Environ. Sci. Technol. 2006, 40, 4666−4671

Kinetics of Uranium(VI) Reduction by Hydrogen Sulfide in Anoxic Aqueous Systems

BIN HUA,[†] HUIFANG XU,[‡]
JEFF TERRY,[§] AND BAOLIN DENG*,[†]

Department of Civil and Environmental Engineering,
University of Missouri-Columbia, Columbia, Missouri 65211,
Department of Geology and Geophysics,
University of Wisconsin, Madison, Wisconsin 53706, and
Department of Biological, Chemical, and Physical Sciences,
Illinois Institute of Technology, Chicago, Illinois 60616

Aqueous U(VI) reduction by hydrogen sulfide was investigated by batch experiments and speciation modeling; product analysis by transmission electron microscopy (TEM) was also performed. The molar ratio of U(VI) reduced to sulfide consumed, and the TEM result suggested that the reaction stoichiometry could be best represented by $UO_2^{2+} + HS^- = UO_2 + S° + H^+$. At pH 6.89 and total carbonate concentration ($[CO_3^{2-}]_T$) of 4.0 mM, the reaction took place according to the following kinetics: $-d[U(VI)]/dt = 0.0103[U(VI)][S^{2-}]_T^{0.54}$ where [U(VI)] is the concentration of hexavalent uranium, and $[S^{2-}]_T$ is the total concentration of sulfide. The kinetics of U(VI) reduction was found to be largely controlled by $[CO_3^{2-}]_T$ (examined from 0.0 to 30.0 mM) and pH (examined from 6.37 to 9.06). The reduction was almost completely inhibited with the following $[CO_3^{2-}]_T$ and pH combinations: [($\geq$15.0 mM, pH 6.89); ($\geq$4.0 mM, pH 8.01); and ($\geq$2.0 mM, pH 9.06)]. By comparing the experimental results with the calculated speciation of U(VI), it was found that there was a strong correlation between the measured initial reaction rates and the calculated total concentrations of uranium-hydroxyl species; we, therefore, concluded that uranium-hydroxyl species were the ones being reduced by sulfide, not the dominant U-carbonate species present in many carbonate-containing systems.

Introduction

Uranium (U) contamination has been detected at numerous U.S. Department of Energy waste sites (*1*). It is also found at other locations such as the agriculture evaporation ponds (3 μg to 22 mg/L) of the San Joaquin Valley, California (*2*) and various U mine tailings (*3*). In aquatic systems, uranium exists primarily as complexed, sorbed, or precipitated uranyl (UO_2^{2+}) carbonate and/or hydroxide species (*4*). The mobility of U in aquatic systems is largely determined by its speciation and interaction with other aquatic constituents, including microorganisms, natural organic matter, inorganic ions, and mineral surfaces. Such interactions may result in U adsorption, redox transformation, and precipitation, all of which are relevant to many geological and environmental processes.

Adsorption of U(VI) onto mineral surfaces has been well explored as one of the potential approaches for U(VI) immobilization (*3*, *5*, *6*). Adsorption, however, could be greatly influenced by the capacity of adsorbents, competition from other species for the surface sites, and reaction with U-complexing agents. For instance, U(VI) adsorption by iron oxyhydroxides depended strongly upon carbonate concentration and pH because of their effects on U(VI)-carbonate complex formation (*7*).

Biotic or abiotic reduction of U(VI) to uraninite (UO_2), which has an extremely low solubility [$K_{sp} = 10^{-60.6}$ (4)], could be an effective approach for uranium immobilization. Some microorganisms, including Fe(III)-reducing *Geobacter metallireducens* (*8*), sulfate-reducing *Desulfovibrio vulgaris* (*9*), and sulfate-reducing *Desulfovibrio desulfuricans* strain G20 (*10*), are known to reduce soluble U(VI) to insoluble U(IV). In heavily contaminated sites, however, biotic reduction of heavy metals and radionuclides could be limited by the lack of microorganisms and suitable electron donors, by the presence of competitive electron acceptors, by the presence of heavy metals toxic to microorganisms, and/or by unfavorable pH conditions (*11*, *12*).

Chemical reduction of U(VI) could be coupled with various reduced iron and sulfur species, including mixed ferrous/ferric hydroxides (*13*), Fe(II) sorbed on hematite surfaces (*14*), zerovalent iron (*15*), and various dissolved and solid sulfide species (*4*, *6*, *16*−*18*). There have been, however, conflicting reports on U(VI) reduction kinetics and products. Wersin et al. (*17*) and Livens et al. (*18*) provided spectroscopic evidence showing the sorption and reduction of U(VI) by sulfide minerals. Laboratory experiments also showed formation of precipitates upon bubbling H_2S gas into $5-10 \times 10^{-2}$ g/L of uranyl solution (free from CO_2) within several hours (*19*), as well as removal of aqueous U(VI) through both enzymatic and chemical reduction that was associated with sulfate-reducing biofilms in the absence of bicarbonate (*20*). In contrast, uranium in anoxic Black Sea water was present as U(VI), rather than the seemingly favored U(IV) species, even though the sulfide concentration was as high as 400 μM (*21*). Another perplexing observation is the production of multiple reaction products. For example, uranium in sulfidic sediments from the San Joaquin Valley of California was determined to be pitchblende (U_3O_8) by X-ray absorption near edge structure spectroscopy (XANES) (*22*), whereas precipitates produced by aqueous sulfide reduction in the laboratory were identified to be uraninite by X-ray diffraction (*19*), as well as by XANES and transmission electron microscopy (TEM) (*20*).

While the detailed kinetics and mechanism of U(VI) reduction by sulfides have not been fully elucidated, available literature has, nevertheless, overwhelmingly suggested that reductive U immobilization by sulfide species could take place under reducing environmental conditions. A contaminant immobilization/site remediation technology, in situ gaseous reduction, has been proposed for the remediation of soils contaminated with redox-sensitive metals (e.g., Cr, U, and Tc) by hydrogen sulfide injection, and has been field-tested for Cr (*23*). The technology could similarly be applied for reductive U immobilization. A better understanding of the kinetics and mechanism of U(VI) reduction by sulfide is needed to apply such reduction-based technologies. The information could also provide insight into other geological and environmental processes such as U ore formation and its biogeochemical cycling.

The objectives of this study were to (i) determine the reaction stoichiometry and the major reaction products of

---

* Corresponding author phone: (573) 882−0075; fax: (573) 882−4784; e-mail: dengb@missouri.edu.

[†] University of Missouri, Columbia.

[‡] University of Wisconsin, Madison.

[§] Illinois Institute of Technology, Chicago.

10.1021/es051804n CCC: $33.50