Monitoring Trace Amounts of Lead and Arsenic Adsorbed under Environmental Conditions by XAFS Combined with Fluorescence Spectrometry

The risk of trace amounts of metals in environmental water to human health has been pointed out [1]. The regulations of metal concentration in water are becoming more severe: e.g., 100 ppb for lead and 10 ppb for arsenic. Co-precipitation and adsorption are promising methods for the removal of trace amounts of metals in water. Information on the removed metal site structure and the chemical state is crucial in the assessment of the removal effectiveness for the most hazardous valence state of metals.

X-ray absorption fine structure (XAFS) has become widely used with the state-of-the-art technology of synchrotron radiation and advanced X-ray detectors to monitor the local structure of noncrystalline and heterogeneous/hybrid materials. However, there are still experimental difficulties in measuring at high-energy resolution the absorption edge of the trace amount of an element in samples containing a high concentration of heavy element(s).

In this account, 0.12 wt% Pb adsorbed from a 100 ppb aqueous solution and 0.20 wt% As adsorbed from a 200 ppb arsenite solution were monitored by the XAFS combined with a high-energy-resolution fluorescence spectrometer [2]. The energy resolutions were 0.3 eV at 5 keV and 1.1 eV at 8 keV. The latter value includes the contribution of the beamline [3]. These values are smaller than the core-hole lifetime widths of Pb L_3 (5.81 eV) and As K (2.14 eV). Thus, the advantages of the method applied in this account are (i) the removal of lifetime broadening [4], (ii) reasonable signal/background ratio, and that (iii) the method is free from the problems associated with photon-counting losses.

The X-ray fluorescence from Pb adsorbed on $Mg_6Fe_2(OH)_{16}(CO_3)\bullet 3H_2O$**(1)** was analyzed by a Rowland-type spectrometer (radius 220 mm) equipped with a Johansson-type cylindrically bent Ge(555) crystal and a scintillation counter at beamline **BL10XU** [5]. The spectrometer was tuned at 10551.5 eV (Pb $L\alpha_1$ emission), and the obtained Pb L_3-edge X-ray absorption near-edge structure (XANES) spectra are shown in Figs. 1(a-c). Based on the comparison of the rising edge and post-edge peak energies, spectrum a for Pd adsorbed from the 1.0 ppm solution resembled only that for $2PbCO_3\bullet Pb(OH)_2$ (Fig. 1(g)). Figures 1(b,c) for Pb adsorbed from a 100 ppb solution resembled each other. The rising edge position shifted from –1.1 to –1.3 eV compared to Fig. 1(a). Figures 1(b,c) resembled only those of PbY zeolite (Fig. 1(d)), Pb mordenite or Pb-ZSM-5. Pb^{2+} ions replace the protons or Na^+ sites of zeolites.

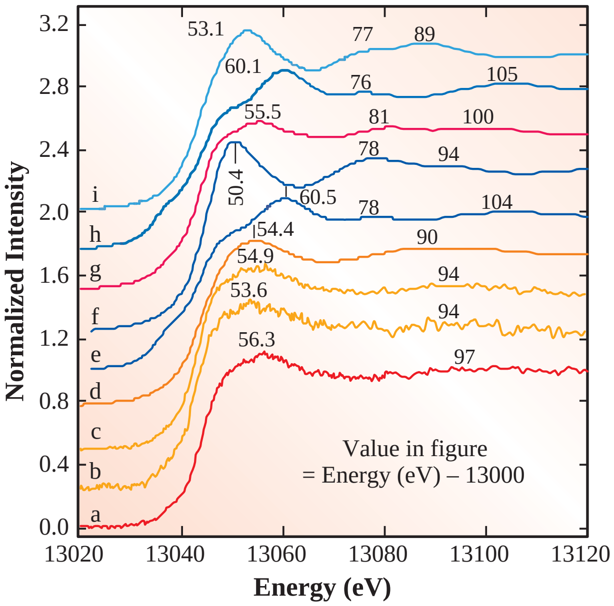

Fig. 1. Normalized Pb L_3-edge XANES spectra for Pb^{2+} on **1** measured utilizing a secondary fluorescence spectrometer **(a – c)**. The Pb content was 1.0 wt% adsorbed from a 1.0 ppm Pb^{2+} solution **(a)** and Pb 0.30 wt% **(b)** and 0.12 wt% **(c)** adsorbed from a 100 ppb solution. XANES spectra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

An unresolved shoulder peak was observed at 13049 eV in Figs. 1(a-c). A similar peak was also observed for $2PbCO_3\bullet Pb(OH)_2$ (Fig. 1(g)). No shoulder peak appeared in this region for PbY (Fig. 1(d)).

