

**TR-99-22**

**Uranium dioxide, SIMFUEL,  
and spent fuel dissolution rates -  
a review of published data**

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October 1999

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

## Abstract

Published data from studies of the dissolution rate of uranium dioxide, SIMFUEL, and spent fuel in aqueous solutions of low ionic strength are reviewed. Data for the dissolution rate of each of the three solid phases are examined for internal consistency and the average or best estimate of the dissolution rate for each of the phases is compared with the rates found for the other phases. The effects of solid phase crystallinity and of environmental conditions such as oxygen concentration in solution on dissolution rate are discussed. The general conclusion of this review is that the kinetics of dissolution of spent fuel as a function of environmental parameters is poorly constrained. Possible experimental methods to better constrain the dissolution rate of spent fuel under potential repository disposal conditions are presented.

## Sammanfattning

En genomgång har gjorts av publicerade data från studier av upplösningshastigheten av urandioxid, SIMFUEL, och använt bränsle i vattenlösningar med låg jonstyrka. Data för upplösningshastigheten för var och en av de fasta faserna har granskats med avseende på samstämmighet och medelvärdet eller bästa uppskattningen av upplösningshastigheten för var och en av faserna jämförs med de hastigheter som bestämts för de andra faserna. Effekterna av fastfasens kristallinitet och av miljöförhållanden, som syrehalt i lösningen, på upplösningshastigheten diskuteras. Den allmänna slutsatsen av denna översikt är att data för kinetiken för upplösningen av använt bränsle som funktion av miljöparametrar har för stor spridning. Tänkbara experimentella metoder för att bättre bestämma upplösningshastigheten för använt bränsle under möjliga förvarsförhållanden presenteras.

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# 1 Introduction

Spent nuclear reactor fuel in Sweden is destined for disposal in a deep underground geologic repository. The host rock for the repository is most likely to be a granitic igneous or metamorphic rock. The groundwater composition may be a dilute sodium/calcium bicarbonate water or a more saline water typical of those found deep in old shield regions of continents. At present, most of the available data on dissolution rates of uranium dioxide, SIMFUEL, and spent fuel have been done in aqueous solutions with low ionic strength. Data for solubilities of these phases and for dissolution rates in saline media are much less abundant due, at least in part, to the analytical difficulties encountered in measuring trace solution components in brines.

The solubility of solids is affected by the degree of crystallinity of the solid phase. Amorphous or poorly crystalline solids have solubilities that can be many orders of magnitude higher than a solid of the same chemical composition that is well crystallized. It is to be expected that degree of crystallinity at constant chemical composition would also have an effect on dissolution rates.

Spent fuel is the product of nuclear reactions occurring in a material that was initially a highly crystalline, low porosity, microcrystalline solid, whose chemical composition was initially  $UO_{2.00}$ . The nuclear reactions that convert the initially pure  $UO_{2.00}$  into spent fuel are fission of uranium nuclei, predominantly  $^{235}U$  in reactors moderated by normal ("light") water, capture of neutrons by  $^{238}U$  to produce actinide isotopes with higher atomic weight, and fission of some of these higher actinides, especially  $^{239}Pu$ . Spent fuel with normal burnup will have had the equivalent of 4% by weight of the original U in the fuel having undergone fission. Each fission reaction produces two product isotopes, one in each of the fission distribution ranges centered near mass 94 and mass 140, as well as a number of neutrons. The fission products remain in the fuel matrix, either in solid solution or as segregated phases.

The fission products can be grouped into categories with similar chemical properties. Table 1 gives a summary of the fission product distribution for a PWR fuel with burnup of 35 MWd/kgU. (The data are recalculated from the concentration data given in /Oversby, 1998/). The total concentration of fission products in this fuel was 3.59% by weight.

**Table 1-1. Distribution of fission products by chemical group in PWR spent fuel with burnup of 35 MWd/kgU.**

Chemical group	Percent by weight
Rare gases (Kr, Xe)	16.75
Halides (Br, I)	0.78
Alkalis (Rb, Cs)	8.21
Alkaline earths (Sr, Ba)	7.06
Zirconium (Zr)	10.13
Y + REE (mainly La, Ce, Pr, Nd, Sm, Eu and Gd)	29.73
Mo + noble metals (Tc, Ru, Rh, and Pd)	24.69
Others (largely Te, Cd, Sn, Ag, Se, Sb)	2.64

Of the fission products found in spent fuel, about 50% can substitute for U in the uranium dioxide lattice; these are Zr, Y + REE, Sr and Ba, and perhaps some of the Mo. Most of the Mo occurs in the separated metallic phase that contains the noble metals. The metallic phase and the gases may occur inside fuel grains, may decorate grain boundaries, or, in the case of the gases, may be segregated to the pellet-cladding gap. When present inside the grains, the segregated phases may cause dislocations and strain in the uranium dioxide lattice. Except for a small amount of Cs found associated with pellet-cladding interaction phases, the alkalis have not been identified as segregated phases in LWR fuels of normal burnup. Since the alkalis cannot form a true solid solution with the uranium dioxide phase, their presence dispersed in the fuel matrix will generate defects in the lattice. Defects are also created when uranium (IV) in the lattice is converted into fission products that remain in solid solution but have valence lower than (IV). Given the complex nature of the "impurities" present in spent fuel, and the near absence of impurities in the starting  $UO_{2.00}$ , it must be expected that this will have an impact on matrix dissolution rate for the spent fuel.

## 2 Factors affecting dissolution rates

There are a number of environmental factors that may affect the rate of dissolution of both uranium dioxide and spent fuel. If we consider only the initial dissolution rate measured in static experiments, a high dissolution rate may be found because the surface of the solid may have a different oxidation state than the bulk material. Exposure of either uranium dioxide or spent fuel to air results in a surface layer with formal oxidation state of  $UO_{2.2}$ . This surface layer may dissolve at a different rate than the bulk material. As dissolution proceeds, the concentration of U in solution increases and the dissolution rate of the solid decreases as the solubility of the solid is approached. If the dissolution medium is decanted after the solution approaches saturation and is replaced by new solution without allowing the solid to dry out and produce a new oxide layer, the dissolution process for the second static test cycle may reflect dissolution of  $UO_{2.0}$ , rather than  $UO_{2.2}$ . To verify that the surface was not oxidized, the replenishment test should be repeated and the same dissolution rate should be found. Note that treatment of the solid with a solution other than the intended dissolution test medium may introduce additional problems. If treatment is done using an oxidizing medium, such as  $HNO_3$  or  $HClO_4$ , the surface layer will be dissolved, but the new surface may be oxidized as well.

A more straight-forward method to measure the initial dissolution rate of solids – i.e., the dissolution rate at infinite dilution – is to use a flow-through test system. In this configuration, the initial surface dissolves rapidly and the dissolved material is removed from the system. The freshly exposed surface of the solid is never exposed directly to the atmosphere, but only to gases dissolved in the fluid phase. If the flow rate is varied and the product of the flow rate of dissolution medium and the concentration of U in solution are constant, the system is not affected by saturation and the initial dissolution rate of the solid may be calculated. This represents the rate of dissolution of the bulk solid, not that of the initial surface layer.

The other parameters that affect the dissolution rate of uranium dioxide and spent fuel are temperature, solution composition, and the presence of oxidizing agents. The latter may be introduced via solution species such as dissolved oxygen or may be produced *in situ* in the case of spent fuel by radiolysis of the solution. In the discussion that follows, we will consider only the dissolution of the bulk solid, with oxidation condition of  $UO_{2.0}$ .

Temperature affects the dissolution rate by supplying additional energy to the system as the temperature is increased. Since dissolution occurs when atoms or molecules at the surface of the solid have enough energy to overcome the bonding forces within the solid, dissolution rates will increase as temperature increases. The magnitude of the temperature effect is determined by the activation energy for the dissolution process. The smaller the increase in dissolution rate with increase in temperature, the lower the activation energy and, thus, the weaker the bonding of the surface atoms to the solid. If the activation energy were zero, there would be no increase in dissolution rate with temperature increase. Note that the solubility of the solid may either increase or decrease as temperature increases.

