



## Project Summary

# A Study of Possible Economical Ways of Removing Radium from Drinking Water

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A study was undertaken to determine variables that control the incidental removal of radium observed to occur as a consequence of treatment to remove iron by oxidation-sand filtration. This study also evaluated the possibility of exploiting these factors to provide an inexpensive means of removing radium using existing or modified iron removal facilities. Emphasis was placed on the use of aeration to oxidize soluble iron. The initial objective was to determine how water chemistry influences  $^{226}\text{Ra}$  sorption to iron oxides produced by aeration. Studies were also conducted to evaluate radium sorption to hydrous manganese oxides produced by permanganate oxidation. A latter objective was to evaluate the potential of exploiting sorption to filter sand as a novel removal technology. Batch and pilot plant studies were conducted in the laboratory and in the field at a city whose supply contains excessive radium.

Sorption of iron and manganese oxides and filter sand appears to be controlled primarily by the presence of calcium and magnesium, which are believed to compete for sorption sites. Excessive pH values would need to be used to obtain significant sorption to iron oxides at concentrations typical of natural waters. Removals obtained by freshly precipitated hydrous manganese oxides in batch studies were much greater than those obtained in systems containing only iron oxides or mixtures of iron and manganese oxides produced by the oxidation of ferrous iron by potassium permanganate. This suggests that sorption to manganese

oxides could possibly be exploited to remove radium if iron did not interfere. The presence of iron may limit the utility of permanganate oxidation of iron as a means to reduce radium.

Filter sand has a potential capacity to sorb significant concentrations of radium at typical hardness concentrations if the capacity is maintained by periodically rinsing the sand with a dilute acid. Removal efficiencies of approximately 80% to 90% could be achieved in laboratory and field studies using a 61-cm (2-ft) deep sand bed at conventional loading rates when daily rinsing with a dilute acid was practiced.

*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

Radium in drinking water is a concern because of suspected detrimental health effects, primarily the formation of cancers. Concentrations exceeding the current EPA-mandated maximum contaminant level (MCL) of 5 pCi/L total radium ( $^{226}\text{Ra} + ^{228}\text{Ra}$ ) have been observed in several areas, the most notable occurrences in the United States being in Florida, North Carolina, Virginia, the New England states, the uranium mining areas of the mountain states, and in the midwestern states of Iowa, Illinois, Wisconsin, Missouri, and Minnesota.

It has been estimated that 500 municipal supplies may contain excessive radium. Lucas reported in 1985 approx-

imately 1.4 million people in a total of 177 cities in the midwest alone are delivered a water containing  $^{226}\text{Ra}$  in excess of 3 pCi/L (the 1962 U.S. Public Health Service drinking water standard and the value above which mandatory analysis for  $^{226}\text{Ra}$  is required). Radium concentrations in the range of 5 to 20 pCi/L are typical of the majority of these supplies although higher levels (up to nearly 50 pCi/L) have been reported. In many cases removal efficiencies in the range of 50% to 75% would be adequate to put these waters into compliance.

Several conventional water treatment practices bring about the removal of radium. Sorg and Logsdon have pointed out that the two most efficient methods are sodium ion exchange and lime-soda softening, each generally removing about 85% to 95% of the influent radium. In those processes radium removal is only incidental to other changes in water quality that may not be needed or even desired. For example, sodium ion exchange causes an increase in sodium concentration, which has been associated with an increased risk of heart disease. In particular, conventional processes are not suited to the many small communities that have excessive radium. Other removal technologies have also been investigated but to date no processes to remove radium alone are in widespread use.

Many supplies having high radium also have unacceptably high concentrations of iron and sometimes manganese that must be removed, commonly through processes involving oxidation and sand filtration. It has been observed that some radium removal occurs during iron removal treatment, presumably by sorption/coprecipitation with the hydrous metal oxides. Radium, like other alkaline earth metals, probably exists in water as a divalent cation and has been shown to sorb to many types of materials. For example, sorption to glass is a common sampling problem that is overcome by acidification. An understanding of the factors that control radium removal in iron removal processes could possibly aid in the development of inexpensive radium removal methods based largely on the use of existing facilities.

The primary objective of this study was to determine what factors control the incidental removal of radium occurring in iron removal plants typical of those operating in the midwest utilizing aeration and sand filtration. The study also evaluated the possibility of exploiting

these factors as an inexpensive means of removing radium from drinking water using existing iron removal facilities. The initial focus was on modification of the water chemistry expected to affect sorption to iron oxides produced by aeration. Studies were also conducted to evaluate radium sorption to hydrous manganese oxides produced by permanganate oxidation. A latter objective was to evaluate the potential of exploiting sorption to filter sand as a novel removal technology.

Tasks included (1) batch studies of the effect of variable water chemistry on sorption of  $^{226}\text{Ra}$  to hydrous iron and manganese oxides, mixtures of iron and manganese oxides coproduced by permanganate oxidation of ferrous ion, and sorption to filter sand; (2) evaluation of radium removal occurring in a laboratory pilot plant simulating an aeration-sand filtration iron removal process under various operating conditions including regeneration of the filter sand using a dilute acid rinse to maintain radium sorption; and (3) field evaluation at Oxford, IA, of the use of a regenerable sand filter to sorb naturally occurring radium.

