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Monitoring Trace Amounts of Lead and Arsenic Adsorption by X-ray Absorption Fine Structure Combined with Fluorescence Spectrometry

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Abstract

X-ray absorption fine structure combined with fluorescence spectrometry was used for the speciation of trace amounts of lead and arsenic adsorbed. The Pb^{2+} species were effectively adsorbed on a layered material $Mg_6Fe_2(OH)_{16}(CO_3)\cdot 3H_2O$ from 100 ppb–1.0 ppm test aqueous solutions. A eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ coagulated in the case of a 1.0 ppm Pb^{2+} solution, and in contrast, the major species was ion-exchanged Pb^{2+} in the case of the adsorption from the 100 ppb aqueous solution. The arsenic species were effectively adsorbed on intercalated Fe-montmorillonite from 50 ppb–16 ppm test aqueous solutions. In this concentration range, As^{3+} in the solution was oxidized upon adsorption. The adsorbed structure was suggested to be $[As^V(OH)_2(\mu\text{-}OFe)_2]$ both in the cases of adsorption of As^{3+} and As^{5+}.

1. Introduction

Speciation of toxic elements, such as Cr^{6+}, Cu^{2+}, Zn^{2+}, As^{3+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} in the environment is important to the understanding of their effects to human health and to investigate the removal and reuse methods. XAFS gives direct information for the speciation of non-crystalline site. Higher-energy-resolution XAFS spectra are desirable for precise speciation. To improve energy resolution, the fluorescence X-rays emitted from a toxic element in the sample were analyzed by a high-energy-resolution Rowland-type spectrometer. This method is free from the problems associated with photon-counting losses (SSD) or spectral broadening effects at higher photon energies (Pb K-edge) [1].

Basic polyhydroxide compound of layered structure $Mg_6Fe_2(OH)_{16}(CO_3)\cdot 3H_2O$ (**1**) was found to be effective for lead(II) adsorption, especially when the flow rate of lead test solution was high [1]. Layered material was also good for arsenic (arsenite, arsenate) adsorption, especially in the case that iron material was intercalated between the layers of montmorillonite.

2. Experimental Section

2.1. *Samples*

Standard lead(II) compounds were used as received and diluted to 5.0 wt% of Pb by mixing with boron nitride. An ion-exchanged standard sample was prepared from lead(II) nitrate aqueous solutions on NaY zeolite (JRC-Z-Y4.8, $Na_{58}Al_{58}Si_{134}O_{384}\cdot 240H_2O$). The cation exchange ratio was 85.5%. An adsorbent **1** was synthesized by adding NaOH to the aqueous solution of $MgCl_2$ and $FeCl_3$ [1]. The specific BET surface area was $110\,m^2\,g^{-1}$. The interlayer spacing was 7.79 Å based on X-ray diffraction (XRD) measurements. A 1.0 ppm or 100 ppb lead(II) nitrate solution was adsorbed at a flow rate (space velocity) of $50\,min^{-1}$ on adsorbent **1**.

Standard As^{III} and As^V compounds were used as received and diluted to 2.0 wt% of As by mixing with boron nitride. An adsorbent was prepared by the following procedure. 8.14 ml of a 0.43 M $Fe(NO_3)_3$ solution and 9.33 ml of a 0.75 M NaOH solution were mixed and left undisturbed in the dark at 290 K for 24 h. 0.5 wt% of Na-montmorillonite (Kunipia F, $Na_{1.5}Ca_{0.096}Al_{5.1}Mg_{1.0}Fe_{0.33}Si_{12}O_{27.6}(OH)_{6.4}$) was suspended in distilled water and the reaction mixture was added. The resultant powder obtained was dried for 72 h at 313 K. The Fe loading was 15.3 wt%. The sample is denoted as Fe-montmorillonite. 20 ml of 1–16 ppm solutions of $As^{III}{}_2O_3$ or $KH_2As^VO_4$ was adsorbed on 50 mg of Fe-montmorillonite in a 30-ml tube at 290 K for 12 h. 500 mg of Fe-montmorillonite was packed and 50–200 ppb solutions of $As^{III}{}_2O_3$ were flowed at a rate of between 1.4–$2.1\,ml\,min^{-1}$. All the samples were pressed into 20 mm-diameter disks for X-ray measurements.

