ZERO DISCHARGE SOFTENER REGENERATION

A new twist on some old technology may hold the key to the long term operation of exchange plants operating in restricted areas.

By Charles F. "Chubb" Michaud

The use of salt-regenerated ion exchange water softeners is not only a convenience for general lime scale prevention but a necessity for certain users of water such as laundries, plating shops, steam generators, bottling plants and food processing plants.

Scale is caused by the presence of "hardness" ions, usually calcium and magnesium contained in the raw water. These ions are generally present as salts of chloride, sulphate and bicarbonate. At elevated temperatures, such as those encountered in a boiler, water heater, steam iron, etc., the bicarbonate ions break down to carbonates. Calcium and magnesium carbonate are marginally soluble under normal water conditions and precipitate as a hard scale, coating the piping or walls of the boiler. In addition, calcium sulphate is less soluble in hot water than in cold and will precipitate as hard scale as well.

Softening is the process of removing the scale causing ions. This can be done through distillation, reverse osmosis (RO) or ion exchange. Since both distillation and RO are prone to fouling from the presence of hard water ions, the preferred method of treatment is salt regenerated ion exchange.

Sodium or potassium chloride are the preferred salts because they are relatively inexpensive, abundant and the chloride salts of calcium and magnesium formed in the regeneration process are soluble.

Assuming a sodium salt regeneration, the reactions for softening and regeneration are as follows:

Softening

$$CaCl_2 + Mg(HCO_2)_2 + \bigcirc^{Na+} \rightleftharpoons \bigcirc^{Ca++Mg++} + Nacl + NaHCO_3$$

Hardness Ions — Softener Resin — Exhausted Resin — Softened Water

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SOFTENING

$$CaCl_2 + Mg(HCO_3)_2 + \bigcirc^{Na+} \rightarrow \bigcirc^{Ca++Mg++} + NaCl + NaHCO_3$$

Hardness Ions — Softener Resin — Exhausted Resin — Softened Water

REGENERATION

$$\bigcirc^{Ca++Mg++} + NaCl \rightarrow \bigcirc^{Na+} + CaCl_2 + MgCl_2 + NaCl$$

Exhausted Resin — Salt — Regenerated Resin — Soluble Hardness — Excess Salt

PRECIPITATION

$$CaCl_2 + MgCl_2 + NaCl + NaOH \rightarrow Ca(OH)_2\downarrow + Mg(OH)_2\downarrow + NaCl + NaOH$$

Soluble Hardness — Excess Salt — Caustic — Hydroxide Precipitate — Excess Salt — Excess Caustic

NEUTRALIZATION

$$NaCl + NaOH + HCl \rightarrow 2\ NaCl + H_2O$$

Salt — Excess Caustic — Hydrochloric Acid — Recovered Salt Brine

Regeneration is accomplished by passing 10-15 lbs. of strong salt solution (NaCl), usually at 10% - 15% or more through the exhausted resin:

Regeneration

$$\bigcirc^{Ca^{++}Mg^{++}} + NaCl \rightleftarrows \bigcirc^{Na^{+}} + CaCl_2 + MgCl_2 + NaCl$$

Exhausted Resin — Salt — Regenerated Resin — Soluble Hardness — Excess Salt

The regenerant waste and excess salt are usually sewered without further treatment.

As the supply of quality water tightens, the need to recycle more and more wastewater is growing. One of the major problems of recycling is the problem of dealing with increased dissolved solids in the wastewater. Water that is too high in salt is unacceptable for agricultural irrigation and/or human consumption. The disposal of brine laden water, especially from softener regeneration plants, has become a political issue. The livelihood of those who depend upon water softener acceptance is definitely being threatened.

Several approaches have been taken to reduce the amount of brine being discharged by softener regeneration plants. One is to use the chloride salt of potassium (KCl) instead of sodium (NaCl). The idea is that some areas that have very low total dissolved solids do not object to the salt levels per se but take exception to the amount of sodium itself being added. KCl can be substituted at only a slight increase in cost. Chloride discharge levels are not reduced however.

Another approach is the "in-house" recycling of the waste brine. Since most of the hardness regenerated off the resin comes off in the first half of the regeneration process, some plants split the brine dose into two halves, saving the second half to reuse as the first half of the next regeneration. Such recycling practices result in a 50% reduction of sewered brine.

Another technique is to regenerate at lower salting levels. Because of the nature of the equilibrium reaction in the regeneration process, lower levels of salt are more efficient on a per pound basis. In other words, there is a higher regain of capacity per pound of salt used at the five pound level than at the 15 pound level. However, the level of regeneration (capacity) is not as high and the hardness leakage is higher. If the softener plant is an "on-site" regenerated plant where regenerations can be performed as needed, this technique has merit as long as the end use of the softened water can tolerate the additional hardness leakage. However, if the regeneration is remote and the softener resin is shipped back and forth in portable tanks, the result is more frequent turnarounds and higher operating costs.

