The Effect of Fuel Chemistry on UO₂ Dissolution

Amanda Casella^a, Brady Hanson^b, William Miller^c

Work was performed at: Pacific Northwest National Laboratory

^a*corresponding author, Pacific Northwest National Laboratory, PO Box 999, MSIN P7-25, Richland WA 99352, USA, phone: (509)375-5622, amanda.casella@pnnl.gov*

^b*Pacific Northwest National Laboratory, PO Box 999, MSIN P7-27, Richland WA, 99352, USA phone: (509) 375-5051, brady.hanson@pnnl.gov*

^c*University of Missouri Research Reactor, 1513 Research Park Drive, Columbia, Missouri 65211, USA*

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ABSTRACT

The dissolution rate of both unirradiated UO₂ and used nuclear fuel has been studied by numerous countries as part of the performance assessment of proposed geologic repositories. In the scenario of waste package failure and groundwater contact with the fuel, the effects of variables such as temperature, dissolved oxygen, and water and fuel chemistry on the dissolution rates of the fuel are necessary to provide a quantitative estimate of the potential release over geologic time frames. The primary objective of this research was to determine the influence these parameters, with primary focus on the fuel chemistry, have on the dissolution rate of unirradiated UO₂ under oxidizing repository conditions and compare them to the rates predicted by current dissolution models.

Both unirradiated UO₂ and UO₂ doped with varying concentrations of Gd₂O₃, to simulate used fuel composition after long time periods when radiolysis has minor contributions to dissolution, were examined. In general, a rise in temperature increased the dissolution rate of UO₂ and had a larger effect on pure UO₂ than on those doped with Gd₂O₃. Oxygen dependence was observed in the UO₂ samples with no dopant and increased as the temperature rose; in the doped fuels less dependence was observed. The addition of gadolinia into the UO₂ matrix resulted in a significant decrease in the dissolution rate. The matrix stabilization effect resulting from the dopant proved even more beneficial in lowering the dissolution rate at higher temperatures and dissolved O₂ concentrations in the leachate where the rates would typically be elevated.

1. Introduction

Long-term geologic disposal is one of the current pathways for used nuclear fuel disposal. In the event of waste package failure, groundwater infiltration provides a mechanism by which radionuclides may be released from the waste form and enter into the surrounding environment. Because of the heterogeneous nature of used fuel, its dissolution has typically been divided into components that originate from three regions: 1) the fuel-cladding gap, crack surfaces, and open porosity; 2) the grain boundaries; and 3) the UO_2 matrix. The dissolution and release of radionuclides from these three regions of the fuel takes place at progressively decreasing rates. The initial dissolution of radionuclides from used fuel is dominated by radionuclides in the gap, which are typically assumed to be dissolved immediately upon contact by water following breach of the waste container and fuel cladding. This is followed by a period in which preferential leaching of radionuclides from the grain boundaries may dominate the dissolution from used fuel. Ultimately, the long-term dissolution rate of radionuclides is expected to be determined by the rate of the dissolution of the UO_2 matrix, which is being examined in this work [1,2,3].

Dissolution rates are also influenced by environmental factors such as temperature and composition of the leachate and fuel. The thermal output of the assemblies due to the decay heat, placement of the waste packages, initial heat load of the waste packages, the ability of the repository to disperse heat, and ventilation during the lifespan of the repository are a few of the factors affecting leachate temperature. In some studies performed, the repository can be maintained below boiling conditions by active ventilation for the first 50 years and then natural ventilation for the rest of its lifespan. In these scenarios, the temperature from the outside of the waste package through the drift wall varies from approximately 90°C at five years to slightly above ambient temperature at 10,000 years. [4]

The composition of the atmosphere and the temperature of the groundwater inside the repository are major controlling factors to the quantity of dissolved oxygen present in leachate that may interact with the failed waste package. Numerous studies have been performed [1,2,5,6,7,8,9,10] and have shown a clear dependence of the UO_2 oxidation and subsequent dissolution rates on dissolved O_2 concentration, although conclusions and trends between the various efforts are not consistent and in some cases large variation was observed within the individual data sets. Additionally, radiolysis alters the chemistry of water interacting with the fuel potentially turning reducing environments into oxidizing ones. [5,11,12] Effects such as reactive surface area relative to fuel size, must be evaluated for both accurate correlation of normalized dissolution rates and radiative attenuation by the fuel, which can reduce radiolysis effects after long time periods where the predominate dose is from alpha radiation. [13]

The primary dissolution mechanism of UO_2 and used fuel under oxidizing conditions is oxidative dissolution. Thus, factors that inhibit or delay oxidation of the matrix uranium from a 4+ valance to the more soluble 6+ valance state would be expected to have similar effects on the dissolution rate, depending on which step is rate limiting. Hanson [14] has shown that the fission products and actinides soluble in the UO_2 matrix of used fuel indeed delay solid state oxidation of used

fuel with an increasing resistance to oxidation to form U_3O_8 with increasing burnup. This same effect of oxidation resistance has been observed in UO_2 doped with Gd_2O_3 [15,16].

