation and settling (and therefore Sr removal) may be influenced by the presence of Ba, as

previous results have shown co-removal of Sr with Ba precipitation when PSS is added to brine

solutions[32]. Addition of an ultrafiltration step increased removal of all cations, as this process captures additional cations that are complexed by PSS or PSSM but do not aggregate and settle from solution. Using ultrafiltration and pH adjustment, PSSM was able to achieve 100% removal of both Ba and Sr from the DC brine. This process also removed 65% and 78% of the initial Mg and Ca, respectively, substantially less than that obtained using precipitative softening. PSS was also able to remove more Sr (> 80% under some conditions) than sulfate precipitation while limiting Ca and Mg removal to less than 60%. While PAA was also able to remove > 90% of Ba and Sr from the DC brine, it demonstrated little selectivity for these ions over Ca and Mg. In the hypersaline RC brine, increased competition from Na molecules reduced the effectiveness of the sulfonate-based polymers (PSSM and PSS), resulting in less than 20% Sr removal. While PAA was able to remove 58% of Sr at pH 9, this removal was accompanied by a greater percentage removal of Ca. Thus, Sr control at very high salinities does not appear to be possible without substantial removal of other divalent cations as well.

These results show potential for development of polymer-based treatment processes for targeted removal of scale-forming compounds, particularly Sr, from produced waters, but additional method development and testing would be required to achieve this potential. Further optimization of polymer selectivity may be able to increase Sr removal over other divalent cations, particularly in moderately saline waters. If this objective could be achieved, it may provide an effective method for controlling Sr concentrations even in the absence of Ba. However, the high concentrations of polymer required would add to the expense of this approach. Treatment costs could be decreased substantially by regeneration and reuse of the added polymers for multiple treatment cycles. For both PSSM and PAA, complexation of divalent cations was sensitive to solution pH, which provides a possible means for polymer de-complexation and recovery. In a previous study [32], cation release from PAA in a synthetic cation solution was accomplished using HCl, and approximately three-quarters of the polymer recovered for reuse. Use of a larger molecular weight polymer could potentially increase this recovery, as even a

200 kDa (nominal) polymer can initially have a substantial fraction of material small enough to pass through a 10 kDa UF filter[31].

In addition to decreasing chemical requirements, such a process could improve process waste management. Polymer regeneration and separation of the removed cation would result in a lower-volume waste brine containing Ba and Sr that could potentially be recovered for commercial purposes. Even if disposal is required, the reduction in brine volume (when coupled with recovery of the treated produced water for industrial reuse) would minimize the impact and cost of waste disposal. Further research into this this recovery process, as well as testing of ultrafiltration capabilities using cross-flow systems more commonly used in real treatment systems, will provide a more complete assessment of the viability of polymer-based treatment processes for produced waters.

5.   Conclusions

A treatment method that removes Sr, Ba, and Ra, while leaving Mg and Ca behind, would result in reduced waste generation, reducing disposal costs. Sulfate addition achieves these goals when the produced water contains a significant excess of Ba over Sr. However,  Sr removal by sulfate addition is not effective when Ba is not present, as in the sulfate-containing produced waters present in parts of the Central Plains and elsewhere.  Precipitative softening (pH adjustment and addition of carbonate salts) will remove Sr even from hypersaline brines at > 90,000 mg/l TDS, but only concurrently with precipitation and removal of Ca as $CaCO_3$. This requires high levels of chemical addition and generates significant waste solids. Increased Sr removal can be achieved by polymer-assisted ultrafiltration, but these processes are still not 100% effective, and become less selective as the overall TDS concentration increases. They will also likely cost significantly more than either precipitative softening or sulfate addition unless efficient methods are developed for polymer recovery and regeneration.
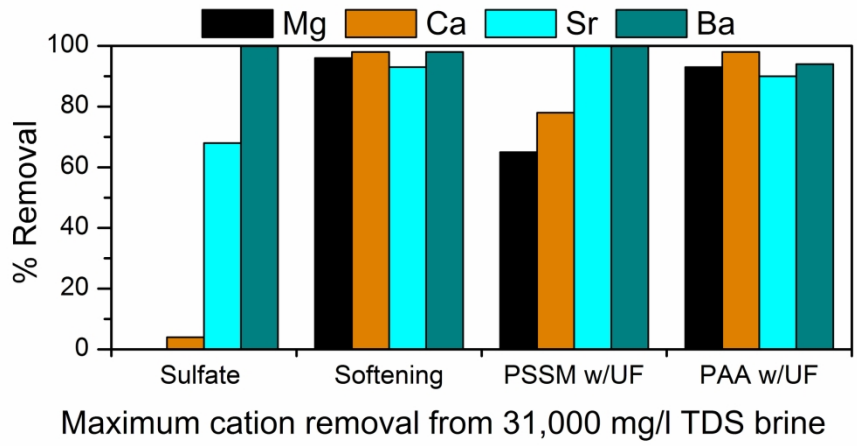
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Maximum cation removal from 31,000 mg/l TDS brine

223x123mm (300 x 300 DPI)