

# Distribution and Speciation of Chromium in Hanford Tank Farm SX-108 and 41-09-39 Core Samples Determined by X-ray Absorption Spectroscopy

J. G. Catalano,<sup>1</sup> J. A. Warner,<sup>1</sup> C-C. Chen,<sup>2</sup> I. Yamakawa,<sup>2</sup> M. Newville,<sup>3</sup> S. R. Sutton,<sup>3</sup>  
C. C. Ainsworth,<sup>4</sup> J. M. Zachara,<sup>4</sup> S. J. Traina,<sup>2</sup> G. E. Brown, Jr.<sup>1,5</sup>

<sup>1</sup>Department of Geological & Environmental Sciences, Stanford University, Stanford, CA, U.S.A.

<sup>2</sup>The Ohio State University, Columbus, OH, U.S.A.

<sup>3</sup>GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS),  
The University of Chicago, Chicago, IL, U.S.A.

<sup>4</sup>Pacific Northwest National Laboratory (PNNL), Richland, WA, U.S.A.

<sup>5</sup>Stanford Synchrotron Radiation Laboratory, Stanford, CA, U.S.A.

## Introduction

Chromium is present in relatively high concentrations in the high-level nuclear waste tanks at Hanford, Washington. It has been found at concentrations as high as 37,000 parts per million (ppm) in contaminated sediments in the vadose zone beneath tanks SX-108 and SX-109. At the high pH values of the tank supernate, aqueous chromium is expected to be dominantly in the chromate ( $\text{CrO}_4^{2-}$ ) form [1]. This form of chromium is highly mobile in aquatic systems [2] and acutely toxic [3], teratogenic [4], and carcinogenic [5]. In order to assess the environmental impact of chromium in tank leachates that have been released to the vadose zone, a quantitative knowledge of chromium speciation is essential. More specifically, it must be determined to what extent Cr(VI) species have been reduced, via electron transfer reactions, to Cr(III) species in the sediments in the vadose zone. In contrast to Cr(VI), Cr(III) species should be relatively immobile in Hanford subsurface sediments and of low toxicity to biological organisms.

We examined the spatial distribution of Cr(VI) and Cr(III) species in thin sections of four of the Hanford tank farm borehole samples prepared at PNNL by using a highly focused beam of x-rays. This method of x-ray microfluorescence elemental mapping and was accomplished on the undulator beamline at GSECARS sector 13 at the APS. By using a  $10 \times 10\text{-}\mu\text{m}$  x-ray beam tuned to an energy just above the Fe K absorption edge (7,112 eV), we mapped K, Ca, Ti, Cr, Fe, and Mn in  $300 \times 300\text{-}\mu\text{m}$  areas on the four thin sections. In separate experiments, we also measured Cr K-edge micro-XANES (x-ray absorption near edge structure) spectra of a number of points on these thin sections to determine Cr speciation. The results of these experiments are reported below.

## Methods and Materials

We examined four subsurface samples obtained from the Hanford S and SX tank farms by using x-ray

absorption fine structure (XAFS) spectroscopy and x-ray microprobe elemental mapping. These consisted of different portions of two samples from the SX-108 slant borehole (samples SX-108-7A and SX-108-8A) and two samples from borehole 41-09-39 (samples 41-09-39-6AB and 41-09-39-7ABC). Prior to examination, these samples were placed in an Al-tube and impregnated with epoxy at PNNL. Once the epoxy had hardened, the samples were cut in cross section and polished to produce 0.1-mm-thick wafers. Each wafer was glued to a  $\text{SiO}_2$ -glass plate, sealed with Kapton™ film, and sent to the APS for micro-XRF (x-ray fluorescence) and micro-XAFS analysis. Once at the APS, the samples were placed into acrylic sample holders and sealed with a second Kapton film.

