



## Project Summary

# Removing Radium from Water by Plain and Treated Activated Alumina

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This research determined the feasibility of using BaSO<sub>4</sub>-impregnated activated alumina and plain activated alumina for radium removal from groundwater by fixed-bed adsorption. The major factors influencing radium adsorption onto the two types of alumina were identified. The radium regenerability of the aluminas was also studied.

Good to excellent radium removals were obtained depending on the chemical composition of the feedwater. For example, BaSO<sub>4</sub>-impregnated alumina treated 25,000 bed volumes (BV) and plain alumina treated 14,000 BV of influent before radium maximum contaminant level (MCL) breakthrough.

The presence of sulfate ions in the feedwater enhanced and the presence of barium inhibited radium adsorption on both types of alumina. The water hardness significantly reduced radium removal by plain alumina although it had little effect on radium removal by BaSO<sub>4</sub>-impregnated alumina. The amount of BaSO<sub>4</sub> contained in the impregnated alumina correlated positively with radium adsorption.

When acid/base regeneration was employed, BaSO<sub>4</sub>-impregnated alumina was about 45% regenerable with respect to radium and plain alumina was about 70% to 95% regenerable. Excellent performance was obtained when using BaSO<sub>4</sub>-impregnated alumina to treat actual radium-contaminated groundwater in Lemont, IL, where 25,000 BV could be treated before the 5 pCi/L MCL was reached. The best performance with plain alumina was 12,000

BV when treating a Houston groundwater spiked with 23 pCi/L of radium.

*This Project Summary was developed by EPA's Risk Reduction Engineering 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

The ability of BaSO<sub>4</sub> precipitates to remove radium from solution has been known for more than 40 yr. Coprecipitation of RaSO<sub>4</sub> with BaSO<sub>4</sub> is the standard technique used to concentrate radium in analysis procedures for radium isotopes. The Dow Radium Selective Complexer (RSC) is an experimental adsorbent that makes good use of the knowledge that BaSO<sub>4</sub> scavenges radium from solution. With the RSC, BaSO<sub>4</sub> is impregnated into cation-exchange beads. The work reported here began with a similar idea, i.e., if BaSO<sub>4</sub> could be effectively precipitated within the pores of activated alumina, the resultant material would serve as a good, inorganic, radium-selective adsorbent. Activated alumina is known to have a good capacity for sulfate and, thus, was expected to be a good host for sulfate before the precipitation of BaSO<sub>4</sub>. Plain activated alumina was not expected to be a good adsorbent for radium but was tested for radium capacity in control experiments. In fact, a survey of the literature indicates that this is probably the first study done on the adsorption of radium onto alumina of any kind.

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BaSO<sub>4</sub>-impregnated alumina was prepared in several ways, both in this study and in field studies. The resultant alumina was used to remove radium by fixed-bed adsorption. Initial results indicated that not only did this material remove radium from spiked Houston tap water from a surface source, but that plain activated alumina, used for the control experiment, also gave good results. Further experimentation with BaSO<sub>4</sub>-impregnated alumina, plain alumina, and different types of feedwaters resulted in widely variable behavior in terms of radium removal. Very good radium removal was obtained with natural waters, whereas essentially no removal was obtained with synthetic waters. At this stage, we concluded that some constituent of the natural waters, not present in the synthetic waters, was responsible for the removal of radium and thus, initiated a study of the influence of pH, chloride, sulfate, and total organic carbon (TOC). A general objective of the lab studies with various waters was to explain how radium is removed from natural waters by BaSO<sub>4</sub>-impregnated alumina and plain alumina.

The effect of naturally occurring organics, measured as TOC, on radium adsorption was thoroughly investigated. We expected that some preferential association of the Ra<sup>2+</sup> ions with the predominantly negatively charged natural organics would exist. Organics were found to enhance radium removal, but not enough to explain the previously observed radium removal, with natural waters. When we again searched the literature to resolve the confusion generated by the experimental results, we found that RaSO<sub>4</sub> ion pairs tend to form in water when sulfate is present and that these uncharged species tend to be adsorbed on all surfaces, particularly glass.

Finally, in an effort to establish the regenerability of the aluminas, acid/base regenerations were attempted on radium-saturated samples of plain and of BaSO<sub>4</sub>-impregnated alumina.

When the experiments were finished, a statistical analysis of the data established the effect of independent variables such as pH, feed <sup>226</sup>Ra activity, and the background concentration of sulfate, barium, hardness, and TOC on the adsorption of radium onto both BaSO<sub>4</sub>-impregnated and plain alumina.

