

Kinetics of zinc and arsenate co-sorption at the goethite–water interface

MARKUS GRÄFE,^{1,*} and DONALD L. SPARKS

Environmental Soil Chemistry Group, Department of Plant and Soil Sciences, University of Delaware, 152 Townsend Hall, Newark, DE 19717, USA

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Abstract—Little or no information is available in the literature about reaction processes of co-sorbing metals and arsenate [As(V)] on variable-charged surfaces or factors influencing these reactions. Arsenic and metal contamination are, however, a common co-occurrence in many contaminated environments. In this study, we investigated the co-sorption kinetics of 250 μM As(V) and zinc [Zn(II)] in 10, 100, and 1000 mg goethite L^{-1} 0.01 M NaCl solution at pH 7, collected complementary As and Zn K-edge extended X-ray absorption fine structure (EXAFS) data after various aging times, and performed a replenishment desorption/dissolution study at pH 4 and 5.5 after 6 months of aging time. Arsenate and Zn(II) formed adamite-like and koritnigite-like precipitates on goethite in 100- and 10-ppm goethite suspensions, respectively, whereas in 1000-ppm goethite suspensions, As(V) formed mostly double-corner sharing complexes and Zn(II) formed a solid solution on goethite according to EXAFS spectroscopic analyses. In all goethite suspension densities, surface adsorption reactions were part of the initial reaction processes. In 10- and 100-ppm goethite suspensions, a heterogeneous nucleation reaction occurred in which adamite-like precipitates began to form 48 h earlier than koritnigite-like surface precipitates. Arsenate and Zn(II) uptake from solution decreased after 4 weeks. Replenishment desorption studies showed that the precipitates and surface adsorbed complexes on goethite were susceptible to proton-promoted dissolution resulting in many cases in more than 80% loss of Zn(II) and $\sim 60\%$ to 70% loss of arsenate. The molar Zn:As dissolution ratio was dependent on the structure of the precipitate and was cyclic for the adamite and koritnigite-like surface precipitates, reflecting the concentric and plane-layered structures of adamite and koritnigite, respectively. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Little or no information is available in the literature about reaction processes and mechanisms of co-sorbing metals and arsenate (As(V)) on variable-charged surfaces or factors influencing these reactions. Arsenic and metal contamination are, however, a common co-occurrence in many contaminated environments (Carlson et al., 2002; Williams, 2001), and it is reasonable to assume that precipitated metal–arsenate phases may exist in co-contaminated soils and sediments. Little or no research has been conducted on the formation and stability of such precipitates. Understanding the mobility and fate of two or more co-occurring contaminants of differing chemical properties is of great importance to make appropriate decisions concerning the stabilization and remediation of such sites.

Waychunas et al. (1993) investigated the effects of arsenate (As(V) = $\text{H}_{3-n}\text{AsO}_4^{0-n}$) on ferrihydrite precipitation using extended X-ray absorption fine structure (EXAFS) spectroscopy and concluded that As(V) inhibited ferrihydrite precipitation by binding to growth sites on the precipitate. Tournassat et al. (2002) observed the precipitation of a manganese(II)–arsenate precipitate at the birnessite–water interface after the oxidation of an 11 mM arsenite (As(III)) solution at the birnessite–water interface. In natural environments, Langner et al. (2001) observed ferric–arsenate precipitation following the oxidation of As(III) in hot sulfur springs. Sadiq (1997) concluded from

thermodynamic data that the solubility of arsenic in acidic environments was controlled by iron and aluminum–arsenates and at alkaline pH by calcium–arsenates. Other metal–arsenates such as copper, zinc, nickel, or cadmium–arsenates were considered less soluble and could accumulate in the environment. First row transition metals form thermodynamically very stable arsenate complexes (K_{so} of $\geq 10^{19}$, Gustafsson, 2004). In mineralogy, several phosphate/arsenate mineral classes are recognized (Gaines et al., 1997). The formation of a solid phase that contains environmentally critical elements, that has low solubility, and that increases in stability over time is favorable from an environmental remediation standpoint. Reaction processes/mechanisms and factors that contribute and inhibit the formation of such solid phases should be understood well to make appropriate decisions for contaminated sites.

Recently, we reported on As(V) and Zn(II) co-sorption at the goethite–water interface as a function of pH (4 and 7). Arsenate and Zn(II) sorbing on goethite above site saturation resulted in the formation of an adamite-like ($\text{Zn}_2(\text{AsO}_4)\text{OH}$) surface precipitate at pH 7 (Gräfe et al., 2004). Extended XAFS spectroscopy analyses showed that an adamite-like precipitate formed on the goethite surface at pH 7, while at pH 4, As(V) and Zn(II) existed as co-sorbed species on the goethite surface. The study suggested that the amount of surface area (and therefore the number of reactive surface sites) may control the precipitation of a zinc–arsenate solid phase. In the current study, we hypothesize that for a given aqueous, undersaturated ($\text{Zn}_3(\text{AsO}_4)_2$: log ion activity product (IAP)/ $K_{\text{so}} < 0$) concentration of Zn(II) and As(V) at a favorable pH (e.g., pH ~ 7), a greater solid–solution ratio will result in the formation of mostly two dimensional or inner-sphere adsorbed species. In lower solid–solution ratios, a

* Author to whom correspondence should be addressed (grafem@agric.usyd.edu.au).

¹ Present address: Faculty of Agriculture, Food, and Natural Resources, Ross Street Building, Rm. #322, The University of Sydney, NSW 2006, Sydney, Australia.

precipitation reaction may occur facilitated by the presence of the goethite surface. The objectives of this study were (i) to investigate the co-sorption kinetics of zinc and arsenate at the goethite–water interface at pH 7 as a function of the solid–solution ratio, (ii) to determine the bonding environment of As(V) and Zn(II) on goethite for certain periods of reaction time using EXAFS spectroscopy, and (iii) to evaluate the stability of the solid phases against background electrolyte adjusted to pH 5.5 and 4.0.

Information gleaned from this study may be useful in predicting the fate and mobility of co-occurring metals and oxyanions and in devising remediation strategies to lower their bioavailability at co-contaminated sites, in ground and surface-waters, and in other applicable situations.

2. MATERIALS AND METHODS

2.1. Materials

The preparation and characterization of goethite (α -FeOOH) was reported elsewhere (Gräfe et al., 2004). Briefly, the specific surface area of the goethite is $\sim 70 \text{ m}^2 \text{ g}^{-1}$, with 2.4% porosity. The average particle size is ~ 30 – 200 nm . All reagents used in the study were ACS grade. A 799 GPT Titrimo automated titrator (Metrohm, Herisau, Switzerland) was used to control the pH of the kinetic reactions for the first 8 h. The setup of the kinetic studies is similar to the one reported earlier (Gräfe et al., 2001). Briefly, kinetic studies were conducted in a Teflon vessel inserted into a glass-jacketed reaction vessel connected to a constant temperature water circulator operating at $25 \pm 1^\circ\text{C}$. The reaction vessel was capped with a glass lid fitted with ports to support two acid/base burettes, a pH electrode, and N_2 gas burette. Nitrogen gas was bubbled through a Teflon straw into the reaction vessel to displace and minimize the effects from dissolved carbonate.

2.2. Methodology

2.2.1. Sorption kinetics

The sorption of Na_2HAsO_4 (As(V)) and ZnCl_2 [Zn(II)] were conducted in 10, 100, and 1000 mg goethite L^{-1} (ppm) suspensions as a function of reaction time. The suspensions were prepared from prehydrated 10-g goethite L^{-1} stock suspensions in 0.01 M NaCl and pH 7-adjusted, 0.05 M Na-(2)-morpholinoethanesulfonic acid (MES) buffer and hydrated overnight before the addition of the sorbates. Both single [As(V) or Zn(II)] and co-sorption [As(V) and Zn(II)] experiments were conducted at concentrations of 250 μM As(V) and Zn(II), ($\text{LOG IAP}/K_{\text{so, Zn}_3(\text{AsO}_4)_2 \cdot 2.5\text{H}_2\text{O}} = -0.92$, $\text{LOG IAP}/K_{\text{so, ZnO (zincite)}} = -1.03$, $\text{LOG IAP}/K_{\text{so, Zn(OH)}_2 (\text{epsilon})} = -1.33$ [Gustafsson, 2004]), in duplicate with averaged results reported. In addition, the precipitation of a homogeneous zinc–arsenate precipitate was monitored over time using 10 mM As(V) and Zn(II) in 0.01 M NaCl and 0.05 M Na-MES (Fig. 1A–F, Fig. 2A–E). Although the aqueous speciation programs we consulted (Gustafsson, 2004; Schecher and McAvoy, 1998) indicated that the solutions were undersaturated with respect to the formation of amorphous koettigite, the possibility of aqueous polymeric solution species forming could not be disregarded. Arsenate and Zn(II) were added simultaneously as independent aliquots (Na_2HAsO_4 and ZnCl_2 salts) on opposite sides of the reaction vessel to minimize their formation before contact with goethite in solution.

Thirty-six samples were collected in 2-, 10-, 20-, 30-, and 60-min intervals during the first 8 h of the experiment. Long-term samples were collected after 24, 48, 72, and 96 h, 7, 14, 21, and 28 d, 6, 8, 10, and 12 weeks, and after 4 and 6 months. Samples were stirred by either an overhead stirrer or a magnetic stir bar at 300 rpm during the first 8 h of the experiment. After 8 h, samples were removed from the glass-jacket reaction vessel and transferred into 250-mL polycarbonate storage containers and placed into a constant temperature ($25 \pm 1^\circ\text{C}$) chamber on a rotary shaker at 150 rpm. After 1-month reaction time, samples were taken off the rotary shaker to avoid effects from abrasion and were left in the constant temperature chamber. Volumes entering or

leaving the vessels were recorded to account for any dilution effects. Samples were syringe-filtered over a $0.22\text{-}\mu\text{m}$ filter paper, and the supernatant was retained for subsequent inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis for As, Fe, and Zn. Field-emission scanning-electron micrographs were collected on a Hitachi 4700 S unit for various co-sorption samples after 4 and 16 weeks for visual comparison (Fig. 3A–D). Sorption rates for single and co-sorption reactions are summarized in Table 1.

2.2.2. EXAFS spectroscopy

EXAFS samples were prepared using the same solid–solution ratios and initial As(V) and Zn(II) concentrations using one to two liter volumes and one sampling at the end of the equilibration periods (24 h, 2 weeks, and 6 months). Samples were placed on a rotary shaker at 150 rpm at $25 \pm 0.1^\circ\text{C}$ for the allotted reaction period and taken off the shaker after 1 month reaction time. The pH (7.00 ± 0.02) of the suspensions was regularly checked and adjusted over the course of the equilibration periods using minute volumes of 1 N NaOH or 1 N HCl as required. EXAFS data were collected for two types of samples: reference phases and experimental samples. The reference phases consisted of mineral standards [adamite ($\text{Zn}_2(\text{AsO}_4)\text{OH}$) and ojuelaite ($\text{ZnFe}_2^{III}(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), obtained from Excalibur], homogeneous zinc–arsenate precipitate reacted for 4 weeks (HZAP), single sorption standards of 250 μM As(V) or Zn(II) reacted in 10-, 100-, and 1000-ppm goethite suspensions for 4 weeks, and aqueous 25 mM Na_2HAsO_4 and 25 mM acidified ZnCl_2 standards. These reference phases served as controls for comparative purposes to the co-sorption samples. The co-sorption samples consisted of 250 μM As(V) and Zn(II) reacting for either 24 h, 2 or 4 weeks, or 6 months in either 10-, 100-, or 1000-ppm goethite suspensions at pH 7. The solids of experimental and reference samples in the 1000-ppm goethite treatment were harvested via centrifugation and pasted into a Teflon sample holder, sealing both ends with Kapton tape. For experimental and reference samples of the 10- and 100-ppm goethite suspensions, between 1 and 2 L of suspensions were syringe-filtered over two to three 25-mm ($0.22\text{-}\mu\text{m}$) filter papers to deposit even layers of the solid phase onto the filter papers. The filter papers were then sealed within two sheets of Kapton tape and were superimposed at the beamline to optimize the transmitted or fluorescence signal, depending on the data acquisition mode. All EXAFS samples are summarized in Table 2 containing pertinent information regarding aging times, loading levels, and Zn:As surface loading ratios.

Arsenic and Zn K-edge EXAFS spectroscopic data were collected at beamline X11-A of the National Synchrotron Light Source (Brookhaven National Laboratories, Upton, NY). The technical operating specifics of the National Synchrotron Light Source and beamline X-11A have been described in detail elsewhere (Arai et al., 2004; O'Reilly et al., 2001; Pandya, 1994; Roberts et al., 2003). The ionization chamber was filled with 90% N_2 and 10% Ar gas for As K-edge EXAFS experiments and 85% and 15% N_2 and Ar, respectively, for Zn K-edge EXAFS experiments. All sorption samples were oriented at 45° to the incident beam, and a Lytle Cell Detector was used to collect spectra in fluorescence mode. For As K-edge EXAFS experiments, the Lytle Cell Detector was purged every 4 to 6 h with Kr gas, whereas for Zn K-edge EXAFS experiments, the Lytle Cell Detector was purged continuously with Ar gas. The cooled monochromator double crystals (Si 111) were detuned by 30% in I_0 to reject higher order harmonics. For signal optimization and removal of elastically scattered radiation, the fluorescence signal was filtered by a Ge (As) or Cu (Zn) foil, one or two Al foils, and Soller slits. The monochromator angle was calibrated to the As(V) K-edge (11.874 KeV) using a diluted Na_2HAsO_4 standard (10 weight percent in boron nitride). The Zn K-edge (9.659 KeV) was calibrated using a metallic zinc foil. These standards were monitored with a reference ion chamber simultaneous to sample collection to check for potential shifts in their respective K-edges due to monochromator drifts. Multiple scans were collected at room temperature for each sample to improve the signal-to-noise ratio for data analysis. Spectra of adamite, ojuelaite, and Na_2HAsO_4 (aq.) and ZnCl_2 (aq.) reference standards were collected in transmission mode. All other spectra were collected simultaneously in transmission and fluorescence mode.

All data were analyzed with WinXAS 2.1 and later versions (Ressler, 1998) using the following procedure (Bunker, 2003). Individual spectra

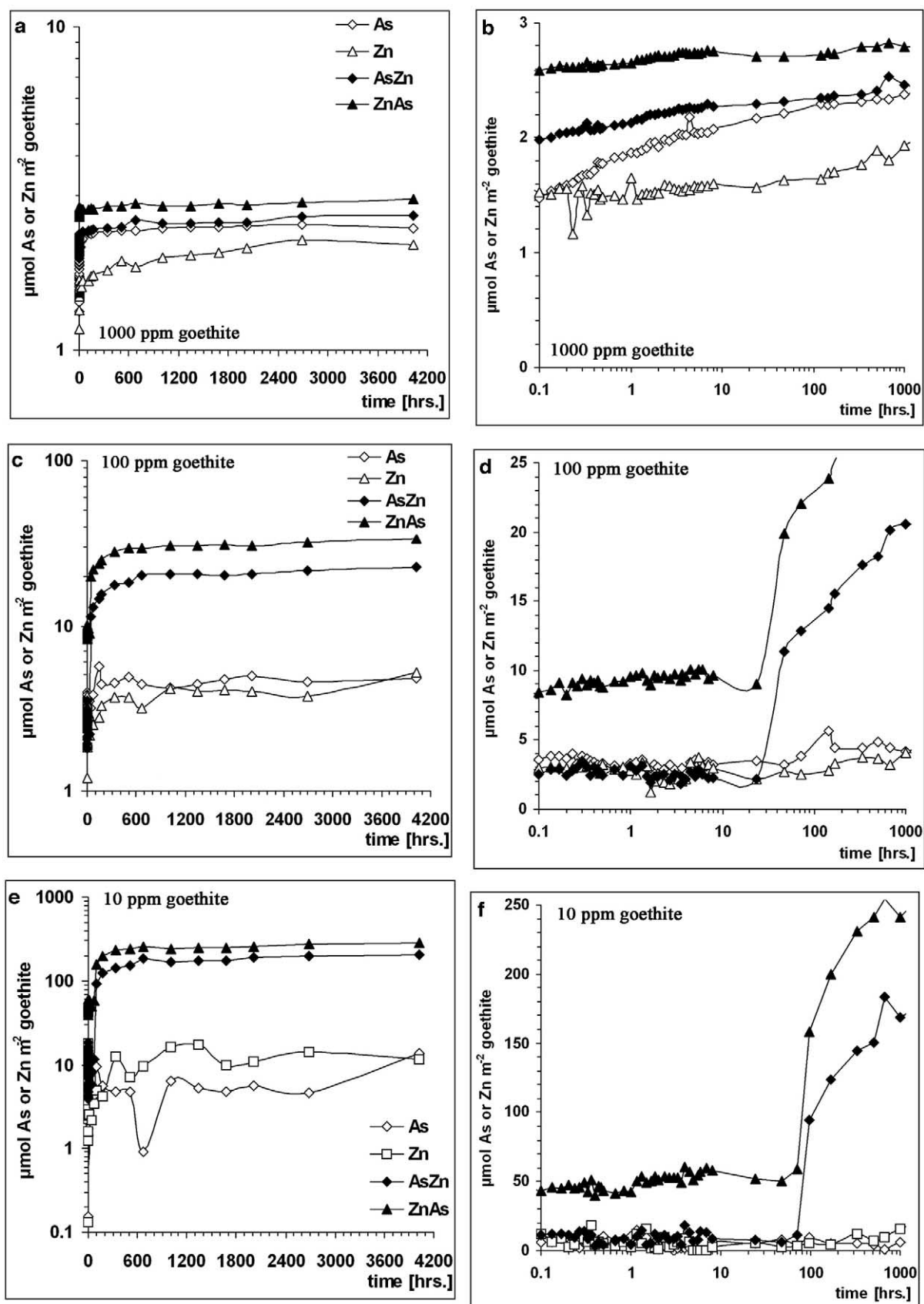


Fig. 1. (A–F) As(V) and Zn(II) single and co-sorption experiments as a function of time in (A and B) 1000-ppm goethite suspension, (C and D) 100-ppm goethite suspension, and (E and F) 10-ppm goethite suspension.

