Crystal Truncation Rod Diffraction Study of U(VI) Adsorption on the α-Fe_2O_3 (1-102) Surface

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Introduction

The partitioning of metal ions from aqueous solutions onto mineral surfaces 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 EXAFS spectroscopy 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 is most often 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 oxygens from water molecules. While this latter assumption is reasonable, it has not been verified except in a few cases where crystal truncation rod diffraction was carried out on the hydrated metal oxide surface free of adsorbates [7-9]. These CTR studies of the hydrated alpha-Al_2O_3 (0001) and (1-102) surfaces showed that the hydrated surface is not a perfect termination of the bulk structure, although the coordination spheres of under-coordinated Al atoms at these surfaces were found to be completed by water molecules.

Knowledge of the coordination geometry of oxygens and metal ions at metal oxide surfaces in contact with aqueous solutions is critical for interpreting the mode of attachment of adsorbate ions on substrate surfaces inferred from EXAFS spectroscopy results (usually from adsorbate atom-2nd neighbor distances). In general, however, the coordination geometries of these surface species are not well constrained because we don't know the surface structure of hydrated sorbents, so a number of different modes of attachment are possible. In this study we examined the structure of U(VI) adsorbed on the α-Fe_2O_3 (1-102) surface under ambient conditions. Uranium(VI) is a contaminant of primary interest to the 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 natural hematite substrates have been well characterized, and work quite well in surface scattering studies [9]. Furthermore, these surfaces are good model systems for commonly occurring iron-(hydr)oxide phases, such as goethite and ferrihydrite. Knowledge of the structure of U(VI) adsorption complexes is essential to developing appropriate surface complexation models to predict the transport of U(VI) in the subsurface, and for interpreting future EXAFS data on both model and natural samples.

Methods and Materials

A natural single crystal of hematite from Bahia, Brazil was cut parallel to (1-102) and highly polished by Princeton Scientific (Princeton, NJ). The wafer was cleaned in 10^{-2} M nitric acid followed by multiple rinses with water. This wash procedure was done to ensure that the surface was fully hydroxylated [10]. After cleaning, The α-Fe_2O_3 (1-102) substrate was reacted with an air-equilibrated, pH 7, 85 μM $UO_2(NO_3)_2$ solution with a 10 mM $NaNO_3$ background electrolyte for 24 hours. The sample was then transferred to a diffractometer for analysis.

Measurements were performed at the APS on beamline 13-ID. X-rays from the first harmonic of an APS undulator “A” were monochromatized to 13 keV by using a double-crystal Si(111) monochromator. Diffraction data were collected under ambient conditions in a water-saturated He atmosphere 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 Trainor et al. [8].

Results

Bond valence and steric constraints limit the the possible sites of adsorption to the following geomtries:

R1. Monodentate, mononuclear to FeOH- sites.
R2. Bidentate, binuclear to adjacent FeOH- sites.
R3. Bi- or tridentate and bi- or trinuclear to Fe_2O- and 1-2 FeOH- sites.

Least squares fits of the full datasets to models of the various possible U(VI) adsorption sites were performed, allowing relaxation of the atomic positions from starting structures. The primary free variables are the atomic fractional coordinates, site occupancies, and Debye-Waller factors, as well as overall roughness and scale factors. Because we found no evidence for reconstructions, the (1x1) symmetries of the surfaces were maintained in the fits as described previously [7]. In-plane displacements were allowed within the first two oxygen layers and for the adsorbed uranium, and z-displacements of all atomic layers were allowed within the first 10 atomic layers; allowing deeper relaxations had an insignificant effect on the fits in previous studies. Based on these constraints, the fits had less than 30 free parameters.

Best-fit relaxed surface structures were obtained by starting with the surface terminations determined by Trainor et al. (2003) with the addition of uranium in positions consistent with the possible binding models discussed above. We note that the (1-102) surface has two chemically equivalent but crystallographically distinct terminations depending on where the unit cell is cut. As these terminations are equally probable, our models for the CTR analyses consisted of a weighted sum of two (1-102) surface models, each with the same chemical termination and the same fit parameters. Surface structural models of the three possible adsorption sites, including constraints on the relaxation of the atoms in the surface layer, of the U(VI)-sorbed α-Fe_2O_3 (1-102) surface were constructed. For the three adsorption models (R1, R2, and R3) there existed two chemically equivalent sites of adsorption. A uranium atom was placed on both sites in each model, and the relaxations of the two were constrained to preserve the symmetry of the surface. The relaxed best-fit surface models were evaluated by comparison of the resulting normalized chi-squared values (χ^2) using the Hamilton R-ratio test [12].

