

# Optimizing Metal-Removal Processes for Produced Water With Electrocoagulation

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## Summary

The combination of advances in hydraulic-fracturing and horizontal-drilling technologies has led to a resurgence in oil and gas activity in multiple regions across the United States. To minimize the impact of the increased water use, many oil and gas companies are pursuing fracture-flowback-water and produced-water recycling for subsequent drilling and fracturing operations. Common processes in a recycling strategy include metal precipitation to minimize scaling potential and electrocoagulation for removing solids that may foul a well when water is reused.

In this study, the precipitation of calcium, magnesium, barium, and strontium was examined experimentally by adding target ligands followed by solids separation with electrocoagulation. In addition, removal efficacy was modeled with a commercially available chemical-equilibrium software (OLI Systems). The experimental results were compared with the predicted data at pH values of 9.5 and 10.2. The differences between the modeled data and the experimental data indicated a deficiency in the solid/liquid-separation process in the laboratory. Results also showed that the pH value did not affect the treatment efficiency, except in the case of magnesium; however, sequencing of softening relative to coagulation was important. An additional finding was that, on the basis of the target metal, either sulfate or carbonate needs to be greater than a threshold concentration to achieve precipitation goals. Chemical consumption at pH values of 9.5 and 10.2 was significantly different. Chemical-equilibrium modeling predicts that the average base usage is 30% lower at a pH of 9.5 compared with a pH of 10.2 and 34% lower for acid usage. The reduction in use experimentally was 27% for base and 43% for acid.

## Introduction

Unconventional oil and gas development has been increasing rapidly throughout the United States, largely because of technical advancements in directional-drilling and hydraulic-fracturing techniques. Shale-oil and -gas production (one form of unconventional development) requires large volumes of water for hydraulic fracturing, and much of this activity occurs in areas of the country that are prone to drought and water shortages (Gregory et al. 2011). The concurrence of large water requirements and water-stressed regions has led to significant interest in reuse of the water that is returned during oil and gas production, commonly referred to as fracture-flowback water and produced water (Fakhru'l-Razi et al. 2009). Historically, water coproduced with oil and gas (produced water) has been disposed of through evaporation or deep-well injection, approaches that do not conserve the resource for beneficial reuse. Reuse of flowback and produced water currently varies significantly from region to region and even within the same oil and

gas basin. For example, recycled produced water is less than 10% of the total water used to drill and fracture in the Barnett, Fayetteville, and Haynesville shale plays. However, the fraction of water recycled is significantly higher in the Marcellus play—greater than 90% of the total water used (Mantell 2011).

Although treatment methods have been developed to recycle produced water for subsequent fracturing operations, widespread adoption of these methods is often limited by costs. Important treatment aspects for fracturing-water reuse include particle removal, reduction of scale-forming metals, and disinfection. Removal of total dissolved solids (TDS) is expensive and therefore avoided, if possible. Fracturing fluids have been developed that are compatible with high TDS concentrations, but the other objectives (solids reduction, scale control, and bactericide) almost always need to be satisfied. The focus of this study was to examine the metal-removal processes associated with reducing scaling potential by use of laboratory-scale data and chemical-equilibrium modeling, with the goal of optimizing chemical use and minimizing cost.

**Softening.** Inorganic elements such as calcium, barium, magnesium, and strontium can cause hardness/scaling issues or failure in fracturing-fluid development. While there are proven methods for the removal of some of these contaminants, data on precipitate removal at high pH for produced water are lacking (Parks and Edwards 2006). Precipitative softening, one of the oldest and most common methods of divalent-cation removal (Lane and Duff 1954; Harden and Hull 1957; Liang et al. 1980; Owen and Humenick 1985), is often less expensive than membrane processes, and it can achieve multiple objectives, including more than 90% hardness removal. Calcium and magnesium are removed from water as calcium carbonate and magnesium hydroxide; strontium and barium are removed as the carbonate and sulfate, respectively.

**Electrocoagulation.** Electrocoagulation (EC) is an electrochemical method of treating polluted water whereby an electrical current induces sacrificial anode corrosion, releasing trivalent iron and aluminum ions. As in chemical coagulation, the iron and aluminum ions hydrolyze to form metal hydroxides that can charge, neutralize, and aggregate with solution particles to form flocculants that can be removed with a range of solid/liquid-separation processes. Accompanying electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode (Matteson et al. 1995). EC has been applied successfully for more than 3 decades as a water-treatment technology to remove an extensive range of pollutants (Pouet and Grasmick 1995; Xu and Zhu 2004; Malakootian and Yousefi 2009; Tezcan et al. 2009; Aoudj et al. 2010; Malakootian et al. 2010; Meas et al. 2010; Zodi et al. 2010). Recently, there has been renewed interest in EC for the treatment of produced water, largely because of the technological improvements that have led to lower electricity consumption and a cleaner output. According to Esmailirad et al. (2015), the use of softening before EC, even at a lower pH, has a higher removal efficiency than the use of softening after EC at a

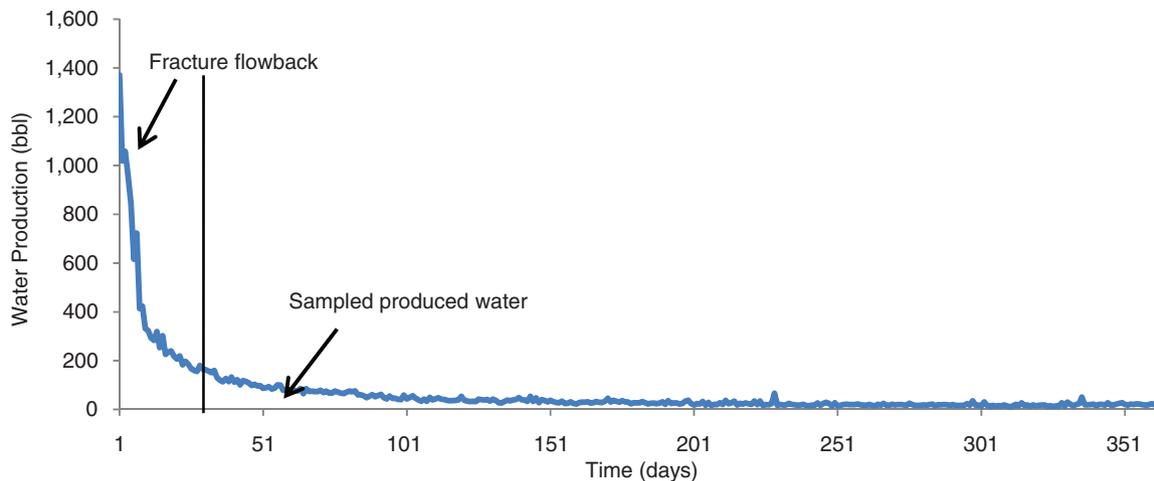


Fig. 1—Typical water-production curve (Bai et al. 2013).

higher pH. However, because the cost of treatment is a major factor when considering water-management options, a full life-cycle analysis must be completed to adequately compare the alternatives.

