

**Dissolution of unirradiated UO_2
and UO_2 doped with ^{233}U under
reducing conditions**

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January 2005

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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 authors and do not necessarily coincide with those of the client.

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Abstract

Experiments have been conducted to determine an upper limit to the dissolution rate of UO_2 under reducing conditions appropriate to those in a geologic repository for spent fuel disposal in Finland and Sweden. Test duration ranged from 52 to 140 days. The total amount of U recovered in each test was converted into a dissolution rate per year for the sample. The dissolution rate was then used to calculate an expected lifetime for the samples under the test conditions. The dissolution rate did not depend on the length of the testing period. Rather, the dissolution rate appeared to decrease as the samples were exposed to sequential testing periods. This indicates that the results are still influenced by transient effects such as high-energy surface sites, which implies that the dissolution rates measured are upper limits. The sample lifetimes calculated from the last two testing periods, which had a total of 269 days, ranged from 7 to 10 million years. There was no indication of an effect of alpha radiolysis on the dissolution rate results for samples with doping levels of 0, 5, and 10% ^{233}U .

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1 Introduction

Posiva in Finland and SKB in Sweden are developing plans for disposal of spent fuel that results from the use of UO_2 fuels in nuclear reactors to generate electric power. At the end of its use, the fuel contains about 4% by weight of fission products and about 1% of actinides with atomic number higher than 92, the atomic number of U. In order to assess the safety of the geologic repository we need to be able to predict how much of the spent fuel might dissolve if it comes in contact with water many years after its disposal.

The dissolution rate of spent fuel can be affected by a number of factors. The radiation from decay of radioactive elements in the fuel can produce radiolysis products in water, which can lead to more rapid dissolution of the fuel as compared to dissolution in the absence of radiolysis products. The matrix of spent fuel is UO_2 , which is thermodynamically stable under reducing conditions, but which oxidizes to produce a surface layer of UO_{2+x} when the $[\text{O}_2]$ is higher than 10^{-65} atm /Shoesmith, 2000; Rai et al. 1990/. The UO_{2+x} contains U(VI) and/or U(V), valence states that give a much higher solution concentration of U than the valence state U(IV), which is found in pure UO_2 . Thus, the dissolution rate of spent fuel in experimental studies will be a strong function of the $[\text{O}_2]$ in the test system. The presence of fission products and actinides in solid solution in the spent fuel matrix might affect the dissolution rate of spent fuel. It is not possible to predict based on available data whether the elements in solid solution would lead to an increase or a decrease in dissolution rate.

A repository constructed at 500 m depth in the granitic bedrock of Finland or Sweden will provide a reducing environment. Any oxygen introduced during repository construction will be rapidly consumed by biological activity and/or reactions with reduced species such as Fe(II) in the minerals present in the host rock or the repository backfill and buffer materials. The spent fuel will be disposed of in a canister with a corrosion-resistant outer layer of copper (50 mm thick) and containing an insert of cast iron to provide structural strength. The copper will ensure that water does not reach the interior of the waste package until a very long time has past. A probabilistic analysis of canister corrosion under repository conditions resulted in the prediction that the time for first penetration of a canister would be somewhere between 400,000 and 1,000,000 years after disposal /SR-Can, 2004/. After water enters the canister, the cast iron insert will corrode by anaerobic corrosion with the production of H_2 gas. The gas pressure will increase until it equals the hydrostatic pressure of the repository – approximately 50 MPa. The redox conditions will be those of the Fe/FeO buffer, sufficiently low to ensure that the spent fuel matrix will be thermodynamically stable.

It is impossible to test directly the dissolution rate of spent fuel under the conditions expected at the time of first water contact hundreds of thousands of years after disposal. The fuel that we have available to test has radiation levels that are much higher than those that are relevant and the radiation type is different from that which will be important in the long term. The level of radioactivity in spent fuel decreases with time. The fission products decay by emission of β and γ radiation, while the decay of the actinides is dominated by α decay. The total radiation emitted by spent fuel in the first hundred years after discharge from the reactor is predominantly due to β and γ radiation; for later times, the dominant activity is α -radiation /Shoesmith, 2000/. Since we do not have 100 year old spent fuel available to test, we must use substitute materials that can give insight into the effects of α -radiation on the dissolution rate of spent fuel. We have chosen to use UO_2 doped with ^{233}U to simulate

the degree of α -radiation that will be present in spent fuel at 3,000 and 10,000 years after disposal. Note that this level of α -radiation is about an order of magnitude higher than that which will be present at the time of first water contact with the fuel.

It is difficult, if not impossible, to establish in a laboratory the redox conditions appropriate to the geologic repository. The best inert atmosphere glove boxes have $[O_2]$ on the order of 0.1 ppm. That means that the O_2 partial pressure is 10^{-7} atm, a value that is very far from the 10^{-65} atm needed to ensure the thermodynamic stability of UO_2 . We can lower the oxygen fugacity in test solutions by using buffer materials, but this can also interfere with the reactions we wish to monitor. Even in the presence of buffers, stray oxygen that diffuses into the test solution might react with the UO_2 before it can react with the buffer. This means that great care must be used in the interpretation of experimental results and that measured $[U]$ in solutions will be upper limits compared with those to be expected in the repository /Werme et al. 2004/.

The conditions inside the disposal canister caused by corrosion of iron can be simulated by adding metallic iron to the test system. In general, the proportions of Fe relative to UO_2 in the test system will be less than those for disposal conditions, so the effects of this difference must be estimated. We may investigate the controlling reactions for the system UO_2 -Fe- H_2 by doing experiments that contain only UO_2 -Fe(II) or UO_2 - H_2 . These experiments will help us to understand the relative reaction rates in the system and help us to evaluate the effects of different mass ratios of UO_2 -Fe.

