

Examination of Mercury Interactions with Iron in the Presence of Chemical Agent Simulant by Using EXAFS and XANES

L.R. Skubal,¹ S.G. Biedron,¹ M. Newville,² J.F. Schneider,¹ S. Milton,¹ P. Pianetta,³ H.J. O'Neill¹

¹Argonne National Laboratory, Argonne, IL, U.S.A.

²Consortium for Advanced Radiation Science, The University of Chicago, Chicago, IL, U.S.A.

³Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Facility, Menlo Park, CA, U.S.A.

Introduction

Under the *Chemical Weapons Convention* [1], the United States is to destroy its current stockpiles of chemical weapons. Two types of destruction techniques are commonly used: incineration and chemical destruction. Often, metal catalysts/contaminants, such as mercury (Hg) and arsenic (As), (from synthesis processes), are present in the containers holding the agent. Before destruction processes via incineration can commence, the contaminant metals must be removed by chemical means to prevent their entry into the atmosphere. To choose an appropriate and successful chemical removal method, the valence state of the metals present in the agent must be known.

The work presented here examines the changes of state that occur in mercury and arsenic as they are introduced into a mustard simulant, thiodiglycol. Metal characterizations were performed by using extended x-ray absorption fine structure (EXAFS) spectroscopy and x-ray absorption near-edge structure (XANES) spectroscopy.

Methods and Materials

In the containers housing agent, high concentrations of other metals, including cadmium, selenium, and iron, are typically present. Chemical reagents were added to simulating metals present in the containers. These included mercuric chloride (HgCl₂), cadmium chloride (CdCl₂), ferrous sulfate (FeSO₄), ferric oxide (Fe₂O₃), and

selenious acid (H₂SeO₃), all from Aldrich. Various combinations of the metals were introduced into both a distilled water matrix and a mustard simulant (thiodiglycol, Aldrich) matrix. Solutions were completely mixed and given a day to equilibrate (Table 1). Then 8 mL of a solution was transferred to an x-ray fluorescence (XRF) cup (Chemplex Industries, Inc.) and covered with Kapton[®] film. The states of mercury and arsenic were determined by using EXAFS and XANES [2] at the GSECARS sector 13 beamline at the APS. The samples were held at 45° to the beam, and the XAFS was recorded by measuring the fluorescent signal from mercury and arsenic as a function of photon energy by using a 16-element Ge detector placed along the polarization vector of the synchrotron radiation.

Results

EXAFS and XANES spectroscopy were used to examine mercury and arsenic in water and in thiodiglycol, with and without the addition of other metals. The added metals were used to simulate concentrations of metals existing in the metal ton containers that are used to house mustard.

Several interesting phenomena occurred:

- The state of mercury (from a HgCl₂ source) in thiodiglycol is different than its state in water in the presence of iron (Fig. 1). The exact state of mercury in simulant was not determined in this preliminary effort.

TABLE 1. Solutions prepared for XANES/EXAFS analyses.

Solution	Solution Constituents (total volume of each solution is 7 mL)
1	1,000 ppm Hg from HgCl ₂ in simulant
2	1,000 ppm Hg from HgCl ₂ , 1,000 ppm Fe from FeSO ₄ , 100 ppm Cd from CdCl ₂ in simulant
3	1,000 ppm Hg from HgCl ₂ , 1,000 ppm Fe from FeSO ₄ , 100 ppm Cd from CdCl ₂ , 100 ppm Se from H ₂ SeO ₃ in simulant
4	150 ppm As from arsenic trioxide in simulant
5	1,000 ppm Hg from HgCl ₂ , 1 mg Fe ₂ O ₃ in simulant
6	150 ppm As from arsenic trioxide, 1,000 ppm Hg from HgCl ₂ , 1 mg Fe ₂ O ₃ in simulant
7	1,000 ppm Hg from HgCl ₂ , 1 mg Fe ₂ O ₃ in simulant
8	1,000 ppm Hg from HgCl ₂ , 1 mg Fe ₂ O ₃ in distilled water
9	1,000 ppm Hg from HgCl ₂ , 1 mg Fe ₂ O ₃ , 150 ppm As from As ₂ O ₃ in distilled water
10	150 ppm As from As ₂ O ₃ , 1 mg Fe ₂ O ₃ in simulant

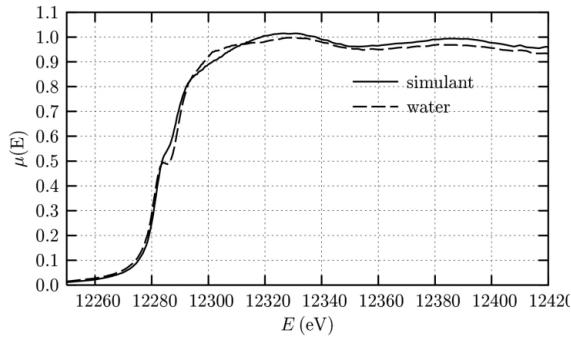


FIG. 1. 1000 ppm Hg with 1% Fe in a simulant and water.

