United States Environmental Protection Agency
Research and Development
Water Engineering Research Laboratory Cincinnati OH 45268
EPA/600/S2-85/006 Mar. 1985

EPA

Project Summary

Barium and Radium in Water Treatment Plant Wastes

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Water Treatment plants at nine locations (10 plants) in Illinois and Iowa were studied to determine the characteristics and disposal practices for the sludge, brine, and backwash water containing radium (Ra) and/or barium (Ba). The treatment processes in these 10 plants include iron (Fe) and manganese (Mn) removal (3 plants), lime softening (4 plants), and ion exchange (3 plants). In the 10 plants, eight had concentrations of radium in their water treatment plants wastes and three had barium. The data are needed to determine whether special procedures are required to dispose of such wastes.

For the eight plants having radium in their wastes, the influent Ra^{226} concentrations ranged from 0.3 to 49 pCi/L. Radium removal averaged 8%, 75%, and 85% for Fe and Mn, lime softening, and ion exchange, respectively. Theoretically, the amount of radium removed estimates the quantity of radium in the waste. The data showed that backwash water from Fe and Mn removal plants contained average Ra^{226} concentrations that ranged from 21.2 to 106 pCi/L, and average Ra^{228} concentrations ranged from 5.7 to 20 pCi/L. Lime softening sludge, on a dry weight basis, ranged from <1.2 to 21.6 pCiRa^{226}/g and from <2.4 to 11.7 pCiRa^{228}/g. Ion exchange plant brine contained peak Ra^{226} concentrations of 217 and 1,144 pCi/L.

Influent barium concentrations for the three plants studied ranged from 4.0 to 16.1 mg/L. Lime softening and ion exchange removed barium to concentrations that were below the maximum contaminant level (MCL) of 1.0 mg/L. Barium removal during lime softening is pH dependent. Theoretically, the amount of barium removed estimates the quantity of barium in the waste. Barium concentrations in the brine and rinsewater from two ion exchange plants that were tested averaged 328 and 1,297 mg/L. Peak concentrations of barium from the two brines were 1,197 mg/L and 5,161 mg/L.

Disposal processes used, for the plants that were studied, were lagooning, discharge to sanitary sewers, and discharge to a water course.

This Project Summary was developed by EPA's Water Engineering 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 (Ba) in drinking water exceeds the MCL of 1 mg/L in some areas of northern Illinois and northeastern Iowa. In these same areas and in some parts of Florida, the concentrations of radium^{226} (Ra^{226}) and radium ^{228}(Ra^{228}) exceed the MCL, which is 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 Ra and Ba 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 calcium (Ca^{2+}) and magnesium (Mg^{2+}), the principal components of hardness in water. The MCL's for Ba and Ra were developed to minimize the attack of these elements on human bones and the replacement of the Ca in bones. Their similarity to Ca, however, means that processes used to soften water are also very useful for removing these contaminants from drinking water.

Water treatment in small communities is often accomplished with iron and manganese (Fe and Mn) removal plants, lime softening plants, and ion exchange plants. The objective of this research was to characterize the backwash samples from all three types of plants, as well as the sludges from the lime softening plants and the brines from ion exchange plants. The concentration data were needed to determine whether special procedures are required to dispose of such wastes. The Ba and Ra removal efficiencies of the plants were also determined.

Materials and Methods

Samples were collected before and after the processes that were likely to cause a change in Ra or Ba concentration. Total alkalinity, total hardness, and Ca concentrations were determined according to *Standard Methods for the Examination of Water and Wastewater* (15th ed., American Public Health Association, Washington, D.C., 1980). Total dissolved solids were measured using a conductivity meter, and Ba was measured with an atomic absorption unit. Chloride was measured using an ion analyzer and an ion chromatograph. The sludge and backwash waters were analyzed for Ra^{226} and Ra^{228} at Argonne National Laboratory by monitoring gamma radiation; the other samples were analyzed by the University of Iowa Hygienic Laboratory by a technique involving co-precipitation of the Ra with $BaSO_4$ and by alpha counting the precipitate with an internal proportional counter.