The basis of this effect is that on a molecular scale, the dopant, representative of many fission products and actinides, is soluble in the UO_2 matrix. In order to maintain charge neutrality and assuming that oxygen vacancies are not created, matrix U ions must oxidize from 4+ to either 5+ or 6+ to compensate for lower valence cation substitutions. Lower valence ions, such as the 3+ Gd, have been shown by Park and Olander [17] to have an effective negative charge compared to the 4+ uranium and repel neighboring interstitial oxygen ions, effectively eliminating these sites from occupation by oxygen and limiting the ability of the matrix to oxidize further. Uranium dioxide forms a cubic fluorite lattice. In this structure each U atom has 12 nearest U neighbors, but when one dopant atom is present in a UO_2 unit cell the 8 surrounding unit cells may be influenced due to a semi-conductor electron transfer effect [18]. Theoretically, for a homogeneous mixture of 15wt% Gd_2O_3 in UO_2 , every UO_2 unit cell will contain one Gd atom. If each Gd atom has the ability to affect all of its nearest neighbors, then, assuming a homogenous distribution, at 3 wt% Gd_2O_3 , every UO_2 unit cell will experience this net negative charge and oxidation resistance.

Grandstaff [19] presented data showing that with increasing concentration of ThO_2 , the dissolution rate of natural uraninites decreased significantly. The dissolution rate decreased by up to two orders of magnitude between samples with negligible ThO_2 present compared to samples with up to 4% ThO_2 . The Th exists only in the 4+ state and is incapable of oxidizing to higher states, thus effectively blocking neighboring oxygen interstitial sites as well. Demkowicz et al. [20] showed similar effects of a decrease in matrix dissolution with the addition of Th. SIMFUEL, containing a variety of dopants to simulate the fission products in used fuel, was shown in a review by Oversby [2], to exhibit a dissolution rate 15 times slower than that of UO_2 when tested under similar conditions.

Tocino et al. [21] also looked at the effect of Th dopants along with other trivalent elements in the fluorite structure under varying acidic conditions. Results demonstrated that under high acid concentrations ($> 2\text{ M HNO}_3$) dissolution was controlled primarily by the oxidation of U(IV) to U(VI), and when tests were performed at lower acid concentrations ($< 0.5\text{M HNO}_3$) oxygen vacancies were the predominate effect. The oxygen vacancies resulting from Th incorporation showed similar trends to Grandstaff [19] although those with Ce were one to two orders of magnitude higher. This deviation is thought to be attributed to U(V) and Ce(III) in the sample. Talip et al. [22] utilized Raman spectroscopy to identify oxygen vacancies in uranium-lanthanum-mixed oxides. These measurements coupled with X-ray diffraction showed a reduction in the formation of M_3O_8 when the La content was increased.

In addition to the semi-conductor electron transfer effect, this dopant effect may also increase as a result from the changing surface chemistry [1,19]. When the U is oxidized and dissolved, any less soluble dopants, fission products, or actinides remain behind. Thus, the surface composition is altered and results in fewer effective sites available for U oxidation and dissolution.

When complexing agents such as carbonate are present the dissolution rate for UO_2 significantly increases. Shoosmith [1] studied the effect of various carbonate concentrations on UO_2

dissolution and concluded that when there is no carbonate in solution, surface complexes such as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ will form and inhibit dissolution. When carbonate is present at concentrations lower than 10^{-3} M, it will increase UO_2^{2+} solubility and prevent surface complexation. As the concentration is increased to the range of 10^{-3} M to 10^{-1} M, the carbonate becomes kinetically involved in the dissolution process. When the carbonate concentration is greater than 10^{-1} M, phases such as UO_2CO_3 begin to form on the surface of the UO_2 and hinder dissolution.

In a report by Gimenez et. al. [23] lower concentrations of carbonate were studied. The experiment was designed to examine bicarbonate concentrations in the range of 10^{-4} to 10^{-2} M. Part of the overall objective of the report was to achieve a better understanding of the rate of oxidation compared to that of dissolution, since previous work had suggested that the dissolution step in bicarbonate media is very fast and oxidation is the limiting step. At 10^{-4} M bicarbonate, the oxidation rate is faster than the dissolution rate by approximately 1.5 orders of magnitude. It is not until around a concentration of 10^{-2} M bicarbonate that the rates began to converge. An overall trend is seen in the range as bicarbonate at low concentrations is increased as the dissolution rate increases. These trends also confirm Shoesmith's [1] conclusions that at low concentrations, the carbonate mostly influences the oxidation, but as the concentration is increased it also contributes to the dissolution of the UO_2 .

