Reductive dissolution of arsenic-bearing ferrihydrite

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Abstract

Ferrihydrites were prepared by coprecipitation (COP) or adsorption (ADS) of arsenate, and the products were characterized using solid-state methods. In addition, the kinetics of reductive dissolution by hydroquinone of these well-characterized materials were quantified. Characterization and magnetism results indicate that the 10 wt\% As COP ferrihydrite is less crystalline and possibly has smaller crystallite size than the other ferrihydrites, which all have similar crystallinity and particle size. The results from reductive dissolution experiments show similar reaction rates, reaction mechanism, and activation energy for ferrihydrite precipitated with or without added arsenate. However, a marked decrease in reactivity was observed for 10 wt\% As ADS ferrihydrite. The decrease is not attributed to differences in activation energy but rather the preferential blocking of active sites on the ferrihydrite surface. Results demonstrate that arsenic may be released by the reductive dissolution of arsenic-bearing ferrihydrite regardless of whether the arsenic is coprecipitated with or adsorbed onto the ferrihydrite. However, under these reaction conditions, release from materials with adsorbed arsenate greatly exceeds that from materials with coprecipitated arsenate. In fact, a considerable amount of arsenic was released from the 10 wt\% ADS ferrihydrite before reductive dissolution was initiated. Therefore, the characterization of arsenate-bearing iron oxide materials to determine the method of arsenate incorporation into structures—perhaps by quantification of Fe–Fe coordination with EXAFS spectroscopy—may lead to improved predictions of the large-scale release of arsenic within aquifer systems under reducing conditions.

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1. INTRODUCTION

Recently, high concentrations of arsenic in groundwater around the world have generated interest in elucidating the mechanisms controlling the geochemical cycling of arsenic in groundwater systems (Smedley and Kinniburgh, 2002). Iron oxides play an important role in attenuating the concentration of arsenic in solution through adsorption and coprecipitation (Pichler et al., 1999). Arsenic may be released from or adsorb onto iron oxide surfaces depending on the groundwater solution properties, especially pH and redox conditions (Smedley and Kinniburgh, 2002). Arsenic has a high adsorption affinity for iron oxide surfaces; however, the mechanisms of adsorption and release in aquifers are not well understood (Sparks, 2003). The development of strongly reducing conditions at near-neutral pH has been suggested as one mechanism that can result in the large-scale release of arsenic from aquifer materials (Appello et al., 2002). Arsenic may be released by simple desorption or through concurrent release from dissolving arsenic-bearing iron oxides (Smedley and Kinniburgh, 2002).

Due to their natural abundance, redox reactivity, and surface adsorptivity, iron oxides play an important role in the transformation and transport of species such as heavy metals and anthropogenic contaminants (Ford et al.,
Precipitation, dissolution, and redox reactivity are strongly affected by the presence of species like arsenate in solution, adsorbed onto mineral surfaces, or incorporated into the bulk of the iron oxide minerals (Stumm and Morgan, 1996). Iron oxides may be reduced through microbial (Straub et al., 2001) or abiotic (LaKind and Stone, 1989) electron transfer reactions with organic compounds, including quinone species and humic substances (Scott et al., 1998). Reductive dissolution can cause the release of adsorbed or incorpo-
rated species and can lead to growth and phase transformations of iron oxides (Scott et al., 1998; Pederson et al., 2006). Bennett and Dudas (2003) reported that the release of As was highly correlated to the release of Fe during reductive dissolution of iron oxides in an As-rich soil. Kocar et al. (2010) found that the As concentration affected the solid-state products formed from reductive dissolution of As-ferrihydrite coated sands. Amorphous iron sulfide and magnetite were produced at low As loading while green rusts, iron sulfide, and magnetite were produced at high As loading. Arsenic was strongly associated with the magnetic and residual ferrihydrite but was excluded from the green rust and iron sulfide.

One iron oxide mineral, ferrihydrite (Fe₂₅H₂O₄·4H₂O), precipitates when iron-rich waters increase in pH and/or become oxidized (Jambor and Dutrizac, 1998; Cornell and Schwertmann, 2003). Ferrihydrite is a poorly crystal-
line, metastable mineral typically ranging in size from 3 to 10 nm and is a precursor to goethite and hematite (Cornell and Schwertmann, 2003; Penn et al., 2007). The high degree of structural disorder and high specific surface area of ferrihydrite make it one of the most reactive of the iron oxide minerals. Due to its high affinity for iron oxides, arsenic concentrations in natural ferrihydrite samples have been documented with values up to 14 wt% As (Rancourt et al., 2001). During the reductive dissolution of arsenic-ferrihydrite by ascorbic acid, Pederson et al. (2006) found that arsenate remained adsorbed on ferrihydrite until the surface area was insufficient to retain the species and the arsenate was desorbed into solution. Although arsenic was not a fo-
cus of the study, Davranche and Bollinger (2000) demon-
strated that the method of incorporation—adsorption or coprecipitation—of Pb, Cd, and Zn into ferrihydrite solids affected the release of the metal cations by reductive and nonreductive mechanisms. The reducing conditions generally increased the amount of metals released, and the desorption behavior of Pb and Zn differed substantially depending on the incorporation method. Paige et al. (1997) found that underoxic conditions, the presence of coprecipitated arsenic hindered the proton-assisted dissolution of ferrihydrite. The authors concluded that arsenate was likely incorporated by a rapid initial adsorption rather than co-deposition because the stability increased in accord with the surface-complex controlled model of dissolution.

X-ray absorption (XAS), infrared, and Raman spectroscopy studies have shown that, when arsenate is adsorbed on iron oxide surfaces, and specifically on ferrihydrite, it typically forms inner-sphere complexes (Sparks, 2003). Extended X-ray absorption fine structure spectroscopy (EXAFS) results (Waychunas et al., 1993, 1995; Manceau, 1995; Sherman and Randall, 2003) from arsenic-bearing ferrihydrite samples indicate that arsenate adsors primarily as a corner-sharing bidentate complex on the apical oxy-
gen of two adjacent edge-sharing iron octahedra or in a monodentate complex. Arsenate may also adsorb as a monodentate complex, but typically only at low arsenate concentrations (Waychunas et al., 1993). EXAFS also re-
vealed that the incorporation of arsenic by either coprecip-
itation or adsorption affects the structure and size of the crystallites formed (Waychunas et al., 1993). With coprecip-
itation of arsenate, the strongly attached arsenate groups effectively poison the crystallites and halt their development during formation. It was predicted that during polymeriza-
tion of iron octahedra, chain crosslinking stopped completely and dioctahedral chain length was reduced with arsenate occupying chain ends, which, led to decreased grain size. In contrast, samples prepared by the adsorption of arsenate were more ordered crystallites and had cross-
linked dioctahedral chains.

Magnetic properties of particles are sensitive to structural and compositional differences; and ferrihydrite, in both doped and undoped forms, has been characterized using magnetic methods by many authors (Stevens et al., 2003; Punnoose et al., 2004; Duarte et al., 2006; Guyo
do et al., 2006; Berquo et al., 2007). It is an antiferromagnetic material and exhibits superparamagnetic behavior at room temperature (Cornell and Schwertmann, 2003; Guyo
do et al., 2006). Fundamental questions include ferrihydrite’s non-zero net magnetization, which was predicted by Néel for nanophase antiferromagnetic materials; magnetic super-exchange interactions within aggregates; and uncompensated magnetic moments. Above the blocking tempera-
ture, superparamagnetic effects suppress important intrinsic magnetic properties of ferrihydrite, such as the Néel tem-
perature (T_N). Recently, T_N of ferrihydrite was estimated to be about 500 K using data from ferrihydrite with small particle sizes from 3.0 to 5.4 nm (Guyo
do et al., 2006) and around 422 K using data extracted from a sample with unusually large particle size of 23 nm (Berquo et al., 2007). Ferritin, an iron-storage protein of mammals in which ferrihydrite appears to be the protein core, is frequently used in magnetic studies (Gilles et al., 2000; Kim et al., 2005). Interparticle super-exchange interactions, a common phe-
nomenon that complicates the interpretation of magnetic data from nanoparticles, are not observed in ferritin because it is isolated from other particles by the surrounding protein matrix.