The R2 model, with U(VI) binding to adjacent FeOH- sites in a bidentate fashion, provided the best fit to the data (Fig. 1), yielding a χ^2 value of 3.11. This was a statistically better fit at the 99.5% confidence level compared to the R1 ($\chi^2 = 3.69$) and R3 ($\chi^2 = 5.21$) models (Fig. 1). The atomic positions, Debye-Waller factors, and site occupancies of the R2 model yield reasonable values for bond valence sums and interatomic distances; the U-$O_{surface}$ bond lengths were 2.2 ± 0.2 Å and 2.4 ± 0.1 Å. The resulting surface structure model differed little from that of the unrelaxed structure with the atoms in the bulk positions, except for the addition of adsorbed uranium (Fig. 2).

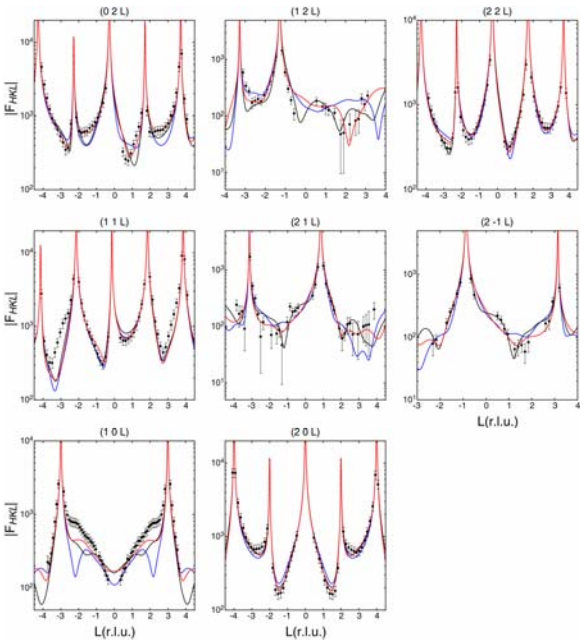

Fig. 1. Experimental structure factors (F_{HKL}) as a function of perpendicular momentum transfer (L, in reciprocal lattice units) for the α-Fe_2O_3 (1-102) surface. The black line is the best-fit R1 model, the red line the best-fit R2 model, and the blue line the best-fit R3 model.

Discussion

On the α-Fe_2O_3 (1-102) surface, U(VI) adsorption occurs only at the singly coordinated oxygen atoms of the surface. The triply coordinated oxygen atoms, while energetically favorable sites of adsorption, are sterically hindered from reacting with aqueous U(VI). The lack of U(VI) adsorption on the doubly coordinated oxygen atoms, while possibly a steric effect, is likely due to the stabilization of such oxygen atoms by protonation and hydrogen bonding [13,14]. Adsorption of large cations to the (1-102) surfaces likely occurs only through reaction with the singly coordinated surface oxygens.

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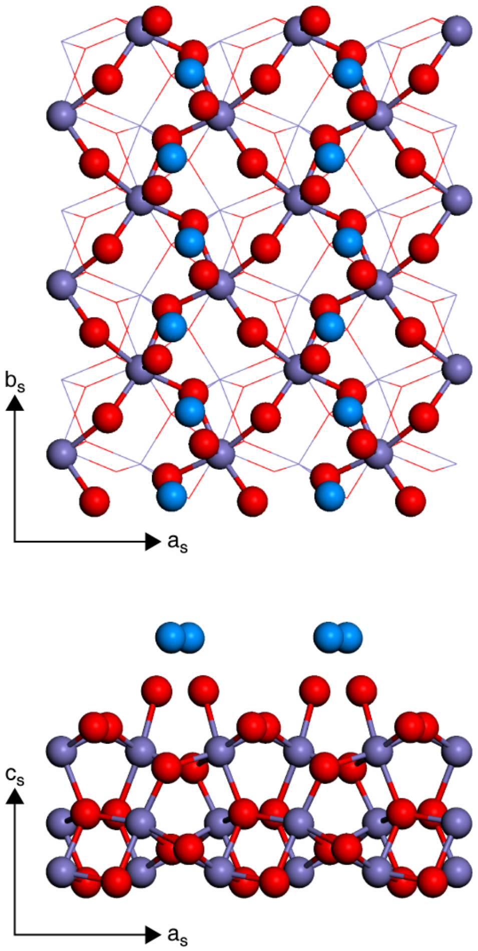

Fig. 2. In-plane and side views of the best-fit models of U(VI) adsorption onto the α-Fe_2O_3 (c and d) surface. Purple sphere are Fe atoms, red spheres are O atoms, and blue spheres are U atoms.

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