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Experimental determination of UO_2(cr) dissolution kinetics: Effects of solution saturation state and pH

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Abstract

To evaluate the release of uranium from natural ore deposits, spent nuclear fuel repositories, and REDOX permeable reactive barriers (PRB), knowledge of the fundamental reaction kinetics associated with the dissolution of uranium dioxide is necessary. Dissolution of crystalline uranium (IV) dioxide under environmental conditions has been studied for four decades but a cardinal gap in the published literature is the effect of pH and solution saturation state on UO_2(cr) dissolution. To resolve inconsistencies, UO_2 dissolution experiments have been conducted under oxic conditions using the single-pass flow-through system. Experiments were conducted as a function of total dissolved carbonate ($[CO_3^{-3}]_T$) from 0.001 to 0.1 M; pH from 7.5 to 11.1; ratio of flow-through rate (q) to specific surface area (S), constant ionic strength (I) = 0.1 M, and temperatures (T) from 23 to 60 °C utilizing both powder and monolithic specimens. The results show that UO_2 dissolution varies as a function of the ratio q/S and temperature. At values of $\log_{10} q/S > -7.0$, UO_2 dissolution becomes invariant with respect to q/S, which can be interpreted as evidence for dissolution at the forward rate of reaction. The data collected in these experiments show the rate of UO_2 dissolution increased by an order of magnitude with a 30 °C increase in temperature. The results also show the overall dissolution rate increases with an increase in pH and decreases as the dissolved uranium concentration approaches saturation with respect to secondary reaction products. Thus, as the value of the reaction quotient, Q, approaches equilibrium, K, (with respect to a potential secondary phase) the dissolution rate decreases. This decrease in dissolution rate (r) was also observed when comparing measured UO_2 dissolution rates from static tests where $r = 1.7 \pm 0.14 \times 10^{-8}$ mol m^{-2} s^{-1} to the rate for flow-through reactors where $r = 3.1 \pm 1.2 \times 10^{-7}$ mol m^{-2} s^{-1}. Thus, using traditional static test methods can result in an underestimation of the true forward rate of UO_2(cr) dissolution. These results illustrate the importance of pH, solution saturation state, and the concentration of dissolved carbonate on the release of uranium from UO_2 in the natural environment.
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1. Introduction

REDOX permeable reactive subsurface barriers (e.g., chemically manipulated soils, microbial manipulated soils, and zero-valent iron) have been demonstrated to be effective in reducing and immobilizing redox-sensitive contaminants (i.e., chromium and uranium) in laboratory

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experiments [1–3] and field experiments [4–6]. Also, uranium reduction in laboratory experiments utilizing both biotic [2,7,8] and abiotic [1,9] permeable reactive barrier (PRB) techniques results in formation of a discrete UO_2 phase. Therefore, to predict the release of soluble uranium and the dissolution of uranium (IV) dioxide from natural ore deposits, spent nuclear fuel repositories, and REDOX permeable reactive barriers, knowledge of the fundamental reaction kinetics must be obtained.

More than four decades of past studies focusing on spent nuclear fuel disposal have quantified the kinetics of UO_2(cr) dissolution [10–23], but the findings, although important, reveal significant gaps in the quantitative understanding of UO_2(cr) reactivity. For a comprehensive discussion of previous results, the reader should consult the review papers by Grambow [24] and Shoesmith [25]. These reviews have identified two factors that have contributed to the uncertainty in dissolution rates, (1) solution saturation state and (2) pH. Therefore, the focus of this study was to determine the effect of pH and solution saturation state in the presence of carbonate on the oxidative dissolution of a crystalline form of uranium (IV) oxide [UO_2(cr)] as a model solid.

Our first concern was that several previous experimental investigations of UO_2 reactivity were conducted using a static reactor (e.g., batch reactor) rather than more applicable flow-through reactors [10–16,19]. Dissolution rates cannot be evaluated accurately under conditions of both near-saturation and dilute dissolved uranium concentrations using the traditional static reactor.

