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**ACTINIDE REMOVAL FROM AQUEOUS SOLUTION  
WITH ACTIVATED MAGNETITE**

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## ACTINIDE REMOVAL FROM AQUEOUS SOLUTION WITH ACTIVATED MAGNETITE

*Robert L. Kochen*

### ABSTRACT

An actinide aqueous waste treatment process using activated magnetite has been developed at Rocky Flats. The use and effectiveness of various magnetites in lowering actinide concentrations in aqueous solution are described. Experiments indicate that magnetite particle size and pretreatment (activation) of the magnetite surface with hydroxyl ions greatly influence the effective use of magnetite as an actinide adsorbent. With respect to actinide removal,  $\text{Ba}(\text{OH})_2$ -activated magnetite was more effective over a broader pH range than was  $\text{NaOH}$ -activated magnetite. About 50% less  $\text{Ba}(\text{OH})_2$ -activated magnetite was required to lower plutonium concentration from  $10^{-4}$  to  $10^{-8}$  g/l.

### INTRODUCTION

The effectiveness of ferrite (magnetite) treatment for actinide removal from Rocky Flats aqueous process waste has been investigated and demonstrated successfully in the laboratory. These ferrite treatment techniques include batch methods<sup>1</sup> as well as continuous methods in which ferrite is added in one or more treatment steps.<sup>2-4</sup> Plutonium concentrations were consistently reduced from  $10^{-4}$  to  $10^{-8}$  g/l or lower. Also, based on laboratory results, solid by-product waste generation was reduced by as much as 80% compared to existing plant operations employing hydroxide precipitation. The use of a ferrite process as an alternative to the existing hydroxide precipitation process is attractive since it reduces reagent handling.

With the preformed ferrite technique, iron ferrite ( $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ) is prepared by adding sodium hydroxide solution to a solution of ferrous sulfate and ferric sulfate. The resulting ferrite slurry is then added to the process aqueous waste to effect actinide removal. This method required 5.0 parts

reagent to produce 1.0 part ferrite with the remainder being 2.4 parts sodium sulfate and 1.6 parts water.<sup>3</sup> The sodium sulfate was ultimately discharged as low-level salt waste, and the water was evaporated. Also, the solubility of sodium sulfate limits the concentration of ferrite slurries that can be prepared.

Other possibilities for improving the preformed ferrite addition technique also were investigated. One of these involves the synthesis of ferrite using air oxidation of ferrous hydroxide slurries under various conditions.<sup>5</sup> Ferrite formed by the oxidative technique was comparable to preformed ferrite in removing actinides from waste solutions. However, ferrite formed by this method still requires preparing ferrous hydroxide slurries from ferrous sulfate and sodium hydroxide reagents. Also, reaction time for ferrite formation varies with volume and depth of slurry as well as contact time between air and slurry. Overall, this method requires 4.7 parts reagent (0.07 part oxygen included) to produce 1.0 part ferrite with the remainder being 1.8 parts sodium sulfate and 1.9 parts water. Again, the sodium sulfate would ultimately be discharged as low-level salt waste.

Another method involves the use of commercially available ferrite (magnetite) that has been activated with either sodium hydroxide<sup>6</sup> or barium hydroxide. Activated commercial magnetite offers a more simplified waste treatment method compared with the preparation of preformed ferrite. Also, there are no by-products generated (e.g., sodium sulfate from the synthesis of preformed ferrite) that would eventually be discharged as low-level salt waste. In this study, four different sources of commercial magnetite are activated and evaluated for actinide removal from aqueous solutions.



## EXPERIMENTAL

### Commercial Magnetite Experiments

Several parameters were varied to examine the effects on actinide removal from aqueous solution with commercial magnetite. These parameters involved the use of four magnetites, wet and dry magnetite, distilled and process water, two activating agents, pH, and magnetite concentration. The magnetites were: Type BK-5599 from Pfizer, Inc., a technical grade magnetite from Sargent-Welch, a purified magnetite from Fisher Scientific, and a refined magnetite ore from Eriez Magnetics of Erie, Pennsylvania.

All actinide solutions consisted of plutonium nitrate [ $\text{Pu}(\text{NO}_3)_4$ ] and americium chloride ( $\text{AmCl}_3$ ). Sodium hydroxide ( $\text{NaOH}$ ) was used to adjust actinide pH values. Unless otherwise noted, distilled water and reagent-grade chemicals were used in the experiments. Process water is defined as treated domestic water that has passed through a Backflow Preventer. All of the experiments were done in a 250-mL beaker at ambient temperature with stirring rates of 200 rpm.

