

## IRREVERSIBLE SORPTION OF CONTAMINANTS DURING FERRIHYDRITE TRANSFORMATION

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### ABSTRACT

A better understanding of the fraction of contaminants irreversibly sorbed by minerals is necessary to effectively quantify bioavailability. Ferrihydrite, a poorly crystalline iron oxide, is a natural sink for sorbed contaminants. Contaminants may be sorbed/occluded as ferrihydrite precipitates in natural waters or as it ages and transforms to more crystalline iron oxides such as goethite or hematite. Laboratory studies indicate that Cd, Co, Cr, Cu, Ni, Np, Pb, Sr, U, and Zn are irreversibly sorbed to some extent during the aging and transformation of synthetic ferrihydrite. Barium, Ra and Sr are known to sorb on ferrihydrite in the pH range of 6 to 10 and sorb more strongly at pH values above its zero point of charge ( $\text{pH} > 8$ ). We will review recent literature on metal retardation, including our laboratory and modeling investigation of Ba (as an analogue for Ra) and Sr adsorption/desorption, during ferrihydrite transformation to more crystalline iron oxides.

Four ferrihydrite suspensions were aged at pH 12 and 50 °C with or without Ba in 0.01 M  $\text{KNO}_3$  for 68 h or in 0.17 M  $\text{KNO}_3$  for 3424 h. Two ferrihydrite suspensions were aged with and without Sr at pH 8 in 0.1 M  $\text{KNO}_3$  at 70°C. Barium or Sr sorption, or desorption, was measured by periodically centrifuging suspension subsamples, filtering, and analyzing the filtrate for Ba or Sr. Solid subsamples were extracted with 0.2 M ammonium oxalate (pH 3 in the dark) and with 6 M HCl to determine the Fe and Ba or Sr attributed to ferrihydrite (or adsorbed on the goethite/hematite surface) and the total Fe and Ba or Sr content, respectively. Barium or Sr occluded in goethite/hematite was determined by the difference between the total Ba or Sr and the oxalate extractable Ba or Sr. The percent transformation of ferrihydrite to goethite/hematite was estimated from the ratio of oxalate and HCl extractable Fe.

All Ba was retained in the precipitates for at least 20 h. Desorption of Ba reached a maximum of 7 to 8% of the  $\text{Ba}^{2+}$  added for samples aged in 0.01 and 0.17 M  $\text{KNO}_3$  after 68 and 90 h of aging, respectively. About 3% of the  $\text{Ba}^{2+}$  added was readsorbed from 90 to 3424 h of aging in 0.17 M  $\text{KNO}_3$ . The amount of Ba sorbed by ferrihydrite or adsorbed on goethite (oxalate-extractable) decreased from 70 to 40% of the  $\text{Ba}^{2+}$  added after 68 h in 0.01 M  $\text{KNO}_3$  and from 80 to 20% of the  $\text{Ba}^{2+}$  added after 400 h in 0.17 M  $\text{KNO}_3$ . The Ba occluded in goethite (HCl-extractable) in 0.01 M  $\text{KNO}_3$  increased rapidly to 30% of the  $\text{Ba}^{2+}$  added in the first 0.4 h and then to 50% of the  $\text{Ba}^{2+}$  added after 68 h. In 0.17 M  $\text{KNO}_3$ , Ba occluded in goethite increased from 60% of the  $\text{Ba}^{2+}$  added by 68 h and to 75% of the  $\text{Ba}^{2+}$  added after 3424 h.

After 68 h at 70°C, ferrihydrite transformation was 99% complete and was slightly inhibited with Sr present during the first few hours. Occlusion of Sr in ferrihydrite or Sr

reversibly adsorbed decreased from 96 to 4% after 86 h. Occlusion of Sr in hematite/goethite increased from 4 to 40% after 68 h. Desorption of Sr increased from 0.2 to 50% after 68 h.

At least 90% of the Ba and 25% of the Sr added to the ferrihydrite suspensions were retained by the iron oxides during the aging periods in this study. At least 75% of the Ba and 15% of the Sr were irreversibly sorbed during ferrihydrite transformation to goethite and/or hematite.

