Title

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ABSTRACT

Arsenic toxicity, mobility, and bioavailability in sediment-water systems are highly depended on its oxidation states and chemical species. Arsenite (As(III)) and arsenate (As(V)) are two main species of arsenic in water ecosystem. As(III) is more toxic and mobile than As(V). In this research both wet chemistry and spectroscopic techniques were applied to study the adsorption and redox transformation of As(III) and As(V) on Fe and Mn iron minerals as well as on soil and sediment. The results indicate that the Fe mineral (goethite) can strongly adsorb both As(V) and As(III) while the Mn mineral Birnessite can effectively oxide As(III) to As(V) both in solution phase and on mineral surfaces. Mn and Fe are closely related in chemical properties and often occur together in soils and sediments. The interaction between of arsenite (As(III)) and Mn-substituted goethite was investigated by both solution chemistry and XANES spectroscopy. This study suggests that the adsorption-oxidation system composed of Fe and Mn minerals may be significant in decreasing arsenic toxicity in terrestrial environments.

The adsorption-desorption and incubation-extraction of As(III) and As(V) on soil and sediment samples collected from Tulare Basin, San Joaquin Valley of California were investigated. Research indicates that the adsorption and redox transformation of arsenic oxyanions on different components of soils and sediments are the major processes for controlling the mobility and bioavailability of arsenic in the terrestrial ecosystem. Results from this study provided useful information for understanding these processes and potentially, possible techniques for arsenic contamination control.

Key words: toxic substances and toxicity, sediments, soil chemistry, soil pollution, minerals and mineralogy, oxidation, water pollution.

1. PROBLEM AND RESEARCH OBJECTIVES OF WORK PERFORMED

An important aspect of the environmental biogeochemistry of As is an improved understanding of the processes controlling its reaction at water - mineral or sediment interfaces. Mineral surfaces play a critical role in controlling the concentrations of soluble As in soil solution or pore water. The processes that influence arsenic distribution on the solid phase in sediments are also partially responsible for the control of aquatic arsenic concentrations. Besides the importance of the kind of mineral surface, the adsorption/desorption of As is very sensitive to pH and Eh conditions. Thus, our management of water resources to prevent potential As toxicity problems is highly dependent on our understanding of the mechanisms and processes controlling its solubility.

High concentrations of arsenic are present in the ground waters (as high as 870 μg/l) and sediments in Tulare Basin, San Joaquin Valley of California(Tanji et al., 1994). Arsenic toxicity is a potential problem for wildlife when subsurface drainage waters are impounded in evaporation ponds. It is also a concern to current and future drinking water supplies if downward migration of contaminated shallow ground waters percolates into the deeper regional ground water basin. Studies indicate that the major processes controlling the solubility of arsenic in the ground water are adsorption and transformation(Tanji et al., 1994). Arsenate (As(V)) and arsenite (As(III)) are the main stable species in natural aquatic ecosystems, but the role of mineral surface for controlling the oxidation states is largely unknown.

Arsenite is much more soluble and mobile in soils and sediments (Ferguson et al., 1972, Deuel et al., 1972, Brannon et al, 1987) than the oxidized form. At high Eh values encountered in oxygenated waters (Matthew et al., 1982), arsenic acid species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) are stable. Arsenous acid species (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) are the stable forms in mildly reducing condition. The mobility, toxicity and bioavailability of arsenic have much to do with its oxidation states. Masscheleyn et al. (1991) investigated the effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Their results indicated that redox status and pH influenced both the speciation and solubility of arsenic. The fate of As in the solid phase of soils and sediments is not well known, however. The formation of As compounds and bonding with minerals has been assumed to be analogous to that of P compounds because of their chemical similarity. Livesey et al.(1981) showed that As(V) retention by soils at dilute concentrations did not involve the precipitation. Its retention evidently proceeds through adsorption mechanisms. They found the As maximum adsorption were linearly related to the amount of oxalate-extractable Al and Fe and content of clay. Brannon et al. (1987) obtained the same results from his studies of As in sediments. None of these studies provide much information about the bonding structures of arsenic on surfaces of clay minerals.

Hydroxyl groups in the mineral surfaces are the most abundant and reactive adsorption sites for many oxyanions. Spectroscopic methods provide bonding information useful for understanding solute-surface interactions. All surface reactions such as adsorption involving OH groups will produce a large perturbation in O-H vibrational modes (Jacques and Herman, 1993) which may be observed in IR spectra. We have obtained evidence from FTIR that shows significant difference in surface bonding structures between As(V) and As(III) on goethite. From these spectral bands, we will be able to evaluate the role of adsorption mechanisms in controlling arsenic migration under different environment conditions.

We propose that the transformation of arsenic is highly modified as the result of adsorption to mineral surfaces. This coupled adsorption and transformation process directly influence the amount and rate of arsenic mobilization.

The objectives of this research are:

1) To investigate the bonding structures of As(III) (the more toxic species) and As(V) on some model clay mineral surfaces by spectroscopic techniques.

2) To evaluate the chemical bonding species of arsenic in natural samples collected from contaminated sites in Tulare Basin by spectroscopic and solvent extraction methods and to analyze the mineral compositions of these samples.

3) To investigate transformation/adsorption of arsenite and arsenate and test the distributions of arsenic species in soluble and adsorbed phases in aged model minerals and incubate natural samples in different pH and Eh environments. These results may provide direction for possible remediation methods of arsenic contamination.

2. REVIEW OF METHODOLOGY USED

2.1. Adsorption and oxidation of arsenite (As(III)) on goethite

2.1.1. Preparation and properties of mineral samples. The synthesis and properties of the goethite used in this study are described elsewhere (Sun and Doner 1996). Briefly, goethite was prepared by mixing $FeCl_3$ and NaOH solutions according to the method described by Atkinson et al. (1968) and Igbene (1985). The sample was oven dried at

60^{o} C for 24 hrs, ground with a mortar and pestle, and passed through a 106 μm sieve. It was verified as goethite by x-ray diffraction and found to have a surface area of 80.2 ± 3.8 m^2/g as determined by the EGME technique (Heilman et al. 1965).

The birnessite sample was synthesized according to the method described by McKenzie (1971) and Traina and Doner (1985). Briefly, 16.5 ml of concentrated HCl were added dropwise to a 500 ml boiling solution of 0.4 M $KMnO_4$. After boiling for one h, the brown precipitate was filtered and washed. The suspension was centrifuged and washed again. This procedure was repeated until the electrical conductivity of the suspension was less than 0.001 dS m^{-1} which was then stored as a suspension.

<u>2.1.2. FTIR studies of As(V) and As(III) mixtures adsorbed on goethite</u> Solutions containing mixture of As(III) and As(V) were added to goethite suspensions for FTIR spectral analysis as follows: Thirty mg of prepared goethite was added to 200 μl arsenate (Na_2HAsO_4) and arsenite ($NaAsO_2$) solutions of various concentrations at pH 5.5 to give the total adsorption densities of 150 μmol As/g goethite. Preliminary adsorption isotherm experiments showed maxima to be 210 and 190 μmol As/g goethite for As(V) and As(III), respectively, at pH 5.5. This was estimated by fitting the Langmuir equation to the data and extrapolation to an adsorption maximum. Thus, all treatments were undersaturated with respect to the adsorption maximum. After equilibrating for one h, films of both untreated and treated goethite were prepared by evaporating a suspension on the surface of AgCl pellet (Sun and Doner 1996) and placing the sample into a cell with KBr windows. The goethite sample was deuterated by evacuating the cell to 0.002 torr, and

exposing it to D_2O. IR spectra were collected in a Matson Galaxy 3000 FTIR Spectrometer. Samples and background were collected on 64 scans at a resolution of 2 cm^{-1} in absorbance-FTIR mode.

Suspensions for adsorption studies of arsenic on goethite were prepared by dispersing 50 mg goethite in 10 ml 0.01 M NaCl solutions. 125 µl of 100 µmol/ml As(V) (Na_2HAsO_4) or As(III) ($NaAsO_2$) was added to goethite suspensions. The pH was adjusted to a range of values between 2 and 10 by addition of 0.1 M NaOH or HCl with constant shaking at room temperature (25 ± 2^oC) for two h. The samples were centrifuged (10,000 x g) for 10 min in a Sorvall RC2-B Centrifuge and filtered through No. 1 Whatman filter paper. Aliquots of the supernatant were taken and As(III) and As(III) + As(V) concentrations were determined by a Perkin-Elmer 2280 atomic absorption spectrophotometer equipped with a Varian VGA-76 hydride generator (Glaubig and Goldberg 1988).

2.1.3. Reaction of As(III) with goethite in suspension and air dry conditions The stability of As(III) against oxidation in goethite suspensions was studied as a function of time and suspension pH. Samples were prepared by adding 1.5 ml of 100 µmol/ml As(III) ($NaAsO_2$) solutions to goethite suspensions (1 g solid to 150 ml of 0.01 M NaCl solution), producing 150 µmol As(III)/g goethite. The pH was controlled at either 5.0 or 8.0 by HCl and NaOH additions and constantly stirred with a magnetic stirrer. Suspension samples were collected at different times up to 100 h. After each collection the suspension was centrifuged and the supernatant was analyzed for As(III) and As(III) + As(V) as described above. About 30 mg of the goethite slurry were collected from the centrifuge tubes for FTIR spectral analysis as described above.

As(III) treated goethite was air dried to evaluate its redox stability under more arid condition. This was done by treating goethite suspensions at the rate of 150 µmol As(III)/g solid at pH 7.0 as described above. After 2 hrs of reaction time, the suspension was centrifuged and about 30 mg of goethite slurry was collected and evaporated on an AgCl pellet (20mm in diameter by 2mm thick). The pellet was placed into a cell with KBr windows and left exposed to the air for different periods of time up to 20 days. Following exposure to air, the cell was evacuated to 0.002 torr, the sample was treated with D_2O vapor and IR spectra were collected.

2.1.4. As(III) treated goethite-birnessite suspensions. Goethite suspensions prepared as described above (1 g solid to 150 ml of 0.01 M NaCl solution) were used to investigate the role of birnessite in As(III) oxidation. One and half ml of 100 µmol/ml (150 µmol) As(III) ($NaAsO_2$) solutions were added to goethite suspensions. The pH was controlled at either 5.0 or 8.0 by HCl and NaOH additions and constantly stirred with a magnet stirrer. After a reaction of 1 h, 1.0 ml of 52 mg/ml birnessite (about 600 µmol δ-MnO_2) was added to the As(III)-goethite suspension with continuous stirring. This resulted in a suspension containing 52 mg birnessite/g goethite. Suspension samples were collected at different time intervals, centrifuged, the supernatant was collected, and As(III) and As(III) + As(V) were determined as described above. Thirty mg slurry samples were collected for FTIR spectral analysis.

2.1.5. XANES study. For sample preparation for the XANES study, all pre-treatments were the same as in the FTIR study. Instead of placing goethite paste on a AgCl pellet as described above, 50 mg goethite paste or air dried samples were mounted in the milled slots of Teflon sample cells and sealed with thin Kapton polymide film to prevent moisture loss during the x-ray absorption scans.

The XANES spectra of As were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) Beam Line 4-3 equipped with a wiggler. The monochromator used Si(220) crystals and was detuned about 50%. Arsenic XANES spectra were collected from 11,650 to 11,950 ev by using Lytle-type fluorescence detector with a Ge-filter. Energy was calibrated from the XANES spectrum of elemental As measured under the same experimental conditions during each experimental run. The half-height edge energy of As(0) was taken to be 11.867 keV. All spectral data are presented without additional smoothing.

2.2 Adsorption and redox transformation of As(III) and As(V) on Mn-substituted goethite.

2.2.1 Preparation and characteristics of Mn-substituted goethite. Mn-substituted goethite was synthesized according to the method described by Schwertmann and Cornell (1991) using analytical grade regents except those mentioned specificly: 175 mL of 2.0 M NaOH was added to 50 mL of a mixed solution of $Fe(NO_3)_3.9H_2O$ and $Mn(NO_3)_2.4H_2O$ having a total Fe + Mn concentration of 0.53 M and Mn/(Mn + Fe) ratios to 0.00, 0.01, 0.05, and 0.10. The products were centrifuged, washed and stored in polyethylene bottles in 250 mL 0.3 M NaOH solution at 60°C for 15 days. The samples were washed and centrifuged again several times with deionized water, placed in molecular porous membrane tubing (VWR Scientific, Catalog No. 25225-281) and dialyzed in deionized water until the electric conductivity of the dialysis water equalled that of deionized water. The samples were oven dried at 60° C, then ground with a mortar and pestle and passed through a 37 μm sieve. All the solid products showed x-ray diffraction patterns identical to pure goethite. The total Mn in Mn-substituted goethite was determined by dissolving the solid products in 6.0 M HCl at 70°C and analyzed by inductively coupled plasma spectroscopy (ICP). The NaCl and $CuCl_2$ extractable Mn from Mn-substituted goethite were determined by addition of 10 ml 0.01 M NaCl or 0.05 M $CuCl_2$ solution to 50 ml centrifuge tubes which contained 0.10 g solid samples. The tubes were shaken for one hr., centrifuged and filtered. The Mn in the supernatant was determined by ICP. Some properties of the products are listed in Table1.