Four groups of actinide removal experiments were conducted with the four commercial magnetites. In the first group, each of the four magnetites (0.1 g each) was equilibrated with 13 mL of 0.02M barium hydroxide [ $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ] (prepared in both distilled and process water, pH 12.7) by stirring (200 rpm) for ten minutes at ambient temperature. The second and third group of experiments were handled in a similar manner, except each of the four magnetites (0.1 g each) was equilibrated with 13 mL of 0.05M  $\text{NaOH}$  (pH 12.7) prepared with both distilled and process water. In the fourth group of experiments, the four magnetites (0.1 g each) were equilibrated 24 hours with 13 mL of 0.05M  $\text{NaOH}$  (pH 12.7) prepared with process water.

After equilibration, the solution from each magnetite solid was decanted. Next, a 50-mL aliquot of actinide solution ( $1.0 \times 10^{-4}$  g/L plutonium and  $1.4 \times 10^{-6}$  g/L americium) at pH 12.0 was added to each equilibrated magnetite solid. These mixtures were stirred (200 rpm) for ten minutes at ambient temperature.

All of the supernatant liquids were then decanted from the magnetite solids and passed at 10 mL/min through a glass column (2.0 cm i.d. by 25 cm) packed with a 10-cm plug of fine No. 431 stainless steel wool. During this procedure, the column was placed between the pole faces of an ANAC Model 3470 laboratory electromagnet (Figure 1), and a field strength of 2000 Gauss was applied.

After each experiment, the stainless steel filled glass column was cleaned for repeated use. This was done by back flushing the column with 20 mL of water. Next, the column was washed with 20 mL of concentrated  $\text{HNO}_3$ , rinsed with 40 mL of water, rinsed with 20 mL of 0.2M  $\text{NaOH}$ , and again rinsed with 20 mL of distilled water.

