The adsorption of Uranium onto goethite and clinochlore

C. Muskett
D. Sherman
V. Ragnarsdottir

Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Road, Clifton, Bristol BS8 1RJ, UK

The aim of this study is to examine the mechanisms involved in the adsorption of uranium from aqueous solutions onto the mineral surfaces goethite (α-FeOOH) and clinochlore ($(Mg_{10}Al_2)(Si_6Al_2)O_{20}(OH)_{16}$).

Adsorption is a major fate process for actinides in natural systems. These results have implications for industry, especially with regards to deep geological repositories for radioactive waste. Also, acid mine drainage in uranium mining areas releases actinides directly into surface and groundwaters.

Goethite was chosen for this study as it is amongst the most common of iron oxyhydroxides, and is found to have a strong affinity for adsorption of the uranyl (UO_2^{2+}) ion (Hsi and Langmuir, 1985). Goethite has a well characterized crystal structure, and is easily prepared under laboratory conditions (Schwertmann and Cornell, 1991). The clinochlore was studied to investigate adsorption onto clay minerals present within the Borrowdale Volcanic group, the rock sequence into which the proposed NIREX repository was to be placed. The clinochlore used was prepared from a single crystal, which was crushed and sieved to give the grain size fraction 63–125 μ. Both minerals were characterized by BET surface area analysis (N_2 adsorption), SEM and XRD. The goethite surface area was 35 m^2/g and clinochlore was 14 m^2/g.

Reaction conditions were varied in order to discover the effect of changing mineral type, pH, surface loading, and carbonate concentration. The surface loading ranged from 0.4–2 wt.%(60, 100, 200 and 1000 ppm U). The solution pH was fixed at 4 and 6. Uranium reactant solutions were prepared from an AAS standard solution (Aldridge Chemicals). A 0.1 M sodium nitrate was used as a background electrolyte. Carbonate concentration was modified either by leaving the reaction vessel open to the atmosphere ($1 \times 10^{-3.5}$ M carbonate), or by using 0.1 M sodium bicarbonate.

The reacted samples were then analysed by ICP-MS to determine the degree of adsorption of the uranium onto the respective minerals. This information, in combination with the surface site density of the minerals, was used to determine the surface loading of uranium adsorbed. The samples were then analysed using EXAFS spectroscopy, conducted at stations 9.2 and 9.3 at the CLRC Synchrotron laboratory at Daresbury, Cheshire.

EXAFS spectra were generated by exposing the sample to a beam of monochromated x-rays, scanning through the range of energies encompassing the x-ray absorption edge of the uranium, L_{III} edge at 17.1 kev. The curve fitting program EXCURV 92 (Binstead *et al.*, 1991) was used to deconvolute the EXAFS spectrua. Radial distribution function plots of K^3 weighted spectra are represented in Figs 1 and 2.

All experiments run using goethite as a sorbent material produced equivalent results. With all clinochlore reactions, all samples also produced

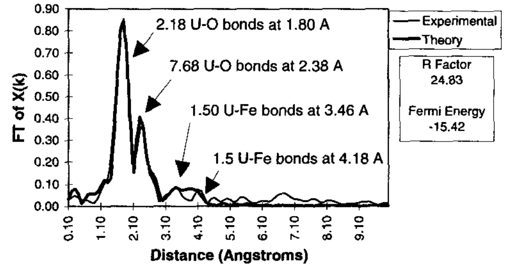

FIG. 1. Radial distribution function of 200 ppm U adsorbed onto goethite with 0.1 M sodium bicarbonate.

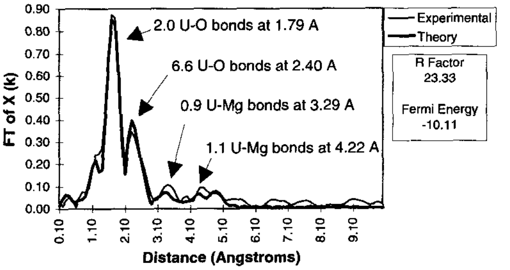

FIG. 2. Radial Distribution Function of 200 ppm U adsorbed onto clinochlore.

