Residence Time Effects on Arsenate Adsorption/Desorption Mechanisms on Goethite

S. E. O'Reilly,* D. G. Strawn, and D. L. Sparks

ABSTRACT

In order to make sound decisions regarding arsenate contamination in soil and water environments, it is necessary to have a thorough understanding of the mechanisms of arsenate sorption and desorption over extended periods. The major objectives of this study were to determine the effects of aging or residence time on the kinetics of arsenate sorption and desorption on goethite, and to combine spectroscopic x-ray absorption fine structure (XAFS) and macroscopic studies in order to determine sorption and desorption mechanisms over time at pH 4 and 6. Sorption studies, conducted from 4 min to ≈12 mo, showed that arsenate sorption on goethite increased with time. Sorption was initially rapid, with over 93% arsenate being sorbed in a 24-h period at pH 6. Similar arsenate adsorption behavior was observed at pH 4. Analysis of the samples with extended x-ray absorption fine structure (EXAFS) revealed that there exist two distinct atomic shells surrounding the adsorbed As. The closest atomic shell was identified as an O atom, the next shell out was identified as an Fe atom. The As–Fe bond distance of 3.30 Å, derived from XAFS data, is indicative of a bidentate binuclear bond forming between the arsenate atoms and the goethite surface. This is in agreement with the findings of previous researchers. Analysis of the As EXAFS from samples incubated for various periods indicated that the molecular environment did not change over time. Complimentary desorption kinetic studies showed that when aging was increased, there was no significant change in the amount of arsenate desorbed from goethite by PO_4^{3-}. Initially, desorption was quite rapid with >35% of the total adsorbed As being desorbed within 24 h at pH 6. After the initial rapid desorption, only a small amount of additional desorption occurred at longer times. A significant amount of arsenate remained bound to the goethite after 5 mo of desorption even though the PO_4^{3-} desorptive solution was three times stronger than the initial arsenate sorptive solution. Sulfate was much less effective at promoting arsenate desorption; at pH 6, no more than 2.5% of the total sorbed arsenate desorbed over a 5-mo period. Desorption results at pH 4 were similar to the desorption behavior at pH 6. The XAFS analyses of PO_4^{3-} desorbed arsenate samples showed that the molecular environment of the adsorbed arsenate did not change.

As a result of natural and anthropogenic sources, the distribution of As is virtually ubiquitous in the environment. The major oxidation states of As in the soil environment are As(III) (arsenite) or As(V) (arsenate). As(III) can be oxidized in soils by manganese oxides to form As(V) which is the dominant species under nonreducing conditions in soils. The acid dissociation constants for H_3AsO_4 are: $pK_1 = 3.60$, $pK_2 = 7.25$, and $pK_3 = 12.52$ (Whitten et al., 1992). The primary sorbent phases for arsenate are hydr(oxides) of Fe and Al (Fordham and Norrish, 1974, 1983; Huang, 1975; Livesey and Huang, 1981; Pierce and Moore, 1982). Arsenate can also sorb to micron-size particles of rutile

Dep. of Geological Sciences, 4044 Derring Hall, Virginia Polytech. Inst. and State Univ., Blacksburg, VA 24061-0420; Dep. of Plant, Soil, and Entomological Sciences, Univ. of Idaho, Moscow, ID 83844-2339; Dep. of Plant and Soil Sciences, Univ. of Delaware, Newark, DE 19717-1303. Received 12 Nov. 1999. *Corresponding author (soreilly@ vt.edu).

and anatase, but it does not sorb significantly to pure clay minerals or soil organic matter (Fordham and Norrish, 1979, 1983; Jacobs et al., 1970). Arsenate sorption on soils and soil components vs. pH increases until maximum sorption is reached and then sorption decreases with further pH increase (Goldberg and Glaubig, 1988; Xu et al., 1988). For example, arsenate sorption on montmorillonite and kaolinite increased at low pH, displayed a peak near pH 5, and decreased at higher pH values (Goldberg and Glaubig, 1988).

Goethite (α–FeOOH), the most common iron oxide in soils, has double bands of $FeO_3(OH)_3$ octahedra which share edges and corners to form 2 by 1 octahedra tunnels (only large enough to accommodate the passage of protons) partially bonded by H bonds (Cornell and Shwertmann, 1996; Schwertmann and Cornell, 1991; Sparks, 1995). Goethite exhibits needle-shaped crystals with grooves and edges (Sparks, 1995).

Researchers have shown that arsenate is specifically sorbed onto iron oxides such as goethite through an inner-sphere complex via a ligand exchange mechanism (Fuller et al. 1993; Fendorf et al., 1997; Grossl et al., 1997; Hsia et al., 1994; Lumsdon et al., 1984; Parfitt, 1978; Sun and Doner, 1996; Waychunas et al., 1993). Sun and Doner (1996), using Transmission-Fourier Transform Infrared (T-FTIR) and Attenuated Total Reflectance-FTIR (ATR-FTIR) spectroscopy, found that arsenate replaced two singly coordinated surface OH groups to form binuclear bridging complexes. Lumsdon et al. (1984), using infrared spectroscopy, discovered that the $HAsO_4^{2-}$ ion participated in ligand exchange reactions displacing singly coordinated surface hydroxl groups to adsorb as a binuclear species. EXAFS studies by Fendorf et al. (1997), Waychunas et al. (1993), and Manceau (1995) found that bidentate binuclear complexation was the major bonding mechanism for arsenate adsorption on goethite. On the basis of a pressure-jump relaxation study and confirmed by EXAFS, Grossl et al. (1997) and Fendorf et al. (1997) demonstrated that arsenate can form three types of surface complexes on goethite depending on the surface coverage level (Fig. 1 and Table 1). At their highest loading level (Γ = mol As/mol Fe; log Γ = −2.05), Fendorf et al. (1997) fit a shell at 3.24 Å dominated with the fits being improved significantly by the addition of a shell at 2.85 and 3.59 Å. Their XAFS data indicated that monodentate surface complexes ($R_{As–Fe}$ = 3.59 Å) dominated at low surface coverages, bidentate mononuclear complexes ($R_{As–Fe}$ = 2.85 Å) dominated at high surface coverages, and bidentate binuclear complexes ($R_{As–Fe}$ = 3.24 Å) dominated at surface coverages near monolayer capacity. Grossl et al. (1997) proposed that, at extremely low surface coverages, a ligand exchange

Fig.1. Schematic illustration of the proposed adsorption mechanisms of arsenate onto goethite.

reaction of $H_2AsO_4^-$ with surface OH groups formed the monodentate complex. At high surface loadings, the sorption of arsenate was dominated by the formation of bidentate surface complexes after a second ligand exchange reaction occurred; however, along with the surface coverage, the pH of the samples was also different (the two lowest loading levels in their study had higher pH values) (Table 1) because the authors adjusted pH to control the loading levels. This may have caused changes in the goethite surface charge and the species of arsenic in solution which in turn could change the favored bonding complex on the goethite. Waychunas et al. (1993) fit an As–Fe peak with 2.35 ± 0.26 As–Fe bonds at 3.29 ± 0.04 Å which indicated bidentate binuclear bridging for most of their samples. They fit a second Fe shell only for the sample with the lowest arsenate loading (As/Fe 0.0015 or log Γ = −2.82) (Table 1). This shell was located at a distance of 3.65 Å from the central As atom, which corresponds to a monodentate arsenate complex. Waychunas et al. (1993) and Fendorf et al. (1997) concluded that As(V) forms inner-sphere bidentate (bridging) complexes on both goethite and ferrihydrite, but, at very low surface coverages, monodentate complexes may form on crystalline goethite under the conditions in their study. Waychunas et al. (1993) found that the fraction of monodentate bonds decreased as the arsenate coverage increased for the amorphous iron oxide samples. Over a 1- to 7-wk period, they did not see an aging effect on the fraction of monodentate bonds in the ferrihydrite samples; however, Manceau (1995) argued that the monodentate structure seen by

Waychunas et al. (1993) was misinterpreted and that a bidentate mononuclear complex (R_{As-Fe} = 2.83 Å), as seen with selenate, was what really formed on the goethite. Manceau (1995) surmised that the bidentate mononuclear complex would not occur in more crystalline samples and that it may also vanish at higher loading rates. Manceau (1995) did agree that the primary sorptive complex was a bidentate binuclear bridging complex. In a rebuttal to the remarks of Manceau (1995), Waychunas et al. (1995) cast doubt on the stability of the edge sharing arsenate group (R_{As-Fe} = 2.83 Å) and showed that the corner-sharing bidentate arsenate model (R_{As-Fe} = 3.26 Å) dominated in most of their samples.

