&EPA **Project Summary**

Barium and Radium Removal from Groundwater by Ion Exchange

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A study was undertaken to develop technology that can be used by small water treatment plants to remove hardness, barium, and radium[226]. Special emphasis was placed on finding an alternative to strong acid ion exchange (which is used in the Na+ form) because this process adds large amounts to Na+ to the treated water. The primary objective of this study was to determine the applicability of weak acid ion exchange resin for removal of hardness, barium, and radium from the types of groundwater encountered in northern Illinois. The capacity of the resin and the regeneration requirements were to be determined and compared with those of strong acid resins for the same application.

Additional tasks included (1) evaluating the performance of the strong acid resin now used at Crystal Lake, Illinois, to remove hardness and barium, (2) determining the barium and radium removal efficiencies of strong acid ion exchange softeners used in homes, and (3) modifying the surface of activated carbon to make it suitable for the selective removal of barium.

Both strong and weak acid resin systems were very effective in removing [226]Ra and Ba^{2+}. The weak acid system in the H+ form does not add Na+ to the water as does the strong acid system, but the weak acid system will cost more to use because of the need for acid-resistant materials and the CO2 stripping.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see

Project Report ordering information at back).

Introduction

Naturally occurring barium in drinking water exceeds the maximum contaminant level (MCL) in some areas of northern Illinois and northeastern Iowa. In these same areas and in some parts of Florida, the concentrations of radium[226] exceed the MCL of 5 pico-Curies (pCi)/L. Most of the contaminated supplies are used by small communities, many of which do not presently treat their water to reduce the concentrations of these substances. Both radium[226] and barium are alkaline earth metals, and both are found in water as divalent cations. Their chemical behavior is very similar, and it is much like that of Ca^{2+} and Mg^{2+}, the principal components of hardness in water. Thus, processes used to soften water are very useful for removing these contaminants from drinking water.

A process particularly suited to small communities where hardness, barium, and/or radium are a problem is ion exchange. The objective of this research was to investigate the applicability of the ion exchange process to this problem in northern Illinois. Strong acid resins in the sodium form were to be evaluated, but because their use results in significant increases in the Na+ content of the water, their performance was to be compared with that of weak acid resins in the hydrogen form. The latter can remove only the equivalents of divalent cations equal to the equivalents of alkalinity present, and ion exchange must be followed by CO_2 stripping and pH adjustment.

The resins were tested with an influent water containing hardness of approximately 200 mg/L as $CaCO_3$, total alkalinity of 250 mg/L as $CaCO_3$, 20 mg/L Ba^{2+}, and 20 pCi/L

The tests used a regenerant dose typical of softening operations.

In addition to investigating the applicability of ion exchange to northern Illinois groundwater, this project also (1) evaluated the performance of the strong acid resin now used at Crystal Lake, Illinois, to remove hardness and barium, (2) determined the barium and radium removal efficiencies of strong acid ion exchange softeners used in homes, and (3) attempted to modify the surface of activated carbon to make it suitable for the selective removal of barium.

Materials and Methods

The resins used in this study were Duolite C-20 and Duolite C-433 manufactured by Diamond Shamrock, Redwood City, CA.* C-20 is a strong acid resin with a polystyrene matrix and sulfonate functional groups. C-433 is a high-capacity weak acid resin with a polyacrylic matrix and carboxyl functional groups. Their capacities are 4.8 and 11.5 meq/g dry resin, respectively, and their properties are typical of resins made by a number of manufacturers. The weak acid resin can be used in solutions with pH > 5, and the strong acid resin can be used for pH > 0.

The solutions used for most of the column tests contained approximately 100 mg Mg^{2+}/L as $CaCO_3$, 100 mg Ca^{2+}/L as $CaCO_3$, 250 mg/L total alkalinity, 20 mg Ba^{2+}/L, and 20 pCi/L of 226Ra. Solutions for selectivity determinations were prepared using reagent-grade chemicals to the specifications required by the test.

Ion chromatography was used for quantitative analysis of cations. Hardness and alkalinity were also determined in accordance with *Standard Methods for Analysis of Water and Wastewater* (15th edition, Amer. Public Health Assoc., 1980). Some samples were also analyzed by atomic absorption spectroscopy. The 226Ra samples were analyzed at the Environmental Research Laboratory, University of Illinois, using the radon emanation method, and at the University Hygienic Laboratory, University of Iowa, by a technique involving coprecipitation of the 226Ra with barium sulfate and by alpha counting with an internal proportional counter.