- Mercury speciation in the thiodiglycol was completely unaffected by the addition of iron (from ferrous sulfate), cadmium, selenium, or combinations of the added metals (Fig. 2).
- Mercury speciation in water was not affected by the presence of iron (from Fe_2O_3) or iron and arsenic (Fig. 3).
- Mercury speciation in thiodiglycol is greatly affected by the presence of iron (from Fe_2O_3) and by the presence of iron and arsenic (Fig. 4).
- Thiodiglycol appears to force arsenic to a reduced state (a 3+ valence state). The presence of iron (from Fe_2O_3) has little to no effect on arsenic speciation (Fig. 5).
- In water and in the presence of mercury, arsenic is oxidized to a 5+ valence state (Fig. 5).

Discussion

EXAFS and XANES were used to evaluate the speciations of mercury and arsenic in a distilled water matrix and in a mustard simulant (thiodiglycol). Results showed that the chemistry of arsenic and mercury in a water matrix and simulant matrix are quite different from each other, greatly depending on the other metals that are

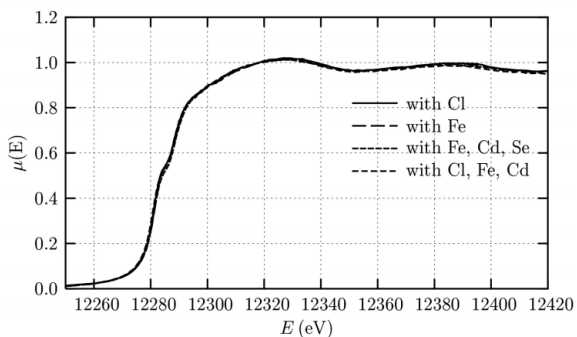


FIG. 2. 1000 ppm Hg in a simulant with various metals present.

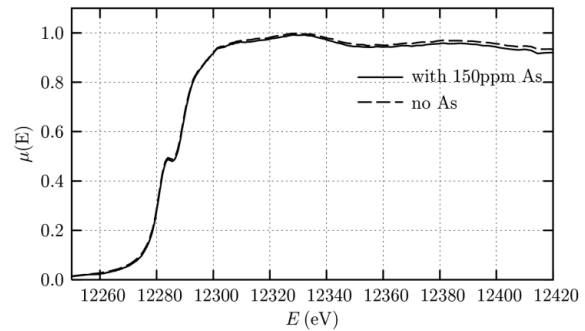


FIG. 3. 1000 ppm Hg with 1% Fe in water.

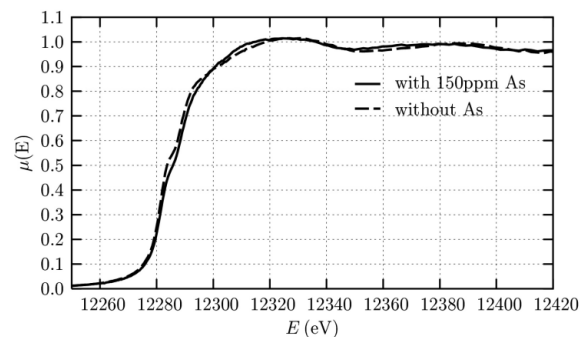


FIG. 4. 1000 ppm Hg with 1% Fe in a simulant.

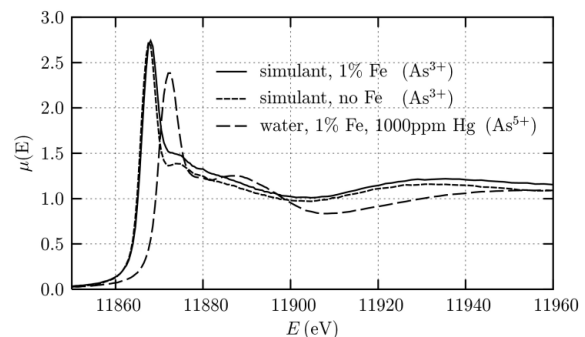


FIG. 5. 150 ppm As in a simulant and water.

present in solution. Although more experiments are required and scheduled, the results from this study were presented to the U.S. Army to use in conceiving a chemical treatment method.

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References

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[2] A.L. Foster, G.E. Brown, Jr., G.A. Parks, T.N. Tingle, D.E. Voigt, and S.L. Brantley, *J. Phys. IV* **7(C2)**, Part 2, 815-816 (1997).