Experiments using freshly prepared crystalline UO_2 may contain some amorphous material if the samples were prepared by precipitation from solution and the material was not subsequently heat-treated. Crystalline UO_2 prepared by sintering at high temperatures will not contain amorphous material, but if the material has been exposed to air even for a few minutes, the outer surface of the material will contain UO_{2+x} . Even if the crystalline UO_2 does not contain higher valence states of U, the structure of the crystalline material may contain defects and high-energy surface sites that will react faster than the bulk material. The higher valence state material and the high-energy surface sites can be removed through sequential dissolution periods, but since the solubility of UO_2 is very low under reducing conditions, this process can be very time-consuming. Defects present in the bulk of the UO_2 lattice can probably never be removed during low temperature dissolution tests. This could be expected to increase the reaction rate over that expected for perfectly crystalline material.

2 Previous Work

The experiments discussed in this report represent the continuation of work begun during the In Can Processes Project supported by the European Commission under the 5th Framework Programme. In this section we will summarize the results of testing of UO₂ samples under reducing conditions. Complete details of the previous testing are given in /Ollila et al. 2003/.

Two types of samples were tested in parallel; all tests were conducted in duplicate. The samples consisted of fragments of unirradiated fuel pellets produced by ABB and samples doped with ²³³U produced by BNFL. The nominal isotopic composition of the samples is given in Table 2-1. The samples were gently crushed and sieved to give fragments in the size range 1.4 to 4 mm. Approximately 1 g of solid was used in each test.

Testing was conducted in a synthetic groundwater called “modified Allard groundwater”. The modification to the original recipe for Allard groundwater was made to ensure thermodynamic stability of the solution concentrations under reducing conditions. The water was prepared in an inert atmosphere (N₂) glove box. The water was conditioned with Fe strips to produce an equilibrium [Fe] in the solution and to control the redox state to the Fe/FeO buffer as well as possible. The composition of the modified Allard groundwater prior to conditioning with the Fe strips is given in Table 2-2.

Samples were pretreated before the start of the main testing to remove any surface material that contained higher oxidation states of U. Samples were placed on a silica saucer and then in a Nalgene bottle and covered with 30 ml of modified Allard groundwater. All work was conducted in a negative pressure inert atmosphere glove box. The solution was left for one or a few days and then changed for fresh solution. Samples were taken for U analysis at each changing to monitor the [U] in solution and, thus, the efficiency of the removal of oxidized material from the surface. After 12 days of pretreatment (7 solution changes and one bottle change) the samples were transferred to new saucers and bottles and an Fe strip was added to the solution. The samples were left for 7 days, then changed to new saucers and vessels with new solution and an Fe strip and left for another 7 days. Finally, samples were given their last pretreatment for a period of 17 days in new saucers and vessels with fresh pretreated modified Allard groundwater.

In the first pretreatment step [U] was as high as 50 to 100 ppb, decreasing with each subsequent change of solution to give 1 to 5 ppb in the last step without Fe strips. In the first week with an Fe strip, 5 of the 6 samples had [U] < 1 ppb, while one sample had 5 ppb. After the second week with an Fe strip, samples had [U] < 0.02 ppb in all cases. This was also the case for the final pretreatment with Fe. We concluded that any surface U with oxidation state higher than (IV) had been successfully removed.

Table 2-1. Isotopic composition of UO₂ samples, in percent.

Sample	[²³³ U]	[²³⁵ U]	[²³⁸ U]
0%	0	2.82	97.18
5%	5.0	4.5	90.5
10%	10.0	4.5	85.5

Table 2-2. Chemical composition of modified Allard groundwater with pH=8.8 (theoretical for $\log p\text{CO}_2 = -4$) /Vuorinen and Snellman, 1998/.

	mg/L	mmol/L
Na ⁺	52.5	2.3
Ca ²⁺	5.1	0.13
Mg ²⁺	0.7	0.03
K ⁺	3.9	0.10
SiO ₂	1.7	0.03
SO ₄ ²⁻	9.6	0.10
Cl ⁻	48.8	1.4
HCO ₃ ⁻	65.0	1.1

Testing of the pretreated samples was done using a method that used successive dilutions of the test solution at the start of the tests. The purpose of this procedure was to remove any traces of higher oxidation states of U that might have formed during the brief exposure of the samples to the 10^{-7} atm of O₂ in the glove box atmosphere during the changing of samples to new reaction vessels. The solution volume was initially 50 ml. After standing (covered) for 2 hr, 30 ml of solution was removed and replaced with fresh modified Allard groundwater. The 20 ml of “old” solution should have protected the samples from any significant contact with oxygen during the dilution step and the dilution would reduce the [U] in solution to 40% of its initial value. The dilution was repeated twice more at 30-minute intervals. After the 3rd dilution, a dose of U spike was added to the samples to give solution [U] of 0.4 ppb, consisting of 0.365 ppb ²³⁵U and 0.035 ppb ²³⁸U. After the spike addition, the solution was stirred and a sample taken to give the starting composition and concentration for the tests. If no further dissolution occurred after the initial pulse of oxidized material, the concentration of the solution before spike addition should have been 6.4% of the value of the solution after the first 2 hr contact period. Analyses of the samples showed that in some cases the predicted dilution of an initial pulse was occurring, while in other cases significant dissolution was occurring during the 30-minute contact periods. This suggests dissolution from high-energy surface sites, perhaps caused by the crushing of the samples to provide fragments.

The tests were conducted for 14 days with samples taken at the start of testing and then after 1, 4, 7, and 14 days of exposure. The change in isotopic composition of the solutions showed that all samples continued to dissolve during the 14 days of exposure; however, for the undoped samples the [U] in solution decreased with time indicating that precipitation was occurring as well as dissolution. The 10% ²³³U samples had higher [U] and lower 235/238 ratio than the 5% samples during the first 7 days of testing, indicating more dissolution during that period. At the end of 14 days, one each of the 10% and 5% samples had [U] < 0.02 ppb, while the duplicate of these samples had [U] of 0.3 and 0.24 ppb respectively. No firm conclusions could be drawn from these data.