Magnetic studies of ferrihydrites prepared with a range of dopants (Ni, Mo, Ir, B, Al, As, Si) have been reported, although such studies lack conclusive data about lattice substitution. In fact, the main effects observed are decreased crystallinity or average particle size for doped versus undoped materials. For natural arsenic-bearing ferrihydrites formed from hydrothermal fluids, Rancourt et al. (2001) observed that incorporation of arsenic prevented particle growth, led to smaller primary particles, and caused structural disorder by distorting the Fe octahedral environments. It was proposed that arsenic was adsorbed at the surface of ~1 nm diameter primary particles and hence did not enter the ferrihydrite lattice. Mössbauer
suspensions were prepared by addition of a 0.48 M NaHCO$_3$ rinsed three times with Milli-Q water. Six-line ferrihydrite (Milli-Q water, Millipore Corporation). All glassware and 2.1. Synthesis of materials

is more likely to lead to substantial release of arsenate from the results lead to a prediction that the reductive dissolution. Combined, the reactivity as measured by reductive dissolution. Samples were prepared by forced hydrolysis of ferric nitrate solutions. Two samples were prepared by coprecipitation with As, three samples were prepared by equilibration of the ferrihydrite with a solution containing arsenate, and one sample was prepared without added As. The composition, particle size, crystallite size, structural properties, magnetic properties, and surface properties of ferrihydrite samples were characterized so as to elucidate the link between physicochemical properties of the nanoparticle and the mechanism of arsenic release to solution as well as the relative reactivity as measured by reductive dissolution. Combined, the results lead to a prediction that the reductive dissolution of ferrihydrite with arsenate located primarially at the surface is more likely to lead to substantial release of arsenate from the solid surface to the solution phase.

2. EXPERIMENTAL METHODS

2.1. Synthesis of materials

Solutions were prepared with 18 MΩ cm resistivity water (Milli-Q water, Millipore Corporation). All glassware and Nalgene bottles were acid washed with 4 M nitric acid and rinsed three times with Milli-Q water. Six-line ferrihydrite suspensions were prepared by addition of a 0.48 M NaHCO$_3$ (Mallinckrodt) solution to an equal volume of 0.40 M Fe(NO$_3$)$_3$, 9H$_2$O (Fisher) solution. The base solution was added over 12 ± 1 min using a Fisher peristaltic pump, and the mixture was stirred constantly using a magnetic Teflon-coated stir bar. Over the course of the base addition, the orange color of the initial ferric nitrate solution changed to a dark red-brown color. Next, the suspension was microwave-annealed (950 W oven) at 30-s intervals until it boiled to improve homogeneity of the ferrihydrite nanoparticles (Burleson and Penn, 2006). The bottle containing the suspension was immediately submerged into an ice bath until it cooled to room temperature and then the suspension was transferred to SpectraPor #7 dialysis bags (MWCO = 2000 g/mol). Dialysis against Milli-Q water was performed for 3 days at room temperature, changing the water at least nine times. The ferrihydrite suspensions were allowed to air dry for several days, ground into powders using an agate mortar and pestle, and then stored in dry glass vials.

Arsenic was added by way of coprecipitation or adsorption after precipitation. The source of arsenic was Na$_2$HAsO$_4$·7H$_2$O (Fluka), which was added to obtain approximately 1 or 10 wt% of arsenic in the synthetic materials (assuming 100% uptake) and was calculated using the Dzombak and Morel (1990) ferrihydrite formula weight of 89 g/mol Fe. For samples with adsorbed arsenic, the ferrihydrite suspension was prepared and dialyzed as above. Then, the appropriate amount of arsenate solution, with the pH adjusted to 3.4 to match that of the ferrihydrite suspension, was added to the ferrihydrite suspension and the solution was equilibrated for 1 or 18 days. Fuller et al. (1993) demonstrated that arsenate was effectively adsorbed onto ferrihydrite within a period of less than 1 day, but the efficiency rose to nearly 100% after at least 8 days. Upon addition of the arsenate solution and after stirring for 1 h the pH of the ferrihydrite suspension rose significantly (from 3.4 to 5.3). The resulting suspension was dialyzed against Milli-Q water over 3 days with a minimum of nine water changes. For samples with coprecipitated arsenic, the arsenate salt was added to the ferric nitrate solution before hydrolysis. Then, dialysis, microwave-anneal, dialysis, and drying steps were performed as described above for ferrihydrite prepared with no arsenic. The pH of the 10% coprecipitated arsenic-ferrihydrite suspension after hydrolysis was somewhat higher than of the unmodified ferrihydrite suspension (pHs of 3.8 and 3.4, respectively). The adsorbed-As- and coprecipitated-As-ferrihydrite suspensions and powders were similar in color to the unmodified ferrihydrite. Hereafter, the samples are named according to their approximate, attempted arsenic content (1% or 10%) and the method of incorporation (COP for coprecipitation or ADS for equilibrium/adsorption), and the pure ferrihydrite sample is referred to as 0% As.

2.2. Materials characterization

Ferrihydrite samples were characterized using inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectroscopy (ICP-AES), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), extended X-ray absorption fine structure spectroscopy (EXAFS), superconducting quantum interference device (SQUID) magnetometry, Mössbauer spectroscopy and potentiometric titrations.

Solid samples were prepared for ICP-MS by dissolving the solid particles in 3.2 M HNO$_3$ and then further diluted with 0.1 M HNO$_3$. For ICP-AES, solid samples were digested with aqua regia, diluted with Milli-Q water, and further diluted with 0.1 M HNO$_3$. The diluted solutions were analyzed for Fe, As, and Na content using a ThermoElemental PX ExCell quadrupole mass spectrometer for ICP-MS or a Perkin-Elmer Optima 3000DV ICP in radial or axial mode for ICP-AES.

X-ray diffraction was performed using a PANalytical X-Pert PRO MPD X-ray diffractometer equipped with a cobalt source and an X-Celerator detector. All scans were collected from front-packed powder samples over the range of 10–90° 20 at a scan rate of 0.6° per minute. The diffraction patterns were compared to the reference powder diffraction file (PDF) for six-line ferrihydrite (#29-0712), goethite (#29-0713), and hematite (#33-0664).

Attempts to obtain BET surface areas of ferrihydrite powders were unsuccessful, so surface areas were estimated from TEM image measurements. Each TEM sample was prepared by drop casting a diluted suspension prepared by adding one drop of dialyzed suspension to 2 mL of
Milli-Q water. A drop of the diluted suspension was placed onto a 3 mm of 200 mesh holey carbon-coated copper grid (Structure Probe, Inc.) and allowed to air dry. Images were collected using an FEI Tecnai T12 TEM operated at 120 kV and equipped with a Gatan CCD camera. The size and morphology of the samples were analyzed using Gatan Digital Micrograph 3.8.2. The lengths and widths of more than 500 particles were measured from the calibrated TEM images. The specific surface area of each sample was calculated using the density of ferrihydrite (3.96 g/cm³) (Cornell and Schwertmann, 2003), the surface area per volume, and modeling of the particles as ellipsoids as in Jentzsch and Penn (2006).