## Materials and Methods

### Waters Used

Batch studies were conducted using synthetic groundwaters and groundwaters obtained from Oxford, IA, and Eldon, IA. A hardness-free synthetic water was prepared by mixing 5 mM  $\text{NaHCO}_3$ , 1 mM  $\text{Na}_2\text{SO}_4$ , and 1 mM  $\text{NaCl}$  to deionized water. Calcium and/or magnesium sulfate were added to vary hardness. Finished waters were obtained from Oxford and Eldon and were filtered through a 0.45  $\mu\text{m}$  filter prior to use. Oxford water had a hardness and alkalinity of approximately 1300 mg/L and 300 mg/L as  $\text{CaCO}_3$ , respectively. Eldon water had a total hardness and alkalinity of approximately 300 mg/L and 200 mg/L as  $\text{CaCO}_3$ , respectively. Oxford and Eldon water contained approximately 10 and 50 pCi/L of natural  $^{226}\text{Ra}$ , respectively. Radium concentrations were generally increased by adding additional  $^{226}\text{Ra}$ .

Laboratory pilot plant studies were conducted using the tap water obtained at the University of Iowa Hygienic Laboratory, which had a total hardness of approximately 150 mg/L as  $\text{CaCO}_3$  and an alkalinity of approximately 300 mg/L as  $\text{CaCO}_3$ . Field studies at Oxford used

water from the existing sand filter effluent (iron floc removed) or water from an existing aeration/flow equalization tank (containing iron floc).

### Batch Studies

Batch studies were conducted using 2-L beakers thermostatted to 25°C and stirred with a Birds and Phipps\* gang stirrer. Mixtures of varying carbon dioxide-air composition were bubbled through to provide pH control although in several experiments pH was adjusted by addition of concentrated sulfuric acid or sodium hydroxide.

Solutions containing pure iron oxides were generally prepared by first deaerating the water by purging with nitrogen gas, adjusting pH to approximately 6.5 by bubbling pure carbon dioxide, then adding ferrous sulfate and  $^{226}\text{Ra}$ . The solutions were then aerated to approximately pH 8 with normal air to oxidize the iron, and the pH adjusted to the desired value by bubbling buffer gas (or acid/base addition) followed by aging for 1 hr. Solutions of pure manganese oxides were prepared similarly except using stoichiometric amounts of permanganate to oxidize added manganous ion. Mixtures of iron and manganese oxides were prepared by addition of enough permanganate to oxidize 90% of the initial added ferrous ion in deaerated solutions followed by aeration to oxidize the remaining iron and then aging for 1 hr at the desired pH. Sorption onto acid-washed and deionized-water-rinsed 0.5 mm filter sand (effective size) was studied using the same apparatus.

After aging, an aliquot was withdrawn and filtered through a 0.45  $\mu\text{m}$  filter and the filtrate acidified for later analyses. In some cases the apparatus and beakers were rinsed with 0.1 N nitric acid and the rinses analyzed for radium to ensure that significant quantities of radium were not sorbing to these components.

### Pilot Plant Studies

Laboratory pilot studies were conducted at the University of Iowa Hygienic Laboratory using an iron aeration-sand filtration pilot plant (Figure 1). The 10.2-cm diameter (4-in.) pressure filter was filled with 61 cm (2 ft) of filter sand and equipped for water backwashing and periodic rinsing with dilute acid.  $^{226}\text{Ra}$  and ferrous iron could be added to the

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

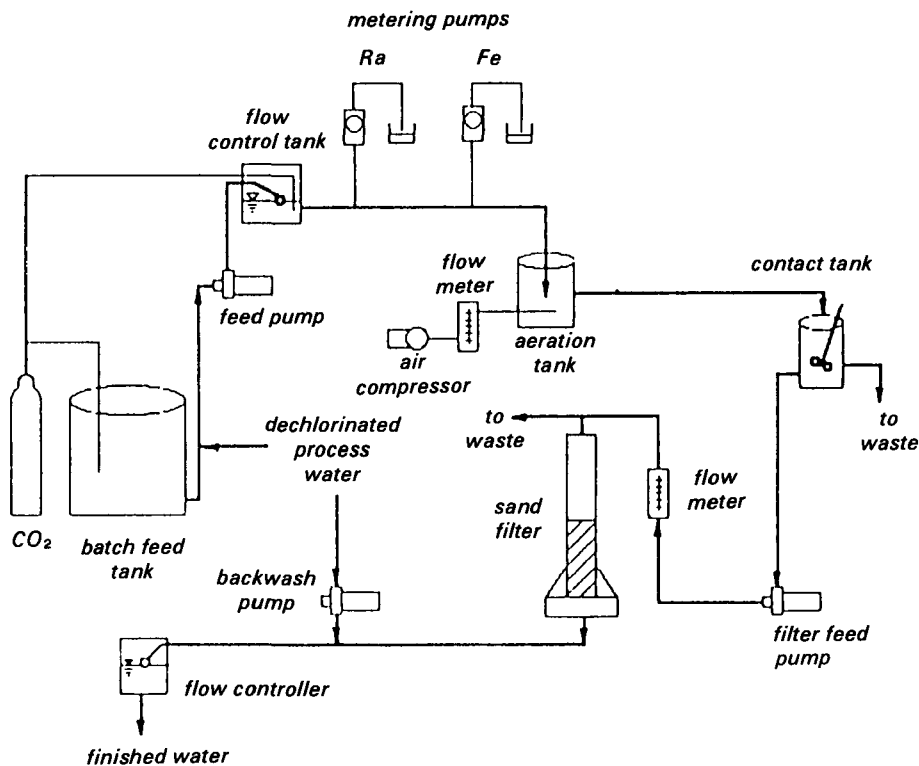


Figure 1. Schematic diagram of pilot plant used in laboratory studies.

water, which was maintained at pH 6.5 prior to aeration by bubbling carbon dioxide through it. Aeration to approximately pH 7.5 was accomplished in a tank having a 10-min hydraulic residence time. Filter influent was withdrawn from a small tank used to moderate flow. Flow rate through the filter was controlled using a small, constant-head tank equipped with a flow control float and valve. Automatic samplers were used to obtain discrete and composite samples. The water supply was usually  $18^{\circ}\text{C} \pm 3^{\circ}\text{C}$ . Field studies at Oxford utilized a similar pressure filter equipped for rinsing with a dilute acid in addition to water backwashing. Water temperature was usually  $15^{\circ}\text{C} \pm 3^{\circ}\text{C}$ .

