New Method to Observe Chemical Reactions at the Solid-water Interface by QXAFS Combined with a Column Reactor

Recently, the environmental and human health impacts of elevated concentrations of arsenic (As) in groundwater have received increased attention because of its toxicity [1]. The predominant forms of As in the environment are as inorganic arsenate (As(V)) and arsenite (As(III)). Unlike the arsenate anions, $H_2AsO_4^-$ and $HAsO_4^{2-}$, the dominant As(III) species up to pH 8 is the nonionic H_3AsO_3, which does not adsorb onto mineral surface as strongly as As(V) [2-4]. The As(III) species is substantially more toxic than As(V). Therefore, it is important for the geochemistry and toxicology of As to determine its oxidation state. In natural systems, amorphous manganese oxide (δ-MnO$_2$) can be the strong oxidizer and sorbent for various trace elements including As. Considering the fate of As in the environment, the oxidation of As(III) by Mn oxide is an important reaction. Although details about the chemical mechanism of As(III) by amorphous Mn oxide have been reported, more information is needed for the kinetics of the oxidation of As(III) to As(V).

In this study, to observe the kinetics and dynamics in the oxidation process of As(III) by Mn oxide, we applied a new method that combines a column reactor with the time-resolved measurement of As species at the solid-water interface using quick XAFS (QXAFS) technique [5], which can measure XAFS spectra within shorter time than the conventional measurement by step scan of monochromator of the incident X-ray. In particular, a short time scale detection is required for the observation of As oxidation by Mn oxide, since the oxidation of As(III) b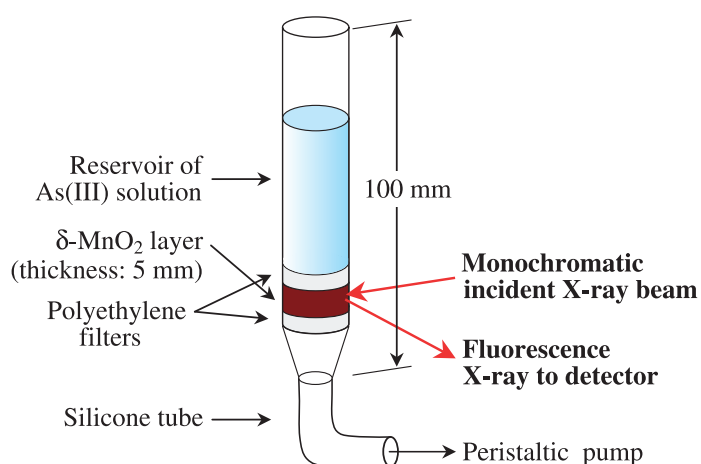y Mn oxide is quite rapid. The application of this method allows us to gain better understanding of the various reaction processes at the solid-water interface.

A small disposable polystyrene column with an inner diameter of 10 mm was used as the reactor to investigate the oxidation of As(III) with Mn oxide (Fig. 1). Arsenite solution was introduced into a column reactor with the outflow port closed. Using a peristaltic pump connected to the outlet of the column, the As(III) solution started to flow into the δ-MnO$_2$ layer, initiating the oxidation reaction.

Quick XAFS measurements at As-K-edge, performed at beamline **BL01B1**, were carried out in fluorescense mode using a Lytle detector. The Si(111) monochromator was moved continuously from 9.63° (11.836 keV) to 9.00° (12.638 keV) in 1 min. The measurements were conducted at 27 ± 2°C under ambient air condition.

In the As(III)/ δ-MnO$_2$ system, the absorption edge of As shifted to higher energy with time (Fig. 2), showing the rapid oxidation of As(III) by δ-MnO$_2$. Figure 3(a) shows the As(III) and As(V) ratio obtained by the simulation of XANES spectra during the oxidation reaction of As(III). Arsenic(III) was rapidly oxidized by δ-MnO$_2$, and about 50% of the original As(III) added was oxidized to As(V) within 20 min (Fig. 3(a)). The net stoichiometry of the oxidation of As(III)
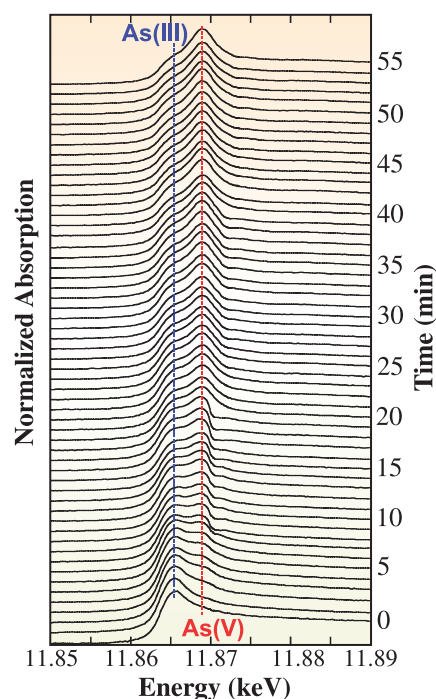
Fig. 1. Schematic figure of the column reactor.