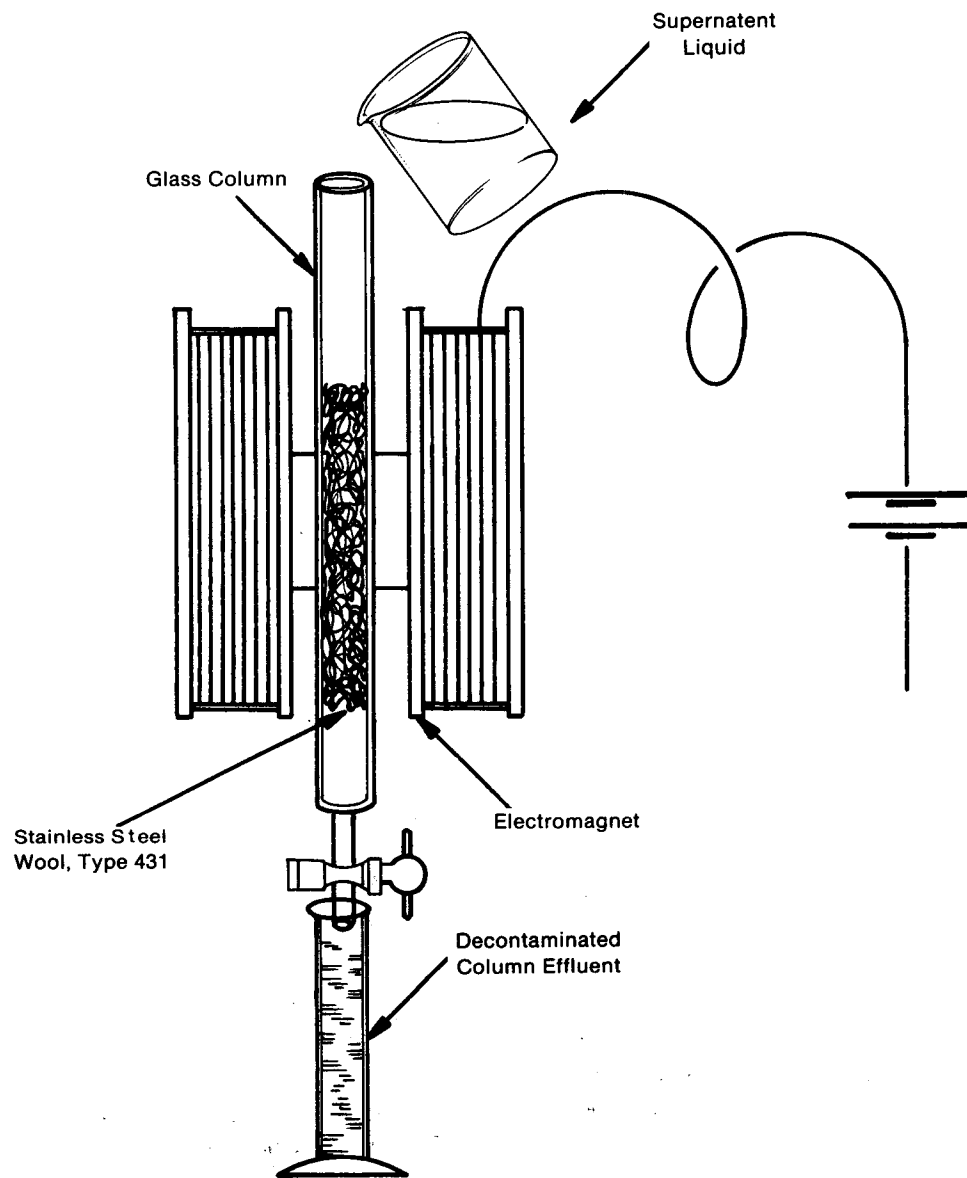
### Wet and Dry Magnetite Experiments

Pfizer magnetite (BK-5599), in both wet and dry form, was evaluated for actinide removal from aqueous solution. The wet magnetite was prepared by adding 13 mL of 0.02M barium hydroxide (pH 12.7), 13 mL of  $1 \times 10^{-6}$  M sodium hydroxide (pH 8.0), 13 mL of 0.05M sodium hydroxide (pH 12.7), and 13 mL of actinide solution ( $1.0 \times 10^{-4}$  g/L plutonium and  $1.4 \times 10^{-6}$  g/L americium) at pH 12.7 ( $\text{NaOH}$ ) to dry magnetite samples (0.1 g each). Process water was used to prepare the solutions. Each of these samples was then equilibrated by stirring (200 rpm) for ten minutes at ambient temperature.

After equilibration, the solution from each magnetite solid was decanted. Next, a 50-mL aliquot of actinide solution ( $1.0 \times 10^{-4}$  g/L plutonium and  $1.4 \times 10^{-6}$  g/L americium) at pH 12.0 was added to each wet, equilibrated magnetite solid. A similar 50-mL aliquot of the actinide solution was also added to a dry BK-5599 sample (0.1 g).

These mixtures were then stirred (200 rpm) for ten minutes at ambient temperature. All of the supernatant liquids were then decanted from the magnetite solids and passed through the glass column described previously.

FIGURE 1. Magnetic Separation Apparatus



### Barium Hydroxide Experiments

Six samples of Pfizer magnetite (BK-5599) were conditioned with six different concentrations of barium hydroxide solution. This was done by adding 13 ml of 0.0075, 0.01, 0.0125, 0.015, 0.02, and 0.05 molar barium hydroxide (prepared with distilled water) to six 0.1-g samples of the magnetite. Each of these samples was then equilibrated by gentle stirring (200 rpm) for ten minutes at ambient temperature.

After equilibration, the solution from each magnetite solid was decanted. Next, a 50-ml aliquot of actinide solution ( $1.0 \times 10^{-4}$  g/l plutonium and  $1.4 \times 10^{-6}$  g/l americium) at pH 12.0 was added to each equilibrated magnetite solid. Again, these mixtures were stirred (200 rpm) for ten minutes at ambient temperature. All of the supernatant liquids were then decanted from the magnetite solids and passed through the glass column described previously.

### pH Experiments

Three groups of experiments were conducted with Pfizer magnetite (BK-5599) to remove plutonium and americium from aqueous solutions at various pH values. The pH values of the actinide solutions were 11.0, 11.5, 12.0, 12.5, 13.0, and 13.5.

In the first group of experiments, six magnetite samples (0.1 g each) were equilibrated with 13 ml of 0.02M barium hydroxide solution (pH 12.7) by stirring (200 rpm) for ten minutes at ambient temperature. Similarly, groups two and three (six 0.1-g samples per group) were equilibrated with 13 ml of  $1.0 \times 10^{-6}$  M NaOH solution (pH 8.0) and 13 ml of 0.05M NaOH solution (pH 12.7), respectively. In all three cases, the solutions were prepared with process water.

After equilibration, the solution from each magnetite solid was decanted. Next, six 50-ml aliquots of actinide solution ( $1.0 \times 10^{-4}$  g/l plutonium and  $1.4 \times 10^{-6}$  g/l americium), with pH values of 11.0, 11.5, 12.0, 12.5, 13.0, and 13.5, were added to each group of the equilibrated magnetite solids. Again, these mixtures were stirred

(200 rpm) for ten minutes at ambient temperature. All of the supernatant liquids were then decanted from the magnetite solids and passed through the glass column as described previously.

### Magnetite Concentration Experiments

Three groups of experiments were conducted to evaluate plutonium and americium removal with various amounts of Pfizer magnetite (BK-5599). The amounts of magnetite for each of the three groups (seven samples per group) were 0.01, 0.025, 0.05, 0.075, 0.1, 0.125, and 0.15 g.

In the first group, each of the seven samples was equilibrated with 13 ml of 0.02M barium hydroxide (pH 12.7) in process water by stirring (200 rpm) for ten minutes at ambient temperature. Similarly, each sample in the second group was equilibrated with 13 ml of 0.05M NaOH in process water (pH 12.7). A third group of seven samples was also equilibrated with 13 ml of 0.05M NaOH (process water). However, the equilibration time for these samples was extended to 24 hours.