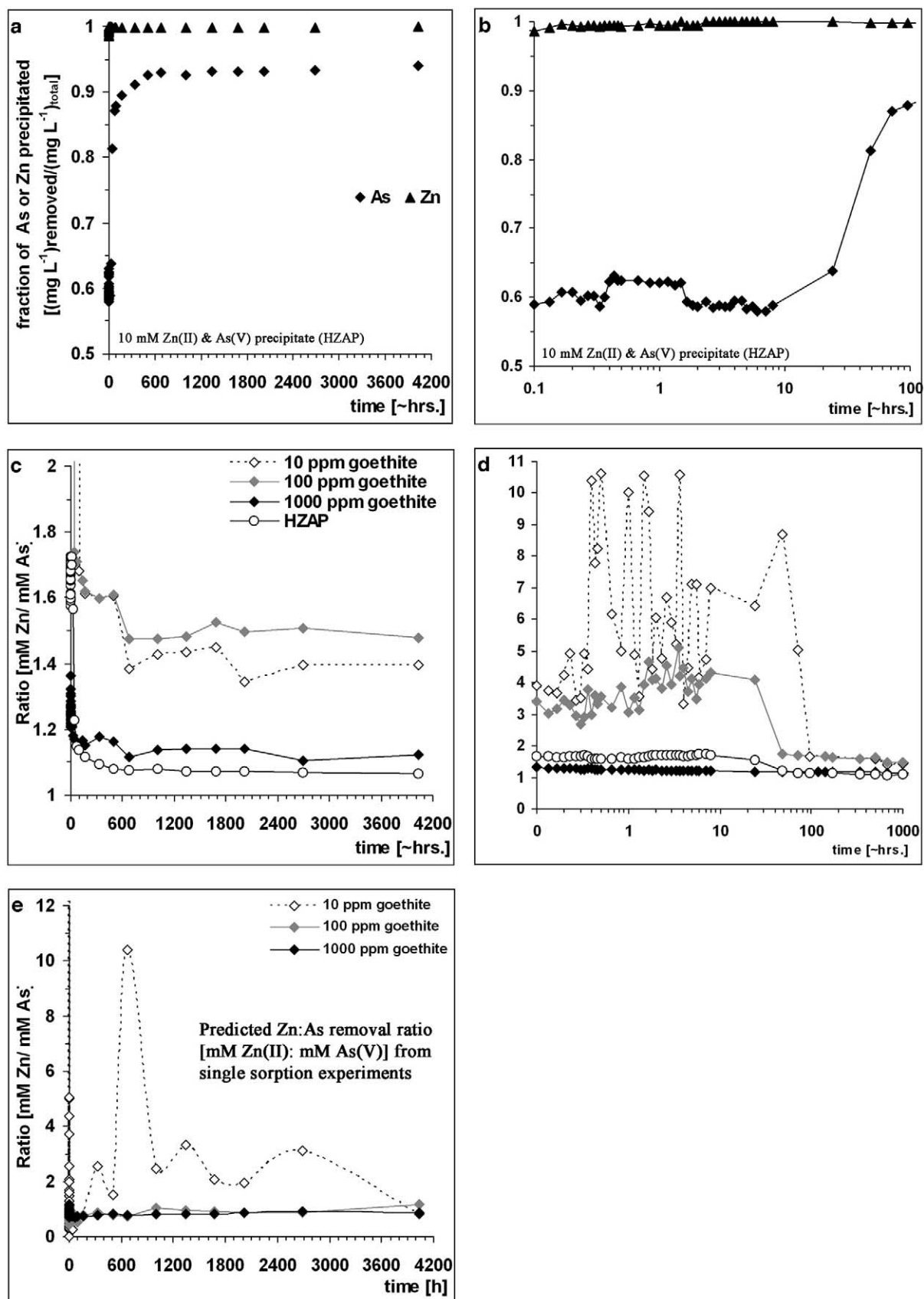


Fig. 2. A-E: (A, B) Formation of a homogeneous zinc-arsenate $[(10 \text{ mM})_i]$ precipitate (HZAP). (C, D) Molar Zn:As removal ratios plotted as a function of time and goethite suspension density. (E) The predicted molar Zn:As removal ratios from single sorption experiments.

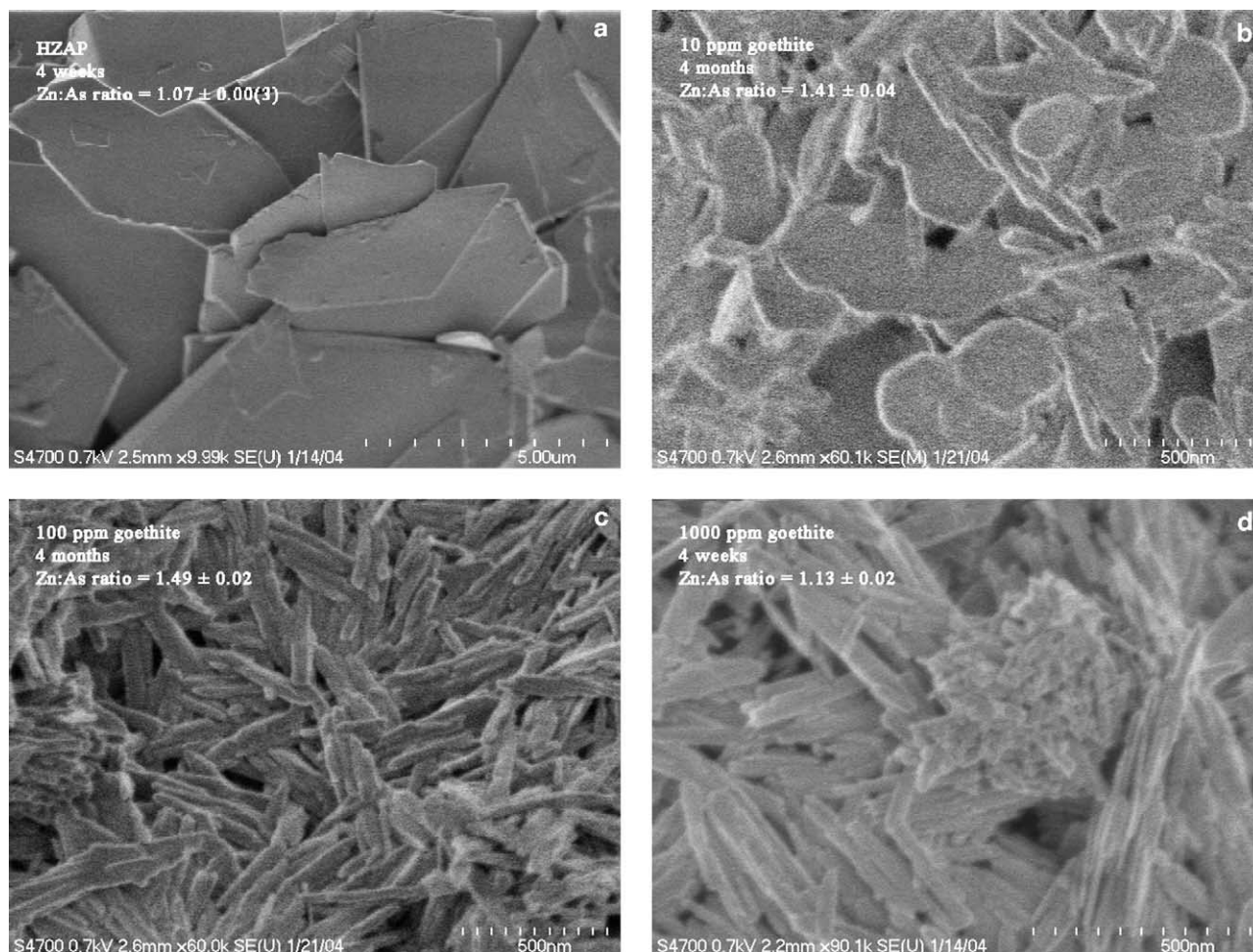


Fig. 3. Field emission-scanning electron micrographs of co-sorbed solid phases after 4 weeks or 4 months. (A) HZAP: a plate like-precipitate (resolution = 5.00 μm). (B) 10-ppm goethite: plate-like precipitate with intermittent goethite particles (rod shapes, resolution 500 nm). (C) 100-ppm goethite: the sorption phase is not distinguishable from goethite (resolution 500 nm). (D) 1000-ppm goethite: the sorption phase is not distinguishable from goethite (resolution 500 nm).

were background corrected and normalized before averaging. Averaged spectra were converted from energy to photo-electron wave vector (k) units (k = is the wave vector number with units of $\text{\AA}^{-1}$) by assigning the origin, E_0 , to the first inflection point of the absorption edge (As(V) = 11.874 KeV; Zn = 9.659 KeV). The EXAFS was extracted using a cubic spline function consisting of ≤ 7 knots applied over an average range in k -space (As: 2.0–13.0 $\text{\AA}^{-1}$; Zn: 1.5–12.0 $\text{\AA}^{-1}$). Fourier transformation of the raw $k^3\chi(k)$ function was performed (As: 2.75–12.50 $\text{\AA}^{-1}$; Zn: 2.0–10.0 $\text{\AA}^{-1}$) to obtain a radial structure function (RSF) using a Bessel window function and a smoothing parameter (β) of 4 to minimize truncation effects in RSFs. The FEFF 7.02 program (Zabinsky et al., 1995) was used to calculate theoretical phase and amplitude functions of As-O, As-Fe, As-Zn, and Zn-O, Zn-As, Zn-Fe, and Zn-Zn scattering paths using input files based on the structural refinement of mapimite ($\text{Zn}_2\text{Fe}_3[\text{AsO}_4]_3(\text{OH})_4 \cdot 10\text{H}_2\text{O}$), adamite, and korinigte ($\text{Zn}[\text{AsO}_3\text{OH}] \cdot \text{H}_2\text{O}$) (Ginderow and Cesborn, 1981; Hill, 1976; Keller et al., 1980). Individual shell contributions in the RSFs of reference standards and model sorption samples were Fourier back transformed for nonlinear least-square shell fitting. The obtained parameters were then used for a sequential fitting procedure that recorded the reduction of the fit's residual until the best fit of the raw k^3 -weighted $\chi(k)$ function was obtained.

The FEFF 7.02 program was used to calculate the theoretical phase and amplitude function of a noncollinear As-O-O-As multiple scattering path using an input file based on the structural refinement

of mapimite and adamite. Noncollinear As-O-O-As multiple scattering (MS) contributions to the EXAFS spectrum were fit to all spectra by correlating (linking to the same value) the mean-square disorder of the radial distance (σ^2) of the As-O single scattering path to σ^2 of the MS As-O-O-As path. The number of permissible free floating parameters (N_{pts}) in all samples ranged between 15 and 18 depending on Zn vs. As EXAFS data (Stern, 1993). For each fit, the coordination number (CN), the radial distance ($R \sim \text{\AA}$), the mean-square disorder of the radial distance (a Debye-Waller parameter, $\sigma^2 \sim \text{\AA}^2$), and a single, cross-correlated (linked to the same value) phase shift value (ΔE_0) for all single and multiple backscattering paths were allowed to vary.

The amplitude reduction factor (S_0^2) was fixed to 0.9 for As fits and to 0.85 for Zn fits. The estimated accuracies for the fit parameters, CN and R , were based on a comparison of our best fit results for adamite with values from refined X-ray diffraction (XRD) measurements published in the literature (Hill, 1976). For the first shell of As(V), the estimated accuracy of the CN was $\pm 5\%$ and $\pm 0.02 \text{ \AA}$ for R ; for the second shell of As, the accuracy of the CN was $\pm 20\%$ and $\pm 0.02 \text{ \AA}$ for R . For the first shell of Zn, the accuracy of the CN was $\pm 3\%$ and $\pm 0.04 \text{ \AA}$ for R ; for the second shell of Zn, the accuracy of the CN was $\pm 50\%$ and $\pm 0.03 \text{ \AA}$ for R . The accuracy of Zn's second shell CN magnitude is a conservative estimate, because the backscattering waves from three distinct second shell neighbors partially cancelled each other out. Hence, approximately only 50% of the true CN magnitude could

Table 1. Sorption rates of As(V) and Zn(II) under single and co-sorbing conditions in 0-, 10-, 100-, and 1000-ppm goethite suspensions.

	$\Delta[\text{As,Zn}]/\Delta[t]^a$						
Time frames	0–8 h	24–48 h	72–96 h	24 h–14 d	72 h–14 d	14 d–6 m	24 h–6 m
ppm goethite							
1000							
As ^b	18.13						3.38*10 ^{−3}
Zn ^b	13.89						9.20*10 ^{−3}
As(Zn) ^c	19.84						5.48*10 ^{−3}
Zn(As) ^c	24.00						3.77*10 ^{−3}
100							
As ^b	2.78						1.73*10 ^{−3}
Zn ^b	2.61						5.34*10 ^{−3}
As(Zn) ^c	1.96	2.68		0.35		9.25*10 ^{−3}	
Zn(As) ^c	8.44	3.15		0.43		9.67*10 ^{−3}	
10							
As ^b	0.63						1.43*10 ^{−3}
Zn ^b	0.22						1.64*10 ^{−3}
As(Zn) ^c	0.72		0.24		0.35	1.07*10 ^{−2}	
Zn(As) ^c	5.03		0.29		0.46	9.49*10 ^{−3}	
0 (HZAP)							
As	735						4.49 ^d
Zn	1250						3.86*10 ^{−2d}

^a [$\mu\text{mol As, Zn L}^{-1}\text{h}^{-1}$] removed from solution.^b Single sorption system.^c Co-sorption system. The sorption rates apply to the element not in parentheses.^d Rate refers to the amount of As and Zn removed from solution between 24 h and 4 weeks.

be fit. For σ^2 , the standard deviation of the population is reported for first and second shell neighbors. Results are reported for multi-shell fits of raw k^3 -weighted $\chi(k)$ -functions (Tables 3a, 3b, Tables 4a, 4b; Fig. 4A,B, Fig. 5A,B, Fig. 6A,B, and Fig. 7A,B).

2.2.3. Dissolution Experiments

Twenty-milliliter aliquots of suspension were extracted from long-term (6-month) single and co-sorption sorption samples (in-

Table 2. EXAFS sample summary and pertinent sample information.