Dissolution tests have been performed using various methods such as semi-static batch [24,25], flow-through [25,26,27,28], and drip [29] tests. Single-pass flow-through tests were used in this work as they have the advantage that the sample size and feedwater flow rate can be controlled, allowing the UO_2 to dissolve under conditions far from solution saturation, thus preventing precipitation of corrosion products and formation of alteration phases [30]. This technique allows the kinetic response of the dissolution to be measured for a number of variables including (specific to this work) dissolved O_2 in the leaching solution, temperature, surface area of the sample, and fuel composition. This approach with flow-through tests was used to develop the model in the commercial spent nuclear fuel (CSNF) Waste Form Degradation: Summary Abstraction [31]. The purpose of this work was to generate additional data for modeling the long-term dissolution behavior of used nuclear fuel for use in developing and validating waste form degradation rates and radionuclide release models. The primary focus was the effect of fuel chemistry, simulated using various concentrations of Gd_2O_3 , on dissolution rates as a function of temperature and dissolved oxygen concentration. It is believed that dissolution rates obtained with a matrix more resistant to oxidation will be more representative of used fuel dissolution rates at long times when the increased dissolution rate resulting from radiolytic production of highly oxidizing species [13,32,33] will significantly decrease with the decay of most beta and gamma producing isotopes.

2. Materials and Methods

Sodium bicarbonate, ACS reagent grade, and Optima nitric acid were used to make the solutions. Solution sparge gases of 10.3% O_2 , 2000 ppm CO_2 with a balance of N_2 and 20.9% O_2 , 2000 ppm CO_2 with a balance of N_2 were purchased from a commercial vendor. All fuel samples were obtained from unirradiated UO_2 pellets with 0 to 4 wt% Gd_2O_3 dopant procured from a commercial fuel vendor. The range of dopant was chosen based upon the estimated used fuel composition after 1000 years [34] and although the wt% Gd is estimated to be only 0.04, the

total rare earth element wt% is 1.26. The higher concentrations simulate the contribution of other soluble fission products and actinides in the used fuel matrix. During preparation of the fuel samples, the as-obtained pellets were crushed and the large fragments removed. The remainder of the pellet was ground to a powder using a mortar and pestle, and then placed in a shaker/tapper sieve system for 48 hours. After sieving, the powder between the 25 μm and 10 μm sieves was collected, coinciding with the vendor-provided and scanning electron microscope (SEM) verified, nominal grain size of 15 μm . Sieving also minimized fines in the powder as the fuel was not washed prior to testing in order to prevent oxidation of the surface.

Dissolved O_2 concentrations were continuously monitoring by in-line Ocean Optics, Inc. FOXY-OR125 Fiber Optic Oxygen Sensors, which were coupled to an Ocean Optics Spectrofluorometer Model USB2000-FL. The sensors were calibrated by using solutions in sample cells maintained at the temperature of the leachate solution to be monitored. Dissolved O_2 in the leachate was varied by altering bath temperature and sparge gas compositions, concentrations were continuously monitored by the in-line sensors. Solution pH was measured continuously in each of the bath set-ups by in-line Quantum Model Q25P pH probes. The probes were calibrated with pH buffers purchased from Environmental Resource Associates. Both the O_2 and pH probes were calibrated prior to start of the experiments and recalibrated on a weekly basis throughout the test.

2.1. Single-Pass Flow-Through Equipment

Three identical setups were used in the single-pass flow-through (SPFT) testing. Each setup consisted of a leachate preparation system with stainless steel lines connecting to eight columns inside an oven. The leachate preparation system consisted of a water bath to maintain temperature of the feed solutions, a feed tank, and a pre-equilibration tank. The pre-equilibration tank allowed for the desired temperature and dissolved O_2 levels to be achieved prior to transferring solution to the feed tank to minimize shocks to the system. The feed tank was continuously stirred through the use of a recirculation line that fed the pumps and was monitored for pH and O_2 . A schematic of the leachate preparation system is shown in Figure 1.

Figure 1. Schematic of leachate preparation system consisting of a feed tank, a pre-equilibration tank, and an outer water bath to maintain temperature. A recirculation line originated in the feed tank and fed the pumps which led to the fuel samples. The remaining solution circulated back to the feed tank and was continuously monitored for pH and O_2 . This schematic is representative of the three identical bath systems that feed each of the three ovens.

Eight solution lines ran from each leachate preparation system and went into an oven (three ovens total, a separate one for each system), displayed in Figure 2. Sixteenth-inch diameter stainless steel tubing connected each pump to a column inside an oven and also extended from the column to a sample collection vial positioned on top of the oven, as shown in Figure 2. Tubing was stainless steel to prevent gas diffusion from influencing the dissolved O_2 concentration and/or pH. Verification was performed prior to testing to ensure levels remained constant. The lines between the feed tank and ovens were not heated; therefore sufficient length was coiled in the oven under the columns to achieve the desired temperature prior to interaction with the fuel.

Figure 2. One of three identical SPFT test ovens containing eight columns housing fuel samples. Leachate solutions were pumped through columns (enlarged on right) and collected in vials on top of the oven.