## Methods

**Experimental.** Produced water was collected from oil and gas wells in the Wattenberg field, which is part of the Denver-Julesburg basin of northeast Colorado. The wells were hydraulically fractured, and water sampling began immediately after flowback was started. Because the objective of the study was to run experiments on flowback and produced water (time period after which most fracturing fluid has flowed back), the sampled wells chosen had an age of 2 to 185 days. A typical production curve for the field is shown in Fig. 1.

Two sets of experiments were run on each water sample. The objective was to investigate the effect of chemical softening and pH on divalent-cation removal during electrocoagulation (EC). Therefore, softening was performed both before and after running EC on each sample by raising the pH value to 9.5 before and to 10.2 after EC. The pH value of 10.2 was chosen for softening after EC because it is the pH that is being used in the treatment process for the water being examined (the control condition in this study). The hypothesis was that softening at a lower pH before EC results in lower chemical costs while still increasing the removal efficacy. Suspended solids after softening and EC-treatment processes were filtered through a 2.5- $\mu\text{m}$  filtration paper (Whatman ashless #42), followed by pH adjustment of the final sample. A schematic of the treatment, sampling, and analysis process is shown in Fig. 2. Softening after and before EC is shown as (1) and (2), respectively. The final sample was taken at the end of each process.

Sodium hydroxide (NaOH) (50% weight/weight concentration from VWR International, Radnor, Pennsylvania, USA) was used to raise the pH of the samples, while hydrochloric acid (HCl) (38% concentration, from VWR International, Radnor, Pennsylvania, USA) was used to lower the pH to 7 at the end of each process. Water-quality analysis of divalent cations such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Ba}^{+2}$ , and  $\text{Sr}^{+2}$  was determined with Environmental Protection Agency method 6010C, with a Varian ICP-AES, Liberty AX (Varian Incorporated, USA).

**Equilibrium Modeling.** OLI Chemical Analyst is a software application used for simulating aqueous-based chemical systems. It is a graphical program developed by OLI Systems (Morris Plains, New Jersey, USA) that uses a predictive thermodynamic framework for calculating the physical and chemical properties of multiphase, aqueous-based systems (Dyer et al. 2003). The software predicts reaction products, phase splits, and complete speciation of all phases for a complex mixture of chemicals in water at a wide range of temperatures and pressures. Stream Analyzer can be used for computing bubblepoint and dewpoint; pH and pH adjustments; precipitation point; acid/base/chelant titration curves; and temperature, pressure, and composition dependence of thermophysical properties (Dyer et al. 2003). Prediction of metal-salt precipitation and scaling tendencies for cations at a range of pH values by use of raw-water quality as the input to the software was performed. The pH range was chosen to be 8.5 to 10.2, with intervals of 0.5. The software reconciled the pH, meaning that the pH was raised with caustic and then was dropped to 7 for all the chosen values with HCl. Standard temperature and pressure conditions were applied in the model (25°C and 1 atm, respectively).

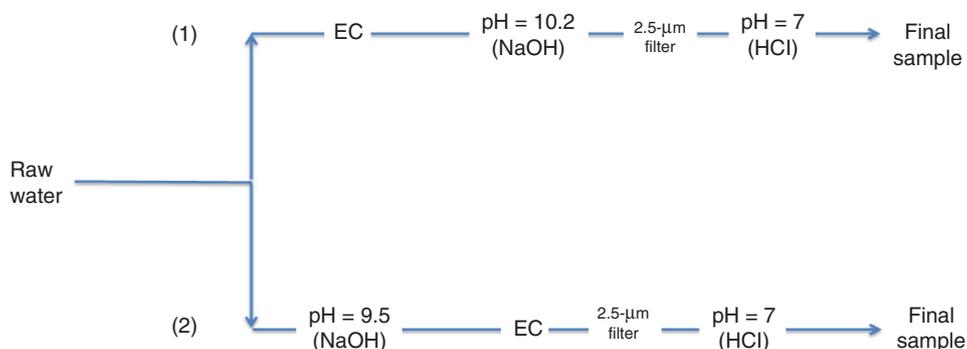


Fig. 2—Schematic of the sampling plan: (1) softening after EC and (2) softening before EC.

Parameters	Case I: Mg <sup>+2</sup> Limitation (mg/L)	Case II: Ca <sup>+2</sup> , Sr <sup>+2</sup> Limitation (mg/L)
Ca <sup>+2</sup>	300	100
Mg <sup>+2</sup>	20	100
Sr <sup>+2</sup>	5	5
Ba <sup>+2</sup>	5	5

Table 1—Water-quality characteristics for Cases I and II.

**Chemical-Use Analysis.** An analysis of chemical requirements for different process scenarios was conducted by comparing two cases (Table 1). Case I water-quality requirements include a “limiting concentration” of magnesium, which requires significant removal of this ion. Concentrations of strontium and calcium are less limiting for this case and requirements should be met with any process that achieves magnesium targets. Magnesium requirements for Case II are not limiting because raw-water concentrations are less than this value. In this case, calcium and strontium removal define the pH conditions of the softening process. In both cases, barium is not important because softening pH will not influence the removal of this ion.

The assumption for the analysis is that a pH of 10.2 will be needed for the Case I precipitation process, but a lower pH of 9.5 will be sufficient for Case II when magnesium removal is not required. These pH values were determined for this analysis on the basis of the availability of experimental and modeled results for each. Both cases should be optimized for chemical use, with an equilibrium model that is based on actual raw-water concentrations and then verified with bench- or pilot-scale testing.