2.3. EXAFS

EXAFS spectroscopy was conducted at Stanford Synchrotron Radiation Laboratory (SSRL) wiggler magnet beamline 10-2 under anaerobic conditions for the 0% As, 1-day 10% ADS, 18-day 10% ADS, and 10% COP ferrihydrites. A 1:10 mass dilution of dry powder sample to boron nitride powder was used to reduce self-absorption effects. The diluted samples were analyzed in 1.5 mm thick Teflon holders sealed with Kapton tape using a double Si 1 1 1 nitride powder was used to reduce self-absorption effects. The diluted samples were analyzed in 1.5 mm thick Teflon holders sealed with Kapton tape using a double Si 1 1 1 nitride powder was used to reduce self-absorption effects. The diluted samples were analyzed in 1.5 mm thick Teflon holders sealed with Kapton tape using a double Si 1 1 1 nitride powder was used to reduce self-absorption effects. The diluted samples were analyzed in 1.5 mm thick Teflon holders sealed with Kapton tape using a double Si 1 1 1 nitride powder was used to reduce self-absorption effects. The diluted samples were analyzed in 1.5 mm thick Teflon holders sealed with Kapton tape using a double Si 1 1 1 nitride powder was used to reduce self-absorption effects.

EXAFS spectra were collected at room temperature in transmission mode using a Fe(0) calibration foil over the energy range 6879–7986 eV.

Data were analyzed using SixPACK software version 0.60 (Webb). EXAFS scans were calibrated for changes in assigned monochromator energy to 7112 eV by using the first derivative of the Fe calibration standard and averaged together. These spectra were deglitched when needed. Background subtraction was performed using SixPACK with \( E_0 \) defined as 7125 eV, the \( k \)-weight = 3, and the \( R \)-background = 1 Å. The resulting spectra were converted to frequency \( k \) space, weighted by \( k^2 \), and Fourier transformed to produce \( R \)-space EXAFS. Quantitative fitting of the background subtracted and \( k^2 \)-weighted spectra was performed using model single scattering paths created in SixPACK using FEFF 6 (Zabinsky et al., 1995).

The shell-by-shell approach to fitting the EXAFS spectra was adapted from Kim et al. (2004, 2008) and initially applied to the 0% As sample. Briefly, the amplitude reduction factor \( S^2(\theta) \) was fixed at 0.9 for all samples. The Debye–Waller factor \( \sigma^2 \) was set at values of 0.007 for the first-shell atomic neighbors and 0.01 for the second- and third-shell atomic neighbors initially. Coordination number \( N \) and \( \sigma^2 \) are highly correlated, and varying both simultaneously can produce unreasonable (nonphysical) uncertainty in the fit result (Waychunas et al., 1986). Therefore, \( N \) values were determined initially by restricting \( \sigma^2 \) to 0.007 for the first shell and 0.01 for subsequent shells and allowing SixPACK to vary \( N \), \( R \), and the energy shift \( E_0 \). \( E_0 \) ranged from 0.1 to 1.2 eV. The 0% As sample was the first spectrum fitted because it represents uncorrupted six-line ferrihydrite and was well characterized. The resulting values for the fitting variables from the 0% As fit were used as the initial values for subsequent fits.

2.4. Magnetism

A commercial SQUID magnetometer (MPMS-XL, Quantum Design) was employed to obtain ZFC/FC magnetization curves and hysteresis loops on the dried 0% As, 18-day 10% ADS, and 10% COP ferrihydrites as a function of temperature. Zero-field-cooled (ZFC) magnetization curves were obtained by cooling the sample in zero field from a high temperature (300 K) to a low temperature (2 K) and then measuring the magnetization at stepwise increasing temperatures from 2 K to 300 K induced in a small applied field \( H = 5 \) mT. The sample was again cooled, in the same field, and field-cooled (FC) magnetization curves were obtained by measuring (in field) at stepwise increasing temperatures, from 2 K to 300 K. Hysteresis loops were obtained by using maximum applied fields up to 5 T at temperatures of 5 K. Mössbauer spectra were measured at room temperature and at 4.2 K. A conventional constant-acceleration spectrometer was used in transmission geometry with a \( ^5\text{Co/Rh} \) source, using \( \alpha-\text{Fe} \) at room temperature to calibrate isomer shifts and velocity scale.

2.5. Potentiometric titrations

The 0% As, 10% COP, 1-day 10% ADS, and 18-day 10% ADS ferrihydrites were used in acid–base potentiometric titrations at three ionic strengths to determine the point of zero net proton charge (PZNPC). Freshly prepared ferrihydrite suspensions were dialyzed but not dried for titration experiments. Standard procedures (Dzombak and Morel, 1990) were followed for the titrations with the exception that \( \text{CO}_2 \) was not excluded from the ferrihydrite suspensions prior to titrations. The presence of \( \text{CO}_2 \) during acid–base titrations was discussed by Gilbert et al. (2007) and was not expected to have a significant effect on the titration of ferrihydrite samples. The titrations were completed manually with 40 mL of suspension with a ferrihydrite solid concentration of 2.5 or 5.0 g/L using 9 M HNO\(_3\) solutions (prepared with CO\(_2\)-free Milli-Q) at ionic strengths of 0.1, 0.01, and 0.001 M NaNO\(_3\) while stirring. The pH was recorded with a Thermo PerpHect Sure-Flow glass pH electrode calibrated with buffers at pH 4 and 10 and Logger Pro 3.6.1 software by Vernier. Titrations took 25–40 min to complete and measurements were recorded 25 s after the aliquot of base was added. Background titrations of pH 4 HNO\(_3\) solutions at each ionic strength were performed. Total surface charge density, or the amount of protons adsorbed, was obtained from the resulting titration curve by subtraction of the blank titration curve data. Charge density was calculated using the adsorbed proton quantity, solids loading, and surface areas determined by TEM analysis. The PZNPC was identified as the common intersection point of the titration curves at different ionic strengths for each ferrihydrite suspension.

2.6. Reductive dissolution kinetics

The reactivity of iron oxides has been quantified previously by measuring the kinetics of reductive dissolution using hydroquinone and monitoring the formation of
benzoquinone (Kung and McBride, 1988; LaKind and Stone, 1989; Anschutz and Penn, 2005; Jentzsch and Penn, 2006). Experiments were performed in duplicate or triplicate and in an anaerobic chamber (Coy Laboratories, 5% H₂/95% N₂) with the pH buffer used containing 40 mM acetate (pH 3.75), acetic acid (Mallinckrodt) and sodium hydroxide (Mallinckrodt) in Milli-Q water). High purity nitrogen gas was bubbled through solutions for at least 30 min to removed dissolved oxygen before transfer into the anaerobic chamber. The oxygen concentration of the anaerobic chamber was monitored during experiments and stayed below 150 ppm but was typically much lower. To prevent exposure to light, 30-mL amber glass vials or 30-mL Nalgene bottles wrapped in aluminum foil were used.

