Geoffrey Brown, Robert Geiger, Daniel K. Pannell and Kris Shelite
Compass Minerals, 9900 West 109th St, Overland Park, KS 66210, USA

Enhancing the Efficiency of Water Softener Regenerants

Salt, Safety and the Environment

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Abstract

Water softener technology was introduced in the early 1900s and the technology continues to evolve and improve to the present day. Currently, the salt-based water softener technology is the most cost-effective against the damaging effects of hard water in household and industrial applications. Despite the tangible benefits provided by the salt-based softener technology, some municipalities have argued that the ongoing use has resulted in excessive chloride discharge into waste and surface waters. In response to softener restrictions proposed in some states, the industry developed divergent strategies to reduce salt usage. One strategy involved the development of water softener technology to allow for more efficient use of salt during the resin regeneration cycle. High-efficiency softeners, as they are known, are commercially available but are more expensive than traditional units. Another strategy involves the development of new chloride-free regenerants containing sodium or potassium salts. While effective, chloride-free regenerants, such as sodium acetate, are significantly more expensive than sodium chloride and have to be used in larger quantities to achieve similar performance. The focus of this present study is about the development of an improved sodium chloride regenerant that requires less salt for resin regeneration. To increase salt efficiency, low levels of anionic polymers capable of chelating Ca^{2+} and Mg^{2+} ions were employed. Although the exact mechanism for increasing efficiency hasn't been completely elucidated, it's understood that traditional regenerants require an overwhelming excess of Na^{+} ions to displace Ca^{2+} and Mg^{2+} ions from the exchange resin. It's also understood that the Ca^{2+} and Mg^{2+} ions can undergo repeated cycles of attachment to and displacement from the softener resin as they travel through the bed. In light of these cycles of displacement from and reattachment to the resin, a large excess of Na^{+} ions is required to thoroughly flush the hardness ions out of the softener. It is posited that the calcium chelator disrupts the cycles of displacement and reattachment by binding to the hardness ions as they are initially displaced by the influent Na^{+} ions. By doing so, the chelator reduces the likelihood that the displaced Ca^{2+} and Mg^{2+} ions will re-reattach to the resin. In water softener experiments, as little as10 ppm of polymeric chelating agents in a 25% brine solution has been able to remove twice as much calcium as a 25% brine solution without chelator. In fact, 25% brine/chelator blend was as effective as a 75% brine solution of equal volume. This type of novel salt-based regenerant system is also environmentally desirable because it significantly reduces the amounts of sodium and chloride discharged in the softener's effluent.

Introduction

While potable water is safe to drink and useful for any number of household and commercial applications, a number of undesirable dissolved substances can affect the water's quality. The levels of two of these dissolved substances, Ca^{2+} and to a lesser degree Mg^{2+}, contribute to what is known as water hardness, which is quantified by the amount of calcium carbonate ($CaCO_3$) in the water. Hard water is defined as having 7 to 10.5 grains per gallon of $CaCO_3$, or 120 to 180 ppm calcium carbonate.

Although hard water is not toxic, its long-term use causes problems in household and industrial fixtures such as hot water heaters, plumbing, boilers and heat exchangers. This is due to the low

pannellda@compassminerals.com phone 9133272401

solubility of calcium and magnesium carbonate, and their tendency to precipitate onto surfaces and form a solid film known as scale. Over time, scale buildup can restrict flow in pipes and fixtures, and can damage or reduce the performance of hot water heaters. To mitigate these adverse effects, water softening devices are commonly used to remove Ca^{2+} and Mg^{2+} ions from source water via a process known as ion exchange.

Water softeners work by passing hard water through a cation exchange resin. The resin has copious negatively charged (anionic) functional groups that bind to positively charged substances (cations), such as calcium and magnesium ions. Over time, the resin becomes saturated, reducing its capacity to remove Ca^{2+} and Mg^{2+} ions from the source water. Therefore, the resin is routinely regenerated by flooding the water softener with another cation (typically Na^+ or K^+), which exchanges with the trapped Ca^{2+} and Mg^{2+} ions allowing them to be rinsed away. As a result of the exchange process, Na^+ or K^+ cations become bound to the softener resin. After regeneration, the softening process begins again as hard water passes through the resin and Ca^{2+} and Mg^{2+} ions displace Na^+ or K^+.

