

# Biological Enhancement of Abiotic Reduction of Pertechnetate in Sediments at the Hanford Site

S. M. Heald, J. P. McKinley, J. M. Zachara  
Pacific Northwest National Laboratory, Richland, WA, U.S.A.

## Introduction

Pertechnetate ( $\text{TcO}_4^-$ ) is a major radioactive component of Hanford tank waste. Since some of the tanks have leaked, it is important to understand the fate of pertechnetate in Hanford sediments. Technetium in the form of pertechnetate is highly mobile and poses a threat to the groundwater. Upon reduction to Tc(IV), the Tc is expected to form less soluble  $\text{TcO}_2$  compounds that are much less mobile. Pertechnetate can be reduced abiotically by ferrous Fe. However, this process can be inhibited by relatively oxidizing Mn(IV) species. In this work, we look at the potential for bacteria to facilitate the abiotic reduction of pertechnetate by the reduction of solid-phase Mn and Fe in Hanford sediments.

## Methods and Materials and Results

Hanford sediments were contacted in slurries with bacteria (*Shewanella p.*) under anaerobic conditions for varying lengths of time. After sterilization and washing, the sediments were exposed to pertechnetate in solution. Experimental evaluations of the removal of Tc from solution in the presence of variable extents of Mn reduction (determined by acid extraction) showed that Tc was removed only after complete reduction of Mn. The x-ray microprobe (XMP) was used to examine the nature of solid-phase Tc.

Samples for XMP were prepared by embedding the sediment in epoxy, cutting and polishing thin disks mounted to glass slides, and mounting the slides on sample holders with Kapton<sup>®</sup> windows. Care was taken to avoid exposure to oxidizing conditions, although later measurements indicated little change upon exposure to air. Bulk measurements of the Mn and Fe edges were made on beamline 20-BM, and microprobe studies with 5- $\mu\text{m}$  resolution were carried out on beamline 20-ID. Fig. 1 shows some bulk measurements of the sediments after treatment with bacteria for various times. The reduction of the Mn is clearly seen, with Mn(II) dominating at longer times. The much more abundant Fe in the samples remains mainly ferric.

The microprobe was then used to locate Tc. Figure 2 shows a typical example of Tc accumulating on an Fe-containing material. Once found, the valence of the Tc was determined from near edge scans. Figure 3 compares the precipitated Tc near-edge with some Tc standards. In all cases, the adsorbed Tc was similar to  $\text{TcO}_2$ . Micro-XANES (x-ray absorption near-edge scattering) showed

the progressive reduction of Mn over time by *Shewanella* and the formation of discrete precipitates of  $\text{TcO}_2$  in sediments where all Mn was bio-reduced. It is likely the Tc was reduced by ferrous Fe on the surface of the Fe-containing minerals. The ferrous Fe could have been preexisting or bio-reduced.

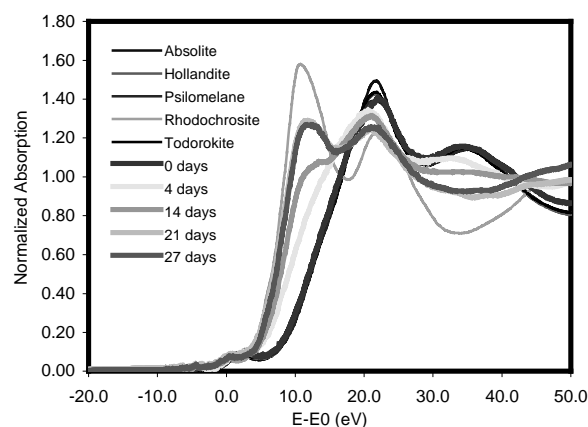


FIG. 1. Comparison of the Mn edge from Hanford sediments treated with bacteria with some Mn minerals. All of the minerals are Mn(IV) except for rhodochrosite, which is Mn(II). The sediments start out as entirely Mn(IV).

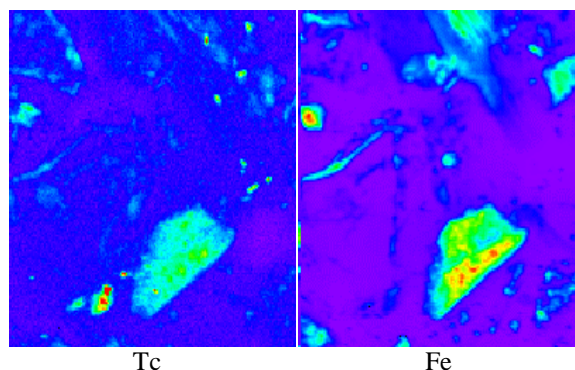


FIG. 2. X-ray microprobe fluorescence images of the Tc and Fe content in a bacteria-treated sediment sample. Tc has accumulated on the Fe-containing particle at the bottom of the image. Some of the smaller Tc hot spots are due to Zr interference.

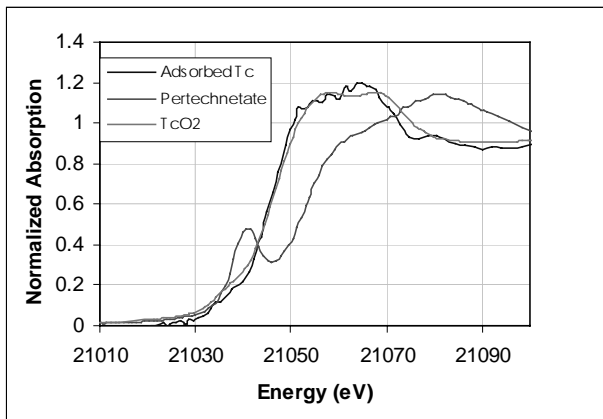


FIG. 3. Comparison of the precipitated Tc XANES with pertechnetate and  $TcO_2$ .

## Acknowledgments

The Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) is supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) and by the Natural Sciences and Engineering Research Council of Canada (NSERC). Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for DOE. Use of the APS was supported by DOE BES under Contract No. W-31-109-ENG-38.