For variable temperature studies, the total volume of suspension was 12.5 mL with 2.0 g/L ferrihydrite loading and 0.2 mM hydroquinone in acetate buffer (40 mM, pH 3.75). For reaction order studies, the total volume of suspension was 25.0 mL with 0.5–2.0 g/L ferrihydrite loading, 0.05–0.80 mM hydroquinone, and 40 mM acetate buffer. Dried powders were weighed into bottles and placed into the anaerobic chamber. Then, 5.0-mL of deoxygenated acetate buffer was added. Samples were sonicated for 20 min, vortexed, and stirred overnight to reduce aggregation of particles. The following day, appropriate volumes of acetate buffer and 10 mM hydroquinone stock solution (prepared with 40 mM acetate buffer) were added to the reaction vessel. At regular time intervals, 1-mL aliquots were removed and filtered using 0.2-μm nylon Acrodisc filters and analyzed within 2 min by high performance liquid chromatography (HPLC), as described below. The filtrate was clear, indicating that the aggregated ferrihydrite solids were effectively removed from the suspension; thus, the reaction was quenched.

Solutions were analyzed with an Agilent HPLC equipped with a Zorbax C18 column. The mobile phase was a 65:35 mixture of acetate buffer (40 mM, pH 3.75) and acetonitrile. The flow rate was 0.75 mL/min and the injection volume was 10 μL. The absorbance was monitored at 235 nm, and hydroquinone eluted at 2.3 min and benzoquinone at 3.4 min. Eight-point calibration curves, ranging from 0.05 to 2.0 mM for hydroquinone and 2 to 150 μM for benzoquinone, were used to determine experimental concentrations.

For a subset of kinetic experiments, [Fe(II)] (aq) was measured by a modified version of the Ferrozine assay (Stookey, 1970). A 0.4-mL aliquot of the filtrate solution was combined with 0.25 mL of Ferrozine solution (5 mg/mL in 40 mM acetate buffer, Acros, 99.9%) and 4.35 mL of 40 mM, pH 3.75 acetate buffer. Absorbance at 562 nm was measured using a Spectrophotometer 20D+ UV–vis spectrophotometer. A Ferrozine/acetate buffer solution was used as a blank, and a six-point calibration curve up to 10⁻⁴ M FeCl₂·4H₂O (Fisher, 99%) was employed. There is no evidence for interference by arsenic complexes with the Ferrozine assay (Stookey, 1970).

To quantitatively compare arsenic release from the 18-day 10% ADS and 10% COP samples during reductive dissolution, a similar procedure was followed as described above, but the initial hydroquinone concentration was 6.0 mM, the ferrihydrite loading was 0.5 g/L, and the reaction vessel was maintained at room temperature. At selected time intervals up to 4 days, sample suspensions were filtered through two Acrodisc filters and analyzed. Benzoquinone and Fe(II) concentrations were measured by methods described above. A subset of filtrates were acidified by adding a known volume of 1 M HCl to a known volume of filtrate and then stored at 10 °C until analyzed by ICP-AES to measure the concentration of dissolved Fe and As. In addition, filtrate was collected from a blank suspension, which was equilibrated with the ferrihydrite solids overnight, for ICP analysis. Attempts to detect and quantify arsenate and arsenite from filtrates using the molybdenylene-blue method (Lenoble et al., 2003) were unsuccessful.

3. RESULTS AND DISCUSSION

3.1. Materials characterization

The Fe, As, and Na content of the solids was determined by ICP-MS or ICP-AES of dissolved samples, and results are presented in Table 1. The arsenic-bearing samples had approximately 1 or 10 wt% of arsenic and the iron content dropped accordingly. For samples prepared with an intended 10 wt% As by equilibration with an arsenate solution, the sample contained 8.5 wt% As after 1 day of equilibration and 9.6 wt% after 18 days of equilibration. These results are consistent with the high affinity of arsenic for iron oxide by adsorption from solution. The results also agree with those of Fuller et al. (1993) on the kinetics of arsenate adsorption, which showed that an initial, rapid arsenate adsorption was followed by arsenate adsorption at a slower rate for at least 8 days. Sodium was a minor impurity and was attributed to the starting material salts; however, the 1-day and 18-day 10% ADS samples had significantly higher sodium content, which can be explained by the co-adsorption of protons and sodium cations with the arsenate anion (AsO₃³⁻) to maintain charge balance.

The powder X-ray diffraction patterns of the ferrihydrite samples, shown in Fig. 1, were consistent with the six-line ferrihydrite powder diffraction file (#29-0712), and there was no evidence for the presence of other crystalline phases. The patterns of the 0% As, 1% ADS, and 1% COP samples were indistinguishable. The XRD pattern for the 10% ADS (18-day) is similar to the aforementioned samples, although a reduction in relative peak intensities of the second through sixth lines relative to the first line and possibly some broadening of the third and fourth lines can be discerned. This indicates that subtle structural changes result from the adsorption of arsenate, perhaps including some diffusion of arsenate into the bulk of the particles. The 10% COP diffraction pattern differed markedly from the other samples. The peaks were poorly defined and broad, indicating a significant difference in particle size and/or crystallinity of the 10% COP sample.

Fig. 2 shows representative TEM images of the 0% As, 10% ADS (18-day), and 10% COP samples. The ellipsoidal particle morphology was confirmed in the images, and the particle size distributions and calculated specific surface areas are reported in Table 2 for the three samples. No significant difference in size was observed, even when consider-
ing a 5% error in absolute size by TEM. Average lengths ranged from 4.2 nm for the 10% COP sample to 4.4 nm for the 10% ADS sample, which yield calculated specific surface areas ranging from 420 to 450 m$^2$/g. Because there is only a small variation in size between the pure ferrihydrite and 10% As-ferrihydrites, it was assumed that the 1% As-bearing ferrihydrites have similar particle size distributions.

The similarity in TEM particle size of the samples suggests that the XRD peak broadening of 10% COP is likely the consequence of decreased crystallinity rather than smaller particle size. Fuller et al. (1993) reported that the presence of adsorbed ions may affect aggregation and crystallite growth, and incorporation of arsenate tetrahedra into the predominantly octahedral crystal structure of ferrihydrite may result in the formation of defects within the particles. However, Waychunas et al. (1995) concluded that coprecipitation of high arsenate content limits the size of ferrihydrite crystallites by poisoning iron octahedral chain corners and edges. Applying the Scherrer equation to wide angle X-ray scattering data, Waychunas et al. (1996) estimated a considerably smaller crystallite size of coprecipitated, 33 wt% As two-line ferrihydrite (5.8 Å) compared to the undoped two-line ferrihydrite (11.7 Å) and concluded that larger particle sizes determined by methods such as TEM could be attributed to agglomerates of smaller individual crystallites. However, despite the low contrast of the TEM images, there is no indication that 10% COP particles are composed of more than one primary ferrihydrite crystallite. Furthermore, the consistent size and aspect ratio over the three samples argues against a fundamental difference in agglomeration state.

### Table 1
Elemental composition of ferrihydrite samples by ICP analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron (wt%)</th>
<th>Arsenic (wt%)</th>
<th>Sodium (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% As</td>
<td>55.0</td>
<td>&lt;0.035</td>
<td>*</td>
</tr>
<tr>
<td>1% ADS</td>
<td>53.9</td>
<td>1.57</td>
<td>*</td>
</tr>
<tr>
<td>10% ADS (1-day)</td>
<td>42.8</td>
<td>8.48</td>
<td>0.546</td>
</tr>
<tr>
<td>10% ADS (18-day)</td>
<td>43.5</td>
<td>9.55</td>
<td>0.754</td>
</tr>
<tr>
<td>1% COP</td>
<td>50.8</td>
<td>1.25</td>
<td>*</td>
</tr>
<tr>
<td>10% COP</td>
<td>41.3</td>
<td>10.5</td>
<td>*</td>
</tr>
</tbody>
</table>

* Concentrations below the instrumental limit of detection.