Adsorption of arsenate has been shown to be rapid initially and decrease with increasing equilibration time (Ferguson and Anderson, 1974; Fuller et al., 1993; Livesey and Huang, 1981; McGeehan et al., 1992; Pierce and Moore, 1982; Raven et al., 1998). In fact, Onken and Adriano (1997) found that As became more recalcitrant in soils over time; however, most kinetic studies have been conducted over very short time periods of minutes and hours. Fuller et al. (1993) found that slow adsorption of arsenate on ferrihydrite continued for a minimum of 192 h, and investigations with Co, Cd, Pb, N, and Zn have also shown continued slow sorption (Ainsworth et al., 1994; Backes et al., 1995; Bruemmer et al., 1988). Longer term studies are more applicable to contaminated soils where the metal or metalloid may have reacted with the soil for months and years (Sparks, 1995). Hypotheses for the slow sorption mechanisms

Table 1. Comparison of pH and loading levels of XAFS studies.

Sorption studies				Desorption studies on sample adsorbed for 1032 h				Waychunas et al. (1993)			Fendorf et al. (1997)		
Sorption	log Γ	pH	Proposed sorption mechanism	Desorption	log Γ	pH	Proposed sorption mechanism	log Γ	pH	Proposed sorption mechanism	log Γ	pH	Proposed sorption mechanism
0.5 h	−1.83	6	bidentate binuclear	24 h	−2.01	6	bidentate binuclear	−2.15	8	bidentate binuclear	−2.05	6	monodentate
24 h	−1.77	6	bidentate binuclear	1 h	−1.81	6	bidentate binuclear	−2.82	8	monodentate	−2.15	8	bidentate mononuclear
168 h	−1.77	6	bidentate binuclear								−2.27	9	bidentate binuclear
741 h	−1.76	6	bidentate binuclear										
1032 h	−1.77	6	bidentate binuclear										

include diffusion, different sites of reactivity, or surface precipitation.

Arsenate is not easily desorbable or removed. Johnston and Barnard (1979) tested many soil extractants (such as 0.5 M NH_4F, 0.5 M $NaHCO_3$, 0.5 M HCl, 0.5 M KH_2PO_4, and 0.25 M H_2SO_4), however, none of the extractants removed more than 80% of the As after 18 h of shaking, which was observed by other researchers (i.e., Waychunas et al., 1993; Woolson et al., 1973). Woolson et al. (1973) showed that arsenate could be leached from soil by PO_4^{3-}, and Melamed et al. (1995) and Davenport and Peryea (1991) showed that arsenate mobility was vastly enhanced by treatments with increasing amounts of PO_4^{3-}. Phosphate-released As was not significantly resorbed in the presence of added PO_4^{3-} (Amacher and Amacher, 1994; Peryea, 1991). Misra and Tiwari (1963) showed that several mineral acids (0.05 M H_2SO_4 and 0.1 M HCl) and PO_4^{3-} solution [0.1 M $(NH_4)_2HPO_4$ and 2.5×10^{-3} M Na-pyrophosphate] extract about the same amount of arsenate. Darland and Inskeep (1997) conducted transport studies using free iron oxides in a sand column and found that PO_4^{3-} effectively competes with arsenate; however, the PO_4^{3-} was not able to desorb all of the applied arsenate, regardless of whether the arsenate was applied concurrently or prior to PO_4^{3-} addition (as in a desorption study). Even when the applied PO_4^{3-} surpassed the column adsorption capacity by twofold, some arsenate remained adsorbed to the free iron oxides in the sand. Similarly, when the authors applied a high concentration of PO_4^{3-} perpetually to a column that had heretofore been spiked with arsenate, recovery of arsenate in the effluent did not exceed 60%, even though the total PO_4^{3-} loading was greater than the calculated column capacity by more than two orders of magnitude (Darland and Inskeep, 1997). In contrast, Pierce and Moore (1982) found that once arsenate was sorbed to a natural surface in an aqueous system, the sorbed arsenate was not affected by the post addition of PO_4^{3-} and SO_4^{2-}; however, sorbed arsenate was affected, at low concentrations, by the prior addition of PO_4^{3-} and SO_4^{2-} to the system.

The ability of PO_4^{3-} to compete with arsenate for goethite surface sites was somewhat expected since PO_4^{3-}, like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism (Parfitt, 1978; Persson et al., 1996; Tejedor-Tejedor and Anderson, 1990). Phosphate is considered an analog of arsenate (they have similar chemical properties and behaviors). They are both oxyanions in aqueous solution with three similar acid dissociation constants. The acid dissociation constants for H_3PO_4 are: $pK_1 = 2.13$, $pK_2 = 7.21$, $pK_3 = 12.44$, and for H_3AsO_4 are: $pK_1 = 3.60$, $pK_2 = 7.25$, and $pK_3 = 12.52$ (Whitten et al., 1992); however, Lumsdon et al. (1984) determined that arsenate may sorb more strongly because, unlike PO_4^{3-}, the arsenate ion is larger in size and interacts more strongly with some of the OH groups that remain on the surface. Additionally, Barrow (1992) concluded that PO_4^{3-} becomes more competitive over time since it is capable of slow sorption.

Sulfate can be sorbed as either an outer- or inner-sphere complex (Gebhardt and Coleman, 1974; He et al., 1997), however, only a few studies have provided direct in situ spectroscopic evidence to suggest inner-sphere complexation (i.e., Parfitt and Russell, 1977; Parfitt and Smart, 1977; Marten and Smart, 1987; Hug, 1997; Peak et al., 1999). Zhang and Sparks (1990) hypothesized that SO_4^{2-} adsorption on goethite resulted in the formation of an outer-sphere complex via electrostatic attraction. Kinjo et al. (1971) proposed that under the conditions of their study (SO_4^{2-} concentration ≤ 0.05 M), SO_4^{2-} was adsorbed via outer-sphere complexation, but at higher concentrations inner-sphere adsorption was the operative mechanism. Myeni et al. (1997), working in alkaline environments with the solid ettringite, reported no arsenate desorption in the presence of SO_4^{2-} in high ionic strength solutions. Xu et al. (1988) suggested that SO_4^{2-} can compete with $H_2AsO_4^-$ and $HAsO_4^{2-}$ and occupy surface sites on the alumina.

In short, since arsenate forms a strong, inner-sphere complex with goethite, to promote desorption an effective ion would have to compete for the same sorption sites (i.e., inner-sphere sorption). As discussed above, studies have shown that PO_4^{3-} is able to form this type of bond with goethite while SO_4^{2-} may or may not form this type of bond with the surface depending on the experimental conditions.

The results of Grossl et al. (1997) showed that desorption was the rate-limiting step in the reaction of arsenate with a hydroxylated goethite surface since the rate constants for desorption of arsenate from goethite were lower than the rate constants for adsorption of arsenate. Fuller et al. (1993) theorized that arsenate desorption from a poorly crystalline iron oxide was limited by diffusional processes. Accordingly, the goals of this study were to combine macroscopic and molecular level studies to ascertain the effects of aging or residence time on the kinetics and mechanisms of arsenate sorption and desorption on goethite. Phosphate and SO_4^{2-} were chosen as desorptive solutions because they are common soil nutrients. Such an understanding is necessary to provide much needed information on the mobility, persistence, and fate of As in the environment.

