



ENVIRONMENTAL RESEARCH BRIEF

Removal of Barium and Radium from Groundwater

Vernon L. Snoeyink, Carl C. Chambers, Candace K. Schmidt, Rick F. Manner,
Anthony G. Myers, Julie L. Pfeffer, Sharon K. Richter, David W. Snyder

Abstract

A research project was undertaken to investigate processes for removing barium and radium from drinking water and to determine their suitability for treatment of small drinking water supplies. Special emphasis was placed on ion exchange processes that can be used without adding large concentrations of sodium to the water. The wastes from radium and barium removal processes were also characterized, and processes suitable for treatment of ion exchange brines were evaluated.

Earlier reports have evaluated the use of strong-acid and weak-acid ion exchange resins for barium, radium, and hardness removal, and they have characterized wastes from barium and radium removal processes. This report discusses two ion exchange processes that can be used for barium and radium removal accompanied by either partial or no hardness removal.

The calcium-form, strong-acid ion exchange resin can be used for barium and radium removal without significant change in hardness or the concentration of other salts. This resin can be regenerated with CaCl_2 brine; the optimum regenerant concentration was established as 0.8M, and the tradeoff between resin capacity and regeneration efficiency was also determined. The resin also gave excellent removals of radium for run lengths of 500 bed volumes, but the length of run to radium breakthrough was not determined. Procedures were developed for regenerating the spent CaCl_2 brine for reuse.

The Radium-Selective Complexer (RSC) will remove radium without altering hardness or other salt concentration. The capacity of this resin for waters with low total dissolved solids (TDS) (<1,000 to 2,000 mg/L TDS) is in excess of 30,000 pCi/dry g; however, if the

TDS is increased to about 40,000 mg/L, the capacity drops to 200 to 300 pCi/dry g. Thus using this resin to remove radium from spent brine does not appear feasible.

Process schematics for various ways of using the calcium form resin and the RSC have been presented.

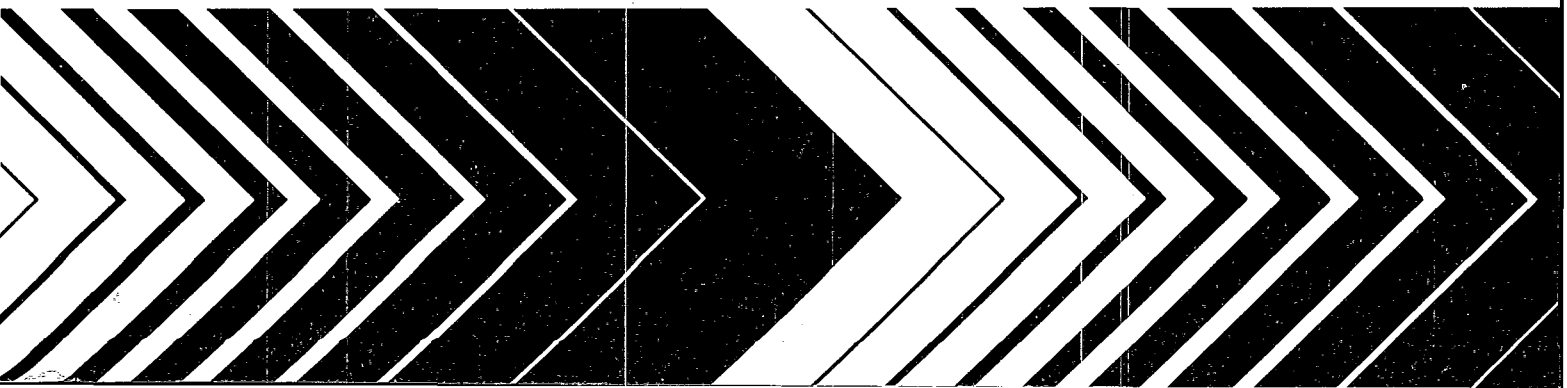
The conditions for precipitating barium (as BaSO_4) and radium (coprecipitation with BaSO_4) from spent brine were also established. The amount of sulfate that must be added relative to the amount of barium in the brine is a function of the barium concentration and the TDS of the brine. If no barium is present in the spent brine, BaCl_2 or BaCO_3 must be added along with the sulfate to remove the radium.

Adsorption of radium by MnO_2 -impregnated acrylic resin was investigated as a removal process, but the experiments were not successful and further research is not recommended.

This Research Brief was developed by the principal investigators and EPA's Water Engineering Research Laboratory, Cincinnati, Ohio, to announce key findings of the research project that is fully documented in the reports and publications listed in the References.

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, some parts of Florida, and other locations, the concentrations of Ra^{226} plus Ra^{228} exceed the MCL of 5 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 and barium are alkaline earth metals and 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.

