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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 Pb2+ species were effectively adsorbed on a layered material Mg6Fe2(OH)16(CO3)·4H2O from 100–1 ppm test aqueous solutions. A mixture of Pb(NO3)2 and Pb(OH)2 coagulated in the case of the adsorption from 100–1 ppm aqueous solution. The arsenic species were effectively adsorbed on intercalated Fe-montmorillonite from 50 ppb–16 ppm test aqueous solutions. In this concentration range, As3+/5+ in the solution was oxidized upon adsorption. The adsorbed structure was suggested to be [AsV(OH)2(µ-Cl)] in the cases of Pb2+ and As3+.

1. Introduction
Speciation of toxic elements, such as Cd2+, Cu2+, Zn2+, As3+, As5+, Hg2+, and Pb2+ 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 Mg6Fe2(OH)16(CO3)·4H2O (I) 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 (arsenate, 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 adsorbent was prepared by the following procedure. 8.14 mL of a 0.43 M Fe(NO3)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 (Kennecott: Na0.75Ca0.25Al8.58Si34.64O102(OH)0.7) 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 AsIII2O3 or KH2AsVO4 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 AsIII2O3 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 Johannson-type Ge(555) crystal (50 × 50 mm2, Cismatec) and a scintillation counter (Oken). The energy resolution was 1.1 eV at the Cu Kα emission (8.0 keV) including the contribution of the beamline [2] and 0.3 eV at the V Kα emission (5.4 keV) based on the peak width of emission and the pre-edge absorption peak [3].

The Pb L3 emission spectrum was measured for Pb2+ adsorbed on compound I (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 L3 peak and the Pb L3-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 Kα 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 eV. The fluorescence spectrometer was tuned to the center of the As Kα 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.
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 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_3-edge Emission and L_3-edge Absorption Spectra

The Pb L_3-edge emission peak appeared at 10551 eV for 0.12 wt% Pb adsorbed on compound 1 from a 100 ppb Pb^{2+} solution. The full width at half maximum (FWHM) obtained by the peak fit using a pseudo-Voigt function was 11.7 eV. The core-hole lifetime width of PbL_{3/2} 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^{2+} inorganic compounds shifted by 2.8–4.3 eV toward higher energy compared to the spectrum for 1.0 wt% Pb on compound 1. The rising edge and maximum point energies for PbO (13043.4 and 13054.3 eV, respectively; d) and PbO_2 (13043.0 ± 0.1 eV and 13054.3 ± 0.7 eV, respectively; g) resembled each other. Based on the rising edge and the maximum point energies, these two spectra (d)–(g) for the samples prepared from the arsenite solution were more similar to (c) than they were to (b). Hence, in the case of the 100 ppb solution, the major lead phase 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 11862 eV for adsorbed on Fe-montmorillonite from a 16 ppm test solution of As^{3+}. 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_L is 3.08 eV and the energy resolution of the spectrometer was evaluated to be 4.8 eV, including the contribution of the beamline. Note that this value will be an overestimation in the case of 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 arsenite solution.

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+} co-agulated 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 PbO(OH)_2 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+} → PbOH^{+} + H^+. A shoulder peak at 13049 eV (Figure 1b and c) suggests a minor contribution from a co-agulated 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].
of the arsenic adsorbed from arsenite solutions in the range of 50 ppb–16 ppm, most of the As\textsuperscript{3+} was oxidized to As\textsuperscript{5+} upon adsorption. A minor peak for adsorbed As\textsuperscript{3+} 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. Based on the crystallographic structure of FeO(OH) where [FeO\textsubscript{6}] octahedral are connected at the edge, the mechanism of oxidative adsorption of As may be formulated as equation 1. [AsO\textsubscript{2}(OH)\textsubscript{2}]\textsuperscript{−} was also suggested for spectrum d adsorbed from arsenate [9–11].

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\textsubscript{3}-edge XANES, it was found that a eutectic mixture of PbCO\textsubscript{3} and Pb(OH)\textsubscript{2} coagulated in the case of the 1.0 ppm Pb\textsuperscript{2+} solution, whereas the major species was ion-exchanged Pb\textsuperscript{2+} in the case of adsorption from 100 ppb Pb\textsuperscript{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\textsuperscript{3+} in solution was oxidized to As\textsuperscript{5+} upon adsorption. Because the As\textsuperscript{3+} is more toxic [8, 9], Fe-montmorillonite effectively trapped trace amounts of As\textsuperscript{7+} in solution and detoxified it.

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