

# Arsenite and Arsenate Adsorption on Ferrihydrite: Surface Charge Reduction and Net OH<sup>-</sup> Release Stoichiometry

AMITA JAIN, KLAUS P. RAVEN, AND RICHARD H. LOEPPERT\*

Department of Soil and Crop Sciences, Texas A&M University, College Station, Texas 77843-2474

Arsenite [As(III)] and arsenate [As(V)] are highly toxic inorganic arsenic species that represent a potential threat to the environment and human health. Iron oxides including poorly crystalline oxides, e.g., ferrihydrite, play a significant role in controlling dissolved As concentration and limit the mobility and bioavailability of As(III) and As(V). Adsorption occurs by ligand exchange of the As species for OH<sub>2</sub> and OH<sup>-</sup> in the coordination spheres of surface structural Fe atoms. The objective of this study was to evaluate H<sup>+</sup>/OH<sup>-</sup> release stoichiometry and changes in surface charge properties of the adsorbent during the adsorption of arsenite and arsenate on ferrihydrite in the pH range of 4–10. This information, which is not directly accessible through spectroscopic studies, provides important clues to bonding mechanism. While arsenate adsorption resulted in the net release of OH<sup>-</sup> at pH 4.6 and 9.2, arsenite adsorption resulted in net OH<sup>-</sup> release at pH 9.2 and net H<sup>+</sup> release at pH 4.6. The amount of H<sup>+</sup> or OH<sup>-</sup> release per mole of adsorbed As varied with the As surface coverage, indicating that different mechanisms of arsenic adsorption predominate at low versus high coverage. The experimentally observed surface charge reduction and net OH<sup>-</sup> release stoichiometry were compared with the theoretical stoichiometry of the surface adsorption reactions that might occur. The results provide evidence that during arsenite adsorption at low pH, i.e., pH 4.6, the oxygen of the Fe–O–As bond remained partially protonated as Fe–O(H)–As. There is evidence that the monodentate bonding mechanism might play an increasing role during arsenate adsorption on ferrihydrite with increasing pH (at pH > 8). The results of this study have provided ancillary evidence to support the experimentally observed reduced adsorption of arsenite at low pH and of arsenate at high pH.

## Introduction

Arsenic is of environmental concern because of its toxicity to plants, animals, and human beings. In oxidized systems, its solubility is largely controlled by adsorption reactions occurring at colloid surfaces. Arsenic adsorption on a wide variety of adsorbents, including phyllosilicates (1, 2), aluminum oxides (3, 4), and iron oxides (5–13) has been studied. Iron oxides, including the poorly crystalline iron oxides, e.g.,

ferrihydrite, have a strong affinity for both arsenite and arsenate. The retention of arsenite [As(III)] and arsenate [As(V)] is predominantly by ligand exchange with surface structural OH<sub>2</sub> and/or OH<sup>-</sup> at surface adsorption sites. The retention of both arsenite and arsenate is strongly pH-dependent, but with opposite trends. At low to moderate arsenic adsorption levels, the adsorption envelopes of arsenite and arsenate usually cross within the pH range of 6–7.5, i.e., ferrihydrite exhibits a relatively greater retention of arsenate at lower pH values, whereas arsenite is more strongly retained at higher pH values (13). The reaction of arsenate with iron oxides has been studied by extended X-ray absorption fine structure (EXAFS) (14–16) and infrared (IR) (17, 18) spectroscopy. These studies have provided strong evidence that arsenate is adsorbed on iron oxide surfaces predominantly by forming bidentate binuclear complexes. Recently, EXAFS (19) and Fourier transform infrared (FTIR) (20) studies have provided evidence that arsenite is also adsorbed on the goethite surface as a bidentate binuclear complex.

The effect of cation and anion adsorption on surface charge of adsorbents has been reviewed by Stumm (21). Anion adsorption by ligand exchange involves the release of surface OH<sup>-</sup> and/or OH<sub>2</sub>. Evaluation of changes in the surface charge properties of the adsorbent and H<sup>+</sup>/OH<sup>-</sup> release stoichiometry provides important clues with regard to the adsorption mechanism and has been especially useful in studies of phosphate and sulfate adsorption mechanisms (22–27).

The objectives of this study were to evaluate H<sup>+</sup>/OH<sup>-</sup> release stoichiometry and changes in net surface charge resulting from the reactions of arsenite and arsenate with ferrihydrite within the pH range of 4–10. A better understanding of these aspects of the adsorption process is helpful to elucidate the reaction mechanism and eventually to optimize strategies for the removal of arsenic from contaminated water and the management of arsenic contaminated soil.

## Materials and Methods

**Ferrihydrite Synthesis.** Two-line ferrihydrite was synthesized using the procedure of Schwertmann and Cornell (28), with slight modifications (13). The ferrihydrite (10 g L<sup>-1</sup>) was stored separately in 0.001, 0.01, and 0.1 M NaCl ionic strength buffers at 2 °C, for use in subsequent experiments. The identity of the two-line ferrihydrite was confirmed by powder X-ray diffraction. Preliminary tests showed that the ferrihydrite transformed partially into goethite upon prolonged storage (>4 weeks at room temperature). Therefore, each batch of ferrihydrite was used within 10 days of its synthesis, at which time there was no evidence for the presence of goethite, as determined by powder X-ray diffraction and diffuse reflectance FTIR spectroscopy of freeze-dried samples.