Experimental Results

Strong Acid Resins

Isotherms and column tests were used to determine the capacity of the strong acid resin with 4.8 meq/g dry resin (hydrogen form). The selectivity sequence was Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > H^+. Alkalinity had no

effect on capacity, but the capacity for divalent cations decreased as the concentration of sodium increased.

Column tests were run using 2.5- x 62-cm columns with the resin in both the Na^+ and H^+ form. Application of the test solution at rates of 2.5 to 5 bed volumes (BV)/hr to virgin resin in the Na^+ form gave the breakthrough curves shown in Figure 1. The

curves for the H^+ form of the resin were similar except for the Na^+ concentration in the effluent. In keeping with the selectivity sequence, Mg^{2+} is the first divalent cation to appear in the effluent, followed by Ca^{2+}, and much later by Ba^{2+}. Regeneration of the H^+ form of the resin with 8 percent HCl at 1.6 BV/hr gave the results that appear in Figure 2; results for regeneration of the Na^+ form
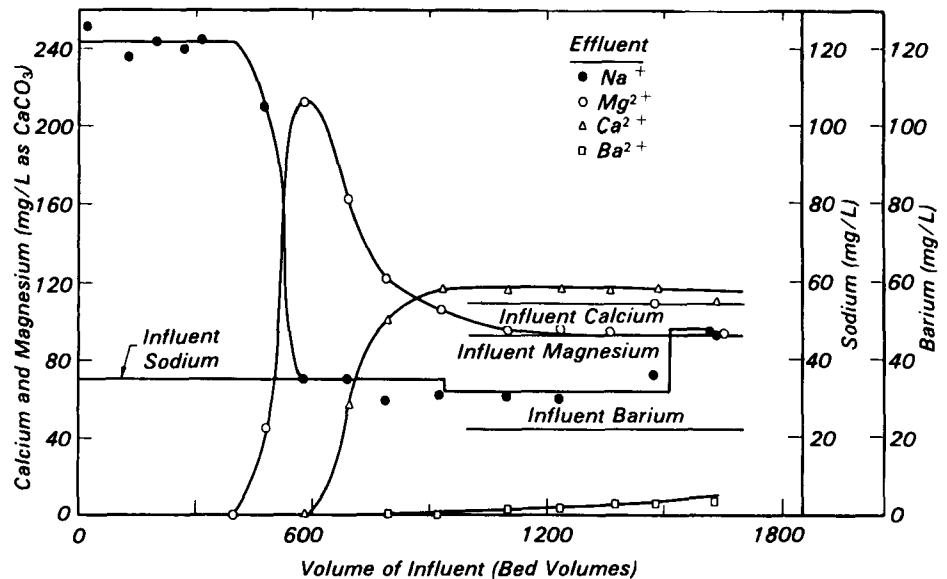

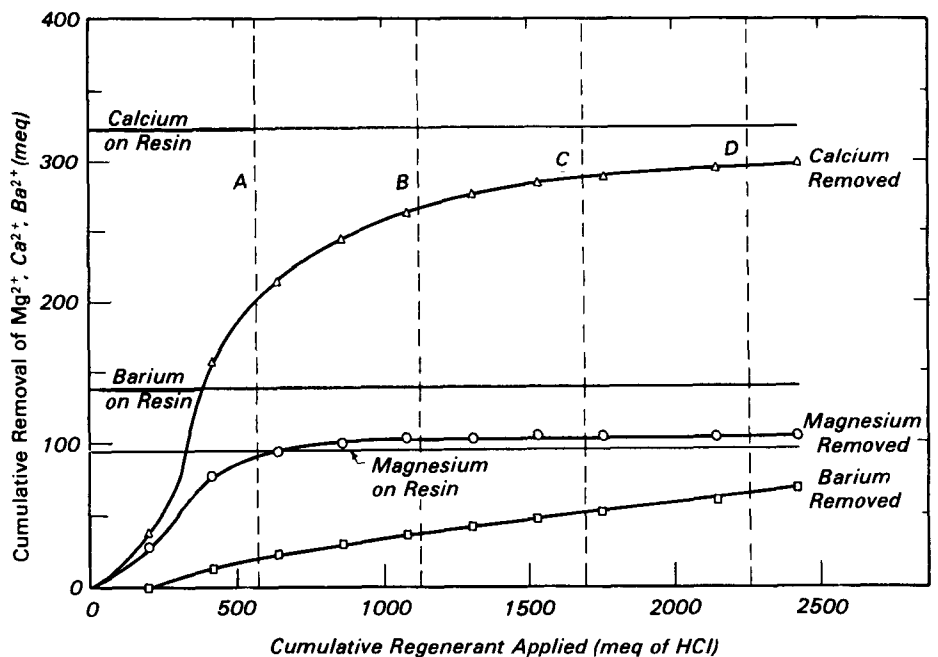Figure 1. Breakthrough curves for virgin strong acid resin in the sodium form.