The solution composition for fluids with low total ionic strength will influence dissolution rates through the formation of complexes involving solution species and atoms on the surface of the solid. For normal dilute groundwater compositions, the most important solution species will be  $H^+$  and  $HCO_3^-$ . The former acts by binding to surface oxygen atoms of the solid and facilitating breaking of the O-U bonds to remove hydrated

uranium atoms from the surface. Bicarbonate acts by forming complex ions with U and facilitating removal of U as the  $\text{UO}_2(\text{CO}_3)_2^-$  ion. Note that the  $\text{HCO}_3^-$  ion should only be effective if there is U(VI) present on the solid surface. If the surface is  $\text{UO}_{2.00}$ , only U(IV) is present and the dissolution rate should not be effected by changes in bicarbonate concentration. The concentrations of  $\text{H}^+$  and  $\text{HCO}_3^-$  are not independent parameters; if  $\text{H}^+$  increases from pH = 9 and continuing toward pH = 4,  $[\text{HCO}_3^-]$  will first increase and then decrease as dissolved carbonate ion is converted to bicarbonate and ultimately the bicarbonate is converted into dissolved carbon dioxide gas. Both  $\text{H}^+$  and  $\text{HCO}_3^-$  can be expected to increase the solubility of U(VI), but  $\text{HCO}_3^-$  should not affect the solubility of U(IV).

The principal oxidizing agent present in natural groundwaters is dissolved oxygen. For dissolution of uranium dioxide and spent fuel, the oxygen in solution can cause an increase in the surface oxidation state from  $\text{UO}_{2.00}$  to  $\text{UO}_{2+x}$ , in effect producing some U(VI) at the surface of the solid. The dissolution process, therefore, involves two steps, either of which may be rate controlling. The first step is to produce the U(VI) at the solid surface and the second step is the removal of the U(VI) species from the surface and into solution.

Radiolysis reactions in the dissolution medium caused by decay energy from spent fuel may create both oxygen in solution and other oxidizing agents. The oxygen produced by radiolysis can be expected to behave the same way as the dissolved oxygen discussed above. Other oxidizing agents produced through radiolysis may be able to more rapidly oxidize the fuel surface to produce U(VI). If it is the oxidation step that is rate-limiting for the dissolution process, and if radiolytic species other than molecular oxygen are the predominant pathway for surface oxidation, it is possible that spent fuel will not show a change in dissolution rate as the amount of oxygen in solution is increased, but that uranium dioxide will.

All dissolution rate studies performed to date have used [U] in solution as the measure of the dissolution rate or have used electrochemical methods. In this report we will only consider the studies based on solution chemistry measurements; the electrochemical measurements will be discussed in a subsequent report.

A number of studies conducted in support of the US repository disposal program have used uranium dioxide or spent fuel that has been intentionally oxidized. These studies have included  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$ , as well as the lower oxidation states of  $\text{UO}_{2+x}$  with  $x \leq 0.4$  for spent fuel and  $x \leq 0.33$  for uranium dioxide. Studies related to the higher oxidation state of U above  $\text{UO}_{2+x}$  will not be discussed in this report since they are unlikely to be relevant to disposal of spent fuel under Swedish repository conditions.

### 3 SIMFUEL dissolution rates

SIMFUEL is a synthetic uranium dioxide polycrystalline material containing additions of Sr, Y, Zr, Mo, Ru, Rh, Pd, Ba, La, Ce, and Nd in proportions intended to be analogous to spent fuel with burnups of 30 and 50 MWd/kgU. These two SIMFUEL batches had significant differences in grain size, which might affect dissolution rates. In addition, the chemical state of the fission product simulants did not match that found in spent fuel for several important elements. Thus, use of the trace element additions to measure dissolution rates of SIMFUEL will not be expected to represent the matrix dissolution rate. It is unclear the extent to which the deviations in chemical state of the "fission products" will affect the actual matrix dissolution rates.

Casas et al /1991/ report results of batch and flow-through dissolution tests using both the 30 and 50 MWd/kgU SIMFUEL materials. The data for U release as a function of time for the static tests, which involved leaching of a single, intact pellet of SIMFUEL in either 100 ml of "Allard" water (depleted with nitrogen prior to use) plus 50 ml of air atmosphere over the solution, or 1000 ml of a synthetic granite groundwater with an atmosphere of 0.97 atm O<sub>2</sub> + 0.01 atm CO<sub>2</sub>, were reported as dissolution rates of moles U/m<sup>2</sup>h. The surface area used in the calculations was 0.12 m<sup>2</sup>/pellet, which is now known to be incorrect /Ollila, personal communication/. If the data are recalculated using a more realistic surface area of 1.52 x 10<sup>-3</sup> m<sup>2</sup>/pellet the results are

Test conditions	Dissolution rate mol/m <sup>2</sup> h	Dissolution rate mg/m <sup>2</sup> d
Allard - 30 Mwd	4 x 10 <sup>-9</sup>	0.023
Allard - 50 Mwd	8 x 10 <sup>-9</sup>	0.046
Granite - 30 Mwd	2.9 x 10 <sup>-8</sup>	0.165
Granite - 50 Mwd	2.8 x 10 <sup>-8</sup>	0.16

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Flow-through experiments for both of the SIMFUEL types in Allard water with nitrogen gas (no air intentionally added) produced uranium release during the period between 10 and 100 hours of dissolution of about 10<sup>-9</sup> moles, which would give a dissolution rate of 7 x 10<sup>-9</sup> mol/m<sup>2</sup>h. With the granite groundwater + oxygen with carbon dioxide system, the rate found was 7 x 10<sup>-8</sup> mol/m<sup>2</sup>h for both burnup simulants, which is about 2.5 times higher than the rate found in the static tests. The same data are also reported in Sandino et al /1991/ and in Bruno et al /1992/.

Ollila /1992/ reports the results of testing the 50MWd/kgU SIMFUEL under anaerobic conditions. She dissolved a single, intact pellet in Allard water, deaerated with nitrogen before use, using 100 ml flasks in a nitrogen atmosphere glove box. The dissolution was done in stages, transferring the pellet to a new flask at each sampling time. The solutions were analyzed, as well as a vessel rinse and acid strip of the vessel at the end of each stage. The vessel rinse and strip samples contained substantial amounts of U; these amounts were added to those found in the solution samples to give a total amount of U removed from the pellet during the test period. (Note: this procedure was not used in the Casas et al /1991/ report). Ollila /1992/ uses the same surface area as Casas et al /1991/

for conversion of the concentration data to dissolution rates, so the reported values need to be corrected to the more appropriate surface area of  $1.52 \times 10^{-3} \text{ m}^2/\text{pellet}$ . If a single low value at the end of the testing is ignored, the average dissolution rate found was  $80 \times 10^{-8} \text{ mol/m}^2\text{h}$  when the acid strip U is included in the reported value, but only  $0.16 \times 10^{-8} \text{ mol/m}^2\text{h}$  if just the [U] in filtered solutions is used. The total amount of U removed from the pellet in static tests is more likely to represent the total dissolution rate, so the higher value of  $80 \times 10^{-8} \text{ mol/m}^2\text{h}$  would be the most appropriate estimate of SIMFUEL dissolution rate under static conditions in Allard water with nitrogen atmosphere. This converts to  $4.6 \text{ mg/m}^2\text{d}$ , a value 100 times greater than that reported by Casas et al /1991/.

Garcia-Serrano et al /1996/ reported results of static dissolution tests of powdered SIMFUEL in synthetic groundwater. While the water composition is not given in the text, reference is made to work by Ollila, so the water is most probably "Allard" water. The tests used 1 gram of powder in 200 ml of solution, with an atmosphere of 90%  $\text{N}_2$  and 10%  $\text{O}_2$ . The test solution was sampled periodically to produce a continuous dissolution description for the samples. The concentration of U rose rapidly over the first week of testing and then more slowly as the solution concentration became higher, indicating approach to saturation, especially for the finer grain-sized sample. Results of the testing were

Size ( $\mu\text{m}$ )	BET area ( $\text{m}^2/\text{g}$ )	R1 ( $\text{mg/m}^2\text{d}$ )	R2 ( $\text{mg/m}^2\text{d}$ )
50-100	0.1	3.1	$3.7 \times 10^{-3}$
100-315	0.026	3.6	$3.6 \times 10^{-3}$

The data for the two different size fractions showed good reproducibility. The rate for the initial period (R1) is in good agreement with the results from Ollila /1992/ for the case where the acid strip U is included in the dissolution rate calculation.