Table 1 Some properties of prepared goethite and Mn-goethite samples

	Pure goethite	1% Mn goethite	5% Mn goethite	10% Mn goethite
Surface area* (m^2/g)	90.8±1.2	83.3±2.0	81.5±3.8	94.5±2.6
pH_{PZNPC}**	8.31±0.03	5.97±0.03	5.74±0.02	5.65±0.15
Total Mn(%, Mn/(Mn+Fe))	0.00	1.10	5.39	10.9
0.01 M NaCl soluble Mn (% of total Mn)	0.00	0.00	0.01	0.02
0.05 M $CuCl_2$ extractable Mn*** (% of total Mn)	0.00	2.30	1.20	1.80
Color****	2.5y 7/8	2.5y 5/8	5y 4/3	5y 3/2

*: EGME method (Heilman et al. 1965) **: Acid-base titration (Sposito 1981)

***: Adapted from Traina and Doner (1985).

****: Munsell color system.

2.2.2. XANES study. The Mn oxidation state in Mn-substituted goethite was examined by using the sample with lowest Mn concentration (1% Mn) in order to minimize self-absorption effects (Schulze et al. 1995). Mn(II) and Mn(VI) standards were prepared by mixing $MnSO_4$ (analytical agent) and MnO_2 (99.5% MnO_2, Matheson Coleman & Bell) with boron nitride powder to give solid mixtures which contained the same amount of Mn as 1% Mn-substituted goethite. The powder samples were mounted in a 2x8x25 mm milled slot cut in a Teflon sheet, and sealed with thin Mylar polymide film to minimize X-ray adsorption.

Mixtures of As(III) and As(V) adsorbed on pure goethite were prepared for XANES analysis by adding 300 µl solution of various concentrations of arsenate (Na_2HAsO_4) and arsenite ($NaAsO_2$) at pH 6.5 to 50 mg of pure goethite to give a total adsorption density of 150 µmol As/g goethite. After two hrs., the paste samples were mounted in the milled Teflon slots as described above. The sample cells were sealed with thin Mylar polymide film to prevent moisture loss while minimizing X-ray absorption during scans. Preliminary adsorption isotherm experiments showed that the adsorption maxima of the various Mn-substituted goethite minerals for As(V) and As(III) were all above 180 µmol As/g goethite at pH 6.5. This was estimated by fitting the Langmuir equation to the data and extrapolation to an adsorption maximum. Thus, all treatments were undersaturated with respect to the adsorption maximum.

Mn-goethite suspensions for kinetic study were prepared as follow: 0.05 g of Mn-substituted goethite was added to 5.0 ml 0.01 M NaCl solution, followed by the addition of 0.1 ml 75 µmol/ml As(III) producing 150 µmol As(III)/g solid. The pH was adjusted to 6.5 with 0.1 M HCl. Samples were then mixed continuously up to 10 days in capped centrifuge tubes on a shaker. Following the different aging periods, the mixtures were centrifuged and sediment-pastes were collected. The paste samples for XANES study were prepared at different time intervals ranging from 2 hrs. to 5 days before scanning.

To examine the effects of dry conditions on As(III) stability, samples were prepared as follows: 0.1 ml of 75 μmol/ml As(III) was added to 1.0 ml of a 5% (w/w) Mn-goethite suspension in a 0.01 M NaCl solution producing 150 μmol As(III)/g solid. The pH was adjusted to 6.5 with 0.1 M HCl, mixed and aged in air dry condition up to 10 days. The air dried samples for XANES study were prepared by using same procedures as above.

The pH and temperature effects on As(III) oxidation by Mn-goethite were studied by adding 0.05 g of Mn-substituted goethite to 5.0 ml 0.01 M NaCl solution. To this suspension 0.1 ml 75 μmol/ml As(III) was added producing 150 μmol As(III)/g solid. The pH was adjusted to 5.0, 6.5, and 8.0 with 0.1 M HCl or NaOH. Samples were then mixed continuously up to 10 days in capped centrifuge tubes on a shaker. The treatments at pH 6.5 were aged in 25°C, 45°C, and 65°C up to 10 hrs. in capped centrifuge tubes. Following the different aging periods, the mixtures were centrifuged. Sediment-paste samples were collected for XANES study. Replicates of the above treatments were used to determine extractable Mn(II) produced from the reaction with As(III). The samples were centrifuged and the supernatant was taken for analysis. Then 10.00 ml 0.05 M $CuCl_2$ was added the mineral residue, shaken for one hr. and centrifuged again. The supernatant was combined with the original supernatant and all Mn(II) released to the solution phase was determined by ICP.

The XANES spectra of both As and Mn were collected at the Stanford Synchrotron Radiation Laboratory as described above. The Mn XANES spectra were collected from 6.000 keV to 7.000 keV by using Mn (0) to calibrate energy (half-height edge energy of Mn metal was taken as 6.539 keV). The Lytle-type fluorescence detector was used to collect spectral data. All data are presented without additional smoothing.

2.3 The adsorption and redox transformation of As(III) and As(V) in Soil and Sediment

2.3.1. Soil Collection and Analyses. The soil and sediment samples for the study were collected from Tulare Lake Basin of the southern San Joaquin Valley, California (N35°52'31", W119 ° 38'32"). Ten experimental field plots using constructed, flow-through wetland cells were built to decrease potential Se toxicity in agricultural drainage water via bioremediation. The soil type in these area is a Westcamp loam (fine-silty, mixed (Calcareous), thermic Aeric Fluvaquents). A composite soil sample was collected from a constructed cell (Cell no. 8) before the application of drainage water and flooding. Because of the construction operation the soil was highly disturbed. The sediment sample was collected from an adjacent cell (Cell no. 10) after flooding for 6 months. Both soil and sediment were collected from 0-20 cm. The soil sample was air dried while the sediment sample was freeze dried. Both samples ground with a mortar and pestle, mixed thoroughly, passed through a 1mm sieve to insure uniformity before use in the incubation study. Selected properties of the soil and sediment samples are listed in Table 2. All analyses are reported on an oven-dry basis at 105°C. The elemental analysis was done by

HNO_3-H_2SO_4 digestion used for As determination and then analyzed by ICP (Huang and Fujii, 1996).

Table 2 Selected chemical properties of the soil and sediment samples.

Elemental analyses are from acid digestion except for carbon.

	Soil	Sediment
Al (g kg^{-1})	20.9	20.0
As (mg kg^{-1})	5.00	5.62
Ca (g kg^{-1})	10.3	11.9
Fe (g kg^{-1})	12.1	12.2
Mn (mg kg^{-1})	254	218
Org. C (g kg^{-1})*	44.7	57.2
pH	7.89	8.45

*: Nelson and Sommers 1996.

2.3.2.Arsenic Treatment Two grams of < 1mm sieved soil or sediment were weighed into 50-ml polypropylene centrifuge tubes and 1.9 ml deionized water was added. To soil and sediment 0.1 ml of 100 µmol/ml As(V) (Na_2HAsO_4) or As(III) ($NaAsO_2$) was added suspensions to achieve a final concentration of 5.0 mmol As/g soil or sediment. Two ml of deionized water was added to 2.0 g soil and sediment samples, which were used as background comparison. All centrifuge tubes containing samples and water were weighed. The pH was then adjusted to 7.5 by addition of 0.1 M NaOH or HCl with constant shaking for 2 h. After that, all samples were incubated at atmospheric conditions up to 10 days at room temperature. Each treatment had 7 replicates. Five of them were used for XANES analysis and 2 for chemical sequential extraction determinations. Deionized water was added daily to original weight to maintain at a constant water content.

2.3.3 Soil and Sediment pH and Redox Status Determination. Soil and sediment suspension pH and redox potentials were determined before the chemical extraction. A Fisher pH electrode, a Accumet platinum combination electrode, and a Accumet 15 pH meter (Fisher Scientific, Haven, CT) were used to determine pH and Eh (converted to the standard hydrogen electrode, SHE) of soil and sediment suspensions with 1:1 ration of solid to water.

2.3.4 Sequential Extraction Before extraction, each sample was weighed again and deionized water was added to give a total water content of 25 ml. All tubes were shaken for 1 h, centrifuged (5,000 x g) for ten min. in a Sorvall RC2-B Centrifuge, and filtered through No. 1 Whatman filter paper. Aliquots of filtered samples were taken and As(III) and As(V) concentrations were determined. The amount of arsenic adsorbed was calculated by difference between the added and the amount left in the equilibrium solution. The water washed samples were extracted by the following sequence (Onken and Adriano 1997): 1.0 M NH_4Cl; 0.5 M NH_4F; 0.1 M NaOH; and 0.5 M H_2SO_4. Each tube was treated with 25 ml solution and shaken for one hr. Supernatants were collected and total extracted As was determined by ICP. The residual As was obtained by subtracting total extractable As from total As in soil and sediment.

2.3.5 XANES Study The paste samples of soil and sediment after each extraction were collected and mounted in a 2x8x25 mm milled slot cut in a Teflon sheet, and sealed with thin Mylar polymide film to prevent moisture loss while minimizing X-ray adsorption. The XANES spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) and the testing condition as same as described above.

3. DISCUSSION OF RESULTS AND THEIR SIGNIFICANCE

3.1. Reaction of As(III) and As(V) on goethite and birnessite surface.

Fig. 1 shows the IR spectra of surface deuterated goethite treated with 150 μmol/g arsenic at different As(V)/As(III) ratios. Goethite treated with 150 μmol/g As(III) has a band at 2701 cm^{-1}. Based on previous assignment (Sun and Doner 1996), this is the absorbance band of deuterated triply coordinated (B-type) hydroxyls. As seen in previously, an adsorption band at 2686 cm^{-1} band observed for the As(V) treated goethite. As the As(V)/As(III) ratio increased, the intensity of 2686 cm^{-1} band increased while 2701 cm^{-1} band decreased. These differences were used to indirectly identify the redox transformation from As(III) to As(V) on goethite surfaces semi-quantitatively. However, since the samples have been dried before collecting IR spectra, the results from this method may not reflect the reactions in a wet system. And also because As(V) on goethite produced from As(III) oxidation may not have the same surface structure as As(V) directly adsorbed from solution, XANES spectral data will be presented below to verify the IR data.

Table 3 shows the results of goethite suspensions treated with As(III) at pH 5 and pH 8. The initial adsorption of As(III) on goethite was very fast, more than 90% of the maximum was adsorbed within 1h. After 100 hrs, a small amount of As(V) may have been present in the pH 5.0 treatment solution while none was detected in the pH 8.0 treatment. According to the thermodynamic calculation, the oxidation of As(III) by Fe(III) should be favorable at low pH values (Oscarson et al, 1980). From colorimetry and x-ray photoelectron spectroscopy studies, Oscarson et al (1981a) found no evidence

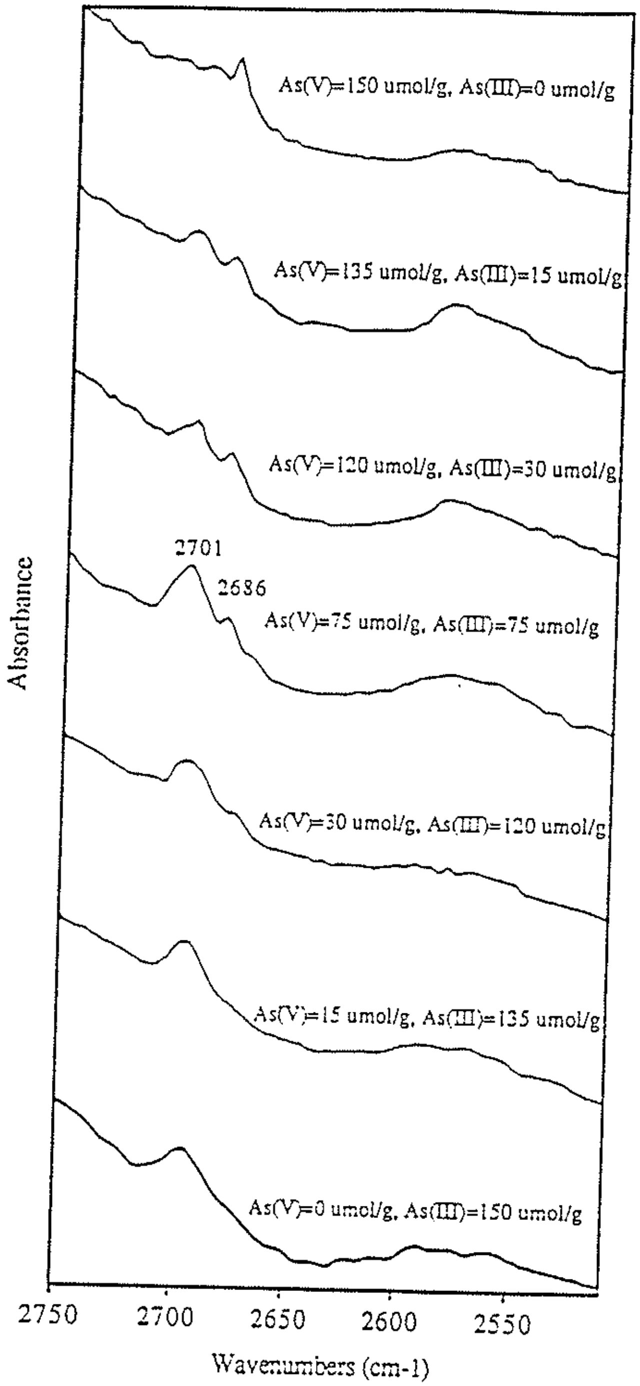

Fig. 1 FTIR absorbance spectra of surface deuterated goethite treated with As(III) and As(V) at As(III)+As(V) = 150 μmol/g.