Figure 2. Regeneration of the hydrogen form of the strong acid resin with HCl. At A, B, C, and D, the equivalents of HCl added per equivalent of divalent cation originally on the resin is 1, 2, 3, and 4, respectively.

with NaCl gave very similar results. At a regenerant dose equal to the equivalents of divalent cation on the resin, 55 percent of the ions were removed, including 80 percent of the Mg^{2+}, 67 percent of the Ca^{2+}, and 15 percent of the Ba^{2+}. A dose of three times the equivalents of the divalent cations on the resin was necessary to remove 50 percent of the Ba^{2+}.

Several exhaustion-regeneration cycles were then carried out to determine the behavior of the strong acid resin at steady-state conditions. The influent was applied at a rate of 17 BV/hr, and a typical NaCl regenerant dose for softening (6.5 lb/ft³, or 4.7 meq/g) was applied co-current at 1.7 BV/hr, followed by a slow rinse at 1.7 BV/hr for 48 min and a fast rinse at 7 to 8 BV/hr for 26 min. The Ba^{2+} accumulated on the resin over successive cycles and thus caused the Ba^{2+} to break through much earlier than it did with virgin resin. The hardness and Ba^{2+} breakthrough curves that developed after several cycles appear in Figure 3. The curves show that approximately 225 BV of water were processed before hardness and Ba^{2+} broke through at about the same time. The regeneration efficiency (equivalents of divalent cations removed per equivalents of NaCl applied) was 58 to 59 percent. Column utilization (column capacity used/maximum capacity) was about 58 percent; a large portion of the remaining 42 percent was occupied by Ca^{2+} and Ba^{2+} that was not removed by the regenerant dose.

The data in Figure 4 show the Ba^{2+} concentration (when $CaCO_3$) effluent hardness was approximately 40 mg/L as $CaCO_3$ as a function of the number of cycles. The Ba^{2+} concentration leveled off at 1.7 mg/L for a regenerant dose of 6.5 lb NaCl/ft³ (4.7 meq/g). An HCl regenerant dose of 4.06 lb HCl/ft³ (4.7 meq/g) was tested on a second column for a few runs, and similar results were obtained. Increasing the regenerant dose by 50 percent to 9.75 lb NaCl/ft³ reduced the Ba^{2+} to about 1.2 mg/L when the hardness was 40 mg/L as $CaCO_3$. The regeneration efficiency dropped to 46 percent; however, the column utilization increased to 68 percent. For the regenerant dose of 6.5 lb NaCl/ft³, 2.4 BV of brine with total dissolved solids (TDS) of 16,400 mg/L were produced per 100 BV of product water.