## INTRODUCTION

An understanding of the surface structure and sorptive properties of soil minerals in contact with dissolved radionuclides is fundamental to modeling metal retardation. Hydrogeochemical transport codes can accurately predict the transport and retardation of dissolved radionuclides only when there is a mechanistic understanding of the adsorption and fixation behavior of metals in near-field soils. While theoretical models exist for modeling surface complexation, sorption, and desorption at mineral surfaces, experimental verification of those models lags, as does atomistic characterization of retardation mechanisms. This project was designed to provide mechanistic and kinetic data about the sorption behavior of metals with iron oxide surfaces. Unraveling the mechanistic controls on sorption under diverse geochemical conditions is necessary to predict metal transport and retardation in soils. These data will provide the technical confidence for regulatory decisions on radionuclide transport and retardation. The regulatory objectives of this project are to provide the NRC, state regulators, and disposal site operators with defensible models describing radionuclide retardation by soil-forming minerals.

Pore fluids in cement-based, low level radioactive waste repositories and waste forms are alkaline, ranging from above pH 13 initially and decreasing to around pH 10 with time (1). Although geochemical modeling predicts that solubility and sorption under these conditions may attenuate Ra in an oxidizing environment (2),(3), estimates of Ra sorption need further refinement. The laboratory work presented here is specifically focused on providing a clearer picture of Ra and Sr migration or retardation under diverse geochemical conditions in soil and concrete environments.

Ferrihydrite is a poorly crystalline Fe(III) oxide structurally similar to hematite, but with less Fe and some O replaced by OH or H<sub>2</sub>O molecules (4). Ferrihydrite precipitates when natural waters high in Fe(II) are rapidly oxidized (acid mine waters, acid soil drainage ditches, hot/cold springs, or streams) and occurs as very small (2-4 nm), highly aggregated, spherical particles that may coat mineral grains or microbes (5-9). As a result, ferrihydrite has a very high specific surface area (200-500 m<sup>2</sup>g<sup>-1</sup>; BET, N<sub>2</sub>) and is a natural sink for contaminants (10).

Although ferrihydrite is a common component of temperate region soils and sediments, it is difficult to isolate or identify in situ (11). Ferrihydrite's effectiveness as a metal sorbent in natural materials is usually determined by selective dissolution techniques (12). Goethite ( $\alpha$ -FeOOH), the most common iron oxide in soils, forms by ferrihydrite dissolution and reprecipitation, while hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) forms from ferrihydrite by internal aggregation and rearrangement (13). Transformation rates are affected by pH (14), ionic strength (15), sorption/coprecipitation of ions (16-18), temperature (19), and rate of initial ferrihydrite precipitation (20). Laboratory studies indicate that Cd, Co, Cr, Cu, Ni, Np, Pb, Sr, U, and Zn are irreversibly sorbed to some extent during the aging and transformation of synthetic ferrihydrite (Table 1). The extent of metal immobilization by this mechanism is dependent on the chemical

and physical parameters of the aging experiments. These experimental conditions can be related to processes occurring in contaminated soils and sediments, or in cement-based waste repositories or waste forms.

Radium 226 ( $t_{1/2} = 1600$  y) is a major radionuclide decay product of the most abundant uranium isotope,  $^{238}\text{U}$ . An  $\alpha$ -emitter with a long half-life,  $^{226}\text{Ra}$  may cause biological damage if ingested, therefore its presence is a major concern in the environmental management of nuclear waste. Radium and Ba, have effective ionic radii of 1.48 and 1.42 Å, respectively (21), and