Radium Removal in Fe and Mn Removal Plants

Fe and Mn removal plants often treat their waters by aeration, detention, and filtration. Ra removal during aeration and detention has been observed, perhaps as a result of Ra adsorption on the Mn oxides or Fe hydroxides. The hydrous oxides of Fe (III) and Mn (IV) have high sorption capacities for bivalent metal ions. Removal of Ra by sand, coal, or greensand media filters is likely attributable to removal of oxides containing adsorbed Ra, or to accumulation of these oxides in the filter followed by sorption of Ra on their surfaces.

Our data, combined with similar data of others, show removal efficiencies that range from a negative value (obtained from a sample taken at the end of a filter run) to more than 50%; but values in the range of 5% to 15% are most common.

Moore and co-workers reported $MnO_{2(s)}$ to have a high affinity for Ra. High removals (~50% of an influent concentration of 14 pCi/L) were reported for Hersher, Illinois, where 0.5 mg/L manganese was being removed as $MnO_{2(s)}$ on the filter. Periodic low removals then would be expected after filter backwashing when the $MnO_{2(s)}$ was removed from the filter. Sufficient data are not available from this study to show the expected relationship, however.

Ra^{226} in the backwash water was found to be 21 pCi/L at Adair, Iowa, and 106 pCi/L at Stuart, Iowa. The average Ra removal indicated by backwash concentration was 11%, which was comparable with the removal figure obtained by measurement of influent and effluent concentrations. Total solids levels in the backwash waters were approximately 2,000 mg/L. These solids could be settled in a lagoon, and the supernatant could be recycled to the plant.

Radium Removal in Lime Softening Plants

The sludges from the lime softening plants samples in this study were discharged to a sanitary sewer (Bushnell, Illinois) or to lagoons (Elgin and Colchester, Illinois, and West Des Moines, Iowa). Sanitary sewers have been noted as being somewhat unfavorable, since they simply transfer any sludge contaminants from the water treatment plant to the sludge of the wastewater treatment plant. Radioactive contaminants in lagooned sludges must be considered when choosing methods for reclaiming the land from permanent lagoon sites. For instance, home building on such sites is not recommended because of the potential hazards from the radon gas.

The softening process may yield Ba and Ra removal by direct precipitation, coprecipitation, or adsorption. Other ionic compounds present in the water and the pH may influence the mechanism and the extent of removal. Removal efficiencies (Table 1) ranged from 43% to 96%, with an average of 75%.

The relationship between hardness and Ra has also been examined and is expressed in the following equation:

$$y = 0.4566\frac{y}{x} + 0.2275$$

where y = the total hardness removal fraction, and x = the Ra^{226} removal fraction. This equation describes the data reasonably well, as shown in Figure 1.

A combination of the data collected in this study with data from the literature shows Ra^{226} concentrations in the sludge ranging from 1,000 to 11,000 pCi/L of sludge. The concentration per dry gram of solids was 10 to 20 pCi. Backwash water concentrations ranged from 6 to 50 pCi/L. Although the relative quantities of Ra in backwash and sludge was not determined, most of the Ra appears in the sludge. A good estimate of the Ra in the sludge can be calculated by multiplying the difference in concentration between influent and effluent by the volume of flow through the plant.

Radium Removal in Ion Exchange Plants

Two ion exchange columns are used in the water treatment plant at Eldon, Iowa. Both columns are usually regenerated with a 100%-saturated (26-37%) by weight) solution of NaCl, but a shortage of available salt resulted in the decision to regenerate one column with a 40%-saturated (10-15% by weight) NaCl solution. Eldon's spent brine is discharged into a storm sewer, which then discharges to a river.

The Ra^{226} removal obtained by ion exchange at Eldon was 60%. However, the regeneration was performed with a limited amount of 40%-saturated salt solution and the regeneration was incomplete. This removal can be compared with 65% to 85% removals found for other plants that were incompletely regenerating their exchange media. The literature indicates that 81% to 97% Ra removal can be achieved in well-operated plants, and that Ra removal is directly related to hardness removal (see Table 2). Laboratory studies cited in the literature using both strong and weak acid resins have indicated that good removal occurred long after hardness breakthrough in both types of resin, although operation through several service cycles with incomplete regeneration may lead to earlier Ra breakthrough.

