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Dissolution Kinetics of UO_2. Flow-through Tests on $UO_{2.00}$ Pellets and Polycrystalline Schoepite Samples in Oxygenated, Carbonate/Bicarbonate Buffer Solutions at 25° C

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The modelling of radionuclide release from waste forms is an important part of the performance assessment of a potential, high-level radioactive waste repository. Since spent fuel consists of UO_2 containing actinide elements and other fission products, it is necessary to determine the principal parameters affecting UO_2 dissolution and quantify their effects on the dissolution rate before any prediction of long term release rates of radionuclides from the spent fuel can be made.

As part of a complex matrix to determine the dissolution kinetics of UO_2 as a function of time, pH, carbonate/bicarbonate concentration and oxygen activity, we have measured the dissolution rates at 25° C of: a) UO_2 pellets; b) $UO_{2.00}$ powder and c) synthetic dehydrated schoepite, $UO_3.H_2O$ using a single-pass flow through system in an argon-atmosphere glove box. Carbonate, carbonate/bicarbonate, and bicarbonate buffers with concentrations ranging from 0.0002 M to 0.02 M and pH values from 8 to 11 have been used. Argon gas mixtures containing oxygen (from 0.002 to 0.2 atm) and carbon dioxide (from 0 to 0.011 atm) were bubbled through the buffers to stabilize their pH values.

Introduction

Many researchers have investigated the dissolution of UO_2, spent fuel and uraninite in aqueous solutions, under either reducing or oxidizing conditions, and as a function of pH, oxygen fugacity, solution chemical compositions, and temperature. The dissolution data of the previous studies are very scattered and vary as much as 6 orders of magnitude (Grambow, 1989). The results are equivocal not only due to the difference in experimental design, or the diverse history of fuel samples but also because of uncertainties regarding redox chemistry of U in solutions and in solid phases, surface area measurements, and the possibility of secondary phase formation. In addition, the previous studies were conducted under experimental conditions which were either unconstrained or which simulated complex repository conditions, making the results of such studies difficult to interpret.

Benefitting from previous studies, we conducted a study to elucidate the dissolution kinetics of UO_2 using the single-pass flow through method, which has been successfully used in the study of dissolution kinetics of glass other minerals (Knauss et al., [1989], [1990]) and of UO_2 (Wilson and Gray, [1990]). The advantage of this technique is that flow rates can be adjusted so that the UO_2 dissolves under conditions that are far from saturation with respect to alteration phases. Under such conditions, the steady-state dissolution concentrations are directly proportional to the effective surface area of the sample (Aagaard [1982], Helgeson et al. [1984], Lasaga [1981]). To elucidate the particle size effect on the dissolution rates, both UO_2 pellets and UO_2 powder were used. Previous studies indicated that UO_2 is easily oxidized to U_4O_9 and U_3O_7 in air (Aronson [1961], Einziger [1988]), and can be further oxidized to either U_3O_8 or schoepite, $UO_3.2H_2O$ (Wadsten, [1977]), which are all more soluble than UO_2. The dissolution rate of the synthetic dehydrated schoepite obtained from this study can be considered as the upper limit for the dissolution rate for UO_2 in carbonate/bicarbonate buffer solution.

Experimental

Materials

UO_2 pellets were supplied by Westinghouse Hanford Co., (Richland, Washington). X-ray diffraction of the pellet indicated that UO_2 is the major phase. Emission spectroscopic analysis revealed the presence of Ca, Si, Al, Fe, B, Cr, Ni in the sample. Electron microprobe analysis of the sample showed equigranular texture with a mosaic of polygonal grains approximately 10 microns in diameter. It also indicated that the sample matrix is exclusively UO_2; with several minor phases such as MgO, Al_2O_3, SiO_2 and NiO located within and among the UO_2 grains. From the dimensions of the pellets (typically 0.87 cm diameter and 0.88 cm, length) the geometric surface area of the pellets were calculated. In order to obtain reliable dissolution rates of UO_2 instead of UO_{2+x}, the original UO_2 pellets were reduced to $UO_{2.00}$ in a hydrogen atmosphere at 1200° C for 15 minutes. After treatment, the pellets were kept in a vacuum desiccator before using. Thermo-gravimetric analysis of the hydrogen-reduced UO_2 pellets showed an O/U ratio of 1.993. The mercury porosity and BET surface area measurements of the hydrogen-reduced pellets were 1.15% porosity and $10 cm^2/g$, respectively.