MATERIALS AND METHODS

The goethite used as a model soil component in this study was synthesized in the laboratory using a modified version of Atkinson et al., 1968. Ferric nitrate (0.2 M) solution was slowly titrated with KOH in a plastic bottle until the pH reached 12; it was then put in an oven at 343 K overnight. The goethite, which had settled to the bottom of the container, was washed with dialysis tubing until the conductivity matched that of distilled deionized water. Once the goethite was dialyzed, it was freeze dried and stored in a vacuum desiccator.

The goethite was characterized by x-ray diffraction (XRD). Surface area (BET N_2 adsorption) measurements were conducted on a Micrometrics Surface Area Analyzer (Micrometrics Instruments Corp., Norcross, GA); the surface area was 87.97 m^2 g^{-1}. The point of zero salt effect (PZSE), calculated via potentiometric titration analysis (Zelazny et al., 1996) was 6.8. Zelazny et al. (1996), and references therein, reported a PZSE value of 7.3 ± 0.2. Our value is slightly low, which may be due to differences in experimental methods or minor differences in the solid itself.
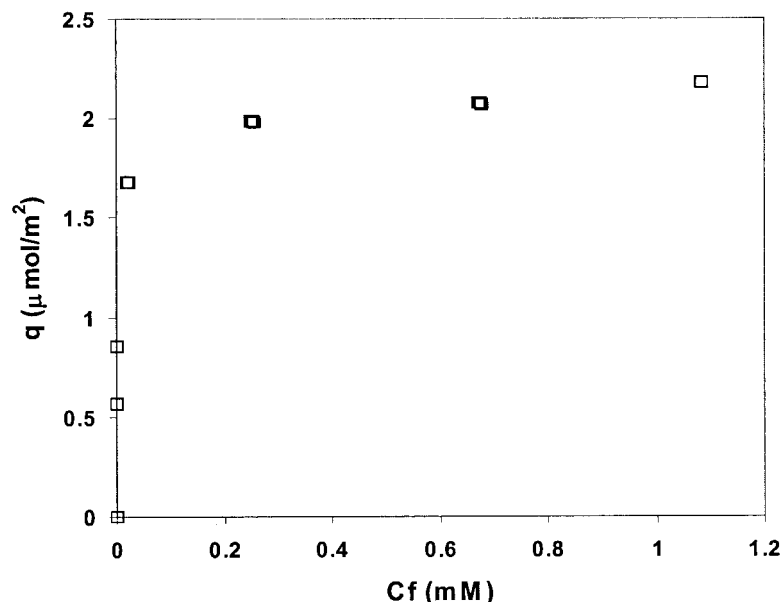
Fig. 2. Arsenate sorption isotherm in triplicate on goethite at pH 6 and 298 K. The ionic strength was 0.1 M in NaNO$_3$, and the solid/solution was 10 g L^{-1}.

A traditional test tube batch sorption isotherm experiment was conducted in triplicate in order to better understand the system. Initial arsenic concentrations of 0, 0.5, 0.75, 1.5, 2, 2.5, and 3 mM sodium arsenate were equilibrated on a reciprocating shaker for 24 h at 298 K. All solutions were pre-equilibrated at pH 6 and the pH was measured at the end of the experiment. The final ionic strength in the tubes was 0.1 M in NaNO$_3$ and the solid–solution was 10 g L^{-1}. These experimental conditions are similar to those described below. The samples were then centrifuged and filtered through a 0.22 αm membrane filter. The filtrate was analyzed via inductively coupled plasma atomic emission spectrometry (ICP-AES, Enviro II, Thermo Jarrell Ash, Franklin, MA) for arsenate as total arsenic. Figure 2 shows the results of the sorption isotherm of As(V) on goethite at pH 6. The shape of the isotherm is similar to those found for arsenate on hydrous iron oxide, and ferrihydrite (see Hsia et al., 1994; Raven et al., 1998).

Kinetic Studies

To study the kinetics of arsenate sorption on goethite, initial arsenate concentrations were selected to meet the following criteria: (i) the reaction pH should be ≈5 to 8, a common range for natural soils, to promote arsenate as the predominant species of As in solution, and (ii) the concentration of arsenate in solution must be high enough to be in the detection range for analysis via ICP and XAFS spectroscopy (in order for complimentary spectroscopic studies and desorption studies to be conducted).

The sorption kinetics experiments were performed with an initial arsenate concentration of 2 mM Na$_2$HAsO$_4$·7H$_2$O, and a constant pH (either 4 or 6) using a stirred pH–stat apparatus. Experiments were conducted using plastic batch reactors and mixed with a stir bar to limit the effects of diffusion. The experiments were primarily conducted at pH 6 (below the PZSE); however, a few kinetic experiments were conducted at pH 4. The sorbents were hydrated (in a 0.1 M NaNO$_3$ matrix) and pH adjusted with 0.1 M HNO$_3$ 24 h before they were reacted with the arsenate. The final solid/solution ratio was 10 g L^{-1}. The pH–stat automatically adjusted the pH and recorded the amount of acid added. The sample was placed in a water bath at 298 K, and CO$_2$ was controlled via N$_2$

purging. Samples were taken from the batch reactor over a period of 4 min to 12 mo. The samples were then centrifuged and filtered through a 0.22 μm membrane filter. The filtrate was analyzed via inductively coupled plasma atomic emission spectrometry (ICP-AES, Enviro II Thermo Jarrell Ashe) for arsenate as total arsenic. The ICP can measure As in the range of 0.05 to 250 mg L^{-1} with 95% accuracy. Arsenate sorption was calculated from the difference between the initial and final arsenate concentrations. Stock solution concentrations were also confirmed via the ICP. External ICP standards were used to confirm the concentration of the samples and the stock solutions used in the experiments. Iron measurements were taken to confirm that dissolution of the goethite was not occurring. After 24 h of sorption, the vessel was removed from the pH–stat since preliminary studies showed that the majority of the reaction took place within this time. The vessel was stored in a constant temperature chamber where it was periodically mixed and the pH was adjusted.

Desorption studies were conducted on goethite samples reacted with arsenate for times ranging from 45 min to 7 mo. The adsorption samples were prepared for desorption by first centrifuging the arsenate-reacted samples and washing by resuspending the samples with 0.001 M NaNO$_3$ (adjusted to pH 6) and then centrifuging to remove entrained As (preliminary studies showed that washing did not result in significant arsenate desorption from the goethite surface). To initiate the desorption experiment the paste was then resuspended in the desorptive solution, 6 mM Na$_2$HPO$_4$ · H$_2$O or Na$_2$SO$_4$ · H$_2$O, by quickly vortexing and sonifying the paste with the added desorptive solution. The solid/solution ratio, ionic strength, pH of the solutions, and sampling methods were the same as for the sorption studies. Desorption sampling times ranged from 30 min to 5 mo. The amount of arsenate desorbed was quantified based on ICP results. The total percentage of arsenate desorbed was calculated by comparing the concentration of arsenate desorbed as total arsenic to the amount of total arsenic sorbed.

Extended X-Ray Absorption Fine Structure Spectroscopy Studies

Although macroscopic kinetic studies are very useful, they cannot be used to determine a specific bonding mechanism. In
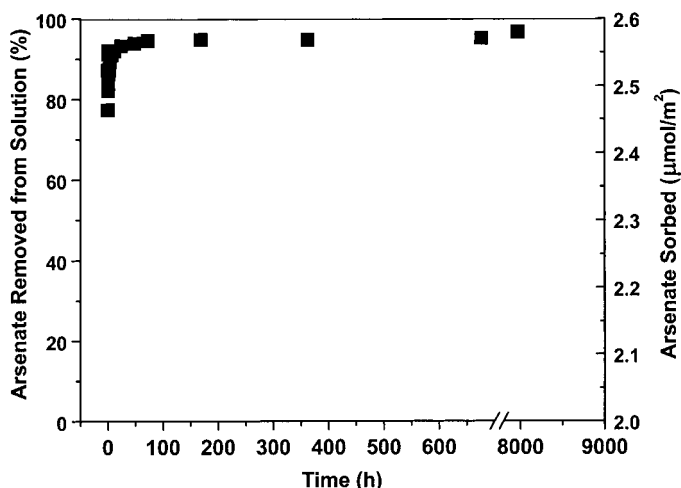
Fig. 3. Arsenate (2 mM) sorption kinetics on goethite at pH 6. The ionic strength was 0.1 M in NaNO$_3$ and the solid/solution was 10 g L^{-1}.

order to glean mechanistic information, detailed spectroscopic and/or microscopic studies need to be performed to uncover molecular and atomic resolution information (Sparks, 1995). Thus, complimentary XAFS studies were conducted to provide information on how the local chemical environment of the sorbed As(V) changes over long time periods and in the presence of desorptive solutions. This information is extremely relevant in situations in which a site has already been contaminated for long time periods and accurate risk assessments and remediation procedures still need to be determined.