The objectives of this research project were to investigate the processes for barium and radium removal to determine their suitability for use, especially for small supplies. Special emphasis was placed on ion exchange processes that can be used without adding large concentrations of sodium to the water. The wastes from radium and barium removal processes also were characterized, and processes suitable for treatment of ion exchange brines were evaluated.

Earlier reports (1,2) have evaluated the use of strong-acid and weak-acid ion exchange resins for barium, radium, and hardness removal, and they have characterized wastes from barium and radium removal processes. The purposes of this Research Brief are: (1) to present information on two ion exchange processes that can be used for barium and radium removal accompanied by either partial or no hardness removal; and (2) to summarize our research on precipitation of barium and radium from spent ion exchange brines and on removal of barium and radium from water with MnO_2 -impregnated resin.

Radium and Barium Removal by Hydrogen-Form Exchange

The sodium-form, strong-acid ion exchange resin is commonly used today to remove barium and radium together

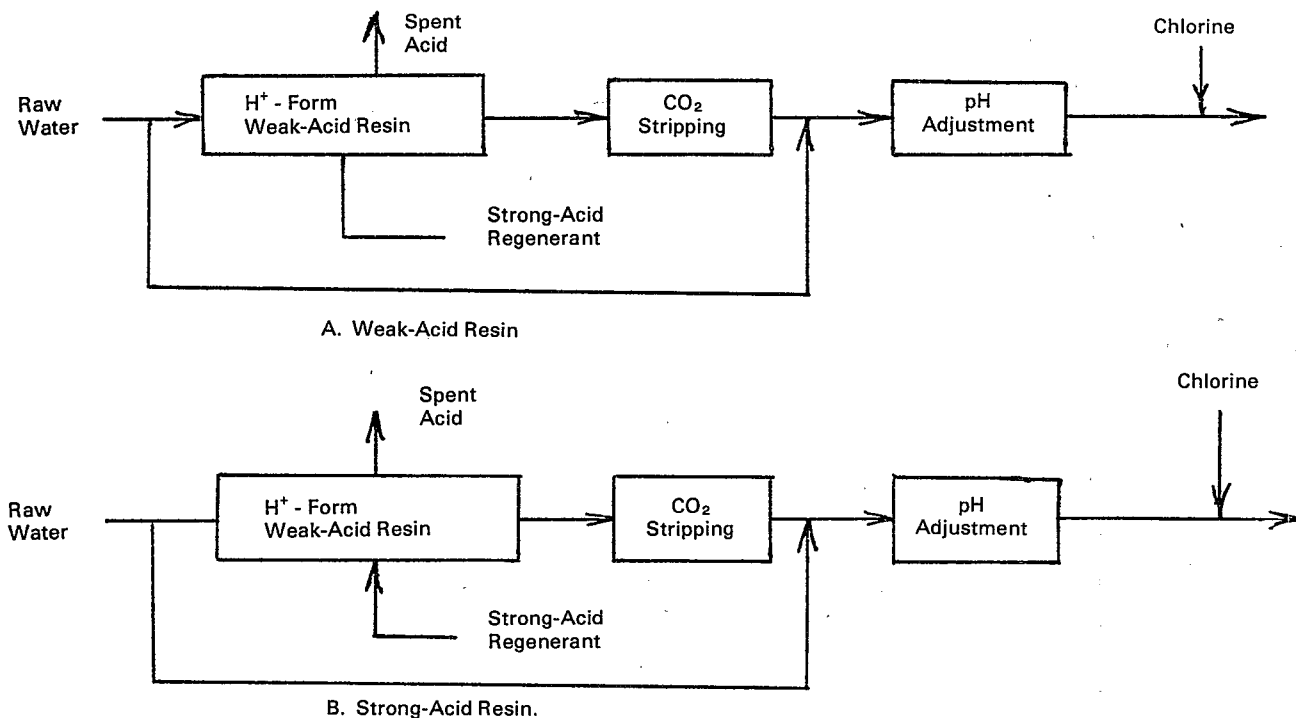
with hardness. The process is effective (see Reference 1), but sodium is added to the product water. The increase in sodium concentration can be avoided if either strong-acid or weak-acid resins are used in the hydrogen form. Hydrogen-form resins must be followed by a carbon dioxide stripping process and a pH adjustment step, as shown in Figure 1. A portion of the raw water can bypass the ion exchange and carbon dioxide removal process; the amount of barium, radium, or hardness desired in the final water may control the quantity of water that is bypassed. The advantages and disadvantages of using resins in the hydrogen-form are given in References 1, 3, and 4. The processes are very effective, and the weak-acid resin is especially useful if there is a need to minimize the volume of waste brine.

Radium Removal without Hardness Removal

Calcium-Form Ion Exchange for Radium and Barium Removal

Complete removal of hardness from water is often not appropriate or desirable. Low-calcium waters are corrosive to some metals, and the cost of removing the hardness may be excessive. The strong-acid resin has a much higher selectivity for barium and radium compared with calcium and magnesium, and thus a resin in the calcium-form should selectively remove barium and radium from a water containing these ions plus hardness. Laboratory experiments were conducted to show the performance of the calcium-form resin, and to develop a method to reclaim the spent calcium chloride brine.