Quiñones et al /1998/ conducted tests of powdered SIMFUEL dissolution in granite groundwater under anoxic ( $\text{N}_2$  atmosphere) and reducing ( $\text{N}_2 + \text{H}_2$  atmosphere) conditions. The concentration of U was essentially constant at long exposure times, giving about  $3 \times 10^{-7} \text{ mol/L}$  for the reducing conditions test and 1 to  $2 \times 10^{-7} \text{ mol/L}$  for the anoxic test. The tests are clearly showing the effects of U saturation, so it is impossible to calculate any dissolution rate for the SIMFUEL samples.

Bruno et al /1995/ report results of a static test using a SIMFUEL pellet and a flow-through test using 100-300  $\mu\text{m}$  SIMFUEL powder. The tests were done in a 0.1M  $\text{NaCl}/0.01 \text{ M NaHCO}_3$  solution at  $\text{pH} = 8.5$ . The test atmosphere is not stated, so was probably air. Results of the static test were interpreted in terms of an initial rate of dissolution (R1) and a long-term rate (R2). The rates were calculated using the BET surface area data given in Casas et al /1993/ -  $0.0113 \text{ m}^2/\text{g}$  for the powder and  $0.00019 \text{ m}^2/\text{g}$  for the pellet. The results for the static test were  $\text{R1} = 1.43 \text{ mg/m}^2\text{d}$  and  $\text{R2} = 0.21 \text{ mg/m}^2\text{d}$ . The rate for the flow-through test was  $0.23 \text{ mg/m}^2\text{d}$ . This low rate, comparable to R2 in the static tests, suggests that the flow-through test may have been affected by U buildup in solution. Data for R1 for the static test are similar to those reported by Ollila /1992/ and Garcia-Serrano et al /1996/ for the first phase of dissolution of SIMFUEL, despite the differences in redox conditions and solution compositions.

LeLous et al /1998/ conducted tests of spent fuel and SIMFUEL in the presence of "environmental materials". The data for the SIMFUEL tests could not be interpreted because of interference from the leaching of the environmental materials. The spent fuel data are discussed below.

## 4 Uranium dioxide

Unlike SIMFUEL, uranium dioxide is a pure chemical compound, which should simplify the interpretation of the dissolution rate data. SIMFUEL, however, all comes from the same source, so the initial material in all tests had the same, known characteristics. With the testing of uranium dioxide, it will be necessary to evaluate the nature of the solid materials – i.e., grain size, porosity, degree of crystallinity, etc. – in order to understand the sources of any differences in dissolution rates.

Bruno et al /1991/ used a flow-through system to measure the dissolution rate of powdered  $\text{UO}_2$  (50  $\mu\text{m}$  size) in 0.008 M  $\text{NaClO}_4$  treated with  $\text{H}_2$  gas in the presence of a Pd catalyst. The solid was supplied by ASEA Atom AB, so should be representative of unirradiated fuel. The BET surface area of the powder was  $0.201 \pm 0.002 \text{ m}^2/\text{g}$ . The dissolution rate measured based on  $[\text{U}]$  in solution was  $4.4 \times 10^{-12} \text{ mol/m}^2\text{s}$ . A correction was made for the effects of precipitation; however, the correction value was applied in the wrong direction and was subtracted from the measured rate based on  $[\text{U}]$ . The correct dissolution rate, after adding the effects of precipitation, would be  $6 \times 10^{-12} \text{ mol/m}^2\text{s}$ , rather than the reported value of  $1.9 \times 10^{-12} \text{ mol/m}^2\text{s}$ . A rate of  $6 \times 10^{-12} \text{ mol/m}^2\text{s}$  corresponds to  $9 \times 10^{-5} \text{ g/m}^2\text{d}$ , or  $0.09 \text{ mg/m}^2\text{d}$ .

Casas et al /1993/ conducted static dissolution tests on unirradiated fuel pellets and crushed material from pellets using 0.01 mol/L  $\text{NaClO}_4$  at pH = 8 with an atmosphere of 5%  $\text{O}_2$  in  $\text{N}_2$ . An initial rapid increase in  $[\text{U}]$  was followed by a slower increase. The initial dissolution was interpreted to represent removal of an oxidized surface layer, while the second rate was interpreted to represent the matrix dissolution rate. For the second dissolution rate, the rate-limiting step was interpreted to be the oxidation of the surface of the  $\text{UO}_2$  by dissolved oxygen, followed by rapid dissolution of the U(VI) from the surface. Rates found were

Size fraction	BET ( $\text{m}^2/\text{g}$ )	R1 ( $\text{mg/m}^2\text{d}$ )	R2 ( $\text{mg/m}^2\text{d}$ )
100–300 $\mu\text{m}$	0.0113	0.12	$2.9 \times 10^{-4}$
900–1100 $\mu\text{m}$	0.0016	0.57	$2.6 \times 10^{-3}$
Pellet	0.00019	0.40	$3.8 \times 10^{-3}$

Casas et al /1994b/ describes experiments similar to (and in some cases probably the same experiments) as those described in Casas et al /1993/, as well as a flow through experiment using the 100–300  $\mu\text{m}$  size fraction. Batch experiments were done in 0.01 mol/L  $\text{NaClO}_4$  in Teflon vessels, pH = 8 (or 4 in one case), with an atmosphere of 5%  $\text{O}_2$  in  $\text{N}_2$ . Samples used in experiments 1, 3, and 4 were pretreated with perchloric acid to remove fine particles and oxidized phases prior to use. XPS data showed 60% U(VI) for unpretreated starting material, which is very oxidized, and 71% for pretreated material. (This suggests that the pretreatment may oxidize the surface, rather than remove oxidized phases.) Experiments 1 and 2 were 100–300  $\mu\text{m}$ ; experiments 3 and 4 were 900–1100  $\mu\text{m}$ .

Flow through experiments used 100–300  $\mu\text{m}$  size fraction in 0.01 mol/L  $\text{NaClO}_4$  in a chromatographic column, pH = 8 or 6.5, with an atmosphere of 5%  $\text{O}_2$  in  $\text{N}_2$ .

Results were

Expt	pH	pretreat	initial rate mg/m <sup>2</sup> d	final rate mg/m <sup>2</sup> d
1	8	yes	0.05	$3.1 \times 10^{-4}$
2	8	no	0.38	$3.8 \times 10^{-3}$
3	4	yes	1.4	$3.0 \times 10^{-3}$
4	8	yes	0.33	$2.5 \times 10^{-3}$
flow	8	no		0.08
flow	6.5	no		0.10

Note: experiments 1 and 4 seem to be the same as those reported in the MRS paper; however, the initial rates given here are lower than those reported in the MRS paper (0.12 and 0.57 respectively). The final rates given here and in the MRS paper correspond to within the number of significant figures reported.

The initial rates reported for the static tests are all for highly oxidized surfaces, much more oxidized than expected for any realistic spent fuel disposal case. The “final rates” for the static tests are all much lower than the rates measured for flow-through tests. This strongly suggests that the static tests are affected by the presence of a significant fraction of the saturation level of  $[\text{U}]$  in solution. The average of the dissolution rates measured in the two flow-through tests is the same as that found by Bruno et al /1991/, despite the use of  $\text{H}_2$  gas and a Pd catalyst to treat the leaching solution in the Bruno et al /1991/ experiments and the use of an atmosphere of 5%  $\text{O}_2$  in  $\text{N}_2$  in the Casas et al /1994b/ tests. This may mean that there is no influence of  $[\text{O}_2]$  on the dissolution rate of uranium dioxide in perchloric acid medium, or that some oxygen leaked into the test solution as it was pumped through the experimental system in the Bruno et al /1991/ tests.

The presence of bicarbonate ion in solution will increase the solubility of U(VI) and will stabilize that oxidation state in solution relative to U(IV). Thus, addition of bicarbonate to an otherwise unreactive dissolution medium could be expected to increase the dissolution rate of uranium dioxide as well. de Pablo et al /1997/ studied the dissolution rate of powdered  $\text{UO}_2$  produced by crushing unirradiated fuel pellets and separating the 100–300  $\mu\text{m}$  size fraction. The powder, with a BET surface area of 0.0113  $\text{m}^2/\text{g}$ , was dissolved in a NaCl solution with total ionic strength of 0.15 and hydrogen carbonate concentrations ranging from 0.05 to 0.0001 mole/L in a thin layer flow-through reactor with normal air atmosphere.