Thus, the major objectives of this study were:

1. to determine the effectiveness of BaSO<sub>4</sub>-impregnated alumina in removing radium from water by fixed-bed adsorption,

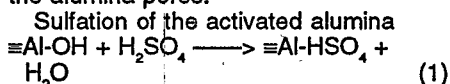
2. to determine the effectiveness of plain activated alumina in removing radium from water by fixed-bed adsorption, and to compare its radium removal performance with that obtained with BaSO<sub>4</sub>-impregnated alumina,
3. to identify the water quality factors influencing radium adsorption onto both BaSO<sub>4</sub>-impregnated and onto plain alumina,
4. to evaluate the regenerability of both BaSO<sub>4</sub>-impregnated and plain alumina, using acid and base, and finally
5. to develop a set of rules for choosing the proper alumina — BaSO<sub>4</sub>-impregnated or plain — to be applied to water to remove radium.

## Materials and Methods

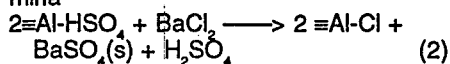
### Preparation of Barium-Sulfate-Impregnated Alumina

Alcoa F-1 activated alumina (28 x 48 mesh, i.e., 0.6 x 0.3 mm diameter) was used throughout the study. To utilize the well-known radium removal capacity of BaSO<sub>4</sub> as well as the large surface area present within the alumina, we attempted to impregnate BaSO<sub>4</sub> into the alumina. To achieve impregnation, sulfate was first adsorbed onto the alumina then BaSO<sub>4</sub> was precipitated within the alumina pores by adding excess barium in the form of BaCl<sub>2</sub>.

The following reaction sequence is proposed for impregnating barium sulfate into the alumina pores:



Precipitation of BaSO<sub>4</sub> in activated alumina



Before being studied in detail in these laboratory studies, BaSO<sub>4</sub>-impregnated alumina was prepared and used in the U.S. Environmental Protection Agency (EPA) funded, Lemont, IL, radium-removal field study (Clifford et al., J. AWWA, 90:94-104; July 1988). The BaSO<sub>4</sub>-loaded alumina was prepared in a 1-in.-diameter glass column by slowly rinsing a 30-in. deep bed of plain alumina with 10 BV of 0.25 N H<sub>2</sub>SO<sub>4</sub> followed by 10 BV of 0.25 N BaCl<sub>2</sub>. The column was extensively rinsed (40 BV) with reverse osmosis (RO) product water to eliminate BaSO<sub>4</sub>(s) fines. Radium adsorption tests with the BaSO<sub>4</sub>-loaded alumina were carried out in the

column used to prepare the medium. A control run with plain alumina was carried out in Lemont in a similar 1-in.-diameter column with a 20-in. depth of medium. A similar impregnation procedure was used for the laboratory experiments except that 0.5 N H<sub>2</sub>SO<sub>4</sub> and 1.0 N BaCl<sub>2</sub> were used. Normally, impregnations were carried out at 22° to 25°C and 1 atm pressure. Higher temperature (70°C), vacuum (25 mm Hg), and higher pressure (2 atm) techniques were, however, briefly experimented with.

### Minicolumn Experiments

To reduce the volume of radium-spiked water needed and to increase the number of column runs that could be completed, we used minicolumns of alumina containing approximately 5 cm<sup>3</sup> of medium. Numerous previous experiments over a period of six yr had shown that such columns could reliably be substituted for the larger (1-in.-diameter) columns normally used for adsorption experiments. The minicolumns used in this research were made of clear acrylic plastic, 10-in. (25.4 cm) long with an i.d. of 0.25 in. (6 mm).

The experimental minicolumn flow system consisted of a feed solution contained in a 13-gal (50 L) polyethylene carboy pumped first through a 5-μm, in-line membrane filter (with porous prefilter) and then through the minicolumn. Although pumping pressures less than 20 psig (138 kPa) were required, a Milton Roy Laboratory Data Control (model 396), high-pressure metering pump was used as the feed pump. Generally the flow rate through the 5 cm<sup>3</sup> of granular 28 x 48 mesh alumina was maintained at 1.5 mL/min for an empty bed contact time (EBCT) of 3.3 min.

The radium adsorption performance of a column run was determined by analyzing the feed and effluent for radium.

The <sup>226</sup>Ra isotope standard used in these experiments for spiking the feedwater, was calibrated and supplied by the EPA's Environmental Monitoring Systems Laboratory in Las Vegas, NV.

One focus of this study was to examine the effect of the presence of natural organics in feedwater on the removal of radium on alumina. The organics were isolated from Lake Houston water with the use of RO concentration, followed by size fractionation using ultrafiltration. The fractions had cut-off limits of 10,000 (10 K), 5,000 (5 K), and 1,000 (1 K), apparent molecular weight units (AMU). The 1 to 5 K and the 5 to 10 K fractions were used for the TOC spiking experiments because these relatively smaller molecules were expected to be at least partially adsorbed by the aluminas.