2.2. *X-ray Emission and Absorption Measurements*

The X-ray measurements utilizing a fluorescence spectrometer were performed on the Undulator Beamline 10XU of SPring-8 (Sayo). The storage ring energy was 8.0 GeV and the ring current was 100–50 mA. A Si(111) double crystal monochromator and a Rh-coated double mirror set were used. All the measurements were performed at 290 K. The X-ray fluorescence from the sample was analyzed by a Rowland-type spectrometer ($R = 220$ mm) equipped with a Johansson-type Ge(555) crystal ($50 \times 50\,mm^2$, Crismatec) and a scintillation counter (Oken). The energy resolution was 1.1 eV at the Cu $K\alpha_1$ emission (8 keV) including the contribution of the beamline [2] and 0.3 eV at the V $K\alpha_1$ emission (5 keV) based on the peak width of emission and the pre-edge absorption peaks [3].

The Pb $L\alpha_1$ emission spectrum was measured for Pb^{2+} adsorbed on compound **1** (Pb 0.12–1.0 wt%) and reference Pb compounds with the excitation energy set at 13064.3 eV. The fluorescence spectrometer was tuned to the center of the Pb $L\alpha_1$ peak and the Pb L_3-edge XAFS spectrum was measured. The Undulator gap and the piezoelement were optimized to maximize the X-ray beam flux at each data point.

The As $K\alpha_1$ emission spectrum was measured for arsenic adsorbed on the Fe-montmorillonite (As 0.13–0.48 wt%) and reference As compounds with the excitation energy set at 11885.0 eV. The fluorescence spectrometer was tuned to the center of the As $K\alpha_1$ peak and the As K-edge XAFS spectrum was measured. Measurements for standard As samples and a part of As adsorbed onto Fe-montmorillonites were carried out in transmission mode to evaluate the energy resolution and signal-to-background ratio of the spectra obtained in each mode.

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2.3. *XAFS Data Analysis*

Background subtraction of the raw XANES spectrum was performed by using a Victoreen parameter. The subtraction was not necessary in the case of XANES utilizing the fluorescence spectrometer. A smooth spline function was calculated in the postedge region, and then the spectrum was normalized. An EXAFS curve fitting analysis was performed using empirical phase-shift and amplitude parameters for the Pb-O and As-O bonds extracted from the EXAFS spectra of PbO_2 and $K[AsO_2(OH)_2]$ and theoretical phase-shift and amplitude parameters of the As•••Fe bond generated using the *ab-initio* calculation code FEFF 8.2 [4] for the coordinates of $AsFeO_4$ crystal [5].

3. Results and Discussion

3.1. *Pb $L\alpha_1$ Emission and L_3-edge Absorption Spectra*

The Pb $L\alpha_1$ emission peak appeared at 10551.5 eV for 0.12 wt% Pb adsorbed on compound **1** from a 100 ppb Pb^{2+} solution. The full width at a half maximum (FWHM) obtained by the peak fit using a pseudo-Voigt function was 11.7 eV. The core-hole lifetime width of Pb L_3 is 5.81 eV and the energy resolution of spectrometer was evaluated to be 10.1 eV, including the contribution of the beamline.

Normalized Pb L_3-edge XANES spectra are depicted in Figure 1. The rising edge for standard Pb^{II} inorganic compounds shifted by 2.8–4.3 eV toward higher energy compared to 13040.6 eV for Pb^0. The rising edge for lead (0.12–1.0 wt%) adsorbed on compound **1** appeared within the range 13042.9–13044.2 eV (a–c), demonstrating that the adsorbed lead state was II. The rising edge and maximum point energies for the spectrum for 1.0 wt% Pb on compound **1** (13044.2 and 13056.3 eV, respectively; Figure 1a) prepared from 1.0 ppm test solution resembled only that for $2PbCO_3{\cdot}Pb(OH)_2$ (13044.0 and 13055.5 eV, respectively; g).