Figure 1. Flow diagrams for removal of radium, barium, and hardness with hydrogen-form resins.



Column runs using virgin resin showed that an empty bed contact time (EBCT, volume of resin/volumetric flow rate) of 2.5 min gave a run length of about 1,800 bed volumes when water with 15 mg barium/L was applied. The number of bed volumes that could be processed did not increase as the EBCT increased (see Table 1 for influent composition). The number of bed volumes that can be processed depends on the quantity of calcium chloride regenerant applied, as shown in Figure 2. Application of 4, 6, and 8 equivalents of calcium/L of resin resulted in runs of 500, 900, and 1,100 bed volumes, respectively, compared with 1,200 bed volumes for virgin resin when the influent water contained 23 mg barium/L. The tradeoff between resin capacity per run and regeneration efficiency

is shown in Figure 3. The optimum regenerant concentration was found to be 0.8M calcium chloride.

The ability of a calcium-form resin column to remove radium from water was evaluated through four exhaustion-regeneration cycles. The fifth cycle consisted of exhaustion only. Influent water was similar to that shown in Table 1, except that 43 pCi radium/L replaced the barium. Exhaustion in the 4.7-in. (12-cm) column was carried out at 1.35 gpm/ft² (3.4 m/hr) for 500 bed volumes. Termination of the run at 500 bed volumes was arbitrary; additional runs are needed to establish the number of bed volumes that can be processed to radium breakthrough. Regenerant brine contained 0.85M calcium and 0.2M magnesium. The brine-loading rate was 0.29 gpm/ft² (0.7 m/hr), and the dose was 6 equivalents of calcium/L resin (27.5 lb CaCl₂ · 2H₂O/ft³ resin). The spent brine from each cycle was reclaimed and reused in the next cycle. Rinse-water volume was 8.5 bed volumes.

The average effluent in each of the five exhaustion runs was <0.5 pCi radium/L (98.8 percent radium removal). The amount of radium placed on the column during exhaustion was 45 pCi/g dry resin (0.02 μCi/L resin). Radium capacity at breakthrough was not determined.

The spent CaCl₂ brine can be reclaimed for reuse. Addition of 10 percent molar excess solid CaSO₄ relative to the barium in the brine resulted in reduction of the barium

Table 1. Composition of Influent Water

Parameter	Concentration
Total Hardness	215 mg as CaCO ₃ /L
Calcium	105 mg as CaCO ₃ /L
Magnesium	95 mg as CaCO ₃ /L
Barium	15 mg/L
Sodium	~23 mg/L
Chloride	~10 mg/L
Total Alkalinity	250 mg as CaCO ₃ /L
pH	7

Figure 2. Barium breakthrough curves at different regenerant dosages.