Table 1. Metal retardation during ferrihydrite aging or transformation

Metal	Sorption Conditions	Sorption Mechanisms	References
Cd	pH 9.5 to pH 4.5 cycles	Adsorption/desorption	(22)
	Alkaline coprecipitation	Isomorphic substitution	(23)
	Aged 86 weeks, pH 7	Partially occluded	(24)
	Coprecipitation, aged 14 d at pH 8, 50 or 70°C	Isomorphic substitution for Fe in hematite	(25)
	Coprecipitation, 100 mg Cd kg <sup>-1</sup> , pH 6, aged 250 d	28 to 59% sorbed at 25°C more after 60d at 70°C	(20, 26)
Co	Coprecipitation, aged 20 d pH 12, 70°C	Isomorphic substitution for Fe in goethite or magnetite	(16)
	Added to ferrihydrite, aged <100 h, pH 10.5-12, 70°C	Isomorphic substitution for Fe in goethite or magnetite	(27)
	Alkaline coprecipitation	Isomorphic substitution	(23)
	Aged 86 weeks, pH 7	Partially occluded	(24)
Cr	pH 9.5 to pH 4.5 cycles	94 – 97% bound 21.5 h	(22)
	Alkaline coprecipitation	Isomorphic substitution for Fe in goethite	(28)
Cu	pH 9.5 to pH 4.5 cycles	10-15% slowly reversible	(22)
	Coprecipitation, aged 20 d pH 12, 70°C	Isomorphic substitution for Fe in goethite, hematite or spinel	(16); (29)
	Alkaline coprecipitation	Isomorphic substitution	(23)
	Coprecipitation, 1500 mg Cu kg <sup>-1</sup> , pH 6, aged 250 d	94% sorbed, constant to more after 60d at 70°C	(20, 26)
Ni	pH 9.5 to pH 4.5 cycles	~20% slowly reversible	(22)
	Coprecipitation, pH 7.5 to 13	Ni-goethite pH > 11.5 Ni-hematite pH 8 – pH 11.5	(30)
	Coprecipitation, pH 6, aged 400 h at 70°C	Incorporation in goethite and hematite	(31)
Np	Coprecipitation, pH 6.0 or 7.7, 90°C, 198 h	100% sorbed at pH 7.7 11% sorbed at pH 6.0	(32)
Pb	pH 9.5 to pH 4.5 cycles	40-60% slowly reversible	(22)
	Alkaline coprecipitation	Isomorphic substitution	(23)
	Coprecipitation, pH 6, aged 400 h at 70°C	Adsorbed on oxides but only 10% occluded	(31)
	Coprecipitation, 1500 or 500 mg Pb kg <sup>-1</sup> , pH 6, aged 250 d	100% sorbed, some desorption after 60d at 70°C	(20, 26)
Sr	Ferrihydrite aged at pH 12, 40°C for 150+h	100% sorbed initially, 60% sorbed on goethite	(33)
U	Ferrihydrite aged	Partial desorption during transformation,	(34)
Zn	pH 9.5 to pH 4.5 cycles plus aging up to 44 h	4 to 43% remained adsorbed	(22)
	Coprecipitation, aged 20 d pH 12, 70°C	Isomorphic substitution for Fe in goethite, hematite or spinel, up to 5 mole %	(16); (35)
	Coprecipitation, 3000 mg Zn kg <sup>-1</sup> , pH 6, aged 250 d	58% sorbed, more after 60d at 70°C	(20, 26)

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consequently have similar chemical reactivity. Radium is known to coprecipitate in a solid solution with barite (36-38). As a result, Ba salt solutions are used to remove Ra from U mine waters and acid sulfate and U mill tailings solutions or effluents (39). Both Ra and Ba are known to sorb on ferrihydrite in the pH range of 6 to 10 (40, 41) and sorb more strongly at pH values above its zero point of charge ( $\text{pH} > 8$ ). It is therefore reasonable to use Ba as an analogue to study Ra sorption on iron oxides.

Earlier workers found that high pH hastens the conversion of ferrihydrite to more crystalline products. Schwertmann and Murad (14) found that half conversion of ferrihydrite to goethite at 25°C at pH 12 occurs in < 4 d while half conversion to hematite and goethite at pH 7 takes 112 d. Heating also hastens ferrihydrite transformation, so we chose to conduct our studies at 50°C (19). We measured the kinetics of adsorption and desorption of  $\text{Ba}^{2+}$  on ferrihydrite during its recrystallization to goethite at pH 12, at two different ionic strengths, in 0.01 M  $\text{KNO}_3$  or in 0.17 M  $\text{KNO}_3$ .