The samples of 0.30 and 0.12 wt% Pb on compound **1** were both prepared from 100 ppb Pb^{2+} solution, and the two spectra (b) and (c) resembled each other. Based on the rising edge and the maximum point energies, these two spectra (13043.0 ± 0.1 eV and 13054.3 ± 0.7 eV, respectively) resembled only that for PbY (13043.4 and 13054.4 eV, respectively; d).

The comparison of post-edge peak at 13094–13097 eV and the unresolved shoulder peak at 13049 eV supported above assignments of lead species in Figure 1a–c. Most of the Pb^{2+} coagulated as a eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ on compound **1** in the case from a 1.0 ppm solution. The hydroxyl groups should be derived from the buffering effect of basic surface of compound **1**. The formation of pure $PbCO_3$ by the reaction with intercalated/dissolved carbonate or pure $Pb_6O_4(OH)_4$ by the reaction with surface hydroxyl groups should be negligible. In contrast, in the case of the 100 ppb solution, the major lead phase was ion-exchanged Pb^{2+} via the surface reaction $-OH + Pb^{2+} \rightarrow -OPb^+ + H^+$. A shoulder peak at 13049 eV (Figure 1b and c) suggests a minor contribution from a coagulated eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ on compound **1**. Pb L_3-edge EXAFS was measured for the sample of Figure 1a. The Pb-O bond was found at 2.4 Å and the coordination number (N) was ≈3 [6].

3.2. *As $K\alpha_1$ Emission and K-edge Absorption Spectra*

The As $K\alpha_1$ emission peak appeared at 10544.7 eV for 0.48 wt% As adsorbed on Fe-montmorillonite from a 16 ppm test solution of As^{5+}. The FWHM obtained by the peak fit using a pseudo-Voigt function was 5.72 eV. The total core-hole lifetime width for As $K\alpha_1$ is 3.08 eV and the energy resolution of the spectrometer was evaluated to be 4.8 eV, including the contribution of beamline. Note that this value will be an overestimation in the case that As^{5+} and As^{3+} co-exist as adsorbed in the sample. The corresponding value of energy resolution was estimated to be 1.3 eV for an arsenic metal sample.

Normalized arsenic K-edge XANES spectra are depicted in Figure 2. The maximum point energy above the edge shifts from 11867.1 for the arsenic metal (a) to 11868.5 for $As^{III}{}_2O_3$ (b) then to 11872.1 eV for $K[As^VO_2(OH)_2]$ (c). The maximum point energy for (d)–(g) was similar to the case of (c). The spectrum pattern of the arsenic adsorbed from the 16 ppm arsenate solution (d) closely resembled that of $K[AsO_2(OH)_2]$. Unexpectedly, spectra (e)–(g) for the samples prepared from the arsenite solution were more similar to (c) than they were to (b). Hence, in the case

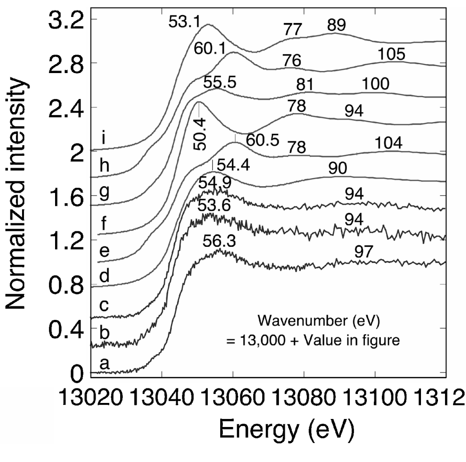


Fig. 1. Normalized Pb L_3-edge XANES spectra for Pb^{2+} on (1) measured utilizing a secondary fluorescence spectrometer (a–c). The Pb content was 1.0 wt% adsorbed from 1.0 ppm Pb^{2+} solution (a) and Pb 0.30 (b) and 0.12 wt% (c) from 100 ppb solution. Reference XANES spectra for PbY zeolite (d), PbO (e), $Pb(NO_3)_2$ (f), $2PbCO_3{\cdot}Pb(OH)_2$ (g), $Pb_6O_4(OH)_4$ (h), and $PbCO_3$ (i). (d)–(i) were measured in the conventional transmission mode.