Rates found at a function of bicarbonate and temperature were

[HCO <sub>3</sub> ] <sup>-</sup> , mmol/L	T(°C)	Dissolution rate, mg/m <sup>2</sup> d
50	25	8.64
50	45	116
50	60	221
10	25	2.20
10	45	17.0
10	60	59.9
1	25	0.84
1	45	1.73
1	60	2.40
0.1	25	0.19
0.1	45	0.30
0.1	60	0.53

These data show clearly that at constant temperature, the rate of dissolution increased with increasing bicarbonate content and at constant bicarbonate content, the rate of dissolution increased with increasing temperature.

The dependence of the rate on carbonate concentration was calculated using the formula

$$r = k [\text{HCO}_3^-]^n$$

Results were	25°C	$k = 2.0 (\pm 0.5) \times 10^{-9}$	$n = 0.58 \pm 0.05$
	45°C	$k = 7.9 (\pm 0.3) \times 10^{-8}$	$n = 0.96 \pm 0.06$
	60°C	$k = 2.0 (\pm 0.2) \times 10^{-7}$	$n = 1.0 \pm 0.1$

Comparison of the rate found at 25°C for the lowest carbonate + bicarbonate concentration of 0.1 mmol/L with that for flow-through experiments in perchloric acid discussed above Casas et al /1994b/ shows that the small amount of bicarbonate increased the dissolution rate only by a factor of 2. Interpolation of the data given above suggests that at normal atmospheric pCO<sub>2</sub> levels, which produce about 2 mmol/L of bicarbonate in dilute solutions, the dissolution rate of uranium dioxide would be expected to be about 1 mg/m<sup>2</sup>d at 25°C.

Bruno et al /1995/ conducted static and flow-through tests of UO<sub>2</sub> pellets and material crushed to 100-300 μm size, as well as a static test of a SIMFUEL pellet and a flow-through test of crushed SIMFUEL. The SIMFUEL results were discussed above, but are repeated here to allow easy comparison with the data for UO<sub>2</sub>. All tests were conducted at room temperature and pH = 8.5, with an unstated atmosphere, which was probably normal air. For the NaCl/NaHCO<sub>3</sub> dissolution medium, the proportions were 0.1M/0.01M - i.e., 10 millimolar bicarbonate + carbonate. Test conditions were

Number/Sample	Leachant	Type
TS1 SIMFUEL pellet	NaCl/NaHCO <sub>3</sub>	replenish
TS2 UO <sub>2</sub> pellet	NaCl/NaHCO <sub>3</sub>	sequential
TS3 UO <sub>2</sub> (100–300 μm)	NaCl/NaHCO <sub>3</sub>	sequential
TS4 UO <sub>2</sub> pellet	0.01 M NaClO <sub>4</sub>	sequential
TS5 SIMFUEL(100–300 μm)	NaCl/NaHCO <sub>3</sub>	flow
TS6 UO <sub>2</sub> (100–300 μm)	NaCl/NaHCO <sub>3</sub>	flow
TS7 UO <sub>2</sub> (100–300 μm)	NaCl/NaHCO <sub>3</sub>	flow
TS8 UO <sub>2</sub> (100–300 μm)	0.01 M NaClO <sub>4</sub>	flow

Note: TS6 and TS7 differ only in the amount of sample used (0.1g and 0.25g respectively).

Rates were calculated using BET data from Casas et al /1993/. Rates were given as mg/m<sup>2</sup>d. For static tests, both initial and long-term rates were given.

TS1 R1 = 1.43 R2 = 0.21	TS5 R = 0.23 mg/m <sup>2</sup> d
TS2 R1 = 2.41 R2 = 1.27	TS6 R = 3.3
TS3 R1 = 1.73 R2 = 0.67	TS7 R = 3.1
TS4 R1 = 0.19 R2 = 0.005	TS8 R = 0.17

The dissolution rate for the flow-through test with powdered uranium dioxide in perchlorate medium (TS8) is about twice as high as that reported by Casas et al /1994b/ and Bruno et al /1991/ for similar test conditions. The uranium dioxide flow-through tests gave consistently higher dissolution rates than the longer-term rates measured in static tests, but the rates for SIMFUEL under the two conditions were the same. The dissolution rate of SIMFUEL under flow-through conditions was about 15 times lower than the rate for UO<sub>2</sub> dissolution, suggesting that the SIMFUEL static tests might not be affected by too high a [U] in solution at a given duration of dissolution time, while the UO<sub>2</sub> static dissolution tests may be. The average value found for TS6 and TS7 of 3.2 mg/m<sup>2</sup>d is about 50% higher than the results for essentially identical conditions (10 mmol/L bicarbonate and 25°C) reported by de Pablo et al /1997/.

Torrero et al /1997/ conducted flow-through tests of unirradiated UO<sub>2</sub> crushed to 100–300 μm size with BET surface area of 0.0113 m<sup>2</sup>/g. (Note: it is likely that this is the same material as that used by Casas et al /1993/, Casas et al /1994b/, de Pablo et al /1997/, and Bruno et al /1995/). One gram of powder was used in a thin layer flow-through reactor with 0.01 mol/L NaClO<sub>4</sub> at ambient temperature. Atmospheres were controlled to be 5, 21, and 100% O<sub>2</sub> in N<sub>2</sub>, which are then stated to produce partial pressures of oxygen of 0.048, 0.18, and 0.98 atm. The Henry's law constant of 1.28 x 10<sup>-3</sup> mole/L-atm was used to convert to solution concentrations of oxygen. [That would give 2, 7.4, and 40 mg/L for the three conditions.]

Conditions were adjusted to give pH values from 3.3 to 11.6. For pH < 6.7, there was a clear dependence of dissolution rate on pH, with the rate decreasing as pH increased. There was also a clear dependence of dissolution rate on [O<sub>2</sub>] for pH < 6.7. Above pH 6.7, there was no evidence for dependence of dissolution rate on either pH or [O<sub>2</sub>]. At the conditions for pH > 6.7, the dissolution rate was about 8 x 10<sup>-12</sup> mole/m<sup>2</sup>s,

corresponding to about 0.17 mg/m<sup>2</sup>d. This is the same value as reported by Bruno et al /1995/ for dissolution in 0.01 M sodium perchlorate, and may reflect the same test data. A rate equation valid for conditions 3 < pH < 6.7, and was calculated, with

$$r(\text{mole/m}^2\text{s}) = 3.5 (\pm 0.8) \times 10^{-8} [\text{H}^+]^z [\text{O}_2]^y$$

where

$$z = 0.37 \pm 0.01 \quad \text{and} \quad y = 0.31 \pm 0.02$$

XPS analyses of the sample surfaces showed that the starting material was highly oxidized, but rapidly reduced after dissolution of the outermost layer from the solid. At pH = 5.0, the surface after leaching was UO<sub>2.00</sub>, while at pH 8.2 and 9.0, the surface was found to be UO<sub>2.25</sub>. Even at the highest oxygen partial pressure, the surface of the solid after leaching was still UO<sub>2.25</sub>.

Garcia-Serrano et al /1996/ dissolved one sample of 100–300 μm UO<sub>2</sub> under the same conditions as those used for their SIMFUEL experiments discussed above. The initial, rapid dissolution rate of the UO<sub>2</sub> was somewhat higher than that of the SIMFUEL, but the longer-term rate was about a factor of 25 greater, giving 0.1 mg/m<sup>2</sup>d. The data for UO<sub>2</sub> dissolution for the period 150 to 350 days were quite erratic, with three abrupt drops in total released U in solution, followed by slow to moderate increases. These effects are highly suggestive of solution saturation and secondary phase formation. In that case, the results cannot be compared in detail with any of the other published data for UO<sub>2</sub> dissolution. These tests probably contained 1.8 millimolar bicarbonate solution ("Allard" water), for which an initial dissolution rate of about 1 mg/m<sup>2</sup>d would be expected based on the results of de Pablo et al /1997/.

Quiñones et al /1998/ conducted dissolution tests with finely powdered material, 50 to 100 μm particle size, with surface area stated as 0.04 m<sup>2</sup>/g. The powder was leached in 250 ml borosilicate glass vessels with 200 ml granite groundwater under anoxic (N<sub>2</sub>) atmosphere and under reducing (N<sub>2</sub> + H<sub>2</sub>) atmosphere. The original leaching solution was changed out after 1 month to remove the effects of initial dissolution of any oxidized layer on the materials. Concentrations at long times (2000 to 7000 hours) were nearly constant, but slowly increasing for the test with UO<sub>2</sub>. U dissolution rates calculated for the long term samples were about 2.4 × 10<sup>-4</sup> mg/m<sup>2</sup>d, which represents a long-term rate clearly affected by solution saturation.