Table 3 Concentration changes of As(III) and changes in ratio of As(III) to total As(As(III)+As(V)) in solutions after different reaction times in goethite suspensions at two different pH values*.

t (hrs.)	pH= 5.0		pH= 8.0	
	As(III) (mM)	$\frac{\mathrm{As(III)}}{\mathrm{(As(III)+(As(V))}}$	As(III) (mM)	$\frac{\mathrm{As(III)}}{\mathrm{(As(III)+(As(V))}}$
0	1.25±0.06	1.00±0.05	1.25±0.06	1.00±0.05
1.0	0.67±0.03	1.00±0.05	0.31±0.02	1.03±0.06
5.0	0.66±0.03	1.01±0.05	0.29±0.02	0.97±0.05
10.0	0.64±0.03	0.99±0.04	0.28±0.01	1.00±0.05
50.0	0.61±0.03	0.96±0.04	0.29±0.01	1.03±0.05
100.0	0.59±0.02	0.95±0.04	0.28±0.01	1.00±0.05

*: The adsorption suspensions were prepared by dispersing 50 mg goethite in 10 ml 0.01 M NaCl solutions.

that redox reaction occurred between Fe(III) and As(III) after 72 hrs at pH 6.9. In our studies at pH 5.0, after 100 h. a small peak appeared at 2686 cm^{-1} in the IR spectrum of As(III) treated goethite (Fig. 2a). By comparing this to Fig. 1, we estimate 10-20% of As adsorbed on goethite was in the As(V) oxidation state. This was a higher amount than was detected in the solution phase (Table 3). At pH 8, no detectable As(V) was observed by IR (Fig. 2b). Fig. 3 shows the XANE spectra of As on goethite. As(III) has an edge peak at 11.873 keV while As(V) has an edge peak peak at 11.876 keV. For the same treatment of paste sample at pH 5, a small shoulder was apparent at 11.876 keV after 5 days (120 ± 8 h), which indicates the existance of a small amount As(V). It is possible a

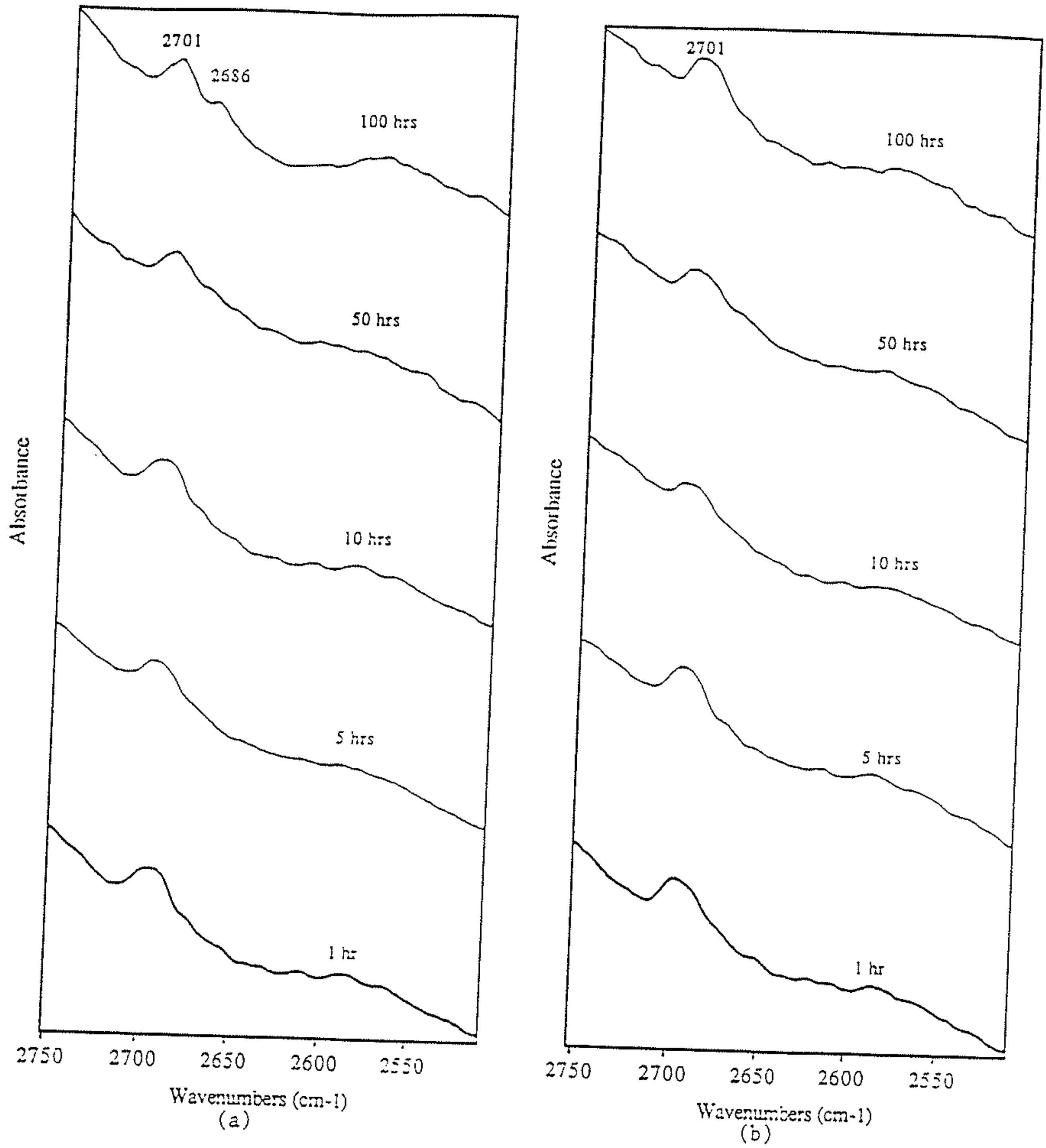

Fig. 2 FTIR absorbance spectra of surface deuterated goethite treated with As(III) at 150 μmol/g. (a) pH=5.0 (b) pH=8.0

small amount of As(III) existed on the goethite after 72 ± 8 h but the shoulder is much more weaker and questionable. The results from XANES spectra support our interpretation of the FTIR results.

Fig. 4 shows that the adsorption envelopes of As(III) and As(V) on goethite as a function of pH are quite different. These results are compatible with the previous studies (Ferguson and Anderson 1974; Pierce and Moore 1980, 1982). H_3AsO_3 is the predominate species of arsenite at low pH since it is a very weak acid (pK_{a1}= 9.3). The adsorption of this undissociated acid is much less than $H_2AsO_4^-$, the main species of arsenate in neutral pH environments. From the adsorption results we can see that at low pH, any As(V) oxyanions produced from the oxidation of As(III) in solution can be selectively adsorbed by goethite and enriched in the solid phase. It may be very misleading if we only use As(V)/As(III) ratio in solution to evaluate the oxidation of As(III) in goethite suspensions. Thermodynamically, the oxidation of As(III) on goethite would not be expected to occur at a high pH (Scott 1991), which is consistent with our results.

Fig. 5 shows that the adsorbed As(III) on goethite in air dry condition was not stable. After 10 days a small band at 2686 cm^{-1} became apparent suggesting As(V) formation. More than 20% of the adsorbed As(III) on goethite was oxidized to As(V) after 20 days as estimated from the band at 2686 cm^{-1}. XANES spectra of As(III) treated goethite (Fig. 6) under similar conditions as used for the FTIR (Fig. 5) also showed arsenic oxidation. The appearance of a shoulder at 11.876 keV became more apparent after 10 days. This provides additional, direct evidence supporting our interpretation of the FTIR spectra. Because the sample was aged in the air, we can not say if the oxidant is

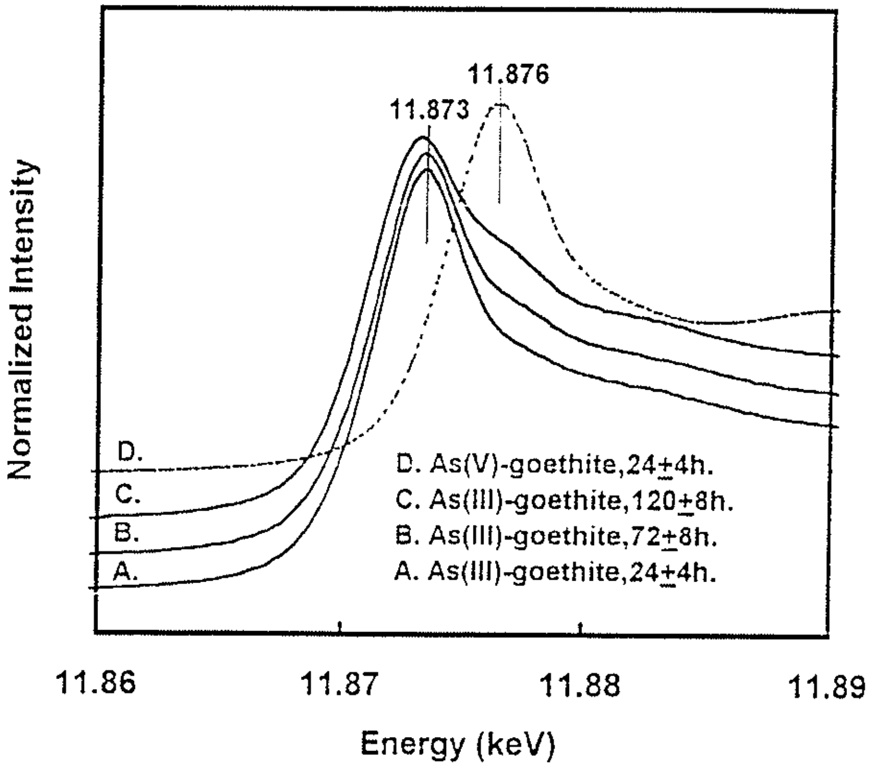

Fig. 3 Normalized XANES spectra of As 150 (μmol/g) on goethite at different time intervals pH=5.0.

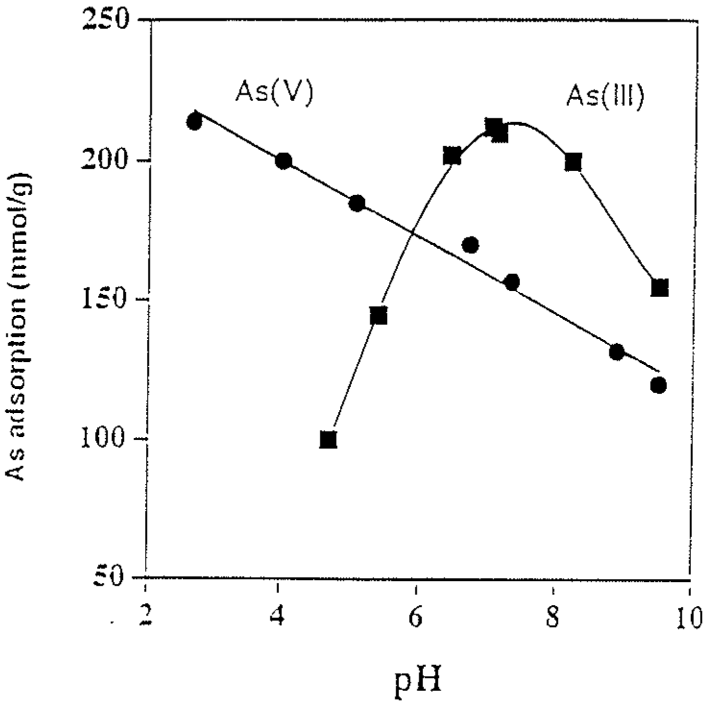

Fig. 4 Adsorption of As(III) and As(V) on goethite at various pH values.

As(III)T = As(V)T = 1.25 mM, goethite = 5.0 mg/ml, in 0.01 M NaCl.

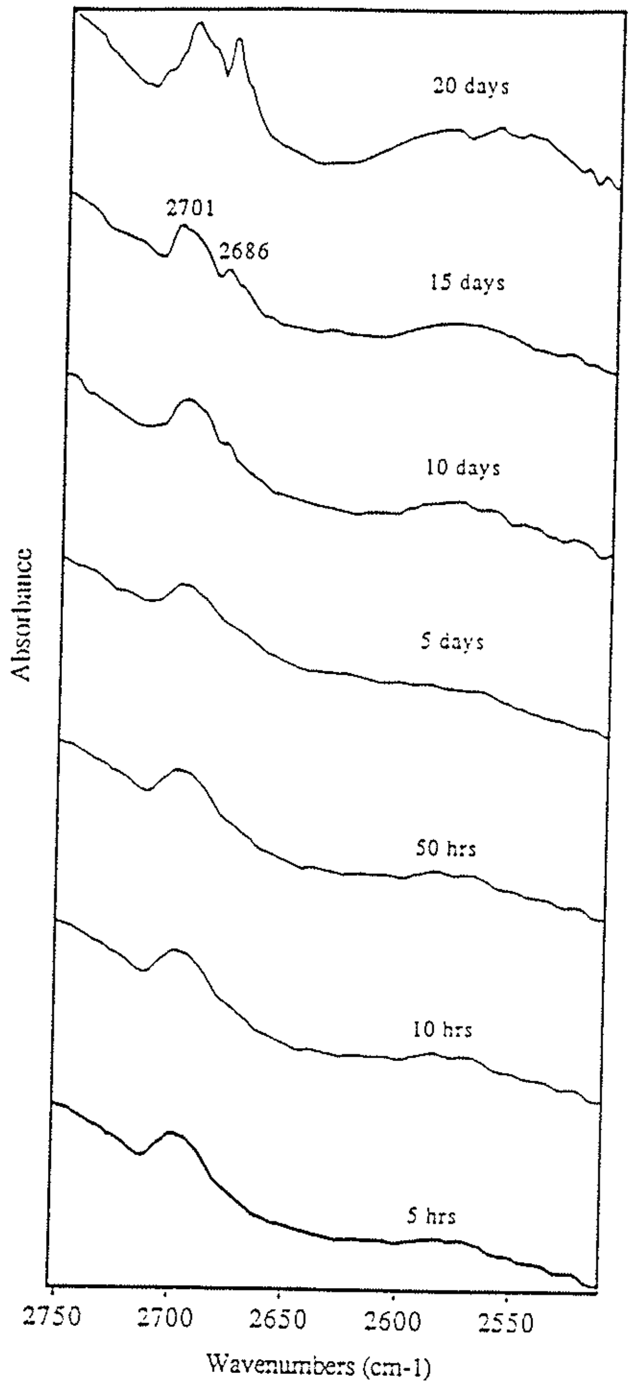

Fig. 5 FTIR absorbance spectra of surface deuterated goethite treated with As(III) (150 μmol/g) and mantained in air dry conditions at different time intervals. Initial pH=7.0.