### Analyses

$^{226}\text{Ra}$  concentration was determined using precipitation with  $\text{BaSO}_4$  and counting of the radioactivity. Iron concentrations were routinely determined using Hach Chemical Kit ISR-18. Iron was also measured in several experiments by the phenanthroline colorimetric method. Hardness ions were determined by EDTA titration, and alkalinity by acidimetric titration.

## Results and Discussion

### Sorption to Hydrous Iron Oxides

Removals in a hardness-free synthetic groundwater by oxides produced by oxidation of 10 mg/L Fe increased with pH from approximately zero at a pH of about 5.5 to over 90% above pH 9.0 and  $25^{\circ}\text{C}$  (Figure 2). A linear isotherm,

$$q = k_d [^{226}\text{Ra}]$$

where  $q$  is the amount of radium sorbed per unit mass of iron, and  $k_d$  is a distribution coefficient, and  $[^{226}\text{Ra}]$  is the concentration of radium remaining in solution, could be used to adequately describe sorption to iron oxides (Figure 3). As a consequence of a linear isotherm, percent removals do not depend on the initial radium concentration and can be equated to,

$$\text{percent removed} = 100 \frac{k_d [\text{Fe}]}{1 + k_d [\text{Fe}]}$$

where  $[\text{Fe}]$  is the total iron concentration.

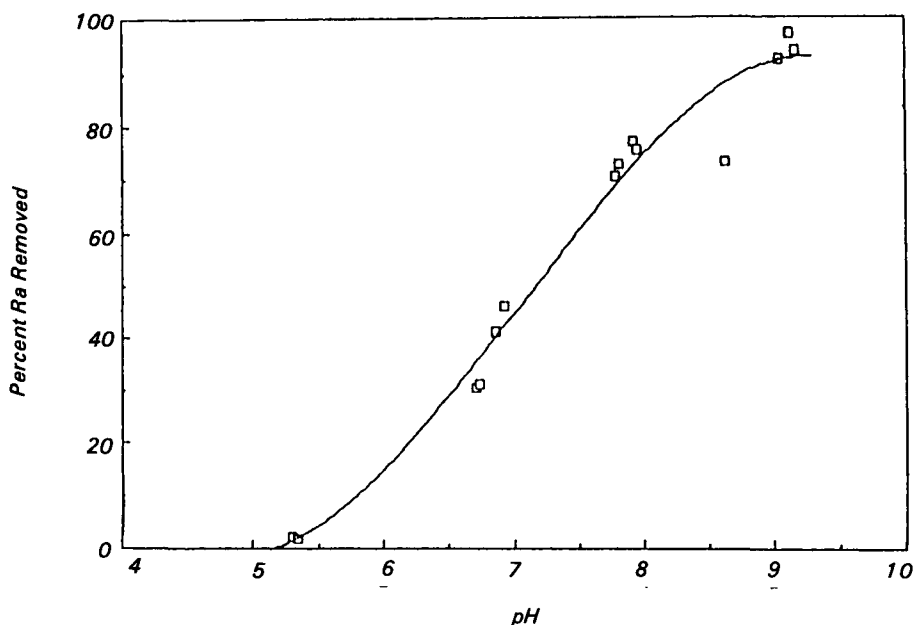
Sorption was significantly reduced by the presence of calcium, magnesium, and barium and was a strong function of pH over the range of 5 to 9. Distribution

coefficients characterizing sorption at  $25^{\circ}\text{C}$  and at approximately pH 8.0, decreased from about 0.3 L/mg obtained in the absence of hardness or barium to approximately 1/10 this value when the calcium was increased to approximately 3mM (300 mg/L as  $\text{CaCO}_3$ ) or when 1 mg/L of barium was present in a synthetic groundwater. Above this hardness level little further reduction in the distribution coefficient was observed. This is consistent with the observation that removals were similar in both Oxford and Eldon water (approximately 10% to 20% in the presence of 10 mg/L Fe) despite a large difference in hardness. Based on measured distribution coefficients, radium reduction due to sorption to iron oxides is not expected to exceed 10% to 20% in typical groundwaters with iron concentrations of approximately 2 to 5 mg/L and hardness in excess of approximately 300 mg/L as  $\text{CaCO}_3$ . The pH would need to exceed at least 10 to obtain significantly better removals in natural waters at typical iron concentrations. Radium removals obtained in laboratory pilot studies designed to simulate an iron oxidation (aeration)-sand filtration plant generally supported the findings anticipated from batch studies.

### Sorption to Hydrous Manganese and Iron/Manganese Mixtures

Sorption to freshly formed manganese oxides was significantly greater than that to iron oxides of comparable molar concentration and does not appear to be sensitive to either pH or hardness. Removals of approximately 80% were obtained in synthetic groundwater containing up to 3 mM Ca (300 mg/L as  $\text{CaCO}_3$ ) and 1 mg/L of freshly formed  $\text{MnO}_2$ . Removals of 40% to 70% were obtained over the pH range of 5 to 9 by 1 mg/L  $\text{MnO}_2$  in Oxford water and Oxford water diluted in half with deionized water (Figure 4).