**H<sup>+</sup>/OH<sup>-</sup> Release Stoichiometry.** The H<sup>+</sup>/OH<sup>-</sup> release during arsenite and arsenate adsorption was studied at pH 4.6 and 9.2 at initial As solution concentrations of 0.133 to 13.3 mol<sub>As</sub> kg<sub>fer</sub><sup>-1</sup>. Reagent-grade NaAsO<sub>2</sub> and Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O were used as the arsenite and arsenate sources, respectively. Stock solutions of arsenite and arsenate were prepared in 0.1 M NaCl to give As concentrations of 1.33, 3.33, 6.67, 13.3, 33.3, 66.7, and 133 mmol L<sup>-1</sup>. Forty milliliters of ferrihydrite suspension (2.5 g L<sup>-1</sup>) in 0.1 M NaCl was placed in a polyethylene container. A combination pH electrode and a buret tip connected to an automatic titrator were introduced into the ferrihydrite suspension through perforations in the lid of the container. The suspension was purged with N<sub>2</sub> continuously throughout the experiment. The pH of the ferrihydrite suspension was adjusted to the experimental pH,

\* Corresponding author telephone: (409)845-3814; fax: (409)-845-0456; e-mail: r-loeppert@tamu.edu.

and 10 mL of As stock solution with preadjusted pH was added to the ferrihydrite suspension with simultaneous addition of acid or base with an automatic titrator in pH-stat mode to maintain the pH. The cumulative consumption of acid and base was recorded throughout the equilibration period. After the 24-h equilibration, the suspension was filtered immediately through a membrane filter (0.45- $\mu\text{m}$  nominal pore size), and the filtrate was stored at 2 °C until analysis.

**Titration Curves and Zero Point of Charge.** The zero point of charge (ZPC) was evaluated for the ferrihydrite alone and with As concentrations corresponding to 0.267 and 0.801 mol<sub>As</sub> kg<sub>fer</sub><sup>-1</sup>, from the intercept of acid–base titration curves obtained for pure ferrihydrite and ferrihydrite treated with arsenic in 0.001, 0.01, and 0.1 ionic strength buffers.

The stock solutions of arsenite (from NaAsO<sub>2</sub>) and arsenate (from Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O) were prepared at concentrations of 2.67 and 8.01 mmol of As L<sup>-1</sup> in 0.001, 0.01, and 0.1 M NaCl. Each titration point (10–14 per curve) was obtained by pre-equilibrating 20 mL of a 2.5 g L<sup>-1</sup> ferrihydrite suspension with 5 mL of As stock solution in a capped 40-mL polyethylene centrifuge tube for 4 h. After pre-equilibration, a given amount of 0.1 M HCl or NaOH was added to each centrifuge tube to give final supernatant pH values ranging from 3 to 11. All sample manipulations were carried out under N<sub>2</sub> purge. The centrifuge tubes were capped and placed on a reciprocating shaker for 24 h. After equilibration, the suspension was centrifuged, the pH of the supernatant was measured, and the supernatant was passed through a membrane filter (0.45- $\mu\text{m}$  nominal pore size) and stored at 2 °C for subsequent As analysis.

**Surface Charge Calculations.** Surface charge calculations were carried out for arsenite and arsenate adsorption on ferrihydrite at initial As solution concentrations of 0, 0.534, and 1.60 mM L<sup>-1</sup>. For each of these cases, the amount of H<sup>+</sup> or OH<sup>-</sup> required to achieve the specified pH from the ZPC was determined, and the surface charge was calculated with the assumption that 1 mol of H<sup>+</sup> or OH<sup>-</sup> added was equivalent to 1 mol of positive or negative charge gained, respectively.

To calculate the surface charge changes attributable to As adsorption, the surface charge vs pH plot for pure ferrihydrite was subtracted from that for a given As treatment at the same ionic strength. These calculations required that the surface charge vs pH plots first be fitted with a fifth-order polynomial function, which in all cases fit the data points closely. The influence of adsorbed As on surface charge was expressed as mol<sub>c</sub> mol<sub>ads As</sub><sup>-1</sup>.

**Arsenic Analyses.** Arsenic analyses were performed using a 3100 EDS atomic absorption spectrophotometer (Perkin-Elmer Corporation, Norwalk, CT), with an electrodeless discharge lamp (EDL) as the radiation source. The flame technique was used for solutions with As concentrations > 0.1 mM L<sup>-1</sup>, at a wavelength of 193.7 nm and with the absorbance signal averaged over 10 s. The hydride generation technique was used for solutions with As concentrations < 0.1 mM L<sup>-1</sup>. Twenty milliliters of test solution, consisting of 10 mL of 12 M HCl and 10 mL of sample solution, was used for each determination. The test solution was transferred into a stoppered 500-mL separatory funnel which was used as the reaction vessel. Six milliliters of 3% NaBH<sub>4</sub> solution in 1% NaOH was then injected into the reaction vessel. The released H<sub>3</sub>As was transported through Tygon tubing by a 3.5 L min<sup>-1</sup> Ar stream to a quartz cell centered on the optical beam of the spectrometer. The quartz cell was heated using a 5-cm burner head. The As atomized in the heated quartz cell was measured with 189.0-nm radiation. The absorbance peak area integrated over 45 s was used as the analytical signal. The As detection limit of the test solution was approximately 4.4 nmol L<sup>-1</sup>.