After equilibration, the solution from each magnetite solid was decanted. A 50-ml aliquot of actinide solution ( $1.0 \times 10^{-4}$  g/l plutonium and  $1.4 \times 10^{-6}$  g/l americium) at pH 12.0 was then added to each equilibrated magnetite solid. These mixtures were then stirred (200 rpm) for ten minutes at ambient temperature. All of the supernatant liquids were then decanted from the magnetite solids and passed through a glass column as described previously.

### Analyses

Samples of column effluent were analyzed for plutonium using a Nuclear Measurements Corporation PC-4 proportion alpha counter. Americium concentrations were determined using a Canberra Series 80 multichannel analyzer in conjunction with a Phoswich-type detector. All of the magnetite experiments were done in duplicate and the experimental results generally agreed to within  $\pm 10\%$ .

A feature analysis was done on each of the four commercial magnetites to determine their particle

size (average diameter). This was done with a Tracor Northern 5700 Image Analyzer in conjunction with a 5200 Scanning Electron Microscope.

The distilled and process water analyses were determined by semiquantitative emission spectroscopy, atomic absorption, and ion chromatography.

## RESULTS AND DISCUSSION

### Commercial Magnetite Tests

Four commercial magnetites (Pfizer BK-5599, Sargent-Welch, Fisher, and Eriez) were each activated with barium hydroxide and sodium

hydroxide in distilled and process water (all at pH 12.7). These magnetites were then compared with each other and evaluated for actinide removal from aqueous solution. Results show that the  $\text{Ba}(\text{OH})_2$ -activated magnetites were more effective in removing plutonium from aqueous solution than were the same NaOH-activated magnetites. In all cases, the Pfizer magnetite removed about ten times more plutonium than did both the Sargent-Welch and Fisher magnetites. The Eriez magnetite was the least effective at removing plutonium from aqueous solution. However, the  $\text{Ba}(\text{OH})_2$ -activated Eriez magnetite removed about 50% more plutonium than did the NaOH-activated Eriez magnetite. There was no significant difference between the distilled and process waters [used to prepare  $\text{Ba}(\text{OH})_2$  and NaOH solutions at pH 12.7] with respect to actinide removal. These results are shown in Table 1.

TABLE 1. Actinide Removal With Activated Commercial Magnetites

Magnetite <sup>a</sup>	Particle Size of Magnetite ( $\mu\text{m}$ ) <sup>b</sup>	Activating Materials [ $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ] <sup>c</sup> and NaOH <sup>d</sup>	Final Actinide Concentration	
			Plutonium <sup>e</sup> (g/l)	Americium <sup>f</sup> (g/l)
Pfizer (BK-5599)	0.28	$\text{Ba}(\text{OH})_2$ Dist. Water	$3.2 \times 10^{-9}$	$2.0 \times 10^{-11}$
			Process Water	$3.5 \times 10^{-9}$
		NaOH Dist. Water	$6.3 \times 10^{-8}$	$8.8 \times 10^{-11}$
			Process Water	$7.7 \times 10^{-8}$
Sargent-Welch	0.68	$\text{Ba}(\text{OH})_2$ Dist. Water	$1.6 \times 10^{-8}$	$4.6 \times 10^{-11}$
			Process Water	$1.9 \times 10^{-8}$
		NaOH Dist. Water	$5.2 \times 10^{-7}$	$2.2 \times 10^{-11}$
			Process Water	$7.9 \times 10^{-7}$
Fisher (Purified)	0.71	$\text{Ba}(\text{OH})_2$ Dist. Water	$4.0 \times 10^{-8}$	$1.1 \times 10^{-10}$
			Process Water	$3.7 \times 10^{-8}$
		NaOH Dist. Water	$8.5 \times 10^{-7}$	$2.9 \times 10^{-10}$
			Process Water	$6.2 \times 10^{-7}$
Eriez (Refined Ore)	1.72	$\text{Ba}(\text{OH})_2$ Dist. Water	$2.6 \times 10^{-5}$	$3.0 \times 10^{-7}$
			Process Water	$2.5 \times 10^{-5}$
		NaOH Dist. Water	$5.6 \times 10^{-5}$	$1.6 \times 10^{-7}$
			Process Water	$6.9 \times 10^{-5}$

a. Two grams of magnetite per litre of actinide solution

b. Average diameter

c. 2.6 mmol  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  per gram of magnetite for 10 minutes (pH 12.7)

d. 6.5 mmol NaOH per gram of magnetite for 10 minutes (pH 12.7)

e. Initial plutonium concentration:  $1.0 \times 10^{-4}$  g/l (pH 12.0) in distilled water

f. Initial americium concentration:  $1.4 \times 10^{-6}$  g/l (pH 12.0) in distilled water

The difference in each magnetite's ability to adsorb actinides from aqueous solution is attributed to the size of the particles comprising each magnetite. The smaller size magnetite particles have a greater surface area and, therefore, more adsorption capability.