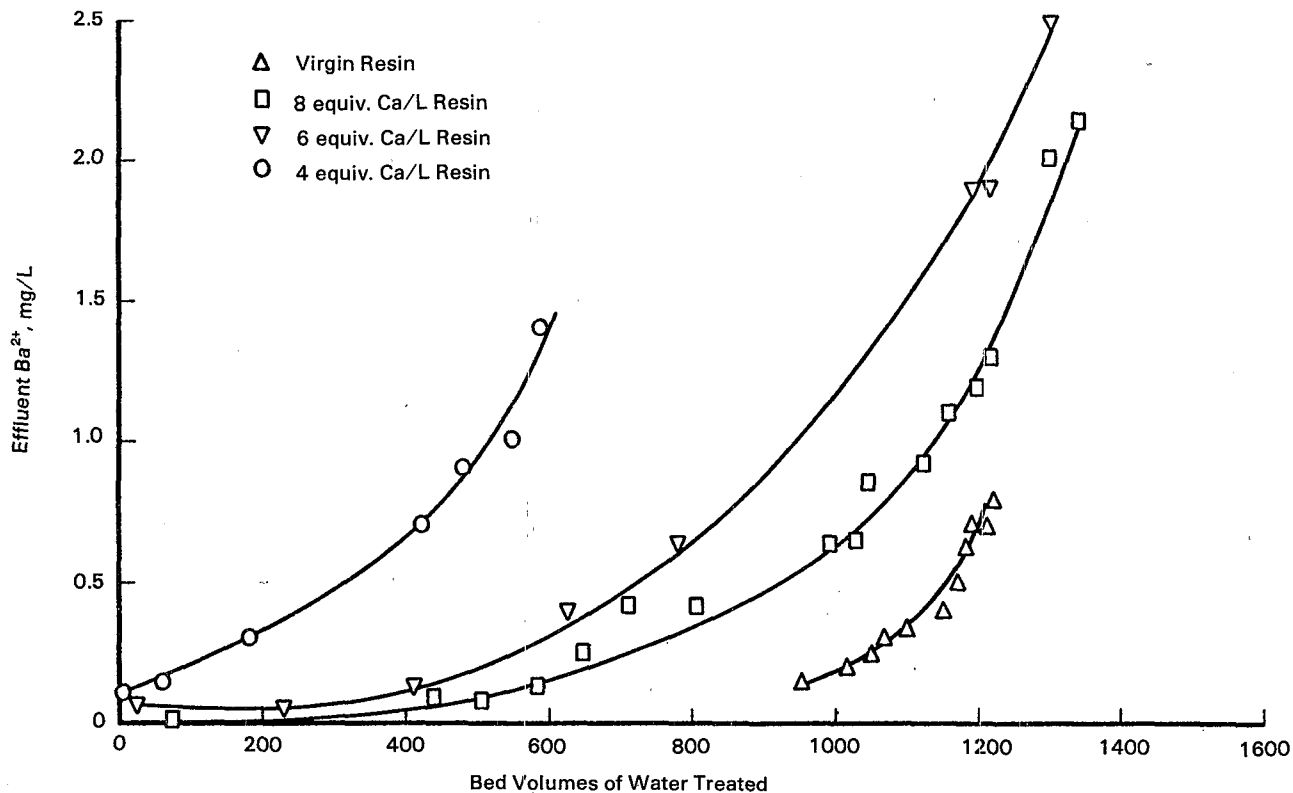
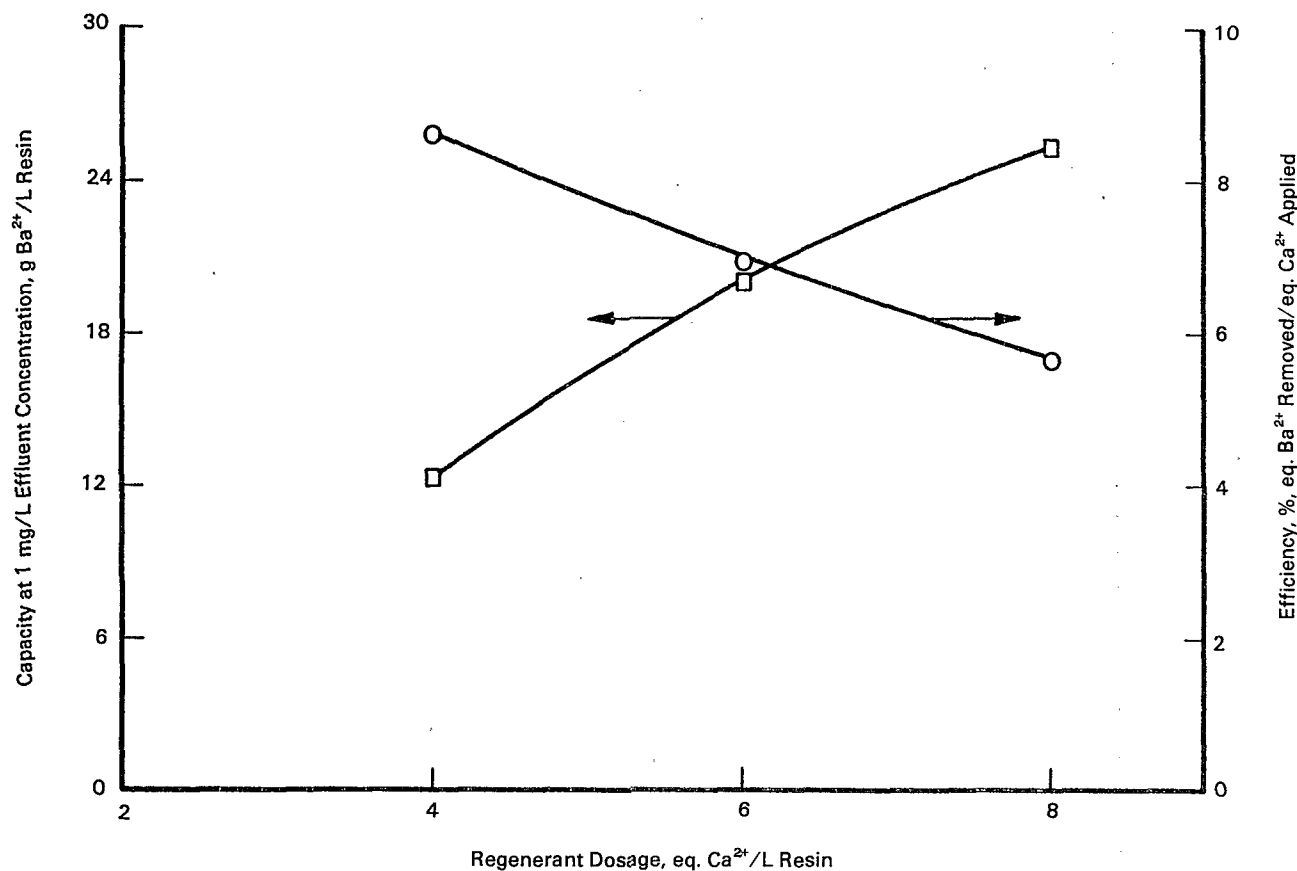