A second cycle of testing using the same procedure gave rather high [U] (0.2 to 0.3 ppb) in the initial sample and had similar concentrations after each dilution step, indicating rapid dissolution of small amounts of U. The samples from exposure for 1, 4, and 7 days showed dissolution for the 10% samples greater than for the 5% samples, which were themselves greater than the undoped samples. After 14 days, the 10% and 5% samples gave similar [U] and 235/238 ratios, while the undoped samples showed lower [U] and higher 235/238. It would be tempting to interpret these results as showing increased dissolution due to alpha radiolysis effects.

At the end of the second cycle of testing, the remainder of the solution, the solid samples on their saucers, and the Fe strip were transferred to a new reaction vessel. The volume was returned to 50 ml and a new dose of spike was added to increase the total [U] by 0.4 ppb. A sample was then taken to determine the starting conditions. The measured starting conditions were consistent with those calculated from the day 14 results plus dilution of the solution and addition of spike, indicating no significant dissolution during the transfer of samples and setting up of the test continuation. Samples taken after one day of exposure showed slight decreases in [U] and no change in isotopic composition, indicating precipitation without significant dissolution. Samples taken after 4 days of exposure had [U] near the detection limit of 0.02 ppb. After 7 and 14 days of exposure, all samples had [U] < 0.02 ppb. To check on the actual [U], a further dose of spike was added to each sample. The measured 235/238 ratios were between 9 and 10, indicating that the final [U] before spike addition was on the order of 0.01 ppb. After 7 days of exposure, all samples again had < 0.02 ppb ²³⁸U.

In the final cycle of testing (after transfer of the solution from cycle 2 and restarting of the tests) there was no difference in behavior of the samples with and without ²³³U. This showed that alpha radiolysis was not the cause of the earlier differences in sample behavior, which fortuitously coincided with the level of ²³³U-doping. It seems more likely now that the differences in behavior were due to differences in the number of active high-energy sites that dissolved preferentially in the early stages of testing. The Fe strips used in the last tests were leached in NaHCO₃ under oxidizing conditions in an attempt to remove any U adhering to the Fe surface. Only very small amounts of U were recovered.

3 Results and Discussion

The samples from the In Can Processes project were left in the inert atmosphere glove box in storage until a new project would be started. The samples were on saucers in Nalgene vessels covered by conditioned modified Allard groundwater and with an Fe strip in the vessel. In this manner, the storage was actually the equivalent of a long duration experiment. On December 17, 2003, the solid samples were moved to new reaction vessels and a series of solution samples were prepared to investigate the progress of the dissolution process. Details of the sampling are in Appendix 1 together with the results of ICP-MS analysis conducted in January, 2004.

Solution samples that were acidified at the time of original sampling and analyzed two days later showed $[U] < 0.02$ ppb. In contrast to this, the remainder of the solution samples, which were acidified and stored for 3 weeks, all showed substantial amounts of U – ranging from 0.3 to 10.5 ppb ^{238}U . The highest concentrations were found for the samples that did not contain ^{233}U . There is no evidence of increased dissolution due to α -radiolysis in the solutions. Rather, there is an indication that dissolution and precipitation have been occurring during the 4 months of storage of the samples in solution. The material recovered from the acidified solution samples after storage is most likely due to dissolution of colloidal UO_2 that has precipitated from solution but has not yet grown to a large enough size to fall out of the liquid phase. Rinsing of the test vessels with deionized water and stripping of the vessels with 1 M HNO_3 gave recovery of U that was similar to that found in the acidified solution samples after 3 weeks of storage.

The vast majority of the U recovered was found as a precipitate or particles associated with the saucers. The saucers had a grayish-greenish precipitate on both the inside and outside surfaces. The total amount of U recovered from the acid stripping of the saucers was 0.42 to 1.15 μg , an amount that would not be sufficient to account for the obvious precipitate. It is most likely that the precipitate was due to some form of hydrous iron oxide. The U recovered probably is due to dissolution in the 1 M acid of small grains of solid that separated from the samples during handling and transfer operations. Thus, the total U that actually dissolved during the testing period is probably much less than the total U recovered at the end of testing.

The results from the 4-month storage experiment can be used to calculate an average dissolution rate for the samples during that time period. The dissolution rate can then be converted into an expected sample lifetime under the test conditions, assuming that the dissolution rate remains the same in the future as it was during the 4-month test. We have calculated the sample dissolution rate and lifetime in two ways: first, using the total U recovered (including material from the saucers), and second, using all U except that associated with the saucers. The results are given in Table 3-1. Regardless of the method used, there is no evidence of any effect caused by α -radiolysis. The lifetimes calculated based on total recovered U are between 0.2 and 0.7 million years, while those calculated from U recovery excluding the U associated with the saucers are between 0.6 and 20 million years.

After sampling on December 17, 2003, the solid samples were transferred to new saucers and new reaction vessels for a new period of storage under modified Allard groundwater and with a new Fe strip. The samples were left in the inert atmosphere glove box until February 9, 2004, at which time they were sampled. Details of the sampling and results of analyses are in Appendix 2.

Table 3-1. Four month leaching of samples after conclusion of In Can Processes tests. Leaching period from August 15 to December 17, 2003 (1/3 year).

Sample	Sample wt g	Σrecovered U, µg	Dissolution ppm/yr	Sample life 10 ⁶ yr	Exclude saucers	Dissolution ppm/yr	Sample life 10 ⁶ yr
10%–1	1.012	0.97	2.87	0.35	0.10	0.29	3.5
10%–2	0.9125	0.45	1.47	0.68	0.03	0.09	11.2
5%–1	1.0085	0.70	2.10	0.48	0.02	0.05	20.5
5%–2	0.9792	0.51	1.56	0.64	0.13	0.39	2.6
0%–1	1.0995	1.75	4.78	0.21	0.60	1.64	0.6
0%–2	1.0558	0.94	2.68	0.37	0.21	0.60	1.7

The solution (except for a few ml that were in the saucer) was transferred to a new vessel (V sample). The remaining solution in the saucer was transferred to a separate bottle (SAV sample). The saucer with the solid sample was transferred to a new bottle together with the same Fe strip and 30 of new modified Allard groundwater was added. The vessel was then closed and left to equilibrate.