The conclusion that Ba^{2+} can be removed to less than the MCL of 1 mg/L as long as the strong acid resin is not saturated with hardness was confirmed by observations at the Crystal Lake, Illinois, municipal ion exchange system. The influent and effluent of several home ion exchange softeners were also sampled, and these too showed Ba^{2+} removal below the MCL.
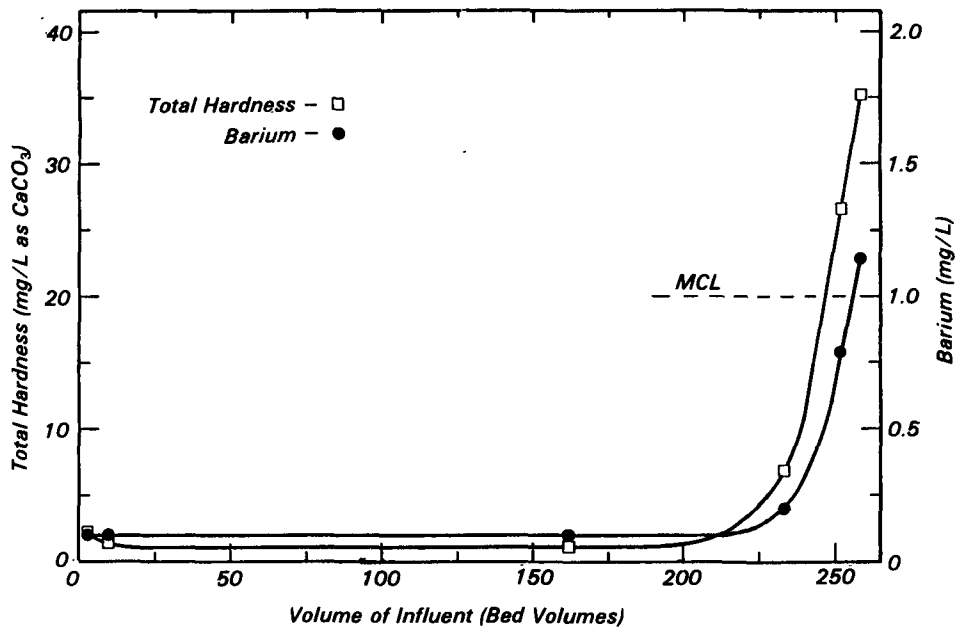

Figure 3.   Breakthrough curves for hardness and barium on a strong acid resin in the sodium form after several exhaustion-regeneration cycles.
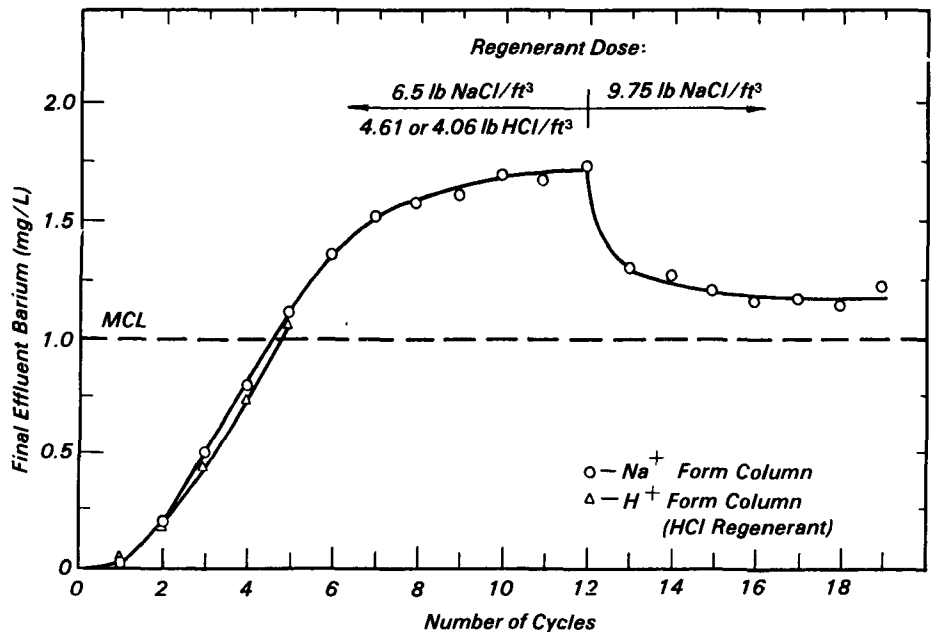

Figure 4.   Barium effluent concentrations for the strong acid resin exhaustion-regeneration cyclic runs. The barium values shown are those when the effluent hardness concentration is 40 mg/L.

Weak Acid Resins

The maximum capacity of the weak acid resin was determined to be 11.5 meq/g dry resin, but the extent of swelling of the resin determined how much of the capacity could be used. For example, exposure of the resin in the H^+ form to a solution containing only $BaCO_3$ salt resulted in a capacity of only 7.5 meq/g, whereas carbonate salts of Ca^{2+} and Mg^{2+}, which cause the resin to swell more

because of their larger hydrated radii, used the full 11.5 meq/g. Addition of salts to the Ba²⁺ solution increased the swelling and allowed Ba²⁺ to use the full capacity.