Removals of  $^{226}\text{Ra}$  in mixed manganese/iron oxides prepared by the oxidation of  $\text{Fe}^{+2}$  by  $\text{KMnO}_4$  were much greater than by aeration produced iron oxides alone but were less than obtained by comparable concentrations of pure manganese oxides. Again, removals were less in Oxford water than in a hardness-free synthetic groundwater. In synthetic hardness-free groundwater, removals increased from approximately 75% at pH 7 to nearly 100% near pH 9 when 1 mg/L Fe was oxidized by  $\text{KMnO}_4$ .



**Figure 2.** Effect of pH on radium removal by sorption to iron oxides in hardness free synthetic groundwater. 10 mg/L Fe,  $^{226}\text{Ra} = 48$  pCi/L.

addition. However, removals were less than 10% over pH 5.5 to 8.7 in a system prepared by permanganate oxidation of 2 mg/L Fe in Oxford water (equivalent  $\text{MnO}_2$  concentration of 0.84 mg/L as  $\text{MnO}_2$ ). A maximum removal of only approximately 40% at pH 9.0 was observed in Oxford water when 5 mg/L Fe was oxidized as described above (Figure 5). It appears that coproduced iron oxides produced by aeration after formation of manganese oxides may interfere with sorption to manganese oxides. This may limit the utility of permanganate oxidation of iron to increase radium removals.

### Sorption to Filter Sand

Sorption to acid-rinsed filter sand was characterized by a linear sorption isotherm in studies conducted in synthetic and natural waters. Sorption generally increased with pH, but was not a strong function of pH in the range of 5 to 8. Magnesium and calcium reduced sorption in a similar manner when at identical molar concentrations. However, the distribution coefficient did not significantly decrease further with increasing hardness levels in excess of approximately 100 to 200 mg/L as  $\text{CaCO}_3$ . Distribution coefficients decreased from approximately 0.3 L/g in hardness-free synthetic groundwater to approximately 1/10 this value in the presence of 1 to 3 mM Ca over the pH range of 5 to 8.

Isotherms obtained at approximately pH 7 for Oxford, Eldon, and a synthetic groundwater containing 6 mM Ca were nearly identical (Figure 6).

Theoretical calculations based on instantaneous equilibrium and a linear isotherm indicate that conventional filter sand beds may have a significant radium removal capacity if this capacity could be maintained by a regeneration step. Table 1 summarizes measured distribution coefficients, theoretical calculations of the ratio and bed volumes potentially treated to empty bed volume, and the breakthrough time,  $t_b$ , for a 1-m deep sand bed fed at a loading rate of 3.7 m/h (1.5 gpm/ft<sup>2</sup>).

### Laboratory and Field Pilot Plant Studies

The daily average amount of radium removed by the filter-fed UHL water (containing 2 mg/L of iron flocs and approximately 80 pCi/L added  $^{226}\text{Ra}$  at a rate of 7.5 m/h (3 gpm/ft<sup>2</sup>) increased from about 30% obtained with only a daily water backwashing, to approximately 85% to 90% when the bed was regenerated with 4 bed volumes of a pH 1 dilute HCl rinse (Figure 7). Performance did not decrease over a 4-day period in which daily regeneration was practiced using 4 bed volumes of regenerant at a loading rate of 7.4 m/h (3 gpm/ft<sup>2</sup>). Removals obtained using a daily pH 2

rinse at the same operating conditions were only slightly less (about 75% to 85%). Mass balances on the cumulative amount of radium removed by the sand filter and recovered during backwashing/regeneration showed that only approximately half of the radium removed prior to initiation of acid regeneration could be recovered in the backwash water, indicating that sorption to filter sand was occurring even when water-only backwashing was practiced. All radium removed by the sand filter was recovered with dilute acid regeneration using either pH 1 or pH 2 rinses.

Operation of the pilot facility at Oxford to treat the existing sand filter effluent using a 3.7 m/h (1.5 gpm/ft<sup>2</sup>) influent loading rate and a daily pH 1 rinse (4 bed volumes, EBCT 5 min) for 4 days resulted in daily composite average removals of approximately 85% and the production of a water containing  $^{226}\text{Ra}$  at concentrations less than 3 pCi/L (Figure 8). Upon termination of dilute acid regeneration, effluent radium concentrations increased greatly. The removals are a consequence of dilute acid regeneration and not sorption to iron flocs since radium is not removed by filtration in Oxford's existing filters nor was any significant amount found to be sorbed to the iron oxides as determined by filtration through a 0.45  $\mu\text{m}$  filter and filtrate analysis. Removals were less when twice the water volume was treated using an influent loading rate of 7.4 m/h (3.0 gpm/ft<sup>2</sup>) but still resulted in a product water containing approximately 3 pCi/L  $^{226}\text{Ra}$ . In general, observed radium sorptive capacities were 3 to 4 times greater than those anticipated based on batch sorption studies. This may be due to lower temperatures used in the pilot studies or an unidentified mechanism.