The V and SAV samples were transferred out of the glovebox and acidified with 1 M HNO₃. Two of the SAV samples were filtered prior to acidification (one each of the 0% and 5% samples). Vessel rinsing and acid stripping was conducted as usual.

The samples were stored for about 3 weeks before aliquots were taken for ICP-MS analysis. Thus, any small particles or colloids in the solutions should have had adequate time to dissolve. Three 5-ml aliquots of the V samples were also taken for isotope dilution analysis to determine the [U] in the solution. The three samples were spiked with different amounts of spike solution so that 3 independent measurements of the [U] could be made. Data for the solution analyses and isotope dilution results are given in Appendix 2.

The [U] in the unspiked solution samples was below the ICP-MS detection limits of 0.02 ppb in all cases. The spiked samples all had both ²³⁵U and ²³⁸U above detection limits. This occurs because the spike contained at least 0.02 ppb of ²³⁸U and 10 times as much ²³⁵U. The data for individual measurements are in Appendix 2. Because the [²³⁸U] in the samples spiked to give 0.24 ppb total U in solution were very close to the detection limits, these data are less reliable than the results for spiking levels of 0.37 and 0.50 ppb total U. The average of all three determinations is given in Appendix 2; the more reliable estimate of [U] given by the average of the 2 higher spiking levels is given in Table 3-2. All determinations are in agreement with the original ICP-MS determination that the [U] is < 0.02 ppb. By using the isotope dilution method we have been able to increase the sensitivity of the measurement of [U] by a factor of about 10. There is no evidence of an effect of alpha radiolysis on [U] is solution.

Table 3-2. Concentration of U in solution at the end of the 52 day dissolution period based on isotope dilution analysis.

Sample	Average [U], ppb
Undoped – 1	0.0062
Undoped – 2	0.0030
5% ²³³ U–1	0.0030
5% ²³³ U–2	0.0020
10% ²³³ U–1	0.0009
10% ²³³ U–2	0.0027

Results for the filtered and then acidified saucer samples (SAV) had [U] < 0.02 ppb, while results for SAV samples that were not filtered before acidification showed measurable U. This suggests that the U in the unfiltered samples is due to colloids or small grains of the original sample being transferred along with the liquid phase during sampling. There is no sample representing the acid stripping of the saucers for this data set because the saucers were reused in the next testing period. Results for vessel rinsing and acid stripping of the vessel show lower [U] for this data set than for the first data set. Data for total recovery of U and calculated dissolution rate and sample lifetime are given in Table 3-3. These data should be compared to the results that exclude the saucer stripping in Table 3-1. In two cases (samples 10%–2 and 5%–1) the dissolution rates calculated from total release data for the 52 day period are higher than for the 4 month period. For the other 4 samples, the dissolution rates in the 52-day test were lower. There is no difference in the behavior of the samples that can be attributed to the presence of ²³³U in the samples.

Table 3-3. Total recovered U and sample dissolution rates for the 52 day dissolution period.

Sample	Sample wt g	Saucer U, ng	Rinse U, ng	Acid strip U, ng	Total U, µg
10%–1	1.012	1.3	2.8	9.4	0.013
10%–2	0.9125	3.2	5.1	4.9	0.013
5%–1	1.0085	4.0	4.1	2.3	0.010
5%–2	0.9792	< 0.02	3.8	2.0	0.006
0%–1	1.0995	5.6	5.9	11.1	0.023
0%–2	1.0558	< 0.02	3.4	6.8	0.010

Sample	Dissolution rate, ppm/yr	Sample life million yrs
10%–1	0.09	10.7
10%–2	0.10	9.9
5%–1	0.07	13.7
5%–2	0.04	24.2
0%–1	0.14	7.0
0%–2	0.07	14.8

The samples were left to equilibrate in the inert atmosphere glove box for a further 129-day period. Samples were taken on June 18, 2004 to monitor progress for the dissolution and total U release. Details are given in Appendix 3. At this sampling period the used saucers were also leached, ensuring that all U released from the samples would be included in the total. Samples of the solution were taken, acidified, and analyzed by ICP–MS for [²³⁸U]. Three aliquots of solution were also taken and spiked with a 10/1 mixture of ²³⁵U/²³⁸U so that the [U] could be measured by the isotope dilution method.

The solution samples for the 129-day leaching period, which used a previously used Fe strip, show measurable amounts of U in solution. This may be due to slower corrosion of the Fe, which already had a protective layer of corrosion products on its surface. Slower corrosion of Fe would provide lower amounts of H₂ in the system. Any trace amounts of O₂ that managed to diffuse through the plastic leaching vessels might be more likely to oxidize the UO₂ surface if the amount of H₂ in the system was low. The rinse and acid strip samples were similar to or lower than those for the previous 52-day leaching period.

The total amount of U recovered was dominated by the U from the saucers; however, the total recovered from the saucers was much less than for the first 4 month leaching period (Appendix 1 data) – 0.8 to 2.3 ppb versus 16 to 52 ppb.

The results of the isotope dilution analyses give [U] values for 5 of the samples that are in excellent agreement with the concentration measurement for the unspiked sample. The high value of 0.45 ppb ^{238}U found in the first ICP-MS measurement for sample 1–10 was not confirmed by the three measurements for spiked samples. The three spiked samples are in reasonable agreement for the calculated [U], but show wider dispersion in the results than for the other 5 samples. Both of these conditions suggest that the solution sample for 1–10 was heterogeneous. The high value of 0.45 ppb is most likely due to dissolution of colloidal material in the acidified sample prior to analysis. The rinse and acid strip data for sample 1–10 are lower than for other samples, suggesting that U in that sample was not able to precipitate as efficiently as in the other samples.

Table 3-4. Comparison of directly measured [^{238}U] and that calculated from the average of the three isotope dilution measurements.