Wilson and Gray /1990/ studied the effects of water composition on the dissolution rate of UO<sub>2</sub> under oxidizing conditions. Unirradiated UO<sub>2</sub> pellets were crushed and sieved to give 1 to 3 mm particle sizes. The particles were conditioned in synthetic J-13 water to remove surface layers and fine fragments. During this conditioning, the solution reached a steady-state uranium concentration of 700 ng/ml. Flow through experiments were then conducted in stainless steel columns using 7 grams of material. The range of linear flow-rate versus concentration was determined and 0.2 ml/min was selected as the appropriate flow rate for the experiments.

The first flow through experiments used synthetic J-13 water and gave a concentration of 3 ng/ml. The leachant was then changed to NaHCO<sub>3</sub> with the same Na and bicarbonate concentrations as the synthetic J-13 water. This produced an increase in the U concentration to 120 ng/ml. Addition, stepwise of Ca and then Si in appropriated amounts to the NaHCO<sub>3</sub> produced a decrease in [U] to values lower than originally measured in the synthetic J-13 water. Temperature increase to 85°C and then decrease to 25°C produced even lower [U]. Changing to DIW<sup>\*</sup> produced an initial decrease, followed by an

increase to about what was expected based on preliminary experiments. Surface analysis of a particle removed from the test prior to the change to DIW showed that a 5 to 10 nm thick layer containing Ca-U-Si-O had formed on the particle. A second experiment with synthetic J-13 water followed by NaHCO<sub>3</sub> produced similar solution concentrations. In this case the temperature was 25°C throughout and the surface layer formed in the synthetic J-13 water contained only U-Si-O (no Ca). The materials formed on the particle surfaces were interpreted to provide a transport barrier to U release rather than a solubility control, since they dissolved when the solution was changed.

Dissolution rate data was cited only for the first column experiment for the NaHCO<sub>3</sub> solution, and was 1 ng/cm<sup>2</sup>-min. This would amount to 10<sup>4</sup> ng/m<sup>2</sup>-min, or 14.4 mg/m<sup>2</sup>d. Since the [U] in the synthetic J-13 water was a factor of 40 lower, the dissolution rate in that solution must have been 2.5x10<sup>2</sup> ng/m<sup>2</sup>-min, or 0.36 mg/m<sup>2</sup>d for the synthetic J-13 water.

Wilson and Gray /1990/ note that the effects they found on changing composition of leaching solutions indicate that great care must be taken in selection of an appropriate solution composition if prediction of repository performance is to be done. It will be equally true that great care must be taken in comparing results from experiments done in different laboratories if different leaching/dissolution solutions are used. It is most surprising to see that the change from synthetic J-13 water to a NaHCO<sub>3</sub> solution with the same total carbonate would change the dissolution rate by a factor of 40. The dissolution rate found in the synthetic J-13 water is in better agreement with the data of de Pablo et al /1997/ for NaHCO<sub>3</sub> solutions than the results reported for NaHCO<sub>3</sub> solutions by Wilson and Gray /1990/.

Nguyen et al /1992/ report results from flow-through dissolution tests of UO<sub>2.00</sub> pellets in solutions of carbonate + bicarbonates, with fixed partial pressures of oxygen and CO<sub>2</sub> in Ar, done in an argon glovebox, at 25°C. Pellets were reacted at 1200°C in H<sub>2</sub> for 15 minutes to ensure that there was no oxidized surface layer. Rates were calculated using geometric surface area for the pellets because BET measurements looked like they gave erroneously high values. [Note: to convert rates to equivalent BET surface, divide by 3.]

Test	Na <sub>2</sub> CO <sub>3</sub> + NaHCO <sub>3</sub> (moles/kg)	p (atm)		pH	Dissolution rate mg/m <sup>2</sup> d
		O <sub>2</sub>	CO <sub>2</sub>		
1	0.02	0.2	0.011	8.16	0.80
2	0.02	0.002	0.011	8.06	2.33
3	0.0002	0.02	0.00012	8.04	0.89
4	0.02	0.2	0.00104	9.08	2.80
5	0.002	0.002	0.00012	9.36	1.20
6	0.0002	0.2	0	9.70	0.24
7	0.0002	0.0002	0	9.82	1.02
8	0.02	0.02	0	11.06	4.05
9	0.002	0.2	0	10.50	1.56

Rates were calculated for data from the 13th day of testing.

Tests were also conducted using UO<sub>2</sub> powder samples, 45-105 μm size, treated to reduce the surface to stoichiometric, and which had BET surface area of 254 cm<sup>2</sup>/g. Dissolution

rates, calculated using the BET SA, for the same conditions as tests 1 and 6 were 0.097 and 0.19 mg/m<sup>2</sup>d respectively.

The data for pellets do not show any systematic variation with oxygen or carbon dioxide content; except for condition 6, which gave a dissolution rate for the pellet that was about 5 times lower than expected if we consider the data found for the crushed samples, there is a suggestion of an increase in dissolution rate as pH increases. The average rate (based on geometric surface area of pellets) is 1.23 mg/m<sup>2</sup>d for total carbonate between 0.2 and 20 mmol/L. If we divide this result by 3 to adjust for the difference between average BET surface area and geometric surface area for pellet-size material, we find an average dissolution rate of 0.4 mg/m<sup>2</sup>d. This compares with the average dissolution rate found by de Pablo et al /1997/ for 100–300 μm size powdered uranium dioxide of 0.8 mg/m<sup>2</sup>d for carbonate + bicarbonate between 0.1 and 10 mmol/L.

Steward and Weed /1994/ present results from a matrix of flow-through dissolution tests at 25, 50, and 75°C and various carbonate and oxygen concentrations and pH values. Material used was a polycrystalline UO<sub>2</sub> with grain size of 1 to 2 cm prepared at PNL in the 1960's for use in physical properties measurements. The material was stated to have "dislocation substructures, i.e., low-angle grain boundaries." The large grain size and the defect structures may influence dissolution rates, so care must be taken when comparing results for this material with uranium dioxide which has average fuel characteristic grain size of 5 to 10 μm. Dissolution rates were calculated using an assumed surface area, which is not given in the text and cannot be deduced from the data given. The paper by Nguyen et al /1992/ is cited, but the data are not discussed, even though there is overlap in conditions for the experiments and Steward and Weed /1994/ probably used the same equipment in some cases. Results of the individual tests are given below. (The 3 tests labelled "U9MM50" are duplicates of the same conditions). Tests have been grouped by temperature as the first sorting parameter and then by decreasing carbonate content, and finally by decreasing oxygen content. The pH for the tests was varied independently from the carbonate content, which will be unlikely to occur under natural disposal conditions. This independent variation of pH will complicate interpretation of the results.

Test	Temp °C	carbonate mmole	oxygen atm	pH	Dissolution rate mg/m <sup>2</sup> d
U8HH25	25	20	.20	8.7	2.42
U9HH25	25	20	.20	9.4	6.72
U10HM25	25.8	20	.02	10.1	1.87
U8HL25	25	20	.002	8.0	0.216
U10MH25	25	2	.20	9.3	9.34
U9ML25	25	2	.002	9.0	1.52
U10LH25	25	0.2	.20	9.0	2.55
U8LM25	25.8	0.2	.02	7.8	0.120
U10LL25	26.1	0.2	.002	9.3	0.233
U10HL50	50	20	.002	9.9	4.60
U9MM50	50	2	.02	8.9	12.3
U9MM50	50	2	.02	8.8	7.96
U9MM50	50	2	.02	8.9	10.4

To be contd.