An earlier study of seven water treatment plants reported that maximum Ra^{226} concentrations in softener brine and rinse effluent ranged from 320 to 500 pCi/L. Iowa ion exchange wastes were found to contain 7.8 to 98 pCi/L of Ra^{226} in the backwash water, and rinse wastewaters ranged from 114 to 1,960 pCi/L of Ra^{226}. Less than 5% of the Ra was

Table 1. Ra and Hardness Removal Efficiencies in Lime Softening Plants

Location and Date	Ra^{226} in Raw Water (pCi/L)	Ra^{226} Removed (%)	Total Hardness Raw Water (mg/L as $CaCO_3$)	Total Hardness Removed (%)
W. Des Moines, Iowa:				
8/1/74*	9.3	75	376	49
6/5/78†	1.9	43	NA	NA
8/2/83‡	6.9	78	389	61
Webster City, Iowa:				
8/13/74*	6.1	85	507	48
2/20/75*	7.8	96	482	78
7/26/78†	1.4	60	NA	NA
Peru, Illinois:				
2/20/75*	6.5	92	329	47
2/25/75*	5.5	70	278	35
3/4/75*	5.5	76	286	57
Elgin, Illinois:				
3/7/75*	7.5	90	246	60
3/14/75*	5.7	86	243	54
3/21/75*	3.5	80	242	61
6/27/83‡	0.3	(-)	253	67
Colchester, Illinois:				
8/83‡	12.1	74	698	57
Bushnell, Illinois:				
8/83‡	12.6	45	354	42

*Data from EPA-600/2-77-073.
†Data from JAWWA, 61:541, 619, and 681.
‡Data from this study.

removed during backwash. Wastewater volumes generated were 2% to 10% of the product water. Wastewater characteristics varied greatly from one plant to another.

Barium Removal in Lime Softening Plants

Barium removal is pH dependent, with an optimum pH occurring in the 9 to 11 range. At Elgin, 90% of the influent barium (4 mg/L) was removed at pH 9.3.

Barium Removal in Ion Exchange Treatment Plants

Crystal Lake, Illinois, has an ion exchange system composed of three separate wells with two strong acid ion exchange columns for each. The spent brine is discharged to a sanitary sewer system, which eventually discharges to the wastewater treatment plant. Data indicate that ion exchange plants typically remove 92% to 99% of the incoming barium. Laboratory studies have shown that hardness and Ba will break through at the same time for a strong acid resin after operation through several exhaustion-regeneration cycles.

The regeneration of Wells 6 and 8 removed 84% and 153% of the exchanged Ba, respectively. At Well 6, 6.5 kg of Ba was contained in the 9,500 gal of wastewater generated from one regeneration cycle. Likewise, Well 8 produced 30 kg Ba in its 10,000 gal of wastewater. Less than 2% of the barium was found in the backwash water, and the remainder was in the spent brine and rinse water. Other researchers report 85% removal or 18 kg Ba in 9,250 gal of wastewater.

Peak hardness (33,000 mg/L) and Ba (1,200 mg/L) concentrations in the spent regenerant coincide at Well 6 (Figure 2), but the peak hardness (44,000 mg/L) occurs before the peak Ba (5,000 mg/L) concentration at Well 8. This phenomenon may be caused by the greater amount of Ba on the column before generation at Well 8 (78.4 g Ba/ft^3) compared with that at Well 6 (40.4 g Ba/ft^3). More Ba accumulates on the resin during the service cycle at Well 8 because the raw water Ba concentration is higher and because less regenerant is applied to the column per unit volume of water produced during the service cycle.

Conclusions

Ion exchange plants, lime softening plants, and Fe and Mn removal plants can remove Ra from water, with varying degrees of success. The Fe and Mn treatment plants removed 0% to 54% of the influent Ra, which ranged in concentration from 6.0 to 49 pCi/L. The lower removals were more common. The average removal, including values taken from the literature, was 23%, but the mean for this study was only 8%. The total Ra content of the waters from a single backwash was 0.02 to 7.6 µCi, and concentrations were typically less than 100 pCi/L. The average Ra removal by the plant was 11%. Though a relationship between MnO_2 accumulation on the filters and Ra removal was expected, sufficient data were not available to show this relationship. Treatment methods such as lime softening or ion exchange seem better suited than Fe and Mn removal plants for removing Ra from water supplies.