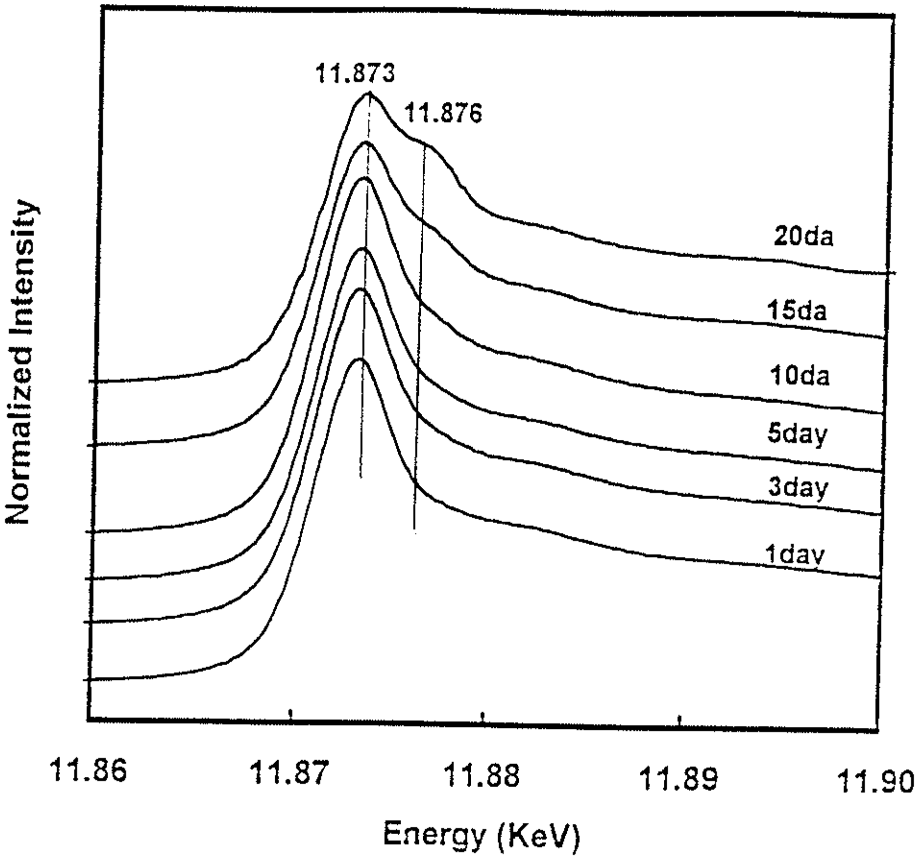

Fig. 6 Normalized XANES spectra of As(III) (150 μmol/g) aged on goethite in air dry conditions at different time intervals. Initial pH=7.0.

Fe(III), oxygen in the air, or a microbial process. As(III) in distilled demineralized water exposed to air is very stable. No oxidation of As(III) was observed after 37 days (Tallman and Shaikh, 1980). Eary and Schramke (1990) reported a half-life of one year for As(III) oxidation in distilled water by atmospheric oxygen. The spectroscopic evidence here indicates that the goethite surface plays an important role in oxidation either as a catalyst or a direct oxidant.

Birnessite is one of the most common Mn oxides in terrestrial and aquatic environments (Moore et al., 1990). The depletion (oxidation and adsorption) of As(III) in the synthetic birnessite suspension is rapid with a time scale of minutes (Scott and Morgan, 1995). Table 2 showed that the addition of 5% birnessite (w/w of goethite) to the As(III)-goethite system completely depleted As(III) in solutions within 50 min at both pH 5.0 and pH 8.0. IR spectra of solid phases shows that most As(III) adsorbed on the goethite surface was As(V) after 10 min reaction time and 1h deuteration period (Fig. 7). The XANES spectra (Fig. 8) collected from the paste samples shows the same results. It should be pointed out that our synthetic birnessite may be more reactive than the natural form. Scott and Morgan (1995) described the mechanism of As(III) oxidation by birnessite as a surface reaction with three steps: (1) As(III) adsorption, (2) oxidation of As(III) to As(V), and (3) desorption of As(V). Table 4 also shows that the pH influence on the reaction between aqueous As(III) and birnessite is slight as indicated by the ratio of As(III)/(As(III)+As(V)). Unlike iron oxides, manganese oxides are capable of As(III) oxidation over a wide pH range in natural waters (Scott and Morgan 1995). In general, the adsorption and redox transformation of arsenic at the water-goethite interface could

Table 4 Concentration changes of As(III) and changes in ratio of As(III) to total As(As(III)+As(V)) in solutions after different reaction times in goethite suspensions with the addition of birnessite at two different pH values*.

	pH= 5.0		pH= 8.0	
t (min.)**	As(III) (mM)	$\frac{As(III)}{(As(III)+As(V))}$	As(III) (mM)	$\frac{As(III)}{(As(III)+As(V))}$
0	0.67±0.03	1.00±0.05	0.31±0.02	1.00±0.06
10	0.13±0.01	0.20±0.01	0.32±0.02	0.53±0.03
20	0.09±0.01	0.13±0.01	0.31±0.02	0.33±0.02
30	0.07±0.01	0.11±0.01	0.30±0.01	0.17±0.01
40	0.04±0.01	0.06±0.01	0.31±0.01	0.12±0.01
50	0.02±0.01	0.03±0.01	0.30±0.01	0.06±0.01
100	0.02±0.01	0.03±0.01	0.31±0.01	0.06±0.01

* The initial As(III) = 1.25 mM, adsorbed on goethite suspensions (by dispersing 50 mg goethite in 10 ml 0.01 M NaCl solutions.) for one hr.

** After the addition of birnessite.

include the following four processes (Fig. 9): (1) the adsorption and desorption of As(III) by goethite, (2) the redox transformation between As(III) and As(V) in the solution, (3) the adsorption and desorption of As(V) by goethite, and (4) the redox transformation between As(III) and As(V) on goethite. The addition of birnessite perturbs the ratio equilibrium of As(III) to As(V) in solution. As a result, more As(III) will be desorbed from the goethite surface, oxidized by birnessite in the solution and then readsorbed as As(V). Finally, nearly all of the adsorbed As(III) will be replaced by As(V). However, in this study, the transformation rate of the adsorbed As(III) on goethite was too fast to be

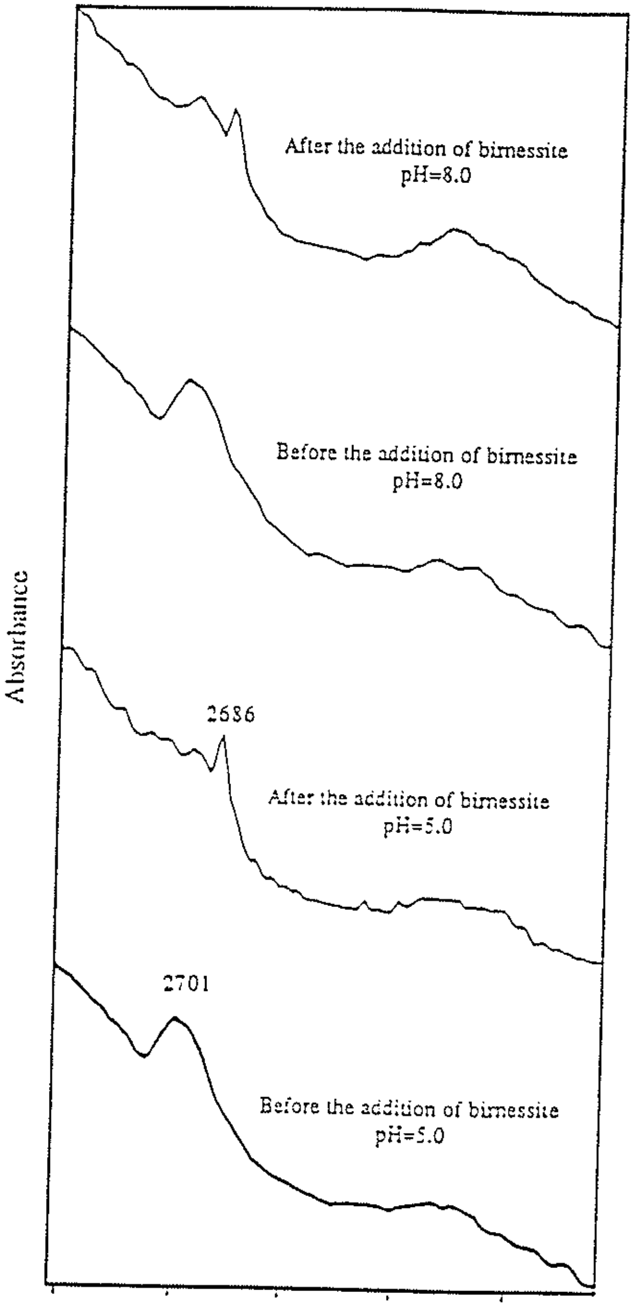

Fig. 7 FTIR absorbance spectra of surface deuterated goethite treated with 150 µmol/g As(III) for 1h, before and after the addition of birnesstie.

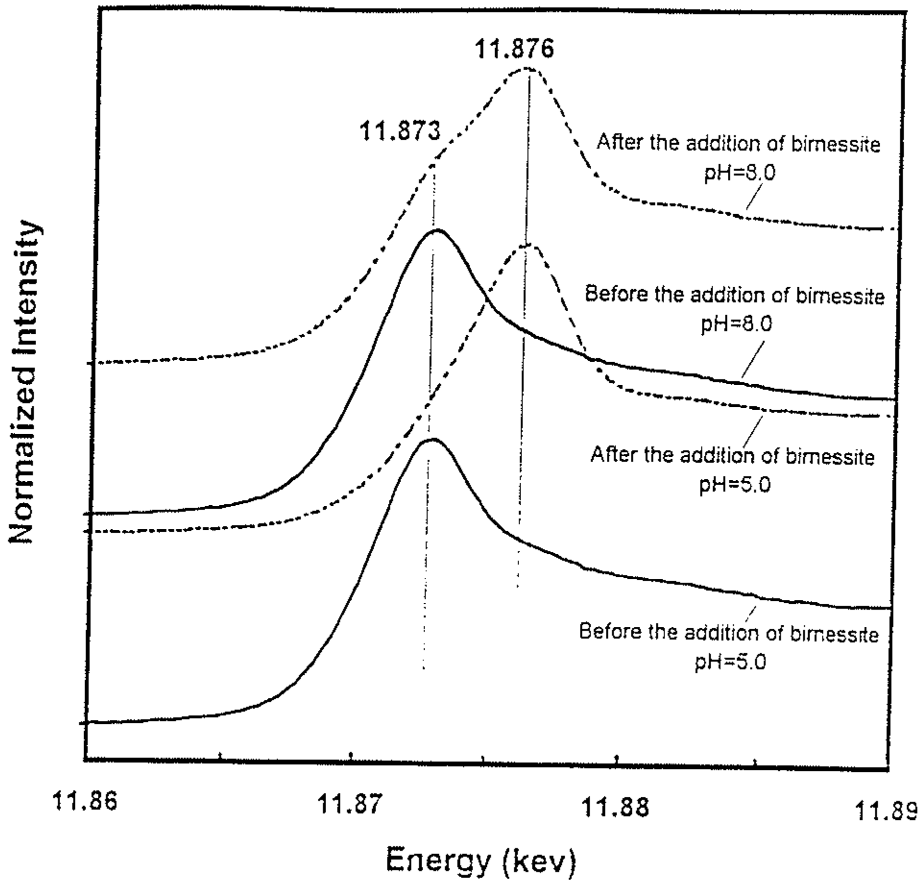

Fig. 8 Normalized XANES spectra of As(III) aged on goethite in suspensions for 1 h followed by birnessite addition and aging another 1 h.

only attributed to the oxidation in the solution phase.

Our previous study (Sun and Doner 1996) indicated that both As(III) and As(V) formed binuclear adsorption complexes on goethite surfaces restricting the rate of desorption. There are several other possible reactions to explain this result: (1) Sung and Morgan (1981) reported that the γ-FeOOH surface could act as a catalyst in the oxidation of Mn(II) by oxygen. The Mn(II) produced from redox reactions in the solution with birnessite may be adsorbed on goethite, then oxidized by oxygen to Mn(III) or Mn(IV). The newly formed Mn(III)/(IV) on the goethite surface could oxidize adsorbed As(III) directly. (2) Natural manganese oxides are present in both the colloidal and non-colloidal particle-size fractions (Oscarson et al., 1981b). The colloidal fraction of synthetic birnessite may be active enough to oxidize the adsorbed As(III) on the goethite surface. (3) Some other surface reactions could occur during the one hour evacuation and deuteration process.

Fujii and Swain (1995) suggested that iron and manganese oxyhydroxides may be an important factor in controlling the concentration of As in shallow ground waters by occluding As(V) in a mineral precipitate. Our results indicate that the combined effect of goethite (an iron oxyhydroxide) and birnessite (a manganese oxide) results in a rapid oxidation of As(III) and adsorption of As(V). This coupled reaction may effectively reduce the concentration of As in soil solutions and ground waters as long as manganese oxides, hydroxides or oxyhydroxides are present. The following reactions illustrate that the oxidation of As(III) to As(V) by oxygen is favored by high pH values while low pH values favor for the oxidation of As(III) by Fe and Mn oxides in the solution:

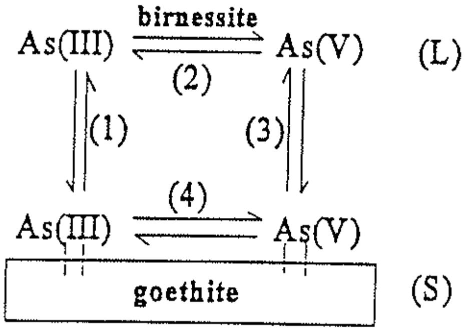

Fig. 9 A schematic depiction of reactions of arsenic at water-goethite interface.

$$O_2 + 4OH^- + 2H_2AsO_3^- = 2AsO_4^{3-} + 2H_2O \qquad E^o = 1.18V \quad (1)$$

$$2Fe(OH)_3 + H_3AsO_3 + 4H^+ = 2Fe^{2+} + H_3AsO_4 + 5H_2O \qquad E^o = 0.40V \quad (2)$$

$$MnO_2 + H_3AsO_3 + 2H^+ = H_3AsO_4 + H_2O + Mn^{2+} \qquad E^o = 0.62V \quad (3)$$

In this study, more As(III) was oxidized at pH 5.0 than at 8.0 both in the solution phase of suspensions (Table 3 and 4) and on the goethite surface (Fig. 2a), suggesting that Fe and/or Mn were involved in the reaction.