Fig. 1. XRD patterns 0% As, 1% ADS, 18-day 10% ADS, and 1% COP, and 10% COP. The PDF pattern for six-line ferrihydrite (#29-0712) is shown as a stick pattern.

![XRD Patterns](image1.png)

Fig. 2. Representative TEM images of 0% As (upper), 18-day 10% ADS (middle), and 10% COP (lower) ferrihydrite samples.

![TEM Images](image2.png)

### Table 2
Average particle length and width distributions (with standard deviations as error) for ferrihydrite samples as determined using TEM and calculated specific surface areas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle length (nm)</th>
<th>Particle width (nm)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% As</td>
<td>4.3 ± 0.3</td>
<td>3.1 ± 0.5</td>
<td>430</td>
</tr>
<tr>
<td>10% ADS (18-day)</td>
<td>4.4 ± 0.3</td>
<td>3.2 ± 0.3</td>
<td>420</td>
</tr>
<tr>
<td>10% COP</td>
<td>4.2 ± 0.3</td>
<td>2.9 ± 0.3</td>
<td>450</td>
</tr>
</tbody>
</table>
Although changes in crystallite size of 10% COP cannot be completely ruled out, we conclude that the broadening of the XRD peaks for 10% COP is primarily due to decreased crystallinity.

3.2. EXAFS

The structural similarities seen in XRD data between the 0% As, 1-day 10% ADS, and 18-day 10% ADS samples, as well as the structural differences between those particles and the 10% COP particles are reinforced by the EXAFS data. Table 3 shows the fitting results for Fe K-edge EXAFS shell-by-shell fitting and Fig. 3 shows the raw data and fitting results. Reductions in the first Fe–Fe coordination number between the 18-day ADS and the COP samples compared to the 0% As sample can be seen qualitatively in Fig. 3 with the fitting results displayed in Table 3. There is no change in Fe coordination environment for 1-day 10% ADS, and the mode of association is likely adsorption. There is, however, a reduction in the first-shell Fe–Fe (R ~ 3.03 Å) coordination number from 1.6 to 1.4 for the 18-day 10% ADS sample. This reduction is likely due to the As replacing surface-bound Fe and possibly incorporating into the bulk ferrihydrite structure. The most prominent effect on N occurred when As was coprecipitated during the formation of ferrihydrite. This alteration can be seen as a reduction in the amplitude in the Fe–Fe paths for the coprecipitated sample in Fig. 3. For coprecipitation, the average N of the first-shell Fe–Fe bonds at ~3.03 Å was reduced to 1.2 from 1.6 for 0% As particles. Fe–Fe bonds in the second shell at a distance of ~3.45 were unaffected by exposure to As post formation, but experienced a reduction in N from 1.2 to 0.7, for the coprecipitated case. The bond distances and coordination numbers, as well as the reduction in N caused by coprecipitation, mimic those seen by Waychunas et al. (1993) for similar systems. Waychunas et al. (1993) also showed that a variety of As bonding geometries result in a bond distance near 3.45 Å, and it is likely that the spectral features that result in the peak at that distance in the Fourier transforms contain some contribution from Fe–As bonds, however attempts by Waychunas et al. (1993), to fit Fe–As shells at that distance often produced unreasonable fitting results, and in the end only three shells, one Fe–O and two Fe–Fe were accepted. The R-factor, a goodness of fit measurement between the data and the model fit, was determined to be <0.03 for all fits; and the

Table 3
Fe K-edge EXAFS fitting results for As-ferrihydrite sorption and coprecipitated samples (see Fig. 3 for EXAFS and Fourier transform spectra).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Figure</th>
<th>% As</th>
<th>Fe-O</th>
<th>Fe-Fe</th>
<th>Fe-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% As</td>
<td>3a</td>
<td>0</td>
<td>2.7(2) 1.97(1) 0.007ab</td>
<td>1.6(3) 3.04(2) 0.01a</td>
<td>1.2(3) 3.46(2) 0.01a</td>
</tr>
<tr>
<td>10% ADS (1-day)</td>
<td>3b</td>
<td>8.12</td>
<td>2.9(2) 1.97(1) 0.007ab</td>
<td>1.5(3) 3.04(2) 0.01a</td>
<td>1.0(3) 3.45(2) 0.01a</td>
</tr>
<tr>
<td>10% ADS (18-day)</td>
<td>3c</td>
<td>9.55</td>
<td>2.8(2) 1.97(1) 0.007ab</td>
<td>1.4(3) 3.04(2) 0.01a</td>
<td>1.0(3) 3.44(2) 0.01a</td>
</tr>
<tr>
<td>10% COP</td>
<td>3d</td>
<td>10.5</td>
<td>2.8(2) 1.97(1) 0.007ab</td>
<td>1.2(3) 3.04(1) 0.01a</td>
<td>0.7(3) 3.44(2) 0.01a</td>
</tr>
</tbody>
</table>

N = number of atoms at distance R, R = interatomic distance, and σ² = Debye–Waller factor. The R-factor, a goodness of fit measurement between the data and the fit, were <0.03 for each fit performed.

Note: the Debye–Waller factor value for the Fe–Fe shells were held constant at values determined for the 0% As sample.

Fig. 3. Fe K-edge k³-weighted EXAFS and corresponding Fourier transforms and fits (black = data, grey = fits) for 0%, 1-day 10% ADS, 18-day 10% ADS, and 10% COP ferrihydrite.
$R$-factor was not significantly improved, nor was the visual quality of the fit, when Fe–As shells were input into the model.

### 3.3. Magnetism

Fig. 4 shows the ZFC/FC magnetization curves for the 0% As, 18-day 10% ADS, and 10% COP ferrihydrite samples. Superparamagnetic behavior was observed; i.e., the occurrence of the peak in each ZFC curve and the overlap of ZFC and FC curves above the temperature at which all particles are unblocked. The blocking temperatures ($T_B$), which were determined from the maximum magnetization of ZFC curves, were estimated to be $45 \pm 2$ K, $33 \pm 2$ K, $27 \pm 2$ K for samples 0% As, 18-day 10% ADS, and 10% COP, respectively. Blocking temperature ($T_B$) is associated with volume ($V$) by the following equation:

$$V = \frac{25k_B T_B}{K}$$

where $k_B$ is the Boltzmann constant and $K$ is the anisotropy constant, which is material specific. As can be seen from the equation above, $T_B$ is proportional to $V$, and when the average particle size becomes smaller, $T_B$ is expected to decrease (Dormann et al., 1997). For 18-day 10% ADS and 10% COP, $T_B$ decreased and the ZFC peak shape, representing the distribution of particle volume, narrowed as compared to 0% As.

Two hypotheses can be associated with the observed decrease in $T_B$. The first one, observed by Rancourt et al. (2001), is related to the decrease in crystallite size. The presence of arsenate during precipitation may inhibit nucleation and growth, resulting in smaller crystallites. By TEM, the average particle size of 10% COP is indistinguishable from that of the other samples (Table 2 and Fig. 2). However, the TEM particle sizes may reflect the size of aggregated crystallites, which may be smaller in the 10% COP ferrihydrite as discussed earlier. The hypothesis does not explain the decrease of $T_B$ for the 10% ADS ZFC curve since arsenic adsorbed after synthesis is not expected to affect the primary particle size, which was confirmed by TEM (Table 2).