Strontium 90 is a toxic and abundant fission product in spent nuclear fuel and fuel processing wastes. Understanding Sr mobility in natural systems can prevent uptake of  $^{90}\text{Sr}$  by plants, animals and humans. Strontium is adsorbed by ferrihydrite and may be occluded during its transformation to hematite and goethite at near neutral pH (40, 42). We chose to study the sorption and desorption of Sr during ferrihydrite aging at pH 8 and 70°C in 0.1 M  $\text{KNO}_3$ .

## METHODS

Approximately 40 g of poorly crystalline ferrihydrite were precipitated by rapid neutralization of 1 M  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with 1 M KOH to pH 8. The resulting suspension was aged for 3 h, washed, and then divided into four parts ( $\sim 0.1 \text{ mol Fe L}^{-1}$ ) which were aged at pH 12 and 50 °C with or without Ba [ $0.0005 \text{ M Ba}(\text{NO}_3)_2$ ] in 0.01 M  $\text{KNO}_3$  for 68 h or in 0.17 M  $\text{KNO}_3$  for 3424 h. In a separate experiment, two ferrihydrite suspensions ( $\sim 0.02 \text{ mol Fe L}^{-1}$ ) prepared in a similar manner, were aged with and without Sr [ $0.006 \text{ mmol SrCl}_2$ ] at pH 8 in 0.1 M  $\text{KNO}_3$  at 70 °C.

To measure Ba or Sr sorption onto or desorption from the precipitates over time, subsamples were periodically removed, centrifuged, the supernatant passed through a 0.2  $\mu\text{m}$  nylon syringe filter, and the filtrate analyzed for Ba or Sr by direct current argon plasma emission spectroscopy (DCP). Solid subsamples were extracted with 0.2 M ammonium oxalate (pH 3 in the dark) and with 6 M HCl to determine the Fe and Ba/Sr attributed to ferrihydrite (or adsorbed on the goethite/hematite surface) and the total Fe and Ba/Sr content, respectively. Barium or Sr occluded in goethite was determined by the difference between the total Ba or Sr and the oxalate extractable Ba or Sr. The percent transformation of ferrihydrite to hematite/goethite was estimated from the ratio of oxalate and HCl extractable Fe.

Subsamples of the precipitates were washed and freeze-dried. Pressed powder mounts of these subsamples were analyzed by X-ray diffraction (XRD) ( $\text{CuK}\alpha$ , 35 kV, 30 mA). Surface areas of selected freeze-dried subsamples were determined by  $\text{N}_2$  adsorption with a multipoint B.E.T. method (43).

## RESULTS

### Sample Characterization

Surface areas of samples aged with and without Ba in 0.01 M KNO<sub>3</sub> decreased rapidly during the first 19.3 h of aging and then approached a constant value of about 50 m<sup>2</sup> g<sup>-1</sup>. The surface area decreased rapidly until the transformation of ferrihydrite to goethite neared completion. The surface areas of samples aged in 0.17 M KNO<sub>3</sub> at pH 12 and 50°C with and without Ba decreased rapidly during the first 90.3 h of aging and then remained constant at about 40 m<sup>2</sup> g<sup>-1</sup>. There was no significant difference in surface areas for samples aged with and without Sr at pH 8 and 70°C. Surface area decreased from 240 to 16 m<sup>2</sup> g<sup>-1</sup> during 68 h of aging.

For subsamples taken during aging in 0.01 M KNO<sub>3</sub>, XRD patterns show a slight decrease in transformation rate in samples with Ba added during the first 12.4 h of aging. No difference can be detected in this study between XRD patterns for samples aged with or without Ba from 12.4 to 68.4 h. The XRD data show that some poorly crystalline goethite formed during the first 0.4 h of aging and that the goethite XRD peaks increase in intensity and decrease in width during the first 12.4 h of aging indicating an increase in the amount of goethite present and its crystallinity. Between 12.4 h and 25.2 h of aging, there are no further changes in XRD peak width, but a slight increase in peak height indicating an increase in the amount of crystalline goethite present. After 25.2 h of aging, when the transformation of ferrihydrite to goethite is 94 to 95 % complete, there are no further significant changes in the XRD patterns of the samples.