A feature analysis was conducted on each of the four magnetites to determine their particle size (average diameter). These analyses showed that the average particle diameters for the Pfizer (BK-5599), Sargent-Welch, Fisher Scientific, and Eriez magnetites were 0.28, 0.68, 0.71, and 1.72  $\mu\text{m}$ , respectively. From this data, it is reasonable to conclude that the Pfizer (BK-5599) magnetite adsorbed more plutonium from solution because it had smaller size particles. The Sargent-Welch and Fisher magnetites responded similarly to actinide removal since both of these magnetites had similar size particles.

Since the NaOH-activated magnetites (pH 12.7) were less effective at removing actinides from solution, the equilibration time was increased from ten minutes to 24 hours. A small improvement in plutonium removal was observed with the longer equilibration period. These results are shown in Table 2. The analyses for the distilled

and process waters used in this study are presented in Table 3.

### Wet and Dry Magnetite Tests

The adsorption mechanism of metals from solution by magnetite is thought to occur through metal hydroxide species.<sup>7</sup> In an alkaline solution, most metal ions form insoluble species and may complex with additional hydroxide ions. Magnetite strongly adsorbs hydroxide ions and metal ions bond to the magnetite surface through these hydroxide ions.

When dry magnetite is prewetted by an alkaline solution, it is more effective than dry magnetite for removing actinides from aqueous solution. For example, two grams of dry Pfizer (BK-5599) magnetite lowers the plutonium concentration in one litre of aqueous solution (pH 12.0) from  $10^{-4}$  to  $10^{-5}$  g/l. If this same magnetite is first activated with NaOH solution (pH 8.0 to 12.7), the plutonium concentration is lowered from  $10^{-4}$  to  $10^{-8}$  g/l. However, if there are actinide ions ( $1.0 \times 10^{-4}$  g/l plutonium and  $1.4 \times 10^{-6}$  g/l americium) present during activation with the NaOH (pH 12.7), the plutonium concentration is lowered to only  $10^{-5}$  g/l.

TABLE 2. Comparison of Actinide Removal With 10-Minute and 24-Hour NaOH-Activated Commercial Magnetites

Magnetite <sup>a</sup>	Particle Size of Magnetite ( $\mu\text{m}$ ) <sup>b</sup>	10-Minute Equilibration		24-Hour Equilibration	
		Final Plutonium <sup>c</sup> Concentration (g/l)	Final Americium <sup>d</sup> Concentration (g/l)	Final Plutonium <sup>c</sup> Concentration (g/l)	Final Americium <sup>d</sup> Concentration (g/l)
Pfizer (BK-5599)	0.28	$7.7 \times 10^{-8}$	$4.0 \times 10^{-11}$	$6.4 \times 10^{-8}$	$7.0 \times 10^{-11}$
Sargent-Welch (Technical)	0.68	$7.9 \times 10^{-7}$	$5.1 \times 10^{-10}$	$7.0 \times 10^{-7}$	$7.3 \times 10^{-10}$
Fisher (Purified)	0.71	$6.2 \times 10^{-7}$	$1.5 \times 10^{-10}$	$1.8 \times 10^{-7}$	$1.5 \times 10^{-10}$
Eriez (Refined Ore)	1.72	$6.0 \times 10^{-5}$	$1.9 \times 10^{-7}$	$5.1 \times 10^{-5}$	$1.0 \times 10^{-7}$

a. Equilibrated with 6.5 mmol NaOH per gram of magnetite in process water (pH 12.7). Two grams of magnetite per litre of actinide solution.

b. Average diameter

c. Initial plutonium concentration:  $1.0 \times 10^{-4}$  g/l (pH 12.0)

d. Initial americium concentration:  $1.4 \times 10^{-6}$  g/l (pH 12.0)

TABLE 3. Water Analyses

Element <sup>a</sup>	Distilled Water (ppm)	Process Water (ppm)
Al	<1.0	<1.0
As <sup>b</sup>	<0.01	<0.01
B	<5.0	<5.0
Ba <sup>b</sup>	<1.0	<1.0
Be <sup>b</sup>	<0.05	<0.05
Ca <sup>b</sup>	6.9	5.1
Cd <sup>b</sup>	<0.01	<0.01
Co	<0.001	<0.001
Cr <sup>b</sup>	<0.05	<0.05
Cu	<1.0	<1.0
Fe	<1.0	<1.0
Hg <sup>b</sup>	<0.002	<0.002
K <sup>b</sup>	0.6	0.1
Li	<1.0	<1.0
Mg <sup>b</sup>	1.9	0.3
Mn	<0.0001	0.0001
Mo	<0.0002	0.0035
Na <sup>b</sup>	5.6	0.1
Ni	<0.0021	0.0044
Pb	<0.0001	0.0009
Se	<0.01	<0.01
Si <sup>b</sup>	<0.01	0.4
Sn	<0.0004	<0.0004
V	<0.0004	<0.0004
Zn	<0.0022	<0.0022
<b>Analysis<sup>c</sup></b>		
T.D.S.	13	44
Hardness	13.1	598
Cl <sup>-</sup>	<1.0	1.9
F <sup>-</sup>	<1.0	<1.0
SO <sub>4</sub> <sup>-2</sup>	3.8	9.8

a. Determined by semiquantitative emission spectroscopy unless otherwise noted.

b. Determined by atomic absorption.

c. Determined by ion chromatography.