Sample	[^{238}U] by ICP-MS, ppb	[^{238}U] by isotope dilution, ppb
1–10% ^{233}U	0.45	0.077
2–10% ^{233}U	0.08	0.059
1–5% ^{233}U	0.07	0.060
2–5% ^{233}U	0.03	0.029
1–0% ^{233}U	0.11	0.086
2–0% ^{233}U	0.02	0.022

Data for the directly measured [^{238}U] and the [^{238}U] calculated from the total [U] from the isotope dilution measurements are compared in Table 3-4. For the samples with the lowest [^{238}U] for the direct measurement by ICP-MS, the agreement between results for the two methods is excellent. For 3 samples, the agreement is good, but the direct ICP-MS results are slightly higher than the results calculated with the isotope dilution method. This suggests that even those three samples might have had some colloids present in the solution samples.

Data for total U release from the samples are given in Table 3-5. It can be seen that the saucer samples contain the highest U amount, but far less than for the first 4 month leaching period. The total amounts of U recovered are now quite similar for all samples, ranging from 24 to 61 ng for the 129-day leaching period. If we assume a constant dissolution rate, we can calculate that the dissolution rates (including the material recovered from the saucers) ranged between 0.07 to 0.16 ppm/yr. This translates into a sample lifetime under the test conditions of 6.1 to 14.2 million years. If we exclude the U recovered from the saucers, which may include particulate material that was never processed through the solution, we find an average dissolution rate of 0.01 to 0.066 ppm/yr corresponding to sample lifetimes ranging from 15 to 99 million years. Again, the differences between duplicate samples is larger than the differences between samples with different [^{233}U], indicating that defects in the samples such as high energy surface sites are much more important than any effects due to alpha radiolysis.

A final testing period for these samples was conducted between 16 June 2004 and 5 November 2004. This testing period involved the use of a fresh Fe strip. The tests were sampled on November 4 by taking a 5 ml sample of the solution, which was acidified and analyzed for [²³⁸U] on 9 November. The results of these analyses showed [²³⁸U] < 0.02 ppb in all cases.

Table 3-5. Total release of U for test period 9 February to 18 June, 2004. All units ng U unless otherwise noted.

Sample	Solution	Saucer	Rinse	Acid strip	Total
10%-1	15.73	33.5	1.54	1.37	52.1
10%-2	2.73	31.8	13.22	5.49	53.2
5%-1	2.47	29.0	4.93	3.84	40.2
5%-2	0.96	17.6	5.38	0.44	24.4
0%-1	3.40	47.9	4.29	5.85	61.4
0%-2	0.62	44.7	1.26	2.00	48.5

Sample	Weight, g	Dissolution rate, ppm/yr	Sample life million yrs
10%-1	1.0120	0.15	6.9
10%-2	0.9125	0.17	6.1
5%-1	1.0085	0.11	8.9
5%-2	0.9792	0.07	14.2
0%-1	1.0995	0.16	6.3
0%-2	1.0558	0.13	7.7

Without U from saucers.

Sample	Total U, ng	Dissolution rate, ppm/yr	Sample life million years
10%-1	18.6	0.052	19
10%-2	21.4	0.066	15
5%-1	11.2	0.032	32
5%-2	6.8	0.020	51
0%-1	13.5	0.035	29
0%-2	3.9	0.010	96

Sampling to terminate the tests was done on 5 November. Details of the samples taken are given in Appendix 4 together with the results of the solution analyses. The acidified solution samples that represent the bulk of the test solution showed measurable [²³⁸U]. This is probably due to a slight disturbance of some colloidal material from the saucers during removal of the solutions. As with previous testing periods, the largest amount of U was found associated with the saucers after the solid samples were removed (except for sample 2-5). Results for total U release, sample dissolution rates, and calculated sample lifetimes are given in Table 3-6.

Table 3-6. Total release of U for test period 18 June to 5 November, 2004. All units are in ng U unless otherwise specified.

Sample	Solution U, ng	Saucers U, ng	Rinse U, ng	Strip U, ng	Total U, ng
1-10	1.02	20.5	4.57	11.9	38.0
2-10	0.87	26.6	0.99	10.0	38.5
1-5	0.69	22.6	2.33	5.7	31.4
2-5	1.24	14.4	1.27	50.9	67.8
1-0	1.95	33.1	0.89	8.7	44.7
2-0	0.57	27.1	12.2	13.4	53.3

Sample	Original Solid, g	Total U, ng	Dissolution rate ppm/yr	Sample life million years
1-10	1.0120	38.0	0.098	10.2
2-10	0.9125	38.5	0.110	9.1
1-5	1.0085	31.4	0.081	12.3
2-5	0.9792	67.8	0.181	5.5
1-0	1.0995	44.7	0.106	9.4
2-0	1.0558	53.3	0.132	7.6

Without U from saucers

Sample	Original Solid, g	Total U, ng	Dissolution rate ppm/yr	Sample life million years
1-10	1.0120	17.5	0.045	22
2-10	0.9125	11.8	0.034	30
1-5	1.0085	8.7	0.023	44
2-5	0.9792	53.4	0.142	7
1-0	1.0995	11.6	0.027	37
2-0	1.0558	26.2	0.065	15

One sample, 2-5, which had shown the lowest total release (including material from the saucers) in the previous testing period showed the highest release in this period. It is possible that some colloidal material associated with the saucers from the previous testing period adhered to the solid sample when it was transferred to start the last testing cycle. This material could then have been processed through the solution phase and turned up on the vessel surfaces. Perhaps a better estimate of total release can be found by adding together the results of the last two testing periods for total U recovery, including the material associated with the saucers. These data are compared in Table 3-7. Total U release seems to be consistent for all samples and shows no indication of any influence of alpha radiolysis on the dissolution rate results.

The total release of U from Table 3-7 for the sum of the 129 and 140 day testing periods can be converted into a dissolution rate and sample lifetime for each of the samples. The results of these calculations are given in Table 3-8. The dissolution rates and sample lifetimes are very consistent for all samples. There is no suggestion of any effect of alpha radiolysis on the results.

Table 3-7. Total recovery of U from testing cycles 3 and 4 – 129 days + 140 days.