Selected arsenate aged samples (0.5 h–1 mo) were analyzed using XAFS. Vessels were setup identically to the adsorption pH–stat kinetic vessels and the contents of the vessel were used as an XAFS sample. The vessel was removed from the pH–stat, constant temperature chamber at the selected aging time, centrifuged, and the supernatant decanted. After decanting the supernatant and analyzing for As and Fe as before, the paste was washed with diluted electrolyte solution (0.001 M NaNO$_3$ adjusted to pH 6) to remove any entrained solution and then centrifuged once again to remove the solution. The pastes were stored in a refrigerator to keep them moist and to hinder microbial growth so the paste could be analyzed using XAFS spectroscopy. Two samples that had sorbed arsenate for 1032 h (about a month and a half) at pH 6 were subsequently desorbed with PO$_4^{3-}$, 6 mM Na$_2$HPO$_4$ · H$_2$O (adjusted to pH 6), for 1 h or 24 h and also were analyzed by XAFS. The 24 h sample was replenished with fresh PO$_4^{3-}$ solution every 12 h after centrifuging and collecting the previ-

ous solution. The goethite was then resuspended in the fresh desorptive solution and all the old previous desorptive solutions were analyzed as in the other experiments. The amount of arsenate desorbed was calculated by adding the arsenate present in each of the PO$_4^{3-}$ solutions used to desorb the arsenate. The remaining experimental parameters were consistent with the methods above (pH–stat, etc.).

The XAFS measurements were made on beamline X-11A at the NSLS (National Synchrotron Light Source), Brookhaven National Laboratory, Upton, NY. The electron storage ring is operated at 2.5 GeV with a current range of about 110 to 300 mA. The K edge of As (11 867 eV) was probed with an unfocused beam. An Si(111) double crystal monochromator was used with a 0.5 mm vertical entrance slit. In order to achieve higher-order harmonic rejection, one of the monochromator crystals was detuned 20% with respect to the other crystal. The spectra were collected in fluorescence mode using a Stern-Herald type detector equipped with a Ge-filter. Krypton gas was bubbled at 10 cm^3 ($\approx$1 bubble per sec) through a Lytle detector (The EXAFS Co., Pioche, NV). The fill gasses used in the ionization chamber were 90% N$_2$ and 10% Ar. Samples were mounted in a 4- by 6- by 25-mm slot cut in a stainless steel block or in thin Al holders with an open slot to allow for both transmission and fluorescence data to be collected if desired. The samples were sealed with Kapton tape (Type K-104) to prevent moisture loss and minimize x-ray absorption. The spectra were obtained at 77 K to reduce thermal disorder of the sample.
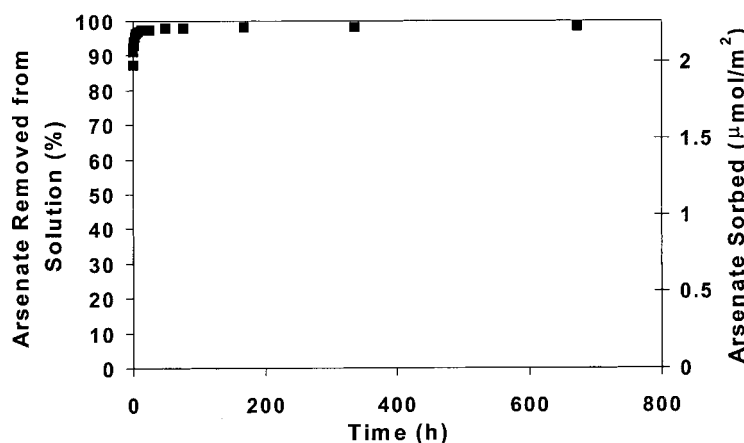

Fig. 4. Arsenate (2 mM) sorption kinetics on goethite at pH 4. The ionic strength was 0.1 M in NaNO$_3$ and the solid/solution was 10 g L^{-1}.
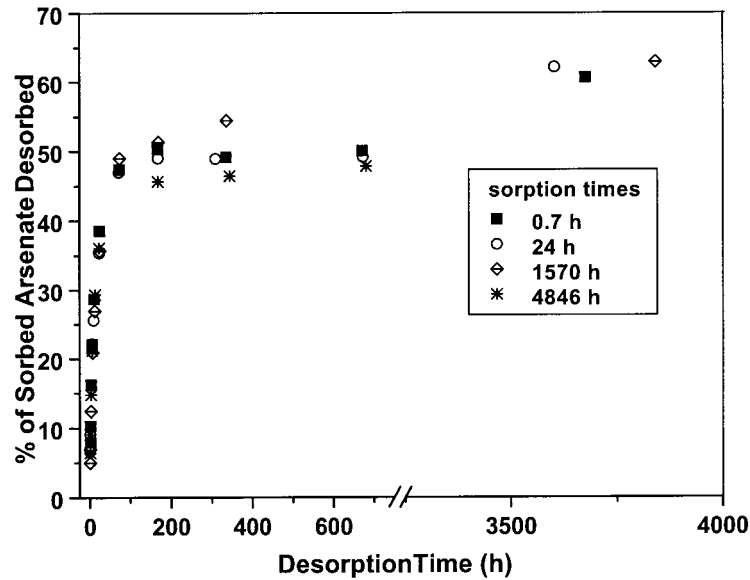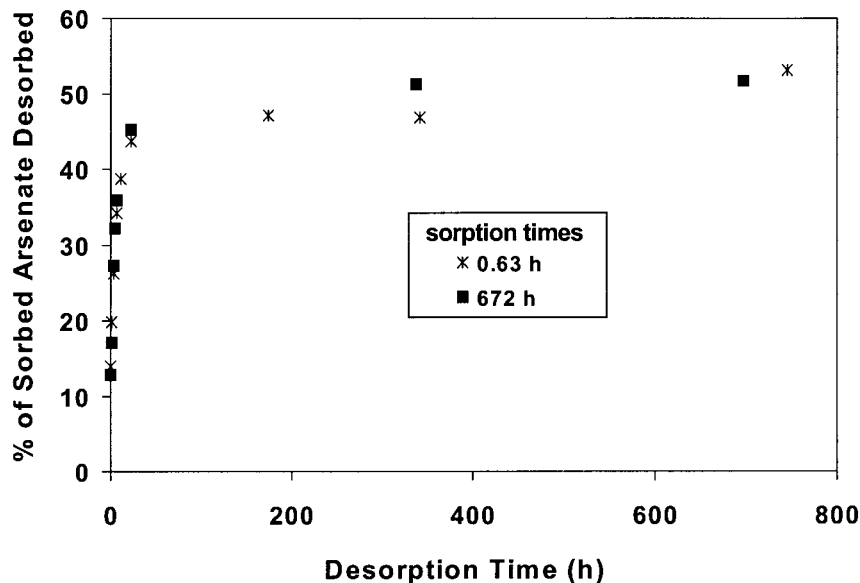
Fig. 5. Arsenate desorption kinetics in the presence of phosphate (6 m*M*) at pH 6. The ionic strength was 0.1 *M* in NaNO₃, and the solid/solution was 10 g L⁻¹.