A more effective activating agent for magnetite is barium hydroxide solution. Pfizer (BK-5599) magnetite, when activated with Ba(OH)<sub>2</sub> solution (pH 12.7), lowers plutonium concentration from 10<sup>-4</sup> to 10<sup>-9</sup> g/ℓ.

Magnetite may have a greater affinity for barium hydroxide than it does for sodium hydroxide. If this is the case, there maybe a greater concentration

of hydroxide ions available to impart more negative charge to the magnetite surface. This would result in greater adsorption by the magnetite of cations such as plutonium and americium. The results for the wet and dry magnetite tests are presented in Table 4.

### Barium Hydroxide Tests

Pfizer (BK-5599) magnetite was equilibrated with various concentrations of barium hydroxide solution. A quantity of barium hydroxide (for activation) was selected that would produce about a ten-fold increase in plutonium removal over the best sodium hydroxide activated magnetite. This quantity was about 2.6 mmol barium hydroxide per gram of BK-5599 magnetite. The effect of magnetite on actinide removal as a function of barium hydroxide concentration is presented in Table 5.

TABLE 4. Actinide Removal With Wet and Dry Pfizer (BK-5599) Magnetite

BK-5599 (2 g/ℓ)	Magnetite (pH)	Final Actinide Concentration	
		Plutonium <sup>c</sup> (g/ℓ)	Americium <sup>f</sup> (g/ℓ)
Dry	—	3.6 × 10 <sup>-5</sup>	7.9 × 10 <sup>-8</sup>
Wet <sup>a</sup> [NaOH, Pu, Am]	12.7	4.6 × 10 <sup>-5</sup>	8.4 × 10 <sup>-8</sup>
Wet <sup>b</sup> [NaOH]	8.0	1.1 × 10 <sup>-8</sup>	1.1 × 10 <sup>-11</sup>
Wet <sup>c</sup> [NaOH]	12.7	7.7 × 10 <sup>-8</sup>	4.0 × 10 <sup>-11</sup>
Wet <sup>d</sup> [Ba(OH) <sub>2</sub> ]	12.7	3.5 × 10 <sup>-9</sup>	2.9 × 10 <sup>-11</sup>

a. Equilibrated (10 minutes) with 6.5 mmol NaOH, 5.4 × 10<sup>-5</sup> mmol plutonium, and 7.6 × 10<sup>-7</sup> mmol americium per gram of magnetite in process water.

b. Equilibrated (10 minutes) with 1.3 × 10<sup>-4</sup> mmol NaOH per gram of magnetite in process water.

c. Equilibrated (10 minutes) with 6.5 mmol NaOH per gram of magnetite in process water.

d. Equilibrated (10 minutes) with 2.6 mmol Ba(OH)<sub>2</sub>·8H<sub>2</sub>O per gram of magnetite in process water.

e. Initial plutonium concentration: 1.0 × 10<sup>-4</sup> g/ℓ (pH 12.0)

f. Initial americium concentration: 1.4 × 10<sup>-6</sup> g/ℓ (pH 12.0)

TABLE 5. Effect of Pfizer (BK-5599) Magnetite on Actinide Removal as a Function of Barium Hydroxide Concentration

BK-5599 Magnetite (g/l)	Barium Hydroxide <sup>a</sup>		Final Actinide Concentration	
	(mmol)	(pH)	Plutonium <sup>b</sup> (g/l)	Americium <sup>c</sup> (g/l)
2	2.0	12.2	$2.3 \times 10^{-8}$	$2.8 \times 10^{-10}$
2	2.6	12.4	$1.3 \times 10^{-8}$	$8.9 \times 10^{-11}$
2	3.2	12.5	$7.2 \times 10^{-9}$	$6.8 \times 10^{-11}$
2	3.9	12.6	$4.6 \times 10^{-9}$	$4.4 \times 10^{-11}$
2	5.2	12.7	$3.2 \times 10^{-9}$	$2.0 \times 10^{-11}$
2	13.0	12.8	$5.0 \times 10^{-10}$	$3.2 \times 10^{-12}$

a. Solutions prepared with distilled water.

b. Initial plutonium concentration:  $1.0 \times 10^{-4}$  g/l (pH 12.0)

c. Initial americium concentration:  $1.4 \times 10^{-6}$  g/l (pH 12.0)

### pH Tests

Results show that NaOH-activated Pfizer (BK-5599) magnetite (2 g/l) lowers plutonium concentrations from  $10^{-4}$  to  $10^{-8}$  g/l if the pH of the actinide solution is between 12.0 and 13.0. If this pH goes below 11.5 or approaches 13.5, plutonium removal is substantially decreased. In contrast, Ba(OH)<sub>2</sub>-activated magnetite lowers plutonium concentrations from  $10^{-4}$  to  $10^{-8}$  and  $10^{-9}$  g/l over the pH range of 11 through 13.5. These results are presented in Table 6.