## Results and Discussion

**Possible Surface Complexation Reactions Involved in the Adsorption of Arsenite and Arsenate on Ferrihydrite.** There are several possible reactions that could occur during the adsorption of arsenite and arsenate on ferrihydrite. These reactions, along with their respective theoretical surface charge changes and net OH<sup>-</sup> release stoichiometries are summarized in Table 1. The experimentally determined net OH<sup>-</sup> release stoichiometries and charge reduction at pH 4.6 and 9.2 are also summarized in Table 1. The acid dissociation constants for H<sub>3</sub>AsO<sub>4</sub> are pK<sub>1</sub> = 2.3, pK<sub>2</sub> = 6.9, and pK<sub>3</sub> = 11.5, and for H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> are pK<sub>1</sub> = 9.2, pK<sub>2</sub> = 12.1, and pK<sub>3</sub> = 12.7 (29). Therefore, the predominant species of arsenate at pH 4.6 and 9.2 are H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup>, respectively. The predominant species of arsenite are H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> at pH 4.6 and approximately an equimolar mixture of H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> and H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> at pH 9.2. The theoretical OH<sup>-</sup> release and surface charge reduction values in Table 1 resulting from arsenite adsorption at pH 9.2 are given with the assumption that the initial concentrations of H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> and H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> are equimolar.

The only surface groups represented in Table 1 are A-type Fe–OH<sub>2</sub> and Fe–OH, in which the surface OH<sub>2</sub> or OH<sup>-</sup> is bound to a single structural Fe. These are the surface groups that are most likely involved in ligand exchange reactions (21). The probable occurrence of surface sites at a specific pH value is based on the pK values of surface sites (Fe–OH<sub>2</sub>, pK = 5.1; Fe–OH, pK = 10.7) for amorphous iron oxide (30). Therefore, at pH 4.6, both Fe–OH<sub>2</sub> and Fe–OH are likely to be present in appreciable concentrations; at pH 9.2, Fe–OH is likely the dominant site. The surface OH<sub>2</sub> and OH<sup>-</sup> groups involved in bidentate bonding by formation of an edge sharing complex, as Fe–O<sub>2</sub>–As(III or V), or corner sharing complex, as (Fe–O)<sub>2</sub>–As(III or V), are both represented in Table 1 as Fe|O<sub>2</sub>As(III or V). In the evaluation of surface complexes by charge reduction and net OH<sup>-</sup> release, it is not possible to differentiate the edge-sharing (bidentate) and corner-sharing (bidentate bridging) complexes. Both monodentate and bidentate complexes are presented, although the current X-ray absorption and infrared spectroscopic evidence indicates that bidentate complexes are likely to dominate.

**H<sup>+</sup>/OH<sup>-</sup> Release Stoichiometry.** The adsorption of arsenate at pH 4.6 and 9.2 and of arsenite at pH 9.2 by ferrihydrite resulted in the net release of OH<sup>-</sup> (Figure 1). In contrast, the reaction between ferrihydrite and arsenite at pH 4.6 resulted in the net release of H<sup>+</sup>. The final equilibrium net OH<sup>-</sup> release is the combined effect of individual net changes in arsenic species protonation and surface hydroxylation. In each case, the cumulative net OH<sup>-</sup> release per mole of As adsorbed was influenced by the quantity of As adsorbed. The net H<sup>+</sup> release during arsenite adsorption at pH 4.6 was attributable to the deprotonation of H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> during the adsorption reaction, e.g., by reactions 1, 6, or 10 (Table 1). The fact that the net release of H<sup>+</sup> was less than the theoretical value of 1 mol<sub>H</sub><sup>+</sup> mol<sub>ads As</sub><sup>-1</sup> indicates that either a portion of the H<sup>+</sup> was neutralized by surface OH<sup>-</sup> released during the adsorption of H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> as in reaction 3 or that the O in the Fe–O–As group remained protonated as Fe–O(H)–As as in reaction 2.

During arsenite adsorption, the net release of H<sup>+</sup> (pH 4.6) or OH<sup>-</sup> (pH 9.2) per mole of adsorbed As increased gradually with an increase in the As surface coverage up to ~2 mol<sub>ads As</sub> kg<sub>fer</sub><sup>-1</sup> and remained relatively constant at higher As adsorption levels. These results could be attributable to different predominant modes of arsenite adsorption at low compared to high surface coverage. During arsenate adsorption at pH 4.6 and 9.2, the net release of OH<sup>-</sup> per mole of adsorbed As was influenced by pH and arsenic concentration. For example, the net OH<sup>-</sup> release, during arsenate adsorption at

TABLE 1. Possible Reactions of Adsorption of Arsenite and Arsenate by Ferrihydrite<sup>a</sup>

