

The effect of bacterial and plant siderophores on U^{IV} oxide dissolution

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Tetravalent actinides such as Plutonium^{IV} or Uranium^{IV} form oxide phases that have very low solubilities. Therefore, tetravalent actinides are often considered immobile in stable reducing environments. However, it was demonstrated that tetravalent actinides are coordinated by siderophores forming exceptionally stable soluble complexes. Siderophores are organic ligands that are exuded by plants and microorganism to increase the bioavailability of iron, an essential nutrient. They are considered iron specific due to their high affinity for iron relative to other common constituents of ground- and surface water. In this context we investigated the effect of plant and bacterial siderophores on the solubility of uranium oxide, and on the rates and mechanisms of uranium oxide dissolution under reducing conditions. We also investigated the effect of the presence of Fe(III) on the dissolution process. The uranium oxide was synthesized by reduction of dissolved uranyl nitrate and precipitation, followed by drying, washing, and further reduction in a pure hydrogen atmosphere at 850 degree C. Dissolution experiments were performed in batch and in continuous flow stirred tank reactors. Siderophore adsorption as a function of soluble siderophore concentrations or of pH were conducted in batch experiments. Plant siderophores (desoxymugineic acid) were purified from root exudates of wheat. Bacterial siderophores (desferrioxamine B) were purchased.

Proton promoted dissolution rates of uranium oxide decreased with increasing pH. In the presence of siderophores, dissolution rates were several times greater than the proton or hydroxide promoted dissolution rates alone. A linear correlation was observed between dissolution rates and surface concentrations of adsorbed siderophores. This is consistent with a ligand controlled dissolution mechanism. However, dissolution rate coefficients had a minimum at pH 7.5 and increased toward lower and higher pH. The presence of Fe(III) had only a minor effect on uranium oxide dissolution rates at molar ratios Fe(III)/siderophore < 0.9. This is consistent with the low redox potential of Fe-siderophore complexes below the redox potential of the U(IV)/U(VI) pair which inhibits oxidation of uranium(IV) by Fe(III). In summary, our observations demonstrate that biogenic ligands can have a significant effect on the mobility of tetravalent actinides in the environment.

Citrate adsorption at the water-goethite interface: A spectroscopic evaluation of surface complexes

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The mobility and bioavailability of organic and inorganic ligands in soils and aquifers are dependent on interactions with mineral surfaces. Carboxylic acids are a group of ligands that are abundant in most soil systems. As complexing agents they are involved in detoxification of metals, chemical weathering of minerals and acquisition of nutrients by plants. The present work focuses on interactions between citrate and goethite (α -FeOOH) surfaces. Citrate is a hydroxyl-tri-carboxylic acid that has been shown to participate in all of the above mentioned processes.

There are disparities in the literature regarding the types and structures of citrate-goethite surface complexes [e.g. 1-2], and the present work was an attempt to resolve this controversy. In order to meet our research objective, both quantitative and qualitative data were collected. In-situ ATR-FTIR spectroscopy was used to evaluate the surface speciation of citrate, and scintillation counting and atomic absorption spectroscopy were used to gain quantitative adsorption and dissolution data. The work was conducted in series of batch experiments and a simultaneous infrared and potentiometric titration, measuring ligand adsorption as a function of pH, time and ligand concentration.

With the methods used, we find evidence for at least three different surface complexes. Two of these are outer sphere complexes of which one is protonated and one is deprotonated. The protonated form transforms to the unprotonated one at around pH 3.5. The third species is an inner sphere complex which exists over the whole pH range investigated (3-9), persisting to unusually high pH values compared to other mono-, di-, tri- and tetracarboxylic acids. This increased stability is ascribed to a polydentate coordination between carboxylic group(s) and the hydroxyl group of citrate and surface Fe(III).

No dissolution was detected above pH 5 at any citrate concentration and only up to 0.15% of an estimated monolayer below that pH.

References

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