### Batch (Isotherm) Experiments

Activated alumina used in the batch isotherm experiments was ground and sieved to less than 250  $\mu\text{m}$  in diameter (100% passed through a U.S. Standard Sieve No. 60) to facilitate the kinetics of the adsorption process. The alumina was then transferred to five different bottles for pH adjustment with 1 N NaOH or 1 N HCl. This was done over a period of 2 days with continuous shaking and monitoring of pH. The water was decanted and the alumina dried in an oven overnight. The alumina was then exposed to the atmosphere for 6 hr to ensure that its weight was stable. pH adjustment of the water was extremely difficult because of the lack of buffer capacity in the deionized water; this insufficient buffering is why the equilibrium pHs were quite different from the initial pHs.

After 1-L polyethylene bottles were filled with the radium-spiked water and the chosen weight of activated alumina, they were placed in a heavy duty tumbler for 7 days for equilibration at 20° to 25°C. One set of bottles for determining one isotherm included a blank with no alumina, and five other bottles contained different chosen weights of pH-adjusted alumina. After the 7-day contact period, the suspension was filtered through a 0.45- $\mu\text{m}$  membrane filter before determining the equilibrium pH and  $^{226}\text{Ra}$  activity of the filtrate.

### Regeneration Experiments

The spent alumina columns were regenerated with 0.5 N HCl followed by 0.25 N NaOH solutions. The runs had a total acid contact time of 45 min and a total base contact time of 60 min. Each regeneration effluent bed volume was collected separately with the use of a fraction collector. Eventually, the samples were analyzed for pH,  $^{226}\text{Ra}$ , and TOC.

### Chemical Analysis

All  $^{226}\text{Ra}$  activity measurements in this study were done by the EPA Method 900.1 (gross radium alpha screening procedure for drinking water) described in "Prescribed Procedures for the Measurements of Radioactivity in Drinking Water" (EPA-600/4-80/032, August 1980).

Because we know this method can produce falsely high  $^{226}\text{Ra}$  results when unwanted short-lived alpha emitters are present, we avoided the problem by waiting typically 21 days to count the samples. With proper allowances for the decay of short-lived radionuclides, the precision of the Method 900.1 analyses for  $^{226}\text{Ra}$  was  $\pm 6\%$  relative standard deviation.

A Perkin-Elmer Model 5500 Inductively Coupled Plasma Spectrometer was used to analyze for barium, calcium, and magnesium.

A Dionex ion chromatograph measured sulfate concentration and a Dohrmann (Model DC-80) ultra-low-level TOC analyzer measured TOC.

The  $\text{BaSO}_4$  loading on the  $\text{BaSO}_4$ -impregnated alumina was analyzed with the use of a hot alkaline tetra sodium ethylenediamine tetraacetate (EDTA) extraction procedure followed by measurement of barium in the extract with the use of the ICP. This procedure was developed specifically for this research because of the failure of the usual acid digestion procedures to dissolve the  $\text{BaSO}_4$ -impregnated alumina.

The City of Houston, Water Quality Control Branch, Laboratory Section provided complete chemical analysis of the Houston surface water used in these experiments.

## Results and Discussion

### Lemont Field Study Results

The performance of plain alumina used to treat the Lemont water was unexpectedly good (Figure 1). Based on published information regarding the poor adsorption of alkaline-earth cations at pH 7.2 (the Lemont water pH), we did not expect any significant radium removal beyond a few hundred bed volumes. Nevertheless, we found that about 3400 BV could be treated before radium reached its MCL (which corresponded to 3.25 pCi/L  $^{226}\text{Ra}$  and 1.75 pCi/L  $^{228}\text{Ra}$  for a total of 5 pCi/L). By way of explanation, we can only state that no previous work has been published on radium adsorption onto activated alumina and apparently published work on mg/L levels of barium adsorption cannot be extrapolated to pg/L levels of radium adsorption.

Although plain alumina performed better than expected,  $\text{BaSO}_4$ -impregnated alumina was outstanding by comparison — 27,500 BV to the radium MCL (Figure 1). Also apparent in Figure 1 is improved radium removal performance following periods of flow interruption (15 days and 7 days). This suggests that intermittent operation of the alumina column would yield higher radium loading and lower radium concentration in the effluent. This is because stopping the flow to the column allows relaxation of the radium concentration gradient in the solid phase, which, upon restarting the flow, results in a greater liquid-solid concentration gradient and,

consequently, a higher radium flux into the alumina granules.