Figure 3. Regeneration efficiency and column capacity at various regenerant dosages.



concentration to about 100 mg/L. The CaSO₄ dissolved, and BaSO₄ precipitated. Use of a very soluble sulfate salt such as sodium sulfate was not successful because high localized concentrations of sulfate caused CaSO₄ as well as BaSO₄ to precipitate. Reuse of brine was possible after removal of the precipitate by filtration. The concentration of magnesium in the brine increased through successive cycles until a plateau value was reached. This resulted in a column that was partially in the magnesium form at the beginning of an exhaustion run, but this does not pose a problem because barium and radium can replace magnesium more easily than calcium. If the brine contains radium as well as barium, the radium will coprecipitate on the BaSO₄ and thus also be removed. However, a barium salt such as BaCl₂ will have to be added along with the CaSO₄ to spent CaCl₂ brine containing only radium to achieve radium removal.

Additional research is needed to refine the process. In particular, the best procedure to precipitate and separate barium and radium needs to be established. A procedure is also needed to control the precipitation process to ensure that the barium and radium have been removed and that too much sulfate has not been added. The brine reclamation process should significantly reduce the brine disposal problem, but ways of disposing of the precipitate

must be found, and the cost involved in using the process must be established.

Radium-Selective Complexer for Radium Removal

The Dow Chemical Company has available a synthetic resin called the Radium-Selective Complexer* (RSC) that has a high affinity for radium. Previous information on this material has been published by R. E. Rozelle and K. W. Ma (5), T. D. Boyce and S. Boom (6), Melis Consulting Engineers (7), and R. E. Rozelle et al. (8). The findings of these studies include the high capacity of the resin for radium when treating water with low TDS, the need to remove iron before the resin because particulate iron can foul the bed, and the desirability of isolating the resin bed to minimize exposure to employees.

The purpose of our work with the RSC resin was to determine its capacity for radium removal from brines compared with typical groundwaters to assess whether it can be used to remove radium from spent ion exchange brines.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

The compositions of two of the waters used in the capacity studies are given in Table 2, the column operating parameters are listed in Table 3, and the radium capacity data appear in Table 4. The 22,000-mg/L TDS and the 9,700-mg/L solutions were made diluting the 40,000-mg/L TDS solution with deionized water and then adjusting the radium concentration. The 11,200-mg/L TDS solution is approximately the same as the 9,700-mg/L TDS solution except that the calcium concentration has been reduced from 1,000 to 400 mg/L. Data from the Melis study are shown in Table 4 for comparison.

Table 2. Influent Composition for RSC Experiments

Parameter	450 mg/L TDS Water	Brine
TDS (mg/L)	272-630	40,000
Hardness (mg/L as CaCO ₃)	81-109	15,472
Calcium (mg/L)	14-17	3,802
Magnesium (mg/L)	10-15	1,455
Sodium (mg/L)	40-120	~10,000
Ra ²²⁶ (pCi/L)	817-1139	668 (avg. of 4 samples)
pH	7.1-8.2	5.85
Alkalinity (mg/L as CaCO ₃)	84-106	--
Chloride (mg/L)	--	~17,250

Table 3. Operating Parameters for RSC Experiments

Parameter	450 mg/L TDS Water	Brine
Column Length	16.3 cm (initial), 12 cm (after shrinking)	25 cm (water), 16.2 cm (after shrinking)
Column Diameter	2.45 cm ID	2.45 cm ID
Bed Volume	76.8 cm ³ (initial)	76.4 cm ³ (after shrinking)
Mass of Dry Resin (Na ⁺ form)	16.3 g	27.8 g
Flow Rate (Downflow)	1.28 gpm/ft ²	1.25 gpm/ft ²
EBCT	2.3 min (after shrinking)	3 min (after shrinking)

Several observations can be made from Table 4. The capacity of RSC resin for radium in ~450-mg/L TDS water is about 200 times greater than its capacity for radium in ~40,000 mg/L TDS brine, and even higher capacities were determined by Melis for RSC in 600-mg/L TDS water. Melis was of the opinion that the difference in capacity at Panel Mine and Key Lake may have been caused by the calcium concentration, which was 400 and 38 mg/L, respectively. More extensive competition between

calcium and radium in the Panel Mine water would result in a lower capacity for radium; a similar effect of calcium was observed by us for the 9,700- and 11,200-mg/L TDS solutions. Further studies are needed to better establish the effect of calcium and other ions on capacity. The data also show that capacity increases regularly as TDS decreases. However, it is not possible to reach a firm conclusion about the effect of TDS until the effect of EBCT is better determined. The 11,200-, 9,700-, 22,000-, and 44,000- mg/L TDS samples were run using a 0.7-min EBCT. Because the RSC resin shrinks 20 to 30 percent as it changes from the sodium to the calcium form and because the resin rapidly converts to the calcium form after the column run is started, the actual contact time was even less than the 0.7 min. Higher capacities might be experienced for the 11,200-, 9,700-, and 22,000-mg/L TDS samples if a longer contact time were used, but additional tests are required to determine this. The 0.7- and 4.6-min EBCT's used for the 44,000- and 40,000-TDS samples, respectively, did show the same low capacity, however.