Sample	ng U, cycle 3	ng U, Cycle 4	ng U, cycle 3+4
1-10% ²³³ U	52.1	38.0	90
2-10% ²³³ U	53.2	38.5	92
1-5% ²³³ U	40.2	31.4	72
2-5% ²³³ U	24.4	67.8	92
1-0% ²³³ U	61.4	44.7	106
2-0% ²³³ U	48.5	53.3	102

Table 3-8. Dissolution rates and sample lifetimes for the last 269 days of testing.

Sample	Dissolution rate, ppm/yr	Sample life, million years
1-10% ²³³ U	0.12	8.3
2-10% ²³³ U	0.14	7.3
1-5% ²³³ U	0.10	10.4
2-5% ²³³ U	0.13	7.8
1-0% ²³³ U	0.13	7.6
2-0% ²³³ U	0.13	7.6

The iron strips used in the fourth cycle of testing were treated with 25 ml NaHCO₃ solution (250 ppm HCO₃⁻) under air atmosphere conditions after conclusion of the tests. The strips were held in solution for 11 days. A sample was taken for analysis after 4 days and after 11 days. As can be seen in Table 3-9, only very small amounts of U were recovered. This shows that the iron strips functioned to control redox and did not serve as a location for precipitation of dissolved U nor as a site for reduction of U (VI) that dissolved from the sample. Reduction of U (VI) and subsequent precipitation of U (IV) hydrous oxide as colloids seems to occur in the solution phase.

Table 3-9. Elution of U from iron strips.

Sample	4 day ²³⁸ U, ppb	11 day ²³⁸ U, ppb
1-10	< 0.02	0.02
2-10	< 0.02	< 0.02
1-5	< 0.02	0.02
2-5	0.03	0.02
1-0	< 0.02	< 0.02
2-0	0.03	0.03

4 Conclusions

Results obtained from four long-term dissolution tests of UO_2 containing 0, 5, and 10% ^{233}U allow us to draw the following conclusions.

1. Early in the history of testing these samples, relatively large amounts of U were recovered by dissolving material associated with the saucers that the samples had been resting on. This material represents colloids that formed by precipitation of U that had been dissolved from the samples and grains that have dislodged from the surface of the crushed sample fragments. Some of the colloidal material may also be U sorbed onto the greyish-green precipitate that is most probably hydrous iron oxide.
2. Dissolution rates estimated from total release of U indicate that release in the early stages of testing is dominated by high-energy surface sites and loosely attached grains that were dislodged from the solid sample during crushing.
3. During these long-term dissolution tests no results that could be attributed to the effects of alpha radiolysis in the leaching solution could be found.
4. Solution concentrations of U were higher when an Fe strip containing corrosion products from use in previous tests was used to control redox state than when a fresh Fe strip was used. This suggests that the amount of corroding Fe is important in acting as a scavenger of tramp oxygen that diffuses into the reaction vessel from the 10^{-7} atm of O_2 that are present in the glove box atmosphere. The active agent may be the H_2 that is generated during anaerobic corrosion of Fe.
5. Sample lifetimes under the conditions of these tests based on total release of U ranged from 7 to 10 my for the sum of the total release from the third and fourth cycles of testing (269 days).

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6 Acknowledgements

The authors take pleasure in thanking Ms R Zilliacus and Ms M Lipponen for performing the ICP-MS analyses.

Dissolution period 15 August to 17 December, 2003

Method and sampling procedure.

The samples used in the final series of tests in the In Can Processes project were transferred on their saucers into new containers. New modified Allard groundwater (30 ml) that had been conditioned with iron strips was added to each container and an iron strip was placed in each container. The samples were left in the inert atmosphere glove box until we were ready to start a new test series.

On December 17 the containers were opened and a series of solution samples were taken so that the progress of the solid sample dissolution history would be complete.

The solution samples were prepared as follows:

1. The leaching solution was stirred with a jet of pipet very carefully (only from the surface). Four samples (3 ml) were taken from the leaching solution. The samples were transferred out of the glove box. They were acidified immediately – two samples with HNO₃ (1 M), two samples with HCl (1 M). The ICP-MS analyses were performed two days later.
2. The rest of the leaching solution was pipetted very carefully and only from outside the saucer to a new bottle. (The idea was to avoid mixing the solution in the saucer with the solution outside the saucer, and in this way to avoid the transfer of small fine particles of the original solid from the saucer.) The remaining solution (2 ml) in the saucer was removed and discarded. The UO₂ fragments were transferred to a new saucer that was placed in a new experimental vessel with 30 ml Allard groundwater and an iron strip (the start of the new dissolution period). The “old” saucer was transferred to a new Nalgene bottle. The “old” leaching solution, saucer and exp. vessel were transferred out of the glove box.
3. The “old” leaching solution was acidified (1 M HNO₃) and kept in a refrigerator over the Christmas vacation period (3 weeks).
4. The “old” experimental vessel was rinsed twice with 10 ml deionized water. The vessel had visible greyish precipitate on the bottom and on the side walls. The rinse solution was acidified (1 M HNO₃) and kept in a refrigerator over Christmas. The precipitate seemed to be easily dissolved in the acidified rinse solution.
5. Deionized water (20 ml) was added to the Nalgene bottle with the “old” saucer. The saucer in the bottle was rinsed gently. The rinse solution was left in the bottle with the saucer and acidified (1 M HNO₃). The saucer had on the surfaces, both on the outside and on the inside, visible greyish, greenish, precipitate. The saucer looked greenish throughout. The precipitate seemed to be dissolved easily in the rinse solution. The rinse solution was kept in a refrigerator over Christmas. This rinse solution probably has original UO₂ particles that dissolved during the storage period; however, it was analyzed because the precipitates on the surfaces were so visible.
6. 30 ml 1 M HNO₃ was added to the “old” experimental vessel. The vessel was kept in a refrigerator over Christmas.

Samples were taken from the solutions – 3, 4, 5 and 6 – on January 12 and analysed with ICP-MS.

Solution analysis results for the 4 month dissolution period August 14–December 17, 2003.