## Results and Discussion

**pH Effects.** Raw-water quality was used as the input values for the OLI model, and simulations were carried out to observe the efficacy of each treatment process. The OLI model was used to simulate

an oversaturated condition (scaling tendency greater than unity) by allowing precipitation of solids at high pH values. The removal rates are based on the assumption of 100% solid/liquid separation. Stated differently, divalent cations that are precipitated by reacting with the proper ligand (hydroxide, sulfate, carbonate) are assumed to be removed completely with sedimentation or filtration.

Chemical compounds and scaling tendencies at different pH values for one of the produced-water samples are shown in Table 2. The higher the scaling tendency, the greater the driving force for precipitation, and therefore, dominant solids are expected to be calcium carbonate (CaCO<sub>3</sub>), strontium carbonate (SrCO<sub>3</sub>), magnesium hydroxide [Mg(OH)<sub>2</sub>], and barium sulfate (BaSO<sub>4</sub>). These compounds are colored in the table [CaCO<sub>3</sub> is blue, Mg(OH)<sub>2</sub> is green, strontium (Sr) is yellow, and BaSO<sub>4</sub> is red].

The effect of pH on precipitation of the four targeted cations is shown in Fig. 3. CaCO<sub>3</sub> precipitation, and therefore removal rate, increases dramatically from 5 to 85% when pH is increased from 6.7 to 8.5. At pH higher than this, the equilibrium removal rate for calcium (Ca) flattens out considerably, but the kinetics of reaction will also need to be considered when designing a treatment operation. Chemical-equilibrium modeling predicts that the removal of Ca at pH values as low as 9.0 can be greater than 97%.

A similar trend was observed for the Sr ion because the aqueous complexation with the same ligand (carbonate) is expected to form SrCO<sub>3</sub> solids. Removal jumped from less than 1 to 95% by increasing the pH from 6.7 to 9.0 before leveling off. Minimal magnesium (Mg) precipitation is predicted until the pH is raised to 10, a significantly higher value than that for the other cations examined. Mg precipitates most effectively as the hydroxide, achieving a relatively modest removal of 72% at pH of 10.2. As discussed, barium (Ba) solubility is lowest when precipitating solid BaSO<sub>4</sub>, and because this ligand is not acid/base active at the expected water-quality conditions, the removal of the compound is not affected by pH.

Solids	Scaling Tendency				
	pH=8.5	pH=9	pH=9.5	pH=10	pH=10.2
Iron (III) hydroxide	28213.3	22951.9	14409.3	6598.79	4504.59
Sodium aluminum dihydroxide carbonate	578.532	163.457	39.4661	7.27151	3.38548
Aluminum hydroxide	228.544	72.641	22.9551	7.23369	4.55752
Calcium carbonate (calcite)	32.8503	63.7667	91.941	107.464	110.693
Strontium carbonate	23.1803	64.173	150.837	269.19	311.235
Barium sulfate	17.8622	17.347	16.2446	14.8394	14.3703
Strontium sulfate	0.054015	0.053581	0.052457	0.050789	0.050167
Barium carbonate	0.045327	0.122853	0.276207	0.465083	0.527179
Magnesium carbonate trihydrate	5.46×10 <sup>-3</sup>	0.014468	0.031029	0.049271	0.054734
Magnesium carbonate	5.18×10 <sup>-3</sup>	0.013715	0.029394	0.046632	0.051786
Sodium bicarbonate	4.53×10 <sup>-3</sup>	4.02×10 <sup>-3</sup>	3.08×10 <sup>-3</sup>	1.80×10 <sup>-3</sup>	1.33×10 <sup>-3</sup>
Calcium sulfate dihydrate	4.49×10 <sup>-3</sup>	3.12×10 <sup>-3</sup>	1.88×10 <sup>-3</sup>	1.19×10 <sup>-3</sup>	1.05×10 <sup>-3</sup>
Calcium sulfate	3.31×10 <sup>-3</sup>	2.30×10 <sup>-3</sup>	1.38×10 <sup>-3</sup>	8.77×10 <sup>-4</sup>	7.72×10 <sup>-4</sup>
Boric acid	1.02×10 <sup>-3</sup>	6.94×10 <sup>-4</sup>	3.46×10 <sup>-4</sup>	1.34×10 <sup>-4</sup>	—
Sodium iron (III) dioxide	4.78×10 <sup>-4</sup>	1.24×10 <sup>-3</sup>	2.51×10 <sup>-3</sup>	3.70×10 <sup>-3</sup>	4.03×10 <sup>-3</sup>
Sodium chloride	4.69×10 <sup>-4</sup>	4.73×10 <sup>-4</sup>	4.80×10 <sup>-4</sup>	4.87×10 <sup>-4</sup>	4.89×10 <sup>-4</sup>
Magnesium hydroxide	4.47×10 <sup>-4</sup>	4.26×10 <sup>-3</sup>	0.038422	0.335999	0.805599
Strontium bicarbonate	1.96×10 <sup>-4</sup>	1.51×10 <sup>-4</sup>	—	—	—
Sodium carbonate decahydrate	—	—	—	1.29×10 <sup>-4</sup>	1.52×10 <sup>-4</sup>

Table 2—Classification of existent compounds at different pH.

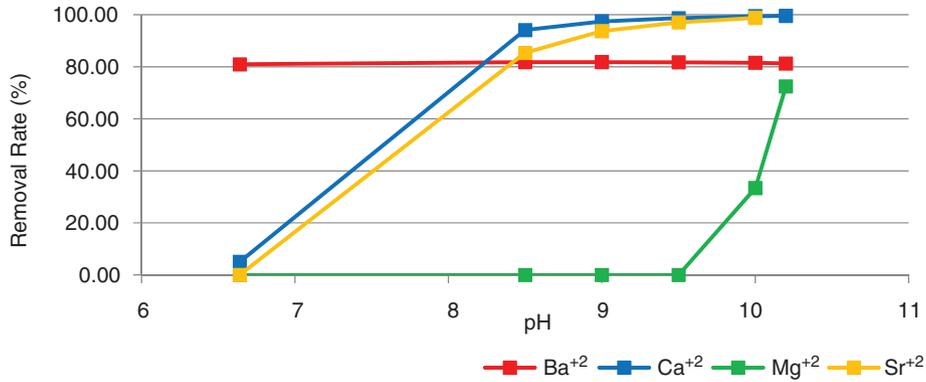


Fig. 3—Precipitation and removal of divalent cations vs. pH (assumes 100% solid/liquid separation following precipitation).

