Uranium Diffusion into Soils from Concentrated Acidic and Alkaline Solutions

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Introduction

Transport of uranium (U) through soil and sediments is of great concern in regions affected by U processing (mining, milling, refining, and waste disposal). While large-scale migration of U contamination in the subsurface is determined by advection along permeable pathways connected to the waste source, its local distribution is controlled by diffusion. Environments contaminated by U can be challenging to understand because extreme disequilibrium is likely, especially during early stages of waste migration. The potential extent of disequilibrium is evident when one recognizes that waste solutions containing high concentrations of U typically are either highly acidic or highly alkaline. Changes in pH encountered by waste solutions contacting soils, combined with the strong pH dependence of aqueous, sorbed, and solid U species, results in a complex series of U transformations during transport [1]. Since U concentrations in both acidic and alkaline waste solutions can be very high, it is important to conduct experiments at elevated U levels in order to understand transport through soils and sediments in regions near contaminant sources.

Because U(VI) forms a variety of strongly pH-dependent solution complexes and surface complexes, its sorption is strongly pH dependent, and so, hence, is its mobility. The impact of pH-dependent sorption on U(VI) diffusion through soils becomes clear when one recognizes that U(VI) partition coefficients (K_d) often vary over three orders of magnitude and that apparent diffusivities are inversely dependent on K_d. Values of K_d can exceed 10^4 cm^3 g^{-1} in the neutral pH region and fall below 10 cm^3 g^{-1} under very acidic (pH of <3) and alkaline (pH of >9) conditions [2, 3]. Sorption of U(VI) at any given pH is nonlinear, with the strongest U(VI) sorption at low concentrations [4-6]. Thus, K_d values obtained from sorption experiments conducted in the μM range of U(VI) concentrations are not representative of sorption from more highly concentrated U waste sources. It has recently been shown that the presence of Ca^{2+} can dramatically alter U(VI) behavior through the formation of the neutral $Ca_2UO_2(CO_3)_3$ solution complex [7]. The high stability of the aqueous $Ca_2UO_2(CO_3)_3$ complex appears to be responsible for suppressing U(VI) sorption at circum-neutral pH [6], and it strongly inhibits bacteria U(VI) reduction [8]. For all of the aforementioned reasons, U(VI) sorption in a system experiencing large changes in U concentration, pH, and solution chemistry is complicated.

Despite the importance of U(VI) diffusion in contaminated soils, information is lacking on the early stages of this process, when either acidic or alkaline solutions containing high U concentrations come in contact with soils. The complex behavior of U under these conditions warrants experiments on natural soils, so that no relevant processes are neglected. This study examines U(VI) diffusion into soils from acidic and alkaline solutions containing high initial U concentrations ($\approx$1 mM). Two different soil types, one neutral and the other slightly alkaline, were exposed to these acidic and alkaline U(VI) solutions. The experiments presented here relied on characterizing spatial distributions of U(VI) during transient diffusion into soils and on measuring time trends in U(VI) depletion from boundary reservoirs.

Methods and Materials

Two different types of soil were used, a slightly alkaline Altamont (AL) soil, and a neutral Oak Ridge (OR) sediment. The AL soil is from Altamont Pass, California. The OR shale saprolite was obtained from the U.S. Department of Energy (DOE), Natural and Accelerated Bioremediation Research (NABIR) Program's Background Area field site at Oak Ridge National Laboratory, Tennessee. Samples were sieved (2 mm) and homogenized before being packed into the diffusion cells. U(VI) solutions were prepared by dissolving $UO_2(NO_3)_2$, and adjusting the pH to either 2.0 or 11.0, by using HCl or NaOH, respectively. Both the initial acidic and alkaline solutions had U(VI) concentrations of 0.94 mM (220 mg L^{-1}) and were in contact with the atmosphere ($P_{CO2} = 10^{-3.5}$ atm).

The soil column design was similar to one used previously, but it did not have a section of the wall removed and sealed with a Kapton® film window for the x-ray measurements [9]. Instead, one side of each 12.7-mm-inner-diameter polycarbonate column was milled to provide a wall thickness of 1.0 mm. The e^{-1} absorption depth for polycarbonate at the U L_{III} edge was about 14 mm, such that x-ray attenuation through the plastic window was negligible. Soils were packed into the columns to a height of 62 mm and porosity of 0.50, then saturated with U-free solutions. Uranium exposure was initiated by ponding 9.0 mL of either pH 2 or pH 11 U(VI) solutions. The pH and U concentration of the boundary reservoir in each column were measured periodically.