Initially, XRF spectra were collected on representative areas of the four core samples. Each sample was moved through the beam over a  $300 \times 300\text{-}\mu\text{m}$  area in  $10\text{-}\mu\text{m}$  steps, in order to determine the elemental associations of Fe, Cr, Mn, K, Ca, and Ti. XANES spectra were collected at the Cr K edge on selected spots in each sample and along linear transects of each sample. In general, high-Cr spots were selected for single analysis spots, but the line scans also sampled lower Cr material. XANES spectra were also collected from the model compounds,  $\text{Na}_2\text{CrO}_4$ ,  $\text{BaCrO}_4$ , and  $\text{Na}_2\text{CrO}_3$ . Additionally, the focused beam was kept on the Cr(VI)-containing models and on Cr(VI)-rich regions of the samples for 1 h to evaluate the potential for x-ray-induced reduction of Cr(VI). No such reduction was observed in this timeframe.

The fraction of total Cr present as Cr(VI) in each sample spot was determined by comparing the area of the pre-edge peak for the unknown samples to that of  $\text{Na}_2\text{CrO}_4$  and  $\text{BaCrO}_4$ . The Cr XANES spectra were normalized to an edge jump defined by the difference of pre-edge background and the height of the spline at 6030 eV, as described above [6]. The area of the pre-edge peak was determined by fitting this peak with mixed Gaussian and Lorentzian functions by using the program Grams/32.

## Results

The spatial distribution of each element within each sample was found to be highly heterogeneous even in an area as small as  $300 \times 300 \mu\text{m}$ . Figure 1 shows the element maps of two samples as examples. Qualitative correlations between certain elements are visible in the maps (e.g., Cr and Mn from Fig. 1a). Scatter plots (Fig. 2) were generated to further investigate the elemental associations by using the data provided from the element maps for the four samples. While sample 41-09-39-6AB shows a moderately strong association between chromium and both manganese and iron, the other samples show a weaker correlation. Samples SX-108-07A, 41-09-39-7ABC, and SX-108-8A (shown in Fig. 2) have weak linear associations, and the shape of their scatter plots suggests a possible weak quadratic association. A filter was applied to the chromium matrix in order to look for correlations with other elements at spatial positions where there are high chromium concentrations (greater than 75th quantile) and low chromium concentrations (less than 25th quantile). This data treatment did not

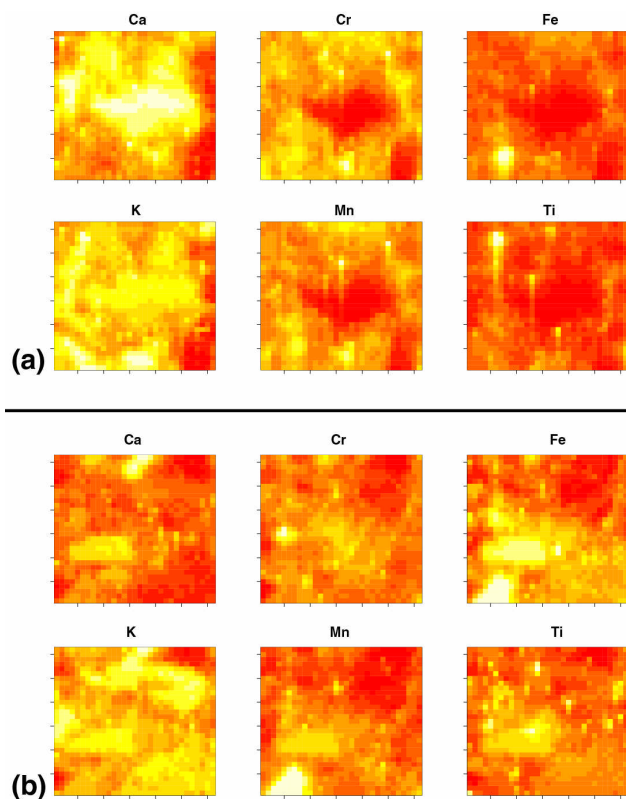


FIG. 1. Element maps of selected areas from (a) sample 41-09-39-6AB and (b) sample SX-108-8A. Total dimensions of the scanned image are  $300 \times 300 \mu\text{m}$ , and each pixel element is  $10 \times 10 \mu\text{m}$ . Light areas have the highest concentrations.

significantly improve the correlations between chromium and any other element. Plotting some of the data by using a quadratic relationship also showed no significant improvement in the correlation between chemical elements.