Application of test solution to 2.5- x 62-cm columns of the virgin resin in the H⁺ form gave the breakthrough curves that appear in Figure 5. The equivalents of alkalinity per liter in the product water exceed the equivalents of divalent cations per liter, so the initial removal of Ca²⁺, Mg²⁺, and Ba²⁺ was complete. Their order of appearance in the effluent was in reverse order of the selectivity series, Ba²⁺ ≅ Ca²⁺ > Mg²⁺, and the breakthrough curves were less steep than those for the strong acid resin, a result caused by a slower rate of exchange by weak acid resins.

A major advantage of using a weak acid resin is the ease with which it can be regenerated by strong acid. The data in Figure 6 show that application of one equivalent HCl per equivalent of divalent ion on the resin resulted in removal of 90 percent of the ions, and 1.5 equivalents HCl per equivalent of divalent cation gave essentially complete removal.

Several exhaustion-regeneration runs were then made to determine resin behavior under continuous operation. Influent was applied at about 17 BV/hr; three cycles were completed, each with a different regenerant dose. The breakthrough curve in Figure 7 resulted after steady-state behavior was obtained for the cycle using 8.5 meq HCl/g. More than 650 BV of product water were obtained before effluent hardness reached a level of 40 mg/L as CaCO₃. The Ba²⁺ concentration leveled off at 0.2 mg/L, as shown in Figure 8. For this regenerant dose, column utilization was about 70 percent, and regeneration efficiency was about 95 percent. The 30 percent of column capacity that was not used was attributable to slow exchange kinetics rather than to buildup of Ca²⁺ ions, as it was for the strong acid resin. Approximately 1.2 BV of spent brine was produced with a TDS of 19,900 mg/L per 100 BV of product water.

Application of less regenerant than the equivalents of divalent cations removed led to a higher Ba²⁺ concentration at hardness breakthrough and to a high leakage of Ba²⁺ and hardness at the start of the subsequent run.

Radium Removal

Radium²²⁶ removal efficiency for both the strong and weak acid resins was excellent. The concentration was reduced from the 20 pCi/L in the influent to much less than the MCL of 5 pCi/L, even after the resins were saturated with hardness and Ba²⁺. Analysis of the ²²⁶Ra in the spent regenerant showed
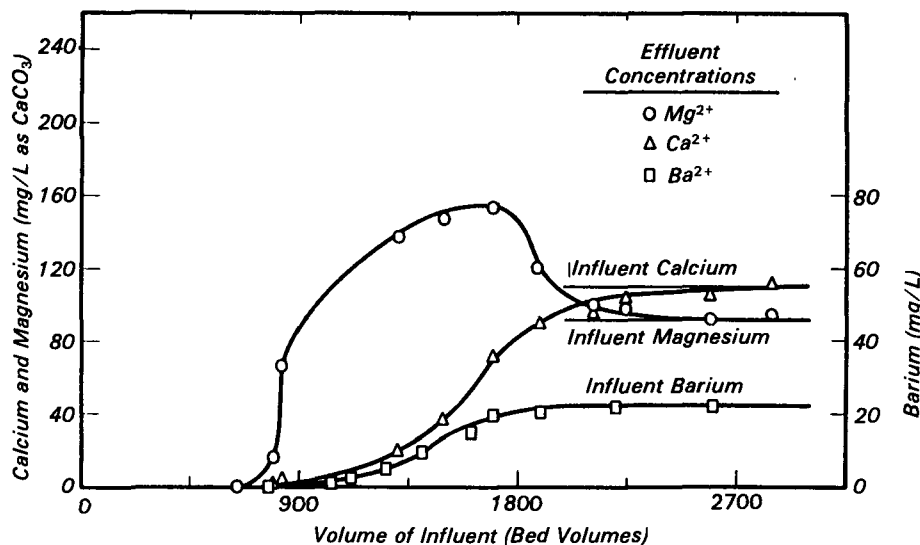