|  | OH <sup>-</sup> release | change in charge |  | OH <sup>-</sup> release | change in charge |
|--|-------------------------|------------------|--|-------------------------|------------------|
| <b>Arsenite, pH 4.6</b>  |                         |                  |  |                         |                  |
| <b>experimental values:</b>  |                         |                  |  |                         |                  |
| at 0.267 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | -0.14                   | -0.73            |  |                         |                  |
| at 0.801 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | -0.23                   | -0.49            |  |                         |                  |
| Fe-OH <sub>2</sub> <sup>+1/2</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe-OAs(OH) <sub>2</sub> <sup>-1/2</sup>                                      | -1                      | -1               | [1] Fe(OH) <sub>2</sub> (OH) <sup>0</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H) <sub>2</sub> AsOH <sup>+1</sup>                              | 1                       | 1                |
| Fe-OH <sub>2</sub> <sup>+1/2</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe-O(H)As(OH) <sub>2</sub> <sup>+1/2</sup>                                   | 0                       | 0                | [2] Fe(OH) <sub>2</sub> (OH) <sup>0</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H)AsOH <sup>0</sup>   | 0                       | 0                |
| Fe-OH <sup>-1/2</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe-OAs(OH) <sub>2</sub> <sup>-1/2</sup>   | 0                       | 0                | [3] Fe(OH) <sub>2</sub> (OH) <sup>0</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> AsOH <sup>-1</sup>   | -1                      | -1               |
| Fe-OH <sup>-1/2</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe-O(H)As(OH) <sub>2</sub> <sup>+1/2</sup>  | 1                       | 1                | [4] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H) <sub>2</sub> AsOH <sup>+1</sup>                                  | 2                       | 2                |
| Fe(OH) <sub>2</sub> <sup>+1</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H) <sub>2</sub> AsOH <sup>+1</sup>            | 0                       | 0                | [5] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H)AsOH <sup>0</sup>   | 1                       | 1                |
| Fe(OH) <sub>2</sub> <sup>+1</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H)AsOH <sup>0</sup>                           | -1                      | -1               | [6] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> AsOH <sup>-1</sup>   | 0                       | 0                |
| Fe(OH) <sub>2</sub> <sup>+1</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> AsOH <sup>-1</sup>                             | -2                      | -2               | [7]  |                         |                  |
| <b>Arsenite, pH 9.2</b>  |                         |                  |  |                         |                  |
| <b>experimental values:</b>  |                         |                  |  |                         |                  |
| at 0.267 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | 0.09                    | -0.80            |  |                         |                  |
| at 0.801 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | 0.13                    | -0.48            |  |                         |                  |
| Fe-OH <sup>-1/2</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe-OAs(OH) <sub>2</sub> <sup>-1/2</sup>    | 0.5                     | 0                | [14] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> (H)AsOH <sup>0</sup> | 1.5                     | 1                |
| Fe-OH <sup>-1/2</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe-OAs(O)(OH) <sub>2</sub> <sup>-3/2</sup> | -0.5                    | -1               | [15] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> → Fe <sub>2</sub> O <sub>2</sub> AsOH <sup>-1</sup>   | 0.5                     | 0                |
| <b>Arsenate, pH 4.6</b>  |                         |                  |  |                         |                  |
| <b>experimental values:</b>  |                         |                  |  |                         |                  |
| at 0.267 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | 0.081                   | -1.40            |  |                         |                  |
| at 0.801 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | 0.15                    | -1.01            |  |                         |                  |
| Fe-OH <sub>2</sub> <sup>+1/2</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe-OAs(O)(OH) <sub>2</sub> <sup>-1/2</sup>                                   | 0                       | -1               | [18] Fe(OH) <sub>2</sub> <sup>+1</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(O)(OH) <sup>-1</sup>   | -1                      | -2               |
| Fe-OH <sub>2</sub> <sup>+1/2</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe-OAs(O) <sub>2</sub> (OH) <sub>2</sub> <sup>-3/2</sup>                     | -1                      | -2               | [19] Fe(OH) <sub>2</sub> (OH) <sup>0</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(OH) <sub>2</sub> <sup>0</sup>                                | 1                       | 0                |
| Fe-OH <sup>-1/2</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe-OAs(O)(OH) <sub>2</sub> <sup>-1/2</sup>  | 1                       | 0                | [20] Fe(OH) <sub>2</sub> (OH) <sup>0</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(O)(OH) <sup>-1</sup>   | 0                       | -1               |
| Fe-OH <sup>-1/2</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe-OAs(O) <sub>2</sub> (OH) <sub>2</sub> <sup>-3/2</sup>                                  | 0                       | -1               | [21] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(OH) <sub>2</sub> <sup>0</sup>                                    | 2                       | 1                |
| Fe(OH) <sub>2</sub> <sup>+1</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(OH) <sub>2</sub> <sup>0</sup>               | 0                       | -1               | [22] Fe(OH) <sub>2</sub> <sup>-1</sup> + H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(O)(OH) <sup>-1</sup>   | 1                       | 0                |
| <b>Arsenate, pH 9.2</b>  |                         |                  |  |                         |                  |
| <b>experimental values:</b>  |                         |                  |  |                         |                  |
| at 0.267 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | 0.95                    | -1.30            |  |                         |                  |
| at 0.801 mol <sub>As</sub> kg <sup>-1</sup> of ferrihydrite  | 0.80                    | -1.20            |  |                         |                  |
| Fe-OH <sup>-1/2</sup> + HAsO <sub>4</sub> <sup>2-</sup> → Fe-OAs(O) <sub>2</sub> (OH) <sub>2</sub> <sup>-3/2</sup>   | 1                       | -1               | [28] Fe(OH) <sub>2</sub> <sup>-1</sup> + HAsO <sub>4</sub> <sup>2-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(O)(OH) <sup>-1</sup>  | 2                       | 0                |
| Fe-OH <sup>-1/2</sup> + HAsO <sub>4</sub> <sup>2-</sup> → Fe-OAs(O) <sub>3</sub> <sup>-5/2</sup>   | 0                       | -2               | [29] Fe(OH) <sub>2</sub> <sup>+1</sup> + HAsO <sub>4</sub> <sup>2-</sup> → Fe <sub>2</sub> O <sub>2</sub> As(O) <sub>2</sub> <sup>-2</sup>   | 1                       | -1               |

<sup>a</sup> The symbol "|" as with Fe<sub>2</sub>O<sub>2</sub>(H)<sub>2</sub>AsOH<sup>+1</sup> in eq 5 represents a surface bidentate complex, either an edge sharing bidentate complex or a corner sharing bidentate-bridging complex.