The $UO_{2.000}$ powder was prepared at Battelle Pacific Northwest Laboratory (PNL, Richland, Washington). Several UO_2 pellets were crushed and ground with mortar and pestle, then sieved through the -140/+325 mesh screens. Only the -140/+325 mesh fraction consisting of particle sizes range from 44 um to 105 um was selected for use in this study. This 140/+325 mesh fraction was washed three times with 2×10^{-4} M Na_2CO_3 and rinsed with deionized water before being air-dried at room temperature. The air-dried particles were heated in a dry He atmosphere for 2 h at 204° C, then were re-heated at 900° C overnight in a flowing stream of 6%H/94%Ar gas that had passed through a water bath at 0° C. The weight loss of the particles during this heat treatment was monitored to ensure the heat-treated powder had an O/U ratio of 2.000. The BET surface area of the reduced $UO_{2.000}$ powder was 254 cm^2/g.

The synthetic dehydrated schoepite, $UO_3.H_2O$, was prepared by hydrolysis of uranyl acetate and distillation of acetic acid from the solution (Gayer and Leider, [1955]). The precipitate in the distillation flask was washed several times with water and the reaction was carried out to completion. The XRD pattern of the solid residue was identified as that of dehydrated schoepite. The BET surface area of the synthetic dehydrated schoepite was 1971 cm^2/g.

Test matrix

The dissolution tests reported in this study were arbitrarily selected from a complex test matrix which had been designed by using R/S Discover Software (Bolt, Beranek and Newman, version 2, 1989) to study the influence of pH, temperature, oxygen and carbonate/bicarbonate activity on the kinetics of the dissolution rate of UO_2 as a function of time. This is the first of a series of dissolution tests. These tests were conducted at 25° C and in basic solutions (pH 8-11).

Leachants

Nine leaching solutions consisting of mixtures of carbonate and bicarbonate buffers at different concentrations were used for dissolution tests on $UO_{2.00}$ pellets (samples 1A-9A) (table 1). The dissolution tests on $UO_{2.000}$ powder were conducted in buffers # 1 and 6 (samples 1B and 6B). The dissolution tests on synthetic dehydrated schoepite were performed in the buffers # 2 and 7 (samples 2B and 7B). To maintain a constant pH for these buffers, argon gas mixtures containing appropriate oxygen and carbon dioxide concentrations were bubbled through the solutions during the entire investigation. The gases were vented outside of the glove box after passing through the solutions.

Table 1. Buffer Chemical Compositions, Argon Gas Mixture Compositions and Solution pH Values for UO_2 and Dehydrated Schoepite Dissolution Experiments

Buffer #	Chemical Composition (moles/kg H_2O)		Partial Pressure (atm)		pH
	Na_2CO_3	$NaHCO_3$	O_2	CO_2	
1		0.02	0.2	0.011	8.16
2		0.02	0.002	0.011	8.06
3		0.0002	0.02	0.00012	8.04
4	0.001541	0.01846	0.2	0.00104	9.08
5	0.0001541	0.001846	0.002	0.00012	9.36
6	0.0002		0.2	0	9.70
7	0.0002		0.002	0	9.82
8	0.02		0.02	0	11.06
9	0.002		0.2	0	10.50

Experimental equipment

The flow-through system was located inside an argon atmosphere glove box (Innovative Technology, Inc.) as shown in Figure 1. A constant temperature in the flow-through sample cell was maintained by an electrical oven. The flow-through cell was made of polymethylpentene (PMP). The sample chamber was located between two sets of filter grids, which were also made of PMP. Teflon filters (0.1 micron pore size, Nuclepore Corp.) were installed at both ends of the sample chamber to retain the particulates and Viton O-rings were used to seal the cell (Figure 2). The oxygen concentration of the glove box was kept below 10 ppm and was constantly monitored by an oxygen analyzer (Innovative Technology, Inc.).