In summary, if treatment processes are being designed to reduce the concentration of divalent cations for either scaling-index control or specific ion interactions with fracturing fluids, process optimization with the approach shown in Fig. 3 should be considered. For example, the sensitivity of fracturing-fluid stability and the

scaling tendency of Mg should be quantified to determine if acid and base chemical use can be reduced by operating at a lower pH.

Removal rates (left axis) for Ca and Sr at different pH values, ranging from 8.5 to 10.2, are shown in Figs. 4a and 4b. Because Ca and Sr both precipitate as a carbonate complex, they have similar

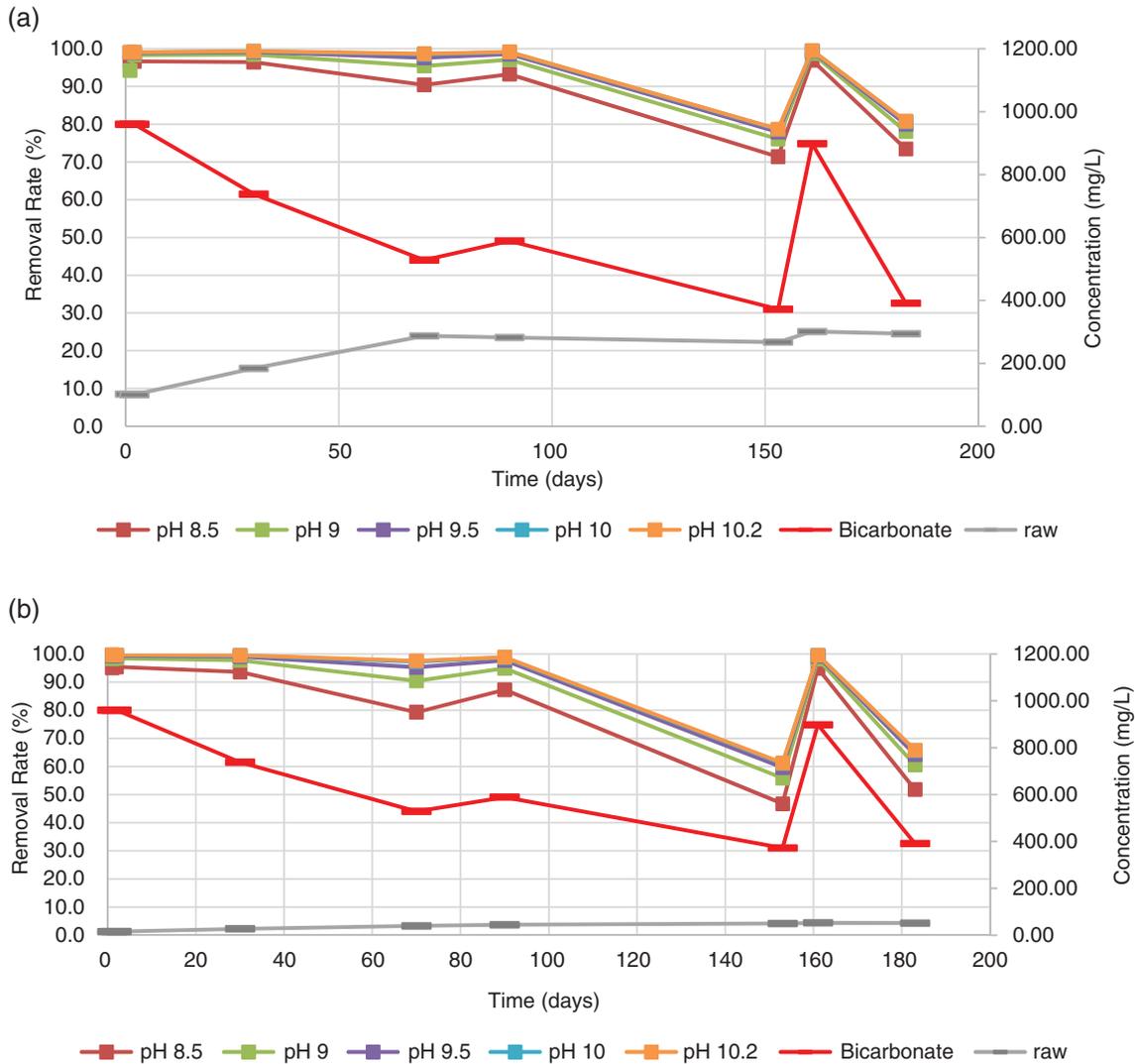


Fig. 4—(a) Calcium (Ca) and (b) strontium (Sr) removal at different pH over time. Ca and Sr removal at different pH values was based on OLI model (left axes), and Sr, Ca, and carbonate concentrations in the raw-water samples (right axes).

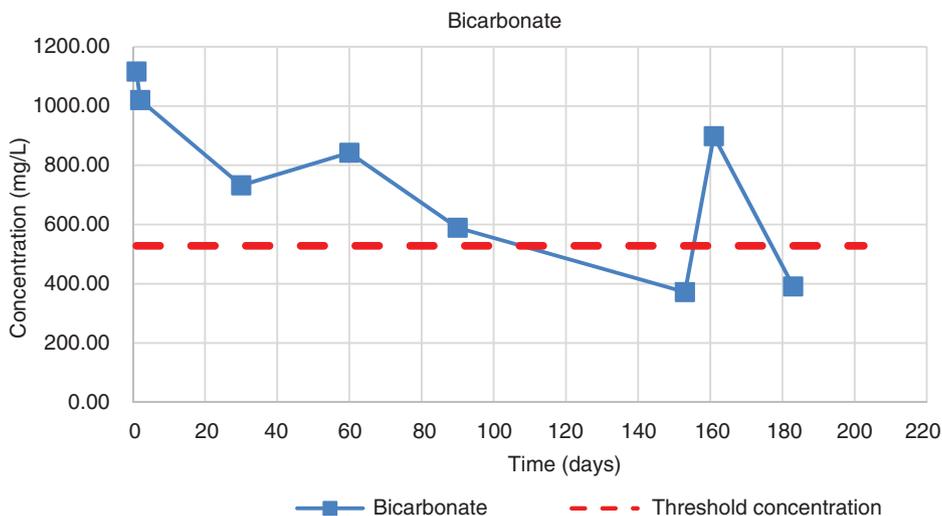


Fig. 5—Bicarbonate concentration in raw-water samples.

sensitivity to pH as removal rates level out at a pH value of greater than approximately 9. Also, the removal rate for both ions (Ca and Sr) was relatively constant, except for a sudden drop at the 153-day sample (Fig. 4). This decline in removal rate could be the result of a reduction in the ligand concentration in the raw water. As shown in Fig. 5, the bicarbonate concentration varies in the raw water and can limit the precipitation of Ca and Sr if it drops below a threshold value. The lowest bicarbonate concentration occurred with the 153-day sample at 372 mg/L, corresponding to an average of 25 and 47% reduction in removal rate for Ca and Sr, respectively. There is another low point with the higher-well-age sample (183 days) at 391 mg/L, corresponding to an average of 41% reduction in Ca and 23% reduction in Sr removal rate.

