

THERMAL TREATMENT OF SOIL CONTAMINATED BY ORGANIC ARSENIC COMPOUNDS

In traditional cases, environmental pollution due to arsenic derived from geological sources has caused ground water contamination by the dissolution of arsenic ions from the vein of ore. As a results of this pollution, people who use the contaminated water for daily purposes suffer from chronic poisoning symptoms. In most of these cases, the original cause of the pollution is the leaching of 'inorganic' arsenic pollutants into the ground water [1]. However, in Kamisu city (Ibaragi Prefecture, Japan), there was an extremely rare case of ground water contamination caused by 'organic' arsenic substances in 2005. From the results of a detailed study, diphenylarsenic acid (DPAA) and phenylarsonic acid (PAA), i.e., organic substances with phenyl radicals, were detected in the ground water of Kamisu city. After more extensive surveying and excavation of the soil in the suspected area, about 100 tons of concrete-like agglomerate and 2000 tons of contaminated soil containing about 1500 mg/kg organic arsenic acids were discovered in the earth at a depth of 4 meters, and they were concluded to be the source of pollution. From the date marked on beverage cans found in the agglomerate, it seems that the organic arsenic acids had been poured into the soil with cement in the 1990s. Because organic substances with phenyl radicals are not present in nature, there was a speculation that the DPAA and PAA found originated from the Imperial Japanese Army. In general, for inorganic arsenic, the toxicity of trivalent arsenic is higher than that of pentavalent arsenic, and the toxicity of organic arsenicals with methyl radicals is much lower than those of inorganic substances. However, the toxicity of organic arsenicals with phenyl radicals is not known [2].

We have confirmed heat treatment as a detoxification process that has been applicable to this unprecedented pollution caused by DPAA and PAA. In this study, we examined the change in the chemical state of organic arsenic compounds in artificially contaminated soil before and after heat treatment by XAFS.

Uncontaminated soil was collected in Ibaraki, Japan. The soil was dried at room temperature and filtered through a 425- μm -opening sieve, and the fine fraction was collected as a substrate. About 500 g of the substrate was mixed with 100 ml of methanol (or ethanol), which dissolved DPAA or PAA. And then, the artificially contaminated soil was dried at room temperature again. In addition, artificially

contaminated cement was also prepared by the above-described method. The total arsenic concentration in these soils and cement were about 2000 mg/kg. The samples were heated at 850°C in a tubular furnace for 30 min under air. XANES analysis was performed on 6 samples and 8 standard compounds at beamline **BL01B1** in the transmission and fluorescence modes.

Figure 1 shows a comparison of the XANES spectra of all the samples and standard compounds. The white-line positions of the heat-treated samples are close to those of pentavalent arsenicals. However, an obvious difference in the shape of the spectra in the vicinity of 11870 eV, i.e., right before the absorption edge, can be seen between the organic and inorganic compounds (except for As and As₂O₃). To clarify these points, **Fig. 2** shows a schematic of the white-line energy positions in terms of relative energy for the samples and standard compounds. White-line peak positions were obtained from the point

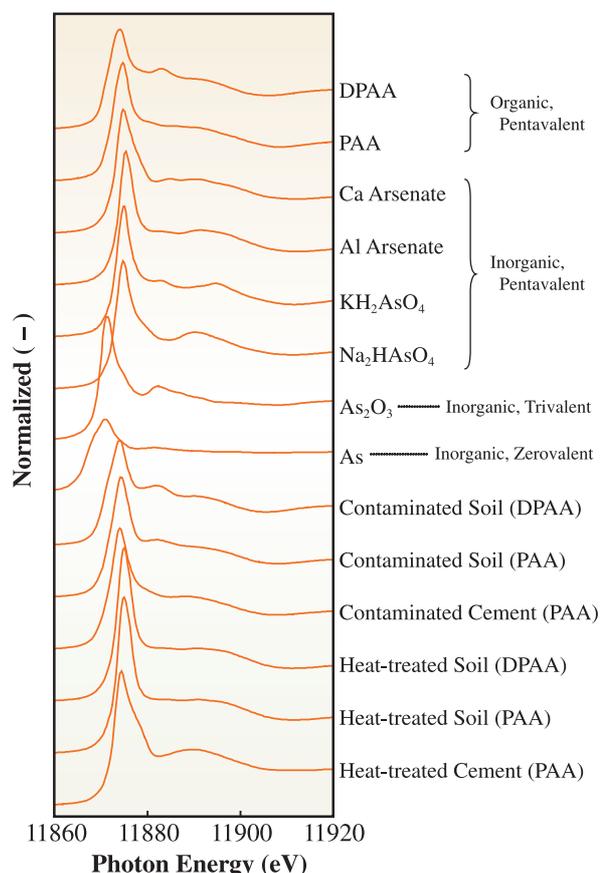


Fig. 1. Normalized As-K XANES spectra of organic and inorganic arsenic samples.