Test	Temp °C	carbonate mmole	oxygen atm	pH	Dissolution rate mg/m <sup>2</sup> d
contd.					
U10HH75	75	20	.20	10.3	77.4
U8HH75	75	20	.20	8.5	93.8
U8HM75	75	20	.02	8.5	5.11
U10HL75	75	20	.002	9.8	9.00
U9MH75	75	2	.20	9.6	23.3
U10LH75	75	0.2	.20	9.5	6.48
U8LH75	75	0.2	.20	9.1	10.9
U10LM75	75	0.2	.02	9.7	9.21
U8LL75	75	0.2	.002	8.7	0.51

We will consider first the 25°C data. Based on the work of de Pablo et al /1997/ we would expect to see a clear decrease in dissolution rate with decreasing carbonate + bicarbonate content in the tests. The data given above are too scattered to see a clear dependence on carbonate content. There is an indication of a decrease in dissolution rate with decreasing oxygen content at constant total carbonate, but again, the trend is far from clear – compare, for example, tests with the same carbonate content, but oxygen of 0.02 and 0.002 atm. If the data above are compared with results for similar conditions used by Nguyen et al /1992/, the case for dependence of dissolution rate on oxygen content becomes even less clear.

The data from tests at 50°C are insufficient to define any relationship of dissolution rate with oxygen or carbonate content. The triplicate tests at 2 mmolar carbonate indicate a range of a factor of 2 in results at constant conditions. The rates found are within a factor of 2 to 4 of those found by de Pablo et al. for 45°C and similar carbonate contents.

The data for 75°C show the expected decrease in dissolution rate with decreasing carbonate content at constant oxygen pressure for  $p = 0.2$  atm. The results for test U8LL75 is far lower than would be expected due to variation in oxygen content alone, and suggests that the result may be erratic. For  $p = 0.02$  atm, the results for total carbonate of 20 and 0.2 millimolar are within a factor of 2, which was the range found for constant conditions at 50°C. The case for a primary dependence of dissolution rate on oxygen content at 75°C is very tenuous based on these data alone. Steward and Weed /1994/, however, conclude that there is a dependence of dissolution rate on  $[O_2]^{1/2}$  based on multivariate regression of all of the data. They also cite an average dissolution rate of 4.3 mg/m<sup>2</sup>d for all of the data.

Gray et al /1993/ report results from testing of spent fuel and unirradiated UO<sub>2</sub>. The spent fuel results will be discussed in the next section. The unirradiated UO<sub>2</sub> was crushed to 44 to 105 μm size and part of it oxidized to make a thin layer of U<sub>3</sub>O<sub>8</sub> on the surface of the UO<sub>2</sub> particles. BET surface areas of both oxidized and unoxidized materials were 270 cm<sup>2</sup>/g.

Test conditions were

Sample	[Na <sub>2</sub> CO <sub>3</sub> + NaHCO <sub>3</sub> ] (millimolar)	O <sub>2</sub> atm	pH	Temp. °C
Unirradiated UO <sub>2</sub> , U <sub>3</sub> O <sub>7</sub> , and U <sub>3</sub> O <sub>8</sub>	20	0.2	8.0-8.2	23
Unirradiated UO <sub>2</sub> and U <sub>3</sub> O <sub>7</sub>	0.2	0.003	9.8-10.2	23

Normalized dissolution rates for UO<sub>2</sub> and U<sub>3</sub>O<sub>7</sub> at O<sub>2</sub> = 0.2 atm converged to about 2.5 mg/m<sup>2</sup>d after 50 days. At O<sub>2</sub> = 0.003 atm, U<sub>3</sub>O<sub>7</sub> rates started at 3 to 4 times higher than UO<sub>2</sub> rates, but UO<sub>2</sub> rates increased with time, while U<sub>3</sub>O<sub>7</sub> rates stayed about constant. Rates after 100 days were 1.5 mg/m<sup>2</sup>d for oxidized and 1.0 mg/m<sup>2</sup>d for unoxidized. Comparing data from the tests at the two different oxygen concentrations and for oxidized versus unoxidized materials, Gray et al /1993/ concluded that air oxidation has no appreciable effect on the long-term rate of dissolution of spent fuel and UO<sub>2</sub> so long as U<sub>3</sub>O<sub>8</sub> is not formed. They suggest that one possible explanation is that the oxide layer formed by air oxidation is different from that formed in water, or that the oxidation process involved in dissolution contains two steps, only one of which is rate limiting.

The final set of data from which a dissolution rate of uranium dioxide can be extracted is that of Ollila /1995/. The work in this report was designed to measure solubility, so the data are for long time periods and represent solutions at steady-state concentrations. The only dissolution rate data that can be extracted are for pretreatment of unirradiated fuel pellets that will be used in tests under anoxic conditions. Pretreatment consisted of ten periods of one day each in 100 ml of solution in a 150 ml bottle, and is believed to represent the removal of a partially oxidized surface layer from the pellet. Tests were done in a nitrogen glovebox using deaerated solutions. Dissolution rates were calculated assuming geometric surface area for the pellet. Solutions used were deionized water, sodium bicarbonate solution (1 to 10 mmol/L), "Allard" groundwater, and a synthetic bentonite-equilibrated water. For the removal of the presumed oxidized layer, there was no difference in dissolution rate as a function of solution composition. Dissolution rates began at about 24 mg/m<sup>2</sup>d and decreased to about 2.4 mg/m<sup>2</sup>d at the second day, followed by a slow decrease to 0.5 to 0.7 mg/m<sup>2</sup>d for day 10. To convert these rates to equivalent BET-based data for pellets, divide the results by 3 to 4. Data for the final pretreatment dissolution periods seem to be reasonably equivalent to those obtained under flow-through test conditions, since the test period was short and the solution volume to pellet surface area was large. This would indicate a dissolution rate under anoxic conditions, based on BET surface area, of about 0.2 mg/m<sup>2</sup>d, with no evidence for dependence of the dissolution rate on solution composition, including carbonate content.

## 5 Spent fuel

The majority of spent fuel dissolution tests have been done under static conditions, with the aim of describing the long-term release of fission products and actinides from the solid to the solution phase. A review of some of the tests is given in Forsyth and Werme /1992/ and in Gray and Wilson /1995/. Some testing has also been done using flow-through test methods to investigate the initial release rate of fission products such as Cs, Sr, and Tc, to investigate the effect of oxidation state on the dissolution rate of the matrix, and to try to determine the effects of oxygen and carbonate on the initial dissolution rate of the fuel matrix.

Gray and Strachan /1991/ present results for two long-term, flow through dissolution tests using ATM 105 (BWR, 28 MWd/kgU) and ATM 106 (PWR, 43 MWd/kgU). The samples had been crushed to pass through a 'sieve' with 32  $\mu\text{m}$  openings and pretreated with 0.1 N HCl to remove the surface grain boundary material. The surface area of the materials was calculated assuming spherical particles in size increments of 0.5  $\mu\text{m}$  and averaging the values based on results of size fraction measurements. The calculated surface area was then multiplied by 2 to take into account surface roughness. The calculated surface area value is not given in the paper. Dissolution rates in aerated DIW were calculated for the two fuels to be

ATM 105, 75–150 days interval: 2 to 2.2  $\text{mg}/\text{m}^2\text{d}$

ATM 106, 100–175 days interval: 1.2 to 1.3  $\text{mg}/\text{m}^2\text{d}$

Gray et al /1992/ conducted flow-through dissolution tests using spent fuel from the PWR Calvert Cliffs (ATM103), 33 MWd/kgU, with fission gas release of 0.25%. The fuel was removed from the cladding, crushed and sieved to pass a 32  $\mu\text{m}$  screen. The sieved fraction was then treated to remove fine particles by adding dilute ( $10^{-4}\text{M}$ )  $\text{Na}_2\text{CO}_3$ , stirring and agitating with ultrasonic, which caused the fines to float so that they could be decanted. This treatment was repeated several times, and finally the fuel particles were rinsed with DIW to remove the bicarbonate. The final particle size was 10 to 15  $\mu\text{m}$ . The geometric surface area was calculated to be 287  $\text{cm}^2/\text{g}$  and a factor of 3 was used to multiple this value by to account for roughness. This gave a "BET equivalent" surface area of 860  $\text{cm}^2/\text{g}$ . [This would be 0.086  $\text{m}^2/\text{g}$ ].