3.2. The reaction of As(III) and As(V) on Mn-substituted goethite.

Manganese substituted goethite has a structure nearly identical to pure goethite according to x-ray diffraction data (data not shown). A previous study (Cornell and Giovanoli 1987) indicated that, in alkali condition (pH=11-13) and with Mn additions of as much as 15 mole %, Mn-substituted goethite was the sole reaction product. With an increase in Mn substitutions (Table 1), the color of goethite samples became darker and the point of zero net proton charge (PZNPC) decreased. Unsubstituted goethite was yellow, but as little as 1 mole % Mn produced an olive color, and highly substituted goethite was gray or black. Fig. 10 shows Mn XANES spectra of MnO_2, $MnSO_4$, and Mn-goethite. Mn(II) ($MnSO_4$) K XANES spectrum was characterized by a pre-edge feature which begins at about 6.540 keV and peaks at 6.552 keV. For Mn(IV) (MnO_2), the edge-peak was at 6.561 keV while for Mn-goethite it was about 6.555 keV. The position of the Mn edge peak for Mn-goethite was between that of Mn(II) and Mn(IV), suggesting the main oxidation state of Mn in Mn-substituted goethite was Mn(III). This is compatible with the suggestion of Schwertmann and Cornell (1991). They proposed that although Mn(II) is used in preparing of Mn-goethite, it is oxidized to Mn(III) by

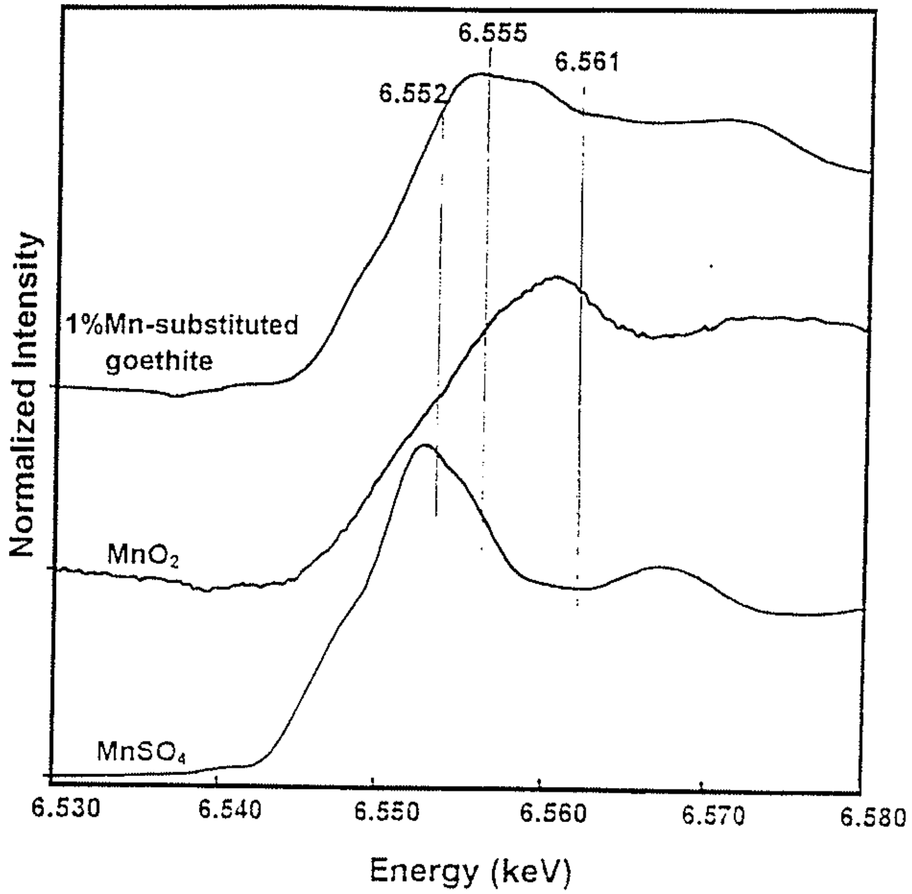

Fig. 10 Normalized K XANES spectra of Mn in 1% Mn -goethite, MnO_2, and $MnSO_4$.

atmospheric oxygen under alkaline conditions and incorporated into the goethite structure as Mn(III). This is favored because of its identical charge and similar ionic radii size to Fe(III).

XANES spectra of pure goethite treated with 150 μmol/g arsenic at different As(V)/As(III) ratios are shown in Fig. 11. It shows that 100% As(III) has a K-edge peak at 11.873 keV while 100% As(V) has a K-edge adsorption peak at 11.876 keV. As the mole fraction of As(III) increased, the intensity of the 11.873 keV peak increased while the 11.876 keV peak decreased gradually. These differences can be semi-quantitatively used as finger prints to identify the oxidation transformation from As(III) to As(V) on goethite surfaces.

Fig. 12 shows the reaction of As(III) on Mn-goethite at pH 5.0 and 8.0. At room temperature, no obvious oxidation occurred on pure goethite after 10 hrs. The oxidation of As(III) to As(V) by Fe(III) is a thermodynamically favorable reaction (Oscarson et al. 1980) at low pH conditions. However, the conversion of As(III) to As(V) by synthetic Fe(III) oxyhydroxide did not occur within 72 hr at neutral pH values, suggesting the reaction is kinetically controlled. Oxidation of As(III) increased with increased Mn substitution in goethite. This indicates that "Mn sites" on Mn-substituted goethite surface are stronger electron acceptors and more active than "Fe sites" for the oxidation of As(III). The influence of pH on the oxidation reaction of As(III) was slight. Lower pH (pH5.0) was favorable for the oxidation, but there was no large difference in the oxidation reaction between pH 5.0 and pH 8.0. The absence of a strong pH influence is predicated from the acid-base chemistry of H_3AsO_3 (pKa = 9.3) (Scott and Morgan 1995). In the pH

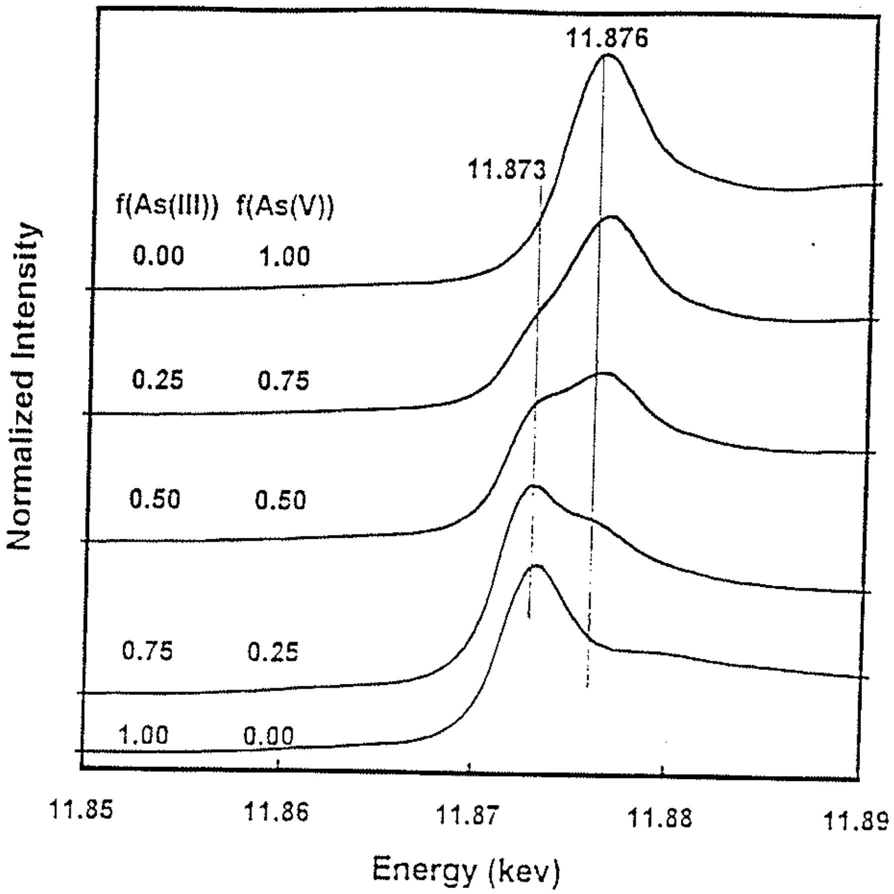

Fig. 11 Normalized As K XANES spectra of As(III) and As(V) mixtures in different As(III)/As(V) ratios on goethite.

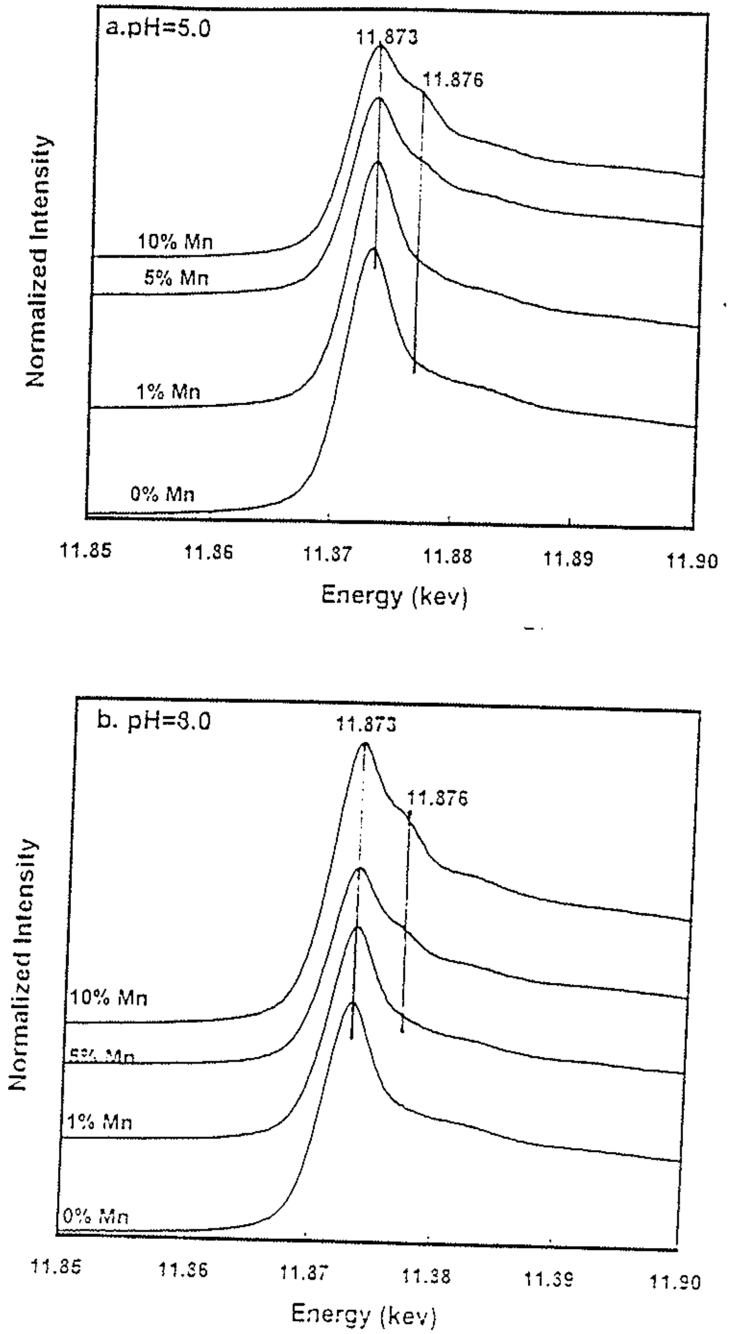

Fig. 12 Normalized As K XANES spectra of As(III) adsorbed on Mn-substituted goethite 10 hrs. after As treatment. a. pH=5.0, b. pH=8.0.

range studied here, the concentration of the $H_3AsO_3^o$ species remains nearly constant.

At room temperature, the oxidation of As(III) on Mn-substituted goethite was slow. Fig. 13 shows the reaction of As(III) on 5% Mn-substituted goethite as a function of time. No obvious oxidation was observed within three days in either suspension or air dry conditions. By day 5, we estimate about 20% of As(III) was oxidized to As(V). McGeehan and Naylor (1994) indicated that the oxidation rate of H_3AsO_3 was slower in soils with higher adsorption capacity, suggesting that adsorption may influence redox transformation of As. Oxidation of As(III) was more favorable in suspension (Fig.13a) than in air dry condition (Fig. 13b). In order for As(III) to oxidize to As(V), it apparently must be in the proximaty of a Mn site in goethite. So the oxidation speed of As(III) may be limited by the adsorption/desorption processes and rate of contact with Mn. Compared to suspension condition, it is more difficult for As(III) anions to desorb move to Mn active sites. Thus, the overall oxidation is less favorable.

Fig. 14 shows that the oxidation of As(III) on Mn-substituted goethite was greatly enhanced at elevated temperatures. At 65°C, nearly all As(III) was oxidized to As(V) on 10% Mn-substituted goethite after ten hrs. On 5% Mn-substituted goethite, As(III) peak was dominate at 45°C while As(V) peak was dominate at 65°C. Even on pure goethite, the oxidation of As(III) was very obvious at 65°C. Temperature may have two effects on overall speed of As(III) oxidation. Firstly, the desorption and transfer rate of As(III) to Mn active site increase as the temperature is raised. Secondly, with increasing temperature, the activation energy of As(III) oxidation reaction decrease, which makes the reaction faster, such as the case on pure goethite.

