Analysis of Chemical States of Heavy Metals in Environmental Samples Using XFAS[†]

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Abstract:

XAFS X-ray absorption fine structure analysis enables to detect chemical states of trace heavy metals in environment directly without any pre-treatment. It was found that the chemical state of Zn in sewage sludge was ZnS, and it changed to Zn^{2+} under aerobic condition. It was also detected that 18% of As_2S_3 existed in excess activated sludge which contained trace of As. This paper shows the method for chemical states analysis of heavy metals in environmental samples using XAFS.

1. Introduction

Heavy metals are indispensable for the support of daily life and even for sustaining life. Their effects on living things, however, depend highly on their chemical states and concentrations. The toxicity of arsenic compounds, for example, is higher when the compounds are inorganic than organic, and higher when the compounds are trivalent than pentavalent. In the case of oral exposure to rats, the 50% lethal dose (LD_{50}) of sodium arsenite is 41 mg/kg, while that for sodium dimethylarsinic acid is 2.6 g/kg[1]. The former is a trivalent inorganic arsenic; the latter, a pentavalent organic arsenic. When evaluating the safety of heavy metals present in the environment, it is therefore necessary to consider the chemical states of the heavy metals as well as their concentrations.

The chemical states of heavy metals present in the environment change under the influence of physicochemical effects and biological effects. In most cases the concentrations are very low, and the environment often provides a wet condition in which aqueous and solid phases coexist. Progress in analytical methods now permits the measurement of concentrations of trace amounts of heavy metals. However, challenges in maintaining the environmental conditions where heavy metals can be found (pH, oxidation-reduction potential, kinds and concentrations of coexisting elements, whether or not microorganisms are present, etc.) still make it difficult to perform these measurements. The analysis of trace amounts of heavy metals requires various pretreatments such as drying, grinding, chemical dissolution, extraction, and concentration. As the environmental conditions specific to samples is often lost during these pretreatments, information on chemical states can only be obtained by estimations.

In an effort to obtain basic information for evaluating the safety of heavy metals present in the environment, the authors have been studying a method of XFAS (X-ray absorption fine structure) analysis based on the X-ray fluorescence mode. This method enables the determination of chemical states under two conditions, i.e., while maintaining the environmental conditions under which heavy metals are present and while changing the environmental conditions. The XFAS analysis is highly effective in identifying chemical states of trace heavy metals in samples in a wet condition, such as those in sludge and soil.

In this paper, the authors present the results of an XAFS analysis of the chemical states of heavy metals in environmental samples using SPring-8, the highest-performance large-scale synchrotron radiation fecility in the world (operated by Japan Synchrotron Radiation Research Institute).

SPring-8 is a public facility for the research of syn-

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Photo 1 Panoramic view of the SPring-8

chrotron radiation. The facility has public beam lines opened to the public, and call for proposal twice a year. **Photo 1** is a panoramic view of the facility. SPring-8 can generate the world's highest-luminance synchrotron radiation in a wide energy range from soft X-rays (photon energy: 300 eV) to hard X-rays (300 keV). Researchers use the facility in many research fields, from fundamental science to industrial applications.

2. Conventional Analysis Methods of Chemical States of Heavy Metals

The sequential fractional method is used for estimating the amounts of the heavy metals contained in environmental samples. The method essentially uses solvents of acid, alkali, and the like to extract heavy metals in samples and determine the heavy metal concentrations in extracts[2,3]. **Figure 1** shows an example of operation of the sequential fractional method applied to the determi-
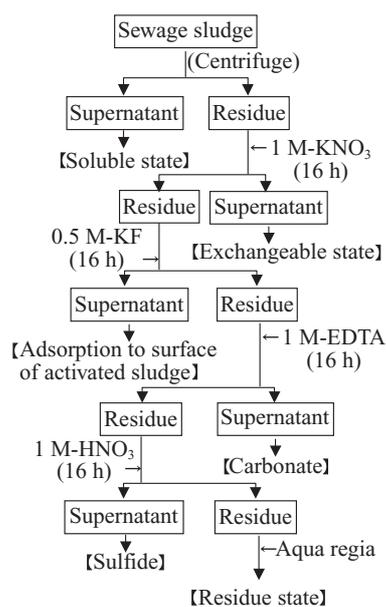
Fig. 1 Schematic diagram of sequential fractional method to detect chemical states of heavy metals in sewage sludge

nation of the chemical states of heavy metals contained in sewage sludge. In this method, the chemical states of heavy metals are estimated by stepwise extraction and separation of the heavy metal elements contained in a sample using four solvents for analysis.