Process Schematics

As shown in Figure 4, the calcium-form resin can be used in several ways to obtain the desired effluent quality. Treatment of 100 percent of the water flow should selectively remove radium and barium. Use of this resin in parallel with a strong-acid, sodium-form resin permits a desired level of hardness removal in addition to radium and barium, but sodium is added to the product water. However, this resin can be used in parallel with a strong- or weak-acid resin in the hydrogen-form followed by carbon dioxide stripping if sodium addition is to be avoided.

The RSC resin can be used in place of the calcium-form, strong-acid resin in the schematics in Figure 4 for removal of radium and varying amounts of hardness. Presumably the resin would be used on a throw-away basis and thus no regenerant would be used. Further studies are necessary to determine whether the RSC resin can be regenerated, however.

Precipitation of Barium and Radium from Brines

Ion exchange treatment of waters containing barium and radium results in brines with high concentrations of these elements. In anticipation of restrictions on the disposal of these brines to surface waters, experiments were conducted to show the effectiveness of precipitation of these ions (9). Addition of a sulfate salt such as Na₂SO₄ to a brine containing barium results in precipitation of BaSO₄, and if radium is present, it will coprecipitate with the BaSO₄. To remove radium from a brine that does not contain barium, a barium salt such as BaCO₃ or BaCl₂ must be added together with a sulfate salt; the BaSO₄ that forms will remove the radium by coprecipitation.

Barium concentrations of 20 to 5,000 mg/L were effectively treated in solutions with TDS up to 30,000 mg/L (9). Below 100 mg barium/L large sulfate-to-barium mole ratios (~90 for 20 mg barium/L in 27,000 mg/L TDS brine) were required to reduce the barium concentration to 0.5 mg/L in 30 min. However, as the initial barium increased,

Table 4. Summary of RSC Radium Capacity

Total Dissolved Solids (mg/L)	Influent Radium (pCi/L)	% Removal at Termination of Run	EBCT (Before Shrinking) (min)	Capacity (pCi/dry g)
11,200 (low Ca)*	560	10	0.7	2,210
9,700 [†]	390	10	0.7	1,300
22,000	810	10	0.7	1,200
44,000 (Run #1)	480	10	0.7	200
40,000 (Run #2)	670	10	4.6	300
~450	1,000	90	3.1	51,000
2,500 (Melis Study, Panel Mine)	180	80	2.6	32,400
600 (Melis Study, Key Lake)	1,620	95	3.8	110,000
600 (Melis Study, Key Lake)	1,620	0	3.8	187,000 (est.)

*Ca = 400 mg/L

[†]Ca = 1,000 mg/L

the sulfate-to-barium mole ratio decreased. For example, a mole ratio of 1.5 was required to reduce the barium from about 1,700 mg/L to 0.5 mg/L in 30 min. As the TDS of the brine decreased, the required mole ratio also decreased. Other factors may also affect the amount of sulfate required.

The radium concentration in a brine can be reduced to less than 1 pCi/L by coprecipitation with BaSO₄. In 40,000-mg/L TDS brines, 30 mg barium/L was sufficient to reduce a 1,000-pCi radium/L concentration to less than 10 pCi/L. The adsorption capacity of the BaSO₄ was approximately 35,000 pCi/g. The adsorption capacity of the BaSO₄ decreased to 5,000 pCi/g when the final radium concentration in the brine was reduced to 1 pCi/L. Also, adsorption capacity increased as the TDS of the brine decreased.

After the barium and/or radium are precipitated, the solids must be removed from the brine. Alternatives are filtration, possibly preceded by coagulation and sedimentation. These processes have been used in the mining industry, but additional studies are needed to determine the best design for small systems and the means of ultimate disposal that should be used.

MnO₂-Impregnated Resin and Fiber

Previous studies by others have established the ability of MnO₂ to adsorb various divalent ions, and MnO₂-impregnated acrylic fiber has been used to remove radium from solution. In this study, acrylic resin beads were impregnated with MnO₂ and then used in a column to adsorb radium and barium from simulated groundwater and brine.