The columns inside the oven containing the fuel had a 6.35-mm inner diameter and were 50.8 mm long. The columns were made of stainless steel and capped at both ends by stainless steel frits with 0.5 μm openings to ensure only dissolved radionuclides or colloids exited the column. The leachate solution entered through the bottom of the column and flowed upwards to prevent a headspace of air in the column and obtain more homogeneous contact with the fuel. After the solution passed through the column containing the fuel, it was transported out of the top of the oven to a three-way valve for collection of the leachate (top of the oven in Figure 2), diversion to a waste stream, or for the line to be closed. During collection of the leachate the flow rate was measured by dividing the mass of the collected effluent by collection time.

2.2. Test Matrix

Three identical bath/oven systems were used in each test, permitting concurrent runs at bath/oven temperatures of 25°C, 50°C, and 75°C. Eight columns containing fuel were inside each oven, allowing for 24 samples per test. Each of the three ovens contained five columns with UO_2 powder (0, 1.25, 2, 3, and 4 wt% Gd_2O_3 dopant) and three columns with UO_2 fragments (0, 2, and 3 wt% Gd_2O_3 dopant). The dissolution solution for all tests was 2×10^{-3} M sodium bicarbonate in deionized water with a pH between 7 and 8.5, flowing at 0.20 ml/min. The spread in pH was due to measured variations and not an evolution over time. The sodium bicarbonate concentration was chosen for similarity to J-13 well water [35]. Four tests were performed by varying O_2 concentrations: 3.0, 4.2, 5.9, and 8.7 ppm in the feed solutions, where 8.7 ppm is the equilibrium concentration for an aqueous solution in contact with air. Dissolved O_2 in the leachate was varied by altering bath temperature and sparge gas compositions. The fuels used in the tests are listed in Table 1. Tests were performed sequentially, with the fuels remaining in the

columns throughout the entirety of all four tests. To prevent formation of alteration phases in stagnant conditions, there were no breaks between tests, only changes to the feed solution to alter the dissolved O₂ content.

Table 1. Location and properties of fuels used in SPFT testing

	Placement	Geometry	Gd ₂ O ₃ wt%	Fuel (mg)	Surface Area (m ² /g)
Oven A, 25°C	A1	powder	0	199	1.47E-01
	A2	powder	1.25	205	1.54E-01
	A3	powder	2	201	2.03E-01
	A4	powder	3	205	1.60E-01
	A5	powder	4	198	1.44E-01
	A6	2 fragments	0	1009	2.93E-03
	A7	4 fragments	2	997	3.07E-03
	A8	5 fragments	3	891	5.35E-03
Oven B, 50°C	B1	powder	0	207	1.47E-01
	B2	powder	1.25	198	1.54E-01
	B3	powder	2	198	2.03E-01
	B4	powder	3	208	1.60E-01
	B5	powder	4	205	1.44E-01
	B6	2 fragments	0	1022	2.01E-03
	B7	4 fragments	2	940	3.06E-03
	B8	4 fragments	3	878	4.39E-03
Oven A, 75°C	C1	powder	0	230	1.47E-01
	C2	powder	1.25	206	1.54E-01
	C3	powder	2	210	2.03E-01
	C4	powder	3	207	1.60E-01
	C5	powder	4	203	1.44E-01
	C6	2 fragments	0	1022	3.23E-03
	C7	4 fragments	2	970	3.63E-03
	C8	5 fragments	3	895	6.10E-03

2.3. Analysis

2.3.1. BET

Surface area measurements of the powder samples, listed in Table 1, were obtained using the Brunauer, Emmett, Teller (BET) method with a Quantachrome Monosorb Model MS-21 single-point gas sorption analyzer. The BET was calibrated with 1cc of air and verified using National Institute of Standards and Technology (NIST) standard reference materials SRM 1899 and SRM 1900. Samples were off-gassed in greater than 99.9999% pure N₂ at 200 °C for at least 30

minutes. Due to the low surface area of the fuel fragments, their dimensions were measured with calibrated calipers to calculate a geometric surface area which was then multiplied by a surface roughness factor of 15 [3,36] to obtain an effective surface area accounting for grain boundaries, pores, and surface irregularities. Specific surface area is a key measurement in dissolution studies, and although this method for fragment surface area creates large uncertainties it is consistent with previous published dissolution studies providing viable comparisons.

2.3.2. SEM

Scanning electron microscopy was performed using a radiation-shielded Amray Model 1610T with energy dispersive X-ray spectroscopy (EDS) capability. Analysis by SEM/EDS was performed on the powder samples both prior to and after testing, along with calibration verification using the NIST-traceable standard MRS-4 by Geller Microanalytical Laboratory.