Figure 5.   Breakthrough curves for weak acid resin in the hydrogen form.
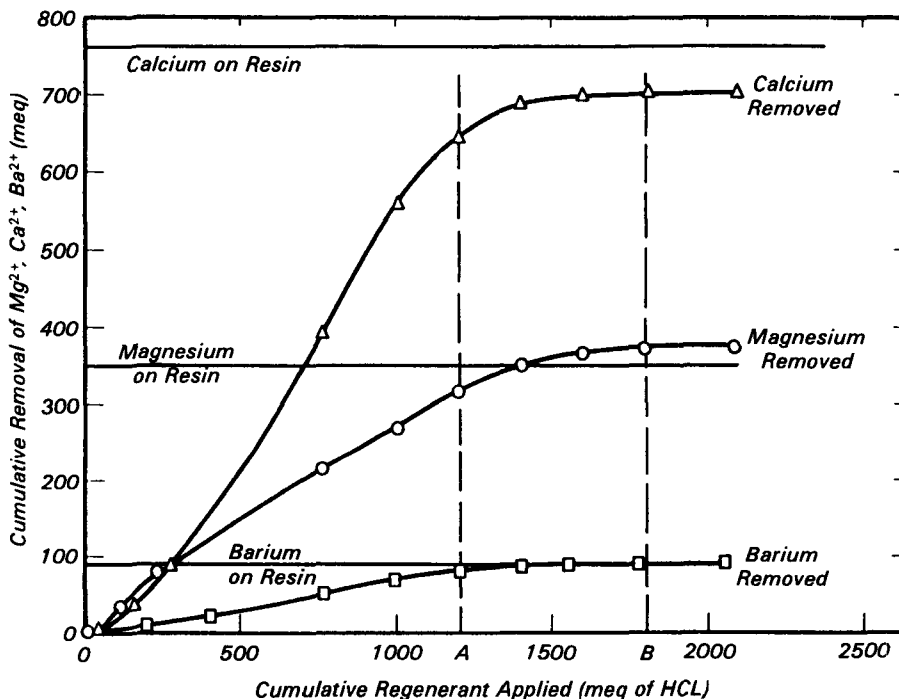

Figure 6.   Regeneration of weak acid resin with HCl. A and B represent 1.0 and 1.5 equivalents of HCl applied per equivalent divalent cation on the resin.

that all ²²⁶ Ra removed during the exhaustion cycle was extracted from the resin during regeneration. Some ²²⁶Ra accumulated on the strong acid resin during the first few exhaustion-regeneration cycles, but after several cycles, no additional accumulation was apparent, and the resin still performed satisfactorily.

Influent and effluent samples taken from home ion exchange softeners using NaCl regeneration also showed that they removed ²²⁶Ra to below the MCL.

Cost

The cost of using strong acid ion exchange softening with NaCl as the regenerant and the type of water used in the laboratory study was estimated to be $1.36/1000 gal and $0.38/1000 gal for a 0.1 and 1 MGD facility, respectively, for the type
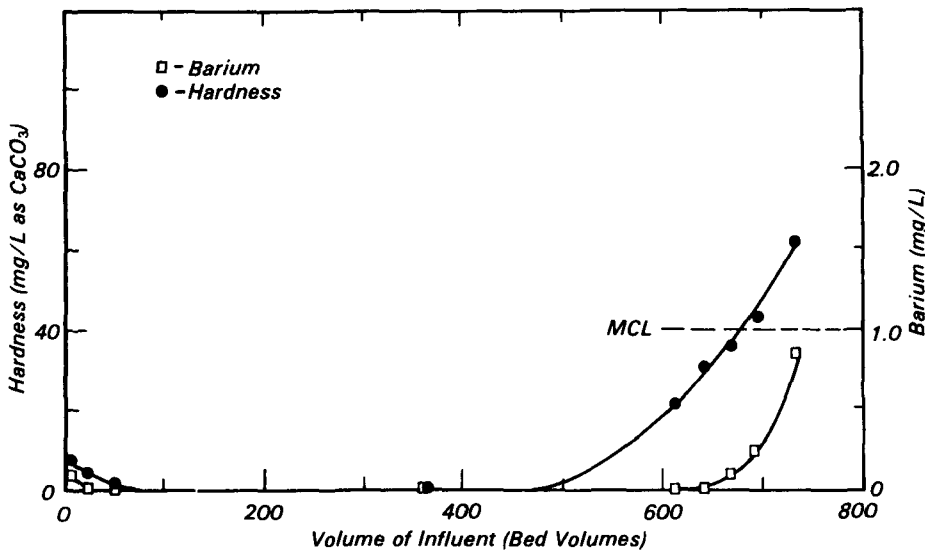
Figure 7. Breakthrough curves for barium and hardness on a weak acid resin in the hydrogen form after several exhaustion-regeneration cycles.
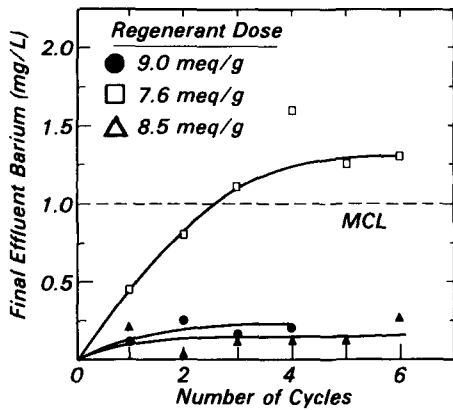