Solution flow rates were usually 0.2 ml/min. as in Wilson and Gray /1990/; [U] versus flow rate was found to be linear over a range of 2 to 15 ml/min. The solution concentration at 0.2 ml/min. was 300 ng/ml (0.3 ppm) as compared to 0.120 ppm for the  $\text{NaHCO}_3$  solution in Wilson and Gray /1990/. Three parameters were varied – pH, temperature, and carbonate + bicarbonate concentration – with the atmosphere held constant at 20%  $\text{O}_2$ . Results were

Temperature °C	[CO <sub>3</sub> <sup>-</sup> + HCO <sub>3</sub> <sup>-</sup> ] millimolar	pH	Dissolution rate mg/m <sup>2</sup> d
25	20	8	3.45
	20	9	2.83
	2	10	2.04
	0.2	10	0.413
50	2	9	6.1 (average of 3)
75	20	10	11.6
	0.2	8	8.60 (average of 2)

Gray et al /1992/ conclude that the dissolution rate depends mainly on temperature and only weakly, if at all, on pH and carbonate + bicarbonate content. These conclusions were based on a multivariate regression analysis of all of the data; the low value at 25°C and 0.2 mmol/L carbonate was not discussed.

Steward and Gray /1994/ provided additional results from flow-through tests of the same fuel type as those presented in Gray et al /1992/, but in this case with oxygen controlled at lower level than atmospheric. The results for the previously reported tests from Gray et al /1992/ for spent fuel and from Steward and Weed /1994/ are also given in the Steward and Gray /1994/ paper, along with the additional information that the unirradiated UO<sub>2</sub> tested by Steward and Weed /1994/ was in the form of pieces about 1 cm across. This suggests that a geometric surface area may have been used in the calculations of dissolution rates. The results for the newly reported tests from Steward and Gray /1994/ are listed below; tests number 1 through 9 were those reported in Gray et al /1992/.

Run No.	Temp. °C	Carbonate mmol/L	Oxygen %	pH	Dissolution rate, mg/m <sup>2</sup> d
12	25	20	2	10.0	2.05
14	23	20	0.3	8.0	2.83
19	21	2	0.3	9.0	1.87
10	27	0.2	2	8.0	1.79
17	19	0.2	0.3	10.0	0.51
18	50	20	0.3	10.0	1.04
20	75	20	2	10.0	4.75
13	77	20	2	8.0	2.89
15	74	20	0.3	10.0	0.69
11	78	0.2	2	10.0	1.49
16	78	0.2	0.3	8.0	1.98

If the data given above are compared with those for O<sub>2</sub> = 0.2 atm, it is clear that there is a dependence of dissolution rate for spent fuel on oxygen concentration at 75°C, but there is no evidence for such a dependence at 25°C. This point was confirmed by Steward and Gray /1994/ by changing the [O<sub>2</sub>] for flow-through tests at each temperature while the test was running. Rates of dissolution increased with increasing temperature, but the effect was small, indicating a low activation energy for dissolution. Steward and Gray /1994/ calculate an activation energy of 6.9 to 7.7 kcal/mol. Multivariate regression

analysis showed a slight dependence of dissolution rate on carbonate content, but no dependence on pH for the range of  $8 \leq \text{pH} \leq 10$ .

The dissolution rate data reported in Steward and Gray /1994/ and in Gray et al /1992/ show considerable scatter. In addition, it is questionable whether multivariate regression analysis is valid, because several of the experimental parameters should be interdependent. Visual inspection of the data above suggest a good dependence of dissolution rate on carbonate content at constant oxygen content, except for the two tests run at 75°C and 0.003 atm oxygen (tests 15 and 16). Given the fairly clear increase of dissolution rate with increasing temperature, comparison of the test 15 rate with that of test 14 at 23°C suggests that the result for test 15 is abnormally low. Also, if one considers variation of dissolution rate with oxygen concentration at constant temperature and carbonate content, the case is clear only for the change in oxygen from 0.2 to 0.02 atm at 75°C. For other conditions, the data show both increases and decreases as oxygen content is changed at constant temperature and carbonate content. This is particularly clear if one looks at the changes in oxygen from 0.02 to 0.003 atmospheres; compare, for example, the results from tests 11 and 16, and from tests 12 and 14.

Gray et al /1993/ report results of tests on spent fuel (ATM 105, BWR Cooper Plant, 31 MWd/kgU, 0.6% fission gas release) crushed into particles of 700 to 1700  $\mu\text{m}$  size and part of it oxidized to  $\text{U}_4\text{O}_{9,x}$  with grain cores remaining  $\text{UO}_2$ . Part of both fractions (as received and oxidized) was crushed to give single grain material, with grain size 15 to 25  $\mu\text{m}$ . Surface area of grain-size fractions was calculated to be 910  $\text{cm}^2/\text{g}$  for oxidized and 980  $\text{cm}^2/\text{g}$  for unoxidized; "particle" fraction surface areas were estimated to be 15 and 17  $\text{cm}^2/\text{g}$ , respectively.

The spent fuel was tested in 2 mmol/L sodium bicarbonate/ carbonate solution at pH 8.8 and temperature of 50°C. The atmosphere used had normal atmospheric oxygen content. The dissolution rates found for spent fuel grains, both oxidized and unoxidized, were  $R = 6 \text{ mg}/\text{m}^2\text{d}$ . For spent fuel particles,  $R$  started higher for oxidized particles, but rates for both oxidized and "as received" particles converged to about 25  $\text{mg}/\text{m}^2\text{d}$  after about 40 days. The higher rate for particles was interpreted by Gray et al /1993/ as probably due to underestimation of normalized surface area ( $A$ ) because grain boundaries were not included in the estimate. If we consider only the grain-size material, the results report here for ATM 105 BWR fuel are in excellent agreement with those reported by Gray et al /1992/ for ATM 103 PWR fuel at 50°C, 0.2 atm oxygen, and 2 mmol/L carbonate.

Gray and Thomas /1994/ reported results from flow-through testing of spent fuel ATM 106 PWR fuel with 50 MWd/kgU burnup and 18% fission gas release with grain size 7 to 17  $\mu\text{m}$ . Results from Gray et al /1993/ for ATM 105 BWR fuel were repeated in this paper, together with new data for Tc. Fuels were tested as grains and as particles (size 700 to 1700  $\mu\text{m}$  aggregates of grains) in "as received" form and after oxidizing to  $\text{U}_4\text{O}_{9,x}$ . One sample of each fuel was also oxidized to  $\text{U}_3\text{O}_8$ . Testing of ATM 106 was done at 25°C, air atmosphere plus 11,000 ppm carbon dioxide to stabilize the pH at 8.0 in 20 mM  $\text{NaHCO}_3$ . Testing of ATM 105 had been done at 50°C at pH 8.8 in 2 mM  $\text{NaHCO}_3$ .

As discussed above, ATM 105 had not shown a difference in dissolution rates of U for "as received" fuel and fuel oxidized to  $\text{U}_4\text{O}_{9,x}$  grains or particles. ATM 106 did show a difference between oxidized and "as received material". For grains, the "as received" material dissolved at about 2  $\text{mg}/\text{m}^2\text{d}$  for U, while the oxidized material dissolved about 5 times faster. Particles of "as received" ATM 106 dissolved at 20  $\text{mg}/\text{m}^2\text{d}$ , while the oxidized particles dissolved about 10 times faster. The faster rates for particles as opposed to grains is believed to be due to underestimation of the surface area of the particles

because the near-surface grain boundaries are not included in the available surface. The difference in dissolution rate for oxidized versus not-intentionally-oxidized fuel for ATM 106, which was not seen for ATM 105, was interpreted by Gray and Thomas /1994/ to be due to the higher fission gas release and more open structure of the grain boundaries in the ATM 106 fuel.

Le Lous et al /1998/ conducted multicomponent tests using spent fuel with combinations of granite, sand plus 10% clay, granite groundwater, and synthetic clay-water, in autoclaves at 90°C and 40 bars. The spent fuel was crushed to produce a 50 to 250 µm size fraction; the atmosphere used was Ar-H<sub>2</sub>-CO<sub>2</sub>. Le Lous et al /1998/ used the <sup>90</sup>Sr activity measured in the solution samples (FIAP) over the period from the end of the 3rd week through the end of the experiment (11 weeks) to calculate dissolution rates for the fuel. [Note: The FIAP for Sr was initially much higher, but decreased during the first few weeks, indicating a rapid dissolution followed by precipitation/sorption somewhere in the system. This casts considerable doubt on the validity of the "dissolution" rates calculated later in the experiment.]