### Minicolumn Results with Radium-Spiked Waters

The minicolumn runs in the laboratory with three different feedwaters provided some hard-to-interpret results. Unlike the Lemont results,  $^{226}\text{Ra}$ -spiked Houston groundwater produced similar performances for both plain and  $\text{BaSO}_4$ -impregnated aluminas. The plain alumina (12,000 BV) performed somewhat better than did the  $\text{BaSO}_4$ -loaded variety (10,000 BV) (Figure 2). The difference in alumina performance between the Lemont and Houston groundwaters is probably due to pH. Plain alumina, as expected, performed better when the pH was increased to 7.6 to 8.2 compared with the 7.2 pH of the Lemont water. This agrees with the general observation that adsorption of cations onto alumina increases as pH increases.

The lower sulfate concentration (17 mg/L) of the Houston groundwater, compared with that of the Lemont water (80 mg/L), may also have contributed to the poorer performance of the  $\text{BaSO}_4$ -impregnated alumina. For, as we found later, sulfate concentration is a major factor in radium adsorption onto both types of alumina.

The performance of both types of alumina on the  $^{226}\text{Ra}$ -spiked synthetic water was dramatically different than the performance on the Lemont and Houston groundwaters. We found nearly immediate breakthrough (500 BV) of radium with the pH 7.5 to 8.0 synthetic water containing a relatively high concentration of barium (0.9 mg/L) and no sulfate. The poor performance of the aluminas was attributed mainly to the high level of barium, an alkaline earth cation similar to radium in chemical behavior.

The performance of the aluminas on  $^{226}\text{Ra}$ -spiked Houston surface water was, again, different from that on the groundwaters and the synthetic water. The plain and  $\text{BaSO}_4$ -impregnated aluminas behaved similarly: the MCL was reached at about 2,000 BV when the feedwater contained 50 pCi/L of  $^{226}\text{Ra}$ . The relatively good performance of the plain alumina was thought to be due to the surface water's 5 mg/L TOC, which was suspected of complexing the radium before being adsorbed by the alumina. For this reason, additional minicolumn tests were performed in which natural organic matter TOC was added to resolve the issue. When 4 mg/L TOC was added to Lemont groundwater during a minicolumn test, no improvement in radium removal was ob-

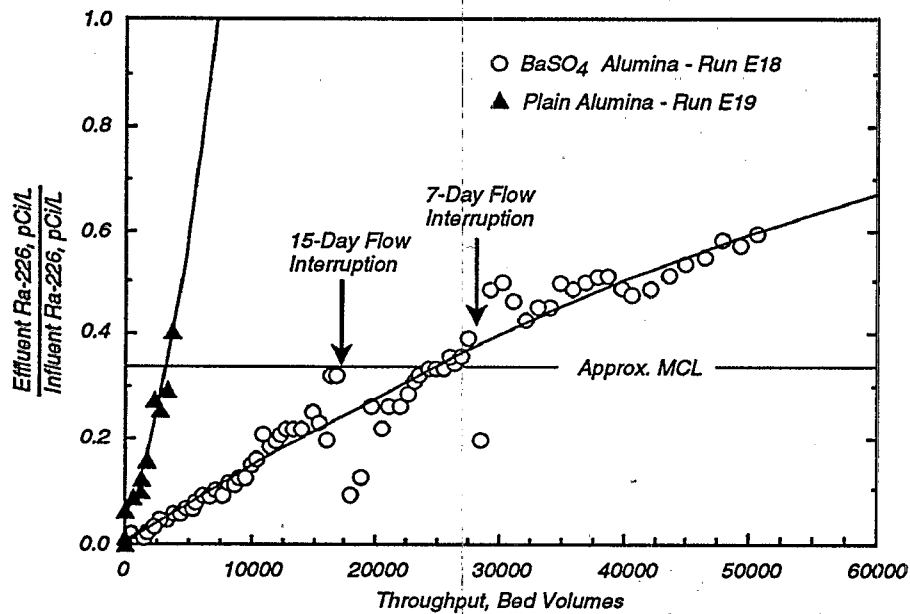


Figure 1. Radium removal from Lemont, IL groundwater by plain (0.5 L) and pressure-impregnated (0.23 L) BaSO<sub>4</sub> alumina columns. Average influent SO<sub>4</sub><sup>2-</sup> = 80 mg/L; TOC = 0.7 mg/L; Ba<sup>2+</sup> = 0.2 mg/L; total radium = 15 pCi/L; and EBCT = 3 min. 20,000 BV corresponds to a 42 - day run length at 3 min EBCT.