2.3.3. Kinetic Phosphorescence Analysis

Uranium concentrations in the leachate solutions were measured by kinetic phosphorescence analysis (KPA) using a Chem-Chek Instruments model KPA-11R uranium analyzer. The KPA was calibrated daily using a set of uranium standards (obtained from Spex and Ultra Scientific) ranging from 10^{-4} $\mu\text{g/mL}$ to 1.0 $\mu\text{g/mL}$ and verification using the second independent set of standards was performed prior to analysis, after every 10 samples, and after analysis completion. Approximately 15 mL of leachate per sample were collected from each of the 24 streams for KPA analysis. A volume of 0.25 mL of concentrated nitric acid was pipetted into all leachate collection vials prior to sampling to ensure that the uranium remained in solution rather than being deposited on vial walls. Also the addition of nitric acid acidified the carbonate solutions for more accurate KPA measurements. Samples were prepared and analyzed within a week of collection, with the majority of samples analyzed the day they were collected.

2.3.4. Dissolution Rate Calculation

The U concentration determined by KPA was used to calculate the normalized dissolution rate (NDR):

$$\text{NDR} = \frac{(\text{Flow Rate}) \times (\text{U Concentration in Leachate})}{(\text{Sample Weight}) \times \left(\frac{\text{grams U}}{\text{grams UO}_2 + \text{Gd}} \right) \times (\text{Specific SA})} \quad (1)$$

where SA is the surface area and (grams U)/(grams $\text{UO}_2 + \text{Gd}$) is the specific fraction of U per sample, which takes into account any Gd and O weight. The dissolution rates presented were taken after steady state was established in order to eliminate effects such as initial oxidation and release of fines. The cumulative fraction (CF) of U released was calculated by:

$$\text{CF}_x = (\text{U Frac}) \times (\text{Day}_x - \text{Day}_{x-1}) + \text{CF}_{x-1} \quad (2)$$

$$\text{U Frac} = \frac{(\text{Flow Rate}) \times (\text{U Concentration in Leachate})}{(\text{Sample Weight}) \times \left(\frac{\text{grams U}}{\text{grams UO}_2 + \text{Gd}} \right)} \quad (3)$$

where U Frac is the fractional release of U over a given time period (usually a day), Day_x is the day number of the specific run, Day_{x-1} is the day prior to Day_x .

The uncertainty associated with the NDR is based upon both associated error of the KPA and BET measurements, which for each sample collected this equated to an uncertainty of 10.8%. Averages were taken of samples collected over the steady state time range with the error propagated via the methods outlined by Meyer [37].

3. Results

3.1. SPFT Analysis

Testing simulated conditions where water breached all outer protection of used fuel (such as drip shields, waste packages and cladding) and the flow rate was sufficiently high to maintain a forward rate of reaction and prevent any secondary phase formation, which would reduce the dissolution rate. Surface examination by SEM of the powders and fragments verified the absence of any alteration phases post-testing. Figure 3 shows the 0 wt% Gd_2O_3 UO_2 powder both before and after testing, and is representative of all the powder fuels.

Figure 3. Grains of 0 wt% Gd_2O_3 UO_2 powder a) after sieving prior to testing and b) after completion of testing

The normalized dissolution rate was plotted as a function of time as shown in Figure 4, where sample C1 (0 wt% Gd_2O_3 at 75°C) is shown to represent how each data set was analyzed. As the UO_2 was not washed prior to testing, an initial drop occurred over the first few days most likely due to fines present from not washing the fuels and/or by removal of an initial pre-oxidized

layer. Once steady state was observed for each of the test conditions, the data was averaged, shown by the shaded regions in Figure 4, for the normalized dissolution rates presented in Table 2 and Table 3.

Figure 4. Normalized dissolution rate and cumulative fraction of uranium released from sample C1 (0 wt% Gd_2O_3 at 75°C) as a function of test time and conditions, shaded regions represent region averaged for steady state dissolution rates

Table 2. Normalized dissolution rates of unirradiated UO_2 powders in $2 \times 10^{-3} \text{ M NaHCO}_3$