Data analysis was done using MacXAFS 4.0 (Bouldin et al., 1995). The analysis proceeded as follows

1. To improve the signal/noise ratio, three spectra were collected and averaged.
2. Merged scans were normalized relative to E_0 (determined from the inflection point of the derivative of the spectra).
3. The chi function was extracted from the raw data using linear preedge and a cubic spline postedge consisting of two knots, and converting the data from energy to k space.
4. The chi function was then weighted by k^3 in order to compensate for dampening of the XAFS amplitude with increasing k.
5. The data were Fourier transformed ($\Delta k = 2.7 - 14.5$ Å⁻¹ or $\Delta k = 2.7 - 12.6$ Å⁻¹ for the 1 h desorption sample) to yield a radial structure function (RSF).

6. The data were fit in R space as discussed in detail below (identical results were found by fitting in k space).

Scorodite ($FeAsO_4 \cdot H_2O$, Ward's Natural Science catalog #46E7180, Rochester, NY) was used as a standard compound because it was a good model for the arsenate/goethite sorption product. The sample originated from the mines of Gold Hill, Toole County, Utah, USA. The scorodite was ground with a mortar and pestle and diluted to 1% by weight in boron nitride. It was then packed into a thin sample holder and analyzed via XAFS in the same manner as the As–goethite samples. Since the chemical structural information is known for scorodite, it can be fit theoretically and an amplitude reduction factor can be calculated to use when fitting the samples. The crystal structure (atomic positions) of scorodite was obtained from Kitahama et al. (1975). The atomic positions and space groups were input into the ATOMS program that generates the input needed for the FEFF 6.01 code (Zabinsky et al.,

Fig. 6. Arsenate desorption in the presence of phosphate (6 m*M*) at pH 4. The ionic strength was 0.1 *M* in NaNO₃, and the solid/solution was 10 g L⁻¹.
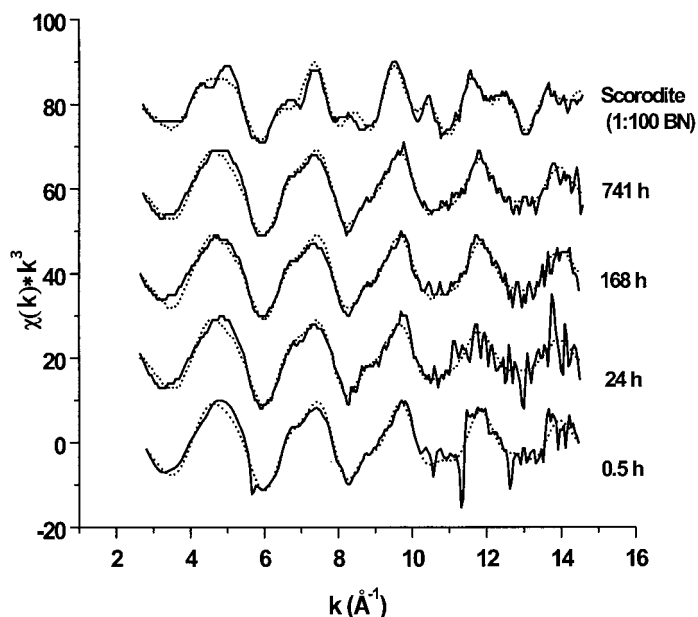
Fig. 7. The k³ weighted normalized χ functions for samples incubated with arsenate for different lengths of time and the scorodite sample diluted 1% by weight in boron nitride. The solid line represents the experimental data, and the dotted line represents the multishell fit to the data.

1995). The FEFF code in turn generates the path files or the single scattering theoretical spectra and phase shifts for the As–O and As–Fe backscatterers. Ionization chamber fill gas corrections (Bunker, 1988) and McMaster's corrections (McMaster et al., 1968) were done for the scorodite and later for the As–goethite samples, but these corrections had no significant effect on the fitting results, so they were not used. After fitting, self-absorption corrections were calculated for the scorodite and this value was used to obtain the new amplitude reduction factor for the samples. The first two shells of the data were fit, and the best fit was obtained by considering all the first shell contributions to be As–O contributions and all the second shell backscatterers to be As–Fe contributions. Errors in the coordination number (N) and the interatomic distances (R) were estimated by comparison of the EXAFS fit results to the values given by Kitahama et al. (1974) for scorodite. The accuracies of the R and N between As and the first shell O backscatterers and the second shell Fe backscatterers were equal or larger than the confidence limits of the least-squares nonlinear fitting procedure. The accuracies were ±0.30% for the interatomic distances, ±12% for the As–O shell coordination number, and ±38% for the As–Fe shell coordination number.

RESULTS AND DISCUSSION

Sorption Kinetics Study

Figure 3 shows the results of the As(V) sorption kinetics on goethite at pH 6. Since the last point plotted on Fig. 3 was taken after almost a year, the ordinate is broken. Initial arsenate sorption was very rapid with over 93% being sorbed within a 24-h period. As time increased, the total amount of As(V) sorption increased. There were slight increases in sorption at the later times, but since the initial sorption was so rapid and extensive, there was not much As(V) left in solution to sorb at the later time periods. After one year, almost 100% of the added As(V) sorbed to the goethite. These results were similar to those obtained by Fuller et al. (1993)

who also observed a period of rapid As(V) uptake followed by continual adsorption, and McGeehan et al. (1992) who saw rapid initial adsorption followed by a plateau phase.

For comparison, an additional sorption kinetic study was conducted at pH 4 (Fig. 4). The results were similar to those obtained at pH 6 (Fig. 3). Initial sorption was very rapid; total sorption increased over time, and after ≈1 mo, 100% sorption occurred; however, the initial arsenate sorption was more rapid at pH 4 than at pH 6 with over 97% being sorbed within the first 24-h period (compared with 93% at pH 6; Fig. 3). This result was not surprising
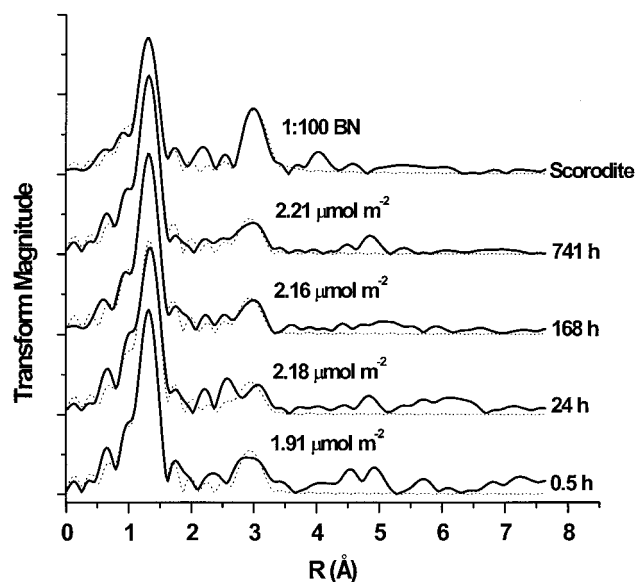

Fig. 8. Fourier transforms (radial structure functions, RSF) of the normalized χ functions in Fig. 7 for samples incubated for different lengths of time, and scorodite diluted 1% by weight in boron nitride. The solid line represents the experimental data, and the dotted line represents the multishell fit to the data.

Table 2. Structural parameters for As adsorption on goethite samples reacted for various lengths of time, and scorodite diluted 1% by BN, derived from the best-fit results of the EXAFS experimental data.

Sorption time	As–O shell				As–Fe shell		
	E_0†	R‡,#	N§,††	σ^2¶	R#	N‡‡	σ^2
		Å		Å²	Å		Å²
0.5 h	−6.04	1.69	4.9	0.0024	3.30	1.76	0.0028
24 h	−7.80	1.70	4.7	0.0025	3.30	2.54	0.0068
168 h	−4.61	1.69	4.2	0.0015	3.29	1.93	0.0049
741 h	−5.96	1.69	4.8	0.0024	3.30	1.84	0.0042
scorodite	−5.11	1.68	3.5	0.0020	3.37	2.48	0.0020

Fit quality confidence limits for parameters: # ±0.30%, †† ±12%, ‡‡ ±38%.
† Phase shift.
‡ Interatomic distance.
§ Coordination number.
¶ Debye Waller factor.

since a sorption envelope experiment, data not shown, revealed the sorption maximum was at pH 4.