The Problem

Theoretically, 7.3 lbs. of NaCl is the total amount required to completely regenerate one cubic foot of ion exchange resin of normal capacity (2.0 meg/ml or 43.66 kilograins/cubic foot). In reality, levels of 10 lbs. of NaCl only recover 25 Kgr/ft^3 and at the 15 lb. level,

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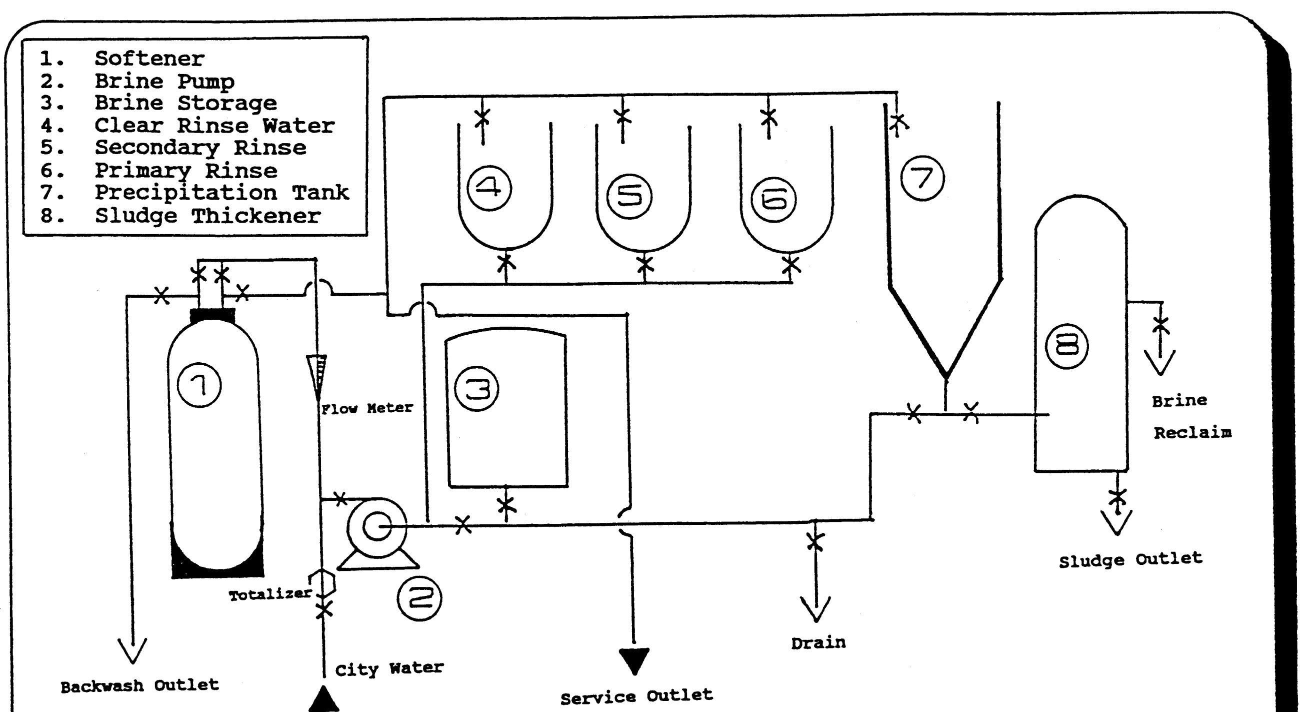

Schematic of Pilot System for Hydroxide Precipitation Study

This process is protected by a US Patent application only Kgr/ft^3. This results in a respective loss of 5.8 to 10 lbs. of salt per regeneration. Attempting to achieve very low leakages of hardness by regenerating with 20 lbs. of salt per cubic foot of resin result in the wasting of 14.56 lbs. of salt for every cubic foot for every cycle.

Hydroxide Precipitation and Recovery of Spent Softening Brine

Past Attempts

Calcium and magnesium salts form insoluble hydrated oxides (hydroxides) when their solutions are elevated in pH. This chemistry gave rise to the development of the "cold lime" and "hot lime" softening processes. In this case, lime (CaO) is added to water, raising the pH and converting the soluble bicarbonates of calcium and magnesium to the insoluble carbonates. Since the pH increase is usually not sufficient to completely precipitate all of the hardness, a stronger base such as magnesium hydroxide or sodium carbonate (soda ash) is also added. The result is a moderately soft water and calcium and magnesium carbonate sludge which is then disposed of. Earlier work by Kreusch and Burton of the Culligan International (Northbrook, IL) describes attempts to apply this system to brine recovery (*WC & P*, Sept. 1974). No further developments have been made and the carbonate sludge is of no commercial value.