Sample name	ppm Goethite	Reaction time	Surface loading ($\Gamma \sim \mu\text{mol m}^{-2}$)		Zn:As [$\Gamma \text{ Zn}:\Gamma \text{ As}$]
			As	Zn	
Single sorption systems ^a					
^{4w} As ₁₀	10	4 wk	5.58	(3.28)	0.59
^{4w} As ₁₀₀	100	4 wk	4.48	(3.01)	0.67
^{4w} As ₁₀₀₀	1000	4 wk	2.16	(1.65)	0.76
^{4w} Zn ₁₀	10	4 wk	(5.58)	3.28	0.59
^{4w} Zn ₁₀₀	100	4 wk	(4.48)	3.01	0.67
^{4w} Zn ₁₀₀₀	1000	4 wk	(2.16)	1.65	0.76
HZAP	0	4 wk	8.06 ^b	9.99 ^b	1.24
Co-sorption systems					
As EXAFS	ZnEXAFS				
^{24h} AsZn ₁₀	^{24h} ZnAs ₁₀	10	12.20	48.06	3.94
^{2w} AsZn ₁₀	^{2w} ZnAs ₁₀	10	115.70	184.48	1.59
^{6m} AsZn ₁₀	^{6m} ZnAs ₁₀	10	196.82	293.86	1.49
^{24h} AsZn ₁₀₀	^{24h} ZnAs ₁₀₀	100	3.34	11.30	3.38
^{2w} AsZn ₁₀₀	^{2w} ZnAs ₁₀₀	100	17.78	27.60	1.55
^{6m} AsZn ₁₀₀	^{6m} ZnAs ₁₀₀	100	20.54	34.31	1.67
^{24h} AsZn ₁₀₀₀	^{24h} ZnAs ₁₀₀₀	1000	2.52	3.02	1.20
^{2w} AsZn ₁₀₀₀	^{2w} ZnAs ₁₀₀₀	1000	2.64	3.01	1.14
^{6m} AsZn ₁₀₀₀	^{6m} ZnAs ₁₀₀₀	1000	2.57	3.03	1.18
Aqueous and mineral phases					
Na ₂ HAsO ₄ (aq.)					
ZnCl ₂ (aq.)					
Adamite					
Ojuelaite					
$\text{Zn}_2(\text{AsO}_4)\text{OH}$ $\text{ZnFe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2-4\text{H}_2\text{O}$					

EXAFS = extended X-ray absorption fine structure.

^a Nomenclature examples: ^{time}As_{ppm goethite} or ^{time}ZnAs_{ppm goethite}.^b $\sim$ mM of As or Zn removed from solution.

Table 3a. Summary of As K-edge EXAFS parameters of reference phases.

Sample	Atom	As-O, As-O-O-As (MS)				As-Fe/Zn					ΔE_0^f
		CN ^a $\pm$ 5%	R ^b $\pm$ 0.02	σ^2 ^c $\pm$ 0.001	Res. ^d	Atom	CN $\pm$ 20%	R $\pm$ 0.02	σ^2 ^e $\pm$ 0.003	Res. ^d	
Na ₂ HAsO ₄ (aq.)	O	4.6	1.69	0.003	14.6					14.6	5.08
	MS	7.7	3.10	0.003	13.7					13.7	
^{4w} As ₁₀₀₀	O	4.3	1.70	0.002	21.4	Fe	2.0	3.32	0.007	13.3	5.09
	MS	18.7	3.23	0.002	17.7	Fe	0.5	2.80	0.007	12.5	
^{4w} As ₁₀₀	O	4.1	1.69	0.002	24.4	Fe	2.0	3.29	0.007	17.6	5.88
	MS	18.9	3.22	0.002	20.7	Fe	0.6	2.80	0.007	17.1	
^{4w} As ₁₀	O	4.0	1.69	0.001	22.7	Fe	1.8	3.29	0.006	14.0	5.86
	MS	19.2	3.21	0.001	18.7	Fe	0.6	2.80	0.006	12.5	
Ojuelaite	O	4.0	1.70	0.001	24.0	Fe/Zn	2.5	3.34	0.011	17.7	4.66
	MS	17.0	3.16	0.001	20.8	Fe/Zn	0.9	2.77	0.011	16.7	
HZAP	O	3.9	1.70	0.002	24.8	Zn	1.3	3.28	0.002	17.6	5.37
	MS	10.4	3.15	0.002	22.7	Zn	1.7	3.42	0.002	16.7	
Adamite	O	4.0	1.70	0.001	49.8	Zn	6.4	3.37	0.006	20.0	6.66
	MS	14.0	3.19	0.001	49.4	Zn ^g	7.4	3.36	0.007	21.8	5.27

EXAFS = extended X-ray absorption fine structure; HZAP = homogeneous zinc–arsenate precipitate.

^a CN = coordination number.

^b R = radial distance, Å.

^c σ^2 = mean square disorder of R (Å²). The σ^2 of As-O scattering and MS paths were correlated (linked to the same value).

^d Res. = residual. The progressive decline of the residual is recorded for each additional shell added to the fit. The listed parameters (CN, R, σ^2 , ΔE_0) reflect the final best fit.

^e σ^2 of second shell scattering paths were correlated (linked to the same value).

^f ΔE_0 = phase shift, eV.

^g Fit result obtained when the CN_{MS} and R_{MS} were fixed at optimized values of 12 and 3.05 Å for adamite, respectively.

Table 3b. Summary of As K-edge EXAFS parameters for AsZn co-sorption samples.

Sample	Atom	As-O, As-O-O (MS)				As-Fe/Zn					ΔE_0^f
		CN ^a $\pm$ 5%	R ^b $\pm$ 0.02	σ^2 ^c $\pm$ 0.001	Res. ^d	Atom	CN $\pm$ 20%	R $\pm$ 0.02	σ^2 ^e $\pm$ 0.003	Res. ^d	
^{24h} AsZn ₁₀₀₀	O	4.3	1.70	0.002	21.3	Fe/Zn	2.0	3.32	0.008	16.5	4.82
	MS	15.2	3.24	0.002	18.4	Fe	0.6	2.83	0.008	15.7	
^{2w} AsZn ₁₀₀₀	O	4.5	1.70	0.002	20.8	Fe/Zn	1.5	3.31	0.008	15.9	4.38
	MS	17.6	3.20	0.002	17.9	Fe	0.5	2.75	0.008	15.0	
^{4w} AsZn ₁₀₀₀	O	4.3	1.70	0.002	20.2	Fe/Zn	1.8	3.31	0.007	14.4	4.59
	MS	16.9	3.22	0.002	17.0	Fe	0.6	2.80	0.007	13.2	
^{24h} AsZn ₁₀₀	O	4.5	1.69	0.002	21.4	Fe/Zn	3.6	3.31	0.016	18.3	6.80
	MS	13.6	3.20	0.002	19.6	Fe/Zn ^g	1.1	3.32	0.007	18.4	6.72
^{2w} AsZn ₁₀₀	O	4.4	1.70	0.002	24.9	Zn ^h	6.2	3.33	0.015	14.6	7.52
	MS	11.9	3.13	0.002	22.4	Zn	2.3	3.30	0.004	14.2	7.43
						Zn	2.0	3.43	0.004	14.2	7.43
^{6m} AsZn ₁₀₀	O	4.5	1.69	0.002	41.8	Zn	6.42	3.34	0.008	16.9	7.22
	MS	11.7	3.11	0.002	40.6	Zn ⁱ	6.9	3.34	0.008	17.6	6.71
						Zn ^j	5.0	3.33	0.006	17.3	7.46
^{24h} AsZn ₁₀	O	4.5	1.69	0.002	17.7	Fe/Zn	2.0	3.28	0.013	15.2	6.72
	MS	11.0	3.16	0.002	16.3	Fe/Zn ^g	0.7	3.29	0.006	15.3	6.43
^{2w} AsZn ₁₀	O	4.2	1.69	0.002	21.9	Zn	2.6	3.28	0.009	14.1	6.72
	MS	9.9	3.08	0.002	19.7						
^{6m} AsZn ₁₀	O	5.0	1.69	0.003	29.0	Zn	4.6	3.46	0.009	21.2	6.33
	MS	11.7	3.07	0.003	28.7	As	3.3	4.04	0.009	19.4	

^a CN = coordination number.

^b R = radial distance, Å.

^c σ^2 = mean square disorder of R (Å²). The σ^2 of As-O scattering and MS paths were correlated (linked to the same value).

^d Res. = residual. The progressive decline of the residual is recorded for each additional shell added to the fit. The listed parameters (CN, R, σ^2 , ΔE_0) reflect the final best fit.

^e σ^2 of As-Me scattering paths were correlated (linked to the same value).

^f ΔE_0 = phase shift, eV.

^g Fit results, when σ^2 was fixed to 0.007, which is σ^2 in ^{24h}As₁₀₀; fit results when σ^2 was fixed to 0.006, which is σ^2 in ^{24h}As₁₀.

^h Fit results, when the second shell is not split over two distinct radial distances. The CN is overestimated due to $\sigma^2 > 0.01$ Å². Fit results below show how σ^2 and CN dropped by distributing second shell Zn neighbors over 3.30 and 3.43 Å, respectively.

ⁱ Fit result obtained when the CN_{MS} and R_{MS} were fixed at optimized values of 12 and 3.05 Å for adamite, respectively.

^j Fit result obtained when σ^2 was fixed to 0.006. The CN is 5.0, which is significantly greater than a CN of 4 indicative of legrandite.

Table 4a. Summary of Zn K-edge EXAFS parameters of reference phases.

Sample	Zn-O					Zn-As/Fe/Zn					ΔE_0^f
	Atom	CN ^a $\pm$ 3%	R ^b $\pm$ 0.04	σ^{2c} $\pm$ 0.002	Res. ^d	Atom	CN $\pm$ 50%	R $\pm$ 0.03	σ^{2e} $\pm$ 0.002	Res. ^d	
ZnCl ₂ (aq.)	O	6.2	2.10	0.009						21.9	3.68
^{4w} Zn ₁₀₀₀	O	4.1	2.04	0.004	39.8	Fe	1.3	3.07	0.010	34.8	3.03
	O	0.8	2.23	0.004	39.7	Fe	2.0	3.24	0.010	34.8	
^{4w} Zn ₁₀	O	5.7	2.05	0.011	36.0	Fe	0.9	3.05	0.008	32.4	1.58
						Fe	1.6	3.26	0.008	31.4	
HZAP	O	5.2	2.09	0.009	34.3	Zn	0.7	3.09	0.008 ^g	28.5	5.08
						As	0.8	3.32	0.008 ^g	26.9	
Adamite	O	5.6	2.04	0.009	48.4	Zn	1.4	3.04	0.006	23.2	3.42
						Zn	1.8	3.63	0.006	16.2	
						As	2.2	3.35	0.006	15.8	

EXAFS = extended X-ray absorption fine structure;

HZAP = homogeneous zinc-arsenate precipitate.

^a CN = coordination number.^b R = radial distance, Å.^c σ^2 = mean square disorder of R (Å²). The σ^2 of two Zn-O backscattering paths were correlated (linked to the same value).^d Res. = residual. The progressive decline of the residual is recorded for each additional shell added to the fit. The listed parameters (CN, R, σ^2 , ΔE_0) reflect the final best fit.^e σ^2 of multiple Zn-Me scattering paths were correlated (linked to the same value).^f ΔE_0 = phase shift, eV.

cluding HZAP), and placed in 35-mL centrifuge tubes. The suspensions were centrifuged for 20 min at 15,000 rpm, and an aliquot of the supernatant was removed and syringe-filtered for ICP-AES analysis of the As, Fe, and Zn content in solution. The solids were

then resuspended with 20 mL of either 0.01 M NaCl (pH 5.5, 10^{-5.5} M HCl) or 0.01 M NaCl (pH 4, 10⁻⁴ M HCl) solutions and placed on a Ferris-wheel (end-over) shaker. Solutions were exchanged twice a day for the first 4 days of the experiments and thereafter

Table 4b. Summary of Zn K-edge EXAFS parameters for ZnAs co-sorption samples.

Sample	Zn-O					Zn-As/Fe/Zn					ΔE_0^f
	Atom	CN ^a $\pm$ 3%	R ^b $\pm$ 0.03	σ^{2c} $\pm$ 0.002	Res. ^d	Atom	CN $\pm$ 50%	R $\pm$ 0.03	σ^{2e} $\pm$ 0.002	Res. ^d	
^{24h} ZnAs ₁₀₀₀	O	4.9	2.04	0.009	35.2	Fe	1.2	3.15	0.007	30.7	2.46
						As/Fe	1.2	3.34	0.007	30.7	
^{2w} ZnAs ₁₀₀₀	O	5.1	2.04	0.010	32.3	Fe	0.6	3.04	0.005	28.0	2.29
						Fe	1.2	3.24	0.005	27.4	
^{4w} ZnAs ₁₀₀₀	O	4.7	2.04	0.010	34.0	Fe	0.8	3.08	0.002	28.8	2.05
						Fe	1.8	3.27	0.002	28.8	
						Fe	0.9	3.46	0.002	27.4	
^{24h} ZnAs ₁₀₀	O	6.0	2.02	0.012	28.2	Fe/Zn	0.9	3.08	0.010	27.0	0.52
						As/Fe	1.2	3.27	0.010	25.8	
^{2w} ZnAs ₁₀₀	O	6.6	2.07	0.009	34.4	Zn	0.9	3.05	0.006	27.6	3.45
						As	0.6	3.26	0.006	26.7	
						Zn	0.4	3.71	0.006	26.4	
^{6m} ZnAs ₁₀₀	O	5.1	2.02	0.006	39.7	Zn	0.6	3.00	0.005	31.0	2.59
						Zn	1.4	3.62	0.005	27.1	
						As	1.4	3.36	0.005	23.4	
^{24h} ZnAs ₁₀	O	5.3	2.00	0.009	27.2	Fe/Zn	1.5	3.17	0.006	24.6	3.30
	O	0.7	2.19	0.009	27.2	As	2.0	3.29	0.006	22.1	
						As	0.7	3.47	0.006	21.6	
^{2w} ZnAs ₁₀	O	4.5	1.97	0.007	41.5	Zn	3.1	3.23	0.008	27.5	2.89
	O	1.5	2.15	0.007	40.3	As	2.8	3.34	0.008	23.2	
^{6m} ZnAs ₁₀	O	4.3	2.00	0.008	39.4	Zn	0.6	3.15	0.006	30.2	3.48
	O	1.9	2.18	0.008	37.6	As	0.6	3.42	0.006	22.8	
						As	0.6	3.72	0.006	20.9	

^gFixed at value indicated.^a CN = coordination number.^b R = radial distance, Å.^c σ^2 = mean square disorder of R (Å²). The σ^2 of two Zn-O backscattering paths were correlated (linked to the same value).^d Res. = residual. The progressive decline of the residual is recorded for each additional shell added to the fit. The listed parameters (CN, R, σ^2 , ΔE_0) reflect the final best fit.^e σ^2 of multiple Zn-Me scattering paths were correlated (linked to the same value).^f ΔE_0 = phase shift, eV.