The information obtained by the sequential fractional method can only be used to determine specific chemical states that have been hypothesized, and the determination remains within the realms of estimation. And when a sample contains heavy metals in only trace amounts, limitations in analytical precision when using fractionated heavy metals often make it difficult to obtain sufficient information.

3. XFAS[4] Analysis

The principle of the XFAS analysis is shown in **Fig. 2**. When an X-ray strikes against an atom of a sample, part of the X-ray is absorbed. When the absorption rate of the X-ray is measured by changing energy, the X-ray absorption rate rises steeply at the excitation energy of a core-level electron and thereafter attenuates gently with increasing energy of injected X-ray.

This spectrum has two structures: a spectral structure with a large change near the absorbed energy and a high-energy region with a small and gentle vibrational structure. The former is called an "XANES" (X-ray absorption near-edge structure), the latter is called an EXAFS (expanded X-ray absorption fine structure), and both are generically called an XFAS. XANES provides information on the local electronic structure of a specific element and EXAFS provides information on a structure around an atom.

In an XFAS analysis of an environmental sample, the spectrum of a standard substance is measured and the chemical state of a substance to be analyzed is determined by comparing the substance to be analyzed with a spectrum obtained from the environmental sample. When a substance to be analyzed is present in multiple chemical states, spectral structures specific to the different chemical states overlap each other. In this case, the relative amounts of the individual chemical states can be determined with the use of a parameter fitting technique
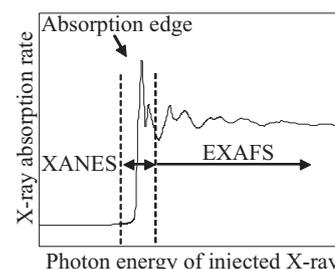
Fig. 2 Schematic diagram of XAFS

to be described later.

Researchers using the public beam line BL01B1 in SPring-8 can perform higher-sensitivity XFAS analyses by applying a multi-element solid-state detector. The XFAS analysis has four useful capabilities:

(1) It can analyze a chemical state without disruption of an environmental state specific to a heavy metal.

(2) It can analyze multiple chemical states of a specified heavy metal by separating the multiple chemical states.

(3) It can determine the chemical states of trace heavy metals.

(4) It can be used for in situ and instantaneous measurements, and changes in a chemical state can be observed by changing measurement conditions.

To give examples of the XFAS analysis and its features, Chapters 4 and 5 of this report present the results of an XFAS investigation on the chemical states of heavy metals in sewage sludge. Chapter 4 describes the chemical states of heavy metals contained in sewage sludge and changes in the chemical states in biological treatment processes. Chapter 5 clarifies the presence of trace arsenic contained in sewage sludge in each chemical state and describes the results of an observation of the chemical states that change in the sewage treatment process.

4. Measurement of Chemical States of Heavy Metals in Sewage Sludge

Trace heavy metals flow into a sewage treatment plant as domestic waste water and industrial waste water. The sewage treatment process decomposes or removes pollution components by biological, physical, and chemical treatments, and almost all of heavy metals move into sludge[3].

Sewage and sewage sludge are basically in an anaerobic condition (a condition which lacks free oxygen). However, the process of aeration changes this anaerobic condition into an aerobic condition (a condition with an abundance of free oxygen), whereupon the decomposition of pollution components by microorganisms proceeds.