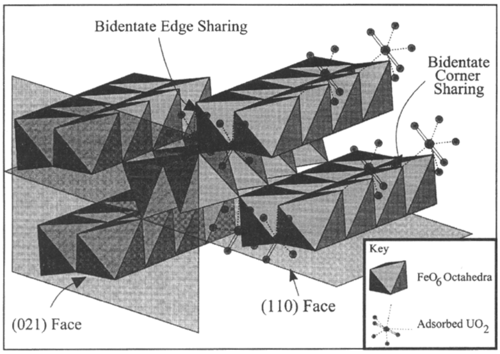

FIG. 3. Proposed structure of the uranyl ion adsorbed onto goethite.

equivalent results (Table 1).

Ambiguity occurs with the interpretation of the EXAFS data for the third and fourth shells in the clinochlore scans, as the atomic numbers of the possible elements were too close together.

Results

The first two shells give speciation information on the adsorbed uranium ion. The number and the distances to the oxygen atoms indicate that the adsorbed species is that of the uranyl oxycation UO_2^{2+}. This is surprising, as the thermodynamically predicted stable solution species where carbonate was predicted to be uranyl carbonate.

A geometrical analysis of the EXAFS data produced gives information on the location of the adsorbed species on the surface of the crystals. Within the goethite system, adsorption occurs initially upon the more reactive (021) sites via edge adsorption. These edge sites have a small surface area due to the acicular shape of the goethite. Uranium also adsorbs onto the less reactive (110) face, by corner sharing onto two iron-oxygen octahedra (Fig. 3). Adsorption onto these sites occurs regardless of solution pH, surface loading, and solution speciation.

TABLE. 1. Parameters produced by deconvolution of EXAFS spectra.

Mineral	Shell no.	No. of atoms	Atom type	Distance
Goethite	1	2	O	1.8 Å
	2	6–10	O	2.35 Å
	3	0.5–1.5	Fe	3.5 Å
	4	0.9–1.3	Fe	4.2 Å
	5*	0.8–2.0	Fe	4.5 Å
Clinochlore				
	1	2	O	1.8 Å
	2	6–7	O	2.4 Å
	3	0.5–1.5	Mg/Si/Al	3.3 Å
	4	0.9–1.3	Mg/Si/Al	4.2 Å

*Only visible at 60 ppm U

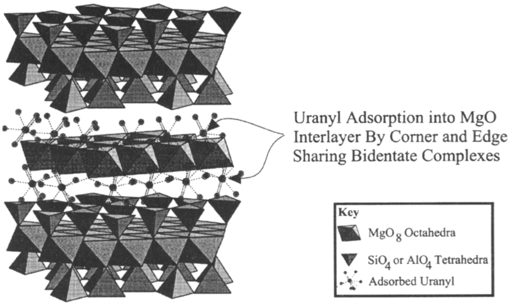

FIG. 4. Proposed location of the adsorbed uranyl ion onto clinochlore. Exact positioning of the uranyl ion into the brucite interlayer is uncertain, due to equal proportions of edge and corner sharing sites on the (110), (110) and (010) faces.

The adsorption of uranyl onto clinochlore from raw analysis of EXAFS data cannot resolve the binding site to which uranium adsorbs to. Geometrical analysis, however, indicates that the uranium is bonding onto an octahedral site, as opposed to a tetrahedral site, hence the uranium bonds onto the brucite interlayer. Adsorption of uranium to the interlayer occurs via corner and edge sharing onto the magnesium-oxygen octahedra (Fig. 4).

The strong adsorption of uranyl onto the magnesium end member chlorite implies even greater adsorption will be observed on to more iron rich members of the chlorite series, due to the substitution of iron into the magnesium oxide layer.

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