X-ray powder diffraction patterns of samples aged without and with Ba in 0.17 M KNO<sub>3</sub> at pH 12 and 50°C were not significantly different from each other. The XRD data of samples aged with Ba show a significant increase in the amount of goethite present in the samples during the first 20.7 h of aging and then a very gradual increase in peak intensity continuing through 3423.8 h of aging.

For samples aged with and without Sr, XRD patterns showed that ferrihydrite transformation to hematite and goethite was nearly complete after 68 h of aging. Strontium slowed ferrihydrite transformation slightly during the first few hours of aging and then had little or no observable affect.

### Barium sorption/desorption

Barium sorption data for ferrihydrite transformation at pH 12 and 50°C in 0.01 M KNO<sub>3</sub> are presented in Figure 1. Analyses of the suspension filtrates indicated that 100% of the Ba added was retained by the iron oxide for at least 25.2 h of aging and that 4 and 7% of the Ba were desorbed after 45.9 and 68.4 h of aging, respectively. Barium sorbed by ferrihydrite and/or adsorbed on goethite decreased from 75 to 40% during 68.4 h of aging. The Ba occluded by goethite increased rapidly to 30 % in the first 0.4 h of aging and then gradually increased to 50% after 68.4 h.

For the samples aged in 0.17 M KNO<sub>3</sub> at pH 12 and 50°C, Ba starts to desorb after 20.7 h of aging (Figure 2). Barium desorption reached a maximum of 6% after 90.3 h of aging, and decreased to 0.4% after 3423.8 h of aging. Barium sorbed by ferrihydrite and/or adsorbed on goethite decreased from 80% after 0.4 h of aging to about 21% after 401.1 h of aging and then remained constant to the end of the experiment at 3423.8 h of aging. Barium occluded in goethite increased to about 77% by 401.1 h of aging and remained constant through 3423.8 h of aging.

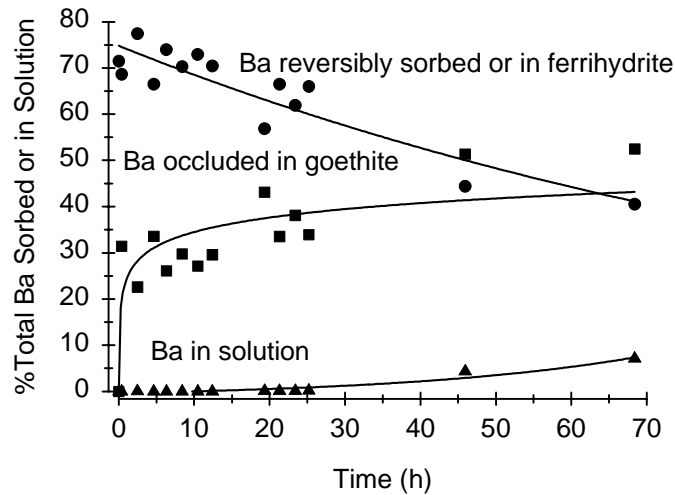


Figure 1. Changes in Ba sorption/desorption during aging of ferrihydrite suspensions at 50°C and pH 12 in 0.01 M KNO<sub>3</sub>.

Occlusion of Sr in ferrihydrite or Sr reversibly adsorbed decreased from 94 to 9% after 68 h of aging and then remained constant through 1476 h (Figure 3). Occlusion of Sr in hematite/goethite increased to 24% after 86 h, but had decreased to 12% by 1476 h. Desorption of Sr increased from 3 to 75% after 68 h and then remained constant through 1476 h.