An Amberlite XAD-7 acrylic resin (Rohm and Haas, Philadelphia, PA), which has a surface area of 450 m²/g, was loaded with MnO₂ by bringing it into contact with hot permanganate solution. A loading of 6 to 10 of manganese/100 g of resin was achieved; similar treatment of acrylic fiber (Monsanto Textiles Co., Decatur,

AL) gave a loading of 10 g of manganese/100 g. The adsorption capacity for barium was very sensitive to ionic strength. Capacity at an ionic strength of 0.03 (typical of groundwater) was ~0.2 g of barium/g of manganese and decreased to 0.005 g of barium/g of manganese at an ionic strength of 0.93 (typical of a spent ion exchange brine). The capacities for radium at the same ionic strengths were 140 and 12 nCi/g of manganese, respectively.

The treatment cost was \$1.80 per 1,000 gal of groundwater if the impregnated resin is used on a throw-away basis. This cost was for chemicals and resin only, using a 0.5-mgd system. The impregnated resin could be regenerated with HNO₃, however. Based on the unverified assumption that the resin could be used six times before it was replaced, chemical and resin costs were \$0.36/million gal. The additional cost of disposal for the neutralized, spent HNO₃ remains to be determined, however. The cost of using fiber is estimated to be somewhat cheaper, although disposal of the spent fiber remains a problem, and thus further research on the resin is not recommended.

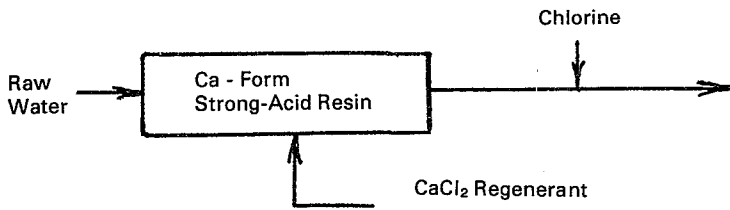
References

Publications 1 to 4 under Literature Cited and 1 to 7 under Bibliography contain the findings of this research project in their entirety. The Master's theses are available from the University of Illinois Library or Vernon L. Snoeyink, Department of Civil Engineering, University of Illinois, 208 North Romine Street, Urbana, IL 61801. The articles that are in press are also available from Vernon L. Snoeyink until they appear in journals.

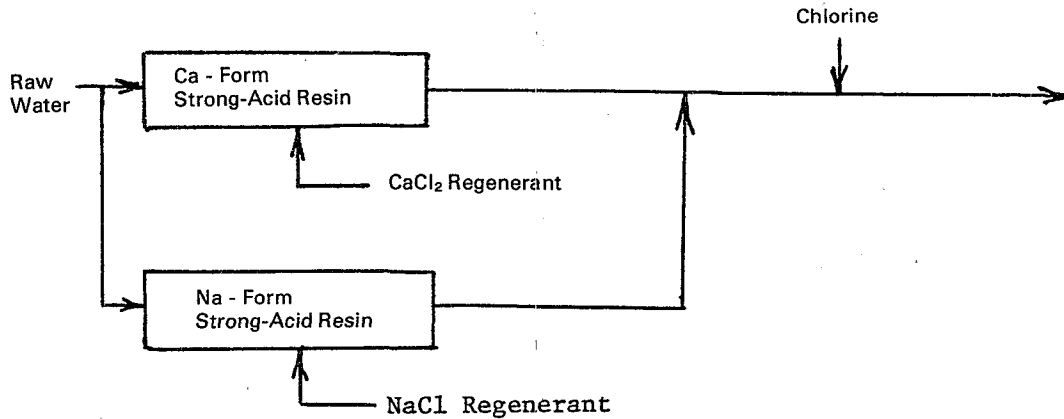
Literature Cited

1. Snoeyink, V. L., J. L. Pfeffer, D. W. Snyder, and C. C. Chambers. "Barium and Radium Removal from Groundwater by Ion Exchange." Report to the U.S. Environmental Protection Agency, Cincinnati, OH, 151 pp. (1983), available from the National Technical Information Service, Order No. PB 84-189810.

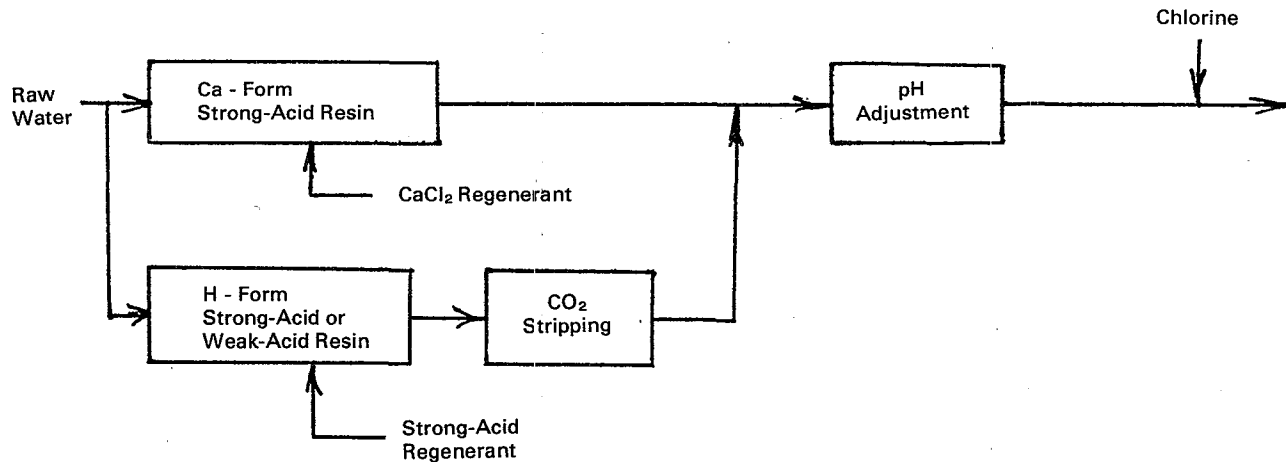
Figure 4. Process schematics for removing barium, radium and varying amounts of hardness.