Dissolved $\text{O}_2 \rightarrow$	Normalized Dissolution Rate ($\text{mg m}^{-2} \text{ d}^{-1}$)			
	3.0 ppm O_2	4.2 ppm O_2	5.9 ppm O_2	8.7 ppm O_2
A1	$4.17\text{E-}01 \pm 1.93\text{E-}02$	$7.07\text{E-}01 \pm 2.69\text{E-}02$	$7.64\text{E-}01 \pm 4.09\text{E-}02$	$6.98\text{E-}01 \pm 3.38\text{E-}02$
A2	$3.04\text{E-}01 \pm 1.41\text{E-}02$	$2.98\text{E-}01 \pm 1.13\text{E-}02$	$3.62\text{E-}01 \pm 1.93\text{E-}02$	$3.48\text{E-}01 \pm 1.15\text{E-}02$
A3	$1.64\text{E-}01 \pm 8.15\text{E-}03$	$1.58\text{E-}01 \pm 5.78\text{E-}03$	$1.87\text{E-}01 \pm 9.99\text{E-}03$	$1.90\text{E-}01 \pm 6.27\text{E-}03$
A4	$2.50\text{E-}01 \pm 1.16\text{E-}02$	$2.44\text{E-}01 \pm 8.94\text{E-}03$	$1.81\text{E-}01 \pm 9.64\text{E-}03$	$2.09\text{E-}01 \pm 7.32\text{E-}03$
A5	$9.05\text{E-}02 \pm 4.23\text{E-}03$	$7.56\text{E-}02 \pm 2.75\text{E-}03$	$8.34\text{E-}02 \pm 4.89\text{E-}03$	$8.71\text{E-}02 \pm 2.87\text{E-}03$
B1	$3.88\text{E+}00 \pm 1.78\text{E-}01$	$4.28\text{E+}00 \pm 1.56\text{E-}01$	$6.04\text{E+}00 \pm 3.21\text{E-}01$	$5.67\text{E+}00 \pm 2.04\text{E-}01$
B2	$5.91\text{E-}01 \pm 2.74\text{E-}02$	$3.57\text{E-}01 \pm 1.33\text{E-}02$	$5.87\text{E-}01 \pm 3.14\text{E-}02$	$6.36\text{E-}01 \pm 1.92\text{E-}02$
B3	$3.27\text{E-}01 \pm 1.51\text{E-}02$	$1.97\text{E-}01 \pm 7.33\text{E-}03$	$3.38\text{E-}01 \pm 1.81\text{E-}02$	$3.74\text{E-}01 \pm 1.13\text{E-}02$
B4	$2.04\text{E-}01 \pm 9.57\text{E-}03$	$1.10\text{E-}01 \pm 4.19\text{E-}03$	$1.96\text{E-}01 \pm 1.16\text{E-}02$	$2.10\text{E-}01 \pm 6.71\text{E-}03$
B5	$1.23\text{E-}01 \pm 5.74\text{E-}03$	$7.09\text{E-}02 \pm 2.68\text{E-}03$	$1.00\text{E-}01 \pm 5.44\text{E-}03$	$1.26\text{E-}01 \pm 3.84\text{E-}03$
C1	$3.58\text{E+}00 \pm 1.65\text{E-}01$	$4.39\text{E+}00 \pm 1.58\text{E-}01$	$5.61\text{E+}00 \pm 2.98\text{E-}01$	$7.49\text{E+}00 \pm 2.25\text{E-}01$
C2	$8.20\text{E-}01 \pm 3.79\text{E-}02$	$6.58\text{E-}01 \pm 2.45\text{E-}02$	$7.07\text{E-}01 \pm 3.79\text{E-}02$	$1.22\text{E+}00 \pm 3.65\text{E-}02$

C3	4.36E-01 ± 2.02E-02	3.81E-01 ± 1.43E-02	3.61E-01 ± 1.95E-02	6.01E-01 ± 1.81E-02
C4	3.36E-01 ± 1.56E-02	2.91E-01 ± 1.11E-02	1.95E-01 ± 1.06E-02	3.25E-01 ± 9.81E-03
C5	1.80E-01 ± 8.36E-03	1.94E-01 ± 7.46E-03	1.19E-01 ± 6.53E-03	1.96E-01 ± 5.88E-03

Table 3. Normalized dissolution rates of unirradiated UO₂ fragments in 2×10⁻³ M NaHCO₃

Dissolved O₂ →	Normalized Dissolution Rate (mg m⁻² d⁻¹)			
	3.0 ppm O ₂	4.2 ppm O ₂	5.9 ppm O ₂	8.7 ppm O ₂
A6	5.35E-01 ± 2.82E-02	1.13E+00 ± 4.36E-02	1.59E+00 ± 9.25E-02	1.49E+00 ± 4.86E-02
A7	1.53E-01 ± 7.11E-03	1.71E-01 ± 6.22E-03	1.71E-01 ± 9.12E-03	1.61E-01 ± 5.28E-03
A8	6.97E-02 ± 3.25E-03	7.57E-02 ± 3.17E-03	5.92E-02 ± 3.46E-03	5.07E-02 ± 1.67E-03
B6	4.87E+00 ± 2.24E-01	7.40E+00 ± 2.71E-01	1.01E+01 ± 7.57E-01	8.99E+00 ± 3.97E-01
B7	4.99E-01 ± 2.31E-02	3.41E-01 ± 1.26E-02	6.65E-01 ± 3.55E-02	8.24E-01 ± 2.58E-02
B8	1.17E-01 ± 5.43E-03	4.64E-02 ± 1.79E-03	1.21E-01 ± 6.67E-03	9.35E-02 ± 2.82E-03
C6	8.97E+00 ± 4.12E-01	1.22E+01 ± 4.44E-01	1.54E+01 ± 8.21E-01	2.19E+01 ± 6.62E-01
C7	3.45E-01 ± 1.62E-02	2.13E-01 ± 8.10E-03	4.02E-01 ± 2.18E-02	5.75E-01 ± 1.73E-02
C8	1.39E-01 ± 6.44E-03	9.65E-02 ± 3.74E-03	1.95E-01 ± 1.06E-02	4.70E-01 ± 1.41E-02