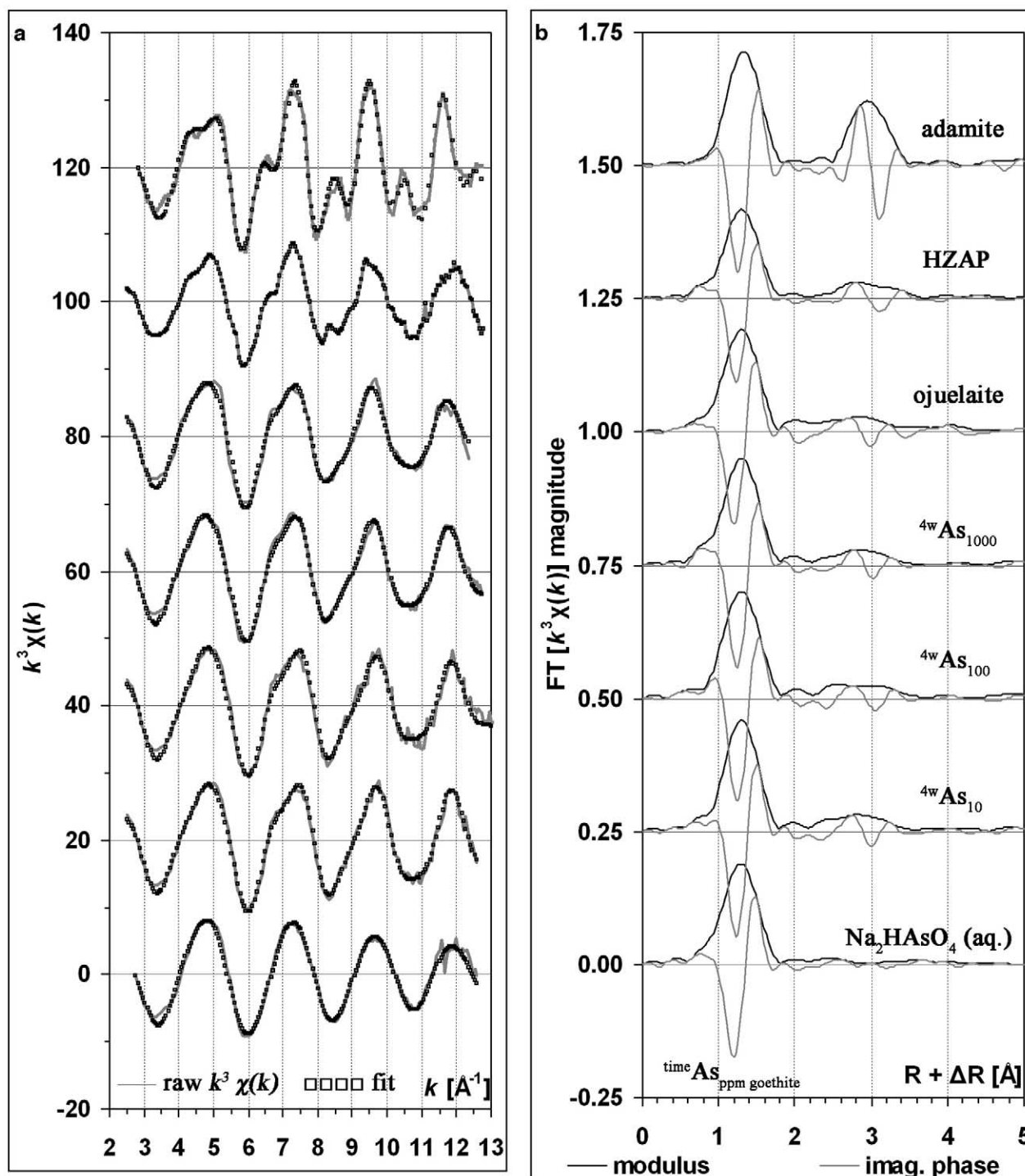


Fig. 4. K^3 -weighted $\chi(k)$ spectra of As reference compounds (A) and their radial structure functions (RSFs) (B).

once a day on every second or third day. Solid-liquid separation was achieved via centrifugation for 20 min at 15,000 rpm, and an aliquot was syringe filtered for ICP-AES or graphite furnace atomic absorption analysis of As, Fe, and Zn. The remaining supernatant was vacuum-siphoned to minimize the loss of solids. The experiments were run in duplicate, and averaged results are reported (Fig. 8A–F, Fig. 9A–F).

3. RESULTS

3.1. Sorption Kinetics

Common, biphasic sorption reactions were observed in both single and co-sorption experiments of As(V) and Zn(II)

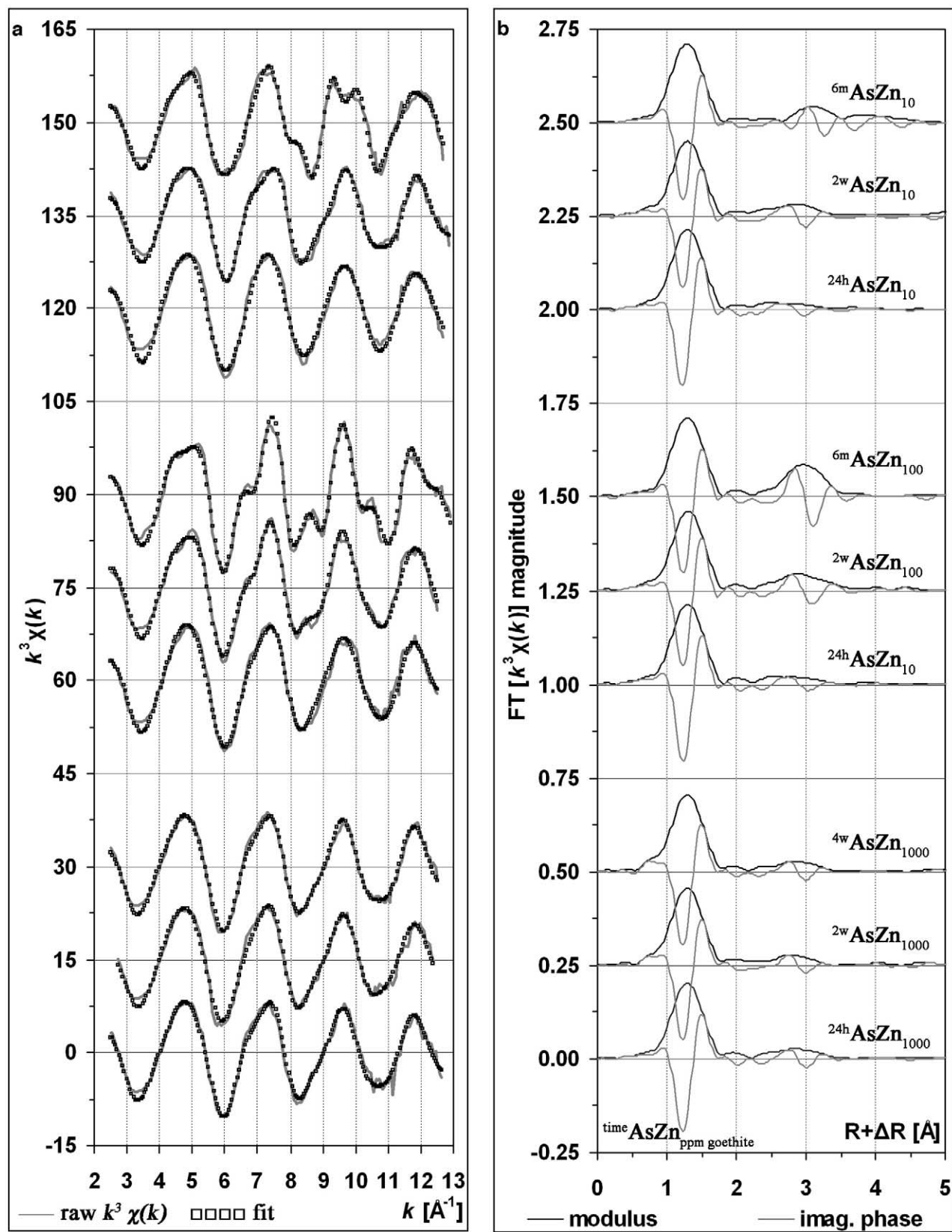


Fig. 5. K^3 -weighted $\chi(k)$ spectra of (A) AsZn co-sorption samples and their radial structure functions (RSFs, B) as a function of goethite suspension density and aging time.

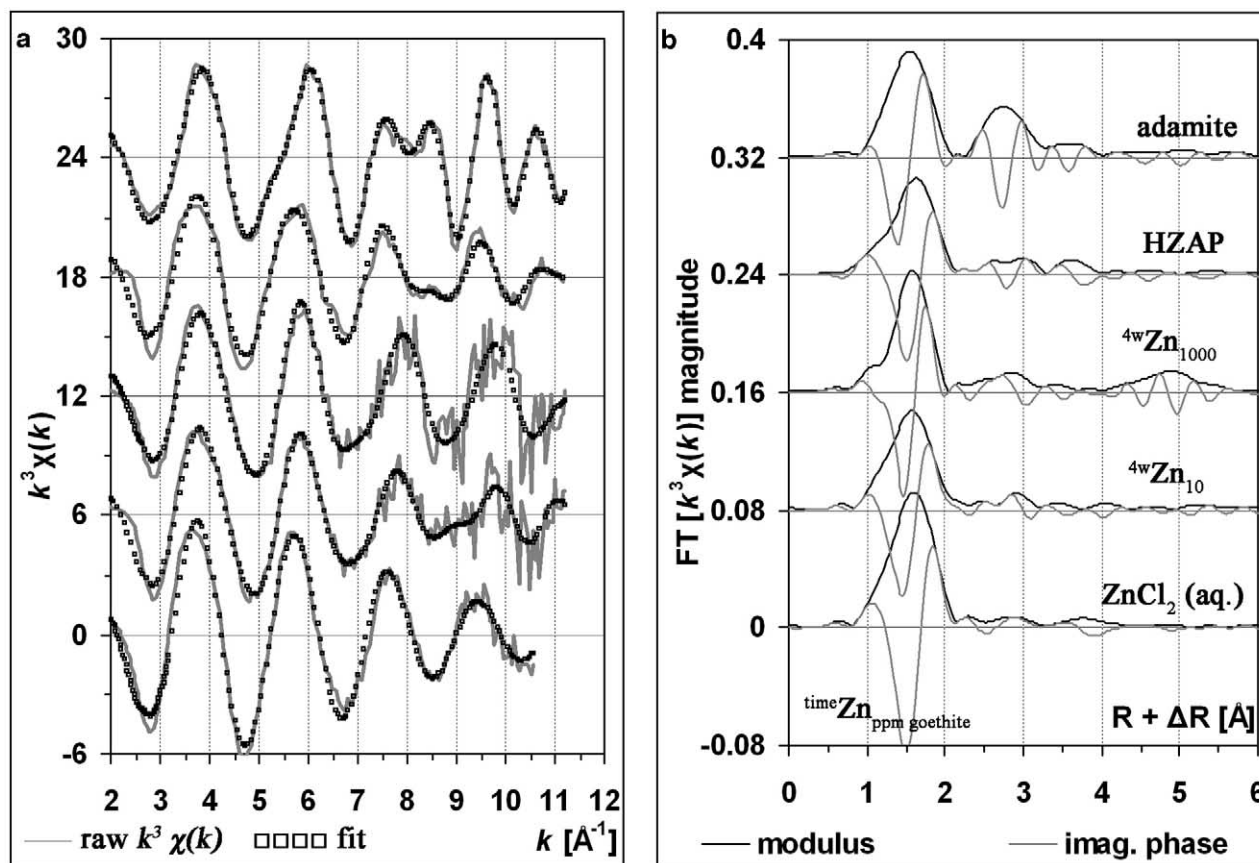


Fig. 6. K^3 -weighted $\chi(k)$ spectra of Zn(II) reference compounds (A) and their radial structure functions (RSFs, B).

in 1000-ppm goethite suspensions (Gräfe et al., 2001; Grossl and Sparks, 1995; McBride, 1994; O'Reilly et al., 2001; Sparks, 2002; Strawn et al., 1998; Xue and Huang, 1995). Approximately 95% As(V) and 72% Zn(II) sorbed on goethite in the first 8 h (Fig. 1A,B). The initial sorption rates (0–8 h) increased by one order of magnitude with every order of magnitude increase in goethite suspension density (Table 1), suggesting that the rate of sorption was dependent among other factors on the number of available surface sites. An apparent equilibrium concentration of As(V) on goethite was reached after 24 h at $\sim 2.5 \mu\text{mol m}^{-2}$, which was similar to site saturation values obtained in previously conducted isotherm experiments (3.2 and $2.2 \mu\text{mol m}^{-2}$ at pH 4 and 7, respectively) (Gräfe et al., 2004). Arsenate sorption did not accelerate or increase in the presence of Zn(II); however, Zn(II) sorption was $\sim 42\%$ faster and yielded a 23% greater uptake (2.2 vs. $2.9 \mu\text{mol Zn(II) m}^{-2}$ goethite) in the presence of As(V) after 6 months.

Single As(V) and single Zn(II) sorption reactions in 10- and 100-ppm goethite suspensions were also biphasic in which 99% and 60%, respectively, of the sorption occurred in the first 24 h (Fig. 1C–F). An apparent equilibrium of As(V) in 10- and 100-ppm goethite was reached after 24 h at ~ 4.5 – $5.0 \mu\text{mol m}^{-2}$, which was greater than site saturation levels observed in single As(V) sorption isotherms on goethite at pH 4 (Gräfe et al., 2004). The equilibrium concentration of Zn on goethite after 24 h increased from ~ 2 to ~ 4

to $\sim 12 \mu\text{mol Zn m}^{-2}$ goethite with decreasing goethite suspension density. Zinc K-edge EXAFS spectroscopy would show later that the Zn(II) solid-phase speciation did not change as a function of the solid solution ratio, and solution measurements indicated that the Zn(II) surface loading did not exceed $3.28 \mu\text{mol Zn(II) m}^{-2}$ goethite for the EXAFS samples (Table 2). Therefore, significant amounts of Zn(II) in 10- and 100-ppm goethite suspensions were likely sorbed as outer sphere or weakly bound complexes.

Arsenate and Zn(II) co-sorption in 10- and 100-ppm goethite occurred as two successive, biphasic sorption reactions. Arsenate and Zn(II) sorption on goethite was rapid in the first 8 h followed by a steady-state period that lasted between 24 and 72 h depending on the goethite suspension density (Fig. 1 D,F). Arsenate sorption did not accelerate in the presence of Zn(II); however, Zn(II) sorption was 2 to 3 times faster in co-sorption experiments than in corresponding single sorption experiments and was 4 to 7 times faster than As(V) sorption in the co-sorption experiments (Table 1). Approximately 4 to $5 \mu\text{mol As m}^{-2}$ were sorbed within 8 h, suggesting that monolayer coverage of As(V) on goethite was not exceeded and a precipitate had not formed. The second biphasic sorption reaction occurred after 24 h in 100-ppm goethite suspensions and after 72 h in 10-ppm goethite suspensions, each significantly exceeding the surface saturations of single As(V) and Zn(II) reactions on

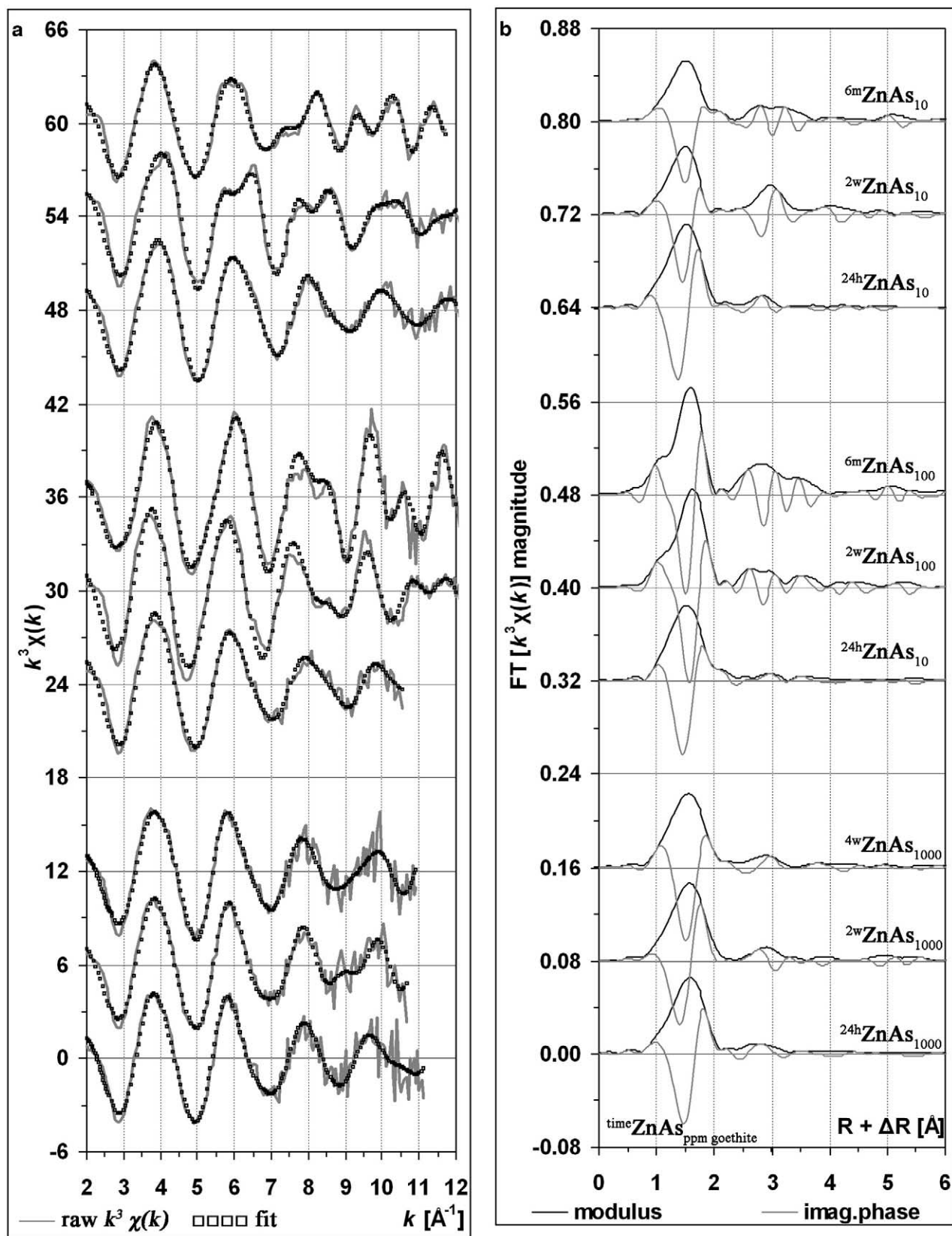


Fig. 7. K^3 -weighted $\chi(k)$ spectra (A) of ZnAs co-sorption samples and their radial structure functions (RSFs, B) as a function of goethite suspension density and aging time.