Lime softening effectively removes Ra from waters. The influent concentrations were 0.3 to 24.2 pCi/L. Typical removal values ranged from 43% to 92%, with an average of 69% if data from the literature are included. The Ra removal at the plants sampled during the summer varied from 45% to 78%, with an average of 75%. Two correlations presented in the report relate hardness removal to Ra removal and can be used to predict Ra removal efficiencies. The Ra concentrations in the softening sludges ranged from <1.2 to 21.6 pCi/g dry solids for Ra^{226} and from <2.4 to 11.7 pCi/g dry solids for Ra^{228}.

Ion exchange plants also produce an effluent with low Ra concentrations. The plant at Eldon removed 60% of the influent Ra of 47 pCi/L, but sufficient salt was not applied to completely regenerate the resin. Common removals reported in the literature are 65% to 90%, and the average approaches 85%. Ra concentrations in the brines at Eldon reached 217 and 1,144 pCi/L for NaCl brines at 40% and 100% saturation with NaCl, respectively.

Ion exchange and lime softening plants were also analyzed for Ba removal. Ion exchange at Crystal Lake removed more than 90% of the influent 9.5 and 16.1 mg/L Ba. Barium concentrations in the brine at Wells 6 and 8 averaged 328 and 1,300 mg/L, with peak values of 1,200 and 5,200 mg/L, respectively. Lime softening at Elgin also removed 90% of the 4 mg/L Ba in the influent water.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-808912 by the University of Illinois at Urbana-Champaign under the sponsorship of the U.S. Environmental Protection Agency.

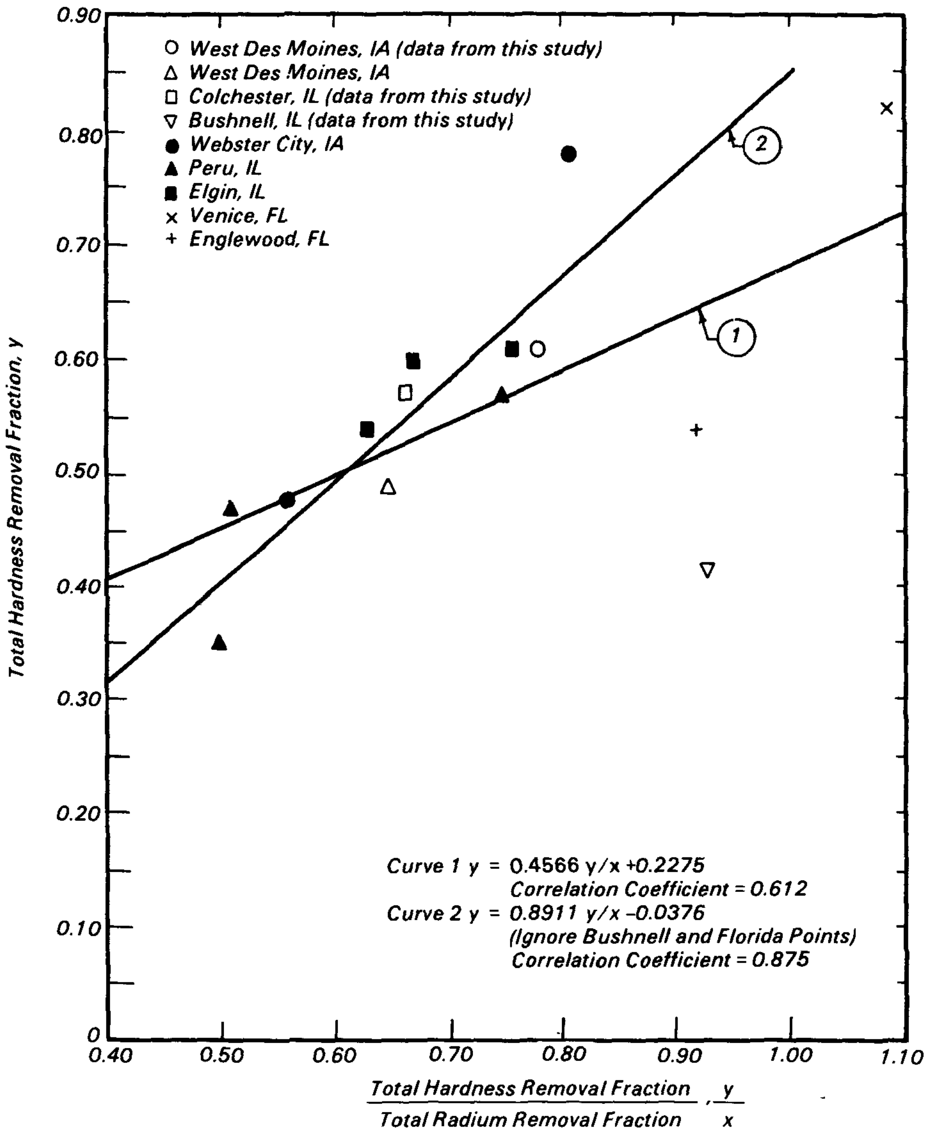

Figure 1. *Proposed correlation between Ra^{226} and total hardness removal fractions for lime softening plants.*