4. Discussion

Dissolution tests in these studies examined four different factors: temperature of the leachate, dissolved oxygen content of the leachate, dopant concentration in the fuel, and surface area of the fuel. Figure 5 shows direct comparisons of the dissolved oxygen concentration in the leachate for the varying dopant concentrations of the fuel powder samples for each temperature. Figure 6 shows the same comparison for the fragment samples of UO₂. Similar trends were observed in the powder and fragment data. In general, a decrease in the normalized dissolution rate was observed for all temperatures and dissolved O₂ ranges when Gd₂O₃-dopant was present in the fuel. This effect was most significant in the 50 °C and 75 °C tests where the dissolution rate dropped, on average, by a factor of 8 for the powders and 27 for the fragments when the Gd₂O₃ concentration was increased from 0% to 1.25%. There was also a general trend of increasing dissolution as the dissolved O₂ in solution was increased. In comparison between the temperature ranges, the decrease in the normalized dissolution rate between the undoped UO₂ and 1.25 to 4 wt% Gd₂O₃ doped UO₂ cases became significantly more predominant at 50 °C and 75 °C.

Figure 5. Normalized dissolution rate of unirradiated UO_2 powders in 2×10^{-3} M NaHCO_3 with O_2 concentration of 3.0, 4.2, 5.9, and 8.7 ppm at a) 25 °C, b) 50 °C, and c) 75 °C.

Figure 6. Normalized dissolution rate of unirradiated UO_2 fragments in 2×10^{-3} M NaHCO_3 with O_2 concentration of 3.0, 4.2, 5.9, and 8.7 ppm at a) 25 °C, b) 50 °C, and c) 75 °C.

Figure 7 and Figure 8 display the comparisons between various temperatures in the leachate for the powders and fragments, respectively. Overall, the samples showed an increasing dissolution rate at the higher temperatures in comparison to the 25 °C rates. For both the powder and fragment samples, the dissolution rate at 50 °C and 75 °C for the undoped samples in the reduced O_2 environments, 3.0, 4.2, and 5.9 ppm, were similar, although at 8.7 ppm dissolved O_2 (the O_2 concentration for deionized water in equilibrium with air) a slight increase was observed.

Figure 7. Normalized dissolution rate of unirradiated UO₂ powders in 2×10^{-3} M NaHCO₃ with O₂ concentration of a) 3.0, b) 4.2, c) 5.9, and d) 8.7 ppm at 25 °C, 50 °C, and 75 °C.

Figure 8. Normalized dissolution rate of unirradiated UO₂ fragments in 2×10^{-3} M NaHCO₃ with O₂ concentration of a) 3.0, b) 4.2, c) 5.9, and d) 8.7 ppm at 25 °C, 50 °C, and 75 °C.

Comparisons between the powder and fragment samples can be seen in Table 4, these data are presented as a factor difference between the powder and fragment samples with similar dopant concentrations for direct comparison of the surface area effects. In the tests where no Gd-dopant was present, the normalized dissolution rate was higher in the fragments than in the corresponding powders, indicated by a factor greater than 1. However, that the factor is greater than one may simply mean that the roughness factor of 15 applied to calculate the effective surface area of the fragments may not be large enough. For most conditions, the dissolution rate of the fragments relative to the powders decreased as the Gd-dopant concentration increased. No distinctive trends were observed for the surface area effects with respect to dissolved O₂ concentration in the leachate.

Table 4. Factor difference between powder and fragment dissolution rates at specific dopant concentrations ($\text{NDR}_{\text{fragment}}/\text{NDR}_{\text{powder}}$)

	Gd_2O_3 wt%	3.0 ppm O_2	4.2 ppm O_2	5.9 ppm O_2	8.7 ppm O_2
25°C	0	1.3 ± 0.1	1.6 ± 0.1	2.1 ± 0.2	2.1 ± 0.1
	2	0.9 ± 0.1	1.1 ± 0.1	0.9 ± 0.1	0.8 ± 0.04
	3	0.3 ± 0.02	0.3 ± 0.02	0.3 ± 0.03	0.2 ± 0.01
50°C	0	1.3 ± 0.1	1.7 ± 0.1	2.1 ± 0.2	1.5 ± 0.1
	2	1.5 ± 0.1	1.7 ± 0.1	2.0 ± 0.1	2.2 ± 0.1
	3	0.6 ± 0.04	0.4 ± 0.02	0.6 ± 0.05	0.4 ± 0.02
75°C	0	2.5 ± 0.2	2.8 ± 0.1	2.8 ± 0.2	2.9 ± 0.1
	2	0.8 ± 0.1	0.6 ± 0.03	1.1 ± 0.1	1.0 ± 0.04
	3	0.4 ± 0.03	0.3 ± 0.02	1.0 ± 0.1	1.4 ± 0.1

The trends shown in Figure 5 through Figure 8 provide evidence that dopant concentration significantly influences the dissolution rate. These data support the matrix stabilization effect presented by Grandstaff and others [15,16,19, 38,39] who also observed in their experiments that the oxidation and/or dissolution rates decreased where Gd_2O_3 and ThO_2 were added and incorporated into the UO_2 matrix. Therefore, having dopants such as Gd present in the unirradiated UO_2 provides a better surrogate for estimating the dissolution rate of used nuclear fuel at long time periods when radiolysis effects are minimal.