Because the low-solubility ligand for both Ca and Sr is bicarbonate, the alkalinity of a produced-water solution (an indicator of total carbonate concentration) can limit the removal of these metals. According to Fig. 5, to reach a 90% removal of both Ca and Sr at all pH values (8.5, 9, 9.5, 10, and 10.2), a threshold carbonate concentration of 528 mg/L is required. In other words, on the basis of the graph in Fig. 5, the minimum concentration of bicarbonate associating with 95% Ca and Sr removal was 528 mg/L, and when the concentration was lower than this, the removal rates for both Ca and Sr decreased. Below this threshold concentration, the system is carbonate deficient, leading to a removal limitation that is not a function of pH. When designing a treatment process for Ca or Sr removal, the alkalinity of the influent water is an important process variable.

The Mg removal rate and raw-water Mg concentrations are shown in Fig. 6. As mentioned in the previous discussion, Mg precipitates as a hydroxide after the pH is increased to greater than 10. The plot shown in Fig. 6a indicates a sudden increase in Mg removal at a pH of 10.2 for the water-quality sample that was collected after 70 days (96%). This appears to be because of the increased raw-water Mg (98.7 mg/L at 70 days vs. 29.7 mg/L for the 30-day sample that was collected immediately before). The predicted treated-water concentrations of Mg were 29.7 mg/L for the 30-day sample and 46.9 mg/L for the 70-day sample, indicating similar equilibrium concentrations at the same pH. It was also seen that the removal rate was 0% until the pH was increased to 10 and higher. Also, the higher pH of 10.2 had a significantly greater efficacy than pH of 10, despite a 0.2 unit difference pH that was equivalent to 1.6 mol/L additional hydroxide ions.

Fig. 7 shows Ba removal over time at different pH values. As anticipated, pH did not influence the Ba removal rate, and in the figure,

all pH values are coincident with the pH = 10.2 trend line. The modeled removal rate has a sudden decrease with the 30-day sample, resulting almost entirely from a decrease in the sulfate concentration.  $\text{BaSO}_4$  is more soluble at higher temperatures (Jiang 1996; Rudie and Hart 2006), and therefore, supersaturated conditions that will lead to precipitation can occur when the solution cools during surface handling. Sulfate concentration and threshold concentration are shown in Fig. 8. Because the Ba concentration in the raw-water samples is between 4 and 30.6 mg/L, removal rates are not influenced significantly, and to achieve 70% Ba removal for the system, the sulfate concentration needs to be above the threshold concentration of 21 mg/L (Fig. 8). If additional Ba needs to be removed, an excess concentration of sulfate will need to be added as a treatment chemical.

**Comparison of Experimental and Modeled Results.** To determine if a treatment is working sufficiently, the target-dissolved-ion concentrations at the effluent are measured and plotted with the goal concentration (Figs. 9 through 11).

Fig. 9 shows the removal of Ca and Sr ions for both experimental and modeled trends and the raw-water and goal concentration. It is shown that the experimental effluent has higher concentration than predicted with the OLI chemical-equilibrium model. The experimental removal efficiencies are lower than the modeled data except for one data point (146-day sample), which could be because of the deficiency of solid/liquid separation (filtration with 2.5- $\mu\text{m}$  paper) in the laboratory. Both experimental and modeled results follow a similar trend, and the sudden rise in the concentration, as mentioned previously, is because of a corresponding drop in the raw-water carbonate concentration. Another major point is that pH value does not cause the difference between the two treatments because the modeled results show there is not any difference between the two pH values of 9.5 and 10.2. Hence, the sequence of softening was the important factor in the increased effectiveness of the softening-before-electrocoagulation (Soft-EC) vs. softening-after-electrocoagulation (EC-Soft) process in this study.

Mg, as discussed in the preceding and shown in Fig. 10, was in the dissolved, divalent-cationic form at a pH of 9.5. By increasing the pH to 10.2, there is a significant decrease in Mg concentration in the OLI-modeled result. However, the same trend (higher efficiency in the modeled result) was observed for Mg as for Ca and Sr.

Ba removal results (experimental and modeled) are shown in Fig. 11. Initially, both treatments (EC-Soft and Soft-EC) had similar removal rates, but the gap increased over time for samples from wells with an age greater than 160 days.