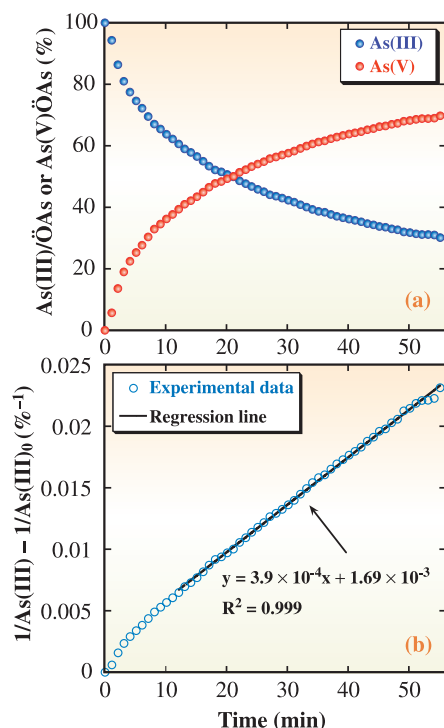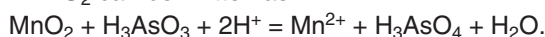Fig. 2. Arsenic K-edge XANES spectra of As(III)/δ-MnO$_2$ system.

Fig. 3. **(a)** Decrease of As(III) and formation of As(V) during the oxidation of As(III) by δ-MnO$_2$. **(b)** Relationship between elapsed time and $1/\text{As(III)} - 1/\text{As(III)}_0$ (As(III): percentage of As(III) fraction; As(III)$_0$ = 100%).

Fig. 4. Radial structure functions (phase shift is uncorrected) for As during the oxidation of As(III) by δ-MnO$_2$.

by δ-MnO$_2$ can be written as

$$\text{MnO}_2 + \text{H}_3\text{AsO}_3 + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_3\text{AsO}_4 + \text{H}_2\text{O}.$$

The decrease of As(III) in this study follows a second order reaction kinetic, as shown by the linear relation in the time dependence of 1/As(III) 1/As(III)0 (As(III): the percentage of As(III) fraction; As(III)0: initial As(III)) in Fig. 3(b).

The rate constant (k') value based on the second order reaction is $3.9 \times 10^{-4}\%^{-1}$ min^{-1} at pH 7.1, which was obtained by the least-squares fitting of the plot (Fig. 3(b)). Several data points before 12 min are not on the regression line. Although the reason is not clear at present for the discrepancy, it is possible that the As(III) oxidation was induced by the incident X-ray beam at the initial time range.

The validity of our k' value is discussed by comparison with other reports. Our k' value is within the range from 2.9×10^{-5} to 2.6×10^{-3} %$^{-1}$min^{-1} reported in previous researches, showing that the present k' value may be valid considering other reported data.

In many previous works, however, the oxidation rate is determined indirectly by measuring concentrations of As(III) and As(V) dissolved in the aqueous phase. The rate constant obtained by such a method includes the sorption/desorption processes of As(III) and As(V). Since the sorption coefficient of As(III) and As(V) are different, the k' value obtain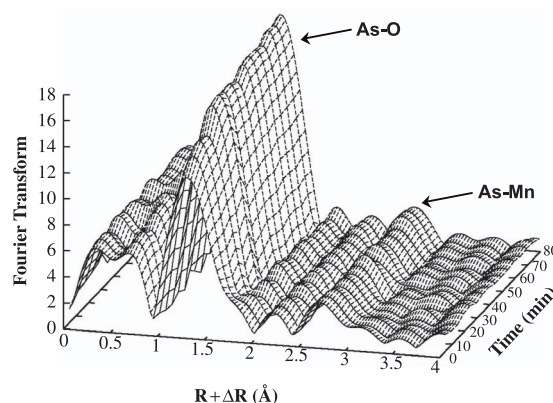ed by the method may include some ambiguities. On the other hand, the k' value obtained in our system reflects only the oxidation of As(III) by δ-MnO$_2$ at the solid-water interface. This point is a highlight of the method based on the observation of the oxidation kinetics using QXAFS and the column reactor.

Time-resolved Fourier Transform of the $k^3\chi(k)$ EXAFS for As(III)/δ-MnO$_2$ system is presented in Fig. 4. The first shell due to As-O shell shifts slightly to shorter distance with time due to the bond length of As(V)-O that is smaller than that of As(III)-O. The magnitude of the As-O shell in Fig. 4 increases with time. Although the variation of EXAFS spectra in Fig. 4 is simply due to the increase of the As(V)/As(III) ratio with time, the present results show that the method can be applied not only to the kinetic study but also to the characterization of local structure of As at the solid-water interface during reaction by EXAFS analysis. Moreover, since this method is very simple, we can apply it to various elements and reaction systems at the solid-water interface.

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