### Magnetite Concentration Tests

Various amounts of activated Pfizer (BK-5599) magnetite were evaluated for actinide removal from aqueous solution. Activation was accomplished by equilibrating this magnetite (ten minutes) with barium hydroxide in process water (pH 12.7) as well as with sodium hydroxide in process water (pH 12.7). Results show that compared with the NaOH-activated magnetite, about 50% less Ba(OH)<sub>2</sub>-activated magnetite was needed to lower the plutonium concentration from  $10^{-4}$  to  $10^{-8}$  g/l. These results are shown in Table 7.

Since the NaOH-activated magnetites (pH 12.7) were less effective in removing actinides from solution, the equilibration time was increased from

ten minutes to 24 hours. A small improvement in plutonium removal occurred with the longer equilibration period. These results are shown in Table 8.

### SUMMARY

In this study, four commercial magnetites were evaluated for actinide removal from aqueous solution. Two major factors appear to greatly influence the effective use of magnetite as an actinide adsorbent. One of these factors is magnetite particle size. (Smaller size particles mean greater surface area for more adsorption capability.) The Pfizer magnetite (BK-5599), with its smaller particle size, was at least ten times more effective at lowering plutonium concentrations than were the Sargent-Welch, Fisher Scientific, and Eriez magnetites.

A second factor that greatly influences the use of magnetite as an actinide adsorbent is pretreatment (activation) of the magnetite surface with hydroxyl ions. The Ba(OH)<sub>2</sub>-activated Pfizer magnetite (BK-5599) was effective over the pH range of 11.0 through 13.5 and lowered plutonium concentrations from  $10^{-4}$  to  $10^{-8}$  and  $10^{-9}$  g/l. This same NaOH-activated magnetite lowered plutonium concentrations from  $10^{-4}$  and  $10^{-8}$  g/l at a pH between 12.0 and 13.0. Also, the presence of actinide ions during magnetite activation with hydroxyl ions greatly lowers the effectiveness of magnetite as an actinide adsorbent.

Compared to NaOH-activated magnetite, about 50% less Ba(OH)<sub>2</sub>-activated magnetite was required to lower plutonium concentrations from  $10^{-4}$  to  $10^{-8}$  g/l. Also, with respect to actinide removal, there was no significant difference between the distilled and process waters [used to prepare Ba(OH)<sub>2</sub> and NaOH solutions for magnetite activation].

The use of activated commercial magnetite as an alternative to using preformed ferrite for actinide waste management is attractive because fewer reagents are needed. Also, compared to preformed ferrite, there is no by-product (e.g., sodium sulfate) that would ultimately be discharged as low-level waste.

TABLE 6. Effect of pH on Actinide Removal With Pfizer (BK-5599) Magnetite

BK-5599 Magnetite <sup>a</sup> (g/l)	Activation <sup>b</sup>		Actinide Solution (pH)	Final Actinide Concentration	
	Material	(pH)		Plutonium <sup>c</sup> (g/l)	Americium <sup>d</sup> (g/l)
2	Ba(OH) <sub>2</sub>	12.7	11.0	1.8 × 10 <sup>-8</sup>	8.1 × 10 <sup>-11</sup>
2	NaOH	12.7		1.7 × 10 <sup>-6</sup>	3.3 × 10 <sup>-9</sup>
2	NaOH	8.0		4.8 × 10 <sup>-6</sup>	9.2 × 10 <sup>-9</sup>
2	Ba(OH) <sub>2</sub>	12.7	11.5	2.9 × 10 <sup>-8</sup>	4.6 × 10 <sup>-11</sup>
2	NaOH	12.7		1.2 × 10 <sup>-7</sup>	2.0 × 10 <sup>-9</sup>
2	NaOH	8.0		5.1 × 10 <sup>-6</sup>	6.7 × 10 <sup>-9</sup>
2	Ba(OH) <sub>2</sub>	12.7	12.0	3.5 × 10 <sup>-9</sup>	2.9 × 10 <sup>-11</sup>
2	NaOH	12.7		7.7 × 10 <sup>-8</sup>	9.0 × 10 <sup>-11</sup>
2	NaOH	8.0		1.1 × 10 <sup>-8</sup>	1.1 × 10 <sup>-11</sup>
2	Ba(OH) <sub>2</sub>	12.7	12.5	3.6 × 10 <sup>-9</sup>	4.9 × 10 <sup>-11</sup>
2	NaOH	12.7		4.6 × 10 <sup>-8</sup>	5.3 × 10 <sup>-11</sup>
2	NaOH	8.0		1.6 × 10 <sup>-8</sup>	4.2 × 10 <sup>-11</sup>
2	Ba(OH) <sub>2</sub>	12.7	13.0	1.4 × 10 <sup>-9</sup>	5.9 × 10 <sup>-11</sup>
2	NaOH	12.7		6.1 × 10 <sup>-8</sup>	4.0 × 10 <sup>-11</sup>
2	NaOH	8.0		3.4 × 10 <sup>-8</sup>	2.3 × 10 <sup>-11</sup>
2	Ba(OH) <sub>2</sub>	12.7	13.5	2.2 × 10 <sup>-9</sup>	6.0 × 10 <sup>-11</sup>
2	NaOH	12.7		1.4 × 10 <sup>-5</sup>	8.6 × 10 <sup>-8</sup>
2	NaOH	8.0		1.4 × 10 <sup>-7</sup>	1.1 × 10 <sup>-10</sup>