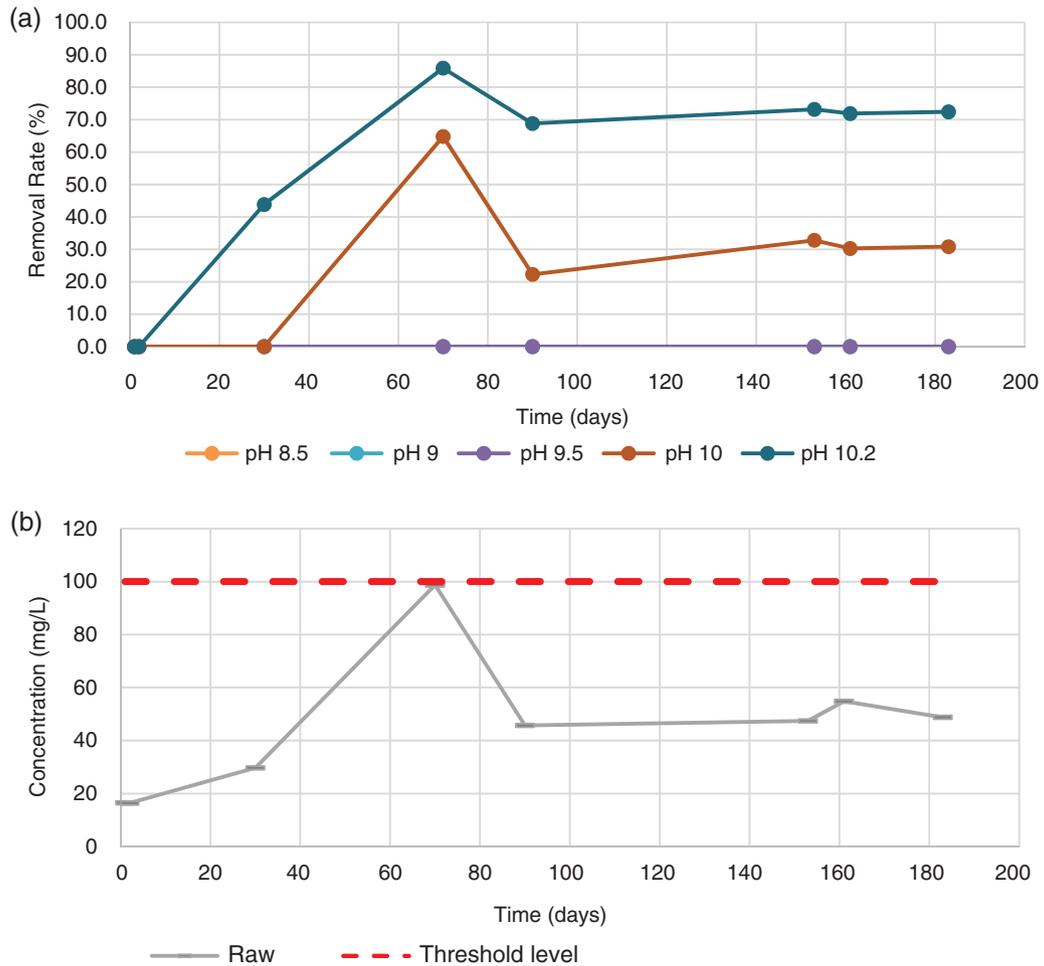


Fig. 6—(a) Mg removal at different pH values over time; (b) Mg concentration in the raw-water samples and threshold concentration.

**Chemical-Use-Analysis Observations.** The required acid/base quantities for the case studies (Case I: Mg limited; Case II: Ca and Sr limited) on the basis of OLI-model results are shown in Fig. 12. It was seen that there is a substantial difference between pH values of 9.5 and 10.2 in terms of chemical consumption. Theoretically, with the required base (e.g., sodium hydroxide) at the pH of 10.2,

base-usage efficiency was 20 to 40% lower at pH of 9.5 compared with 10.2; likewise this amount was 21 and 48% for acid usage. The observed reduction for the experiments ranged from 10 to 62% for base usage and 22 to 73% for acid usage. Also, it appears that there is a large difference between flowback water and produced water in terms of chemical usage. Much more chemical (acid and

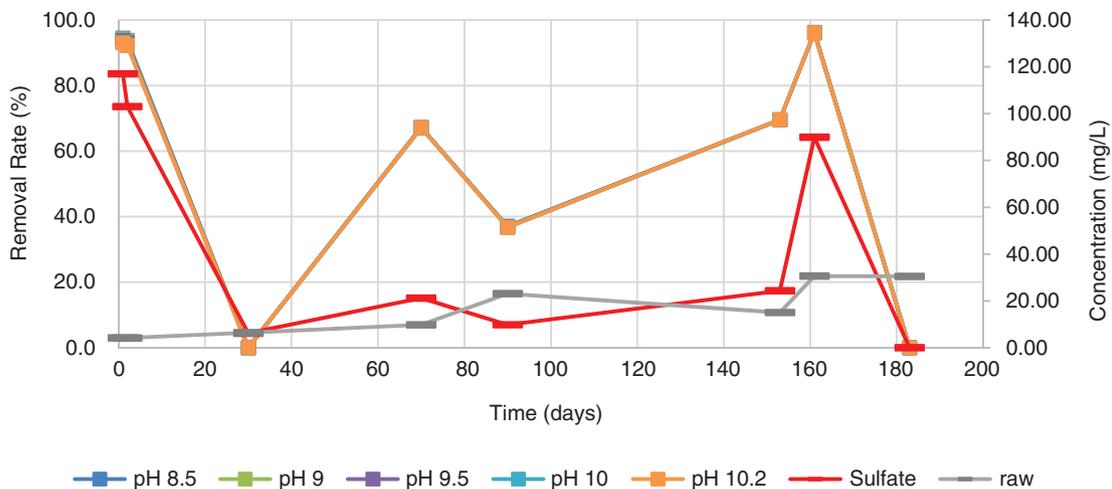


Fig. 7—Ba removal rates at different pH values (left axis); Ba and sulfate concentrations in the raw-water samples (right axis) over time.

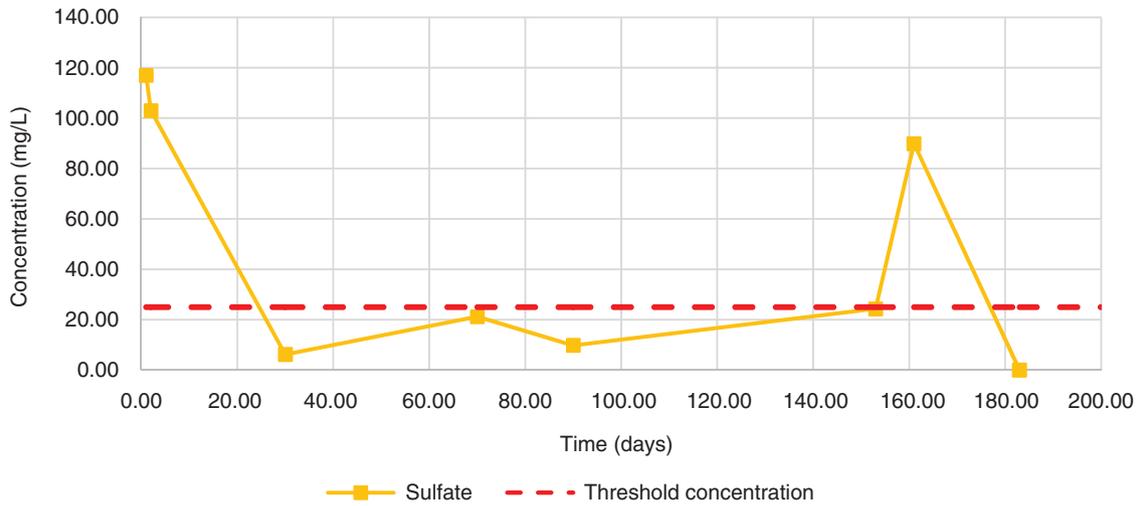


Fig. 8—Sulfate concentration in raw-water samples over time and threshold concentration.