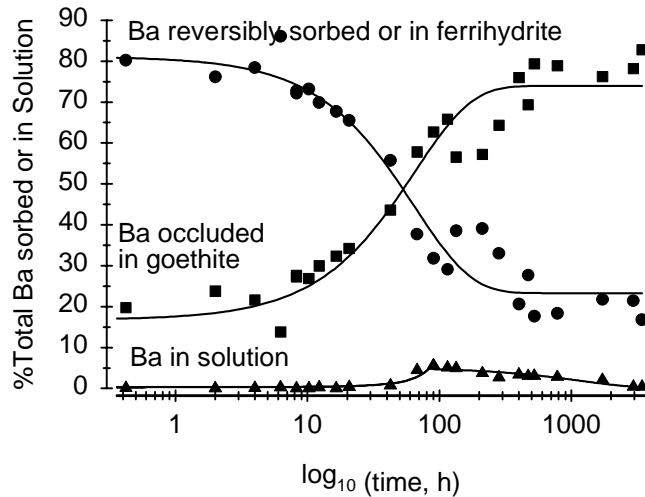


Figure 2. Changes in Ba sorption/desorption during aging of ferrihydrite suspensions at 50°C and pH 12 in 0.17 M KNO<sub>3</sub>.

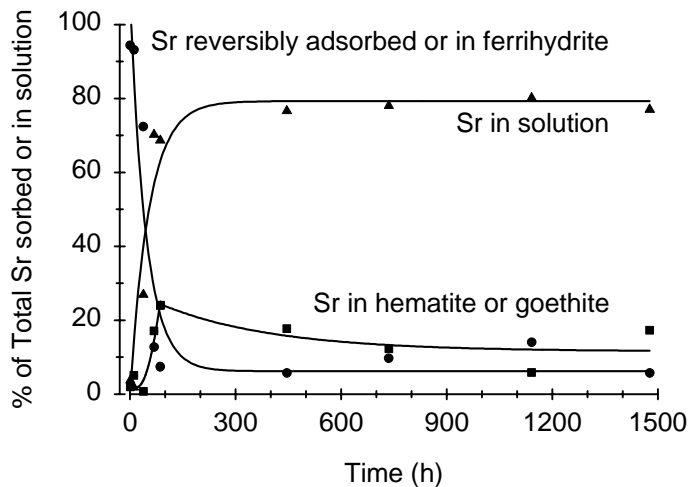


Figure 3. Changes in Sr sorption/desorption during aging of ferrihydrite suspensions at 70°C and pH 8 in 0.1 M KNO<sub>3</sub>.

## DISCUSSION

At least 90% of the Ba added to the suspensions was retained by the iron oxides during the aging periods in this study. Sakamoto and Senoo (33) also found that large amounts of Sr were occluded in goethite during alkaline ferrihydrite transformation. They aged ferrihydrite suspensions (17 g L<sup>-1</sup>) with 0.003 M Sr in 0.03 M NaClO<sub>4</sub> at pH 12 and 40°C. Transformation of ferrihydrite to goethite in their samples reached completion between 75 and 100 h of aging. They found that 53% of the Sr added to their system remained sorbed on goethite after 200 h of aging. Their results, from a sequential extraction of the Sr sorbed in freeze-dried samples, indicated that about 70% was reversibly sorbed (extracted with 1 M MgCl<sub>2</sub>), a negligible amount was sorbed on poorly crystalline iron oxides (extracted with 0.04 M NH<sub>2</sub>OH·HCl in 25% acetic acid), and 30% was occluded in the goethite (extracted by HF-HClO<sub>4</sub>).

Barium desorption began when ferrihydrite transformation to goethite was 92 to 94% complete. Maximum desorption of Ba coincided with 95 to 99% transformation of ferrihydrite to goethite and a resulting decrease in precipitate surface area. Barium desorption may be caused by this decrease in surface area.

Although Ba<sup>2+</sup> is too large to replace Fe(III) in the goethite structure, Ba released after ferrihydrite dissolution may have been adsorbed and then occluded during rapid nucleation and growth of goethite crystals. As the transformation of ferrihydrite to goethite neared completion, surface area decreased and the number of sites for Ba sorption and/or occlusion also decreased causing some Ba to be desorbed.

For samples aged in 0.17 M KNO<sub>3</sub>, the gradual readsorption of Ba may reflect the presence of multiple sorption sites with different sorption rates or diffusion of Ba into goethite pores. Calculations show that this system was supersaturated with respect to witherite and that



relatively slow precipitation of witherite also might be causing the gradual decrease in solution Ba, after desorption.