The second hypothesis is related to effects of magnetic super-exchange interactions resulting from particle agglomeration. Magnetic interaction effects have been the focus of many studies since they have a strong influence on the magnetic properties of nanoparticles. It has been documented that $T_B$ decreases when particles are well dispersed (Dormann et al., 1997). Frandsen and Morup (2003) documented a marked decrease in $T_B$ for coated hematite nanoparticles. Additionally, a reduction of interaction effects has been demonstrated for ferrihydrite by coating with sugar or alginate, as evidenced by a drastically lowered $T_B$ (12 K) and sharper ZFC peak for each coated sample as compared to the uncoated sample (Berquó et al., 2009).

This second hypothesis suggests that arsenic likely forms a partial coating on the arsenic-bearing ferrihydrite particles, particularly for the 10% ADS, which could slightly increase interparticle separation within aggregates and consequently lower magnetic interactions and decrease $T_B$. The ZFC peak shape for 10% ADS is also substantially sharper than for 0% As, which suggests the presence of As at particle surfaces and interfaces, which narrows the volume distribution due to attenuated particle–particle interactions. For future magnetism studies of arsenic-bearing ferrihydrites, coating the particles with sugar or alginate after synthesis may better resolve if decrease in $T_B$ is due to decreased crystallite size or a reduction in super-exchange interactions for each incorporation method.

The magnetic hysteresis loops of the 0% As, 18-day 10% ADS, and 10% COP samples collected at 5 K for are presented in Fig. 5. The behavior for all three samples was similar, and they did not achieve saturation even at 5 T, which is consistent with behavior usually observed for antiferromagnetic materials. Saturation magnetization and coercive force both decrease with arsenic adsorption and coprecipitation. The 10% COP sample has the lowest saturation magnetization, consistent with arsenic substitution within the ferrihydrite lattice (O’Reilly, 1984).

Mössbauer spectra collected at 4.2 K of the 10% COP, 18-day 10% ADS, and 0% As samples (Fig. 6) show sextets corresponding to magnetic ordering below the $T_B$ and $T_N$. The Mössbauer spectra taken at room temperature (not shown) are represented only by doublets due to thermal effects. The distribution of particle volume, narrowed as compared to 0% As.
fluctuations (superparamagnetism), indicating the particles were unblocked at this temperature. The magnetic hyperfine parameters at 4.2 K are presented in Table 4. The magnetic hyperfine field ($B_{HF}$) for the 0% sample, 49.6 T, was close to standard values available for ferrihydrite ($B_{HF} = 50.0$ T) (Murad and Cashion, 2004). The parameter $B_{HF}$ was lower (48.5 T) for 18-day 10% ADS but even lower (47.9 T) for 10% COP. The decrease in $B_{HF}$ relates to the crystallinity of the ferrihydrite samples and suggests that lattice defects, such as isomorphic substitutions and lattice vacancies, are introduced with the incorporation of arsenic both by equilibration and coprecipitation (Murad and Cashion, 2004). These magnetism results compliment the XRD and EXAFS and support the conclusion that the incorporation of arsenate by coprecipitation causes structural changes and decreased crystallinity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B_{HF}$ (T)</th>
<th>QS (mm/s)</th>
<th>IS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% As</td>
<td>49.6 ± 0.2</td>
<td>-0.07 ± 0.01</td>
<td>0.46 ± 0.01</td>
</tr>
<tr>
<td>10% ADS (18-day)</td>
<td>48.5 ± 0.2</td>
<td>-0.08 ± 0.01</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>10% COP</td>
<td>47.9 ± 0.2</td>
<td>-0.03 ± 0.01</td>
<td>0.54 ± 0.02</td>
</tr>
</tbody>
</table>

3.4. Potentiometric titrations

The data from potentiometric titrations of the 0% As and 10% COP suspensions are shown in Fig. 7. The point of zero net proton charge (PZNPC) was pH 8.8 ± 0.1 for the 0% As sample and pH 6.3 ± 0.1 for the 10% COP sample. Experiments to determine the PZNPC of 1-day and 18-day 10% ADS ferrihydrite were complicated by the influence of CO$_2$ and desorption of arsenate with the increasing pH of the titration procedure. However, the semi-quantitative titration results clearly indicate a PZNPC greater than 10.5 for both samples (results not shown). This is consistent with the prediction of Dzombak and Morel (1990) regarding an increase in the PZNPC due to co-adsorption of arsenate, protons, and sodium (as determined by ICP-AES analysis). The coprecipitation of arsenic had the opposite effect and shifted the PZNPC to a lower pH as compared to the 0% As sample. Few studies have considered the effect on PZNPC with coprecipitation of ions, but the shift to lower pH parallels the effect observed by Mikutta et al. (2008), in which acid polysaccharides were coprecipitated with ferrihydrite. Electrophoretic mobility experiments determined the isoelectric point of pure ferrihydrite to be near pH 7 and the isoelectric point of the coprecipitated-acid polysaccharide ferrihydrites was less than 2.

In summary, the six-line ferrihydrite samples all have similar average particle size, and their XRD patterns are consistent with six-line ferrihydrite. However, the 10%...
COP sample exhibits a lower degree of crystallinity, as evidenced by the results from XRD peak broadening, decreased $T_B$ in ZFC/FC analysis, and increased disorder in the crystal lattice (lower $B_{HF}$) by Mössbauer studies. Reduced crystallite size of the 10% COP sample may also lead to lower $T_B$ in ZFC/FC experiments and peak broadening in XRD. Therefore, it is also possible that the 10% COP crystallite size may be smaller than for the other samples, which would be consistent with the conclusions of Waychunas et al. (1995, 1996). If the lower $T_B$ in ZFC/FC experiments was attributed only to decreased crystallite size, the 10% COP crystallite volume would be calculated as 60% of the volume of an unmodified ferrihydrite crystallite using the relationship in Eq. (1). The measured average particle sizes in TEM would require the aggregation of two or three crystallites and the morphology would be expected to change in the 10% COP sample. The lack of evidence for aggregation of smaller crystallites in TEM images of 10% COP suggests that arsenate initially adsorbs to ferrihydrite but that incorporation of arsenate into the ferrihydrite structure does not occur.

3.5. Reductive dissolution kinetics

The reductive dissolution was monitored for the arsenic-bearing and 0% As-ferrihydrite powders. During the reaction, hydroquinone (QH$_2$) is oxidized and ferric iron reduced to produce benzoquinone (Q) and ferrous iron (Eqs. (2)-(4)). The rate of reaction can be measured by monitoring the benzoquinone and Fe(II) concentrations as a function of time.

$$2\text{Fe}_3\text{O}_4 \cdot \text{4H}_2\text{O}(s) + 10e^- + 30\text{H}^+(aq) \longrightarrow 10\text{Fe}^{2+}(aq) + 24\text{H}_2\text{O}(l)$$  
$$5\text{QH}_2(aq) \rightarrow 5\text{Q}(aq) + 10e^- + 10\text{H}^+(aq)$$  
$$2\text{Fe}_3\text{O}_4 \cdot \text{4H}_2\text{O}(s) + 5\text{QH}_2(aq) + 20\text{H}^+(aq) \longrightarrow 10\text{Fe}^{2+}(aq) + 5\text{Q}(aq) + 24\text{H}_2\text{O}(l)$$  

Using the method of initial rates (Espenson, 2002), the rate was determined using the first 3–7 data points from each trial (9–21 points for each sample). The concentration of benzoquinone versus reaction time is presented in Fig. 8 for five ferrihydrite samples with 2.0 g/L ferrihydrite loading and 0.2 mM hydroquinone at 25 ± 1°C. With the exception of the 18-day 10% ADS sample, the reductive dissolution rates are statistically indistinguishable. The significantly lower reaction rate of the 10% ADS sample, approximately one-fifth the rate of the other four samples, suggests that the high concentration of arsenic on the particle surface inhibits the redox reaction. Using the calculated surface area for the 10% ADS sample from Table 2 combined with the elemental analysis and a reactive surface site density of 17 μmol sites/g (Dzombak and Morel, 1990), one can estimate the fraction of sites occupied by arsenate. Assuming a 1:1 stoichiometry (i.e., one arsenic per reactive surface site) and that all of the arsenic is located on reactive surface sites yields an estimate that 20% of the reactive sites are bound to arsenate. However, the rate of reduction of 10% ADS is reduced by 80% as compared to the other four samples. One hypothesis for this dramatic drop in reactivity with such modest surface coverage is that arsenate preferentially adsorbs at the most reactive surface sites.