Radium removals decreased significantly to approximately 25% to 30% when the pilot plant was used to simultaneously remove both radium and iron flocs (0.5 to 1.0 mg/L as Fe) from the aerator effluent. Figure 9 shows results being obtained using an influent loading rate of 3.7 m/h (1.5 gpm/ft<sup>2</sup>) and a pH 1 regenerant of either dilute hydrochloric or sulfuric acid at rates of 3.7 and 7.4 m/h (1.5 and 3.0 gpm/ft<sup>2</sup>). Sulfuric and hydrochloric acid appear equally effective at either of the regenerant loading rates.

The decrease in radium removal efficiency occurring as a result of a dual-use mode of operation was not expected based on the laboratory pilot plant

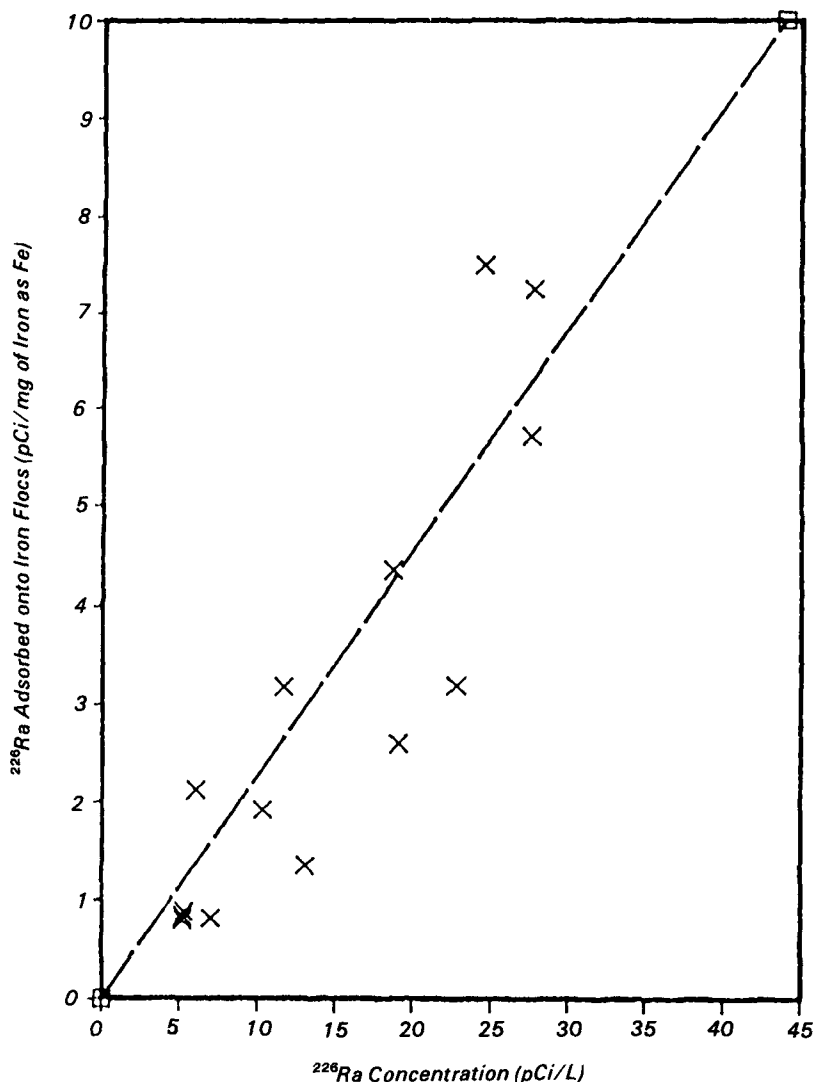


Figure 3. Radium sorption isotherm obtained in hardness free synthetic groundwater at pH 8.1.

results, which indicated little iron floc interference. While it may be supposed that the flocs coated the sand, thereby blocking radium sorption, it is believed that most of the iron flocs were removed in the first few inches of sand bed. Therefore, significant amounts of "clean" sand probably existed below the iron floc removal zone even after 1 day of operation. Poor removals may be attributable to the presence of significant concentrations of soluble iron.

### Conclusions

Increasing sand filter influent pH to increase sorption to hydrous iron oxides produced by aeration does not appear to be a realistic strategy to increase radium removals. Differences in radium remo-

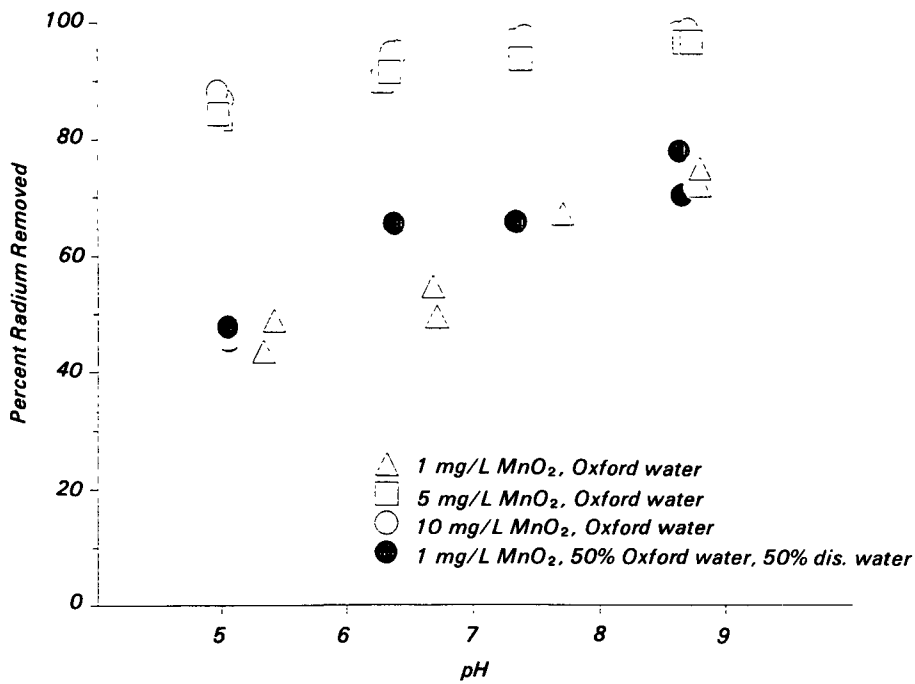
vals occurring as a result of iron removal processes involving aeration-sand filtration are probably due to differences in pH, iron concentration, and hardness. Regardless of these differences, little removal is expected.