Calculated results for each spent fuel system were

- |             |                          |             |                          |
|-------------|--------------------------|-------------|--------------------------|
| (1) g + ggw | 0.74 µg/m <sup>2</sup> d | (2) c + ggw | 0.37 µg/m <sup>2</sup> d |
| (3) c + cgw | 3.33 µg/m <sup>2</sup> d | (4) g + cgw | 3.37 µg/m <sup>2</sup> d |

where g = granite, c = sand + 10% clay, ggw = granite groundwater, and cgw = clay groundwater.

These calculated dissolution rates based on <sup>90</sup>Sr for long term exposure at 90°C are at least 3 orders of magnitude less than those reported by Steward and Gray /1994/ for the initial dissolution rate for spent fuel at 75°C and oxygen atmospheric content of 0.003 atm.

Wilson /1990/ reports the results from leaching of spent fuel samples in dilute groundwater. Data for cycles 4 and 5, which represent results after 2 years of previous leaching cycles, show an increase in concentration over a 50 day period from an early measured value of about 0.5 ppm to a value of about 1 ppm. If this is assumed to be indicative of dissolution of a fresh UO<sub>2</sub> surface, a dissolution rate can be calculated. The H. B. Robinson fuel sample weighed 81 g, and the solution volume was 250 ml. Thus, the amount of UO<sub>2</sub> dissolved was 125 µg over approximately 50 days. Using Forsyth's /1995/ values for spent fuel surface area of 72 cm<sup>2</sup>/g, we estimate the fuel surface area to be 5832 cm<sup>2</sup> or 0.58 m<sup>2</sup>. Converting to dissolution rate in mg/m<sup>2</sup>d, we find 4.3 x 10<sup>-3</sup> mg/m<sup>2</sup>d. Since the solution concentration was 0.5 ppm after 5 to 7 days, the initial dissolution rate for these tests was much higher than the dissolution rate after some U was in solution. The first sample was taken at 7 days, and gives an average dissolution rate over 7 days of about .03 mg/m<sup>2</sup>d.

Grambow et al /1990/ suggest that the release rate of <sup>90</sup>Sr may provide a better estimate of the long term degradation of the spent fuel matrix than measurements based on uranium itself. This is because uranium concentration in solution is limited by solubility, even in solutions that contain bicarbonate ion. Wilson /1990/ reports a release rate of <sup>90</sup>Sr of approximately 1.5 x 10<sup>-7</sup> parts of the inventory in the test per day, with 80% of the <sup>90</sup>Sr recovered in solution samples. This compares with about 75% and 60% of the U recovered in cycles 4 and 5 in solution samples. The <sup>90</sup>Sr release rate would correspond to a matrix "dissolution" rate of about 0.02 mg/m<sup>2</sup>d, or a bit less than the initial rate of U dissolution found in these tests, but about 5 times higher than the rate estimated for the period from 7 to 57 days from U in solution. This may be due to inhibition of U

dissolution through back reaction onto the fuel surface even in the early stages of fuel-water interaction, long before the steady-state uranium concentrations have been reached.

Grambow et al /1990/ selected a value of  $3 \times 10^{-7}$  as the fraction of the  $^{90}\text{Sr}$  inventory dissolved per day to represent the long term behavior of spent fuel in tests conducted at Studsvik for SKB under oxic conditions (water with normal air atmosphere above it). This translates to a dissolution rate of .04 mg/m<sup>2</sup>d for the fuel matrix. This is two times higher than the value found by Wilson /1990/. Grambow et al /1990/ note that the release rate of  $^{90}\text{Sr}$  under anoxic conditions (oxygen excluded from the test vessel atmosphere) was about 10 times lower than that under oxic conditions. This would correspond to a dissolution rate or degradation rate of the fuel matrix of 0.004 mg/m<sup>2</sup>d. Note that this does not correspond necessarily to zero oxygen concentration in solution, because oxygen may be formed *in situ* by the radiolysis of water. This estimate of dissolution rate under anoxic conditions is in good agreement with that calculated by Le Lous et al /1998/ based on  $^{90}\text{Sr}$  under anoxic conditions.

## 6 Discussion and conclusions

Studies of dissolution rates of SIMFUEL, unirradiated uranium dioxide, and spent fuel show a wide range of results. In many cases it is not possible to determine whether the results are affected by oxidation on the surface of the solid starting materials. The effect of build-up of U in solution on lowering the dissolution rate cannot be ruled out even in flow-through tests, if it has not been shown that the product of the flow rate and concentration of uranium is constant over a range that includes the flow rate used in the experiments. Variation of several experimental parameters at once and the artificial fixing of pH in systems where there is covariance of pH with concentration of solution species further complicates the interpretation of the experimental data.

For SIMFUEL, there is a range of a factor of 100 in dissolution rates (0.04 to 4.6 mg/m<sup>2</sup>d) for conditions that should be expected to give similar results. In contrast, for conditions where a difference in rate might be expected, little or none was found. The ambiguity in the condition of the starting solid surface, the effects of solution saturation, and the actual redox condition of some of the tests makes it impossible to compare the SIMFUEL dissolution rate data to those for unirradiated uranium dioxide and spent fuel.

Dissolution rate data for unirradiated uranium dioxide seem to provide a clearer picture than those for SIMFUEL, especially if allowance is made for the possible differences in dissolution rate caused by the use by some workers of material with unusually large grain size. There are, however, many ambiguities concerning the effects of oxygen in the system on dissolution rate and the effects of variation of solution chemistry at constant bicarbonate concentration.

The lowest dissolution rates found for unirradiated UO<sub>2</sub> were those for dissolution in dilute NaClO<sub>4</sub>, with or without oxygen in the system, and those for anoxic conditions with any solution chemistry. These rates were in close agreement within the range of 0.1 to 0.2 mg/m<sup>2</sup>d. In contrast to this, changing the dissolution medium from a synthetic dilute groundwater with about 2 mM bicarbonate concentration to a pure solution of NaHCO<sub>3</sub>, produced a factor of 40 increase in dissolution rate. In NaClO<sub>4</sub>, the dissolution rate was shown to depend on pH and [O<sub>2</sub>] for pH up to 6.7, but to be independent of these parameters for pH above 6.7.

The study that appears to provide the best controlled case for variations of dissolution rate with environmental parameters is that of de Pablo et al /1997/. They showed that for a solution of NaHCO<sub>3</sub> in dilute NaCl, the dissolution rate at 25°C and air atmosphere increased from 0.2 to 2 mg/m<sup>2</sup>d as NaHCO<sub>3</sub> increased from 0.1 to 10 mM. At constant NaHCO<sub>3</sub> = 1 mM, dissolution rate increased from 0.8 to 2.4 mg/m<sup>2</sup>d as temperature increased from 25°C to 60°C. At higher bicarbonate concentrations, the effect of temperature was larger.

Dissolution rate data for tests using spent fuel show a rather surprising similarity in results. Tests with deionized water gave dissolution rates in air atmosphere of 1 to 2 mg/m<sup>2</sup>d. Tests in 0.2 to 20 mM NaHCO<sub>3</sub> at 25°C gave dissolution rates of 0.4 to 3.5 mg/m<sup>2</sup>d with no dependence on oxygen concentration at 25°C, but with a documented increase in dissolution rate with increase in [O<sub>2</sub>] at 75°C.

Long-term dissolution rates of spent fuel have been estimated using  $^{90}\text{Sr}$  release data for anoxic conditions by two groups and the same results of  $0.004 \text{ mg/m}^2\text{d}$  was found. Using the same approach for tests conducted under oxic conditions gave an estimated dissolution/degradation rate of  $0.02 \text{ mg/m}^2\text{d}$  to  $0.04 \text{ mg/m}^2\text{d}$  for spent fuel. An estimate based on early rise in  $[\text{U}]$  in solution for spent fuel tests under oxic conditions gave an estimated dissolution rate of  $0.004 \text{ mg/m}^2\text{d}$  for a 50 day period following an initial 7 day dissolution, which occurred at an average rate of  $0.03 \text{ mg/m}^2\text{d}$ .

The long-term dissolution rate, which is affected by the presence of U in solution, is the rate that is appropriate for performance assessment calculations. This is the rate that should be measured in new experiments that use a method that can measure the rate of degradation of the U matrix, rather than relying on the use of Sr, which may or may not be released at the same rate as the matrix dissolves. A test using a fuel pellet with normal enrichment of  $^{235}\text{U}$  and a solution with differing levels of  $^{238}\text{U}$  can be used to make the direct measurement of dissolution rate by measuring the 235/238 ratio in solution as a function of time and environmental parameters.

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