Second, numerous studies have been conducted to evaluate the effect of pH (3.0–11.0) on the dissolution of UO_2 under oxidizing and reducing conditions [11,13–15,17,22,26]. All investigators have observed a linear relationship of pH on the dissolution rate from the acidic to near neutral range (i.e., from $pH = 3.0$ to 6.8) and a dissolution rate that becomes insensitive to pH from the near neutral to alkaline range (i.e., from $pH = 6.8$ to 11.0). The scatter shown in the data obtained by Torrero et al. [22] under oxidizing conditions and at pH values greater than 6.8 was attributed to the formation of a partially oxidized surface layer. Other investigators [22,27] have also observed the formation of a partially oxidized surface film within this pH range (e.g., from 7 to 11), when evaluating the dissolution of UO_2 under oxidized conditions with a total dissolved carbonate concentration ($[CO_3^{2-}]_T$) less than 10^{-3} M. The formation of this surface film has led to the conclusion that UO_2 dissolution is insensitive to pH within this range.

The X-ray photoelectron spectroscopy (XPS) results presented by Casas et al. [18] and Torrero et al. [22] suggested the surface film had a U/O ratio similar to $UO_{2.25}$ (e.g., U_4O_9). Previous experiments [12,27–30], in the absence of bicarbonate, illustrated that this surface film formed numerous intermediate uranium phases over time resulting in a final composition of $UO_3 \cdot xH_2O$(cr). The apparent mechanism for the formation of this oxidized surface film is slow detachment of the oxidized metal species from the surface of the UO_2 crystal lattice. In the presence of a total dissolved carbonate concentration of 10^{-3} M or greater, strong aqueous uranyl carbonate complexes prevent the formation of this surface layer, allowing an investigator to evaluate the reactivity of the pure UO_2 surface within the near neutral to alkaline pH range. The inhibitive effect of high carbonate concentrations on formation of the oxidized surface film was proven by the XPS results of Pablo et al. [23].

Pablo et al. [23] investigated the effects of $[CO_3^{2-}]_T$ on the reactivity of UO_2(cr) at a pH of 8.0 as a function of temperature (from 10 to 60 °C) and $[CO_3^{2-}]_T$ (from 10^{-4} to $10^{-1.5}$ M). In this investigation, Pablo et al. [23] confirmed by XPS that a surface film was not detected. They attribute the lack of the surface film to the complexation of surface oxidized uranium with dissolved carbonate and subsequent transport of the $U^{VI} - HCO_3^-$ complex into solution. They propose several step-wise mechanisms for this process that begin with UO_2 surface oxidation, then uranium surface coordination and complexation with the bicarbonate ion, and finally detachment of the uranyl–carbonate complex into solution. Although the results obtained by Pablo et al. [23] provide critical information on the mechanisms of UO_2 dissolution, other factors that affect uranium dissolution, such as the effect of the solution saturation state and pH, were not addressed and thus merit investigation.

The purpose of this study was to determine the dissolution kinetics of UO_2(cr) in the presence of atmospheric oxygen as a function of temperature, solution saturation state, and pH. Accordingly, the principal objective was to determine the dissolution rates over a large flow-rate-to-surface-area interval to examine the effects of solution saturation state. Examining the dissolution process of UO_2(cr) as a function of these variables provides information on the rates near and far from saturation with respect to potential secondary phases. These and other factors will affect the release of uranium from natural and repository environments; as well as subsurface REDOX permeable reactive barriers, once oxidizing conditions prevail.

2. Experimental details

2.1. Sample preparation

Commercially available crystalline uranium(IV) dioxide (UO_2) was obtained from Alfa Aeasar® as a powdered specimen containing an average particle diameter of 213 μm. The UO_2 sample was calcined at approximately 900 °C using a Lindberg™ furnace in a reducing atmosphere of 92% argon and 8% hydrogen to remove any surface oxidation. Once calcined, the UO_2 sample