Solution samples (step 1) were all less than detection limits (< 0.02 ppb).

Sample 3 = Acidified remainder of the leaching solution

Sample 4 = Vessel rinse, acidified

Sample 5 = Acidified rinse solution from the saucers

Sample 6 = Acidified strip of the vessel

Samples 3–6 were stored for 26 days prior to analysis

Test number	²³³ U (%)	Original wt. (g)	Sample 3 ²³⁸ U, ppb	Sample 4 ²³⁸ U, ppb	Sample 6 ²³⁸ U, ppb	Sample 5 ²³⁸ U,ppb
1–10	10	1.0120	0.75	0.48	1.69	35.0
2–10	10	0.9125	0.35	0.10	0.36	16.9
1–5	5	1.0085	0.29	0.08	0.15	29.2
2–5	5	0.9792	3.18	0.19	0.53	16.3
1–0	0	1.0995	10.48	2.95	6.91	52.3
2–0	0	1.0558	4.11	0.46	2.37	33.3

Total ²³⁸ U, ng				
Test #	Solution*	Rinse	Acid strip	Saucers
1–10	23	10	51	749
2–10	11	2	11	361
1–5	9	2	5	626
2–5	95	4	16	349
1–0	314	63	207	1,119
2–0	123	10	71	713

* Solution calculated for total of 30 ml original volume.

Dissolution period 19 December, 2003 to 9 February, 2004 (30 ml modified Allard groundwater, Fe strip, no spike)

Method and sampling procedures

1. The saucer with the solid samples and the Fe strip were transferred with the help of tweezers to a new experimental vessel (60 ml). The remaining leaching solution, that was left in the saucer, was pipetted to a separate bottle (~4 ml). -----> SAV solution.
A new portion of Allard groundwater (30 ml) was added to the experimental vessel and the vessel was closed.
2. The “old” leaching solution (about 25 ml) was poured into a new bottle ---- > V solution.
3. The SAV and V samples, and the experimental vessel were transferred out of the glove box.

The V samples were acidified (1 M HNO₃).

The SAV samples were acidified. Some SAV samples were filtered prior to the addition of the acid:

1–10 SAV, 2–10 SAV: not filtered

1–5 SAV: not filtered, 2–5 SAV: filtered

1–0 SAV: not filtered, 2–0 SAV: filtered

4. The “old” experimental vessel was rinsed with 5 ml deionized water three times. ----> R solution.

The rinse solution (15 ml) was acidified (1 M HNO₃).

5. 30 ml 1 M HNO₃ was added to the ‘old’ exp. vessel. ----> S solution
6. 5 ml samples were taken on February 11 from the V-, SAV-, R- and S solutions for ICP-MS analysis. (Measurements were done on 1–3 March, 2004).
7. Three 5 ml aliquots were taken from the remaining V sample. These were spiked with a dose of U containing $^{235}\text{U}/^{238}\text{U} = 10.14$. The doses contained sufficient U to give 0.24, 0.37, and 0.50 ppb ^{235}U respectively added as spike. The spiked aliquots were measured for [^{235}U] and $^{235}\text{U}/^{238}\text{U}$ with ICP-MS. This provides three independent determinations of the concentration of U in the solutions prior to spike addition.

Results of solution analyses for the 52 day leaching period, 19 December, 2003 to 9 February, 2004.

Test	^{233}U %	Original solid, g	SAV samples ^{238}U , ppb	R samples ^{238}U , ppb	S samples ^{238}U , ppb
1–10	10	1.0120	0.27	0.16	0.27
2–10	10	0.9125	0.69	0.29	0.14
1–5	5	1.0085	0.92	0.25	0.07
2–5	5	0.9792	< 0.02	0.23	0.06
1–0	0	1.0995	1.35	0.38	0.36
2–0	0	1.0558	< 0.02	0.22	0.22

Analyses of V samples after spike addition.

Test	Spike = 0.24 ppb ²³⁵ U		Spike = 0.37 ppb ²³⁵ U		Spike = 0.50 ppb ²³⁵ U	
	²³⁵ U, ppb	²³⁵ U/ ²³⁸ U	²³⁵ U, ppb	²³⁵ U/ ²³⁸ U	²³⁵ U	²³⁵ U/ ²³⁸ U
1-10	0.25	6.05	0.38	9.89	0.51	10.01
2-10	0.25	8.76	0.40	9.48	0.50	9.74
1-5	0.26	5.90	0.38	9.37	0.53	9.66
2-5	0.26	8.86	0.39	9.78	0.50	9.69
1-0	0.26	8.53	0.37	8.73	0.50	9.03
2-0	0.25	9.04	0.37	9.47	0.49	9.51

All V samples had [U] < 0.02 ppb when analyzed without spike addition.

Concentrations of U in solution before addition of spike to the "V" samples after 52 day dissolution period.

Undoped	²³⁵ / ²³⁸ measured	Conc U ppb	Average [U] ppb
1-0-0.24	8.53	0.0046	0.0057
1-0-0.37	8.73	0.0061	
1-0-0.50	9.03	0.0063	
2-0-0.24	9.04	0.0030	0.0030
2-0-0.37	9.47	0.0027	
2-0-0.50	9.51	0.0034	
5% doped			
1-5-0.24	5.90	0.0189	0.0083
1-5-0.37	9.37	0.0033	
1-5-0.50	9.66	0.0027	
2-5-0.24	8.86	0.0038	0.0026
2-5-0.37	9.78	0.0015	
2-5-0.50	9.69	0.0025	
10% doped			
1-10-0.24	6.05	0.0187	0.0069
1-10-0.37	9.89	0.0011	
1-10-0.50	10.01	0.0007	
2-10-0.24	8.76	0.0044	0.0032
2-10-0.37	9.48	0.0030	
2-10-0.50	9.74	0.0024	

Dissolution period 9 February 2004 to 18 June 2004. Total time = 129 days, 30 ml modified Allard groundwater, same saucers and Fe strip as for leaching period 2