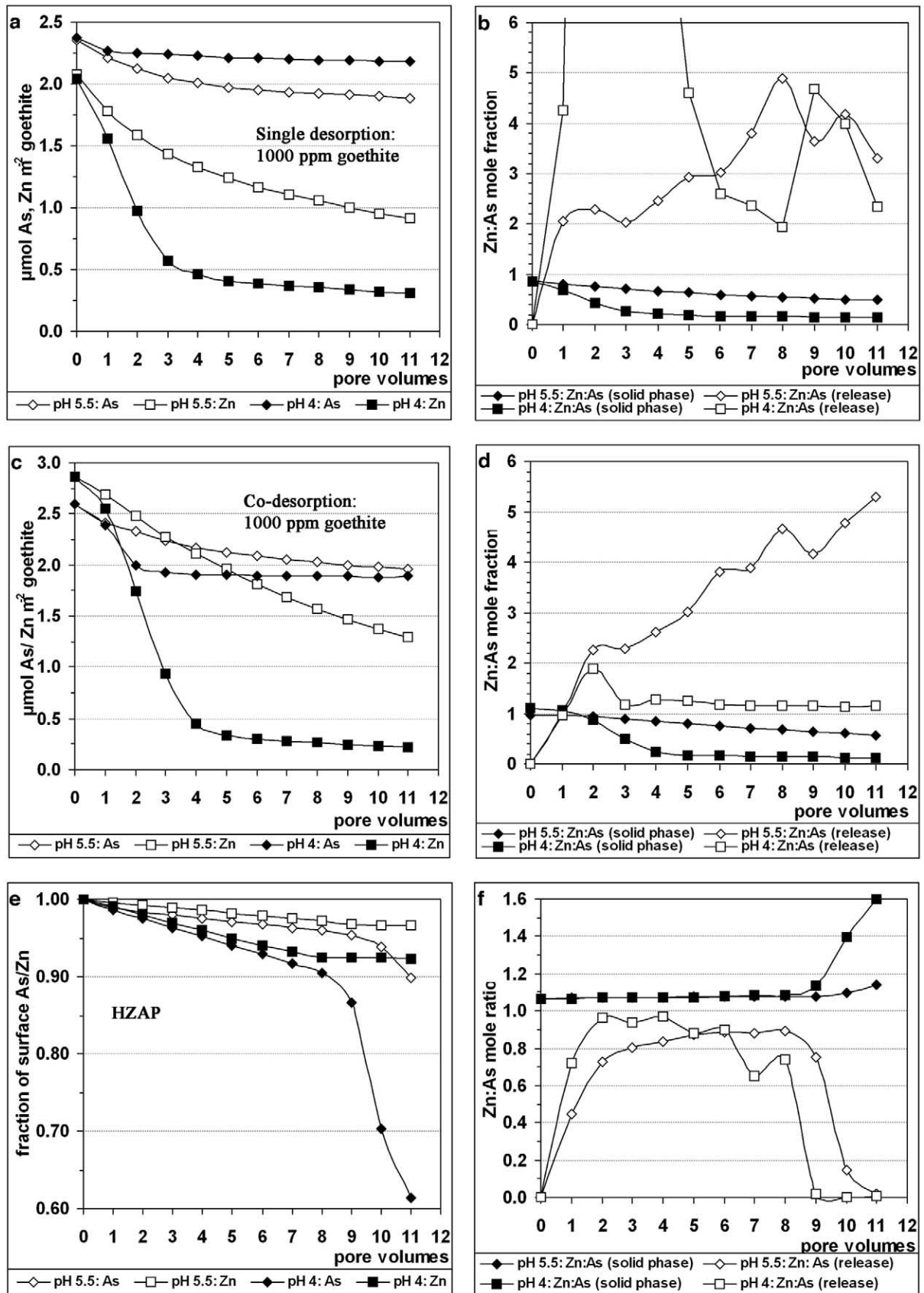


Fig. 8. Replenishment desorption. Desorption of As(V) and Zn(II) from 6-month aged, singly sorbed (A, B) and co-sorbed (C, D) phases in 1000-ppm goethite with Zn:As mole ratio of remaining surface density and release into solution. (E, F) Dissolution of the HZAP with Zn:As mole ratio of remaining solid phase and release into solution.

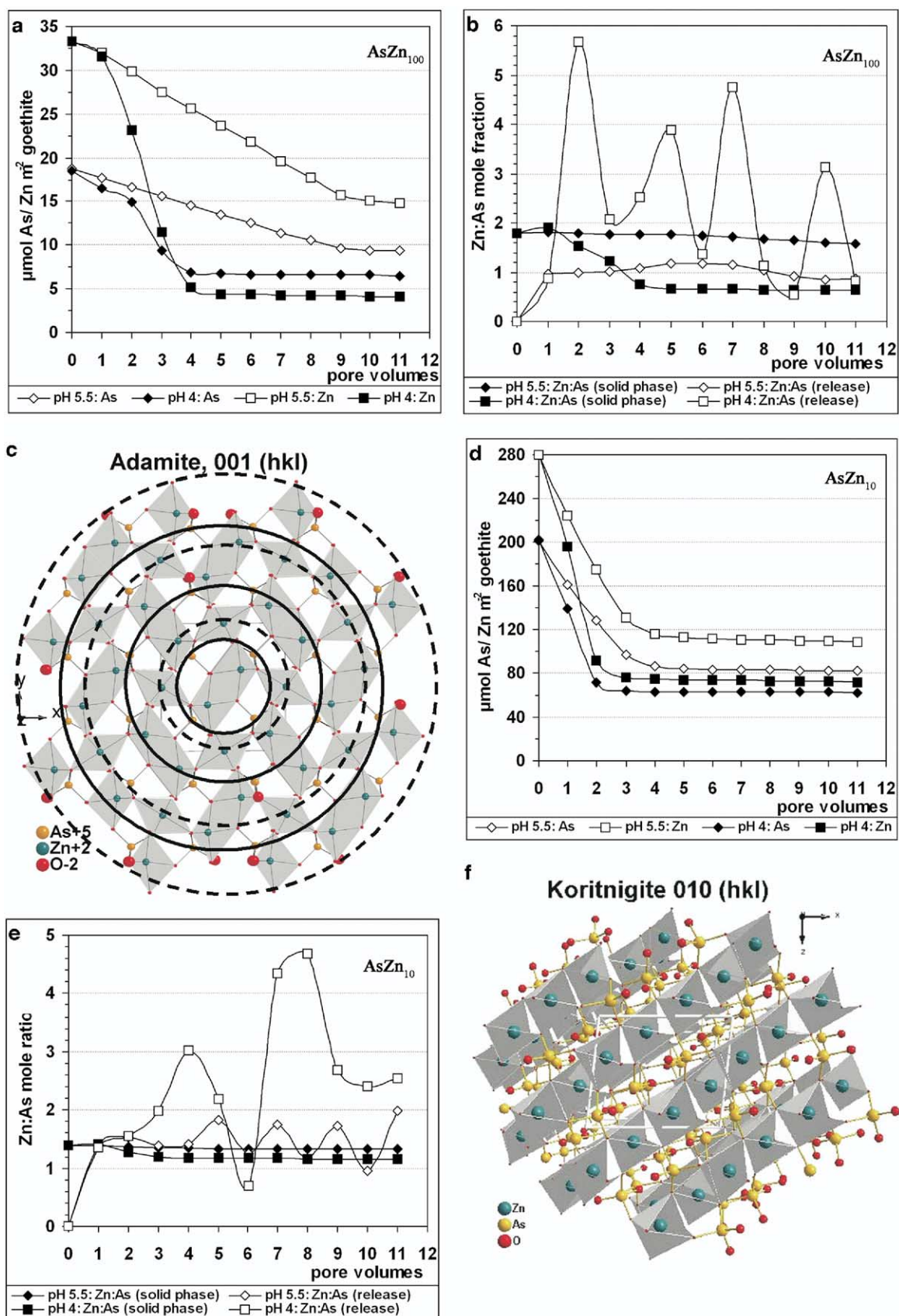


Fig. 9. Replenishment desorption of the adamite-like phases in 100-ppm goethite (A–C) and the koritnigite-like phase in 10-ppm goethite (D–F) after 6 months of aging time showing the remaining surface area density of As(V) and Zn(II) and the molar Zn:As ratio of the remaining solid phase and the release into solution.

goethite, suggesting that a precipitation reaction had occurred (Fig. 1). The initial sorption/precipitation rate of As(V) and Zn(II) (24–48 h and 72–96 h) was as rapid as the initial (0–8 h) sorption rates of As(V) and Zn(II) in 100-ppm goethite suspensions, and even the rate of sorption between 24/72 h and 14 d was as fast as initial (0–8 h) As(V) and Zn(II) sorption reactions in 10-ppm goethite suspensions (Table 1). After 14 d, the sorption rate dropped by two orders of magnitude and after 4 months, 90/71 and 77/55 percent Zn(II)/As(II) were removed from solution in the 10- and 100-ppm goethite suspensions, respectively.

The formation of a homogeneous zinc–arsenate precipitate (HZAP) from pH 7 adjusted, 10 mM Na_2HAsO_4 and ZnCl_2 solutions occurred in less than 2 min and removed more than 60% and 99% of As(V) and Zn(II) from solution in the first 4 minutes, respectively (Fig. 2A,B). A white precipitate formed within seconds of adding 10 mM Zn(II) to a 10 mM As(V) solution buffered at pH 7. The reaction conditions were oversaturated with respect to the saturation index ($\text{Zn}_3(\text{AsO}_4)_2 \cdot 2.5\text{H}_2\text{O}$: $\log \text{IAP}/K_{\text{so}} = +6.47$ at 10 mM As(V) and Zn(II); Gustafsson, 2004). Sorption occurring at and beyond 2 min reaction time was hence a heterogeneous nucleation/precipitation reaction “mediated” by the precipitate’s surface (Stumm, 1992). Between 8 h and 4 weeks, an additional 30% of As(V) were removed from solution, resulting in more than 90% removal of As(V) from solution. This reaction may have been due to adsorption reactions at external and internal surface sites of the precipitate. The initial precipitation rate (0–8 h) was one to five orders of magnitude greater than any of the initial Zn(II)/As(V) adsorption rates, and As(V) sorption onto the precipitate between 24 h and 4 weeks was as rapid or faster than the initial (0–8 h) As(V) sorption rates in 100-ppm goethite suspensions and initial Zn(II)/As(V) precipitation rates in 10- and 100-ppm goethite suspensions (Table 1).

The sorbed Zn:As ratio [mM Zn(II) vs. mM As(II) removed from solution] in co-sorption experiments was compared as a function of time and goethite suspension to predictions based on sorbed Zn:As ratios in single sorption experiments (Fig. 2C–E). Initially, the sorbed Zn:As ratio was $\gg 1$, indicating a more favorable uptake of Zn(II) over As(V) from solution. With increasing reaction time, however, the sorbed Zn:As ratio dropped below 2 reaching a steady state after ~ 4 weeks with distinguishable ratios that differed from the predicted single As(V) and Zn(II) sorption ratios (Fig. 2): 1.07 ± 0.003 (HZAP), 1.41 ± 0.04 (10-ppm goethite), 1.49 ± 0.02 (100-ppm goethite), and 1.13 ± 0.01 (1000-ppm goethite). The sorbed Zn:As ratios suggested that As(V) and Zn(II) co-sorption was an interdependent process in which the goethite suspension density could be dictating the formation of a specific zinc–arsenate solid phase. To corroborate this hypothesis further, field emission–scanning electron micrographs were collected of freeze-dried HZAP and 1000-ppm goethite system samples (4 weeks) and of 100- and 10-ppm goethite (4 months) samples (Fig. 3A–D). Micrographs of the 10-ppm goethite system and the HZAP showed a similar plate-like precipitate suggesting the formation of a similar precipitate. The 100- and 1000-ppm goethite micrographs showed only the needle-like goethite structure and were inconclusive concerning the formation of a zinc–arsenate precipitate.

3.2. EXAFS Spectroscopy

To ascertain the formation of a zinc–arsenate precipitate, the local bonding environments of As(V) and Zn(II) were investigated by EXAFS spectroscopy in single and co-sorbed samples. Table 2 summarizes the EXAFS experiments including pertinent information about goethite suspension density, reaction time, surface loading ($\Gamma \sim \mu\text{mol m}^{-2}$ goethite), and sorbed Zn:As ratio. For consistency and ease of communication, a specific nomenclature was adopted in which the first element denotes the type of K-edge EXAFS, the superscript to the left states the aging period, and the right-hand subscript reveals the goethite suspension density: e.g., $^{2\text{w}}\text{AsZn}_{100}\text{-As}$ K-edge EXAFS of an As(V) and Zn(II) co-sorption sample aged for 2 weeks in a 100-ppm goethite suspension. Tables 3a and 3b summarize the fitting parameters of the single and co-sorbed As K-edge spectra.

3.2.1. As K-edge EXAFS: As Reference Phases

All k^3 -weighted $\chi(k)$ As reference spectra were dominated by contributions from backscattering oxygen (O) atoms as evident from their similarity to the Na_2HAsO_4 (aq.) $\chi(k)$ spectrum (Fig. 4A). Contributions from backscattering O atoms were expressed by the first RSF peak at $R + \Delta R \sim 1.2\text{--}1.4 \text{ \AA}$ (all $R + \Delta R$ quotations from RSFs are uncorrected for phase shift) (Fig. 4B). Nonlinear least-square fitting indicated that on average ~ 4.1 O atoms occurred at $1.70 \text{ \AA}$, which was in good agreement with previously observed tetrahedral coordination of As by four O atoms (Table 3a) (Arai et al., 2004; Fendorf et al., 1997; Ladeira et al., 2001; O’Reilly et al., 2001; Sherman and Randall, 2003; Waychunas et al., 1993).

Contributions from As–O–O–As MS were observed in all reference and experimental samples. In the RSF of the Na_2HAsO_4 (aq.) sample, the As–O–O–As MS contributions were noticeable between $R + \Delta R$ 2.5 and $2.6 \text{ \AA}$. The magnitude of the CN_{MS} and the R_{MS} was distinctly dependent on the type of reference phase. In the single As(V) sorption samples ($^{4\text{w}}\text{As}_{10, 100, 1000}$), MS was observed above $3.20 \text{ \AA}$ with an average CN of 18.9. In the aqueous, precipitated, and mineralized reference spectra, MS was observed below $3.20 \text{ \AA}$ with an average CN magnitude of 12.3. On average, the fit’s residual decreased by 17% in the single As(V) sorption experiments, and by ca. 7% in the aqueous, precipitated, and mineralized reference spectra. This difference may be attributed to the increasing contribution from higher order shells (except for the Na_2HAsO_4 (aq.) spectrum, which is dominated by contributions from O atoms) decreasing the overall contribution from As–O–O–As MS. Overall, the CN_{MS} and R_{MS} fit results were similar to those obtained for K_2CrO_4 solutions (Pandya, 1994).