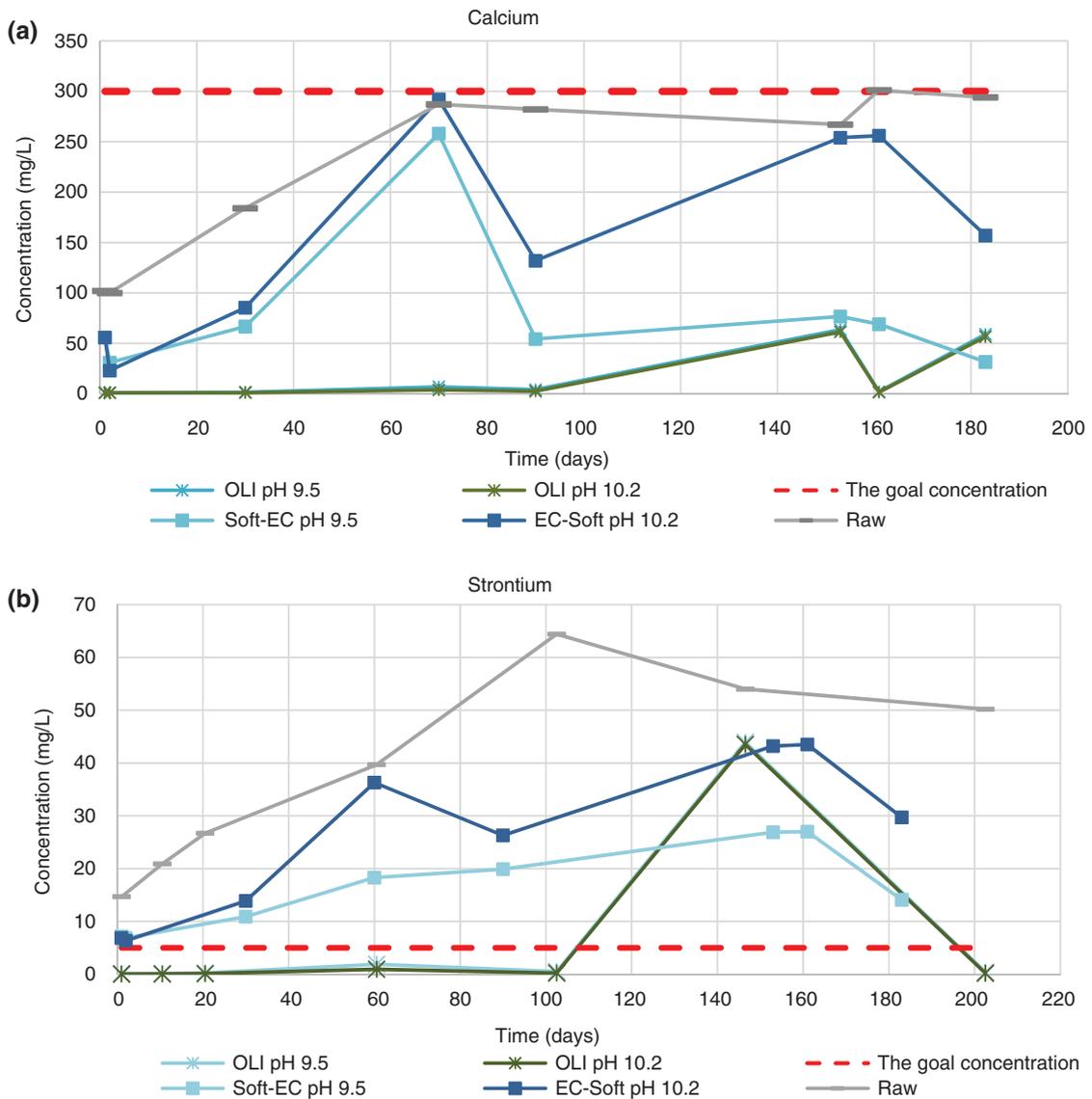


Fig. 9—Comparison between the experimental and modeled ion concentrations in the effluent at pH values of 9.5 and 10.2: (a) Ca and (b) Sr.

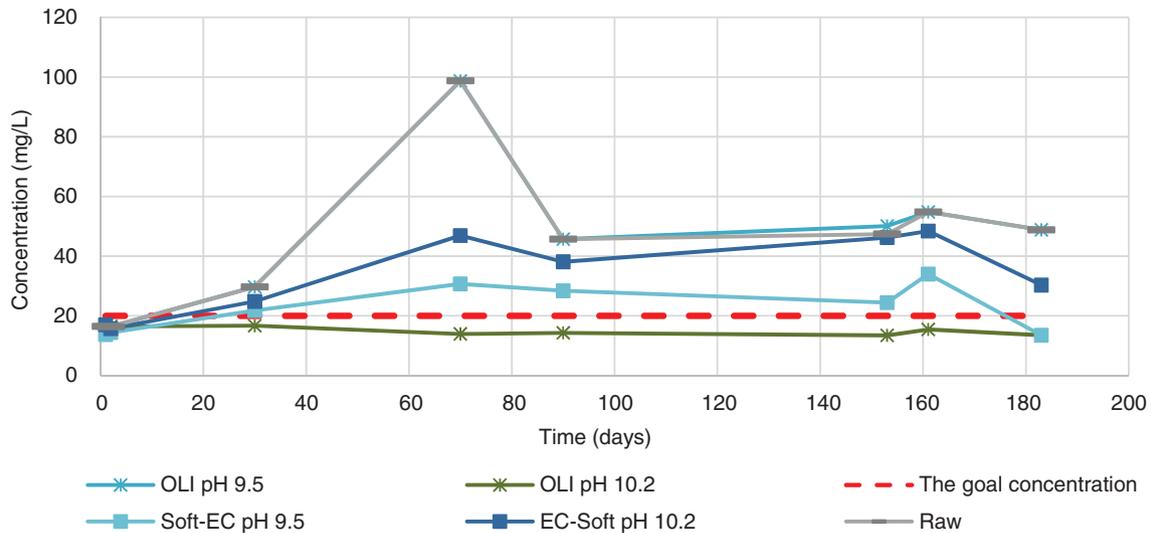


Fig. 10—Comparison between the experimental and modeled Mg concentration in the effluent at pH values of 9.5 and 10.2.