The effect of sorption residence time (2 m*M* initial arsenate concentration) on arsenate desorption kinetics in the presence of 6 m*M* PO_4^{3-} at pH 6 is shown in Fig. 5. Initially, desorption was very fast with >35% being desorbed within 24 h. After the initial rapid desorption the release slowed down. Total desorption increased with time reaching about 65% total desorption after ≈5 mo. These results showed that a significant amount of arsenate was still retained on the goethite after 5 mo of desorption even though the PO_4^{3-} desorptive solution was three times more concentrated than the initial arsenate sorptive solution. There was no measurable effect of aging or residence time on the desorption of the arsenate in the presence of PO_4^{3-} (Fig. 5). For example, the amount of arsenate desorbed at ≈1 mo after a residence time of 0.7 h was 50% compared with 48% after a sorption residence time of ≈7 mo.

Arsenate desorption kinetics in the presence of PO_4^{3-} at pH 4 is shown in Fig. 6. The goethite was reacted with arsenate for 0.63 and 672 h (≈1 mo) and then subsequently desorbed for up to ≈1 mo. The results are similar to those at pH 6. The initial arsenate desorption was rapid with about 45% desorbed within the first 24 h. Desorption then leveled off and the total percentage arsenate desorbed at pH 4 after one month was ≈53%. Similar to the pH 6 desorption data, there was no effect of sorption residence time on arsenate desorption at pH 4. These results (i.e., Fig. 3 and Fig. 5, or Fig. 4 and Fig. 6) indicate that desorption is much slower than sorption which is expected for a ligand exchange reaction (McBride, 1994).

Although not shown, very little arsenate was desorbed by SO_4^{2-} at pH 6 or 4 and residence time had little, if any, effect on arsenate desorption. The maximum amount of arsenate desorbed was <3%. The results from our study are not surprising since SO_4^{2-} is less strongly sorbed than PO_4^{3-} and is thus a much less effective desorbent (Geelhoed et al., 1997; Haque and Walmsley, 1973; Parfitt, 1978). The mechanisms for adsorption of arsenate and SO_4^{2-} were probably not identical because arsenate adsorption should have decreased with increased SO_4^{2-} concentration if the mechanisms were
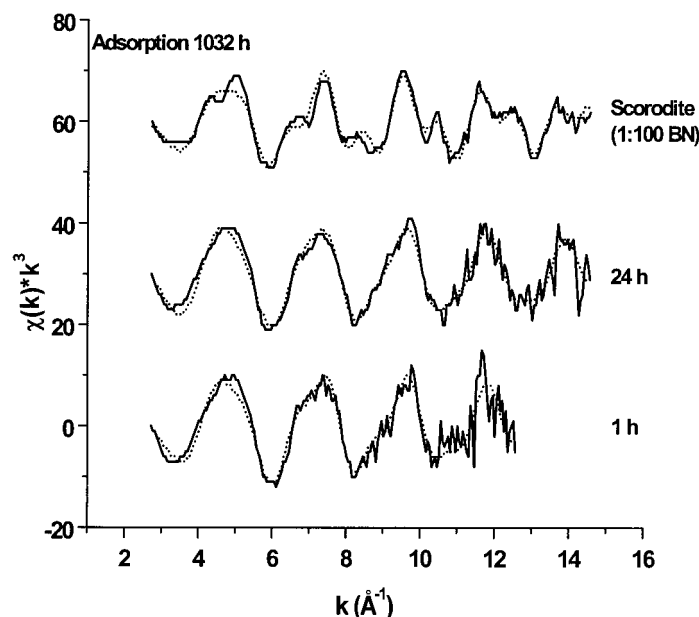

Fig. 9. The k³ weighted normalized χ functions for samples incubated for 1032 h with arsenate and then desorbed for various times in the presence of 6 m*M* phosphate solution and the scorodite sample diluted 1% by weight in boron nitride. The solid line represents the experimental data, and the dotted line represents the multishell fit of the data.
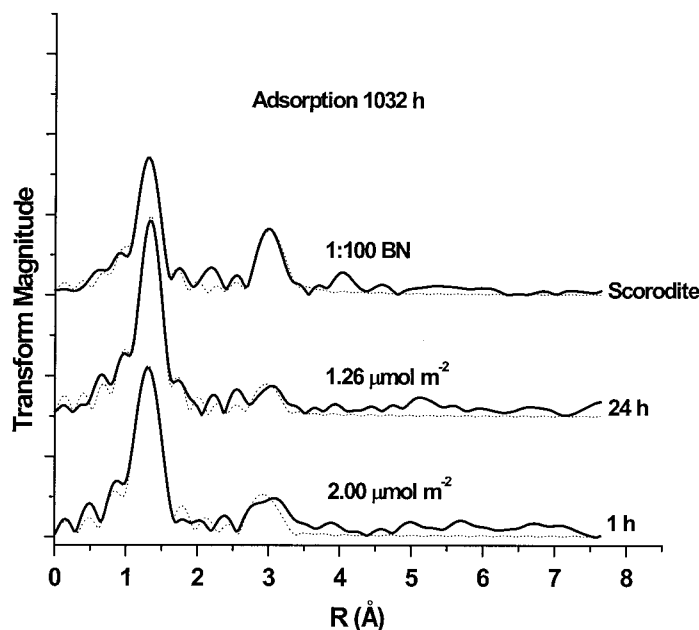
Fig. 10. Fourier transforms (radial structure functions, RSF) of the normalized χ functions in Fig. 9 for samples adsorbed for 1032 h and desorbed for various times in the presence of 6 mM sodium phosphate solution. The scorodite standard diluted 1% by weight in boron nitride is also shown for comparison. The solid line represents the experimental data, and the dotted line represents the multishell fit to the data.

the same. In fact, Geelhoed et al. (1997) found that PO_4^{3-} was a stronger competitor for adsorption on goethite than SO_4^{2-} in competitive adsorption systems with PO_4^{3-} and SO_4^{2-}.

Extended X-Ray Absorption Fine Structure Spectroscopy Studies

Figure 7 shows the background subtracted k^3 weighted χ functions (solid lines) along with their best fit (dotted lines) for the samples reacted with arsenate for 0.5 to 741 h (≈1 mo) and the scorodite standard [diluted 1:100 in boron nitride (BN)]. A sinusoidal beat pattern characteristic of a strong first neighbor O–shell backscattering atom is present in all of the sorption samples. The existence of numerous frequencies due to second shell backscattering would result in dampening or additive amplitude effects on the peaks, or the formation of shoulders due to a strong frequency differing from the primary frequency; however, these characteristics are rather difficult to discern in the χ function if their contributions are small. The RSFs are generated by Fourier transforming the χ spectra. The representative frequencies of the individual components in the χ function are more clearly illustrated in the RSF and thus can be more readily detected in the RSF then in the χ function. The RSFs (uncorrected for phase shift) derived from the XAFS data for the samples and standard are given in Fig. 8 (solid lines) along with their best fit (dotted lines) for the samples and the diluted standard. The structural parameters (the number of coordinating atoms (N), the interatomic distance (R), and the Debye-Waller factor ($σ^2$) (which is indicative of disorder) derived from the fitting procedure are given in Table 2. As was discussed earlier, the best fit was obtained by considering all the first shell contributions to be As–O contributions and all the second shell backscatterers to be As–Fe contribu-

tions. The first shell centered at about 1.30 Å (uncorrected for phase shift; Fig. 8) can be fit with 4.2 – 4.9 O backscatterers at $R = 1.69 – 1.70$ Å from the central As atom. The second peak, centered at about 2.90 Å (uncorrected for phase shift; Fig. 8), can be fit with 1.8 – 2.5 Fe backscatterers 3.29 – 3.30 Å from the central As atom. To infer the arsenate sorption mechanisms from the XAFS data fits, we used the structural parameters from Szytula et al. (1968) in ATOMS (note that the space group of goethite has been reassigned since the paper has been published; see Cornell and Schwertmann, 1996) and assumed a zero tilt angle for arsenate, an ideal octahedral coordination for goethite, and no bond relaxation. The As–O distance used was an average of our XAFS value ($R_{As–O} = 1.69$ Å). For a monodentate bond we calculated $R_{As–Fe} = 3.71$ Å, for a bidentate mononuclear bond $R_{As–Fe} = 2.36$ Å, and for a bidentate binuclear bond $R_{As–Fe} = 3.17$ Å. The $R_{As–Fe}$ value derived from our XAFS data is 3.30 Å, which is close to the calculated distance for bidentate binuclear bonding. Thus, we conclude that in our samples, arsenate is bound to goethite via a bidentate binuclear complex.