Our group determined the chemical states of heavy metals in sewage sludge by performing an XFAS analysis in SPring-8. Using a measurement container capable of receiving an air flow, we carried out the XFAS analysis by aerating the sewage sludge in this measurement container in order to elucidate the changes in the chemical states of heavy metals in the biological treatment process.

4.1 Experimental Method

We performed an XFAS analysis on primary sludge

and excess activated sludge sampled from a medium-scale wastewater treatment plant (Treatment Plant A) in Japan.

To keep the sewage sludge is an anaerobic condition, each of the samples was kept in a $40\,\mu m$ thick polypropylene bag and refrigerated in a hermetically sealed condition, as shown in **Photo 2**. In order to simulate the aeration in sewage treatment (to confer the aerobic condition), we fabricated an acrylic measurement container (**Photo 3**) and performed measurements by blowing air in.

The XFAS spectrum can be quantified by either measuring the transmitted X-rays (the transmission mode) or measuring the fluorescent X-rays (the X-ray fluorescence mode)[4]. In this study we needed to handle very low element concentrations of several milligrams/kg or so. To accomplish this effectively, we made the measurements in a high-sensitivity X-ray fluorescence mode using a Ge 19-element solid-state detector for X-ray detection. The transmission mode was adopted for the spectra of standard substances, and an XFAS spectrum of the K-absorption edge was measured for each of the elements.

As the standard substances, oxides and sulfides of specified heavy metals were selected from commercially available reagents. Aqueous solutions of chlorides were used as metal ions.
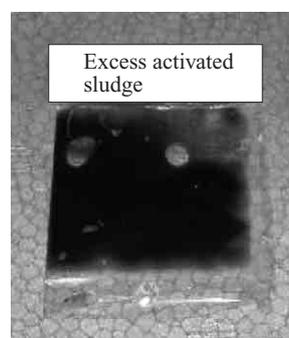
Photo 2 Sample for measurement under anaerobic condition
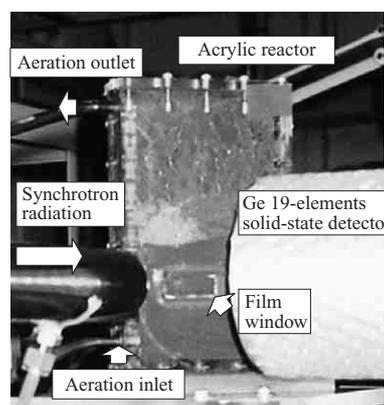
Photo 3 Apparatus of XAFS measurement for aerobic conditions

4.2 Results

4.2.1 Change in the state of Mn

Figure 3 shows K-absorption edge XANES spectra of Mn contained in the sludge of Treatment Plant A. In an anaerobic condition, the Mn in both the primary sludge and excess activated sludge consisted of bivalent ions (① and ② of Fig. 3).

When the aerobic condition was produced in the excess activated sludge, a peak of MnO_2 appeared near 6 550 to 6 560 eV (③ of Fig. 3) and part of the Mn(II) was oxidized to form Mn(V). When the aerobic condition was produced in the primary sludge, the valence remained unchanged (④ of Fig. 3). This difference was attributed to the compositions of the two types of sludge: while the excess activated sludge was mainly composed of microorganisms, the primary sludge was mainly composed of coarse organic and inorganic substances. In the excess activated sludge mainly made up of microorganisms, the aerobic condition may have oxidized the Mn via the action of the iron-oxidizing bacteria contained in the sludge and the like.

4.2.2 Change in the state of Zn

Figure 4 shows the K-absorption edge XANES spectra of Zn contained in the sludge sampled in Treatment Plant A. In the anaerobic condition, the Zn in both the primary sludge and excess activated sludge was apparently ZnS (① and ② of Fig. 4).

In the excess activated sludge in the aerobic condition, a wide portion appeared in the right shoulder of a spectrum peak. This suggests that part of the ZnS might have been eluted as Zn^{2+}. In the aerated primary sludge, part of the ZnS changed into Zn^{2+} (④ of Fig. 4). This result agrees with research results of Shirakabe at al.[5] demonstrating an increase in the elutability of heavy metal ions when sludge is brought into an aerobic condition.