The Solution

This process pertains to the use of sodium hydroxide (NaOH) or potassium hydroxide (KOH) to precipitate the calcium and magnesium salts from waste brine as the insoluble hydroxides. Hydrated lime $Ca(OH)_2$ and $Mg(OH)_2$ can be collected and have commercial value for use in the precipitation of plating waste, neutralization of waste acids and increasing the pH of acidic soils. The clarified solution above the precipitate contains the recovered salt plus a slight excess of sodium or potassium hydroxide. This solution can be readily neutralized with the addition of hydrochloric acid (HCl) resulting in further recovery of usable salt for future regeneration of resin. The following describes the reactions:

Precipitation

$$\underbrace{CaCl_2 + MgCl_2}_{\text{Soluble Hardness}} + \underbrace{NaCl}_{\text{Excess Salt}} + \underbrace{NaOH}_{\text{Caustic}} \rightarrow \underbrace{Ca(OH)_2\downarrow + Mg(OH)_2\downarrow}_{\text{Hydrogen Precipitate}} + \underbrace{NaCl}_{\text{Excess Salt}} + \underbrace{NaOH}_{\text{Excess Caustic}}$$

Neutralization

$$\underbrace{NaCl}_{\text{Salt}} + \underbrace{NaOH}_{\text{Excess Caustic}} + \underbrace{HCl}_{\text{Hydrochloric Acid}} \rightarrow \underbrace{2\,NaCl + H_2O}_{\text{Recovered Salt Brine}}$$

Pilot Study

A 0.5 cubic foot softener containing typical strong acid cation exchange resin such as Purolite C-100, Sybron C-249, Amberlite IR-120 or Dow HCRS, was run to exhaustion on city water containing approximately 14.0 grains per gallon or hardness. Upon a hardness break of 1/2 grains/gal. the column was regenerated with the equivalent of 30 lbs. of NaCl/cu. ft. with a 10% brine solution.

On each of two successive runs, the capacities were determined by multiplying the number of gallons treated by the average grains per gallon hardness. Typical values of 36 Kgr/Cu. ft. were achieved with leakages of 0.1 gr/gallon. After the third exhaustion cycle, recovered brine from the third cycle was used as the sole regenerant for the fourth cycle. Rinse water was also captured for re-use.

This was repeated for a total of five more complete cycles using only the recovered brine as the sole regenerant. The average softening capacity regained for the five cycles was 36.44 Kgr/cu. ft. The equivalent brine efficiency was 5623 grains/lb. NaCl equivalent. Leakages were typically <0.1 gr/gal. The total rinse water used was five gal./cu ft. The total amount of sludge generation was approximately four gal./cubic ft/cycle. The sludge was approximately 10% total solids. Some brine was trapped in the wet sludge. This would have to be made up with fresh saturated brine at the calculated rate of one lb./cu. ft./cycle.

Most Important: There is No Brine Discharge

Economics

The chemical costs of regenerating a cubic foot of cation resin with this method is about $0.80. This compares favorably with the cost of 15 lbs. of NaCl (about $0.75). In addition, the chemical recovery of the lime saves $0.15 per cubic foot. Handling charges for the portable exchange plant are estimated at a savings of $0.37 per foot (fewer exchanges) and if you are now hauling brine, the savings adds another $2.00 per foot. The use of this technique can result in a net savings over the use of salt. It may prove to be an attractive advance, even in non-restricted areas.

Retrofitting of an existing plant can be done with very little additional tankage and very little added floor space.

Conclusion

Hydroxide precipitation has been shown as an effective and economical as well as a practical method of brine recovery for softener regeneration plants. Brine utility of over 5500 grains/lb. of salt equivalent are readily achievable and capacities of 36+ Kgr/cu. ft. the norm. Together with a concerted program of conservation, water usage can be reduced by 80% in the regeneration/rinse process.

No water was discharged above 1500 ppm TDS (influent was 600 ppm TDS). Sludge consisting of calcium and magnesium hydroxides plus some excess sodium hydroxide is a recoverable and resalable by-product. ❑

About The Author

Charles F. "Chubb" Michaud is a chemical engineering graduate of the University of Maine and has been involved in ion exchange water treatment for 13 years. He is founder of Systematix Co. of Brea, CA and represents the Purolite Co in the western states.