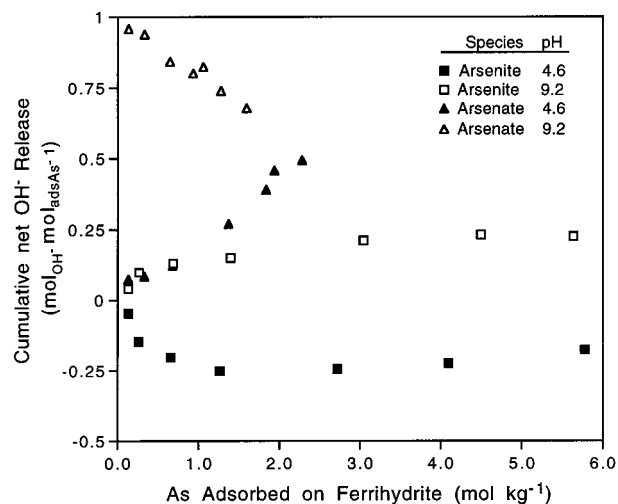


FIGURE 1. Relationship between As adsorbed and net OH<sup>-</sup> release during the reaction of arsenite and arsenate with ferrihydrite at pH 4.6 and 9.2.

pH 4.6, increased from 0.07 to 0.49 mol mol<sub>As</sub> kg<sup>-1</sup> with the increase in As surface coverage from 0.13 to 2.28 mol<sub>ads</sub> As kg<sub>fer</sub><sup>-1</sup>. This phenomenon is attributable to the initial preferred desorption of OH<sub>2</sub> versus OH<sup>-</sup> from the ferrihydrite surface. An opposite trend was observed for the reaction between arsenate and ferrihydrite at pH 9.2, i.e., the net OH<sup>-</sup> release per mole of adsorbed As decreased as the As surface coverage increased. These results also indicate a changing predominant adsorption reaction with the increased surface coverage of adsorbed arsenate.

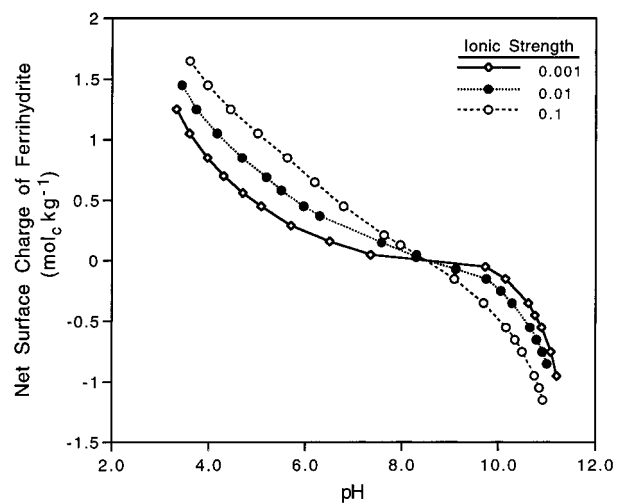


FIGURE 2. Net surface charge of ferrihydrite at three ionic strengths as determined by the ZPC titration procedures.

**Titration Curves and Zero Point of Charge.** The zero point of charge (ZPC) of pure ferrihydrite was approximately 8.5 (Figure 2). Similar values have been previously reported, as reviewed by Stumm (21). The titration curves for ferrihydrite with adsorbed As followed the same general trends as pure ferrihydrite, but had lower ZPC values (Figure 3). Similar results have been observed for other specifically adsorbed anions (23). Adsorption of arsenic resulted in reduction of ZPC by as much as 2.4 pH units for arsenate and slightly less reduction for arsenite (Figure 3). Reduction of ZPC resulting from the adsorption of anionic species is

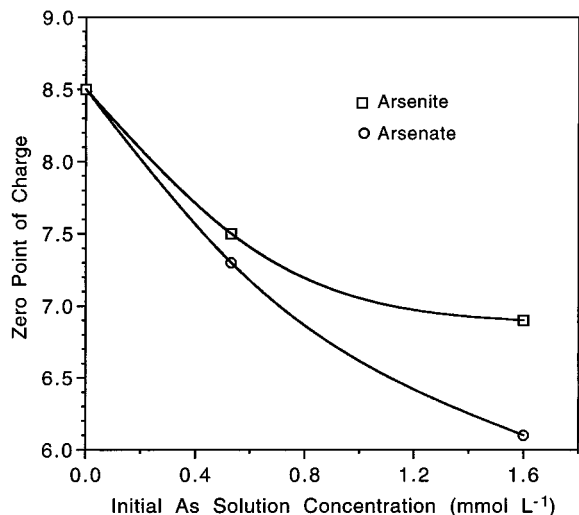


FIGURE 3. Relationship between the initial As solution concentration and the zero point of charge of ferrihydrite.

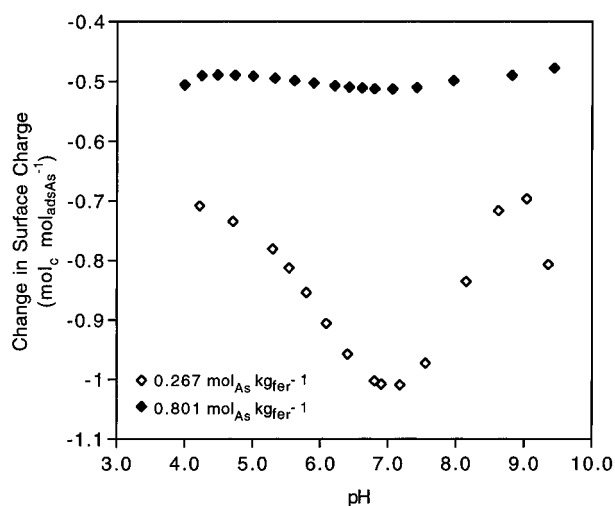


FIGURE 4. Influence of pH on the change in surface charge of ferrihydrite at 0.1 ionic strength during adsorption of arsenite at two initial As solution concentrations.

generally indicative of the formation of inner-sphere complexes rather than outer-sphere complexes (31).