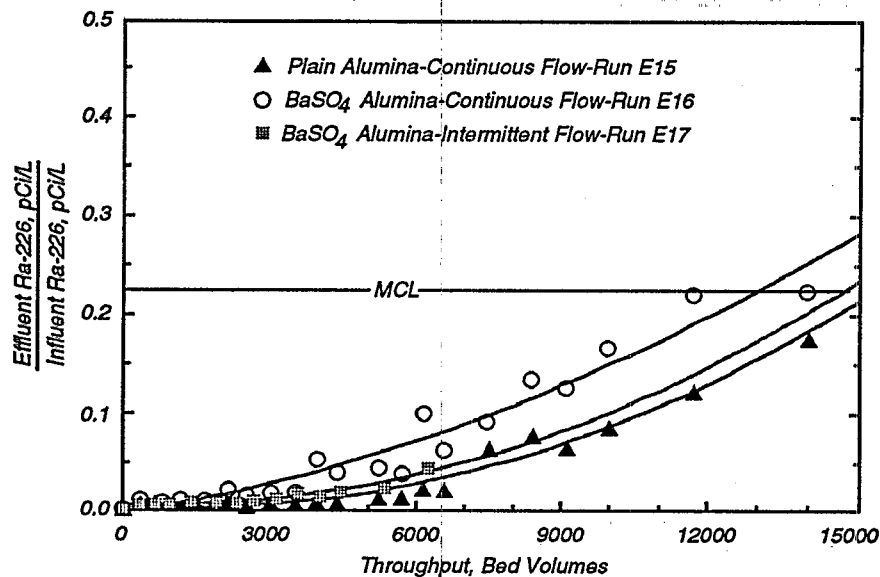


Figure 2. Radium removal from Ra - 226 - spiked Houston groundwater by vacuum impregnated BaSO<sub>4</sub> alumina — continuous and intermittent flow. Average influent SO<sub>4</sub><sup>2-</sup> = 17 mg/L; TOC = 0.6 mg/L; Ba<sup>2+</sup> ≤ 0.02 mg/L; average influent Ra-226 = 23 pCi/L; feed and effluent pH = 7.6 to 8.2; BV = 5.2 mL; and EBCT = 3.3 min. 12,000 BV corresponds to a 28-day run length at 3.3 min EBCT.

served. Thus, the influence of TOC was not as significant as suspected.

### Statistical Evaluation of Results

Because of the number of variables involved, the results obtained with column experiments were statistically analyzed. The objective was to establish the effects of the independent variables, including pH, feed  $^{226}\text{Ra}$  activity, sulfate, barium, hardness, and TOC concentrations, on the adsorption of radium onto both  $\text{BaSO}_4$ -impregnated and plain alumina.

The analysis was done by means of a correlation matrix in which an attempt was made to correlate the dependent variable, pCi/g radium loading, with the independent variables just mentioned.

Table 1 summarizes the effects of the various independent variables on the radium loadings obtained onto both  $\text{BaSO}_4$ -impregnated alumina and plain alumina.

### Batch Isotherm Studies

The radium isotherm studies were done after the column experiments in an attempt to obtain a better understanding of the effects of pH and sulfate concentration on radium removal by plain alumina.

The initial isotherm tests with synthetic water of variable radium activity were conducted in glass bottles to determine the effect of pH on radium removal. In these tests, we observed significant radium adsorption onto the glass. After correcting for the influence of radium adsorption onto the glass, it was clear that, as expected, the higher the pH the greater the radium adsorption. For example, as pH was increased from 6.8 to 7.9, the radium loading on plain alumina in equilibrium with 5 pCi/L  $^{226}\text{Ra}$  increased from 100 to 350 pCi/g.

The results of the second set of isotherms designed to determine the influence of sulfate versus chloride as background anions are shown in Figure 3. Polyethylene bottles were used in these tests to overcome the problems caused by radium adsorption onto glass. Obviously, the presence of sulfate dramatically increased the adsorption of radium onto plain alumina. At 5 pCi/L in the water, the increase in solid phase radium loading is approximately four-fold. This verifies the conclusion from the column studies regarding the importance of sulfate.

The mechanism of improved radium uptake is thought to be one of enhanced adsorption of neutral  $\text{RaSOS}(\frac{0}{2})$  ion pairs — the mechanism presumed to be responsible for enhanced radium adsorption onto glass.

### Barium in the Column Effluent

There was concern about barium leaking from the  $\text{BaSO}_4$ -impregnated alumina because a drinking water MCL of 2 mg/L exists for barium. Thus, the column effluents from the Lemont field study and the lab study were checked for increased barium. In both the field and lab study, an increased effluent barium level of approximately 0.2 mg/L was found. This was not considered serious because it is so far below the existing 2 mg/L and proposed 5 mg/L MCLs.

