

# CTR Diffraction Study of U(VI) Adsorption to the $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(1-102) Surface

J.G. Catalano,<sup>1</sup> T.P. Trainor,<sup>2</sup> P.J. Eng,<sup>2,3</sup> G.E. Brown, Jr.,<sup>1,4</sup> G.A. Waychunas<sup>5</sup>

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

<sup>2</sup>GSECARS and <sup>3</sup>James Franck Institute, The University of Chicago, Chicago, IL, U.S.A.

<sup>4</sup>Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University,  
Menlo Park, CA, U.S.A.

<sup>5</sup>Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, U.S.A.

## Introduction

The partitioning of metal ions from aqueous solutions onto mineral surfaces plays an important role in many geochemical and environmental processes. However, it is not well understood at an atomistic level, except for a few simplified model systems where variables have been carefully controlled and appropriate spectroscopic methods have been employed. For example, a number of extended x-ray absorption fine structure (EXAFS) spectroscopic studies over the past decade have revealed information on the structure, composition, and mode of attachment of selected cations and oxoanions at metal-oxide/water interfaces, usually involving powdered substrates [1]. In a few cases, more surface-sensitive grazing-incidence EXAFS spectroscopy studies have been carried out on adsorbate ions on oriented, single-crystal surfaces [2-6]. These studies have placed constraints on the average types of sites to which the adsorbate ions specifically bind. In most cases, however, interpretation of the EXAFS data is complicated and based on assumptions that the surface of the metal oxide substrate is a perfect termination of the bulk structure (i.e., no relaxation or reconstruction) and that the coordination sphere of each coordinatively unsaturated metal ion is completed by oxygen from water molecules.

While this latter assumption is reasonable, it has not been verified except in a few cases where crystal truncation rod (CTR) diffraction was carried out on the hydrated metal oxide surface free of adsorbates [7, 8]. These CTR studies of the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) and (1-102) surfaces showed that the hydrated surface is not a perfect termination of the bulk structure, although the coordination spheres of undercoordinated Al atoms at these surfaces were found to be completed by water molecules. Knowledge of the coordination geometry of oxygen and metal ions at metal oxide surfaces in contact with aqueous solutions is critical for interpreting the mode of attachment of adsorbate ions on a substrate surface inferred from EXAFS spectroscopy results (usually from adsorbate-atom/second-neighbor distances). In general, however, the coordination geometries of these surface species are not well constrained because we do not know

the surface structure of hydrated sorbents, so a number of different modes of attachment are possible.

We conducted a CTR diffraction study of aqueous U(VI) adsorbed onto the (1-102) surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. U(VI) is a contaminant of primary interest to the U.S. Department of Energy (DOE) because it has leaked into the subsurface in large quantities at a number of DOE sites, including Hanford, WA, and Savannah River, SC. The aluminum oxide substrate we have chosen is a well-characterized single crystal suitable for surface scattering experiments [8]. Furthermore, this surface is a good model system analog for commonly occurring aluminum-(hydr)oxide phases, such as gibbsite and clay minerals. Knowledge of the structure of U(VI) adsorption complexes is essential for developing appropriate surface complexation models to predict future transport of U(VI) in the subsurface and for interpreting future EXAFS data for both model and natural samples.

## Methods and Materials

The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample substrate used in the CTR measurements was a 2-in.-diameter (0.5-mm-thick) single-crystal wafer obtained from Saint-Gobain Crystals and Detectors. The wafer, with a (1-102) orientation, was cleaned in 10<sup>-2</sup> M nitric acid followed by multiple rinses with water. This wash procedure was done to ensure that the surface was fully hydroxylated [9]. After cleaning, the wafer was reacted with a pH 4.5, 1 mM UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution overnight, followed by multiple rinses with water. The sample was then transferred to a diffractometer for analysis.

Measurements were performed at the APS at beamline 13-ID. X-rays from the first harmonic of an APS undulator-A beam were monochromatized to 10 keV by using a double-crystal Si(111) monochromator. Diffraction data were collected under ambient conditions in a water-saturated He atmosphere by using a kappa-geometry diffractometer in trajectory scanning mode. Each individual structure factor was determined by rocking scans through the CTR and corrected for active area, polarization, and Lorentz factor after background subtraction. Least squares analysis of the CTR data was

performed using the methods and surface termination of Ref. 8.

## Results

An initial comparison of the CTR data of the U(VI)-reacted surface to that of the clean, hydrated (1-102) surface of  $\alpha$ - $\text{Al}_2\text{O}_3$  shows significant difference in the profiles, especially on the (10L) rod (Fig. 1). We attribute these changes to the presence of U(VI) adsorbed on ordered surface sites. An initial fit to part of the data set (Fig. 2) suggests that U(VI) binds to the singly coordinated O atoms on the surface (Fig. 3). However, the U- $\text{O}_{\text{surface}}$  distances obtained (2.96 and 3.55 Å) are too long for U(VI) to be adsorbed in an inner-sphere fashion (typical U- $\text{O}_{\text{surface}}$  distances are 2.3-2.5 Å) [10-12]. Since a mononuclear, bidentate, inner-sphere complex is the commonly assumed form of U(VI) adsorbed on metal oxide surfaces, the measured distances are significantly different from what we anticipated.