We did not observe monodentate or bidentate mononuclear bonds in our system. There is some evidence at 24 h (18 $μM$ m^{-2} or $Γ = -1.77$) of a shell at 2.85 Å (about 2.55 Å if one does not account for phase shift), but most of the scans do not show significant evidence of these peaks above noise or contributions from other backscatterers other then those involved in bidentate bridging. This could be because of lower pH values or higher loading levels (log $Γ = -1.83$ to -1.76) used in our study compared with Fendorf et al. (1997) and Waychunas et al. (1993) (see Table 1). Fendorf et al. (1997) and Waychunas et al. (1993) observed the bidentate bridging bonds at higher loading levels on crystalline goethite. Our findings agree with Waychunas et al.

Table 3. Structural parameters for As desorption from goethite in the presence of phosphate. The samples were reacted with arsenate for 1032 h, and the sorbed geothite samples reacted with phosphate for various amounts of time. The scorodite standard (diluted 1:100 in BN) is shown for comparison. The parameters were derived from the best-fits results of the EXAFS experimental data.

Desorption time	As–O shell				As–Fe shell		
	E_0†	R‡,#	N§,††	σ^2¶	R#	N‡‡	σ^2
		Å		Å²	Å		Å²
1 h	−7.39	1.69	5.2	0.0021	3.31	2.30	0.0041
24 h	−7.18	1.70	4.5	0.0013	3.30	1.08	0.0021
scorodite	−5.11	1.58	3.5	0.0020	3.37	2.48	0.0020

Fit quality confidence limits for parameters: # ±0.30%, †† ±12%, ‡‡ ±38%.
† Phase shift.
‡ Interactomic distance.
§ Coordination number.
¶ Debye Waller factor.

(1993) in that precipitates are not occurring in this system.

Overall, we did not see any clear differences in the bonding mechanism of arsenate onto goethite among samples reacted for different times. Arsenate appears to be bound as a bidentate binuclear (bridging) complex at pH 6, and it does not appear to alter its bonding mechanism over a period of ≈1 mo.

Figure 9 shows the background subtracted k^3 weighted chi functions (solid lines) along with their best fit (dotted lines) for the samples incubated with arsenate for 1032 h and then subsequently desorbed with PO_4^{3-} for 1 h up to 1 wk, and the Scorodite standard (diluted 1:100 in BN). The RSFs derived from the XAFS data for the samples and standard are given in Fig. 10 (solid lines), along with their best fit (dotted lines). The structural parameters derived from the fitting procedure are given in Table 3. The best fit was obtained by fitting the first peak with O atoms and the second peak with Fe atoms, just as with the adsorption samples. The first shell centered at about 1.30 Å in the RSF (Fig. 10) was fit with 4.5 – 5.3 O backscatterers at R = 1.67 – 1.70 Å from the central As atom (Table 3). The second peak in the RSF centered at about 2.90 Å was fit with 1.1 – 7.2 Fe backscatterers 3.29 – 3.30 Å from the central As atom.

The arsenate that remained on the surface of the goethite was examined to see if any changes in the bonding mechanism occurred following the competitive desorption process with PO_4^{3-}. The $R_{As–Fe}$ value derived from our XAFS data was 3.30 Å, which is close to the calculated value of bidentate binuclear bonding. Thus, we conclude that in our desorption samples, arsenate was still bound to goethite via a bidentate binuclear complex as it was observed in the adsorption studies. The small peak appearing at 2.55 Å in the RSF (Fig. 10) could indicate bidentate mononuclear bonding at the lower loading levels, but this peak did not appear in all cases; however, because of the lower loading levels (relative to adsorption studies), the signal/noise ratio was lower. This makes the peak at 2.55 Å indistinguishable from the noise and other backscatterer contributions (Table 2). During the desorption process arsenate seems to be predominantly sorbed as a bidentate binuclear bridging complex, and we did not observe any changes in bonding mechanism following the one week PO_4^{3-} treatment.

In summary, our research showed that As forms bidentate binuclear complexes on goethite under the experimental conditions used in this study, and that this bond was stable for extended time periods. The amount of arsenate desorbed from the goethite using PO_4^{3-} to promote the desorption was much higher than the amount of As desorbed using SO_4^{2-}.

REFERENCES

Ainsworth, C.C., J.L. Pilon, P.L. Gassman, and W.G. Van Der Sluys. 1994. Cobalt, cadmium, and lead sorption to hydrous iron oxide: Residence time effect. Soil Sci. Soc. Am. J. 58:1615–1623.

Amacher, M.C., and J. Kotuby-Amacher. 1994. Selective extraction of arsenic from minespoils, soils, and sediments. Agron. Abstr. p. 256.

Atkinson, R.J., A.M. Posner, and J.P. Quirk. 1968. Crystal nucleation in Fe (III) solutions and hydroxide gels. J. Inorg. Nucl. Chem. 30:2371–2381.

Backes, C.A., R.G. McLaren, A.W. Rate, and R.S. Swift. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. Soil Sci. Soc. Am. J. 59:778–785.

Barrow, N.J. 1992. The effect of time on the competition between anions for sorption. J. Soil Sci. 43:421–428.

Bouldin, C., L. Furenlid, and T. Elam. 1995. MacXAFS: An EXAFS analysis package for the Macintosh. Physica B. 208/209:190–192.

Bruemmer, G.W., J. Gerth, and K.G. Tiller. 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. J. Soil Sci. 39:37–52.

Bunker, G. 1988. Basic techniques for EXAFS. Beamline X-9 documentation (National Biostructures PRT), NSLS, Upton, New York.

Cornell, R.M., and U. Schwermann. 1996. The iron oxides: Structures, properties, reactions, occurrence and uses. VCH Publishers, New York.

Darland, J.E., and W.P. Inskeep. 1997. Effects of pH and phosphate competition on the transport of arsenate. J. Environ. Qual. 26:1133–1139.

Davenport, J.R., and F.J. Peryea. 1991. Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead arsenate. Water Air Soil Pollut. 57–58:101–110.

Fendorf, S., M.J. Eick, P. Grossl, and D.L. Sparks. 1997. Arsenate and chromate retention on goethite: I. Surface structure. Environ. Sci. Technol. 31:315–320.

Ferguson, J.F., and M.A. Anderson 1974. Chemical forms of arsenic in water supplies and their removal. p. 137–158. In A.J. Rubin (ed.) Chemistry of water supply, treatment, and distribution. Ann Arbor Sci. Publ., Inc., Ann Arbor, MI.

Fordham, A.W., and K. Norrish. 1983. The nature of soil particles

particularly those reacting with arsenate in a series of chemically treated samples. Aust. J. Soil Res. 21:455–477.

Fordham, A.W., and K. Norrish. 1979. Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. Aust. J. Soil Res. 17:307–316.

Fordham, A.W., and K. Norrish. 1974. Direct measurement of the composition of soil components which retain added arsenate. Aust. J. Soil Res. 12:165–172.

Fuller, C.F., J.A. Davis, and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochim. Cosmochim. Acta 57:2271–2282.

