

Cr(OH)₃(s) oxidation by birnessite under common groundwater pH conditions

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Contamination of soil and groundwater by hexavalent chromium (Cr(VI)), which is the 2nd most common inorganic contaminant, was generally considered to be generated from anthropogenic sources. Recently, natural groundwater contamination by Cr(VI) without any anthropogenic sources have also been reported over the world. Previous studies showed that various Mn oxides effectively oxidized aqueous- or solid-phase Cr(III) under acidic pH conditions but not under neutral or higher pH conditions. Yet, the geochemical processes causing the natural contamination of Cr(VI) have not been clearly unravelled. This study examined the oxidation of Cr(OH)₃(s) by birnessite, under common groundwater pH conditions. Both solids are ubiquitous in the environment. Practically, Cr(OH)₃(s) has been thought to hinder the oxidation of dissolved Cr(III) by Mn oxides because the precipitation of this solid on Mn oxide would block the reactive surface sites.

Particle suspensions were prepared with synthetic Cr(OH)₃(s) and/or birnessite in 50 mM NaNO₃ at pH 7, 8, or 9 open to the atmosphere. The individual solid concentration was 1 g/L in every case and the solution pH was maintained with a 10 mM buffer (Na-MOPS for pH 7 and 8, CHES for pH 9). In the presence of birnessite, Cr(VI) concentrations increased with increasing pH and reached up to 209, 613, 836 μM at pH 7, 8, and 9, respectively, within a month. These Cr(VI) concentrations were substantially higher than those in the absence of birnessite at all pHs. These results indicate that birnessite could effectively oxidize Cr(OH)₃(s), where the solubility of this solid is minimum. In addition, the apparent rate and extent of Cr(OH)₃(s) oxidation appeared to be controlled by several accompanied reactions, the effects of which mainly depend on the pH of the system. It is noteworthy that the rate of Cr(OH)₃(s) oxidation increased with time during the first 10 hr followed by a decrease in the rate with time for the rest of the reaction. These results suggest that the overall oxidation would likely be accelerated by a reaction intermediate in the early stage of the reaction. A potential reaction pathway of Cr(OH)₃(s) oxidation will be briefly discussed.

Ternary surface complexes probed by attenuated total reflection-infrared spectroscopy

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Attenuated Total Reflection-Infrared spectroscopy (ATR-IR) is amongst the most developed spectral techniques during the last decades to study the solid/solution interfaces. Its efficiency in determining the speciation of adsorbed ions has been proved in numerous works using different metallic oxides [1]. Its advantage is to probe the system in presence of solution, avoiding the modification of the structure consequently to the dehydration. Indeed, this phenomenon can occur for inner-sphere complexes, even though it is not systematic, while for outer-sphere complexes, the dehydration step has always a dramatic effect. Another field where the possibilities of ATR-IR are underexploited is the characterization of ternary surface complexes including the mineral surface / a bridging species / a second adsorbed species. The main question which can be addressed by ATR-IR is to determine which is the bridging species, and what type of chemical groups are bonded to the mineral surface or to the other adsorbed species. In literature, such studies have been performed on goethite/sulfate/Pb (II) [2] or hematite/carbonate/U (VI) [3], goethite/glyphosate/Cu (II) [4] for example. The purpose of our current works is to characterize the surface reactivity of silica towards uranyl ions in presence of small organic molecules to evaluate the role of organic matter on the transport of radionuclides in environment. We have first studied the system silica/uranyl/acetate, using ATR to show the presence of a ternary complex. The same work with more complex organic molecules is in progress.

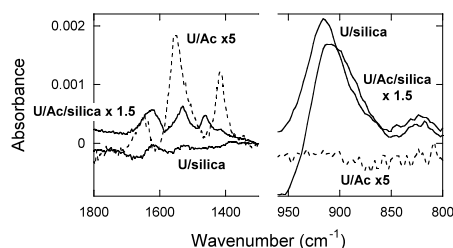


Figure 1: Spectra of U(VI) 0.05 mM in presence of acetic acid 10 mM (pH 5.5) and/or silica

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