3.2. Comparison to Model-predicted Dissolution Rates

The current model used to predict the dissolution rate for used fuel was developed for Yucca Mountain and is based upon data collected from SPFT testing performed at Pacific Northwest National Laboratory (PNNL) and Lawrence Livermore National Laboratory (LLNL) [31]. The data for the model were obtained over the ranges shown in Table 5, and the model is only assumed applicable over these ranges. The pH range tested was from 2 to 10 and the data was separated into two groups: one for alkaline conditions (pH 8-10, the focus of this work) and one for acidic conditions (not discussed here). Previous work demonstrated that, in the range of neutral pH conditions, [10,40] small variations in the pH have minimal effect on the dissolution rate and therefore this variable was not used in three of the four alkaline models discussed below. A fourth model was included (labeled as “Combined Model Comparison, Model 2”) which takes this variable into account.

Table 5. Range of applicability for the alkaline dissolution rate prediction model

Variable	Range
Temperature	25°C to 75°C
ppO ₂	0.002 atm to 0.2 atm
[CO ₃]	2×10^{-4} to 2×10^{-2} M

Four equations were generated to fit the collected data [31]: an equation for CSNF, one for unirradiated UO₂, and two which combined the full data set (one with a pH dependence and one without). The general equation for the models is:

$$\text{Log}_{10}(\text{DR}) = a_0 + \frac{a_1}{T} + a_2 \text{pCO}_3 + a_3 \text{pO}_2 + a_4 \text{pH} \quad (4)$$

where DR is the dissolution rate in mg m⁻² d⁻¹, T is the temperature in Kelvin,

$$\text{pO}_2 = -\text{Log}_{10}(\text{ppO}_2) \quad (5)$$

$$\text{pCO}_3 = -\text{Log}_{10}([\text{HCO}_3^-] + [\text{CO}_3^{2-}]) \quad (6)$$

$$\text{pH} = -\text{Log}_{10}(\text{H}^+) \quad (7)$$

ppO₂ is the partial pressure of O₂, and a₀, a₁, a₂, a₃, and a₄ are the model parameters defined in reference [31].

In the development of the models derived above, all solutions were initially at room temperature and pO₂ represented the partial pressure of the sparge gas for the system. Therefore, for applicability to the models, when calculating pO₂, if the initial solutions are not at room temperature then the dissolved O₂ content at that temperature must be converted to the equivalent partial pressure, via Henry's Law, needed at room temperature to achieve the same dissolved O₂ levels in solution.

Comparisons were made of the predicted values by the model, using equations 4 through 7, for the conditions tested in this work. The results, displayed as the factor difference (model predicted divided by measured value), are presented in Figure 9 and Figure 10. The models predicted the dissolution of the non-doped UO₂ fairly well, especially at the higher temperatures. In the cases with Gd₂O₃ dopant the models over predicted the normalized dissolution rate by roughly one order of magnitude, and in some cases up to two orders of magnitude. In general, the over-prediction increased with the Gd₂O₃ content and with temperature. Out of the four models, the one developed using a combination of unirradiated and CSNF that included a variable for pH (model 2), performed the best overall for all Gd₂O₃ doped samples with the prediction not exceeding a factor of 20. Although this model did well for the Gd₂O₃ doped samples, it also had the highest under-prediction for non-doped samples, especially at the higher temperatures.

Figure 9. Comparison of model predicted normalized dissolution rates with those experimentally measured in this work (Data presented are model predicted values divided by measured results) Left: CSNF Model, Right: UO₂ Model. The P in the legend denotes data from powder samples; the F denotes data from fragment samples

Figure 10. Comparison of model predicted normalized dissolution rates with those experimentally measured in this work (Data presented are model predicted values divided by measured results) Left: Combined CSNF and UO₂ Model 1, Right: Combined CSNF and UO₂ Model 2. The P in the legend denotes data from powder samples; the F denotes data from fragment samples

4. Conclusions

The results presented in this work support the basis that UO_2 is a conservative substitute for used nuclear fuel after radiolysis is no longer a significant factor. The dopants, representative of fission products in the UO_2 matrix, proved beneficial in lowering the dissolution rate with larger effects at higher temperatures and dissolved O_2 concentrations where the rates would typically be elevated. At room temperature the increased dopant concentration reduced the dissolution rate up to an order of magnitude, while at elevated temperatures reductions of almost two orders of magnitude were seen over the tested dopant range.

The results from this study were compared with their values predicted by existing dissolution models. The dissolution rates for pure UO_2 compared reasonably well for most of the models, varying by less than an order of magnitude (model predicted/measured). The samples containing Gd_2O_3 dopant were over-predicted by all models, with the maximum varying from one to two orders of magnitudes. The most significant deviations were those observed in the high dopant samples, measured at elevated temperatures.

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