The distinct decrease in reactivity of 18-day 10% ADS warranted further kinetic experiments to investigate the empirical rate law and quantify the activation energy for the reductive dissolution of the 10% ADS ferrihydrite compared to the 10% COP and 0% As samples. Reaction orders were determined for the 0% As, 18-day 10% ADS, and 10% COP samples, and the results are reported in Table 5.

Rate constants were calculated using the measured rate of reaction and experimental orders with respect to hydroquinone and the particle surface area (S) concentrations according to the empirical rate law

$$\frac{d[Q]}{dt} = k[H^+]^{\alpha}[\text{QH}_2]^{\beta}[S]^n = k'[\text{QH}_2]^{\beta}[S]^n$$  

where $k$ is the rate constant; $k'$ is the observed rate constant; and $l$, $m$, and $n$ are the empirical orders with respect to the proton concentration, hydroquinone concentration, and surface area, respectively. Because all experiments were performed at a buffered pH of 3.75 and the pH was constant during each trial, the proton concentration has been incorporated into the observed rate constant, $k' (k = k[H^+]^l)$. The ionic strength of the reaction solution was controlled by the acetate and sodium ions of the acetate buffer solution and because the pH was constant with only very small changes in solution composition over the reaction period, ionic strength was considered constant. Over the reaction period studied, less than 0.2% of the total Fe(III) was reduced; hence, there was no significant change in the particle surface area concentration. The reaction orders for 0% As and 10% COP are similar, although $m$ is statistically larger for 10% COP than for 0% As. However, the reaction orders for 18-day 10% ADS are substantially different, suggesting
To quantify the activation energy of reductive dissolution, the kinetic data for each sample were collected at four or five temperatures (2.0–50.0 °C) and evaluated using the following Arrhenius equation:

$$\ln k' = \ln A - \frac{E_a}{RT}$$ (6)

Plotting ln $k'$ against 1/T produced a linear trend, from which the pre-exponential factor ($A$) and the activation energy ($E_a$) were calculated (Espenson, 2002). To calculate rate constants, reaction orders were assumed to be independent of particle size and reaction temperature (Anschutz, 2006; Jentzsch and Penn, 2006). The Arrhenius plots for the 0% As, 10% COP, and 18-day 10% ADS, samples are shown in Fig. 9. Arrhenius parameters calculated using linear regression analysis are reported with standard errors in the table embedded within Fig. 9. The activation energies of a significant change in reaction mechanism as a consequence of the adsorption of arsenate. This could result from the preferential adsorption of arsenate onto one type of reactive surface site or simply indicate a change in the overall mechanism of reductive dissolution for the 18-day 10% ADS ferrihydrite due to the presence of adsorbed arsenate. The very modest difference in $m$ observed for 10% COP is maybe the result of a portion of the arsenate residing on the ferrihydrite surface.

To quantify the activation energy of reductive dissolution, the kinetic data for each sample were collected at four or five temperatures (2.0–50.0 °C) and evaluated using the following Arrhenius equation:

$$\ln k' = \ln A - \frac{E_a}{RT}$$ (6)

Plotting ln $k'$ against 1/T produced a linear trend, from which the pre-exponential factor $(A)$ and the activation energy $(E_a)$ were calculated (Espenson, 2002). To calculate rate constants, reaction orders were assumed to be independent of particle size and reaction temperature (Anschutz, 2006; Jentzsch and Penn, 2006). The Arrhenius plots for the 0% As, 10% COP, and 18-day 10% ADS, samples are shown in Fig. 9. Arrhenius parameters calculated using linear regression analysis are reported with standard errors in the table embedded within Fig. 9. The activation energies of all mechanism of reductive dissolution for the 18-day 10% ADS ferrihydrite solids. And Rea et al. (1994) documented a 50% decrease in labile Fe sites for Fe$^{57}$-isotope exchange for ferrihydrite with arsenate adsorbed on 32% of the sites. These published results demonstrate that not all surface sites—only active surface sites—must be blocked to have a pronounced effect on the kinetics of surface reactions. In this body of work, the adsorption of arsenate on one-fifth of the surface sites of 10% ADS produced an 80% drop in the reaction rate for reductive dissolution. The similarity of $E_a$ for 0% As, 10% COP, and 10% ADS indicates that the rate-determining step is unaffected by the structural defects within crystallites/particles or the presence of arsenate on the ferrihydrite surface. However, the reaction orders for the 10% ADS rate law differ from the other two samples, indicating a change in reaction mechanism or, more likely, a change in the relative importance of the parallel reactions at each type of reactive site. Arsenate at the most reactive sites would prevent those sites from participating in the

### Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>$m$</th>
<th>$n$</th>
<th>Initial rate (mM/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% As</td>
<td>0.26 ± 0.02</td>
<td>0.65 ± 0.08</td>
<td>0.020 ± 0.002</td>
</tr>
<tr>
<td>10% ADS (18-day)</td>
<td>0.62 ± 0.09</td>
<td>0.89 ± 0.07</td>
<td>0.0042 ± 0.0003</td>
</tr>
<tr>
<td>10% COP</td>
<td>0.37 ± 0.07</td>
<td>0.64 ± 0.15</td>
<td>0.020 ± 0.001</td>
</tr>
</tbody>
</table>

According to Zinder et al. (1986), the rate of proton-promoted reductive dissolution ($R_{\text{SI}}$) for iron oxides is dependent on the surface concentration ($E$) of potentially detachable surface metal species per area as described by the following equation:

$$R_{\text{SI}} = \frac{d[M(II)]}{dt} = k(E)$$ (7)

and $E$ is statistically related to the probability of finding a reduced, surface metal center with two protonated nearest-neighbor oxide or hydroxide sites. Real oxide surfaces have different kinds of surface sites, including surface defects, kinks, steps, and pits, with varying activation energies (Wieland et al., 1988). Dissolution occurs at the sites with the lowest activation energies, which are called active sites. The detachment of M(II) at active sites and less active sites are parallel reactions but reaction at the most active sites is dominant and rate determining (Zinder et al., 1986). The adsorption of arsenate leads to an increase in surface protonation as indicated by the increase in PZNPC; however, the presence of arsenate at the surface decreases the sites available for protons to adsorb. Arsenate forms binuclear bridging surface complexes and essentially extends the crosslinking of the solid’s lattice. For dissolution at binuclear arsenate adsorption sites, the activation energy is high because dissolution requires the simultaneous removal of two metal centers (Biber et al., 1994). Paige et al. (1997) observed marked decreases in proton-promoted dissolution rates when arsenate (3–50 mol%) was coprecipitated into ferrihydrite solids. And Rea et al. (1994) documented a 50% decrease in labile Fe sites for Fe$^{57}$-isotope exchange for ferrihydrite with arsenate adsorbed on 32% of the sites. These published results demonstrate that not all surface sites—only active surface sites—must be blocked to have a pronounced effect on the kinetics of surface reactions. In this body of work, the adsorption of arsenate on one-fifth of the surface sites of 10% ADS produced an 80% drop in the reaction rate for reductive dissolution. The similarity of $E_a$ for 0% As, 10% COP, and 10% ADS indicates that the rate-determining step is unaffected by the structural defects within crystallites/particles or the presence of arsenate on the ferrihydrite surface. However, the reaction orders for the 10% ADS rate law differed from the other two samples, indicating a change in reaction mechanism or, more likely, a change in the relative importance of the parallel reactions at each type of reactive site. Arsenate at the most reactive sites would prevent those sites from participating in the