We attribute this deviation either to an inadequacy in our preliminary structural model or to the errors induced by the interaction of the x-ray scattering from the surface O atoms and the U atoms. As U has a site occupancy of only 0.056, it may be that the scattering from this is too weak to accurately model, although its contribution to the CTR profiles appears significant considering the changes in the (10L) rod. Alternatively, scattering from components not included in the analysis, including the “yl” O atoms of the  $\text{UO}_2^{2+}$  moiety and possibly structured

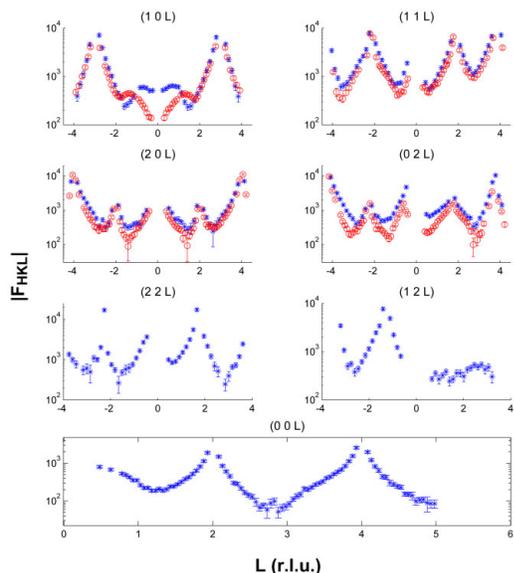


FIG. 1. Comparison of the CTRs measured on the  $\alpha$ - $\text{Al}_2\text{O}_3(1-102)$  clean (red) and U(VI)-reacted (blue) surfaces. Plot at the bottom shows the magnitude of the experimental CTR structure factor vs. perpendicular momentum transfer  $L$ .

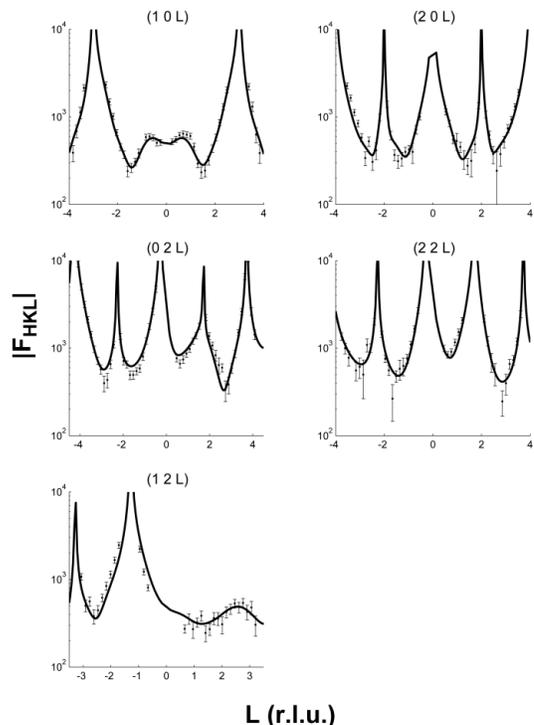


FIG. 2. CTRs measured on a U(VI)-reacted  $\alpha$ - $\text{Al}_2\text{O}_3(1-102)$  surface. Plotted is the magnitude of the experimental CTR structure factor vs. perpendicular momentum transfer  $L$ . Solid line represents the initial fit to the dataset, which resulted in the model shown in Fig. 3.

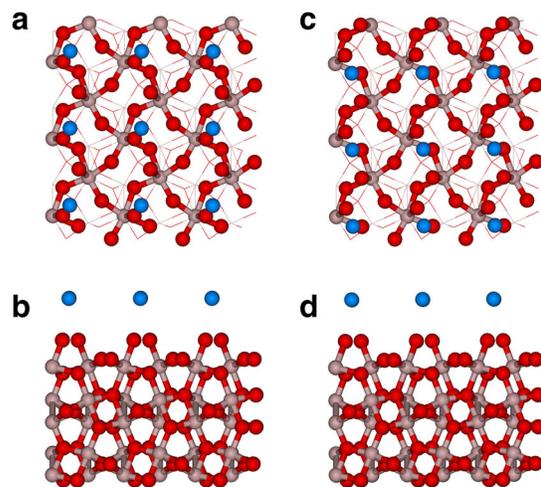


FIG. 3. Section of the  $\alpha$ - $\text{Al}_2\text{O}_3$  unit cell showing the structural model of U(VI) adsorbed to the (1-102) surfaces. Panels (a) and (c) are topviews, and panels (b) and (d) are side views. Note that there are two chemically identical yet symmetry-distinct surface sites that U(VI) may bind to. U(VI) on site 1 is shown in (a) and (b), and site 2 in (c) and (d). Red spheres are O atoms (or hydroxyls or water), gray spheres are Al, and blue spheres are U.

water at the surface, may be responsible for a significant part of the observed CTRs. We will include such components in a future, more complex surface model.

## Discussion

Clear changes are observed in the CTR profiles of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(1-102) surface upon adsorption of U(VI). While an initial fit to the data set identified a possible site of U(VI) adsorption on this surface, validation of this site requires further analysis of other scattering atoms that are likely present.

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