The favorable results obtained using hydrous manganese oxide suggests that they could potentially be used to effectively remove radium if iron did not interfere. If a significant interference is caused by precipitation of iron oxides onto manganese oxides, then a two-stage oxidation process may be warranted when both iron and manganese are present. Iron could be oxidized by aeration in the first stage, followed by permanganate addition in the second to oxidize manganese. Filtration of the iron

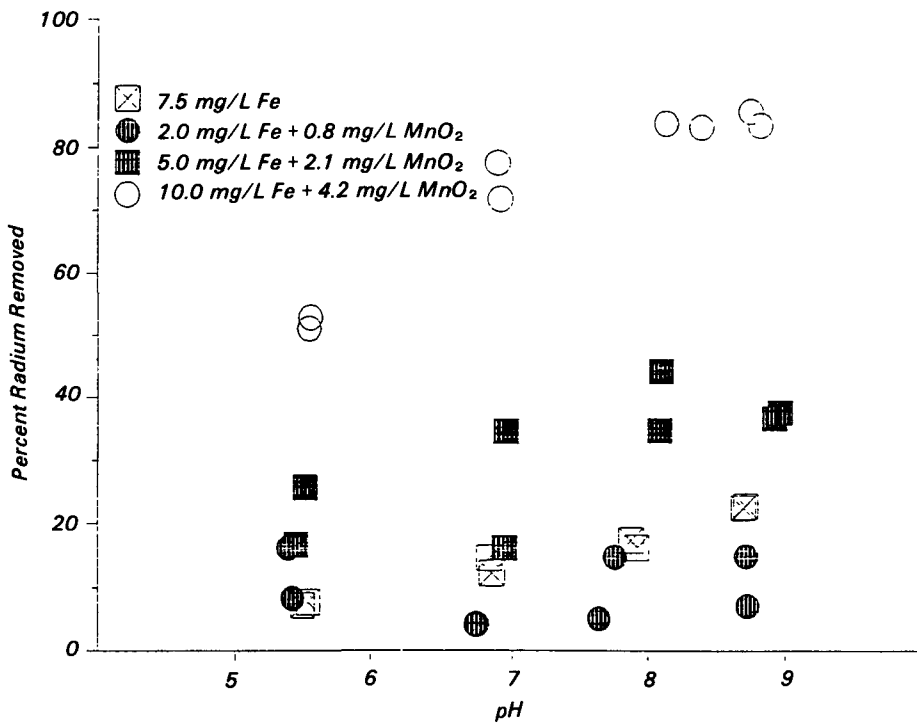
oxides prior to hydrous manganese oxide formation may also be desirable. Addition of manganous ion to waters containing low concentrations of naturally occurring soluble manganese might be useful to increase concentrations of hydrous manganese oxides. Direct addition of preformed hydrous manganese oxides may also be technically feasible and a relatively easily controlled approach to radium removal. In either strategy, filter runs are expected to decrease when a single filter is used to remove both iron and manganese precipitates. Length of filter run might, therefore, limit the utility of adding hydrous manganese oxides or manganous ion.

Radium removal using a regenerable sand filter has been demonstrated. While sorption to filter sand is believed an important mechanism, another is possibly involved. Significantly increased capacities are probably needed before use of a regenerable sand filter process could be generally recommended unless frequent rinsing with a dilute acid was acceptable. Further work is needed to better characterize the removal mechanisms, and to determine maximum possible removals and sorptive capacities. Studies should be conducted in a variety of waters and, in particular, its performance evaluated when operated to simultaneously remove both radium and iron flocs. Studies should also be conducted over much longer time periods than those used in this study. A trade-off between dilute acid strength and volume is expected to lead to a least-cost regeneration scheme. However, even with a 4 bed volume pH 1 daily regeneration scheme, acid costs to treat Oxford water are estimated to be \$0.12/1,000 gal (based on a cost of \$7/100 lb of sulfuric acid). Neutralization of the spent regenerant will probably be required before discharge but since pH control is probably not critical, an inexpensive system utilizing crushed limestone may be adequate. However, sludges may be produced that must be disposed of. Other anticipated costs are associated with possible modifications to make the sand filter resistant to damage by dilute acid.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-810575-01 by the University of Iowa, under the sponsorship of the U.S. Environmental Protection Agency.



**Figure 4.** Radium removal by freshly precipitated MnO<sub>2</sub> in Oxford water and 50% Oxford water. Ra = 32 pCi/L.



**Figure 5.** Radium removal by freshly precipitated (coproduced) iron and manganese oxides in Oxford water. Manganese oxides produced by addition of permanganate sufficient to oxidize 90% of the initial ferrous iron. Removal by 7.5 mg/L as Fe pure iron oxides shown for comparison. Ra = 32 pCi/L.