![Fig. 9. Arrhenius plot of reactions with 0.2 mM hydroquinone and 2 g/L ferrihydrite loading, including the trendlines representing 0% As (---), 18-day 10% ADS (---) and 10% COP (---) ferrihydrites.](image-url)
reductive dissolution, and the reaction orders of 10% ADS may reflect that the reaction at less active sites dominates as a consequence of arsenate occupying the most active sites.

Arsenate is an important species to consider when studying the kinetics for reductive dissolution of the arsenic-bearing ferrihydrite samples; because, in addition to iron, the arsenate ion (AsO$_4^{3-}$) is redox active (Eq. (8)) and may be reduced to arsenite (AsO$_3^{2-}$) during reductive dissolution.

$$\text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}(l) \quad E^- = 0.575 \text{V} \quad (8)$$

In this study, attempts to quantify arsenite and arsenate using the molybdenum-blue method (Lenoble et al., 2003) were unsuccessful. As an alternative, kinetic experiments were conducted using the Ferrozine assay (Stookey, 1970) to investigate the Fe(II):benzoquinone stoichiometry during reductive dissolution of arsenic-bearing ferrihydrites. The aqueous Fe(II) and benzoquinone concentrations of filtered solutions from reductive dissolution experiments using 18-day 10% ADS and 10% COP were measured. The method of initial rates was used to quantify the rate of Fe(II) and benzoquinone formation (Table 6). The slopes (in meq/L) cannot be differentiated for either sample and implies that no significant reduction of arsenate occurred during the reaction period. If arsenate reduction occurred and dominated the reaction, the expected rate of benzoquinone formation would be considerably higher than the stoichiometric rate of Fe(II) formation.

To quantitatively compare arsenic release during reductive dissolution of the As-bearing materials, the samples were reacted for longer periods and with higher concentrations of hydroquinone. The release of iron and arsenic was monitored for 4 days during the reductive dissolution of 10% COP and 18-day 10% ADS samples (Table 7). The most notable distinction is the almost one order of magnitude difference in the final amount of arsenic released from the two solids. In the case of 10% COP the release of Fe far outpaces that of As, but the opposite is true for 18-day 10% ADS. After 95 h of reaction, approximately 12% of the total iron and less than 0.7% of the total arsenic were dissolved from the original 10% COP ferrihydrite solid. These results indicate that (1) arsenic remains incorporated in the ferrihydrite and possibly (2) dissolved arsenate slowly readsores onto the ferrihydrite surface. In contrast, 5% of the total iron and about 4% of the total arsenic were dissolved from 10% ADS (18-day). About 2% of the arsenic was released just by resuspension and equilibration of the 10% ADS sample with the buffer solution overnight. The release of arsenate during equilibration was not expected because samples were resuspended at pH 3.75, which was similar to the 10% ADS suspension pH before drying. A modest drop in dissolved arsenate concentration was observed after 95 h, which was attributed to the readsorption of some arsenate onto ferrihydrite. For these high-yield dissolution experiments, the concentrations of iron measured by ICP-AES were similar to concentrations measured using the Ferrozine method. The formation of Fe(II) closely matched the stoichiometric formation of benzoquinone (2:1 as can be seen in Eq. (4)) for the 10% COP reactions but was slightly lower for the 18-day 10% ADS reactions. Therefore, a small fraction of the arsenate (<2% of total) from the 10% ADS samples may have reduced during the reaction period.

These results demonstrate that arsenic can be released from arsenic-bearing ferrihydrite prepared both by coprecipitation and adsorption, but the release from the ferrihydrite with adsorbed arsenate is substantially greater than from ferrihydrite with coprecipitated arsenate. These results suggest that understanding the mode of arsenic incorporation—either by coprecipitation or adsorption—could lead to improved predictions regarding arsenic release from naturally occurring arsenic-bearing iron oxides under reducing conditions.

### 4. CONCLUSIONS

Structural results indicate that the incorporation of arsenic by coprecipitation leads to decreased crystallinity. The results from reductive dissolution experiments show similar reaction rates, reaction mechanism, and activation energy for ferrihydrite precipitated with or without added arsenate. However, a marked decrease in reaction rate was observed for ferrihydrite after equilibrium with an arsenate solution. The decrease is not attributed to differences in activation energy but rather the preferential blocking of active sites on the ferrihydrite surface, which also affects the rate law for reductive dissolution.

This body of work demonstrates that indeed strongly reducing conditions in groundwater systems may be linked to the large-scale release of arsenic by reductive dissolution of arsenic-bearing ferrihydrite and likely of other arsenic-bearing iron oxide aquifer materials. Arsenic may be released by ferrihydrite materials prepared by either coprecipitation or adsorption of arsenate. However, under these reaction conditions, release from materials with adsorbed

---

**Table 6**

Rates of benzoquinone and Fe(II) formation for the reductive dissolution of 10% ADS and 10% COP ferrihydrites for reactions at room temperature with 0.05 mM hydroquinone and 2 g/L oxide loading.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzoquinone slope (meq/L/h)</th>
<th>Fe(II) slope (meq/L/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% ADS (18-day)</td>
<td>0.0049 ± 0.0020</td>
<td>0.0050 ± 0.0007</td>
</tr>
<tr>
<td>10% COP</td>
<td>0.030 ± 0.002</td>
<td>0.032 ± 0.003</td>
</tr>
</tbody>
</table>

**Table 7**

Percentages of dissolved Fe and As compared to the total amount contained in the ferrihydrite solids for equilibrium and filtrate samples of a long-term reductive dissolution reaction.

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>10% ADS (18-day)</th>
<th>10% COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe dissolved (wt%)</td>
<td>0.020</td>
<td>0.039</td>
</tr>
<tr>
<td>As dissolved (wt%)</td>
<td>1.92</td>
<td>3.07</td>
</tr>
<tr>
<td>1.5 h</td>
<td>0.714</td>
<td>3.37</td>
</tr>
<tr>
<td>19 h</td>
<td>3.25</td>
<td>4.33</td>
</tr>
<tr>
<td>95 h</td>
<td>5.18</td>
<td>3.70</td>
</tr>
</tbody>
</table>

arsenate greatly exceeds that from materials with coprecipitated arsenate. In fact, a considerable amount of arsenic was released from 10% ADS ferrihydrite before the initiation of reductive dissolution. Therefore, characterization of arsenate-bearing iron oxides to determine the mode of arsenate incorporation—perhaps by quantification of Fe-Fe coordination with EXAFS spectroscopy—may lead to improved predictions of the large-scale release of arsenic within aquifer systems under reducing conditions.

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