at which the first derivative gives the top of the peak in part of the near-edge. Looking at the energy positions of the absorption edge of the inorganic arsenicals and heat-treated samples, were higher than those of organic arsenicals, it is clear that the chemical state of arsenic in the soil and cement have been changed from the organic state to the inorganic state. This tiny but visible difference in the energy positions of the absorption edge between organic and inorganic arsenicals is attributed to the change in the electron state of arsenic atoms induced by the loss of phenyl radicals during heat treatment [3].

Table 1 shows the result of spectrum fit analysis applied to the XANES spectra. By superimposing each sample spectrum on each standard spectrum, the similarity of each combination is evaluated using 'R' values, which were calculated using the following equation [4].

$$\text{residual } R \text{ value} = \frac{\sum(XANE_{measd} - XANES_{calcd})^2}{\sum(XANE_{measd})^2}$$

All of the R value ranges obtained are represented by one of four kinds of symbol in the table. Similarly to the result of energy position analysis, the result of the curve fitting analysis indicates that the organic arsenic had been changed to inorganic arsenic by heat treatment. Furthermore, the arsenic chemical compounds in the heat-treated soil and cement are proximate to aluminum arsenate and calcium arsenate, respectively. This observation agrees with the fact that As₂O₅ reacts with major components of soil and cement such as Al₂O₃ and CaO, respectively, and becomes an insoluble arsenate compound when

Table 1. Similarities of organic and inorganic arsenic samples with standard compounds.

	Standard Compounds						Samples				
	DPAA	PAA	Ca Arsenate	Al Arsenate	KH ₂ AsO ₄	NaHAsO ₄	Contaminated Soil (DPAA)	Contaminated Soil (PAA)	Contaminated Cement (DPAA)	Heat-treated Soil (DPAA)	Heat-treated Soil (PAA)
Contaminated Soil (DPAA)	○	○					-	-	-	-	-
Contaminated Soil (PAA)	△	○					△	-	-	-	-
Contaminated Cement (DPAA)	△	◎					△	◎	-	-	-
Heat-treated Soil (DPAA)				○	△					-	-
Heat-treated Soil (PAA)				○						◎	-
Heat-treated Cement (PAA)			○			△					

*Notation
 - : Not calculated,
 ◎ : 0 < R ≤ 0.06, ○ : 0.06 < R ≤ 0.09, △ : 0.09 < R ≤ 0.12, blank : R > 0.12

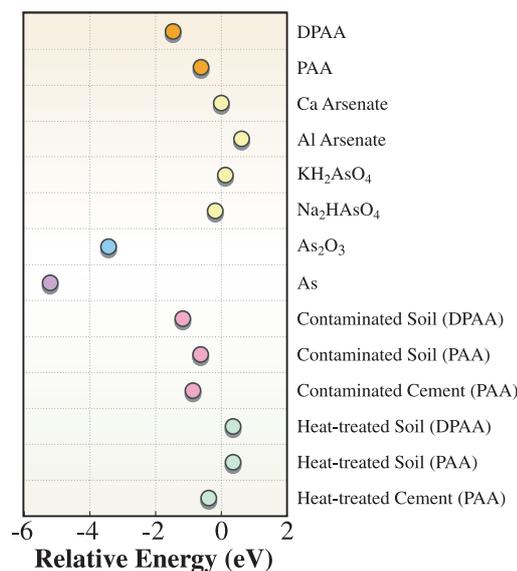


Fig. 2. Relative white-line peak positions obtained from point at which first derivative gives top of peak in vicinity of edge.

it is generated by the thermal decomposition of DPAA or PAA in soil or cement [5].

As discussed above, strong evidence of the effectiveness of heat treatment applied to the detoxification of organic arsenic contamination has been successfully obtained through experiments performed using XAFS analysis in SPring-8. Analysis using synchrotron radiation, which makes chemical form analysis intended for low-concentration elements in bulk samples possible, is expected to grow in application in the environmental field.

Hiroki Harada^{a,*}, Shuji Hamano^a and Masaki Takaoka^b

^a Hitachi Zosen Corporation
^b Department of Urban & Environmental Engineering, Kyoto University

*E-mail: h_harada@hitachizosen.co.jp

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