Even though water softeners play an important role in water quality, some state regulatory bodies and local municipalities have banned softeners or expressed concerns due to the ongoing continual sodium and/or chloride discharges by softeners into public (1,2) or private septic systems (3,4). The industry has partnered with regulators to explore options for reducing the amount of chloride in softener effluents. For example, a research project conducted by the Madison (Wisconsin) Metropolitan Sewerage District assessed the impact of water softener optimization on chloride reduction. The project was sponsored by private industry and the Salt Institute (5). Water softeners were the focus of the research since they were estimated to be responsible for 57% of all chloride discharged to waste treatment. Chlorides can't be readily removed by waste treatment plants, so they build up over time in surface waters. Chloride negatively impacts aquatic life and can also affect vegetation. Therefore, technologies that minimize chloride release are generally viewed as environmentally friendlier.

In addition to sponsoring important research, the water softening industry also responded to the burgeoning regulatory concerns by developing 'high efficiency' water softeners. Unlike traditional water softeners, high efficiency units incorporate technologies that allow them to meter in the appropriate amount of salt that a particular household actually needs. Therefore, the salt is used more efficiently since the minimum amount of salt is used to regenerate only that portion of resin requiring regeneration. However, a drawback of high efficiency softeners is that they can cost several hundred dollars more than traditional units. As a result, they may be cost prohibitive for many households. Other approaches include the use of non-traditional regenerants such as sodium or potassium acetate, but these are also costly and require larger quantities for regeneration. Furthermore, the residual acetate discharged will contribute to BOD (Biochemical Oxygen Demand), which is a surrogate indicator of organic pollution in water (6).

The goal of this research was to develop a cost-effective, high efficiency softener regenerant based on sodium chloride that could be used in any type of water softener.

Experimental

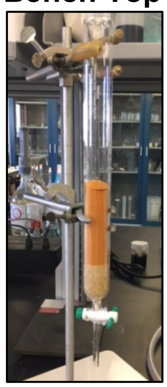
The efficiency of water softener regenerants was evaluated using small-scale bench top softener replicas and with full size units. The small scale units were comprised of plastic bottles filled with

250 mL of Culligan® Cullex® water softening resin (Benzene, Diethyl-, Polymer with ethenylbenzene and ethenylethylbenzene sulfonated sodium salt).

To wet the resin, 250 mL of ultrapure water were poured through each conditioner, followed by 1.25 L of tap water. The resin was subsequently exhausted by pouring concentrated calcium chloride brine through the bench top units. Exogenous, unbound Ca^{2+} ions were flushed from the units by several rinses with tap water (ca. 290 ppm hardness).

Two small-scale water softeners (Fig. 1) were used to compare the performance of 500 mL of diluted sodium chloride brine (100 mL saturated brine + 400 mL water) with 500 mL of a brine dilution (50 mL saturated brine + 450 mL water) containing 100 ppm of a low molecular weight polyacrylic acid (PAA). A third bench top conditioner was treated with an aqueous solution containing only 100 ppm PAA. The purpose of the PAA-only solution was to determine if the polymer could also displace Ca^{2+} from the exchange resin.

Figure 1. Bench Top Softener.



Once the proof of concept studies with the bench top units were completed, confirmatory experiments were performed using a full-sized softener equipped with a Culligan® Medallist Series™ control module and Culligan® Cullex® water softening resin (Figure 2). The housing contained ca. 0.85 ft^3 of Cullex resin. The softener was connected to two clear brine tanks fitted with valves to allow the introduction of different regenerants. A third brine tank was filled with calcium chloride and used to saturate the resin prior to regeneration studies (Fig 2). The calcium chloride brine was prepared by adding 5 kg of calcium chloride flake to approximately 20 liters of water. The other brine tanks were filled with sodium chloride pellets or salt brine solutions, with and without a polymeric calcium chelator. Prior to regeneration, sodium chloride pellets were allowed to brine (i.e., dissolve) for no less than three days before regenerating the resin. For the purposes of these studies, sodium chloride pellets or brine, served as the control (i.e., unenhanced) regenerant.

The water softener was programmed according to the following schedule for all experiments: Backwash cycle - 10 minutes at 1 gal/min; slow brine regeneration - 60 minutes at 0.4 gal/min and fast rinse - 21 minutes at 1 gal/min. The effluents from these cycles were collected in a 100-gallon, plastic tank and analyzed for sodium and calcium contents via Inductively Coupled Plasma or ICP.

Figure 2. Water Softener with Clear Brine Tanks.

Results

Bench top experiments in small-scale softeners indicated that PAA significantly increased NaCl's regeneration efficiency (Table 1). In fact, the addition of 100 ppm PAA removed almost 28% more calcium ions than expected based on the NaCl concentration. Moreover, the data confirmed that PAA alone was not an effective resin regenerant. This indicated that PAA was enhancing the efficiency of NaCl and not displacing calcium ions on its own.

