Speciation and Imaging of Cr Adsorption in Hanford Sediments

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

Introduction

Chromium in the form of chromate is a major component of the waste stored in tanks at the Hanford site. Since some of this waste has leaked, it is important to understand its interactions with Hanford sediments. Chromium is highly mobile and toxic. It becomes much less hazardous if reduced to Cr(+3). Such reduction can occur by number of processes, with an important process being reduction by ferrous iron. The x-ray microprobe at the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) sector was used to image the relationship of chromium with other minerals in Hanford sediments obtained from underneath leaking tanks. Micro-XANES (x-ray absorption near-edge surface) was then used to determine the chromium valence.

Methods and Materials

Samples were prepared from a core sample obtained from underneath tank SX-108. Sediment from several depths was mixed with epoxy, cut into thin disks, and polished to provide a flat surface. The samples were examined in the electron microscope to determine likely areas for study. For the x-ray measurements, a 5-μm x-ray beam was used, and the fluorescence was detected by using a 13-element Ge detector. Typically, fluorescence maps for K, Ti, Mn, and Fe were obtained in addition to the Cr signal. Figure 1 shows a Cr x-ray fluorescence map overlain on a backscattered electron image. For the Fe-rich particle in the center (identified as magnetite), it is clearly seen that Cr has collected on the surface. For this sampling depth, most of the Cr has been converted to Cr(+3). Figure 2 shows some Cr XANES collected by using a large beam (1 × 5 mm) to sample the average valence. The chromate fraction as determined from the height of the pre-edge peak is small. However, a measurable amount of chromate is present. By imaging at two different energies, these chromate regions can be highlighted. The energy of the chromate pre-edge peak is 5993 eV, and the chromium signal is primarily from chromate. At high energies, all of the Cr contributes equally, and a difference map can be used to isolate the regions high in chromate. This is shown in Fig. 3. The energy 7110 eV was chosen for the high energy to allow Fe and Mn to be also imaged. Near-edge spectra at the chromate hot spots confirmed that the signal was indeed due to chromate.

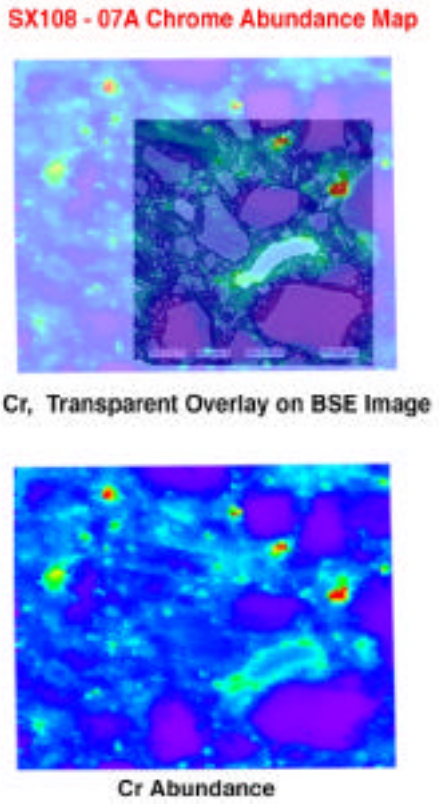

FIG. 1. Top: Overlay of chromium abundance determined by the x-ray microprobe with a backscattered electron image of the same area. Bottom: The same x-ray image shown alone for clarity.

Results

These results demonstrate the power of x-ray microscopy for determining elemental distributions and valence. They confirm that ferrous Fe plays an important role in the reduction chromate in the Hanford sediments. While this has been demonstrated in laboratory measurements, the environment under the tanks has been modified by a complex set of radiological, thermal, and chemical interactions. These results demonstrate the importance of surface reduction in immobilizing Cr in the unsaturated subtank environment.

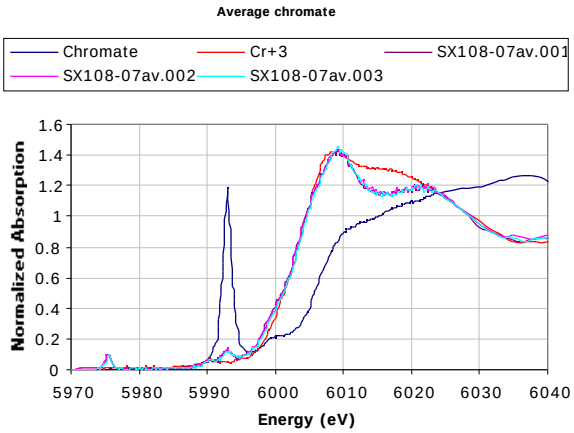

FIG. 2. Cr near-edge spectra taken at three different 1 × 5-mm regions in an SX-108 core sample. For comparison, a chromate and Cr(+3) standard are shown.

Acknowledgments

The 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 the DOE BES under Contract No. W-31-109-ENG-38.

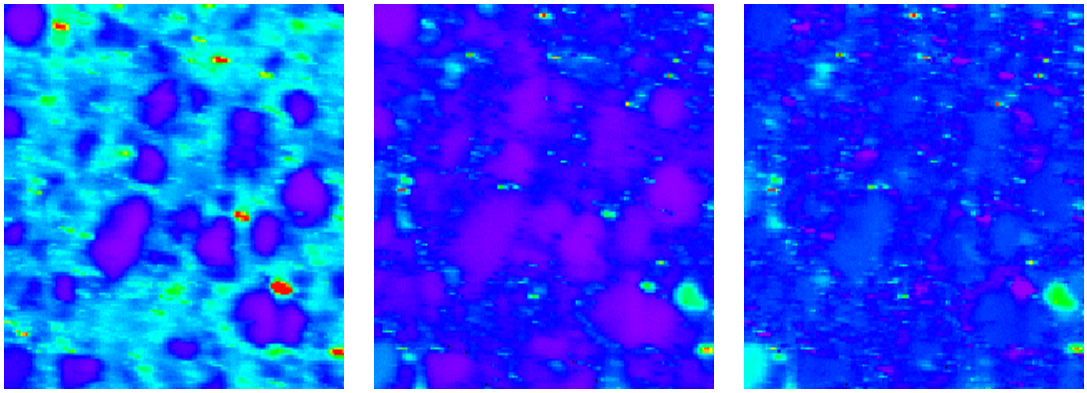

FIG. 3. Example of chromate imaging. The difference map highlights the regions with a high chromate fraction.