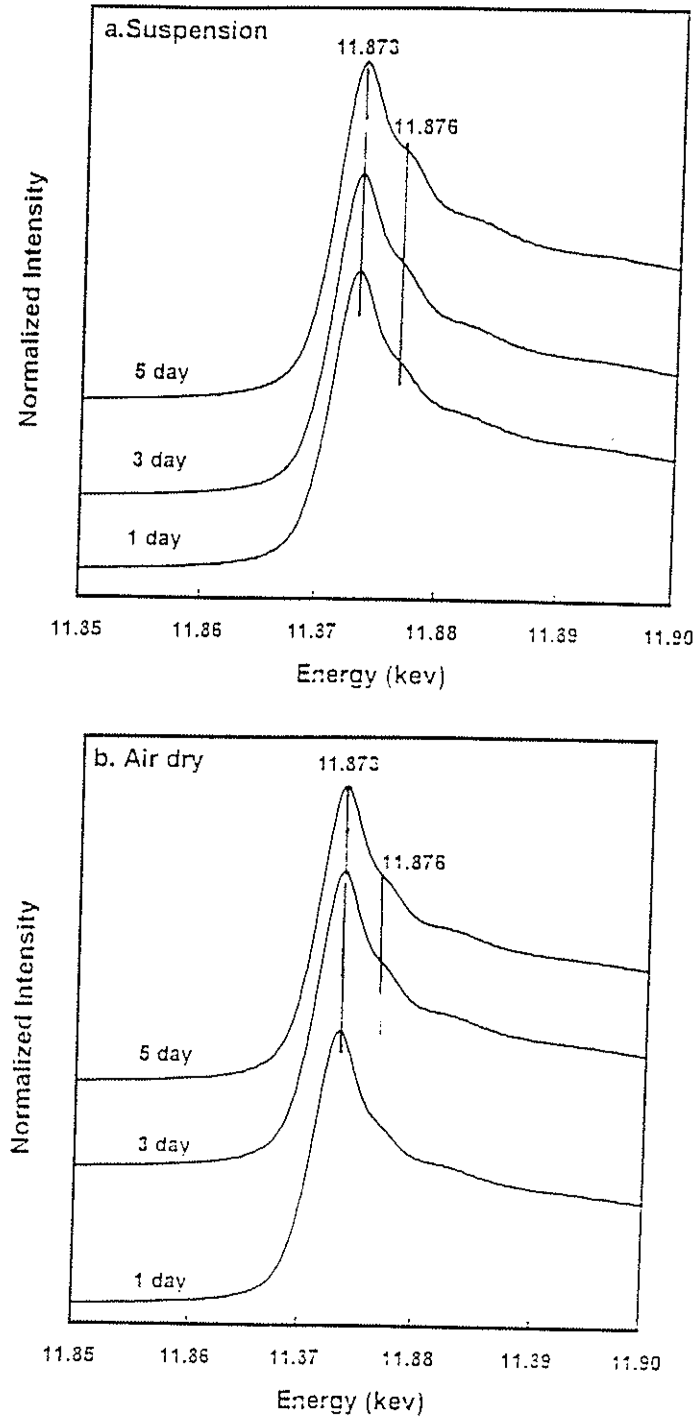

Fig. 13 Normalized As K XANES spectra of As(III) adsorbed on 5% Mn-substituted goethite as a function of time. a. Suspension, b. Air dry.

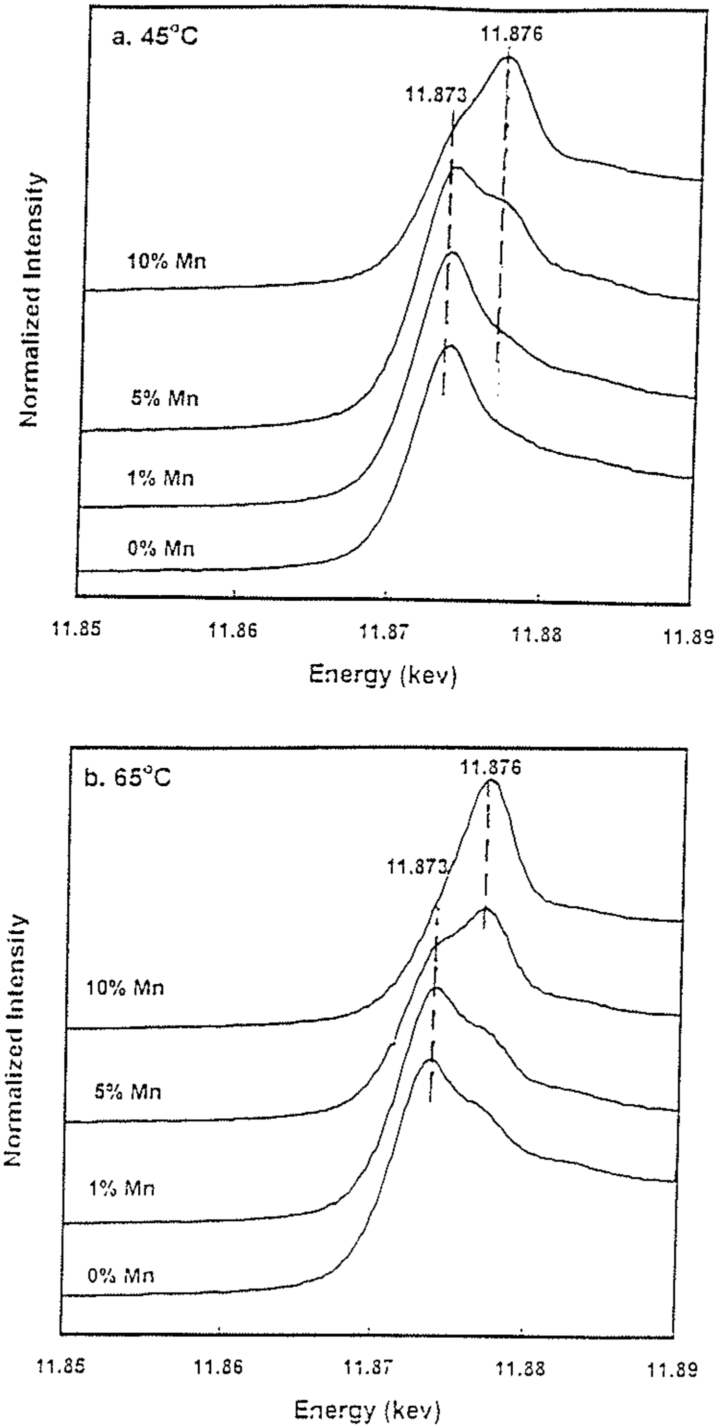

Fig. 14 Normalized As K XANES spectra of As(III) reaction with different Mn-substituted goethite as a function of temperature. a. 45°C, b. 65°C.

Fig. 15 shows the total extracted Mn(II) by $CuCl_2$ from Mn-substituted goethite after it was reacted with As(III) at 65°C. As was shown in Fig. 14, almost all As(III) (150 µmol/g) was oxidized to As(V) on 10% Mn-substituted goethite after ten hrs. Assuming the reaction:

$$\mathrm{As(III)} + 2\mathrm{Mn(III)} = \mathrm{As(V)} + 2\mathrm{Mn(II)}, \qquad (1)$$

Then 300 µmol/g Mn(II)/g would have been produced. However, the extracted Mn(II) from 10% Mn-goethite was much lower than calculated from the reaction (1). For 1% Mn-goethite, Fig. 14 showed that about 30% of As(III) was oxidized to As(V). The Mn(II) produced from reaction (1) should be 90 µmol/g Mn(II)/g, which was about 80% of total Mn in 1% Mn-goethite. If this amount of Mn(II) were not extractable and stayed in solid phase, it would have a significant change in Mn XANES spectrum. However, there was no apparent difference on Mn oxidation states in 1% Mn-goethite before and after the reaction with As(III) (Fig. 16).

The results suggest that the oxidation of As(III) to As(V) may be catalyzed by Mn-substituted goethite surface. McBride (1994) proposed that in many cases, Mn and Fe minerals act as oxidizing agents in soil and sediment. However, these minerals are only catalysts, because oxygen ultimately reoxidizes the reduced Mn and Fe in the minerals. Previous research (Oscarson et al. 1981b) indicated that in a natural, open system, Mn in Mn oxides was able to catalyze As(III) oxidation. The sediments which contained Mn oxides could oxidize unlimited amounts of As(III) because Mn(II) would be reoxidized by oxygen in the air. Davis and Morgan (1989) found that the oxidation of Mn(II) to Mn(III) was very slow at pHs less than 8.5, but it could be catalyzed on goethite surface and the

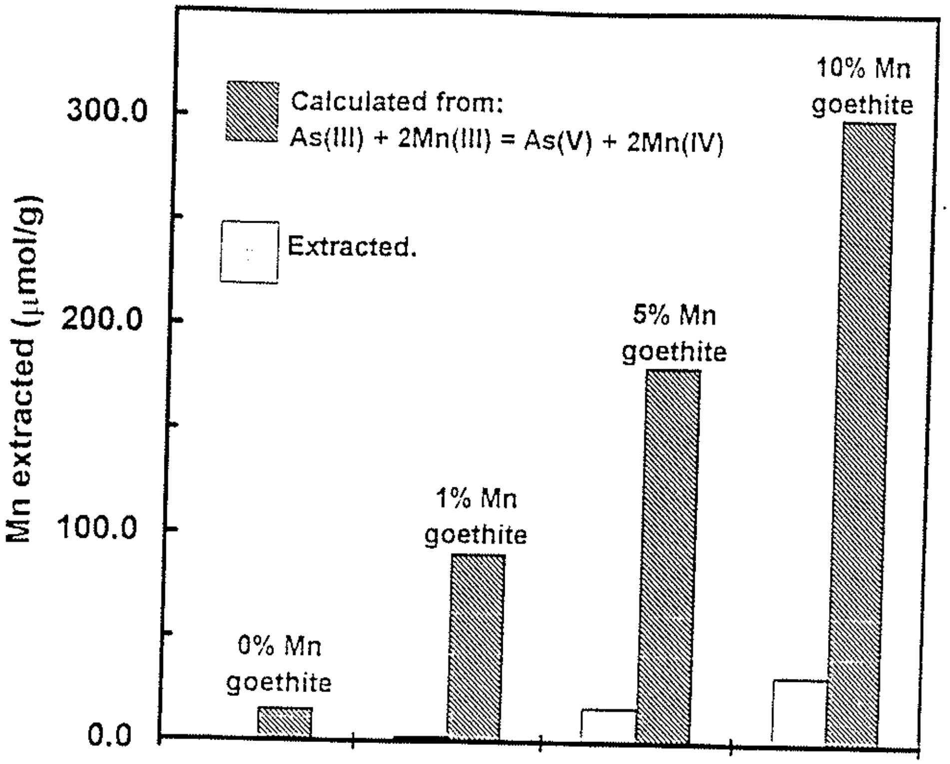

Fig. 15 The Mn released from Mn-substituted goethite after reaction with As(III) at 65°C.

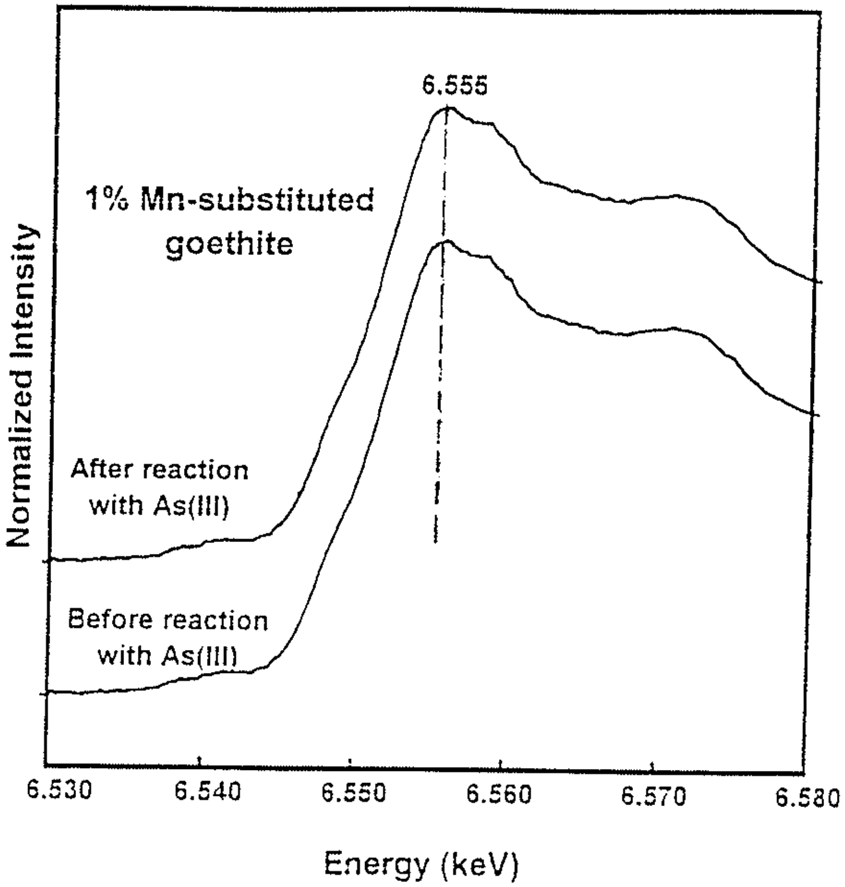

Fig. 16 Normalized K XANES spectra of Mn in 1% Mn-substituted before and after reaction with As(III) at 65°C.

oxidation was strongly temperature dependent.