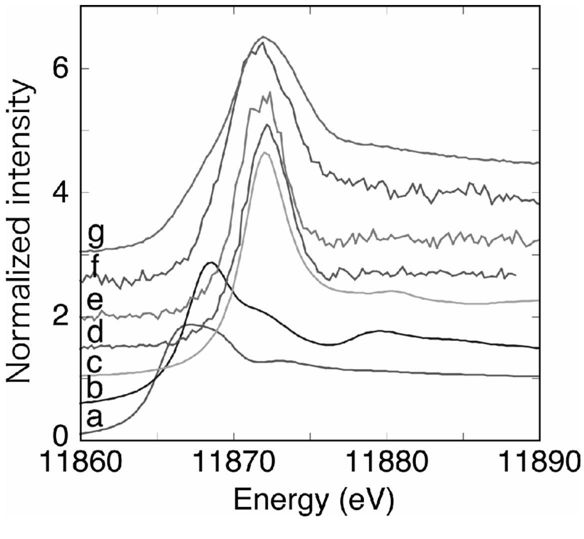
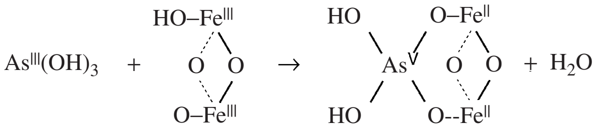


Fig. 2. As K-edge XANES spectra measured at 290 K for As metal (a), As_2O_3 (b), KH_2AsO_4 (c), and As adsorbed (d–g) on Fe-montmorillonite (Fe 15.3 wt%) from test solutions of 16 ppm of KH_2AsO_4 (d), 16 ppm of As_2O_3 (e), 200 ppb of As_2O_3 (f), and 50 ppb of As_2O_3 (g). Spectra (a)–(c) and (g) were measured in transmission mode and (d)–(f) were measured in fluorescence mode utilizing a secondary fluorescence spectrometer.

of the arsenic adsorbed from arsenite solutions in the range of 50 ppb–16 ppm, most of the As^{3+} was oxidized to As^{5+} upon adsorption. A minor peak for adsorbed As^{III} appeared as a shoulder feature at 11868.8–11869.8 eV in (e) and (f). Arsenic K-edge EXAFS was measured for arsenic adsorbed from 200 ppb–16 ppm on Fe-montmorillonite. The As-O and As•••Fe distances were 1.68 Å ($N \approx 3$) and 3.22–3.25 Å ($N \approx 2$), respectively. Also based on the crystallographic structure of FeO(OH) where $[FeO_6]$ octahedral are connected at the edge, the mechanism of oxidative adsorption of As may be formulated as equation **1**. $[AsO_2(OH)_2]^-$ was also suggested for spectrum d adsorbed from arsenate [9–11].



$$\mathrm{As^{III}(OH)_3} + \begin{array}{c}\mathrm{HO{-}Fe^{III}}\\ \mathrm{O\quad O}\\ \mathrm{O{-}Fe^{III}}\end{array} \rightarrow \begin{array}{c}\mathrm{HO\qquad O{-}Fe^{II}}\\ \mathrm{As^{V}\quad O\quad O}\\ \mathrm{HO\qquad O{-}{-}Fe^{II}}\end{array} + \mathrm{H_2O} \qquad (1)$$

4. Conclusions

X-ray absorption fine structure combined with fluorescence spectrometry was successfully applied to trace amounts of lead and arsenic adsorbed from aqueous solutions containing 50 ppb–16 ppm of lead or arsenic. Based on Pb L_3-edge XANES, it was found that a eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ coagulated in the case of the 1.0 ppm Pb^{2+} solution, whereas the major species was ion-exchanged Pb^{2+} in the case of adsorption from 100 ppb Pb^{2+} solution. Both arsenate and arsenite species were adsorbed on Fe-montmorillonite (Fe 15.3 wt%) from 50 ppb– 16 ppm solutions containing of As. In this concentration range, As^{3+} in solution was oxidized to As^{5+} upon adsorption. Because the As^{3+} is more toxic [8, 9], Fe-montmorillonite effectively trapped trace amounts of As^{3+} in solution and detoxified it.

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