Sampling procedures

1. The leaching solution was pipetted with caution to a new bottle (V sample).
2. The solid samples were transferred to new saucers, new reaction vessels, and 30 ml of modified Allard groundwater was added. A new Fe strip was added to each vessel.
3. The V samples and the used experimental vessels were transferred out of the glove box. The V samples were acidified (1 M HNO₃).
4. The used experimental vessel was rinsed with 5 ml deionized water three times. The three rinse solutions were combined (15 ml) and acidified (1 M HNO₃). R samples.
5. The used saucers were placed in a new bottle. 20 ml of 1 M HNO₃ was added. SA samples.
6. 30 ml of 1 M HNO₃ was added to the old experimental vessel. S samples.
7. 5 ml of each sample was taken for ICP-MS analysis.
8. The remaining V samples were split into 3 parts. A dose of U solution with $^{235}\text{U}/^{238}\text{U} = 10.4$ was added to each sample. The dosing rates were sufficient to give 0.26 ppb ^{235}U , 0.40 ppb ^{235}U , and 0.52 ppb ^{235}U . These samples were analyzed for [^{235}U] and $^{235}\text{U}/^{238}\text{U}$.

Results of solution analyses for the 129 day leaching period from 9 February, 2004 to 18 June, 2004.

Test	^{233}U , %	Original Solid, g	V samples ^{238}U , ppb	SA samples ^{238}U , ppb	R samples ^{238}U , ppb	S samples ^{238}U , ppb
1-10	10	1.0120	0.45	1.44	0.09	0.04
2-10	10	0.9125	0.08	1.37	0.76	0.16
1-5	5	1.0085	0.07	1.32	0.30	0.12
2-5	5	0.9792	0.03	0.80	0.33	0.01
1-0	0	1.0995	0.11	2.33	0.28	0.19
2-0	0	1.0558	0.02	2.17	0.08	0.06

Analysis of V samples after spike addition

Test	Spike, 0.26 ppb ^{235}U		Spike, 0.40 ppb ^{235}U		Spike, 0.52 ppb ^{235}U	
	^{235}U , ppb	$^{235}\text{U}/^{238}\text{U}$	^{235}U , ppb	$^{235}\text{U}/^{238}\text{U}$	^{235}U , ppb	$^{235}\text{U}/^{238}\text{U}$
1-10	0.26	2.83	0.40	3.27	0.55	4.10
2-10	0.26	3.03	0.40	4.25	0.54	4.76
1-5	0.27	3.07	0.39	4.21	0.53	4.73
2-5	0.26	5.05	0.40	5.44	0.52	6.86
1-0	0.25	2.37	0.42	3.36	0.54	3.69
2-0	0.25	5.66	0.40	6.79	0.53	7.04

Concentrations of U in solution before addition of the spike to the “V” samples after 129 days of dissolution using old Fe strips. Calculated from the measured 235/238 ratio after spike addition.

Undoped	235/238 measured	Conc U ppb	Average [U] ppb
1-0-0.26	2.37	0.0883	0.089
1-0-0.40	3.36	0.0839	
1-0-0.52	3.69	0.0943	
2-0-0.26	5.66	0.0217	0.023
2-0-0.40	6.79	0.0213	
2-0-0.52	7.04	0.0249	
5% doped			
1-5-0.26	3.07	0.0667	0.066
1-5-0.40	4.21	0.0631	
1-5-0-52	4.73	0.0668	
2-5-0.26	5.05	0.0295	0.032
2-5-0.40	5.44	0.0390	
2-5-0.52	6.86	0.0288	
10% doped			
1-10-0.26	2.83	0.0792	0.089
1-10-0.40	3.27	0.0989	
1-10-0-52	4.10	0.0904	
2-10-0.26	3.03	0.0721	0.069
2-10-0.40	4.25	0.0657	
2-10-0.52	4.76	0.0696	

Dissolution period 18 June to 5 November, 2004. Method and sampling procedure

November 4

1. A 5 ml sample was pipetted from each of the leaching solutions and acidified in preparation for ICP-MS analysis. Analyses were done on November 9.

November 5

2. The remainder of the leaching solution (about 25 ml) was pipetted with caution to a new bottle (V solutions). The V solutions and the experimental vessels were transferred out of the glove box. The V samples were acidified (1 M HNO₃). The solid sample was transferred to a storage location in waiting for new experiments to start.
3. The saucer was placed in a new bottle. 20 ml of 1 M HNO₃ was added. (SA samples).
4. The reaction vessels were rinsed with 5 ml deionized water 3 times. The rinse solution (15 ml) was transferred to a new bottle and acidified (1 M HNO₃). (R samples).
5. 30 ml of 1 M HNO₃ was added to the rinsed experimental vessel. (S samples).

November 11

6. 5 ml samples were taken from each of the V, SA, R, and S solutions for ICP-MS analysis. Analyses were performed on November 12.

ICP-MS results for [²³⁸U] for the leaching period 18 June to 5 November, 2004.

Sample	V, solution ²³⁸ U, ppb	SA, saucer ²³⁸ U, ppb	R, rinse ²³⁸ U, ppb	S, strip ²³⁸ U, ppb
1-10	0.04	0.88	0.26	0.34
2-10	0.03	1.15	0.06	0.29
1-5	0.03	1.03	0.14	0.17
2-5	0.05	0.65	0.08	1.54
1-0	0.08	1.61	0.06	0.28
2-0	0.02	1.32	0.79	0.44

The 5 ml samples taken on November 4 all < 0.02 ppb

Sample	Solution ²³⁸U, ng	Saucers ²³⁸U, ng	Rinse ²³⁸U, ng	Strip ²³⁸U, ng	Total ²³⁸U, ng
1-10	0.88	17.7	3.94	10.3	32.7
2-10	0.75	22.9	0.86	8.6	33.1
1-5	0.63	20.6	2.12	5.2	28.5
2-5	1.13	13.1	1.16	46.3	61.6
1-0	1.90	32.2	0.86	8.5	43.4
2-0	0.55	26.4	11.87	13.1	51.9

ISSN 1404-0344

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