Correlation coefficients were calculated in order to estimate the linear dependence between pairs of elements in the samples (not shown). As expected, there is a strong association between manganese and iron in all of the core samples and a very weak association between calcium and all other elements except potassium. Sample 41-09-39-6AB also shows a strong correlation between chromium and manganese (0.94) and iron (0.81). However, this strong association with chromium is not repeated in the other samples, with their correlation coefficients ranging between 0.46 and 0.60 for manganese and between 0.32 and 0.59 for iron. The correlation coefficient for chromium and titanium ranged from 0.29 to 0.58 for the four samples. The lack of strong correlations between Cr, Fe, and Mn suggests that sorption reactions between Cr and Fe- or Mn-oxide particles are limited.

The analyses of Cr micro-XANES spectra taken at 53 spots on the four thin sections yielded average Cr(VI) percentages of 13%, 28%, 23%, and 12% for SX-108-7A, SX-108-8A, 41-09-39-6AB, and 41-09-39-7ABC, respectively. All but two spots analyzed contained mixtures of Cr(III) and Cr(IV). Of the two end member spots, one was Cr(III) and the other was Cr(VI). These results indicate that, in general, the two species are intermixed at the  $10\text{-}\mu\text{m}$  scale (approximate analysis scale).

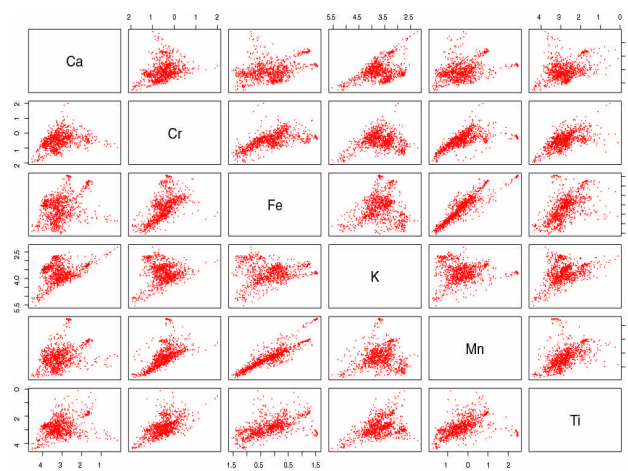


FIG. 2. Scatter plots between Cr, Mn, Fe, and Ti for sample SX-108-8A. The plots in the same row as the elements have that element's normalized fluorescence intensity plotted along the x axis. The y axis of that plot corresponds to the element in the column.

## Conclusions

Microfluorescence elemental mapping of Cr, Fe, Mn, Ti, Ca, and K at  $10 \times 10\text{-}\mu\text{m}$  spatial resolution in  $300 \times 300\text{-}\mu\text{m}$  areas on thin sections of four of the borehole samples showed that they are highly heterogeneous with respect to these elements, with Cr(III) hot spots (diameters of several  $100\ \mu\text{m}^2$ ) occurring, presumably as a result of the precipitation of Cr(III)-hydroxides or chromite or sorption of Cr on Fe(III)-hydroxides. Trivalent and hexavalent chromium are intermixed on a very fine scale (less than  $10\ \mu\text{m}$ ). The spatial correlation between Cr and Fe-bearing minerals, which are likely reductants for Cr(VI), is strong in only one of the four thin sections, indicating that such reactions are limited and occur to varying degrees in these materials.

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