ESRF	**Experiment title:** Tracking changes in Cr speciation in an in-situ contamination treatment project	**Experiment number**: ME 1134
Beamline: BM 26	**Date of experiment**: from: 26.06.2005 to: 03.07.2005	**Date of report**: 20.06.2009
Shifts: 24	**Local contact(s)**: Dr. S. Nikitenko	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jakob FROMMER*
Prof. Dr. Ruben KRETZSCHMAR

Department of Environmental Sciences, Institute of Biogeochemistry and Pollutant Dynamics, Swiss Federal Institute of Technology,
ETH Zurich, CHN, Universitätstr. 16, CH-8092 Zurich, Switzerland

Dr. Maarten NACHTEGAAL*
General Energy Research Department, Laboratory for Energy and Materials Cycles, Paul Scherrer Institute, PSI, CH-5232 Villigen, Switzerland

Report:

The release of toxic hexavalent chromium (Cr(VI)) in the environment and aquifers is of worldwide concern. *In situ* treatments with the goal of the reduction of toxic and mobile Cr(VI) to non-toxic and immobile Cr(III), by permeable reactive barriers or microbial activity is preferable over excavating the sediments. Knowledge of the Cr speciation in the phases formed as a result of the remediation is needed to identify the key processes controlling the Cr(VI) reduction and the subsequent metal sequestration. Synchrotron based XAFS spectroscopy is a unique tool that provides element-selective information on the metal speciation. Cr(VI) and Cr(III) can be readily identified by an intense pre-edge peak, which is only present in the X-ray absorption spectrum of Cr(VI) compounds.

In a first step we collected Cr K-edge XANES and EXAFS spectra on a series of reference and model compounds. Our objectives were to (i) test the occurrence of X-ray beam-induced artefacts that change the Cr redox state in the sample, to (ii) elucidate the structural environment around Cr in these reference samples, and to (iii) better understand the factors affecting the less intense pre-edge resonances in Cr(III) compounds. The latter aspect is particularly interesting if XAFS is used as a microprobe to link the Cr speciation to reactive micro-environments, since in this case the collection of EXAFS spectra with a good enough signal-to-noise ratio is often not possible. Figure 1 shows the XANES and EXAFS spectra of three exemplary reference phases. We found that beam-induced redox changes are likely to occur for Cr(VI) in organic rich matrices under X-ray irradiation, while we did not observe changes between different scans for Cr(III) phases and for Cr(VI) associated with inorganic phases. For future experiments with organic rich samples containing Cr(VI) we will therefore develop a cooling scheme to mitigate the beam-induced redox state changes. In addition, the Cr(III) pre-edge spectra were found to correlate with the type of next-nearest metal atom (Fe or Cr) and the degree of octahedral polymerization. The analysis of the Cr(III) pre-edge spectra can therefore be used to deduce structural information and can contribute to the study of Cr in both, amorphous and crystalline solids.

In a second step we analyzed reactive material sampled from a permeable reactive barrier (PRB) recently installed into a chromate contaminated aquifer. XANES and EXAFS analysis showed that the sequestrated Cr in this sample occurs as Cr(III) bound in mixed Fe-Cr-oxyhydroxides. Furthermore two Cr contaminated soils for which the Cr speciation is unknown were analyzed (floodplain soil and soil contaminated by the activity of a Cr smelter).
Data of good quality could be collected even from dilute samples. The results have been evaluated and contributed to two manuscripts, which are submitted for publication, and to presentations held at international conferences (listed below). In addition, based on these results, follow-up experiments were designed (beam-induced redox state changes, fundamental studies on the factors affecting the Cr(III) pre-edge).