Based on the results above, we propose a possible mechanism of As(III) oxidation on Mn-substituted goethite (Fig. 17). Mn(III) was reduced as As(III) was oxidized. Since Mn(III) ([Ar]3d^4) has one electron less than Fe(III) ([Ar]3d^5), Mn-substituted goethite may act as a p-type semiconductor. In this case the electron transfer might be better described as insertion into the overlapping electronic orbitals of the solid (McBride 1994). So the electrons accepted from As(III) oxidation by Mn-goethite may be delocalized over the solid instead of associated with a specific surface atom. Only those of Mn(II) on the surface could be desorbed and released to the solution. This may account for the relatively small amount of Mn(II) extracted from the Mn-goethite shown in Fig. 15. In terms of charge and size, Mn(II) atoms were not stable in goethite structure and they were easily reoxidized to Mn(III). This reoxidation should be a fast reaction because no oxidation state change of Mn was observed.

3.3. Solubility of As(III) and As(V) in soil and sediment.

Table 5 shows the pH and redox potential status of soil and sediment samples incubated with As(III) and As(V) for ten days. The initial pH (pH=7.50) and final pH values in all treatments were very similar. The redox potentials of soil samples were much higher than that of sediment samples. Table 1 shows that the total organic C was higher in the sediment than in the soil. During flooding, some elements, such as Fe(III) and NO_3^-, may be reduced to lower oxidation states contributing to the lower Eh values in sediment samples. Table 5 also shows that the Eh values of As(III) and As(V) treated soil

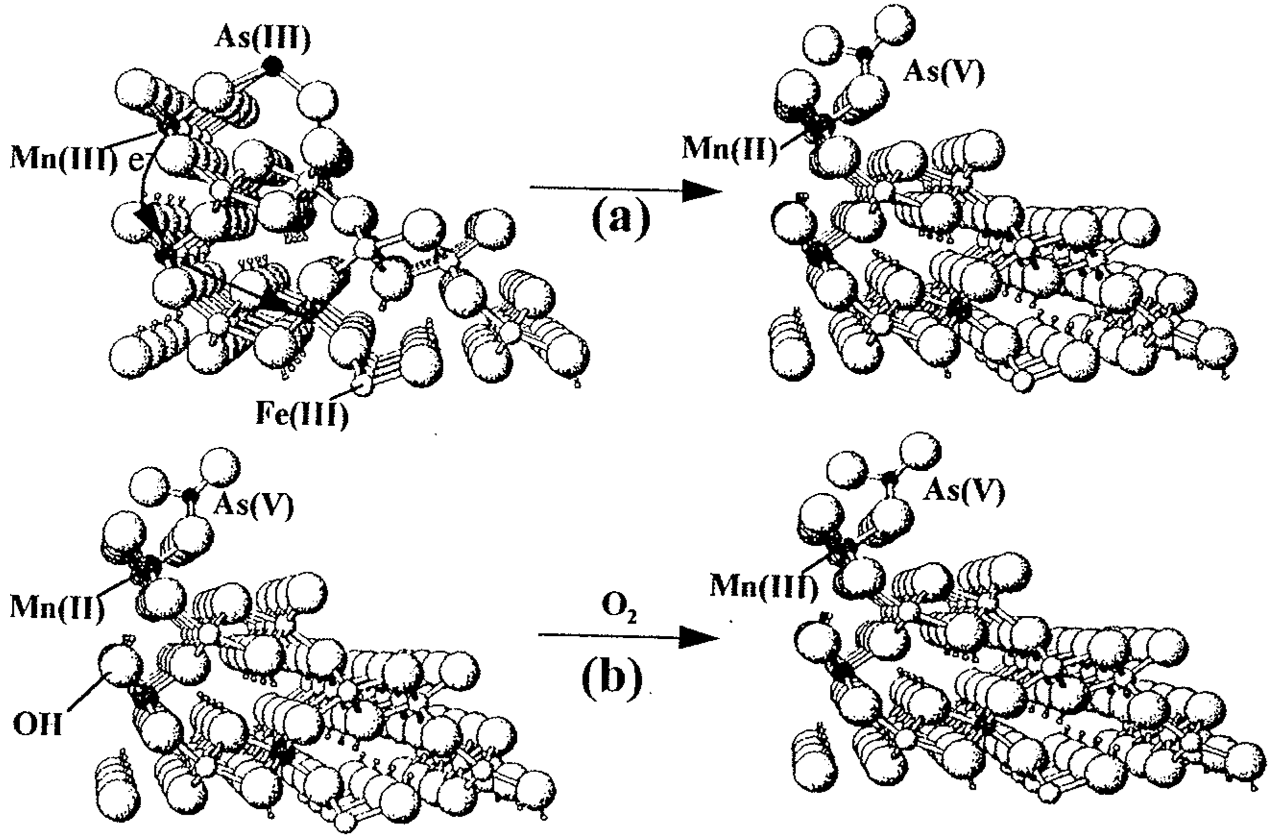

Fig. 17 A mechanism of As(III) oxidation on Mn-substituted goethite.

A. Oxidation of As(III) to As(V). B. Reoxidation of Mn(II) to Mn(III).

Table 5 pH and redox status (SHE) of As incubated soil and sediment samples

	pH	Eh (mV)
As(III) + soil	7.52±0.04	455±15
As(V) + soil	7.66±0.03	433±25
As(III) + sediment	7.77±0.04	130±11
As(V) + sediment	7.69±0.05	240±12

samples were not significantly different while As(V) treated sediment had a 100 mV higher Eh value than As(III) treated sediment. Assuming the redox transformation between As(III) and As(V) has reached equilibrium in soil and sediment suspensions after ten days, the ratio of $HAsO_4^{2-}/H_3AsO_3$ in solution can be calculated from the following reaction by Nernst equation:

$$HAsO_4^{2-} + 4H^+ + 2e^- = H_3AsO_3 + H_2O \qquad Eh^\circ = 0.86\ V \qquad (1)$$

For the As(III)-soil system (pH=7.66, Eh=0.45 V), the calculated $HAsO_4^{2-}/H_3AsO_3$ ratio equals to 10^{15}, and for the As(III)-sediment system (pH=7.77, Eh=0.13 V), the calculated $HAsO_4^{2-}/H_3AsO_3$ ratio equals to $10^{7.1}$. These calculated results suggest that over 99.99% As(III) in soil and sediment suspensions should be oxidized to As(V). However, this thermodynamic calculation can not be simply extrapolated to a soil or sediment system because the kinetics of the As(V)-As(III) transformation is very slow (Masscheleyn et al.,1991).

Fig.18 is XANES spectra of As(III) and As(V) incubated in soil and sediment for ten days. The spectra show that pure As(V) in water had an edge peak at 11876 eV (Fig. 18(1)) while the edge peak was at 11873 eV for pure As(III) (Fig. 1(6)). After 10 days, a small shoulder appeared at 11876 eV in the As(III) treated sediment (Fig. 18 (3)),

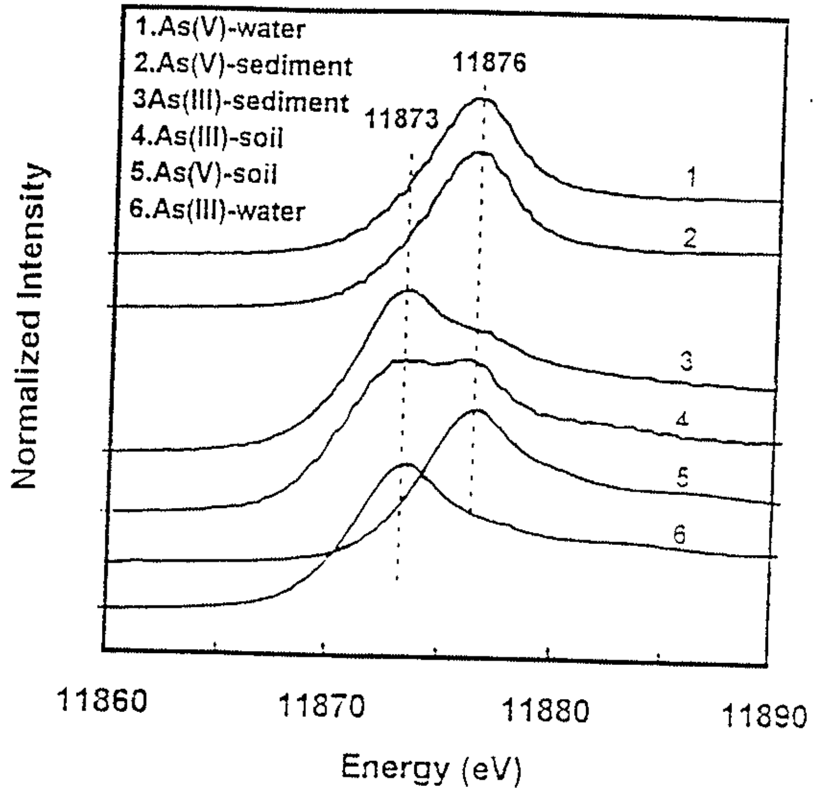

Fig. 18 XANES spectra of As with different treatments.

indicating small amount of As(III) in sediment was oxidized to As(V). Compared to the sediment, there was apparent more As(III) oxidized to As(V) in the soil based on the relative size of the shoulder at 11876 eV (Fig. 18 (4)). In both treatments As(III) peaks could be still be seen after 10 days of incubation. The distributions of different oxidation states of As in solid phases obtained from spectroscopic data were not compatible with that from thermodynamic calculations, which suggested above 99.99% of As should be As(V) species. These results implied that the ratio of As(V) to As(III) in solid phases could not be correctly estimated from pH-Eh conditions.

Table 6 gives the distributions of extracted As and some other selected elements in the untreated soil and sediment.

Table 6 Some elements extracted from untreated soil and sediment
(Total concentrations are shown in Table 1)

	As(%)	Al(%)	Ca(%)	Fe(%)	Mn(%)
Soil					
NH_4Cl	0.00	0.01	11.6	0.01	0.00
NH_4F	4.80	0.01	0.01	0.01	0.00
NaOH	0.20	0.01	0.20	0.01	0.02
H_2SO_4	11.2	10.1	43.6	9.64	28.1
Residual*	86.6	89.9	43.1	89.3	71.8
Sediment					
NH_4Cl	0.89	0.08	24.5	0.08	0.02
NH_4F	3.57	0.01	0.01	0.01	0.00
NaOH	0.53	1.23	0.31	0.00	0.16
H_2SO_4	11.6	12.1	42.7	12.3	34.2
Residual*	82.5	86.6	32.2	87.5	64.8

* Residual fractions were determined by the difference between HNO_3-H_2SO_4 digestion and total extractable forms.

Table 6 showed that the largest amount of As as well as Fe, Mn, Al, and Ca in both untreated soil and sediment was extracted by H_2SO_4, suggesting that most As in untreated soil and sediment was associated with Fe, Mn, Al, and Ca. A previous study showed that there was a high correlation between As and iron (Fe) and manganese (Mn) but a low correlation with total organic carbon (Faust et al., 1987). Arsenic added to sediments became associated with relatively immobile iron and aluminum minerals and long term As release was related to sediment total Fe, extractable Fe, and $CaCO_3$ (Brannon and Patrick 1987). Our results were compatible with their study, except NH_4F extracted As (in %) was significantly greater than other elements. Fluoride forms relative strong ligand bonds on Fe and Al oxides (Hingston et al., 1974) and may desorb As oxyanions from these adsorption sites effectively. There was a large amount of soluble Ca in the sediment because the drainage water was very saline and contains about 2.5 mmol/L Ca. Like other elements, most native As was in relatively insoluble forms which was probably less bioavailable.

Fig. 19 shows sequential extracted total As (As(III)+As(V)) from soil and sediment treated with As(III) and As(V) and incubated for ten days.

Fig. 19a shows that the soluble form (NH_4Cl extractable) As in As(III) treated soil was much higher than that of As(V) treatment after 10 days of incubation. In the pH range of this study, the main species of As(III) is H_3AsO_3 , which is a neutral species and a very week acid (pka1=9.2). The adsorption of H_3AsO_3 by a non-specified mechanism (electrostatic force) on soil components is unlikely because this acid is in direct

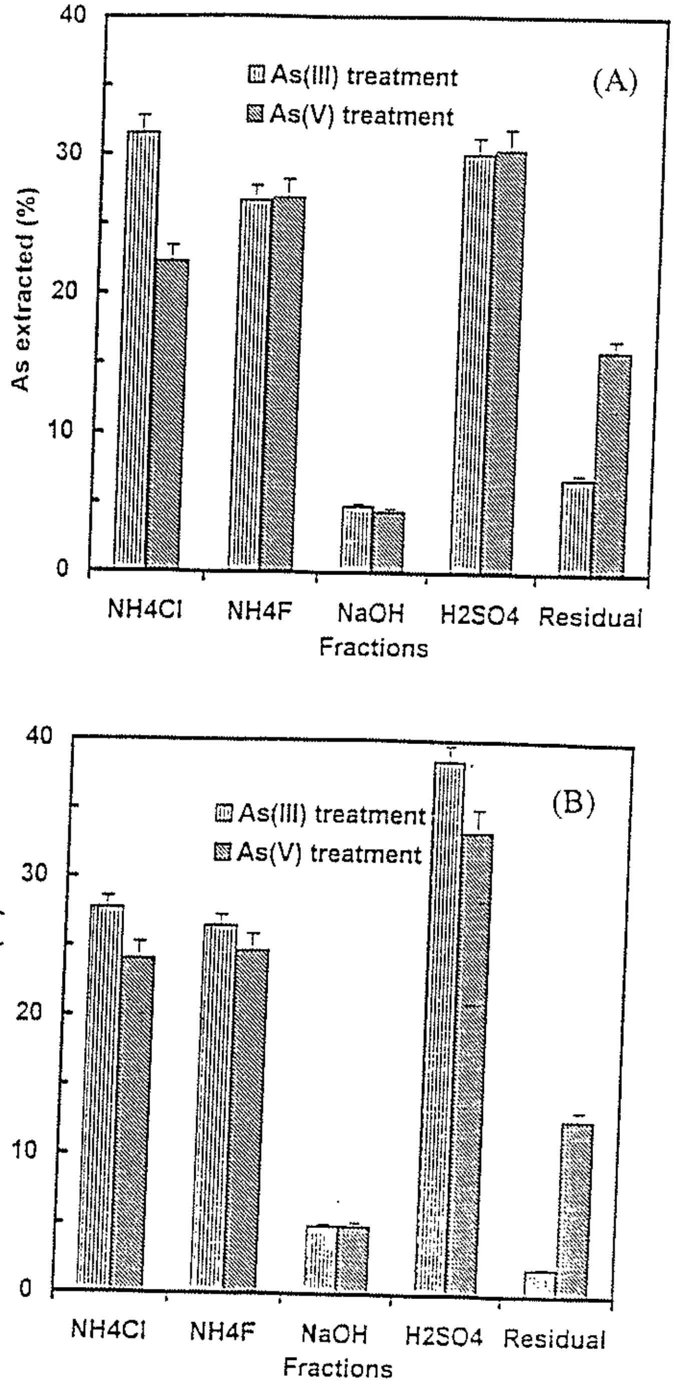

Fig. 19 Distributions of extracted As from the soil (A) and sediment (B) treated with As(III) and As(V) for 10 days. Total As in the soil (375 mg kg^{-1} added + 5.0 mg kg^{-1} background) = 380.0 mg kg^{-1}, total As in the sediment (375 mg kg^{-1} added + 5.6 mg kg^{-1} background) = 380.6 mg kg^{-1}.