Similar solid-phase speciation of As(V) in 10-, 100-, and 1000-ppm goethite suspensions after 4 weeks of aging time suggested that no changes occurred as a function of the solid–solution ratio in the absence of zinc. Arsenate was coordinated to ca. 2 Fe atoms at $\sim 3.30 \text{ \AA}$ and to ~ 0.6 Fe atoms at $\sim 2.80 \text{ \AA}$. These fit results suggested that As(V) was coordinated at the goethite surface as a bidentate binuclear (also known as double corner sharing, ^2C) and a bidentate mononuclear (also known as edge-sharing, ^2E) complex (Fendorf et al., 1997; O’Reilly et al., 2001; Randall et al., 2001; Sherman and Randall, 2003; Waychunas et al., 1993). On average, the fit residual value decreased by 21% with the inclusion

of Fe neighbors at 3.30 Å and by 7% with the inclusion of an additional Fe atom at ~2.80 Å. Thus, we may assume that As(V) coordination at the goethite surface via bidentate binuclear bridging complexes was greater than the edge-sharing complexes, which is consistent with outcomes of density functional theory (DFT) calculations for As(V) coordination by a simple Fe(III) edge-sharing cluster (Sherman and Randall, 2003).

In ojuelaite, contributions from 2.5 Fe and Zn atoms at 3.34 Å agreed well with the coordination environment of As(V) in ojuelaite (Hughes et al., 1996). The mean-square disorder of R ($\sigma^2 = 0.011 \text{ Å}^2$) was larger than for most other reference phases, which may be attributable to the presence of ca. 2 Fe and 1 Zn neighbors at similar distance (3.30 and 3.32 Å) from the central absorber.

A useful fingerprinting index to differentiate As(V) sorption phases may be observed in the position of the imaginary phase in RSFs at $R + \Delta R$ 3.0 Å provided that the k^3 -weighted $\chi(k)$ data are consistently cut on the left and right margins. For adsorbed As(V), as in samples $^{4w}\text{As}_{10, 100, 1000}$ and ojuelaite, the trough of the imaginary phase sits to the left of the vertical guideline at $R + \Delta R$ 3.0 Å and indicated an adsorbed, bidentate binuclear sorption complex at or near 3.30 Å according to the fit results (Fig. 4B). In the RSF of the HZAP and adamite, the trough of the imaginary phase is shifted to $R + \Delta R \geq 3 \text{ Å}$ and was either dissected by the vertical guide at $R + \Delta R$ 3.0 Å or it sat slightly to its right. This shift occurred, because As(V) was coordinated by Zn(II) octahedra at $R > 3.30 \text{ Å}$ in these solid phases (Fig. 4B). In the HZAP, As(V) was coordinated by 1.3 and 1.7 Zn atoms at ~ 3.27 and 3.41 Å, respectively, which is in good agreement with the average bonding environment of As(V) in the mineral koettigite (Hill, 1979). Fit results of our adamite sample suggested that As(V) was coordinated by ca. 6.4 Zn atoms at an average distance of 3.37 Å. Ideally, As(V) is coordinated by 8 Zn atoms in adamite at an average distance of 3.34 Å (Hill, 1976). When the CN_{MS} and R_{MS} were fixed to optimized values for adamite (12 and 3.05 Å, respectively), the $\text{CN}_{\text{As-Zn}}$ and $R_{\text{As-Zn}}$ also became more optimal: 7.4 and 3.36 Å, respectively. Both fits were provided for comparison with sample $^{6m}\text{AsZn}_{100}$ (see section below).

The reference materials selected for this study provide a range of As(V) coordination environments that could be expected to form in reactions with Zn(II) on goethite. As the first shell of As(V) is quasi invariable, the focus of As(V)'s coordination falls onto its second and higher order shells and possibly the CN magnitude and radial distance of the As-O-O-As MS feature. With respect to the adsorbent, goethite, and the cosorbate, Zn(II), As(V) may occur as an outer-sphere complex (Na_2HAsO_4 (aq.)), as a surface-coordinated species with and without Zn(II) as an immediate neighbor ($^{4w}\text{As}_{10, 100, 1000}$, ojuelaite) or in the form of a zinc-arsenate precipitate. Their differentiation is based on the magnitude of the CN and the radial distance of the second shell atoms from the central absorber. The differences between ojuelaite and the single As(V) sorption complexes are quite subtle, but should be recognizable by higher σ^2 values in high signal-to-noise ratio spectra. Outer-sphere As(V) is identified through the absence of a second shell and minor contributions from MS (As-O-O-As) at ca. 3.10 Å. The As-O-O-As MS feature occurred consistently above 3.20 Å for all adsorbed As(V) surface complexes, while

the aqueous, precipitated, and mineralized species had MS occur below 3.20 Å.

There are five zinc-arsenate minerals with crystallographic records: (i) monoclinic-beta (C2/m) koettigite ($\text{Zn}_3[\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$), monoclinic-beta (C2/m) legrandite ($\text{Zn}_4[\text{AsO}_4]_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$), orthorhombic (Pnnm) adamite ($\text{Zn}_2\text{AsO}_4[\text{OH}]$), triclinic (P1(-)) paradamite ($\text{Zn}_2\text{AsO}_4(\text{OH})$), and triclinic (P1(-)) koritnigite ($\text{Zn}[\text{AsO}_3(\text{OH})]\text{H}_2\text{O}$) (Hawthorne, 1979; Hill, 1976; Hill, 1979; Keller et al., 1980; McLean et al., 1971). Koettigite and koritnigite have plane layered structures, and are hence possible solid phases forming in the 10-ppm goethite suspensions. The HZAP was identified as a koettigite-like material with two Zn(II) shells near 3.28 and 3.44 Å. Koritnigite has a unique second shell environment with an average of 5 Zn atoms at 3.47 Å and 2 As atoms near 4.0 Å. Adamite was observed previously to form in 1000-ppm goethite suspensions reacted sequentially with $10 \times 0.25 \text{ mM}$ Zn(II) and As (V) (Gräfe et al., 2004). It is therefore a likely phase to form in the 100- and possibly 1000-ppm goethite systems. Legrandite has a Zn(II) shell at a similar radial distance as in adamite, but the magnitude of the As-Zn CN does not exceed 4, whereas that of adamite is closer to 8. Paradamite's second shell has ca. 3 Zn atoms between 3.15 and 3.20 Å, which would be readily differentiable from any of the other zinc-arsenate minerals.

3.2.2. As K-edge EXAFS: AsZn co-sorption

All k^3 -weighted $\chi(k)$ AsZn co-sorption spectra were dominated by contributions from backscattering O atoms as evident from their similarity to the Na_2HAsO_4 (aq.) $\chi(k)$ spectrum (Fig. 5A). A RSF peak at $R + \Delta R \sim 1.2\text{--}1.4 \text{ Å}$ stemming from backscattering O atoms was observed for all AsZn co-sorption samples (Fig. 5B). Nonlinear least-square fitting indicated that on average ~4.5 O atoms occurred at 1.69 Å, indicative of tetrahedral coordination of As(V) by O atoms in all co-sorption samples (Table 3b).

Contributions to the EXAFS from second shell Fe(III) and/or Zn(II) neighbors were observed in all co-sorption spectra. Using the previously identified fingerprinting index at $R + \Delta R$ 3.0 Å in RSFs, the trough of the imaginary phases of all spectra in the 1000-ppm goethite system and all other 24-h samples ($^{24h}\text{AsZn}_{10, 100}$) were to the left of $R + \Delta R$ 3.0 Å, suggesting a similar coordination environment around As(V) as in $^{4w}\text{As}_{10, 100, 1000}$ (Fig. 5B). Fit results of the raw $^{24h, 2w, 4w}\text{AsZn}_{1000}$ $\chi(k)$ spectra showed that contributions from ~1.8 Fe or Zn atoms occurred at ~3.31 Å and minor contributions from 0.6 Fe atoms at 2.80 Å. Multiple scattering was observed in these samples above 3.20 Å with an average CN magnitude of 16.6. Thus, the solid-phase speciation of As(V) in co-sorption samples of 1000-ppm goethite did not appear to be significantly different from its single sorption counterpart, $^{4w}\text{As}_{1000}$ (Table 3b). With increasing reaction time, σ^2 did not decrease in the second shell of AsZn_{1000} samples, with contributions from Fe and/or Zn atoms at 3.31 Å and contributions from Fe atoms at 2.80 Å remaining constant over the 4-week reaction period (Table 3b). Therefore, no zinc-arsenate precipitate seemed to have formed in the 1000-ppm goethite suspensions.

In the AsZn_{100} series, a beat pattern developed in the k^3 -weighted $\chi(k)$ spectra with increasing reaction time between 6 and 7, 8 and 9, 10 and 11, 12 and 13 Å⁻¹ (Fig. 5A). The 24-h $\chi(k)$ spectrum had only minor contributions from this beat

pattern, and the As(V) speciation was similar to all the other reported adsorbed phases (Table 3a,b). An increasing amplitude of the second shell RSF peak between $R + \Delta R$ 2.2 and 3.6 Å of the 2-week and 6-month AsZn₁₀₀ samples suggested increased coordination of As(V) by Zn atoms (Fig. 5B). The CN_{MS} and R_{MS} (<3.20 Å) also suggested that a precipitate was forming as early as 2 weeks. The 2-week sample had a CN_{As-Zn} of 6.2 at 3.33 Å and σ^2 of 0.015, when fit with only one As-Zn scattering path. The high disorder in this shell suggested that the single As-Zn distance could be split over two populations of distinct Zn neighbors occurring at two different radial distances. Fit results with two As-Zn scattering paths showed that As(V) was coordinated by 2.3 and 2 Zn atoms at 3.27 and 3.41 Å, respectively, after 2 weeks ($\sigma^2 = 0.004$). This fit result was similar to the results obtained for the HZAP. In a previous study (Gräfe et al., 2004), the formation of an adamite-like precipitate appeared to be preceded by the formation of a koettigite-like material. Zinc K-edge EXAFS suggested, however, that the precipitate was a precursor phase to adamite that had similar intermediate structural elements. A similar observation and conclusion was made in this study from the corresponding Zn K-edge EXAFS spectrum (see section 3.2.4). The $\chi(k)$ spectrum of the 6-month sample was similar to that of adamite (Fig. 4A,B); however, the beat pattern in the 6-month $\chi(k)$ spectrum was not as refined, which caused its second shell peak to be broader and its amplitude to be lower (Fig. 5A,B). After 6 months, As(V) was coordinated by ~ 6.4 Zn atoms at an average distance of 3.34 Å, which was nearly identical to the results we obtained for adamite, suggesting that an adamite-like surface precipitate was forming. It is important to note that the ^{6m}AsZn₁₀₀ spectrum could not be fit as ^{2w}AsZn₁₀₀ and that adding a second Zn(II) shell at 3.44 or 3.55 Å did not provide meaningful results. The σ^2 parameter of the 6-month sample was insignificantly higher than the adamite sample (0.008 vs. 0.006 ± 0.002 Å²). Fixing σ^2 to 0.006 dropped the CN magnitude in this sample to 5, which was more than 20% greater than 4. Hence, adamite, and not legrandite formed in this sample. The increased As(V) and Zn(II) sorption observed in the macroscopic experiments beyond 24 h could thus be associated with the heterogeneous nucleation of As(V) and Zn(II) at the goethite surface forming an adamite-like precipitate.

In the AsZn₁₀ series, k^3 -weighted $\chi(k)$ spectra differed from each other with increasing reaction time with second shell RSF peaks shifting to greater $R + \Delta R$ distances (Fig. 5A,B). After 24 h, there were little or no contributions noticeable from backscattering atoms other than O, suggesting that most As(V) may have sorbed as outer-sphere complexes. This would be consistent with As(V) surface concentrations exceeding the sited saturation limit by ca. four times. The fit results showed contributions from ~ 2.0 Fe/Zn atoms at ~ 3.27 Å, but the magnitude of the CN appeared to stem mostly from σ^2 , which was ca. 1.6 times larger than σ^2 (0.008 Å²) of the AsZn₁₀₀ series and approximately two times larger than σ^2 (0.006 Å²) in the ^{4w}As₁₀ spectrum (Table 3b). When σ^2 was fixed to 0.006, the CN_{As-Fe/Zn} dropped to 0.7, suggesting that the contributions from bidentate binuclear surface complexes were diminished in this sample. The absence of Fe(III) neighbors at 2.80 Å and the CN magnitude (11) and R (3.16 Å) of the MS path corroborated a greater degree of outer-sphere coordination at the goethite surface. After 2 weeks reaction time, a noticeable RSF peak

emerged between $R + \Delta R \sim 2.8$ Å that shifted to ~ 3.20 Å after 6 months. The nonlinear least-square fit suggested that As(V) was coordinated by ~ 2.6 Zn atoms at 3.28 Å. From the scanning electron micrograph, we knew that by the fourth month, a planar precipitate had formed. After 6 months, As(V) was coordinated by 4.6 Zn atoms at 3.46 Å and 3.1 As atoms at 4.04 Å (Table 3b). This coordination environment was consistent with that of koritnigite (Zn[AsO₃OH]H₂O), and corroborated by the sample's Zn:As solid phase molar ratio of 1.18 (Table 2). The transition of the Zn-As radial distance from 3.27 to 3.46 Å suggested a continuous transformation of the precipitate's structure over time. In 10-ppm goethite suspensions, a koritnigite-like precipitate occurred after four to six months. The minor contributions from Fe(III) in the second shell of the 24-h sample, and the relatively discrete planar particles (Fig. 3B) suggested that this precipitate may have formed from a local oversaturation of zinc-arsenate solution complexes near the goethite surface. The structural difference between the koritnigite-like sample after 6 months and the 4-week sample of the HZAP suggest that the precipitate was formed via a heterogeneous nucleation process at or near the goethite-water interface.

3.2.3. Zn K-edge EXAFS: Zn reference phases

k^3 -weighted $\chi(k)$ spectra of Zn reference compounds were dominated by contributions from backscattering O atoms as evident from their similarity to the $\chi(k)$ spectrum of ZnCl₂ (aq., Fig. 6A). These contributions were expressed by the first RSF peak at $R + \Delta R \sim 1.5$ Å (Fig. 6B). Nonlinear least-square fitting suggested that on average ~ 5.6 O atoms were coordinated around a central Zn atom at 2.07 Å, which was overall in good agreement with an octahedral coordination environment of 6 O atoms around zinc (Manceau et al., 2002; Manceau et al., 2000; Roberts et al., 2003; Schlegel et al., 1997; Trainor et al., 2000; Trivedi et al., 2001; Waychunas et al., 2002). In two instances (^{4w}Zn10, ₁₀₀₀), we observed two discrete distances from backscattering O atoms. This split may have been induced by the second shell neighbor. Similar splits were observed in all other reference spectra except the ZnCl₂ (aq.) spectrum; however, the use of an additional Zn-O scattering path into the fit did not result in a significant drop of σ^2 (± 0.002 Å²), which we applied as a criterion. Elongated metal-oxygen distances for metal-arsenate minerals of Co, Ni, Cu, Zn, and Pb have been observed before in structure analysis from XRD data and Rietveld refinements (Barbier, 1996; Effenberger and Pertlik, 1986; Hill, 1976; Keller et al., 1980; Toman, 1977). In adamite, for example, the split into two Zn-O distances stems from apical oxygen (O) atoms around octahedral Zn atoms at 2.26 Å and the remaining O atoms located ~ 2.02 Å from the central atom (Hill, 1976). To date, there is no explanation as to why these elongated distances occur. Common theories include metal-center repulsion or steric arrangements of the metals into more than one coordination environment. Changes in the average Zn-O bond distance according to coordination environment are well recorded (Waychunas et al., 2002). A possible explanation for the split Zn-O distances may be related from a recent study by Ding et al. (2000) who studied net electron transfers between substrate-Fe(III, akaganeite, β -FeOOH), O and its adsorbates (Zn(II), As(V), Cr(VI), a.o.). The authors

found that Zn(II) sorption on akaganeite caused a net electron transfer from O to Fe^{3+} , making Fe^{3+} less positive and the O atoms less negative. Hence the attraction between Zn(II) and the shared O was lower, which could have caused at least one Zn-O bond to relax and elongate. Alternatively, As(V) sorbed on akaganeite caused a shift of electrons from Fe^{3+} (Lewis base) to O atoms (Lewis acid). In the case of Cr(VI) sorption on akaganeite, Cr(VI) attracted electrons (Lewis acid) from O and Fe^{3+} (both Lewis bases). Hence the extent and direction of the electron shift appeared to be dependent on the charge difference between the metal centers, which would be congruent with the hypothesis of distorted coordination environments due metal-center repulsion. More research (X-ray photoelectron spectroscopy, XRD) and computational methods such as density functional theory calculations are necessary to link such charge transfers conclusively to metal-O radial distances.

