Speciation of chromium in a polyacrylamide hydrogel by μ-XANES imaging

Gerald SCHMIDT\textsuperscript{1}, Michael KERSTEN*\textsuperscript{1}, Mari MIZUSAWA\textsuperscript{2} and Kenji SAKURAI\textsuperscript{2}

\textsuperscript{1}Gutenberg University, D-55099 Mainz, Germany
\textsuperscript{2}National Institute for Materials Science, Sengen, Tsukuba, Ibaraki 305-0047, Japan

Introduction
Chromium has become an important soil contaminant at many sites, and facilitating in situ reduction of toxic Cr(VI) to nontoxic Cr(III) is becoming an attractive remediation strategy. A variety of natural substances have been tested for this purpose, including Mn(II) and Fe(II) as potential reductants in presence of organic carbon, but the complex reaction kinetics are not yet fully understood.

Experimental
A PMMA hydrogel was first soaked in a K$_2$CrO$_4$ solution and transported to the Photon Factory in a sealed Petri dish. The role of the PMMA gel is to allow diffusive transport of the reacting components. The experiment was started by applying a drop of Mn(II) solution to the center of the gel. A couple of hours later, XANES imaging experiments were conducted at BL-16A1 in fluorescence mode. The XRF microscope described elsewhere \cite{1} was used to collect the image data. The monochromator was run through an energy range from 5968 to 6101 eV in 221 steps. At each individual energy step the CCD recorded a fluorescence image at a spatial resolution of 20 µm per pixel. Exposure times were between 1.5 and 10 seconds. I$_0$ data were recorded by an ionization chamber.

Absorption coefficients (I$_1$/I$_0$) were calculated for each pixel in each image. Remote sensing software was used to process the large amount of spectral image data \cite{2}. Classes of identical XANES spectra were selected by applying a Minimum Noise Fraction (MNF) transformation \cite{3} and selecting specific areas in a scatter plot of the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ MNF eigenimages.

Results and Discussion

Two classes of XANES spectra were identified (Fig. 1). The spatial distribution of pixels selected in the scatter plot (b) is shown in the 2$^{\text{nd}}$ eigenimage map (a). Pixels assigned to class 2 (green) are to be found not only at the center of the sample, but mostly at compositional oscillation halos comprising of the reaction product MnO$_2$. The remaining sample area is assigned to the dominating class 1 (red). The normalized XANES plots (c) show a difference in the amplitude of the pre-edge peak for both areas. A significant reduction in the pre-edge height indicates partial reduction of the Cr(IV) to Cr(III) in the oscillating halos. Development of the oscillatory zoning is driven by a complex interplay between the relatively slow kinetics of the redox reaction, and buildup of a diffusional front of Mn(IV)/Cr(III) reactants until super-saturation of the Mn(IV) reactant is reached at some distance, and subsequent adsorption of the Cr(III) reactant onto the thus formed halo of colloidal MnO$_2$ precipitates within the hydrogel matrix.

References
\cite{3} A.A. Green et al., \textit{IEEE Transactions on Geoscience and Remote Sensing} 26, 65 (1988).

* michael.kersten@uni-mainz.de

Figure 1: a) 2$^{\text{nd}}$ eigenimage of the MNF transformation, b) scatter plot of the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ eigenimages, and c) averaged XANES spectra of the classes 1 (red) and 2 (green) selected from the scatter plot. The sample map (a) shows the spatial distribution of chromium phases that are assigned to the classes 1 and 2.