**Influence of Arsenic Adsorption on Surface Charge of Ferrihydrite.** Both arsenite and arsenate adsorption resulted in a reduction in the surface charge of ferrihydrite (Figures 4 and 5), although the charge reduction throughout the pH range of 4–10 was greater with arsenate. This result was predominantly due to the higher negative charge of adsorbed arsenate compared to arsenite species at any given pH. The surface charge reduction per mole of adsorbed arsenite decreased with increasing adsorbed arsenite concentration (Figure 4). A similar result was observed with arsenate at low pH; however, at pH > 8, there was little influence of adsorbed arsenate concentration on surface charge reduction per mole<sub>ads As</sub> (Figure 5).

**Mechanism of Arsenic Adsorption. Arsenite at pH 4.6.** The adsorption of arsenite by ferrihydrite at low pH, e.g., pH 4.6, is partially attributable to reactions that result in a net release of H<sup>+</sup> and a reduction in surface charge, such as monodentate reaction 1 and bidentate reaction 6 (Table 1). These reactions involve FeOH<sub>2</sub> surface sites, which are the predominant A-type sites based on the pK values (Fe–OH<sub>2</sub>, pK = 5.1; Fe–OH, pK = 10.7) for amorphous iron oxide (30), and H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> (pK<sub>1</sub> = 9.2) species in solution at pH 4.6. Reaction

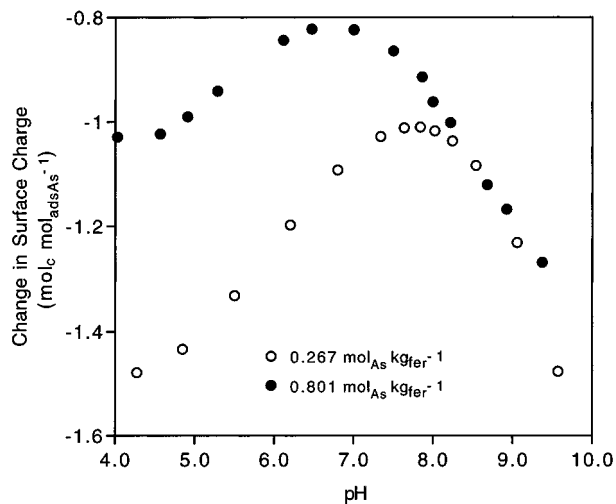


FIGURE 5. Influence of pH on the change in surface charge of ferrihydrite at 0.1 ionic strength during adsorption of arsenate at two initial As solution concentrations.

10, which also results in the net release of H<sup>+</sup> and net reduction in surface charge could also contribute to the overall reaction. The magnitude of the decrease in surface charge and H<sup>+</sup> release per mole<sub>ads As</sub> predicted by these reactions are higher than the experimental values. For example, to achieve an As surface coverage of 0.801 mol<sub>ads As</sub> kg<sub>fer</sub><sup>-1</sup> at pH 4.6 and 0.1 ionic strength, 0.23 mol H<sup>+</sup> (Figure 1) was released on average per mole<sub>ads As</sub> and the surface charge decreased by 0.49 mol<sub>c</sub> mol<sub>ads As</sub><sup>-1</sup> (Figure 4). These results imply that reactions yielding either OH<sup>-</sup> or H<sub>2</sub>O and causing no change in surface charge per mole<sub>ads As</sub> should also occur simultaneously with reactions 1, 6, or 10. Candidate reactions that have these characteristics are monodentate reactions 2 and 3 and bidentate reactions 5, 9, and 13. Monodentate reaction 2 or bidentate reaction 5, which each involve the dominant A-type Fe–OH<sub>2</sub> surface sites, are likely major contributors to the overall reaction. These latter reactions each involve protonation of the surface Fe–O–As complex, as Fe–O(H)–As. The results of this study provide evidence to suggest the presence of surface structures in which the oxygen involved in the Fe–O–As bond remains partially protonated as in reactions 2 and 5. Monodentate reactions 1 and 2 and bidentate reactions 5, 6, and possibly 9 likely contribute significantly to the overall reaction in the monodentate and bidentate scenarios, respectively. Reactions resulting in the net release of OH<sup>-</sup> and an increase in surface charge, such as reactions 4, 8, 11, and 12, or reactions resulting in the release of 2 mol H<sup>+</sup> mol<sub>ads As</sub><sup>-1</sup>, such as reaction 7, are less likely to substantially contribute to the overall reaction. From the results of this study it is not possible to determine the relative likelihood of monodentate vs bidentate bonding, or in the case of bidentate bonding whether the surface complex is predominantly edge sharing (bidentate) or corner sharing (bidentate bridging).

**Artenite at pH 9.2.** At pH 9.2, Fe–OH (pK = 10.7) is expected to be the predominant A-type surface site, and an equimolar mixture of H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> (pK<sub>1</sub> = 9.2) and H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> represent the predominant arsenic species in solution. At pH 9.2 and ionic strength of 0.1, the addition of 0.801 mol<sub>As</sub> kg<sub>fer</sub><sup>-1</sup> resulted in the release of 0.13 mol<sub>OH</sub><sup>-</sup> mol<sub>ads As</sub><sup>-1</sup> (Figure 1) and a surface charge decrease of 0.48 mol<sub>c</sub> mol<sub>ads As</sub><sup>-1</sup> (Figure 4). Likely candidate reactions contributing to this stoichiometry are monodentate reactions 14 and 15 and bidentate reaction 17. Only reaction 16 can be eliminated as contributing substantially to the overall reaction. The trend of the OH<sup>-</sup> release curve (Figure 1) suggests that at very low adsorbed arsenite concentration, monodentate reaction 15



is more likely to contribute significantly to the overall reaction, and at high adsorbed arsenite concentrations, monodentate reaction 14 or bidentate reaction 17 likely play an increasing role in the overall reaction. At the low arsenite level, the larger reduction in surface charge per adsorbed As (Figure 4) also supports the probable role of reaction 15.