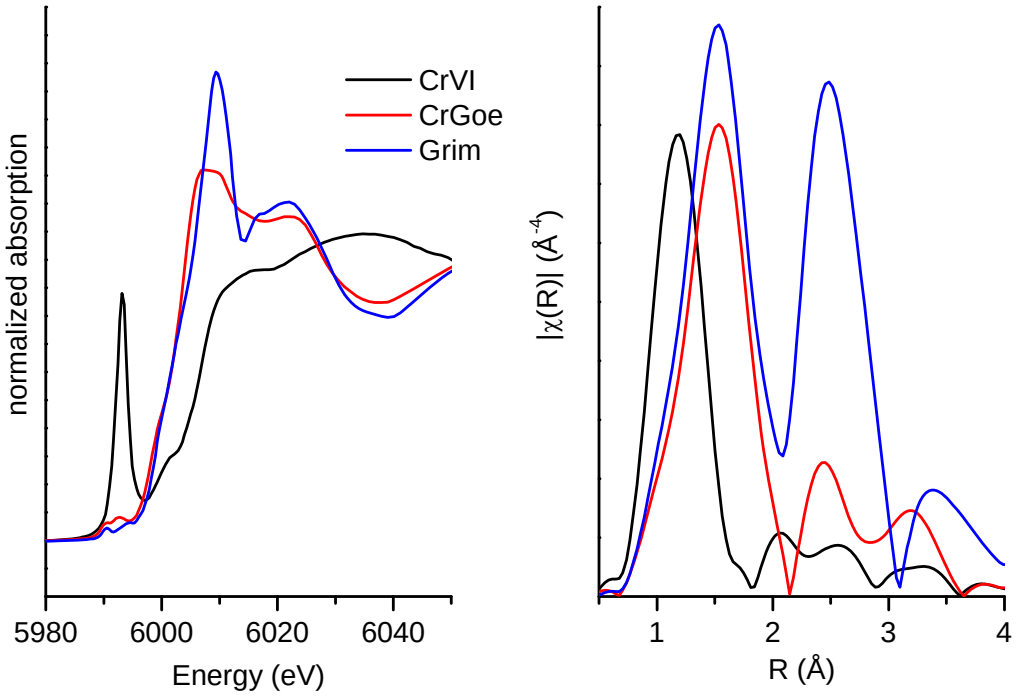

Figure 1: Cr K-edge XANES (left) and magnitude of the Fourier transformed EXAFS (right; *k*-range: 2.5-10 $Å^{-1}$; Kaiser-Bessel window; sill width 2 $Å^{-1}$) of three exemplary Cr reference compounds: potassium-dichromate (CrVI); 5%-Cr substituted goethite (CrGoe; α-FeOOH) and grimaldiite (Grim; α-CrOOH).

Acknowledgements:
We acknowledge the European Synchrotron Radiation Facility for the provision of beamtime at the beamline BM26 and would like to thank Dr. Serge Nikitenko for his excellent support.

Publications:

Flury, B., Frommer, J., Eggenberger, U., Mäder, U., Nachtegaal, M., and Kretzschmar, R. Assessment of long-term performance and chromate reduction mechanisms in a field scale permeable reactive barrier. **submitted.**

Frommer, J., Nachtegaal, M., Czekaj, I., and Kretzschmar, R., Absorption and resonant X-ray emission spectroscopy of poorly crystalline chromium-hydroxides. XAS08 workshop, PSI. Oral presentation. October **2008**.

Frommer, J., Nachtegaal, M., Czekaj, I., Weng, T.-C., Kretzschmar, R., X-ray absorption and emission spectroscopy of Cr(III) (hydr)oxides: Analysis of the K pre-edge region. **submitted**.

Frommer, J., Nachtegaal, M., Czekaj, I., and Kretzschmar, R. (in preparation) The Cr X-ray absorption near K-edge structure of poorly crystalline Fe(III)-Cr(III)-Oxyhydroxides. **submitted**.

Frommer, J., Kretzschmar, R., and Nachtegaal, M. (2007) Exploring the Pre-edge and the XANES of Poorly Crystalline Cr-Phases. American Chemical Society National Meeting; Chicago. Oral presentation. March **2007**.