Contributions from second shell neighboring metal atoms were observed in all Zn(II) reference phase spectra except the ZnCl_2 (aq.) spectrum. Little or no change occurred in the bonding environment of Zn(II) with decreasing goethite suspension density. Zinc was coordinated by ~ 0.9 to 1.3 Fe(III) atoms at ca. 3.06 Å and ca. 1.8 Fe(III) atoms at ~ 3.26 Å, suggesting that Zn(II) was coordinated at the goethite surface as edge-sharing (^2E) and bidentate-binuclear (^2C) surface complexes, respectively (Table 4a) (Manceau et al., 2000; Schlegel et al., 1997). These Zn-Fe radial distances also agree well with aspects of the Fe(III) coordination environment in goethite, suggesting that Zn(II) partially complemented the goethite structure. The absence of Fe(III) neighbors near 3.45 Å also suggested that Zn(II) did not form a solid solution with goethite in the control samples after 4 weeks. HZAP, aged for 4 weeks, contained Zn(II) coordinated by ca. ~ 0.7 Zn(II) atoms at 3.07 Å and 0.8 As(V) atoms at 3.32 Å, consistent with edge-sharing Zn-octahedra and vertex-sharing Zn(II)-As(V) complexes. The structural parameters were in agreement with aspects of a koettigite-like precipitate, but were overall compromised by amplitude reductions from deconstructive interference of several Zn(II) and As(V) backscattering atoms (Table 4a) (Hill, 1979). Fit results of our adamite sample suggested that Zn(II) was coordinated by 1.4 Zn atoms at 3.02 Å, 2.2 As(V) atoms at 3.36 Å, and 1.8 Zn atoms at 3.62 Å, which was in good agreement with the average coordination of Zn(II) in adamite (Table 4a) (Hill, 1976). The fit residuals decreased on average by 23% with the inclusion of the first second shell feature and thereafter on average by 7%. Those reference spectra ($^{48}\text{Zn}_{10,1000}$) which had low signal-to-noise ratios often had very low fit residual declines, whereas the HZAP and adamite had greater fit residual declines, because of greater signal-to-noise ratio and greater second shell contributions to the EXAFS in general.

Several constraints with respect to Zn EXAFS in the presence of iron oxides and As(V) deserve mentioning. In well aerated environments, the first atomic shell of Zn(II) may be occupied by either four, five, six, or seven O atoms (Manceau et al., 2002; Roberts et al., 2003; Schlegel et al., 1997; Trainor et al., 2000; Trivedi et al., 2001; Waychunas et al., 2002). Due to common distortions in Zn(II)'s first atomic shell and the possibility of mixed Zn coordination (e.g., adamite, CN = 5 and 6; hydrozincite, CN = 4 and 6), the Debye-Waller parameter (σ^2) is high, which distorts the true magnitude of the CN. Therefore the true first shell coordination environment has

often been derived from characteristic bond distances: for four-fold coordination by O atoms, the Zn-O bond distance is ≤ 1.98 Å and for sixfold coordination by O atoms, the Zn-O bond distance is ≥ 2.06 Å (Waychunas et al., 2002). With respect to iron oxide sorbents, Schlegel et al. (Schlegel et al., 1997) observed edge-sharing complexes between Zn(II) and Fe(III) octahedra at 3.00 Å and a vertex-sharing complex at 3.20 Å on goethite. Schlegel's findings are consistent with our single Zn(II) sorption experiments showing Zn(II) to be mainly in octahedral coordination as edge- and vertex-sharing complexes at the goethite surface. Other researchers observed Zn(II) in tetrahedral coordination as vertex-sharing complexes at ferrihydrite and goethite surfaces (Trivedi et al., 2001; Waychunas et al., 2002).

The five zinc-arsenate minerals have first shell Zn-O coordination environments ranging from purely sixfold (koritnigite, koettigite) to mixed six- and fivefold (adamite, legrandite) to purely fivefold (paradamite). The average Zn-O radial distance in paradamite ($\text{CN}_{\text{Zn-O}} = 5$) is 2.06 Å, which makes it practically indistinguishable from koettigite ($\text{CN}_{\text{Zn-O}} = 6$, $R = 2.11$ Å), koritnigite ($\text{CN}_{\text{Zn-O}} = 6$, $R = 2.13$ Å), or adamite ($\text{CN}_{\text{Zn-O}} = 5$, $R_{\text{Zn-O}} = 2.03$ Å; $\text{CN}_{\text{Zn-O}} = 6$, $R_{\text{Zn-O}} = 2.12$ Å, average $\text{CN}_{\text{Zn-O}} = 5.5$, $R_{\text{Zn-O}} = 2.08$ Å) based on first shell fits alone. Therefore the identity of zinc-arsenate precipitates and co-sorbed complexes has to be ascertained from specific features in the second shell. The EXAFS contributions from higher order shells are, however, also somewhat problematic, because the backscattering waves from second and higher order shells partially cancel each other out. This causes amplitude reductions in the EXAFS and subsequently, the CN magnitude cannot be determined accurately. In our powder-on-tape adamite sample, for example, approximately only one-half of the true CN magnitude of all possible backscatterers ($\text{Zn-Zn} \sim 3.00$ Å, $\text{Zn-As} \sim 3.34$ Å, and $\text{Zn}_{\text{oct}}\text{-Zn}_{\text{pent.}} \sim 3.60$ Å) was observed (Hill, 1976). A conservative estimate for the second shell accuracy based on adamite was hence at best 50%, but in reality the fit was probably more accurate given the second shell scattering constraints. A similar effect was observed for koettigite. In koettigite, single and edge-sharing Zn(II) octahedra are coordinated around As(V) according to the O-As-O angles ($\sim 109^\circ$) in the As(V) tetrahedron. Ideally, two to three As(V) neighbors should be measurable at an average distance of 3.25 to 3.29 Å, and ca. 2 As(V) neighbors at 3.44 Å. In addition, minor ($\text{CN} \sim 0.5$) EXAFS contributions from edge-sharing Zn(II) neighbors should be measurable. Therefore the description of the Zn(II) bonding environment in mixed zinc-arsenate-goethite systems is likely compromised by the scattering nature of the precipitates and best described by radial distances from the central absorber. Hence the presence of a second shell Zn neighbor near 3.60 Å is an important indicator for the formation of adamite even when the CN magnitude is suppressed by deconstructive interference.

3.2.4. Zn K-edge EXAFS: ZnAs co-sorption

K^3 -weighted $\chi(k)$ spectra of ZnAs co-sorption spectra were dominated by contributions from backscattering O atoms as evident from their similarity to the $\chi(k)$ spectrum of ZnCl_2 (aq.) and the similar position of the first RSF peak at $R + \Delta R \sim 1.5$ Å (Fig. 6A,B, Fig. 7A,B). Nonlinear least-square fitting showed

that on average ~ 5.5 O atoms were at $2.04 \text{ \AA}$ around Zn(II), suggesting a mixed pentahedral–octahedral coordination environment of Zn(II) in the first shell (Table 4b). Two Zn–O contributions were noticed for the entire ZnAs₁₀ series. With increasing residence time, a distribution of the Zn–O distances into a set of ca. 4 O atoms at $\sim 2.00 \text{ \AA}$ (equatorial O) and 2 (apical) O atoms at $\sim 2.17 \text{ \AA}$ resulted (Table 4b). This may have been due to the increasing coordination with As(V) over time.

The k^3 -weighted $\chi(k)$ spectra in the ZnAs₁₀₀₀ series had a slight beat pattern between 6 and 7 and 8 and $10 \text{ \AA}^{-1}$ (Fig. 7A). This beat pattern appeared as a broad and low-amplitude RSF peak between $R + \Delta R$ 2.5 and $3.0 \text{ \AA}$ (Fig. 7B). Changes of the imaginary phase over time suggested changes in coordination and a possible change in neighboring atoms. For example, the imaginary phase of the 24-h sample was similar to that of ZnCl₂ (aq.) and that of the 2-week sample was similar to the imaginary phase of ^{4w}Zn₁₀₀₀, suggesting an increasing inner-sphere complexation of Zn(II) at the goethite surface over time. Nonlinear least-square fitting suggested the formation of edge-sharing ($0.6\text{--}1.2$ Fe atoms at 3.04 to $3.15 \text{ \AA}$) and corner-sharing complexes (1.2 to 1.8 Fe atoms at $3.24 \text{ \AA}$) at the goethite surface within 24 h and 2 weeks (Table 4b). After 6 months, an additional 0.9 Fe/Zn atoms could be fit at $3.46 \text{ \AA}$, suggesting an additional vertex-sharing complex with Fe(III) or Zn(II). Zinc(II) coordination by Fe(III) at ~ 3.05 , 3.25 , and $3.45 \text{ \AA}$ is consistent with the average structural environment of Fe(III) in goethite (Scheinost et al., 2001) and suggested that Zn(II) may have formed a solid solution with goethite over time. With increasing aging time, σ^2 dropped by more than 50%. Some contributions from As(V) at $3.34 \text{ \AA}$ were observed in the 24-h and subsequent samples; however, fit results had significantly greater σ^2 and ΔE_0 values than fits using only Fe(III) backscattering atoms. These fit results are consistent with those from As K-edge EXAFS that As(V) and Zn(II) did not form a precipitate in 1000-ppm goethite suspensions.

In the AsZn₁₀₀ series, a broad beat pattern developed over a 6-month period that became more distinct with aging time and was similar to that of the HZAP after 2 weeks and to adamite after 6 months (Fig. 7B). Similar RSF peaks and imaginary phases were observed between $R + \Delta R \sim 2.3$ and $4.0 \text{ \AA}$, suggesting the formation of an adamite-like precipitate over time consistent with results from As K-edge EXAFS. Nonlinear least-square fitting showed the formation of a mixed AsZn solid phase, which became less disordered between 2 weeks and 6 months (see decreasing σ^2 with time, Table 4b). After 24 h, Zn(II) had formed mixed edge- and vertex-sharing complexes on the goethite surface similar to the ones observed after 24 h in the ZnAs₁₀₀₀ series. After 2 weeks, Zn(II) had formed edge-sharing Zn–Zn complexes (0.9 Zn atoms at $\sim 3.05 \text{ \AA}$) that were coordinated to ~ 0.6 As atoms at $\sim 3.26 \text{ \AA}$, suggesting a corner-sharing complex. In addition, weak scattering contributions from 0.4 Zn(II) atoms at $3.71 \text{ \AA}$ were noticed, which could be related to the Zn_{oct.}–Zn_{pent.} distance ($3.63 \text{ \AA}$) observed in adamite. After 6 months, Zn(II) was coordinated to 0.6 Zn atoms coordinated at $3.00 \text{ \AA}$, 1.4 As atoms at an increased Zn–As distance of $3.36 \text{ \AA}$, and 1.4 Zn at $3.62 \text{ \AA}$. This fit was nearly identical to that of adamite with Zn K-edge EXAFS. Backscattering from one to two Zn atoms at $3.62 \text{ \AA}$ indicated that the solid phase in question was not legrandite, but the

formation of the unique fivefold coordinated Zn-dimers (Zn₂(OH)₈) in adamite (Hill, 1976; McLean et al., 1971). Overall, this reactions series was consistent with the corresponding As K-edge EXAFS data, and showed that after 2 weeks, As(V) was not precipitated as a koettigite-like phase, which was consistent with As and Zn K-edge EXAFS results in our previous study (Gräfe et al., 2004).

Similar to its AsZn₁₀ counterparts, $\chi(k)$ spectra of the ZnAs₁₀ series were increasingly dominated by a beat pattern emerging in the O wave pattern. This beat pattern emerged above $6 \text{ \AA}^{-1}$ and caused splitting of the oscillations at 6, 8, and $10 \text{ \AA}^{-1}$. No obvious trend in the pattern was noticeable with aging time similar to the way spectra behaved at the As K-edge. With increasing aging time, a second shell RSF peak developed between $R + \Delta R$ $2.8\text{--}3.00 \text{ \AA}$, which changed into a broader split peak after 6 months. Changes in the imaginary phase suggested a changing second shell coordination environment over time.

After 24 h, Zn(II) was coordinated by 1.5 Fe(III) or Zn(II) neighbors at $3.17 \text{ \AA}$ in addition to the 2 and 0.7 As atoms at 3.29 and $3.47 \text{ \AA}$, respectively. This fit result suggested the possible formation of a koettigite-like precipitate given the distribution of As(V) at 3.29 and $3.47 \text{ \AA}$ around Zn(II). After 2 weeks, Zn(II) was coordinated by 3.1 Zn atoms at $3.23 \text{ \AA}$ and 2.8 As atoms at $3.34 \text{ \AA}$. After 6 months aging time, Zn(II) was coordinated by 0.6 Zn atoms at $3.15 \text{ \AA}$ and 0.6 As atoms at 3.42 and $3.72 \text{ \AA}$. These parameters corroborate As K-edge EXAFS data that the precipitate was not koettigite, but rather koritnigite-like in phase. The magnitude of the CN in this sample was diminished, which stems from the aforementioned destructive interference of several backscattering waves, but the radial distances of the backscatterers corroborate the corresponding As K-edge EXAFS that a koritnigite-like precipitate had formed. From scanning electron micrographs and As and Zn K-edge EXAFS spectroscopy, we surmise that As(V) and Zn(II) formed a planar, koritnigite-like precipitate in 10-ppm goethite suspensions at pH 7.

3.3. Dissolution Experiments

Arsenate desorption from 6-month-old aged 1000-ppm goethite suspensions was greater at pH 5.5 than at pH 4 with $\sim 80\%$ and 90% of the sorbed As(V) remaining on the goethite surface after 11 replenishments, respectively (Fig. 8A). In contrast, Zn(II) desorption was greater at pH 4 than at pH 5.5 for the same aging period and suspension densities (Fig. 8A). Fifteen percent and 44% of the total sorbed Zn(II) remained on the goethite surface at pH 4 and 5.5, respectively, after 11 replenishments. The desorption behavior of As(V) and Zn(II) at pH 4 and 5.5 was therefore consistent with the stability of adsorbed As(V) and Zn(II) complexes on goethite at higher and lower pH (Gräfe et al., 2004; Sparks, 2002; Stumm, 1992). The predicted molar release ratio suggested that in the case of an independent sorption event between As(V) and Zn(II), the ratio would increase with increasing number of replenishments at pH 4, whereas at pH 5.5, an initial sharp spike would be followed by a more constant molar release ratio (Fig. 8B).

Zinc(II) desorption from co-sorbed samples in 1000-ppm goethite behaved similar to its single-sorption counterpart, i.e., more Zn(II) desorbed at pH 4 than at pH 5.5 (Fig. 8C) and

suggested Zn(II) was primarily adsorbed and not precipitated. The desorption of As(V), however, was greater at pH 4 than at 5.5, which was inversely related to its single-sorption counterpart and contrary to the accepted theory that As(V) surface complexes are more stable at lower than at higher pH. This reversed trend suggested that As(V) was partially coordinated by Zn(II) octahedra at the goethite surface. Although the Zn:As molar surface ratios were quite similar (Fig. 8B,D), the different patterns of the Zn:As molar release ratios suggested that the desorption of Zn(II) and As(V) was dependent on the sorbate.

The dissolution of the HZAP against pH 5.5 and pH 4 background electrolyte solution was greater at pH 4 than at pH 5.5 (Fig. 8E). Slightly more As(V) than Zn(II) desorbed at pH 4 and 5.5. After nine replenishments, the amount of As(V) released from the precipitate increased, decreasing the molar Zn:As release ratio and increasing the remaining Zn:As mole fraction in the solid phase (Fig. 8F). The increased release of As(V) from the koettigite-like material was inconclusive as the reaction did not reach a steady state; however, the loss of ~30% of As(V) from the surface by replenishments 9, 10, and 11 was similar to the additional sorption of 30% As after 8 h in the kinetic experiment.