### Acid/Base Regeneration of Alumina

Figure 4 presents the data from the regeneration of the plain and  $\text{BaSO}_4$ -impregnated alumina columns, which had adsorbed approximately equal amounts of radium. Clearly, the plain alumina is better regenerated in terms of radium elution

than is  $\text{BaSO}_4$ -impregnated alumina, probably because of the difference in the mechanism of adsorption onto the two types of alumina. The hypothesis is that the major mechanisms of removal of  $^{226}\text{Ra}$  onto plain alumina include the adsorption of  $\text{RaSOS}(\frac{0}{2})$  ion pairs,  $\text{Ra}^{2+}$ -organic ligand complexes, and  $\text{Ra}^{2+}$  ions. The removal of radium by  $\text{BaSO}_4$ -impregnated alumina is mainly because  $\text{Ra}^{2+}$  ions are incorporated into the  $\text{BaSO}_4$  crystals. While  $\text{BaSO}_4$  is being impregnated into the alumina, a fraction of the plain alumina adsorption sites presumably remains unaffected. Therefore, removal of radium onto  $\text{BaSO}_4$ -impregnated alumina also takes place by all the mechanisms mentioned above for plain alumina. The removal of radium by plain alumina is a surface phenomenon, whereas the incorporation of radium into the matrix of  $\text{BaSO}_4$  crystals can proceed beneath the surface. Therefore, one can expect radium to be desorbable, either by displacement or by dissolution of the various radium species, during the acid/base regeneration of plain alumina. In the case of the  $\text{BaSO}_4$ -impregnated alumina, complete radium desorption can only occur when the  $\text{BaSO}_4$  dissolves, which is difficult to achieve because of its low solubility. Removal of radium can also occur by the slow diffusion of radium out of the  $\text{Ba}(\text{Ra})\text{SO}_4$  matrix.

Another noticeable difference between the regeneration of plain and  $\text{BaSO}_4$ -impregnated alumina is that, whereas all of the  $^{226}\text{Ra}$  comes off during the acid regeneration in the case of the plain alumina, a significant amount of  $^{226}\text{Ra}$  also comes off during the base regeneration in the case of the  $\text{BaSO}_4$ -impregnated alumina. This can be explained on the basis of slower desorption of radium that has been incorporated into the  $\text{BaSO}_4$  crystals. Mass balances on radium indicate about 95% regenerability of plain alumina and about 45% regenerability of  $\text{BaSO}_4$ -impregnated alumina under the rather exhaustive regenerant conditions tested.

### Conclusions

1. Adsorption onto both  $\text{BaSO}_4$ -impregnated alumina and plain alumina are technologically attractive means to remove radium from small-community water supplies, as demonstrated by the long column runs and the high radium loadings obtained in field and laboratory studies. Radium loadings of 380 pCi/gm for the  $\text{BaSO}_4$ -impregnated alumina and 280 pCi/gm for plain alumina were obtained with typical

Table 1. Summary of the Effects\* of Various Independent Variables on the Adsorption of Radium onto  $\text{BaSO}_4$  - Impregnated and Plain Alumina

Variable	$\text{BaSO}_4$ - Impregnated Alumina	Plain Alumina
Feed hardness content	0	--
Feed sulfate concentration	++	++
Feed barium concentration	--	--
Amount $\text{BaSO}_4$ loaded	++	N/A
Feed $^{226}\text{Ra}$ activity	++	++
Feed TOC concentration	+	+
Feed pH	+	+

\* The effects of the independent variables on  $^{226}\text{Ra}$  loading were judged as significant when R-squared was > 0.1, and F - statistic was > 1.0.

++ Causes very significant increase in radium adsorption.

+ Causes significant increase in radium adsorption.

-- Causes very significant decrease in radium adsorption.

0 Not significant.

N/A Not applicable.