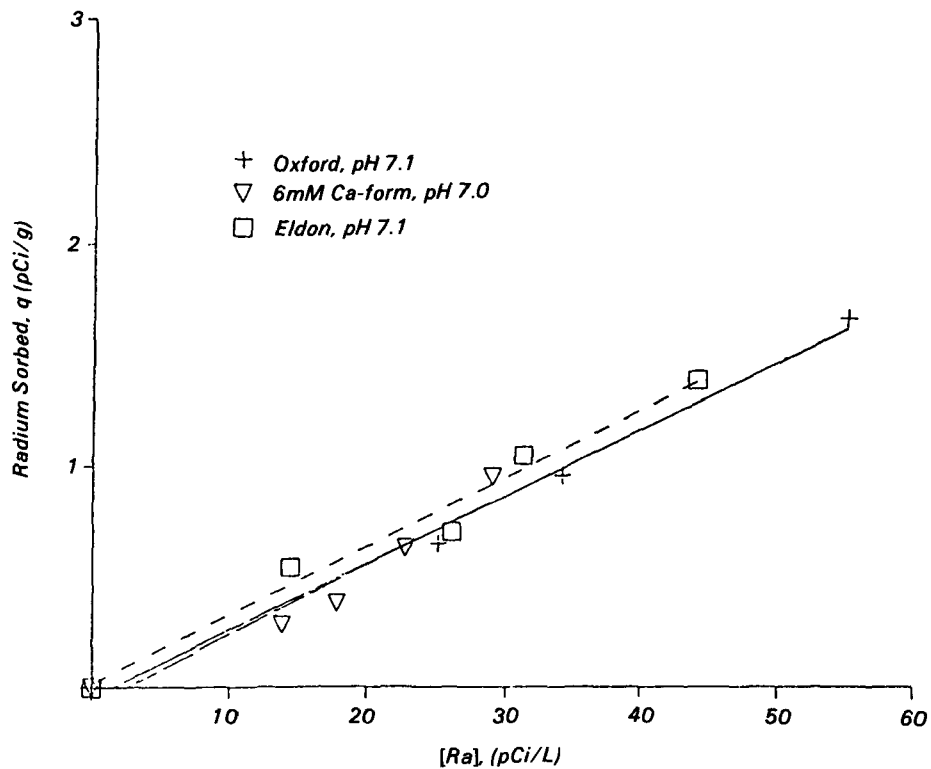
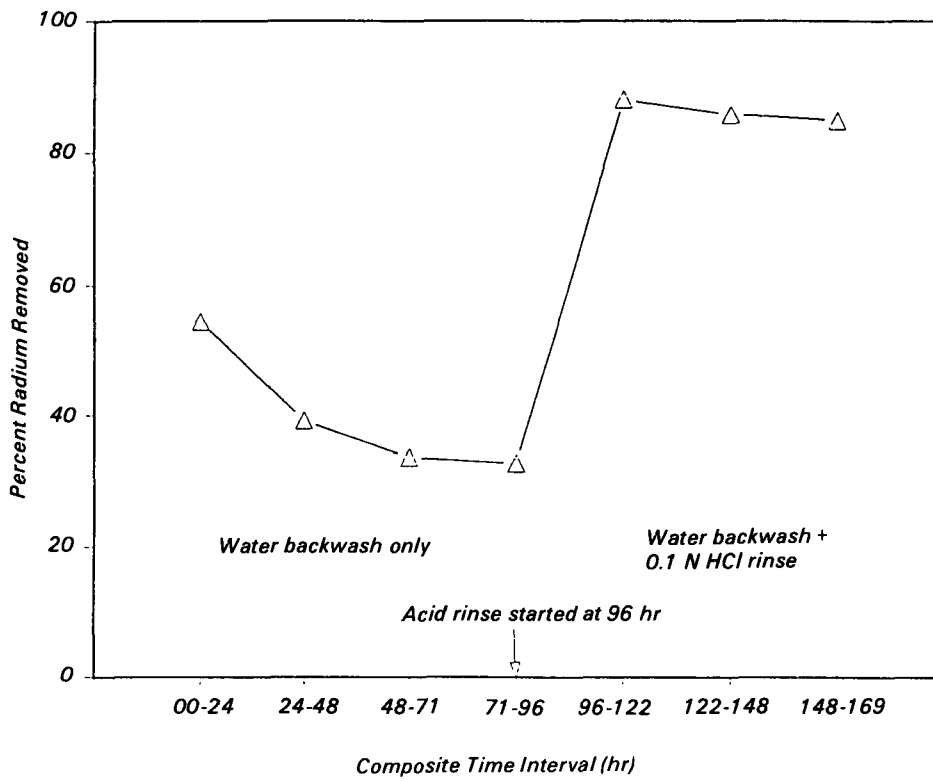


Figure 6. Comparison of  $^{226}\text{Ra}$  sorption isotherms (filter sand) as developed for Eldon (pH 7.1), Oxford (pH 7.1), and synthetic groundwater (pH 7.0) containing 6 mM calcium.