In summary, most of the Pb^{2+} coagulated as a eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ on **1** in the adsorption from a 1.0 ppm solution. In contrast, in the adsorption from a 100 ppb solution, the major Pb phase was ion-exchanged Pb^{2+} via surface reaction A.

$$-\mathrm{OH} + \mathrm{Pb}^{2+} \rightarrow -\mathrm{OPb}^{+} + \mathrm{H}^{+} \qquad \text{(A)}$$

A shoulder peak at 13049 eV suggests a minor contribution from the coagulated eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ on **1**. The interpretation of this difference that depends on the Pb concentration is illustrated in Fig. 2. The surface of **1** has a buffering effect and the pH value in the proximity of **1** becomes 7 – 8 due to the effect of coagulant chemicals released through a slight dissolution of **1** [5]. In the pH region, a forward reaction of B proceeds from a 1.0 ppm solution.

$$Pb^{2+} + nCO_3^{2-} + 2(1-n)OH^- \rightarrow nPbCO_3 \bullet (1-n)Pb(OH)_2 \qquad \text{(B)}$$

In the adsorption from a 100 ppb Pb^{2+} solution, equilibrium shifted to the left-hand side of equation B. The ratio of free Pb^{2+} in the solution dramatically increased, and thus the, ion exchange reaction (equation A) dominantly proceeded. Hence, the major species of ion-exchanged Pb^{2+} and the minor phases of the coagulated eutectic mixture of $PbCO_3$ and $Pb(OH)_2$ were detected (Figs. 1(b,c)).

The As K-edge XANES spectra were also measured similarly to the Pb L_3-edge spectra described above. The fluorescence spectrometer was tuned to 10544.3 eV (As $K\alpha_1$ emission). Samples of 0.48 – 0.20 wt% As adsorbed from 16 ppm of arsenate, 16 ppm of arsenite, and 200 ppb of arsenite aqueous solutions were studied (Figs. 3(d-f)) on an Fe-impregnated montmorillonite ($Na_{1.5}Ca_{0.096}Al_{5.1}Mg_{1.0}Fe_{0.33}Si_{12}O_{27.6}(OH)_{6.4}$)**(2)** [3]. The three spectra resembled one another. The strong peak positions in the post-edge region were very close to that for the spectrum of $KH_2As^VO_4$ (Fig. 3(c)) rather than that for the spectrum of $As^{III}{}_2O_3$ (Fig. 3(b)). Thus, the observed oxidation of trace amounts of arsenite upon adsorption on **2** to arsenate is important in the preservation of the environment because arsenate affects far less human health than arsenite.

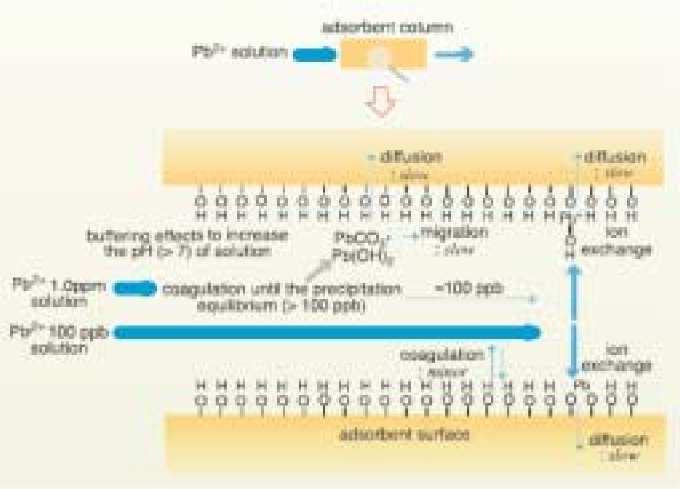

Fig. 2. Pb^{2+} adsorption mechanism on **1** from 1.0 ppm and 100 ppb aqueous Pb^{2+} solutions.

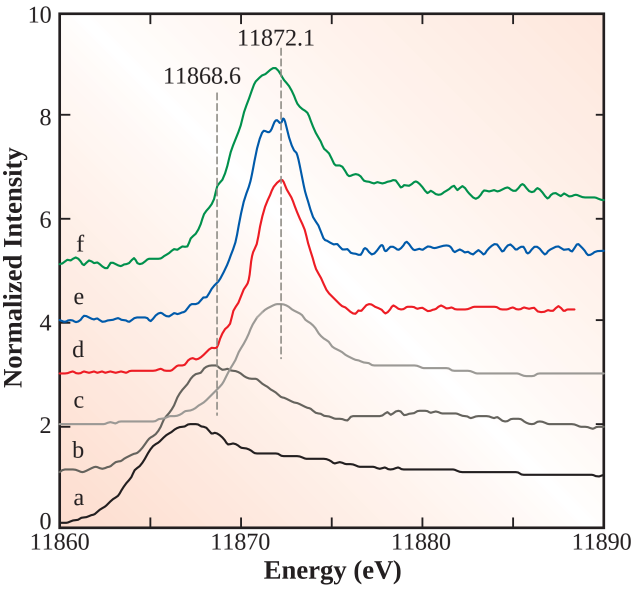

Fig. 3. Normalized As K-edge XANES spectra for As metal **(a)**, As_2O_3 **(b)**, KH_2AsO_4 **(c)**, and As adsorbed on **2** (Fe 15.3 wt%, **d – f**) from solutions of 16 ppm of KH_2AsO_4 **(d)**, 16 ppm of As_2O_3 **(e)**, and 200 ppb of As_2O_3 **(f)**. Spectra **(d – f)** were measured utilizing a high-energy-resolution fluorescence spectrometer. The spectra **(a – c)** were measured in the conventional transmission mode.

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