4.2.3 Change in the state of Cu

Figure 5 shows K-absorption edge XANES spec-
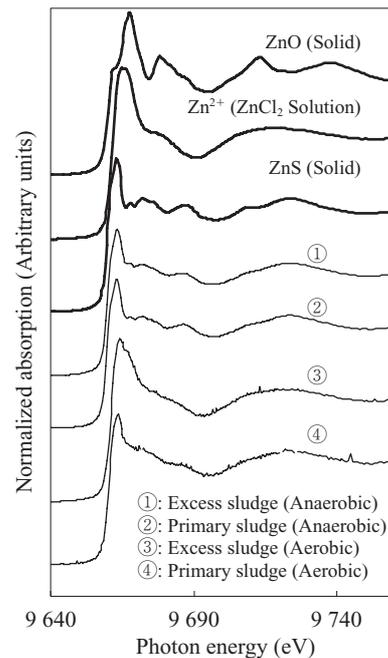
Fig.4 Zn K-edge spectrum of sewage sludge corrected from wastewater treatment plant A
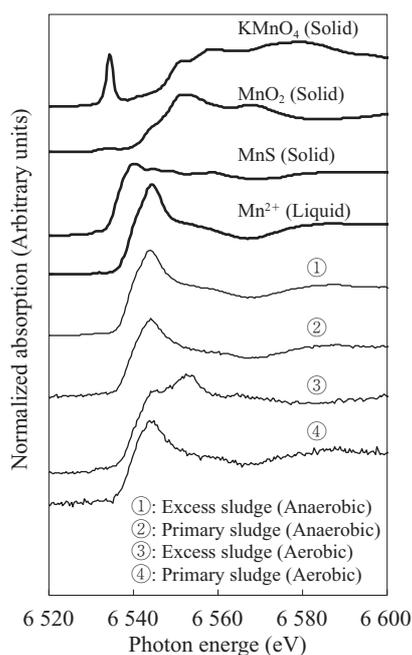
Fig.3 Mn K-edge spectrum of sewage sludge corrected from wastewater treatment plant A
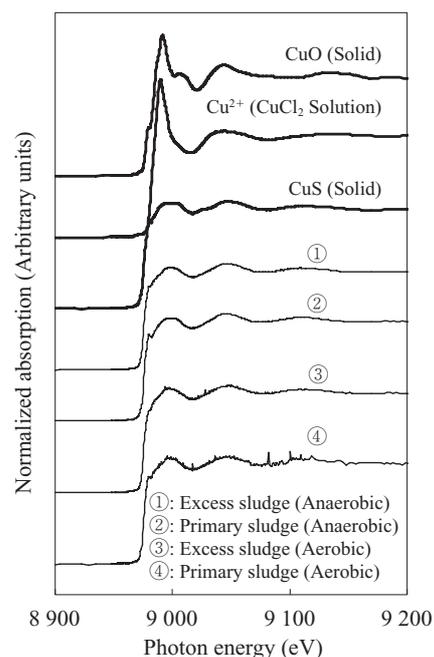
Fig.5 Cu K-edge spectrum of sewage sludge corrected from wastewater treatment plant A

tra of Cu contained in the sludge sampled in Treatment Plant A. The Cu in both the primary sludge and excess activated sludge in the anaerobic condition was CuS (① and ② of Fig. 5). And in contrast to the observations with Mn and Zn, the Cu remained CuS in both sludges even after the aerobic condition was produced (③ and ④ of Fig. 4). Kawashima et al. determined the chemical states of heavy metals in sewage sludge using the state fractionation method by continuous extraction. According to their results, the Cu contained in sewage sludge was all CuS[3]. Our experiments here corroborate this finding.