Although the exact mechanism for increased efficiency hasn't been completely elucidated, it's understood that traditional regenerants require an overwhelming excess of Na^+ ions to displace Ca^{2+} and Mg^{2+} ions from the exchange resin. It's also understood that the Ca^{2+} and Mg^{2+} ions undergo repeated cycles of attachment to and displacement from the softener resin as they travel through the bed. In light of these cycles of displacement from and reattachment to the resin, a large excess of Na^+ ions is required to thoroughly flush hardness ions out of the softener. Therefore, it is posited that the calcium chelator disrupted the cycles of displacement and reattachment by binding to the hardness ions as they were displaced by the influent Na^+ ions. By doing so, the chelator reduced the likelihood that the displaced Ca^{2+} and Mg^{2+} ions would re-reattach to the resin.

Table 1. Impact of PAA on Regeneration Efficiency.

SAMPLE	Ca^{2+} in Effluent (ppm)	Ca^{2+} Expected (ppm)	% DIFFERENCE
NaCl (100 mL brine)	3,716	3,716	-
NaCl (50 mL brine)+ 100 ppm PAA	2,370	1,858	+27.6
100 ppm PAA (no NaCl brine)	2.2	0	0

While the small-scale studies were encouraging, broader studies in full-size water softeners were required. Therefore, a series of experiments were performed using a water softener. For the experiment summarized in Table 2, 50 pounds of salt were added to the brine tank for the ensuing regeneration experiments. Since these data were generated using unenhanced NaCl, they provided baseline expectations for the amounts of Na^+ and Ca^{2+} in the softener effluents. Although only two regenerations were achieved, the concentrations of Na^+ and Ca^{2+} in the effluents from both regenerations were fairly consistent.

Table 2. Regeneration with Sodium Chloride.

REGENERATION NUMBER	Na^+ (PPM) IN EFFLUENT	Ca^{2+} (PPM) IN EFFLUENT
1	7892	3589
2	7668	3594

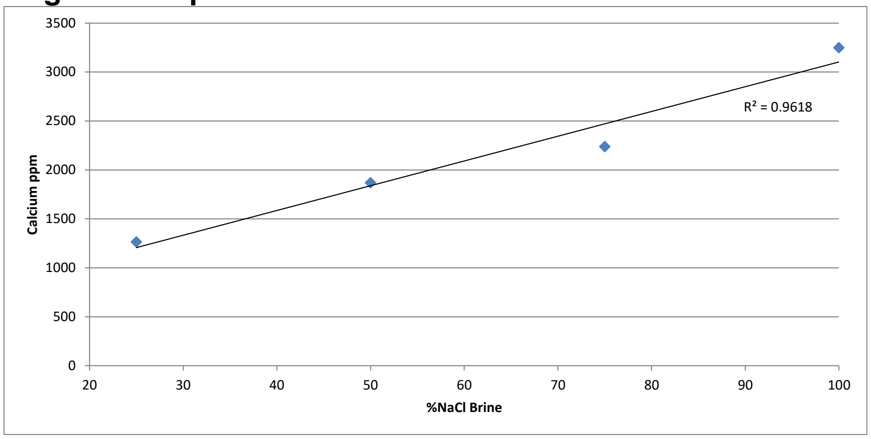
Once the baseline expectations for the traditional regenerant (i.e., NaCl) had been established (Table 2), subsequent experiments focused on the ability of polymeric calcium chelating agents to increase the efficiency of sodium chloride. For these experiments, saturated brine solutions were prepared by dissolving solar salt in municipal water and adding them to the brine tanks. Brine solutions were used in lieu of solid NaCl in order to accurately control the strength of the brines. In each instance, the volume added to the brine tank was about 10 gallons. As with previous experiments, regeneration efficiency was determined by measuring the concentrations of calcium in the effluent tank.

Not surprisingly, Table 3 and Figure 2 show that the amount of calcium removed from the resin was dependent upon the amount of NaCl (i.e., brine concentration) used during regeneration. Lower concentrations of NaCl resulted in less efficient resin regeneration. For example, when the brine strength was lowered to 75%, there was a concomitant decrease in efficiency of 31%.

Table 3. Effect of Brine Concentration on Calcium Removal.

Brine Dilution	Ca^{2+} in Effluent	Impact on Efficiency
Undiluted Brine	3248	-
75% Brine	2238	31% Decrease
50% Brine	1869	42% Decrease
25% Brine	1263	61% Decrease

Figure 3. Impact of Brine Concentration on Ca^{2+} Removal.



