Sorption of Arsenate and Arsenite on $RuO_2 \cdot xH_2O$: Analysis of Sorbed-Phase Oxidation State by XANES

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Introduction

Arsenic (As) contamination in water, soil, and sediment is a global problem. Awareness of the problems created by As contamination has increased in recent years as a result of reports from Asia that described immense health problems from As in drinking water [1, 2]. Changes in U.S. regulations for the value for the maximum contaminant level (MCL) of As in drinking water (from 50 μg/L to 10 μg/L) have also increased interest in and research on As in the environment.

The research presented here was performed in conjunction with macroscopic studies on the sorption of arsenate and arsenite by $RuO_2 \cdot xH_2O$. These consisted of batch sorption experiments and kinetic experiments in a continuously stirred reactor. The use of x-ray absorption spectroscopic (XAS) techniques in this work confirmed results from the macroscopic-scale batch sorption and kinetic experiments. The objectives of the study were to examine the effects of pH on the sorption of arsenite and arsenate on $RuO_2 \cdot xH_2O$, study the kinetics of sorption, and assess the solution and solid-state As speciation associated with $RuO_2 \cdot xH_2O$. This work provides fundamental data on the potential efficacy of $RuO_2 \cdot xH_2O$ for use in remediation of As-contaminated water, soils, sediments, and mine wastes.

Methods and Materials

Details on the methods and materials used for the macroscopic studies may be found in Ref. 3. For the x-ray absorption near-edge spectroscopy (XANES) work, all samples were prepared at 22 ±2°C. A 2.0-g sample of $RuO_2 \cdot xH_2O$ was equilibrated (at pH = 7) with 10-mL solutions of 500-mg/L As (V) or As(III) for periods of 1 month, 2 weeks, 1 week, and 24 hours. The samples were equilibrated until the pH remained at 7 for 24 hours (3 days total). For the 24-hour samples (only oxic samples were examined for this time period), the required base was estimated from the other samples and added along with the As, then the mixture was equilibrated for 24 hours. The oxic samples were centrifuged and washed three times in a 0.01 M $NaNO_3$ background electrolyte (BG), vacuum-filtered through a 0.1-μm cellulose filter, covered, and left to dry in a dessicator. The anoxic samples were purged with N_2 and kept in a zero head space container for the specified time period. Immediately prior to analysis, the anoxic samples were vacuum-filtered in a N_2-purged glove box and washed with N_2-purged BG, and the resulting paste was transferred to Teflon® sample holders for analysis. Pure $NaAsO_2$ and $NaHAsO_4 \cdot 7H_2O$ (reagent grade, Fisher Scientific, Fairlawn, NJ) was mixed with KBr in different proportions for a total As concentration of 10,000 mg/kg. The different quantities (0-100%, 25-75%, 50-50%, etc.) allowed semiquantitative analysis of the samples for percent ranges of As(III) and As(V) in the samples. This semiquantitative approach was modeled after work by Schulze et al. on Mn oxidation states [4]. Arsenic K-edge spectra (11,867 eV) were collected at DND-CAT beamline 5-BM at the APS. XANES spectra were collected in both transmission and fluorescence mode with a solid-state detector. The electron storage ring operated at 7 GeV, with the horizontal entrance slit set at 6 mm and the vertical one set at 2.3 mm. Scans ranged from 11,767 to 12,245 eV. Data were analyzed by WinXAS version 1.3 [5]. Individual spectra were background-corrected by using a two-polynomial fit, then three spectra per sample were averaged, and finally the first derivative was calculated for each averaged spectra. The results for the samples were compared with those from the fabricated reference materials in order to assess the solid-state speciation of As.

Results

Details on results from the bench experiments can be found in Ref. 3. Essentially, at the pH values studied (pH's of 4 through 8), $RuO_2 \cdot xH_2O$ showed a high affinity for As regardless of the initial As species present. Sorption was higher at all pH values when the initial As species was As(III). Oxidation of As(III) (250 mg/L solution) to As(V) (as detected in solution) was virtually complete (98-100%) within 5 seconds. It is speculated that changes in the $RuO_2 \cdot xH_2O$ structure due to oxidation reactions caused the higher total As sorption capacity when As(III) was the initial species.

Figure 1 shows the results for the fabricated reference materials and selected samples. There was no evidence of the presence of As(III) on the solid phase for any of the combinations examined. For the longest time period in anoxic conditions of 4 weeks, there was no evidence of As(III); thus, irrespective of the initial species, no reduction of As occurred in this time frame. Data from the shortest exposure of As(III) to

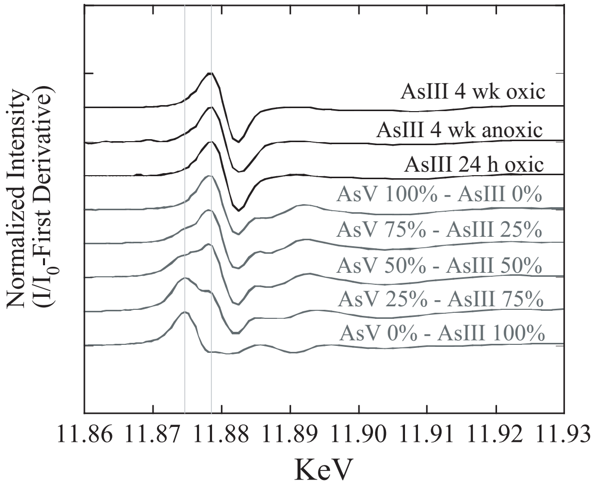

FIG. 1. XANES results for the As reference standards and representative samples.

$RuO_2{\cdot}xH_2O$ conclusively illustrated the association of As(V) alone with the solid state.

Discussion

This study combined XANES and macroscopic studies to assess sorption of arsenate and arsenite by $RuO_2{\cdot}xH_2O$. Researchers at the EPA's National Risk Management Research Laboratory are also examining $RuO_2{\cdot}xH_2O$ sorption of Pb and obtaining encouraging results. It is speculated that $RuO_2{\cdot}xH_2O$ would also have a significant effect on organic contaminants (e.g., dioxins). After further research, $RuO_2{\cdot}xH_2O$ may make current remediation processes more effective in the oxidation, removal, and degradation of a wide variety of contaminants. Research is also underway on the production of engineered Fe-Ru mixed precipitates in which Ru acts as an oxidizer and the Fe-oxide acts as the sorbing media.

Acknowledgments

The EPA has not subjected this report to internal review. Therefore, the research results presented herein do not, necessarily, reflect EPA policy. Mention of trade names of commercial products does not constitute endorsement or recommendation for use. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. The authors would like to extend their deep appreciation to the staff of the DND-CAT, especially research engineer J. Kulpin for his expertise and professionalism during the production of the XANES results presented in this report.

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