Maximum Sr desorption occurred when the transformation of ferrihydrite was 99% complete. Ferrihydrite transformation caused a large decrease in sorbing surface area. At least 25% of the added Sr was irreversibly sorbed during the initial stage of ferrihydrite transformation to hematite and goethite, but a further decrease in iron oxide surface area caused 10% of this Sr to be desorbed. These results differ from those of Sakamoto and Senoo (33) since ferrihydrite is transformed much more slowly at pH 8 than at pH 12.

In order to test the suitability of the conceptual models for the mechanism of  $\text{Ba}^{2+}$  sorption onto goethite we have initiated a computer simulation study. The availability of sophisticated molecular mechanics and molecular orbital software combined with recent advancements in the computational power of workstations has allowed us to examine the energetics of metal sorption onto mineral surfaces (44). Optimized configurations and relative binding energies of  $\text{Ba}^{2+}$  on the different goethite surfaces are obtained using conventional forcefield parameters, energy minimization, and molecular dynamics methods. A comparison can be made of metal binding on the (020) and (110) growth surfaces and on the terminating (111) and (021) edges surfaces associated with the acicular morphology of goethite. The computer simulations suggest that  $\text{Ba}^{2+}$  binds as an inner sphere complex and is coordinated to two of the surface oxygens of the  $\text{Fe}^{3+}$  octahedron with  $\text{Ba}^{2+}$ -O distances of 2.7 Å and 3.1 Å (Figure 4). These values are similar to the observed (2.9 Å) and simulated (2.7 Å) mean distances for the solvated  $\text{Ba}^{2+}$ - $\text{H}_2\text{O}$  complex in solution (45).

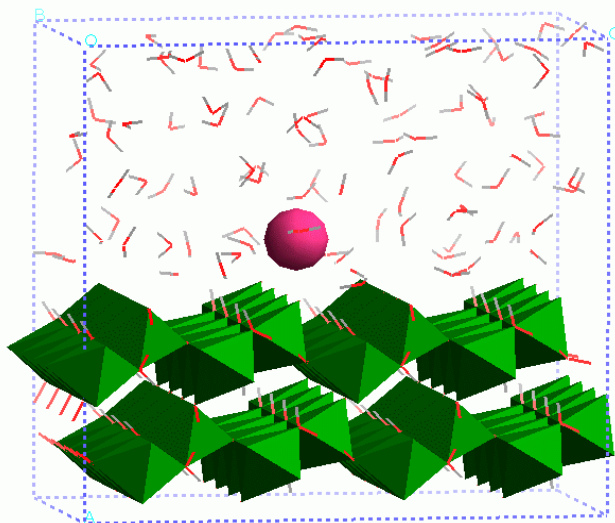


Figure 4. Equilibrated configuration of  $\text{Ba}^{2+}$  sorbed on (110) surface of goethite based on NVT (300 K) molecular dynamics simulation.

## CONCLUSIONS

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Barium (or Ra) in or near the alkaline pore waters of a cement waste form or repository would be significantly retained by the transformation of ferrihydrite to goethite, though this would depend on the amount of iron present in the pore waters, its oxidation state and the presence of other sorbents. Beneš et al. (41) calculated that at pH values < 7, a ferric hydroxide concentration > 5 mg L<sup>-1</sup> would be required to have a significant effect on Ra mobility in natural waters. At alkaline pH, a smaller ferrihydrite concentration should be effective at retaining Ba or Ra. Radium sorption on ferric hydroxide at pH 6 and 7 was found to be reversible (41), while our data show that at least 75% of the added Ba was occluded during ferrihydrite transformation to goethite at pH 12. Irreversible sorption of Sr at pH 8 was not as effective as sorption at pH 12 (33), but at least 15% of the added Sr remained occluded after ferrihydrite aging.

Contaminants may be irreversibly sorbed during ferrihydrite transformation to goethite or hematite. The extent of contaminant immobilization depends on the chemical and physical environment of ferrihydrite aging. Some Ba and Sr are irreversibly sorbed during ferrihydrite transformation to goethite and/or hematite.

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