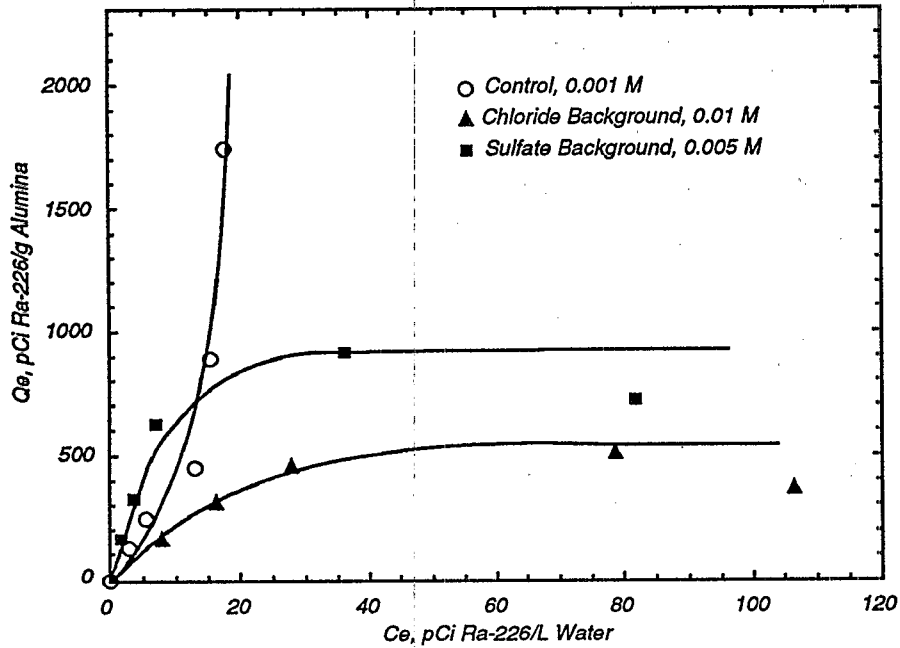


Figure 3. Isotherms for the adsorption of Ra-226 onto activated alumina — ionic composition study. Polyethylene bottles were used. Equilibrium time was 7 days and the pH was 6.77.

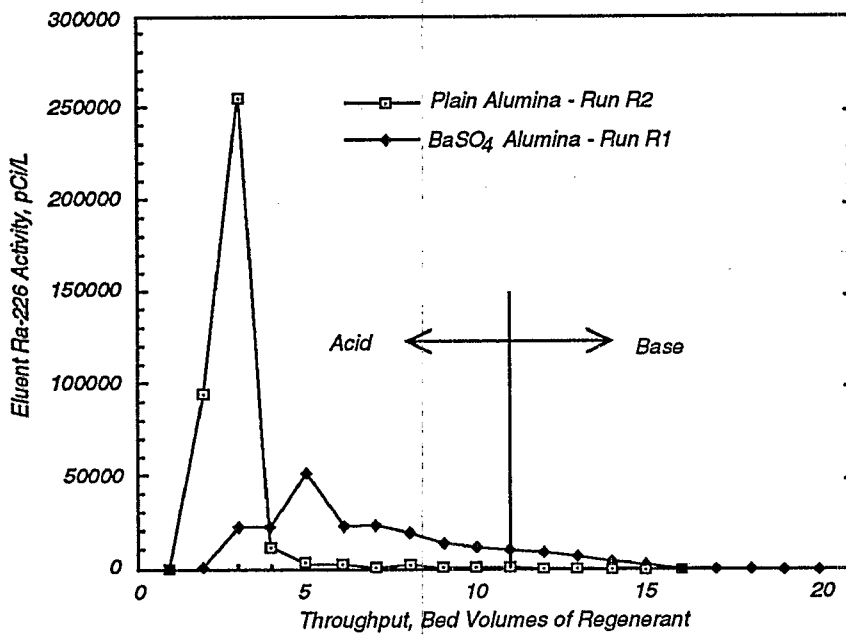


Figure 4. Regeneration of plain and  $BaSO_4$  alumina columns exhausted with Ra-226 spiked Houston surface water. Acid regeneration EBCT = 4.5 min; base regeneration EBCT = 6 min; and regenerant = 11 BV 0.5 N HCl followed by 9 BV 0.25 N NaOH.

groundwaters containing about 12 pCi/L of radium.

2. For the Lemont groundwater with a total radium activity of 18 pCi/L, radium MCL breakthrough was reached at approximately 25,000 BV for the fixed-bed process of adsorption with BaSO<sub>4</sub>-impregnated alumina. With plain alumina, radium MCL breakthrough was reached with a run length of 12,000 BV with a 23 pCi/L radium-spiked Houston groundwater.
3. The presence of hardness inhibits radium removal onto plain alumina through direct competition for adsorption sites by calcium and magnesium. Hardness, in the range found in groundwaters, however, did not greatly influence radium removal by BaSO<sub>4</sub>-impregnated alumina because the major mechanism of radium adsorption onto BaSO<sub>4</sub>-impregnated alumina seemed to be the selective exchange of Ra<sup>2+</sup> for Ba<sup>2+</sup> ions.
4. The presence of sulfate in waters enhances radium removal onto both types of alumina probably through the formation of RaSO<sub>4</sub><sup>0</sup> ion pairs. In batch experiments with plain alumina, for an equilibrium <sup>226</sup>Ra activity of 5 pCi/L, approximately 450 pCi/gm <sup>226</sup>Ra loading was obtained from a sulfate background water; 100 pCi/gm was obtained from a chloride background water. In the case of the BaSO<sub>4</sub>-impregnated alumina, the influence of sulfate ions was not experimentally verified by batch experiments. A high, positive correlation was, however, obtained between feed sulfate concentration and the <sup>226</sup>Ra loading obtained with column experiments.
5. The presence of barium in feedwaters inhibits radium removal onto both BaSO<sub>4</sub>-impregnated alumina and plain alumina because of the chemical similarities of barium and radium and the direct competition for adsorption sites.
6. Some components of natural organics present in feedwaters increase radium removal onto alumina. This was experimentally verified with plain alumina. The components that enhance radium removal, however, were not identified in this study. The influence of organics on radium removal by BaSO<sub>4</sub>-impregnated alumina was