Table 2. Hardness and Ra^{226} Removals in Ion Exchange Plants

Location and Time of Removal	Ra^{226} in Influent (pCi/L)	Ra^{226} in Effluent (pCi/L)	Ra^{226} Removed (%)	Total Hardness in Raw Water (mg/L as $CaCO_3$)	Total Hardness in Product Water (mg/L as $CaCO_3$)	Total Hardness Removed (%)
Hersher, Illinois:*						
3/25/75:						
Just after regeneration	6.64	1.25	81.2	412	18	95.6
Midpoint	6.94	0.42	93.9	427	12	97.2
Near breakthrough	6.88	2.07	69.9	417	184	55.8
Dwight Correctional Center, Illinois:*						
2/13/75-2/14/75:						
Just after regeneration	3	0.4	88.0	286	16.0	94.3
Midpoint	3	0	92.5	284	4.1	98.6
Near breakthrough	3		70.7	279	131.0	53.7
Eldon, Iowa:†						
8/83:						
Just after regeneration‡	NA	14.2	66.5	NA	175	50
Midpoint	42.4	NA	NA	350	NA	NA
Near breakthrough	NA	20.1	52.6	NA	232	33.7

*Data from EPA-600/2-77-073.
†Data from this study.
‡40% saturated brine.

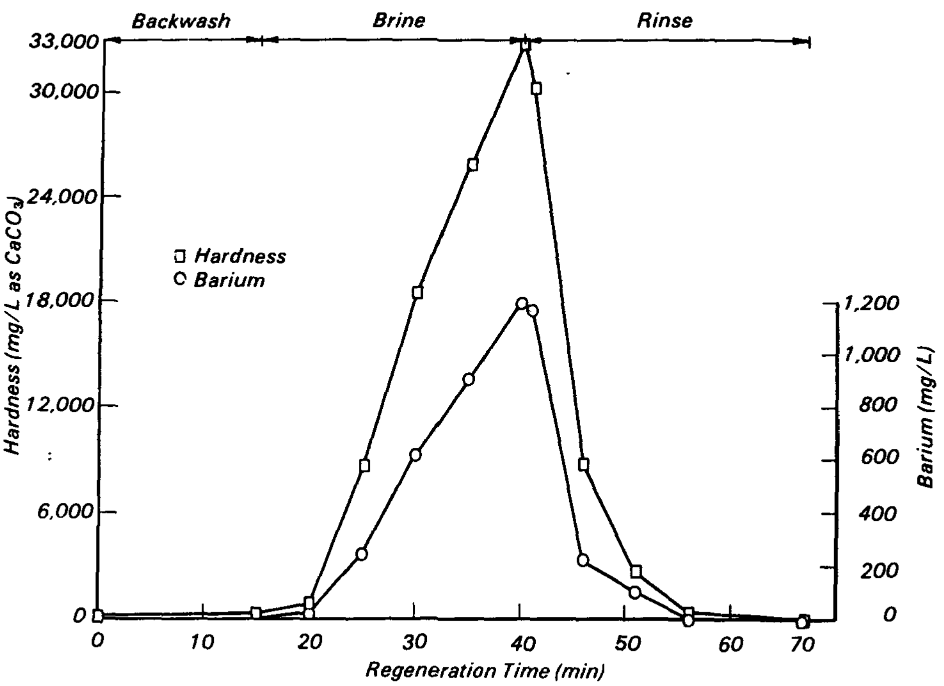

Figure 2. Barium and hardness concentrations in spent brine at Crystal Lake, IL Well #6.

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***Richard P. Lauch** is the EPA Project Officer (see below).*
The complete report, entitled "Barium and Radium in Water Treatment Plant Wastes," (Order No. PB 85-165 777/AS; Cost: $10.00, subject to change) will be available only from:
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