The dissolution of the adamite-like surface precipitate ($^{6m}\text{AsZn}_{100}$) was greater at pH 4 than at pH 5.5 and required fewer replenishments at lower than at higher pH to come to a steady state (Fig. 9A). After 11 replenishments at pH 5.5, ca. ~45 to 50% of As(V) and Zn(II) remained in the solid phase at a surface loading above maximum theoretical mono-layer coverage ($2\text{--}3\ \mu\text{mol m}^{-2}$), suggesting that a core of the precipitate may have remained intact. After five replenishments at pH 4, 12% and 35% of Zn(II) and As(V), respectively, remained in the solid, lowering the surface loading to levels close to theoretical monolayer coverage, and suggested that the precipitate had dissolved. The molar Zn:As release ratio was cyclic at pH 5.5, showing that after 2, 5, 7, and 10 replenishments, more Zn(II) was released than As(V), and after 3, 6, and 9 replenishments, more As(V) than Zn(II) was released into solution (Fig. 9B). This cyclic release ratio may be related to the concentric-layered structure of adamite, suggesting that the precipitate eroded in layers (Fig. 9C).

The dissolution of the koritnigite-like surface precipitate ($^{6m}\text{AsZn}_{10}$) was slightly greater at pH 4 than at pH 5.5, but required fewer replenishments at lower than at higher pH to come to a steady state (Fig. 9D). After five replenishments, ca. ~40% of As(V) and Zn(II) remained in the solid phase at pH 5.5 with a surface loading above maximum theoretical mono-layer coverage, suggesting that a core of the precipitate remained intact. After three replenishments at pH 4, 25% to 30% of Zn(II) and As(V) remained in the solid phase but the site saturation remained above the maximum theoretical mono-layer coverage. The molar Zn:As release ratio was also cyclic at pH 5.5, showing that after four and eight replenishments, relatively more Zn(II) was released than As(V), and after 6 and 10 replenishments, relatively more As(V) than Zn(II) was released into solution (Fig. 9E). The cyclic release ratio is likely related to the plane layered structure of the koritnigite-like precipitate (Fig. 9F).

One reason for the susceptibility to proton promoted dissolution may be the elongated apical Zn-O bonds when the O

atoms are shared with Fe^{3+} and/or As^{5+} centers. The elongated Zn-O bond is weaker and more prone to attack by H_3O^+ . Ding et al. (2000) assessed the strength of the surface sorption complex by comparing energy differences in the highest occupied molecular orbital (HOMO) of nonbonding O ligands on the sorbent (akaganeite) and the lowest unoccupied molecular orbital (LUMO) of the adsorbate for sorbed As(V) and zinc. The authors concluded that Zn-Fe complexes were weaker than As-Fe surface complexes due to greater energy differences between the LUMO of the adsorbate and the HOMO of the sorbent and the consequently lower potential molecular energies of the Zn-Fe vs. As-Fe sorption complex. Their predictions are in good agreement with the experimental results of this study.

4. DISCUSSION

4.1. Heterogeneous Nucleation

The literature recognizes two types of nucleation reactions: homogeneous and heterogeneous (Stumm, 1992). In the absence of a sorbent, a *homogeneous* nucleation reaction may occur when the solution is saturated with the precipitating ions (i.e., $\log \text{IAP}/K_{\text{so}} = 1$), but is kinetically limited until a critical oversaturation ($\log \text{IAP}/K_{\text{so}} > 1$) of the solution has occurred. The Gibbs free energy of the precipitation reaction (ΔG_{rxn}) is dependent on the energy gained from making bonds (ΔG_{bulk}) and the amount of work (ΔG_{surf}) required to make a new surface in the solvating medium (e.g., aqueous solution) (Stumm, 1992). In other words, the term ΔG_{surf} is related to the amount of energy that is required to overcome the interfacial tension between the forming precipitate and its solvent. In soils, sediments, and natural waters, the omnipresence of solid surfaces from clays and metal-oxides such as goethite may induce a catalytic effect on the precipitation reaction by decreasing or removing ΔG_{surf} . These reactions are referred to as *heterogeneous* nucleation reactions. When the surface catalytic effect lowers the surface tension between the precipitate and the substrate surface below the surface tension of the precipitate and its solvating medium (Steeff and van Cappellen, 1990; Stumm, 1992; van Cappellen, 1991), a state of well-matching substrates exists.

Goethite catalyzed the formation of koritnigite- and adamite-like precipitates in 10- and 100-ppm goethite suspensions, respectively, from undersaturated zinc and arsenate solutions. We recall from As and Zn K-edge EXAFS data that in all three suspensions (10-, 100-, 1000-ppm goethite) part of the initial reactions were *surface adsorption* reactions of As(V) and Zn(II) on goethite and that precipitation did not occur until 24 to 72 h after the reaction started in 100- and 10-ppm goethite suspensions, respectively. This suggested that 1) certain surface properties of goethite changed as a result of the initial As(V) and Zn(II) adsorption, 2) without these changes precipitation could not have occurred, and 3) a certain remaining solution concentration of As(V) and Zn(II) was required for precipitation to occur, because the precipitation reaction did not occur in 1000-ppm goethite suspensions.

After 24 h, 248 μM As(V) and 214 μM Zn(II), 238 μM As(V) and 187 μM Zn(II), and 94 μM As(V) and 61 μM Zn(II) remained in 10-, 100-, and 1000-ppm goethite suspensions,

respectively, showing that the amount of As(V) and Zn(II) remaining in solution was significantly higher in 10- and 100-ppm goethite after 24 h than in 1000-ppm goethite, and therefore inversely related to the amount of goethite present in solution. With respect to the bonding environments of As(V) and Zn(II) after 24 h (Tables 3b and 4b), this suggested that initially the surface adsorption reaction of As(V) and Zn(II) was kinetically more favorable than an immediate zinc–arsenate precipitation reaction.

In the first 8 h of the experiments, the rate of Zn(II) sorption was ca. 4 (100-ppm goethite) and 7 (10-ppm goethite) times faster than the rate of As(V) sorption, but only 1.20 times faster in 1000-ppm goethite suspensions (Table 1). After 24 h, the surface concentration of Zn(II) was consistently greater than that of As(V) and significantly greater in 10- than 100- or 1000-ppm goethite (Table 4). Approximately 48 and 11 $\mu\text{mol Zn m}^{-2}$ were sorbed in 10- and 100-ppm goethite, respectively, whereas no more than 3.28 $\mu\text{mol Zn m}^{-2}$ were sorbed in the single Zn(II) sorption systems of 10 and 100 ppm goethite as well as the $^{24}\text{hAsZn}_{1000}$ sample. In comparison, the surface concentration of As(V) was ca. 11 $\mu\text{mol m}^{-2}$ in 10-ppm goethite, but remained within the limits of the theoretical site saturation in 100- and 1000-ppm goethite after 24 h (Gräfe et al., 2004). Higher Zn:As sorbed ratios ($\mu\text{mol Zn m}^{-2} : \mu\text{mol As m}^{-2}$, Table 2) in the systems with subsequent precipitation could therefore suggest that the surface tension between the zinc–arsenate precipitates (koritnigite and adamite) and the goethite surface was lowered by the kinetically favored retention of Zn(II) over As(V). Alternatively, one could argue that the goethite surface induced a concentration effect of Zn(II) [and As(V)] near the surface that led to oversaturated concentrations of Zn(II) and As(V) near the surface. This would explain why we observed a higher degree of outer-sphere Zn(II) and As(V) complexes in the 24-h samples of the 10-ppm goethite suspensions.

As the cohesive bonding between ions in a precipitate becomes stronger relative to the bonding with the substrate, the precipitate will grow in all three dimensions (Stumm, 1992). From scanning electron micrographs, it was possible to distinguish a three-dimensional, plate-like precipitate in the 10-ppm goethite system, but the precipitate in the 100-ppm goethite system could not be identified (Fig. 3B,C). The plate-like precipitates were large and continuous, which gave the impression that the precipitates may have had little or no association with the needle-shaped goethite particles. The goethite surface may have promoted the formation of aqueous polymeric solution species near the surface leading to a surface-induced oversaturation and subsequent precipitation. This could explain why the surface concentrations of Zn(II) and As(V) in the 10-ppm goethite system were significantly above site saturation (Gräfe et al., 2004) and why the As and Zn K-edge EXAFS data suggested a second shell environment filled with Zn(II) and As(V), rather than Fe(III).

The possible role of polymeric solution species requires due attention in future research concerning precipitation reactions. Based on wet-chemistry and EXAFS data, however, we propose that the precipitates formed in 10- and 100-ppm goethite suspensions occurred via heterogeneous nucleation reactions. These reactions were undersaturated with respect to the formation of amorphous koettigite ($\log [\text{IAP}/K_s] = -0.92$, Gustafs-

son, 2004), and the precipitates were not isostructural with the koettigite-like precipitate that formed in oversaturated solutions ($\log [\text{IAP}/K_s] = +6.47$). Hence, a surface-induced effect appeared likely. Based on the experimental results presented in this study, we propose that the surface tension (ΔG_{surf}) of zinc–arsenate precipitates in goethite suspensions was lower for koettigite < koritnigite < adamite as these precipitates formed in increasing goethite suspension concentrations, i.e., ΔG_{surf} was lower for every magnitude increase in goethite suspension density. This order agrees well with the average density of the mineral forms: 3.33, 3.54, and 4.4, respectively (Roberts et al., 1990). Above 100-ppm goethite, however, surface adsorption reactions will deplete the solution concentration of the sorbates (250 mM Zn(II) and As(V) in this study) to levels below the possibility of precipitation.

4.2. Summary of Reaction Processes

Spectroscopic analysis of As(V) and Zn(II) co-sorption samples in 10- and 100-ppm goethite after 24 h, 2 weeks, and 6 months has suggested that a distinct sequence of reactions occurred (Fig. 10).

I. The initial reactions (0–24 h) consisted of surface adsorption reactions in which Zn(II)-octahedra formed edge-sharing complexes on the goethite surface and As(V) formed bidentate binuclear complexes with apical oxygen atoms from Fe(III) and possible Zn(II) octahedra (see Table 3b and 4b: 10-, 100-, and 1000-ppm goethite systems: 24-h sample). The amount of goethite determined whether a precipitation reaction occurred: 1) too much goethite (1000-ppm) in solution decreased the concentration of As(V) and Zn(II) in solution such that a precipitation reaction could not occur (at least within 6 months, see Fig. 1A,B); 2) whereas when the As(V) and Zn(II) concentrations in solution remained high enough after adsorption onto goethite, the goethite suspension density determined the type of precipitate and the onset of precipitation (see Fig. 1D,F and compare the onset of precipitation between the 10- and 100-ppm goethite suspensions). The initial surface adsorption reaction may be the critical first step in the precipitation reaction to lower the surface tension between the precipitate and the goethite surface. Other factors such as local oversaturation and the formation of aqueous polymeric solution species cannot be disregarded.

II. Possible aqueous polymeric zinc–arsenate solution species concentrating near the goethite surface may have initiated the precipitation reactions in the 10-ppm goethite suspensions. The precipitation reactions began by the uptake of more Zn(II) than As(V) from solution in both 10- and 100-ppm goethite (see Fig. 2C,D). The first structural elements to form were Zn–Zn edge-sharing complexes that provided apical Os for the coordination of As(V) as bidentate binuclear complexes (see Tables 3b and 4b: 10- and 100-ppm goethite systems: 2-week samples).

III. The bulk of the precipitation reaction was complete when the molar Zn:As removal ratio became constant and less than 2:1. Additional uptake of Zn(II) or As(V), or both, occurred and may have caused the formation of specific structural elements, e.g., pentahedral Zn–Zn dimers in the adamite-like precipitate of the 100-ppm goethite suspensions. Otherwise, the precipitates began to mature by defining their structures (see Table 3b

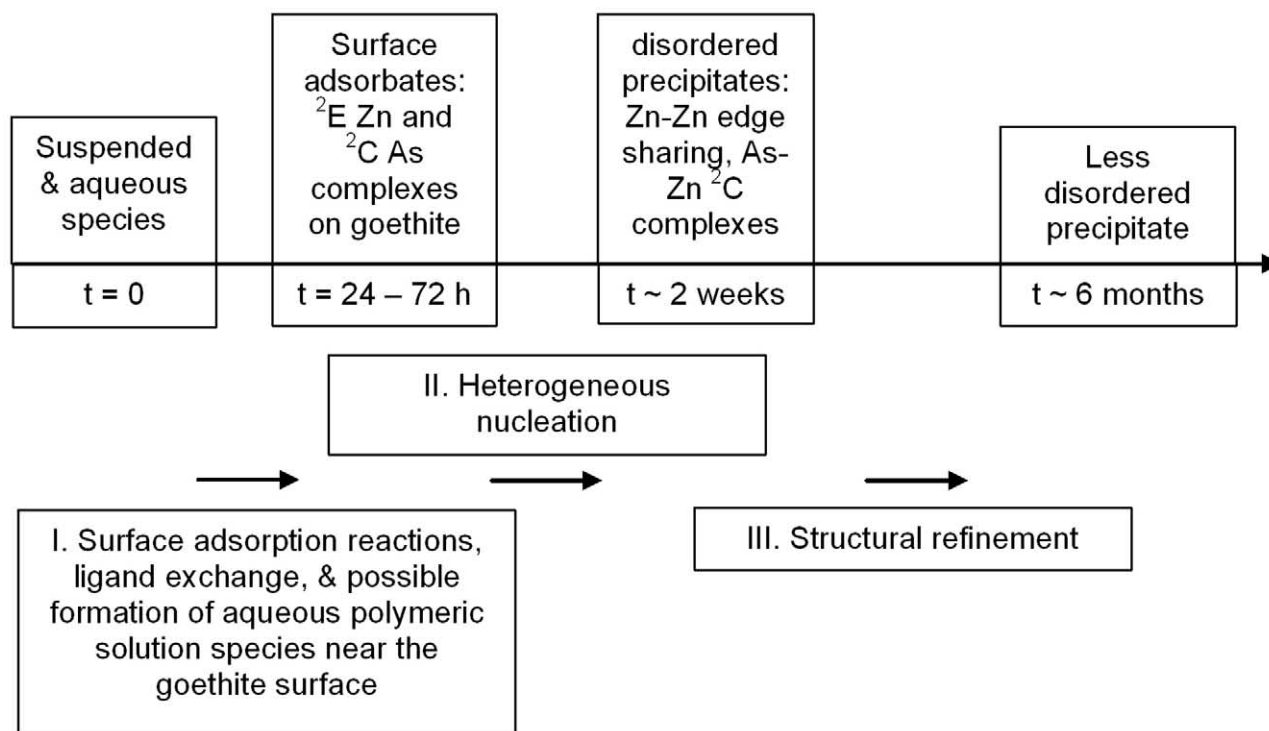


Fig. 10. Reaction processes and solid phases in zinc-arsenate heterogeneous precipitation.

and 4b: 100-ppm goethite: structural transition 2-week samples to 6-month samples).

5. CONCLUSIONS

Heterogeneous nucleation reactions and possibly the formation of poly-nuclear zinc-arsenate solution species near the goethite surface are likely responsible for the reactions that are presented in this study. Four different zinc-arsenate solid phases formed depending on the solid-solution ratio of goethite: koettigite-like precipitates (0-ppm goethite, $\log(\text{IAP/Ks}) = 6.49$), koritnigite-like precipitates (10-ppm goethite, $\log(\text{IAP/Ks}) = -0.92$), adamite-like precipitates (100-ppm goethite, $\log(\text{IAP/Ks}) = -0.92$), and surface-adsorbed species (1000-ppm goethite, $\log(\text{IAP/Ks}) = -0.92$). Long-term (exceeding 6 months) sorption and dissolution experiments with complementary spectroscopic (e.g., EXAFS) data are needed to further evaluate the stability and long-term fate of the metal-arsenate complexes as they may form in co-contaminated environments. The precipitates' crystallinity could be ascertained from collecting XRD data at various intervals. X-ray photoelectron spectroscopy would be useful to ascertain the Lewis acid/base behavior of the sorbates and sorbents and in conjunction with EXAFS spectroscopy shed light into the possible connection between substrate-sorbate charge transfers and first shell metal-oxygen distances. The formation of aqueous polymeric solution complexes and their role in the precipitation of ions deserves due attention to help explain transitions of ions from the aqueous into the solid phase. Generally, more research is required that recognizes the chemistry of binary and tertiary

ion systems as they are more applicable to (contaminated) environments than single ion systems.

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