Profiles of the total U and U(VI) distribution within the sediment columns were obtained by x-ray microprobe and micro-x-ray absorption near-edge structure (micro-XANES) spectroscopy at GSECARS beamline 13-ID-C at the APS [10]. These measurements were obtained on days 150 and 600 relative to initial exposure to the U(VI) solutions. The x-ray beam was defocused to provide a spot size of about 100 μm (vertical) by 1,000 μm (horizontal) on the vertically oriented columns. Total U and U(VI) profiles were obtained by moving columns along the vertical direction in front of the stationary x-ray beam. At each measurement location, a micro-XANES spectrum was obtained by scanning the monochromator through several energies below, within, and above the U_{LIII} edge. Total U concentrations of unknowns were calculated on the basis of a comparison of the magnitudes of background-subtracted edge step heights with concentration standards ($UO_2(NO_3)_2$ mixed into soils at concentrations ranging from 0 to 5,000 mg kg^{-1}. The local oxidation state of U in columns was calculated on the basis of comparisons of energies at the edge half-height with energies of oxidation state standards [11].

Fitting experimental results to model predictions allowed the determination of K_d values and the evaluation of the possible significance of surface diffusion. Because of periodic mixing (during pH and redox measurements and during sampling for U analyses) of the reservoir solution, the experiment approximated 1-D diffusion from a well-stirred finite reservoir into a finite soil column. Analytical solutions for concentrations in the reservoir [12] and along the soil column [13] were modified to include linear sorption.

Results

Micro-XANES spectra confirmed that U remained in hexavalent forms, within measurement uncertainty (about ±10%). The U profiles from day 150 are incomplete, especially for the AL soils, because short diffusion distances were originally anticipated on the basis of assumed larger K_d values. Measured and calculated total U profiles are shown in Fig. 1. Calculated U profiles were obtained by using K_d values of equal or similar magnitude to those inferred from their associated reservoir U time trends. Generally good agreement is obtained between K_d values inferred from reservoir U concentration time trends and soil column U profiles in the initially acidic and initially alkaline AL systems. U diffusion within the AL soils is best described by very low K_d values. Uranium diffusion profiles were fairly well matched in the acidic OR soil with a K_d of 20 cm^3 g^{-1}, despite the less satisfactory fit of its reservoir U concentration time trends. The OR soils exposed to alkaline U solutions exhibited the shortest diffusion distances (Fig. 1d), consistent with both high K_d values and precipitation. Referencing the example model profiles for a K_d of 2,000 cm^3 g^{-1} (matched to the data from day 150), U mobility apparently decreased with time, since the measured profile from day 600 lags significantly behind its calculated profile.

Discussion

These diffusion experiments yielded several new insights into U transport in soils. Although exposed to initially pH 2 or pH 11 U(VI) solutions, the soils provided strong pH buffering (especially the calcareous AL soils), resulting in diffusion at a nearly constant pH. Time trends of U(VI) depletion from reservoirs and U(VI) profiles within soil columns generally yielded similar apparent diffusivities and K_d values. The K_d values inferred from the diffusion experiments were in fair agreement with batch K_d values obtained at similar high concentrations [0.05 to 0.5 mM U(VI)], but they were much lower than values found in the literature obtained in the nM to μM range, reflecting nonlinearity in sorption. Diffusion of U(VI) into the calcareous AL soil is relatively efficient regardless of the initial solution pH, probably because of the stability of aqueous $Ca_2UO_2(CO_3)_3$ and consequent weaker sorption in these calcite-buffered systems. Diffusion into the OR soil under acidic conditions was also significantly faster than expected on the basis of sorption data obtained at lower concentrations. The initially alkaline U(VI) solution diffusing into the OR soil quickly stabilized at neutral pH, such that precipitation prevented analysis of this system strictly in terms of diffusion and sorption. Inclusion of surface diffusion was unnecessary in any of these systems but may be important for U(VI) diffusion at low concentrations and neutral pH, where sorption is strongest.