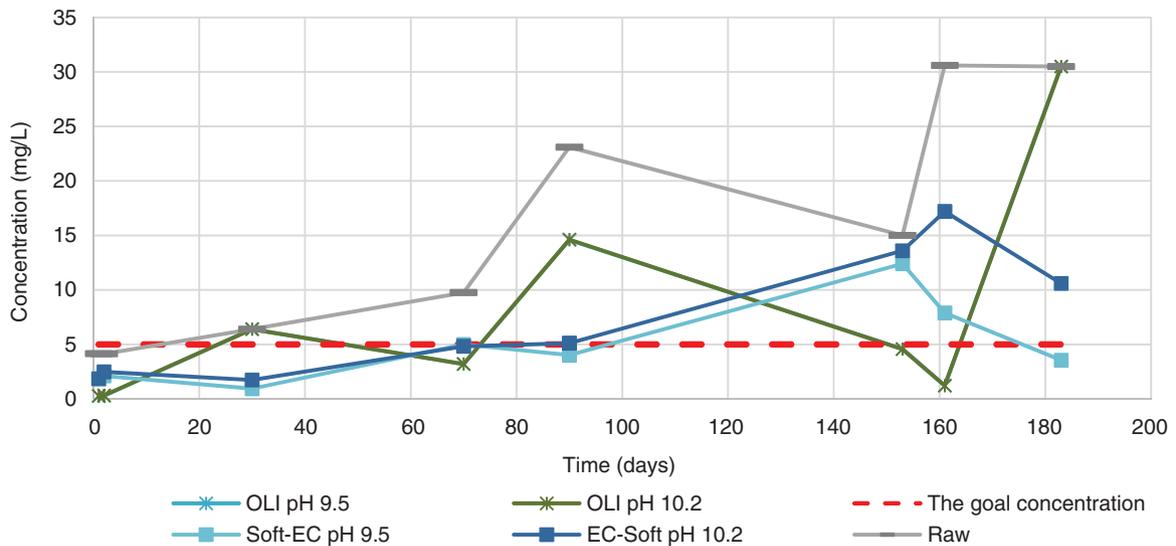


Fig. 11—Comparison between the experimental and modeled Ba concentration in the effluent.

base) was used for the early flowback water (water samples earlier than 1 month) vs. produced water (later water flows). This observation was highly visible, particularly for base consumption in the first 30 days.

It is concluded that, on the basis of the target water quality, optimizing pH conditions could save substantial amounts of acid and base chemicals and therefore reduce the cost of treatment. Hence, a comprehensive water analysis would be necessary to optimize the produced-water treatment in terms of cost and chemical usage.

## Conclusion

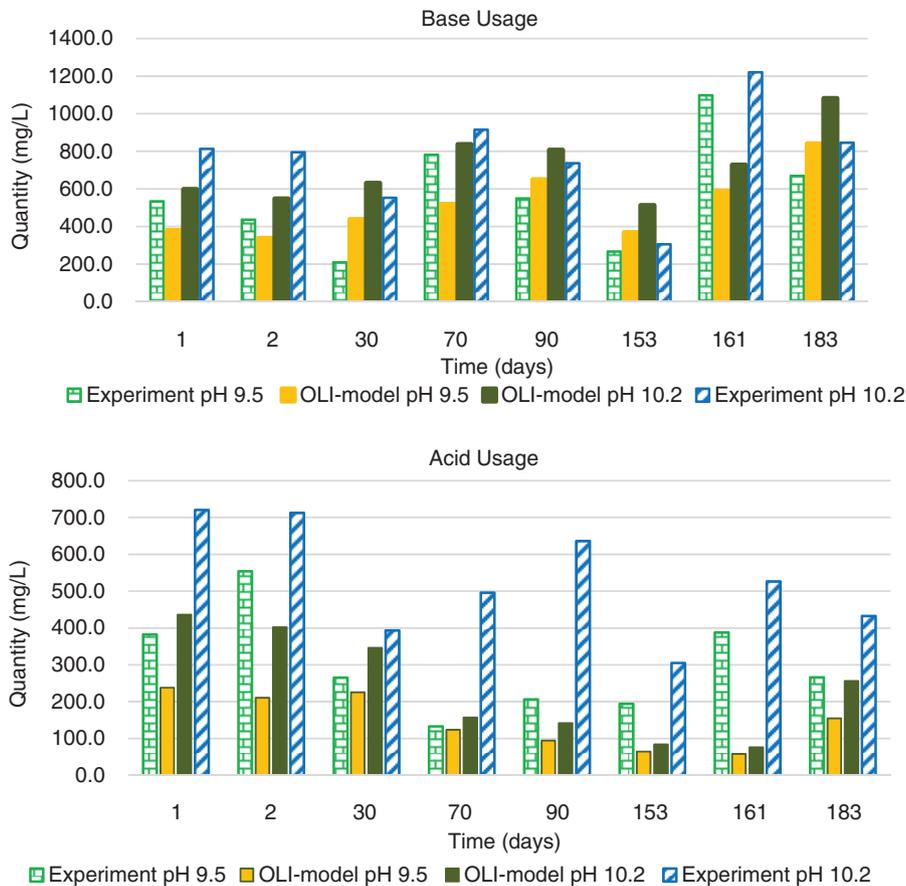
- Magnesium removal targets will dictate the pH required for softening or metal-precipitation processes.
- Equilibrium-modeling results predict that removal efficacy for calcium and strontium will be minimally impacted by lowering pH from 10.2 to 9.5.
- The differences in removal rates for the modeled and experimental results for all of the metals may be a result of a de-

ciency in the solid/liquid-separation process. Coagulation with electrocoagulation after precipitating the solids could result in a more-effective solid/liquid-separation process.

- Chemical consumption at pH values of 9.5 and 10.2 was significantly different. Chemical-equilibrium modeling predicts that the average base usage was 30% lower at pH of 9.5 compared with a pH of 10.2 and 34% lower for acid usage. The reduction in use experimentally was 27% for base and 43% for acid.
- Broad knowledge of water chemistry and quality not only would save considerable amounts of chemicals and the associated costs, but also would reduce sludge production and might lead to a more-effective coagulation process.

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**Fig. 12—Acid and base consumption.**

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