not clear, although a small positive correlation was obtained between feed TOC concentration and the <sup>226</sup>Ra loading obtained with column experiments using BaSO<sub>4</sub>-impregnated alumina.

7. Adsorption of Ra<sup>2+</sup> ions onto plain alumina increases with an increase in pH. Because the number of negatively charged sites (AlO<sup>-</sup>) on activated alumina increased with pH, the positively charged Ra<sup>2+</sup> ions were, presumably, better adsorbed.
8. Radium removal on BaSO<sub>4</sub>-impregnated alumina is a direct function of the amount of BaSO<sub>4</sub> loaded into the alumina matrix.
9. BaSO<sub>4</sub>-impregnated alumina used to adsorb radium is only about 45% to 50% regenerable by acid/base regeneration. This is because BaSO<sub>4</sub>-impregnated alumina was mainly regenerated by extracting radium from the highly insoluble BaSO<sub>4</sub> crystals; however, plain alumina was regenerated by displacing radium from the alumina surface.
10. Plain alumina used to adsorb radium is about 70% to 95% regenerable through acid/base regeneration. The regeneration efficiencies of plain alumina depended mainly on the characteristics (barium and TOC concentration) of the feedwater to which the alumina had been exposed. The presence of barium in the feedwater caused a decrease in regeneration efficiencies because of the coprecipitation of radium with BaSO<sub>4</sub>. The presence of TOC caused part of the <sup>226</sup>Ra to come off during the base regeneration.
11. The performance of BaSO<sub>4</sub>-impregnated alumina or the plain alumina depends on the water chemistry; which is the better to use can be decided after an in-depth evaluation of the water chemistry of the water supply in question. Clearly, the BaSO<sub>4</sub>-impregnated alumina performed better with high-hardness waters (≥ 250 mg/L as CaCO<sub>3</sub>), whereas plain alumina performed equally well or better with low-hardness waters (< 100 mg/L).
12. In light of the above conclusions, BaSO<sub>4</sub>-impregnated alumina seems to be a good candidate for the radium decontamination of ion-exchange regeneration brine solutions

or other brackish waters. (More work, however, needs to be done on the effects of calcium and barium on radium adsorption in brines.) Plain alumina is probably a better choice to remove radium from low-hardness well waters, containing > 40 mg/L sulfate, particularly if the regenerability of the alumina is required.

## Recommendations

More work is needed to optimize the preparation of BaSO<sub>4</sub>-impregnated alumina. The radium loading capacity of the BaSO<sub>4</sub>-impregnated alumina is directly related to the amount of BaSO<sub>4</sub> loaded into its matrix. Industrial-scale manufacture of this material will be possible only after the impregnation process is optimized on a laboratory-scale.

Laboratory and field studies should be done to determine the feasibility of using the BaSO<sub>4</sub>-impregnated alumina to decontaminate spent ion-exchange brine before its reuse in processes that would selectively remove radium without softening. Such processes would (a) not introduce sodium into the product water, (b) not use any salt for regenerant, and (c) not produce a brine to be disposed of into the sanitary sewer. They would, however, produce a spent adsorbent media for ultimate disposal.

More work is needed to clearly identify the role of metal-ligand complexation on the adsorption of metal ions onto iron-oxides as it pertains to the radium-alumina system. The role of natural organics is especially important, and a clear understanding of their influence on radium adsorption as related to the molecular size and component constitution is necessary.

The regeneration of both BaSO<sub>4</sub>-impregnated and plain alumina should be further studied using acid and base regenerations. The primary objectives should be to determine (a) the various desorption mechanisms involved, (b) the usefulness of the regenerated media, (c) the maximum possible concentrations of radium in the spent regenerants, and (d) the possible means of final disposal of radium-contaminated spent regenerant wastewaters.

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*The complete report, entitled "Removing Radium from Water by Barium Sulfate - Impregnated Activated Alumina," (Order No. PB92-164 789/AS; Cost: \$19.00; subject to change) will be available only from:*

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