In order to assess efficiency gains due to calcium chelating agents, diluted brines were dosed with polymeric chelating agents prior to regeneration. The chelating agents were: Aquatreat® 921A (polyacrylic acid), VersaFlex One® (a specialized acrylic acid-based polymer), Versa TL® 3 Dry (sulfonated polystyrene). The data summarized in Table 4 corroborate the findings of the initial experiments performed in the bench top softeners (Table 1). Specifically, brine diluted to 25% of its original strength, and containing as little as 10 ppm of PAA, removed as much calcium as the 75% brine solution shown in Table 3.

Table 4. Effect of PAA on Regeneration Efficiency.

PAA Concentration	Ca^{2+} in Effluent	Impact on Efficiency[1]
500 ppm	2126	68%
50 ppm	2164	71%
25 ppm	2614	107%
10 ppm	2324	84%

[1]Increase in efficiency relative to the 25% brine solution in Table 3.

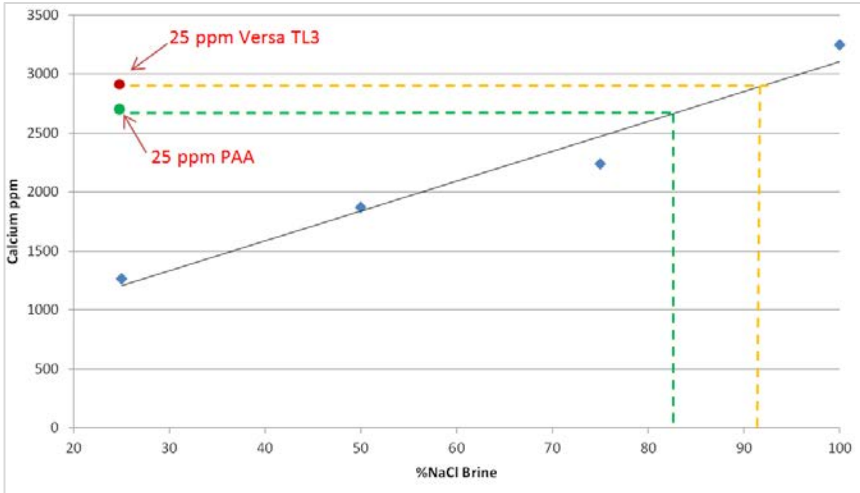
In addition to PAA, 25 ppm of VersaFlex One and Versa TL3 were also able to significantly increase the efficiency of a 25% brine solution (Table 5). Twenty five percent brine solutions containing 25 ppm of PAA and Versa TL3 were as effective as about 83% and 92% brine solutions, respectively (Fig 4).

Table 5. Effect of VersaFlex One and Versa TL3 on Efficiency.

Polymer	Ca^{2+} in Effluent	Impact on Efficiency[1]
VersaFlex One	2608	106%
Versa TL3	2925	132%

[1]Increase in efficiency relative to the 25% brine solution in Table 3.

Figure 4. Enhanced Efficiency Regenerants Relative to Sodium Chloride.



Conclusion

Water softeners provide tenable benefits for consumers in regions of the United States with hard water. However, some state and local regulatory agencies have raised concerns about the continual discharge of chlorides into surface waters. As a result, some municipalities have banned the use of softeners and others are considering steps to help mitigate the environmental impact.

In response to ongoing regulatory concerns, the industry has taken steps to reduce the amount of chloride entering waste treatment facilities as well as lakes, streams and rivers. Chief among these chloride reduction strategies involves the use of high efficiency water softeners and non-chloride based regenerants.

Current strategies notwithstanding, the focus of this research was to harness the benefits of sodium chloride-based resin regeneration while enhancing its environmental profile. A re-engineered sodium chloride regenerant would provide benefits for the environment and for the end user. Specifically, a more efficient regenerant would discharge less chloride than traditional sodium chloride regenerants. The results of these studies indicate that the impact of polyacrylic acid on efficiency was significant (Fig. 4). From an environmental perspective, polyacrylic acid is already being used in a wide variety of household products such as hand sanitizers, moisturizers, aftershave products (7) and the sodium salt is approved as a food additive (8).

While additional studies are required to buttress the extant body of research, the initial findings are promising. To elaborate, sodium chloride is readily available, inexpensive, and well understood by industry professionals and consumers alike. With that, it is an ideal choice for regeneration. If subsequent optimization studies confirm that consumers can use at least 70% less of the enhanced salt in their water softeners, then the impact on chloride discharge could be substantial.

In addition to this, there are additional environmental benefits associated with an enhanced sodium chloride regenerant. Since less product would be required, the enhanced regenerant could be packaged in smaller bags since less salt would be required to achieve the same level of performance. Since less plastic would be required, the resulting carbon footprint would also be reduced. The smaller packages would also be easier to carry, which is an especially important consideration for older customers.

Additional studies are planned that will fully investigate the potential of this new technology.

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