a. Grams of magnetite per litre of actinide solution.

b. Ten minutes with solutions prepared in process water.

c. Initial plutonium concentration: 1.0 × 10<sup>-4</sup> g/l

d. Initial americium concentration: 1.4 × 10<sup>-6</sup> g/l



TABLE 7. Actinide Removal as a Function of Magnetite Concentration

BK-5599 Magnetite <sup>a</sup> (g/l)	Activation <sup>b</sup> Materials at pH 12.7	Final Actinide Concentration	
		Plutonium <sup>c</sup> (g/l)	Americium <sup>d</sup> (g/l)
0.2	Ba(OH) <sub>2</sub> NaOH	3.5 × 10 <sup>-7</sup> —	6.3 × 10 <sup>-11</sup> —
0.5	Ba(OH) <sub>2</sub> NaOH	1.1 × 10 <sup>-7</sup> 1.6 × 10 <sup>-6</sup>	3.8 × 10 <sup>-11</sup> 9.0 × 10 <sup>-11</sup>
1.0	Ba(OH) <sub>2</sub> NaOH	4.9 × 10 <sup>-8</sup> 4.4 × 10 <sup>-7</sup>	3.0 × 10 <sup>-11</sup> 4.6 × 10 <sup>-11</sup>
1.5	Ba(OH) <sub>2</sub> NaOH	9.8 × 10 <sup>-9</sup> 3.4 × 10 <sup>-7</sup>	2.8 × 10 <sup>-11</sup> 5.0 × 10 <sup>-11</sup>
2.0	Ba(OH) <sub>2</sub> NaOH	3.5 × 10 <sup>-9</sup> 7.7 × 10 <sup>-8</sup>	2.9 × 10 <sup>-11</sup> 4.0 × 10 <sup>-11</sup>
2.5	Ba(OH) <sub>2</sub> NaOH	— 4.9 × 10 <sup>-8</sup>	— 3.8 × 10 <sup>-11</sup>
3.0	Ba(OH) <sub>2</sub> NaOH	— 2.8 × 10 <sup>-8</sup>	— 2.8 × 10 <sup>-11</sup>

a. Grams of magnetite per litre of actinide solution.

b. Ten minutes with solutions prepared in process water.

c. Initial plutonium concentration: 1.0 × 10<sup>-4</sup> g/l (pH 12.0)

d. Initial americium concentration: 1.4 × 10<sup>-6</sup> g/l (pH 12.0)

TABLE 8. Actinide Removal With NaOH-Activated (24-Hours) Pfizer (BK-5599) Magnetite

BK-5599 Magnetite <sup>a</sup> (g/l)	Final Actinide Concentration	
	Plutonium <sup>b</sup> (g/l)	Americium <sup>c</sup> (g/l)
0.2	2.6 × 10 <sup>-7</sup>	1.8 × 10 <sup>-10</sup>
0.5	1.1 × 10 <sup>-7</sup>	1.5 × 10 <sup>-10</sup>
1.0	1.2 × 10 <sup>-7</sup>	1.2 × 10 <sup>-10</sup>
1.5	7.4 × 10 <sup>-8</sup>	7.3 × 10 <sup>-11</sup>
2.0	6.4 × 10 <sup>-8</sup>	7.0 × 10 <sup>-11</sup>
2.5	3.3 × 10 <sup>-8</sup>	2.5 × 10 <sup>-11</sup>
3.0	2.3 × 10 <sup>-8</sup>	2.0 × 10 <sup>-11</sup>

a. Equilibrated with 6.5 mmol sodium hydroxide in process water (pH 12.7)

b. Initial plutonium concentration: 1.0 × 10<sup>-4</sup> g/l (pH 12.0)

c. Initial americium concentration: 1.4 × 10<sup>-6</sup> g/l (pH 12.0)

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