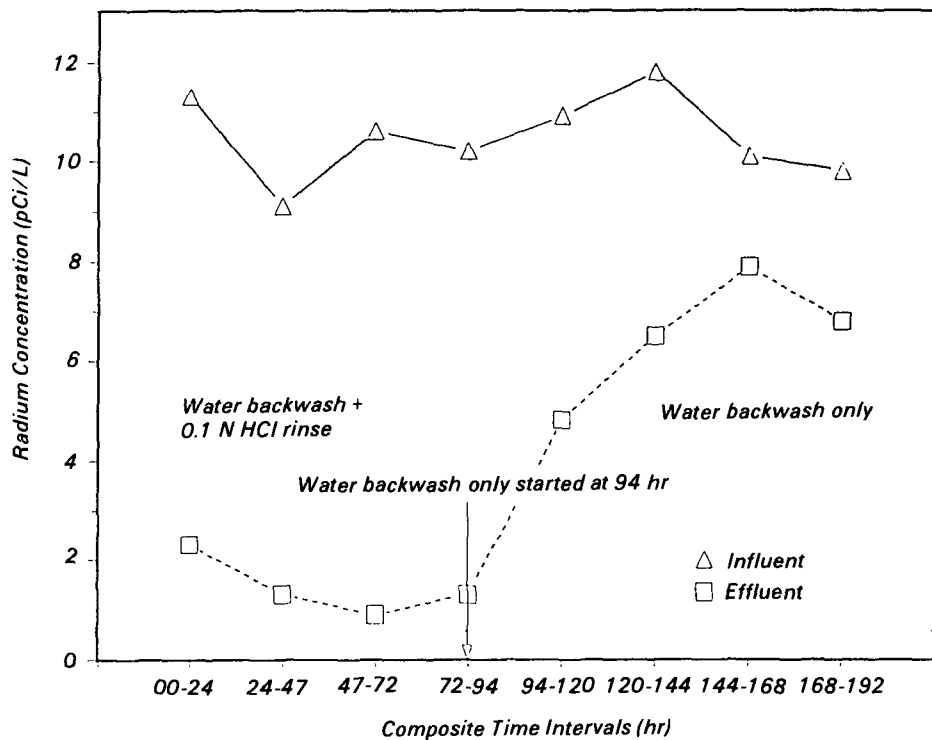
Table 1. Summary of Distribution Coefficients, Bed Volumes Treated and Run Durations

Water Type	pH	$K_d$ , L/g	$V_t/V_b$	$t_b$ , hr
Na-Form	7.0	0.240	384	104
Oxford	6.3	0.037	59	16
Oxford	7.1	0.027	43	12
Oxford	8.7	0.027	43	12
Eldon	7.1	0.031	50	13
Eldon	8.6	0.046	74	20
6 mM Ca	7.0	0.032	51	14
6 mM Ca + 6 mM Mg	8.7	0.026	42	11

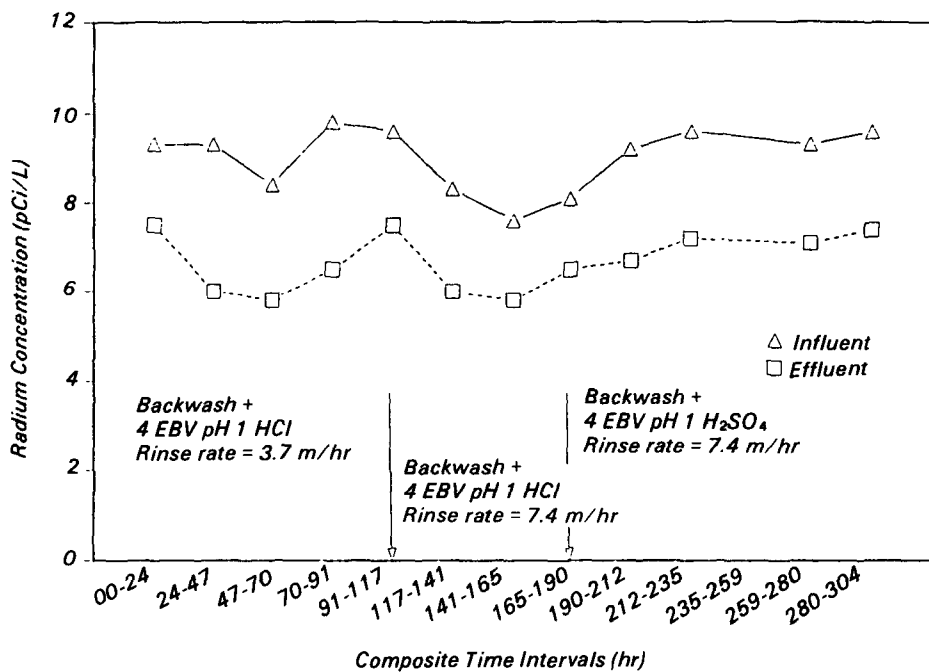


**Figure 7.** Percent of influent radium removed with and without daily pH 1 regeneration. Laboratory pilot plant experiment using an influent radium concentration of approximately 80 pCi/L. Fe = 2 mg/L. Total hardness  $\approx$  150 mg/L as CaCO<sub>3</sub>. Filter influent pH 7.5. Dilute acid regeneration scheme started after 96 hr.





**Figure 8.** Influent and effluent  $^{226}\text{Ra}$  concentrations from pilot studies at Oxford, IA. Existing filter effluent used as regenerable filter feed. Daily dilute acid regeneration terminated after 94 hr.



**Figure 9.** Influent and effluent  $^{226}\text{Ra}$  concentrations from pilot studies at Oxford, IA. Simultaneous iron and radium removal from existing aerator effluent.  $\text{Fe} = 0.5\text{--}1.0$  mg/L. Comparison of sulfuric and hydrochloric acid regeneration at two regenerant rinse rates.

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**Richard P. Lauch** is the EPA Project Officer (see below).

*The complete report, entitled "A Study of Possible Economical Ways of Removing Radium from Drinking Water," (Order No. PB 88-158 464/AS; Cost: \$19.95, subject to change) will be available only from:*

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