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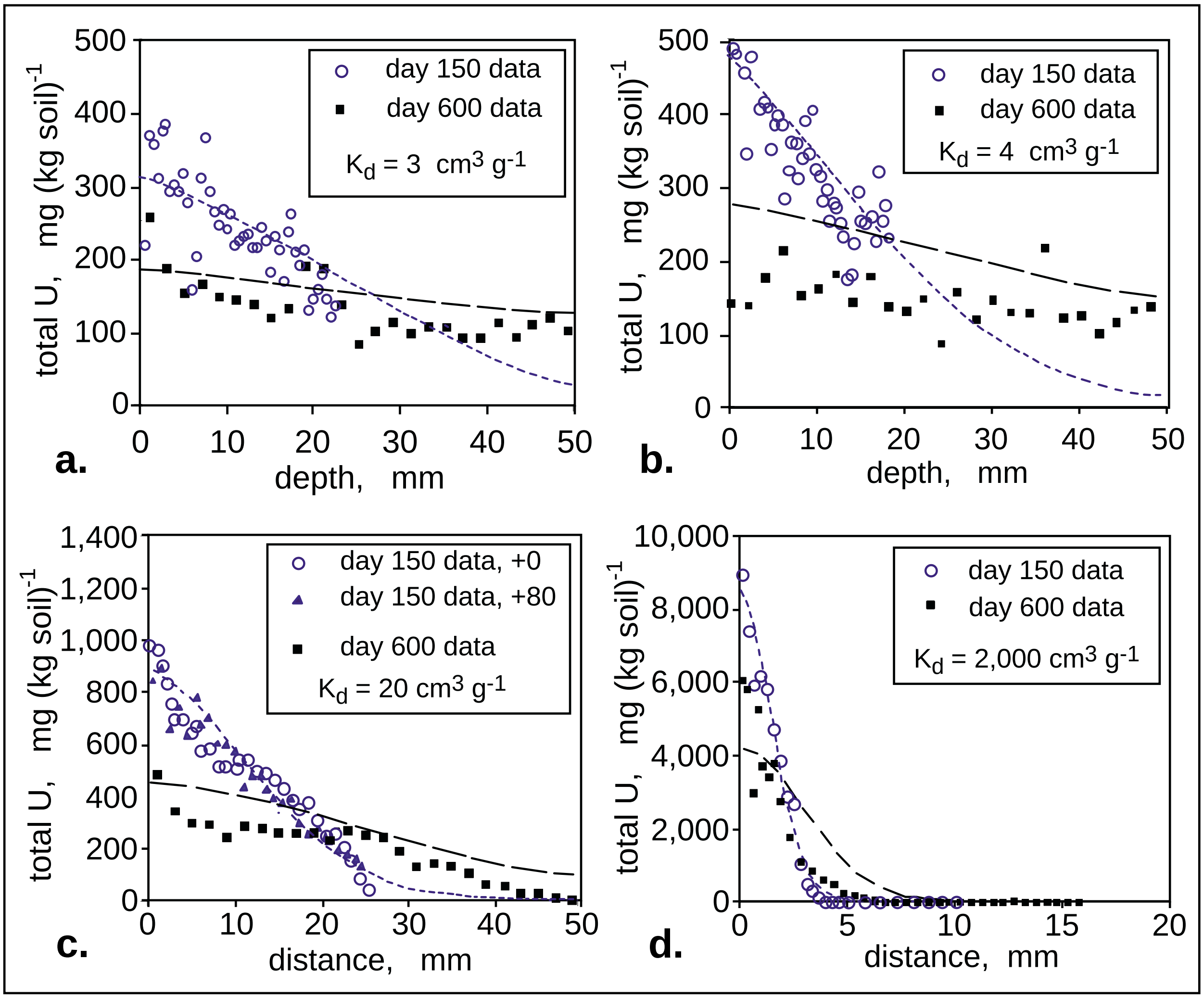

FIG. 1. U(VI) concentration profiles in soil columns at 150 and 600 days (data points) for (a) Altamont soil with an initial pH of 2.0, (b) Altamont soil with an initial pH of 11.0, (c) Oak Ridge soil with an initial pH of 2.0, and (d) Oak Ridge soil with an initial pH of 11.0. Curves are solutions to the diffusion-sorption equation obtained with the indicated K_d *values.*

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