Methods

Different flow rates were used (~100 g solution/day for the $UO_{2.00}$ pellets and ~200 g solution/day for the $UO_{2.000}$ powder and synthetic dehydrated schoepite) so that the solutions in contact with the samples remained undersaturated at all times. Leachates were collected at selected intervals during each run and their U concentrations and pH values were determined to monitor the dissolution rates. The U concentrations were measured using a laser phosphorescence analyzer (KPA-11, Chemchek Instruments, Inc., Richland, Washington). After steady state conditions had been observed, the flow rates were doubled and the leachates were again monitored until the steady states were re-established.

Results

Calculation of Dissolution Rates

Dissolution rates were calculated as:

$$R(\text{mole. } m^{-2}. \text{ sec}^{-1}) = [U](\text{mole. } mL^{-1}) \,.\, \phi(mL. \text{ sec-1}) / A(m^{2})$$

where [U] is the concentration of uranium in the leachate, ϕ is the flow rate of the leachate and A is the surface area of the sample. Thus dissolution rate corresponds to the number of moles of uranium dissolved per unit surface area per unit time.

Aqueous Phase

We reported the dissolution rates of $UO_{2.00}$ pellets in the aforementioned 9 buffers at 25° C (Table 2). Since the dissolution tests are on-going and less than half of the test matrix has been completed, detailed data interpretation and dissolution modelling are not yet possible at this point. For comparison purposes, the dissolution rates of $UO_{2.000}$ powder in buffers # 1 and 6 and of synthetic dehydrated schoepite in buffers # 2 and 7 are also shown in Table 2.

Table 2. Dissolution rates of $UO_{2.00}$ Pellets, $UO_{2.000}$ Powder and Synthetic Dehydrated Schoepite in Carbonate/ Bicarbonate Buffers at 25° C.

Sample I.D	Buffer #	Dissolution Rate(mol/m2.sec)
$UO_{2.00}$ Pellets		
	1	3.88×10^{-11} (a)
	2	9.11×10^{-11} (a)
	3	4.32×10^{-11} (a)
	4	1.36×10^{-10} (a)
	5	5.84×10^{-11} (a)
	6	1.15×10^{-11} (a)
	7	4.98×10^{-11} (a)
	8	1.97×10^{-10} (a)
	9	7.61×10^{-11} (a)
$UO_{2.000}$ Powder		
	1	4.18×10^{-12} (b)
	6	8.38×10^{-12} (b)
Synthetic Dehydrated Schoepite		
	2	5.85×10^{-9} (b)
	7	9.25×10^{-11} (b)

(a) Dissolution rate was calculated using the geometric surface area of the sample.
(b) Dissolution rate was calculated using the BET surface area of the sample.

As expected, synthetic dehydrated schoepite dissolved very fast and it reached steady-state conditions almost instantaneously. The dissolution rates for the synthetic dehydrated schoepite in buffers # 2 and 7 were calculated after adjusting for sample weight loss and the resulting sample surface area reduction.

It was observed that the BET technique overestimates the surface area of the $UO_{2.00}$ pellets. Based on that observation, the geometric surface area was used to calculate the dissolution rate for $UO_{2.00}$ pellets while the BET surface ares were used in the calculation of the dissolution rates for $UO_{2.000}$ powder and synthetic dehydrated schoepite samples.

A preliminary interpretation of the data in Table 2 indicates that the dissolution rate of UO_2 is somewhat independent of oxygen fugacity, is certainly correlated to the carbonate or bicarbonate concentration in the leaching solution. The dissolution rates of $UO_{2.00}$ pellets and $UO_{2.000}$ powder in Table 2 are lower than the dissolution rates measured for spent fuel under the identical experimental conditions (Gray and Wilson,[1991]). Surface analysis of the leached samples is being conducted. Additional results and detailed interpretation will be presented in a future publication.

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