competition with water. On the other hand, the main form of As(V) under the pH conditions here is $H_2AsO_4^-$, an anion which could be adsorbed on positive charged sites of soil components, such as oxides and broken edges of clay minerals. However, the amounts of As extracted by NH_4F, NaOH, and H_2SO_4 were nearly the same for both the As(III) and As(V) treatments after 10 days. Fig. 19b showed that the soluble As (NH_4Cl extractable) in As(III) treated sediment was greater than that in the As(V) treatment, which was similar to soil. Comparing extracted As in the soil and sediment, we can see that for untreated samples (Table 6), there is little difference in As distributions between the soil and sediment. For both As(III) and As(V) treated samples, Fig. 19 showed that H_2SO_4 extracted As (Ca-bound As) from the sediment is significant higher than that from the soil.

Fig. 20 are XANES spectra of As(III) and As(V) treated soil samples after each step of sequential extraction. Fig. 20a clearly showed that after the NH_4Cl extraction, the intensity of As(III) peak (at 11873 eV) decreased greatly, indicating most As(III) was removed by the NH_4Cl extractant from the soil. Meanwhile, As(V) peak was still present and became dominate. This spectroscopic result suggested that if As(III) and As(V) co-exist in soil, As(III) is more extractable than As(V). Fig. 20b showed that only As(V) was apparently present in soil under this pH-Eh incubation condition. XANES data showed that only As(V) species remained in both As(III) and As(V) treated soil after extracted by NH_4Cl. The next several extracted fractions of As in As(III) and As(V) treatments soil were similar. However, the amount of non-extractable As (residual form) in As(V)

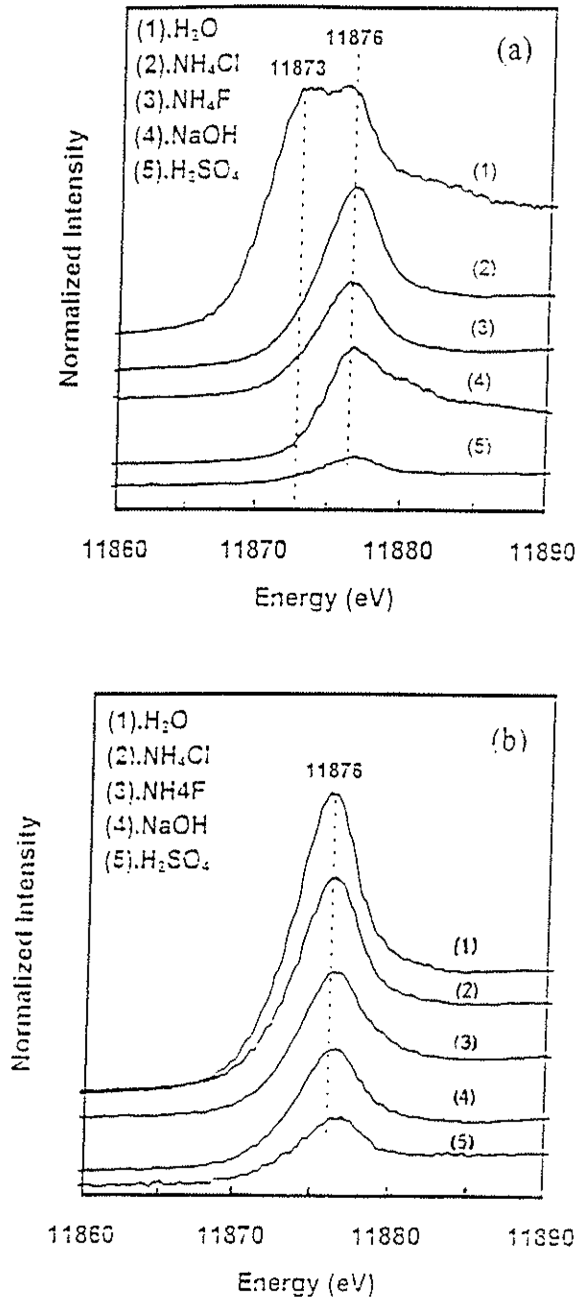

Fig. 20 XANES spectra of As in the soil after each extraction step.

(a) As(III) treatment. (b) As(V) treatment.

treatment was larger than that in As(III) treatment, even though the oxidation states in both treatments were all As(V). Onken and Adriano (1997) found that As(V) became more tightly bound with soil components and recalcitrant in soil with time.

Fig. 21 are XANES spectra of As(III) and As(V) treated sediment after each step of sequential extraction. Before extraction, As(III) predominated with a small amount of As(V) produced from As(III) oxidation in As(III) treated sediment. After extraction with NH_4Cl, the As(III) peak apparently decreased while As(V) peak remained without much change. With subsequent extraction by NH_4F and NaOH, the As(III) peak disappeared while As(V) peak became dominate (Fig. 21a), which suggests As(III) was more easily desorbed from solid phases than As(V) by NH_4Cl , NH_4F and NaOH. Fig. 19b shows that the amounts of NH_4F and H_2SO_4 extracted As (Al-bound and Ca-bound) were greater in the As(III) treatment than in the As(V) treatment. However, for NaOH extractable As (Fe-bound), there was little or no difference between As(III) and As(V) treatments. Previous studies indicated that both As(III) and As(V) were strongly adsorbed on iron oxides (Ferguson and Gavis 1972; Anderson et al. 1976; Gupta and Chen 1978; Pierce and Moore 1980,1982; Matthew and Carleton 1982) by forming binuclear complexes (Waychunas et al. 1993; Waychunas et al. 1995; Manceau 1995; Sun and Doner 1996; Fendorf et al. 1997). On the other hand, As(III) is not stable and easily oxidized to As(V) at high pH in the solution:

$$O_2 + 4OH^- + 2H_2AsO_3^- = 2AsO_4^{3-} + 2H_2O \qquad E^o = 1.18V \qquad (2)$$

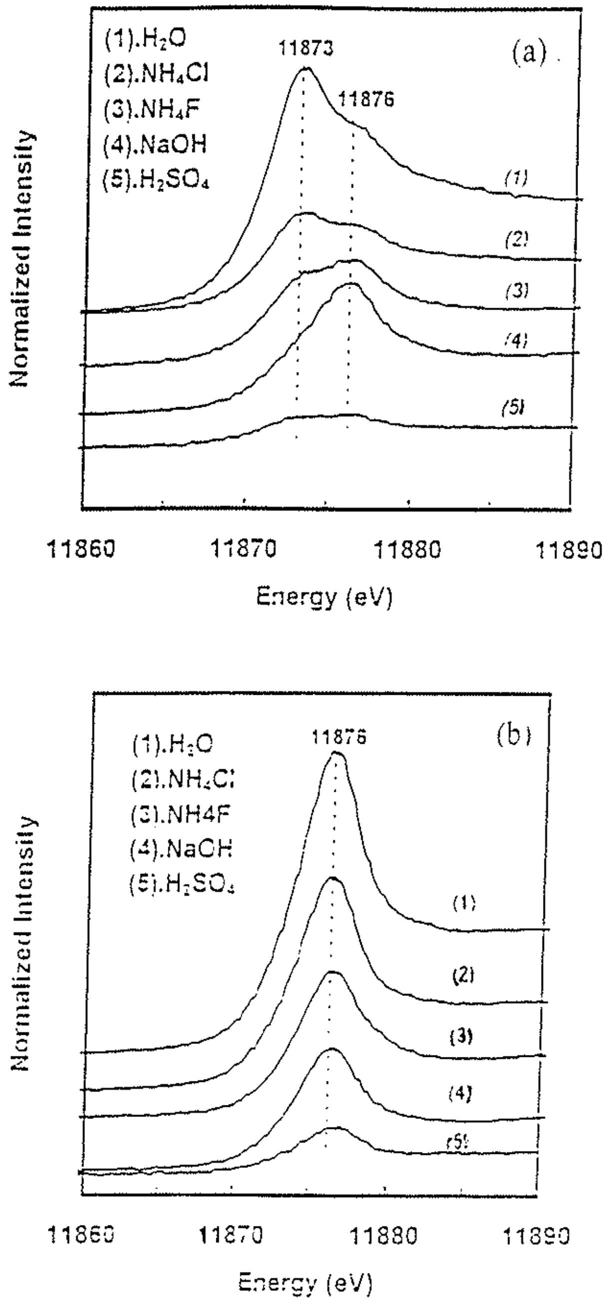

Fig. 21 XANES spectra of As in the soil after each extraction step.

(a) As(III) treatment, (b) As(V) treatment.

During the extraction process by NaOH, As(III) may be oxidized to As(V) by oxygen in the air. Fig. 21a showed that after NaOH extraction, all As in the sediment existed in As(V) form.

Sequential extraction techniques imply that the different bonding forms of trace elements in soils or sediments can be selectively extracted by different solvents and that the trace elements released during the dissolution of one soil component are not readsorbed by remaining components. However, studies (Gruebel et al., 1988; Onken and Adrino 1997) indicated that extraction steps are not always as specific as desired. Incomplete extraction, readsorption of extracted target fractions always occur. For some elements like As the solvent may cause a change in oxidation state. Even qualitative interpretation of data from selective sequential extraction is difficult. In this study, sequential extraction technique was only used to evaluate the relative solubility and potential mobility of As(III) and As(V).

By using the same extraction process, Onken and Adriano (1997) found that most of As in soil was extracted by NaOH. However, the results of this study indicated that the largest amount of As in both untreated and As incubated soil and sediment was extracted by H_2SO_4. The area where the soil and sediment were collected for this study was affected by saline shallow ground water which resulted in the high Ca content in the soil and the sediment (Table 2). On the other hand, the extractable Fe from the soil and the sediment (1.29 and 1.53 g kg^{-1} , calculated from Table 1) for this study is lower than from the soil used by Onken and Adriano (1997) (6.1 g kg^{-1}). These may account for the larger amount of As was extracted by H_2SO_4 (Ca-bound As) than by NaOH (Fe-bound As) in this investigation.

4. PRINCIPAL FINDINGS AND CONCLUSIONS

1. Both indirect (IR) and direct (XANES) spectral properties of As(III) and As(V) were used to investigate the oxidation of As(III) on the goethite surface. The results indicated that at low pH, some As(III) could be oxidized to As(V) and adsorbed on goethite. Because of the higher adsorption capacity goethite for As(V) compared to As(III) below pH 6, the As(V)/As(III) ratio in solid phase is higher than in solution phase. Thus, it is not accurate to evaluate the As(III) oxidation only by the As(V)/As(III) ratio in solutions. As(III) adsorbed on goethite in the air-dry condition was not stable. More than 20% of the As(III) was oxidized to As(V) after 20 days. Because As(III) in pure water is very stable in the air, we conclude that goethite surface may play an important role in its oxidation. Birnessite can actively oxidize As(III) to As(V) and influence the As form both in solution and on the goethite surface. Several transformation mechanisms could account for this. The oxidation rate of As(III) to As(V) on goethite surface by birnessite was faster than expected considering a purely solution controlled process. This study suggests that the adsorption-oxidation system composed of goethite and birnessite may be significant in decreasing the arsenic toxicity in terrestrial environments.

2. The oxidation of As(III) to As(V) can be catalyzed by Mn-substituted goethite. This reaction is more sensitive to temperature than to pH. The possible mechanism of this catalyzed reaction may be explained by the delocalization of electrons in the whole mineral, as a semiconductor, instead of only associated with surface atoms. Since Mn-

substituted goethite can both convert As(III) to As(V) and adsorb As(V) strongly, under certain conditions the reactions may be useful in decreasing As toxicity in As(III) contaminated environments.

3. Previous studies suggested that As(III) was more soluble and mobile than As(V). This conclusion was verified by XANES spectroscopic and sequential extraction results in this study. The redox transformation reactions between As(III) and As(V) may occur during the incubation period of soil and sediment. However, the distributions of As(III) and As(V) in solid phases may not be correctly estimated by pH-Eh values because the transformation between them could be kinetically controlled. The conversions between different oxidation states of arsenic will complicate the sequential extraction results and the data may be misinterpreted if no other information is available. The interpretation of data from selective sequential extraction of arsenic based on the "chemical forms" is very difficult, but, when combined with spectroscopic technique such as XANES spectroscopy, sequential extraction method can be used to evaluate the solubility of different oxidation species of some trace elements.

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