**Arsenate at pH 4.6.** At pH 4.6 and 0.1 ionic strength, the adsorption of approximately  $0.801 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$  resulted in the release of  $0.15 \text{ mol}_{\text{OH}^-} \text{ mol}_{\text{ads As}}^{-1}$  and reduced the surface charge of the ferrihydrite by  $1.01 \text{ mol}_c \text{ mol}_{\text{ads As}}^{-1}$  (Figures 1 and 5). Under similar conditions and at an arsenate addition of  $0.267 \text{ mol}_{\text{fer}}^{-1}$ , the drop in surface charge was even higher, i.e.,  $1.40 \text{ mol}_c \text{ mol}_{\text{ads As}}^{-1}$ . This observed decrease in surface charge is consistent with monodentate reactions 18, 19, and 21 and bidentate reactions 22, 23, and 25. The only reactions that can contribute to the observed large change in surface charge at low As surface coverages are reactions 19 and 23. EXAFS studies (14) have shown that arsenate adsorption on ferrihydrite occurs predominantly as a bidentate bridging complex and that the formation of monodentate surface complexes occurs to only a limited extent. These results, although obtained at pH 8, suggest that reactions 22, 23, and 25 should be favored. Reaction 23 is inconsistent with the observed  $\text{OH}^-$  release, especially at high arsenate surface coverage (Figure 1). Therefore, some other reaction that results in the release of  $\text{OH}^-$  must be occurring simultaneously and to an extent that compensates reaction 23. A possible reaction is 24. With an increase in the As surface coverage, the net  $\text{OH}^-$  release increased (Figure 1) and the charge reduction decreased per mole of adsorbed arsenic (Figure 5). These results indicate a changing predominant mechanism of adsorption with increasing surface coverage, e.g., reactions 22, 23, and 25 to reactions 24 and 27. The results also indicate an initial preferential reactivity of surface Fe—OH<sub>2</sub> sites compared to Fe—OH sites.

**Arsenate at pH 9.2.** At pH 9.2 and ionic strength of 0.1, the adsorption of  $0.801 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$ , resulted in the release of  $0.8 \text{ mol}_{\text{OH}^-} \text{ mol}_{\text{ads As}}^{-1}$  and a surface charge reduction of  $1.2 \text{ mol}_c \text{ mol}_{\text{ads As}}^{-1}$ . The only reaction that would result in a surface charge decrease  $> 1 \text{ mol}_c \text{ mol}_{\text{ads As}}^{-1}$  is monodentate reaction 29. Therefore, this reaction likely contributes to the overall reaction. Bidentate reaction 31 and possibly monodentate reaction 28, which result in the release of  $1 \text{ mol}_{\text{OH}^-} \text{ mol}_{\text{ads As}}^{-1}$ , and reduction in surface charge of  $1 \text{ mol}_c \text{ mol}_{\text{ads As}}^{-1}$  are also likely to contribute to the overall reaction. The reduction in net  $\text{OH}^-$  release with increasing surface coverage (Figure 1) indicates a changing predominant reaction with increasing arsenate adsorption and the possible increasing role of monodentate reaction 29 versus monodentate reaction 28 and bidentate reaction 31. The influence of increasing pH on the increase in surface charge reduction per mole of adsorbed As also supports the increasing role of monodentate reaction 29 with increasing pH. This apparent increase in ratio of monodentate/bidentate complexes with increasing pH or increasing surface coverage would result in a net weakening of bond strength between surface structural Fe and adsorbed arsenate. This result indicates that arsenate would be less strongly adsorbed at high pH, which is consistent with arsenate adsorption envelopes (13). The results of this study differ from results of EXAFS studies (14), which have suggested that monodentate complexes are more prevalent at low surface coverage compared to bidentate complexes at high surface coverage. These opposite conclusions from the EXAFS and stoichiometry studies need to be reconciled.

**Comparative Adsorption of Arsenite and Arsenate.** In the presence of adsorbed arsenate, there is a significant increase in surface charge reduction at  $\text{pH} > 7$  (Figure 5), attributable predominantly to change in surface speciation of adsorbed arsenate with increasing pH, e.g., Fe—OAs(O)<sub>2</sub>—

(OH) in reaction 28 to Fe—OAs(O)<sub>3</sub> in reaction 29. The increases in negative charge character of the surface adsorbed arsenate and of the hydroxylated surface probably each contribute to the significant decrease in retention of arsenate by ferrihydrite above pH 7 observed in other studies (13). The arsenite-treated ferrihydrite does not exhibit this substantial increase in surface charge reduction above pH 7 (Figure 4); hence there is a relatively greater retention of arsenite compared to arsenate at  $\text{pH} > 7$ . The results of the current study also indicate that the monodentate bonding mechanism might play an increasing role during arsenate adsorption by ferrihydrite at high pH ( $> 8$ ). EXAFS studies would be helpful to further elucidate arsenate adsorption reactions at  $\text{pH} > 8$ .