Figure 8. Barium effluent concentration for the weak acid resin exhaustion-regeneration cyclic runs. The barium values shown are those that occur when the effluent hardness concentration is 40 mg/L as $CaCO_2$.

of water used in the laboratory study. The additional cost for using a weak acid system with HCl regeneration will be $0.15 and $0.08/1000 gal, respectively.

The system designs were based on the performance observed when 4.7 meq NaCl/g and 8.5 meq HCl/g were used to regenerate the strong and weak acid resins, respectively. The flow scheme for the weak acid system included the resin columns, a CO_2 stripping column, pH adjustment, and chlorine addition. The strong acid resin system was similar except that the CO_2 stripping column was excluded. The costs were based on cost data supplied by the Illinois Water Treatment Company in Rockford, Illinois. The strong acid ion exchange units included the columns, the resin, regenerant day tanks, brine tanks, and interface piping. The weak acid unit included all of these plus a carbon dioxide stripping tower. A comparison of the two types of exchange systems was used to evaluate the additional costs required for weak acid exchange systems at these different treatment capacities. Complete treatment costs for strong acid ion exchange softening were determined from previously published data and appropriate price indices.

The costs do not include the costs of pumping raw, in-plant, or finished water. Brine disposal was also not included, since costs are very site specific. They do include the cost of adjusting product water pH, however, and this may not be necessary in all cases.

Conclusions

After several exhaustion-regeneration cycles at a regenerant dose typical of softening operations, Ba^{2+} and ^{226}Ra were effectively reduced well below their MCL's. For both types of resin, significant concentrations of Ba^{2+} appeared in the effluent at about the same time as did hardness, but ^{226}Ra continued to be removed even after saturation of the resins with hardness. These conclusions were consistent with the performance of an operating municipal ion exchange plant in northern Illinois and with the results obtained using home ion exchange softeners.

Though both strong and weak acid resin systems can effectively remove hardness, ^{226}Ra, and Ba^{2+}, the weak acid system in the H^+ form does not add Na^+ to the water as does the strong acid. The weak acid system will cost more to use, however, because of the need for acid-resistant materials and the CO_2 stripping. But this cost is offset as the plant size increases. The additional cost for the weak acid system declines from about $0.15/1000 gal for a 0.1-MGD plant to $0.08/1000 gal for a 1-MGD facility. In addition, the weak acid resin will remove only the divalent cations that are balanced by an equivalent amount of alkalinity. If a water contains divalent ions in excess of the alkalinity, the hardness left in the water may be desirable because it should make the water less corrosive during distribution. Whether the weak acid resin will remove Ba^{2+} from such a water must still be shown, however.

Conversion of an existing system that uses strong acid resin in the sodium form to one that uses weak acid resin in the hydrogen form must be done with care. In most cases, acid-resistant materials will have to be installed, and provision must be made to neutralize the spent acid before its discharge. Additional design considerations include that the capacities of the two resins are different and that the weak acid resin is subject to more swelling. Use of a weak acid resin will also require the installation of a CO_2-stripping process.

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The complete report, entitled "Barium and Radium Removal from Groundwater by
Ion Exchange," (Order No. PB 84-189 810; Cost: $14.50, subject to change) will
be available only from:
    National Technical Information Service
    5285 Port Royal Road
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The EPA Project Officer can be contacted at:
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