5. Analysis of the Chemical State of Trace Arsenic (As) in Sewage

This section gives an example of an XFAS analysis conducted to determine trace amounts of As in sewage sludge. In some geographical areas, sewage treatment facilities treat sewage containing As discharged from hot springs[6]. Sludge samples taken from each step in the treatment process were assessed by XFAS analysis to elucidate changes in the chemical state of As during sewage treatment.

5.1 Experimental Method

Primary sludge, excess activated sludge, sludge cases, and incinerator ashes were sampled from two treatment plants, one which treats hot spring water (Treatment Plant B) and one which does not (Treatment Plant C into), for XFAS analysis. The sample storage method and XFAS analysis method described in paragraph 4.1 above were adopted.

5.2 Experimental Results

Figure 6 shows K-absorption edge XANES spectra of the arsenic in the sludge sample from Treatment Plants B, the sample from Treatment Plant C, and sediment sampled from a riverbed downstream of Treatment Plant B. The Figure also shows energy positions in which the peaks of As_2S_3, As(III), and As(V) appear. **Figure 7** shows changes in the amounts of arsenic contained in the analyzed sludge, as calculated by the parameter fitting technique for estimating the presence ratio of arsenic by multiplying data on the XANES spectrum of a standard substance by a coefficient and selecting a coefficient that agrees with an XANES spectrum obtained from the samples.

5.2.1 Chemical state of As in biological reaction tank

Almost all of the As measured in the influent sewage and treated sewage of Treatment Plant B was As(V)(② and ③ of Fig. 6). In the excess activated

Fig. 6 As K-edge spectrum of sewage samples and river sediment sample
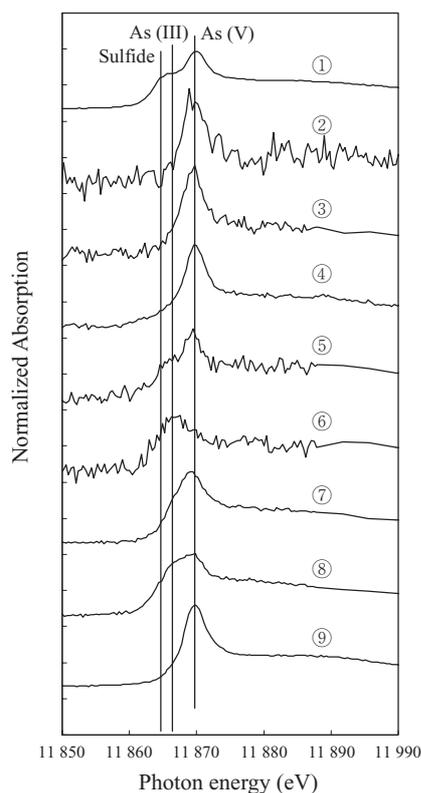
①: Excess activated sludge
②: Influent sewage
③: Treated sewage
①−③: Collected from wastewater treatment plant (WTP)-B
④: River sediment collected from downstream of WTP-B
⑤: Primary sludge
⑥: Excess activated sludge
⑦: Sludge cake 1
⑧: Sludge cake 2
⑨: Incinerator ash
⑤−⑨: Collected from WTP-C

sludge, As(III) and As_2S_3 were detected in concentrations of 15% and 23%, respectively (① of Fig. 6). Nakahara et al. detected As(III) and As_2S_3 in excess activated sludge in an investigation of the chemical state of arsenic in sludge samples taken from a sewage treatment plant in another district[7]. As is generally thought to be present as As(III) and As_2S_3 in sewage sludge, regardless of whether treated hot spring water flows in.