The results of the current study have provided evidence for the presence of ferrihydrite-arsenite surface structures at low pH in which the oxygen involved in the Fe—O—As bond remains partially protonated, such as Fe—O(H)As(OH)<sub>2</sub> in reaction 2 and Fe|O<sub>2</sub>(H)<sub>2</sub>AsOH in reaction 5. These surface arsenite species (H<sub>3</sub>AsO<sub>3</sub><sup>0</sup>) are electrically neutral. The uncharged adsorbed arsenite species would likely be less strongly retained than the charged (−1 or −2) arsenate species (H<sub>2</sub>AsO<sub>4</sub><sup>−</sup> or HAsO<sub>4</sub><sup>2−</sup>) by the positively charged hydroxylated surface of ferrihydrite. This conclusion supports previous observations that arsenite is less strongly retained than arsenate at  $\text{pH} < 6$  (13).

## Acknowledgments

This research was financed by grants from ARCO Exploration and Production Technology, and Elf Atochem North America.

## Literature Cited

- (1) Frost, R. R.; Griffin, R. A. *Soil Sci. Soc. Am. J.* **1977**, *41*, 53–57.
- (2) Manning, B. A.; Goldberg, S. *Environ. Sci. Technol.* **1997**, *31*, 2005–2011.
- (3) Anderson, M. A.; Ferguson, J. F.; Gavis, J. J. *Colloid Interface Sci.* **1976**, *54*, 391–399.
- (4) Gupta, S. K.; Chen, K. Y. J. *Water Pollut. Control Fed.* **1978**, *50*, 493–506.
- (5) Ferguson, J. F.; Anderson, M. A. In *Chemistry of water supply, treatment, and distribution*; Rubin, A. J., Ed.; Ann Arbor Science: Ann Arbor, MI, 1974; pp 137–158.
- (6) Pierce, M. L.; Moore, C. B. *Environ. Sci. Technol.* **1980**, *14*, 214–216.
- (7) Pierce, M. L.; Moore, C. B. *Water Res.* **1982**, *16*, 1247–1253.
- (8) Singh, D. B.; Prasad, G.; Rupainwar, D. C.; Singh, V. N. *Water Air Soil Pollut.* **1988**, *42*, 373–386.
- (9) Hsia, T. H.; Lo, S. L.; Lin, C. F. *Chemosphere* **1992**, *25*, 1825–1837.
- (10) Hsia, T. H.; Lo, S. L.; Lin, C. F.; Lee, D. Y. *Colloids Surf. A* **1994**, *85*, 1–7.
- (11) Fuller, C. C.; Davis, J. A.; Waychunas, G. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 2271–2282.
- (12) Wilkie, J. A.; Hering, J. G. *Colloids Surf. A* **1996**, *107*, 97–110.
- (13) Raven, K. P.; Jain, A.; Loeppert, R. H. *Environ. Sci. Technol.* **1998**, *32*, 344–349.
- (14) Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 2251–2269.
- (15) Manceau, A. *Geochim. Cosmochim. Acta* **1995**, *59*, 3647–3653.
- (16) Fendorf, S.; Elck, M. J.; Grossl, P.; Sparks, D. L. *Environ. Sci. Technol.* **1997**, *31*, 315–320.
- (17) Lumsdon, D. G.; Fraser, A. R.; Russel, J. D.; Livesey, N. T. *J. Soil Sci.* **1994**, *35*, 381–386.
- (18) Harrison, J. B.; Berkheiser, V. E. *Clays Clay Miner.* **1982**, *30*, 97–102.
- (19) Manning, B. A.; Fendorf, S. E.; Goldberg, S. *Environ. Sci. Technol.* **1998**, *32*, 2383–2388.
- (20) Sun, X.; Doner, H. E. *Soil Sci.* **1996**, *161*, 865–872.
- (21) Stumm, W. *Chemistry of the solid-water interface*; John Wiley & Sons: New York, 1992.
- (22) Rajan, S. S. S.; Perrott, K. W.; Saunders, W. M. H. *J. Soil Sci.* **1974**, *25*, 438–447.
- (23) Rajan, S. S. S. *Nature* **1975**, *253*, 434–436.
- (24) Rajan, S. S. S. *Soil Sci. Soc. Am. J.* **1978**, *42*, 39–44.
- (25) Ryden, J. C.; McLaughlin, J. R.; Syers, J. K. *J. Soil Sci.* **1977**, *28*, 72–92.

- (26) Zhang, G. Y.; Zhang, X. N.; Yu, T. R. *J. Soil Sci.* **1987**, *38*, 29–38.
- (27) He, L. M.; Zelazny, L. W.; Baligar, V. C.; Ritchey, K. D.; Martens, D. C. *Soil Sci. Soc. Am. J.* **1996**, *60*, 442–452.
- (28) Schwertmann, U.; R. M. Cornell. *Iron oxides in the laboratory, Preparation and characterization*; VCH: Weinheim, Germany, 1991.
- (29) Sadiq, M.; Zaidi, T. H.; Mian, A. A. *Water Air Soil Pollut.* **1983**, *20*, 369–377.
- (30) Davis, J. A.; Leckie, J. O. *J. Colloid Interface Sci.* **1978**, *67*, 90–107.
- (31) Singh, U.; Uehara, G. Electrochemistry of the double layer: Principles and Applications to soils. In *Soil physical chemistry*; Sparks, D. L., Ed.; CRC Press: Boca Raton, FL, 1998; pp 1–56.

*Received for review July 15, 1998. Revised manuscript received January 4, 1999. Accepted January 26, 1999.*

ES980722E