a. Schematic for Barium and Radium Removal Without Hardness Removal



b. Schematic for Barium, Radium and Partial Hardness Removal with Sodium Addition



c. Schematic for Barium, Radium and Partial Hardness Removal with No Sodium Addition

2. Snoeyink, V. L., C. K. Jongeward, A. G. Myers, and S. K. Richter. "Barium and Radium in Water Treatment Plant Wastes." Report to the U.S. Environmental Protection Agency, Cincinnati, OH, 50 pp. (1984), available from the National Technical Information Service, Order No. PB 85-165777/AS.
3. Snyder, D. W., V. L. Snoeyink, and J. L. Pfeffer. "Weak-Acid Ion Exchange for Removal of Barium, Radium and Hardness." *Journal American Water Works Association*, 78, 98 (Sept. 1986).

4. Snoeyink, V. L., C. C. Chambers, and J. L. Pfeffer. "Strong-Acid Ion Exchange for Removal of Barium, Radium, and Hardness." Submitted for publication (1986).
5. Rozelle, R. E., and K. W. Ma. "A New Potable Water Radium/Radon Removal System." *Proc. AWWA Seminar on Inorganic Contaminants*, June 5-9, 1983, American Water Works Association, Denver, Co.
6. Boyce, T. C., and S. Boom. "Removal of Soluble Radium from Uranium Minewaters by a Selective

Complexer." *Soc. of Mining Engineers of AIME*, 272:82-83 (Feb. 1982).

7. Melis Consulting Engineers. "Radium Removal from Canadian Uranium Mining Effluents by a Radium-Selective Ion Exchange Complexer." Saskatoon, Sask. (1984).
8. Rozelle, R. E. et al. "Potable Water Radium Removal Update on Tests in Missouri, Iowa and Wyoming by the Dow Chemical Company." Internal Report, Dow Chemical Company, Midland, MI.
9. Jongeward, C. K. "Radium and Barium Precipitation from Ion Exchange Brines." M.S. thesis, Department of Civil Engineering, University of Illinois at Urbana-Champaign, Urbana, IL (1984).

Bibliography

1. Chambers, C. C. "Hardness, Barium and Radium Removal from Groundwater by Strong-Acid Exchange Resins." M.S. thesis, Department of Civil Engineering, University of Illinois at Urbana-Champaign, Urbana, IL (1984).
2. Myers, A. G. "Calcium Cation Exchange with Brine Reuse for Barium and Radium Removal." M.S. thesis,

Department of Civil Engineering, University of Illinois at Urbana-Champaign, Urbana, IL (1984).

3. Myers, A. G., V. L. Snoeyink, and D. W. Snyder. "Removing Barium and Radium Through Calcium Cation Exchange." *Journal American Water Works Association*, 77, 60 (May 1985).
4. Pfeffer, J. L. "Equilibrium Studies of Barium Removal from Groundwater by Weak-Acid and Strong-Acid Ion Exchange Resins." M.S. thesis, Department of Civil Engineering, University of Illinois at Urbana-Champaign, Urbana, IL (1984).
5. Richter, S. K. "Radium and Barium Removal from Water with MnO₂ Impregnated Resin and Fiber." M.S. thesis, Department of Civil Engineering, University of Illinois at Urbana-Champaign, Urbana, IL (1984).
6. Snoeyink, V. L., C. K. Jongeward, A. G. Myers, and S. K. Richter. "Characteristics and Handling of Wastes from Groundwater Treatment Systems." Proc. Seminar on Experiences with Groundwater Contamination, American Water Works Association, Dallas, TX (June 10-14, 1984), Denver, CO (1984).
7. Snyder, D. W. "Column Studies of Hardness, Barium and Radium Removal from Groundwater by Weak-Acid Ion Exchange Resins." M.S. thesis, Department of Civil Engineering, University of Illinois at Urbana-Champaign, Champaign, IL (1984).

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use \$300