Gebhardt, H., and N.T. Coleman. 1974. Anion adsorption by allophanic tropical soils: Sulfate adsorption. Soil Sci. Soc. Am. Proc. 38:259–262.

Geelhoed, J.S., T. Hiemstra, and W.H. Van Riemsdijk. 1997. Phosphate and sulfate adsorption on goethite: Single anion and competitive adsorption. Geochim. Cosmochim. Acta 61(12):2389–2396.

Goldberg, S., and R.A. Glaubig. 1988. Anion sorption on a calcareous, montmorillonitic soil-arsenic. Soil Sci. Soc. Am. J. 52:1297–1300.

Grossl, P.R., M. Eick, D.L. Sparks, S. Goldberg, and C.C. Ainsworth. 1997. Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique. Environ. Sci. Technol. 31:321–326.

Haque, I., and D. Walmsley. 1973. Adsorption and desorption of sulfate in some soils of the West Indies. Geoderma 9:269–278.

He, L.M., L.W. Zelazny, V.C. Baligar, K.D. Ritchey, and D.C. Martens. 1997. Ionic strength effects on sulfate and phosphate adsorption on γ-alumina and kaolinite: Triple-layer model. Soil Sci. Soc. Am. J. 61:784–793.

Hsia, T.-H., S.-L. Lo, C.-F. Lin, and D.-Y. Lee. 1994. Characterization of arsenate adsorption on hydrous iron oxide using chemical and physical methods. Colloids Surfaces A: Physicochem. Eng. Aspects. 85:1–7.

Huang, P.M. 1975. Retention of arsenic by hydroxy-aluminum on surfaces of micaceous mineral colloids. Soil Sci. Soc. Am. Proc. 39:271–274.

Hug, S.T. 1997. *In situ* fourier transform infrared measurements of sulfate adsorption on hematite in aqueous solutions. J. Colloid Interface Sci. 188:415–422.

Jacobs, L.W., J.K. Syers, and D.R. Keeney. 1970. Arsenic sorption in soils. Soil Sci. Soc. Am. Proc. 34:750–754.

Johnston, S.E., and W.M. Barnard. 1979. Comparative effectiveness of fourteen solutions for extracting arsenic from four western New York soils. Soil Sci. Soc. Am. J. 43:304–308.

Kinjo, T., and P.F. Pratt. 1971. Nitrate adsorption: II. In competition with chloride, sulfate, and phosphate. Soil Sci. Soc. Amer. Proc. 35:725–728.

Kitahama, K., R. Kiriyama, and Y. Baba. 1975. Refinement of the crystal structure of scorodite. Acta Crystallogr. B31:322–324.

Livesey, N.T., and P.M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci. 131:88–94.

Lumsdon, D.G., A.R. Fraser, J.D. Russell, and N.T. Livesey. 1984. New infrared band assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH). J. Soil Sci. 35:381–386.

Manceau, A. 1995. The mechanisms of anion adsorption on iron oxides: Evidence for the bonding of arsenate tetrahedra on free Fe(O,OH)$_6$ edges. Geochim. Cosmochim. Acta 59:3647–3653.

Marten, R.R., and R.C. Smart. 1987. X-ray photoelectron studies of anion adsorption on goethite. Soil. Sci. Soc. Am. J. 51:54–56.

McBride, M.B. 1994. Environmental Chemistry of Soils. Oxford Univ. Press, New York.

McGeehan, S.L., D.V. Naylor, and B. Shafii. 1992. Statistical evaluation of arsenic adsorption data using linear-plateau regression analysis. Soil Sci. Soc. Am. J. 56:1130–1133.

McMaster, W.H., N. Kerr Del Grande, J.H. Mallett, and J.H. Hubbell. 1968. Compilation of X-ray Cross-sections, UCRL-50174, Section II, Revision I, Univ. of CA, Livermore, CA.

Melamed, R., J.J. Jurinak, and L.M. Dudley. 1995. Effect of adsorbed phosphate on transport of arsenate through an Oxisol. Soil Sci. Soc. Am. J. 59:1289–1294.

Misra, S.G., and R.C. Tiwari. 1963. Studies on arsenite-arsenate system adsorption of arsenate. Soil Sci. and Plant Nutr. 9:10–13.

Myneni, S.C., S.J. Traina, T.J. Logan, and G.A. Waychunas. 1997. Oxyanion behavior in alkaline environments: Sorption and desorption of arsenate in ettringite. Environ. Sci. Technnol. 31:1761–1768.

Onken, B.M., and D.C. Adriano. 1997. Arsenic availability in soil with time under saturated and subsaturated conditions. Soil Sci. Soc. Am. J. 61:746–752.

Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. Adv. Agron. 30:1–50.

Parfitt, R.L., and J.D. Russell. 1977. Adsorption on hydrous oxides. IV. Mechanisms of adsorption of various ions on goethite. J. Soil Sci. 28:297–305.

Parfitt, R.L., and R.C. Smart. 1977. Infrared spectra from binuclear bridging complexes of sulfate adsorbed on goethite. J. Chem. Soc. (Faraday Trans.). 73:796–802.

Peak, J.D., D.L. Sparks, and R.G. Ford. 1999. An *in situ* ATR-FTIR investigation of sulfate bonding mechanisms on goethite. J. Colloid Interface Sci. 218:289–299.

Persson, P., N. Nilsson, and S. Sjoberg. 1996. Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface. J. Colloid Interface Sci. 177:263–275.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301–1306.

Pierce, M.L., and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16:1247–1253.

Raven, K.P., A. Jain, and R.H. Loeppert. 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32:344–349.

Schwertmann, U., and R.M. Cornell. 1991. Iron oxides in the laboratory: Preparation and characterization. VCH Publishers, Inc., New York.

Sparks, D.L. 1995. Environmental soil chemistry. Academic Press, New York.

Sun, X., and H.E. Doner. 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. Soil Sci. 161:865–872.

Szytula, A., A. Burewicz, Z. Dimitrijevic, S. Krasnicki, H. Rzany, J. Todorovic, A. Wanic, and W. Wolski. 1968. Neutron diffraction studies of α-FeOOH. Phys. Stat. Sol. 26:429–434.

Tejedor-Tejedor, M.I., and M.A. Anderson. 1990. Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. Langmuir 124:79–110.

Waychunas, G.A., J.A. Davis, and C.C. Fuller. 1995. Geometry of sorbed arsenate on ferrihydrite and crystalline FeOOH: Re-evaluation of EXAFS results and topological factors in predicting sorbate geometry, and evidence for monodentate complexes. Geochim. Cosmochim. Acta 59:3651–3661.

Waychunas, G.A., B.A. Rea, C.C. Fuller, and J.A. Davis. 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochim. Cosmochim. Acta 57:2251–2269.

Whitten, K.W., K.D. Gailey, and R.E. Davis. 1992. General chemistry with quantitative analysis. 4th ed. Saunders College Publ., Orlando, FL.

Woolson, E.A., J.H. Axley, and P.C. Kearney. 1973. The chemistry and phytotoxicity of arsenic in soils: II. Effects of time and phosphorus. Soil Sci. Soc. Am. Proc. 37:254–259.

Xu, H., B. Allard, and A. Grimvall. 1988. Influence of pH and organic substance on the adsorption of As(V) on geologic materials. Water Air Soil Pollut. 40:293–305.

Zabinsky, S.L., J.J. Rehr, A. Ankudinov, R.C. Albers, and M.J. Eller. 1995. Multiple scattering calculations of x-ray absorption spectra. Phys. Rev. B. Condens. Matter 52:2995–3006.

Zelazny, L.W., L. He, and A.M. Vanwormhoudt. 1996. Charge analyses of soils and anion exchange. p. 1231–1254. *In* D.L. Sparks (ed.) Methods of soil analysis: Chemical methods. Part 3. Soil Sci. Soc. Am. J., Madison, WI.

Zhang, P.C., and D.L. Sparks. 1990. Kinetics and mechanisms of sulfate adsorption/desorption on goethite using pressure-jump relaxation. Soil Sci. Soc. Am. J. 54:1266–1273.