When excess activated sludge is kept in a biological reaction tank, the aeration usually creates an aerobic condition. Later, when the sludge is extracted from the biological reaction tank, it becomes anaerobic. Saito et al. demonstrated that As_2S_3 forms from AsO_4^{3-} through the action of anaerobic bacteria[8]. These results might indicate that the As(V) that had been extracted together with the sludge was reduced into As(III) by the action of anaerobic bacteria, and further that the S^{2-} formed from AsO_4^{2-} and the like reacted under anaerobic conditions with As(III) under the formation of As_2S_3.
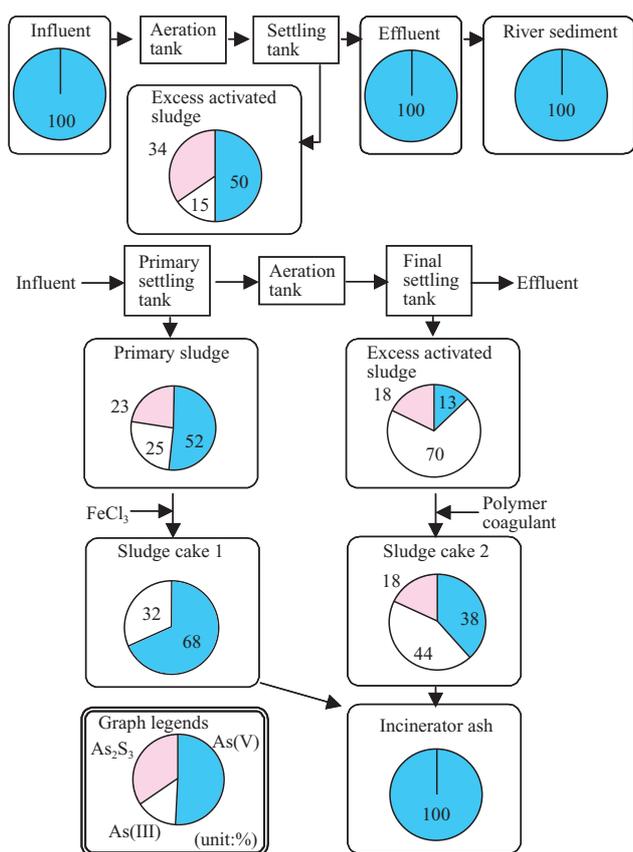
Above: WTP-B, Below: WTP-C

Fig. 7 Change of chemical states of As in wastewater treatment plants

5.2.2 Chemical state of As in dewatering and incineration treatment

Though the analytical values were all less than the lower limits of determination (5 mg/kg-dry), the K-absorption edge XANES spectra of As were obtained all of the sludges sampled from Treatment Plant C: the primary sludge (⑤ of Fig. 6), the excess activated sludge (⑥, ⑧ of Fig. 6), sludge cake 1 (⑦ of Fig. 6), and sludge cake 2 (⑧ of Fig. 6).

The analytical results indicated the following ratios of arsenic: in the primary sludge, As(V) 52%, As(III) 25%, and sulfides 23%; in the excess activated sludge, As(V) 13%, As(III) 70%, and sulfides 18%.

The As concentration of the sludge in a wet condition was less than 0.1 mg/kg-wet for the primary sludge and less than 0.2 mg/kg-wet for the excess activated sludge. Thus, our method successfully determined the chemical state of trace As incapable of being determined by the conventional sequential fractional method. Nagoshi et al. reports that the trace As in sewage sludge has different chemical states in dry and wet conditions[9]. This is a result only obtainable by XFAS analysis. As is oxidized in the dewatering process, but the ratio at which it is oxidized differs when different coagulants are used. From the incinerator ashes, As was detected at a concentration of 14 mg/kg-dry, and all of the As was As(V)(⑨ of Fig. 6).

6. Conclusions

Using a method of XFAS analysis with high-luminance synchrotoron radiation of SPring-8, the authors performed the first XFAS investigation of the chemical states of heavy metals contained in sewage sludge. Our results clarified the changes in the chemical states of the heavy metals of trace heavy metals contained in the sewage sludge, and changes in the chemical states during the treatment process.

As described above, the XFAS analysis can determine the chemical states of trace heavy metals without changing the environmental conditions specific to heavy metals. This analysis is therefore expected to serve as a powerful tool for the analysis of environmental samples, including ecological systems themselves.

The authors intend to use the XFAS analysis as a means of obtaining basic information for the safety evaluation of heavy metals discharged to the environment and the development of more environmentally friendly techniques for treating heavy metals.

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