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Dissolution rates of unirradiated UO_2, UO_2 doped with ^{233}U, and spent fuel under normal atmospheric conditions and under reducing conditions using an isotope dilution method

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1 Introduction

Sweden and Finland plan to dispose of spent fuel from commercial nuclear power plants in deep underground repositories sited in granitic rocks. The fuel assemblies will be placed in canisters consisting of an outer corrosion-resistant copper shell and an inner cast iron form that gives mechanical strength and reduces void space in the canister. The canister will be placed in a disposal borehole lined with compacted bentonite blocks. After sealing of the borehole, groundwater seepage will saturate the bentonite. The water flow path and transport mechanism between the host rock and the canister will be via diffusion through the swollen bentonite. Any oxygen trapped in the repository will be consumed by reaction with the host rock and/or pyrite in the bentonite, giving long-term conditions with low redox potentials. Under these conditions, uranium dioxide – the matrix of unirradiated fuel – is a stable phase.

To evaluate the safety of repository disposal, the implementing agencies in Sweden (Svensk Kärnbränslehantering AB) and Finland (Posiva) need to understand the expected performance of the spent fuel under repository conditions after the canisters have failed and the fuel might come in contact with groundwater. While pure uranium dioxide is stable under the expected repository conditions, two things might make spent fuel less stable and cause dissolution of the matrix to occur. First, the spent fuel contains fission products and higher actinides, so the fuel is uranium dioxide containing about 4% impurities, some in solid solution in the UO_2 matrix and some present as separate phases. This might cause the fuel to undergo a type of zone refining process in the repository by which the fuel dissolves and recrystallizes as a pure phase (or a phase containing those elements that are in true solid solution in the matrix), excluding the elements that are present as segregated phases. During this type of process, the [U] in solution would remain constant, but the fuel matrix would dissolve and recrystallize, releasing the elements from the segregated phases to solution.

A zone-refining process might also occur with pure uranium dioxide if the solid sample contains defects in the crystal structure. Dissolution and reprecipitation might eliminate defects in the structure and produce a solid with a lower Gibbs free energy. The defect-free solid would probably have a lower enthalpy than the original, defect-containing solid, but it would have a lower entropy. Since a lower Gibbs free energy would be produced by a lower enthalpy, this favors the process, but the decrease in entropy counteracts this. A test to see whether the pure UO_2 undergoes a type of zone refining to eliminate defects would allow us to evaluate this process.

The isotope dilution technique, which is used in geochemistry to measure the concentration of elements in natural samples, can be used to determine whether a system of solid in contact with solution is continuing to dissolve and reprecipitate even though the solution concentration is constant, or even decreasing. One takes a solid of known isotopic composition and exposes the solid to a solution that contains an appropriate concentration of the element in question, but with an isotopic composition far from that of the solid. In our case, we take unirradiated UO_2 containing about 3% ^{235}U and put it into a solution that contains either depleted U (nearly pure ^{238}U) or highly enriched ^{235}U ($^{235}U/^{238}U=10$). By measuring the [U] in solution and the ratio of $^{235}U/^{238}U$ in the solution sample we can calculate whether there is material being added to solution from the solid phase. This gives us an unambiguous answer to whether the solid is continuing to dissolve, even if the [U] in solution is constant or decreasing. For each measurement point we have a starting [U] and isotopic composition of the system based on the last measurement point. From this we calculate the initial amounts of ^{235}U and ^{238}U in the solution. When the next sample is taken and the [U] and $^{235}U/^{238}U$ in the solution are measured, we use the isotopic ratio to calculate how much ^{235}U and ^{238}U have been added to the solution.

$$(^{235}U/^{238}U)_{measured} = (^{235}U_{inital} + {}^{235}U_{dissolved})/\ (^{238}U_{inital} + {}^{238}U_{dissolved})$$

We compare the results of the calculations with the measured concentration of each isotope. This lets us see whether precipitation is occurring. For example, if [U] is constant, but the $^{235}U/^{238}U$ in the solution sample shows that new solid has been added to the solution, then precipitation has occurred to balance the addition of new U, indicating that the solid is undergoing a type of zone-refining process.

The second process that may affect spent fuel performance in the long term in the repository is the effect of radiation from the fuel itself. The radiation will produce some level of radiolysis products in the groundwater that contacts the fuel. This may cause oxidation of the fuel surface and increase the tendency for the fuel matrix to dissolve. In the long term, it is alpha decay that is the dominant radioactive process in the fuel. The beta and gamma radiation that are present in spent fuel samples that are available for laboratory testing will have diminished to low levels.

To investigate the effects of alpha radiation on dissolution of UO_2, we have used samples doped with a relatively short-lived isotope of U, ^{233}U, with a half-life of 1.6×10^5 y. The doping levels were chosen to simulate the alpha activity in “average” spent fuel at times of 3000 and 10,000 years after disposal. Comparison of results of testing using the isotope dilution method of undoped UO_2 and doped UO_2 will allow us to determine the effect, if any, of alpha radiolysis in solution on the rate of processing of solid through the solution phase under conditions of interest.

Tests with spent fuel have also been conducted to answer the following questions. 1) Does the presence of impurities in the spent fuel cause it to continue to dissolve even though the matrix UO_2 should be stable? And 2) does the presence of beta and gamma radiation increase the rate of processing of solid through the solution phase?

This report contains the results of testing of unirradiated UO_2 fuel pellet materials, specially prepared unirradiated UO_2 fuel pellet materials that also contained 5 or 10% ^{233}U, and spent fuel. The unirradiated UO_2 was tested under both air atmosphere and under actively reducing conditions. The work with the ^{233}U-doped materials concentrated on actively reducing conditions with a limited amount of work in air atmosphere to evaluate the quality of the pellets. The work on spent fuel was conducted under anaerobic conditions only.

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2 Dissolution of unirradiated UO_2 fuel pellet material

2.1 Tests under air atmosphere conditions

The first series of tests conducted were done under air atmosphere conditions. The purposes of these tests were to provide experience for the laboratories in using the isotope dilution method, refine the experimental procedures prior to starting tests under reducing conditions, and to be able to compare the results from two laboratories using the same test procedure. Tests were conducted at VTT in Finland and at AEA Technology in Harwell, England.

Tests were done using fuel pellets supplied by commercial nuclear fuel manufacturers. Based on our experience with testing of spent (irradiated) fuel under air atmosphere conditions, we expected the steady-state solution concentrations to reach 2 ppm U in solutions of the type we were planning to use within a few months and to remain at this concentration for long periods of time /Wilson, 1990; Forsyth and Werme, 1992/. Some tests of spent fuel at long contact times had shown higher concentrations of U, but there was no consistent trend and the data were scattered /Forsyth and Werme, 1992/.

Testing of spent fuel samples in air atmosphere at room temperature conducted by /Wilson, 1990/ showed initial [U] that was higher than the long-term [U]. That means that an initial pulse of U was released to solution and during subsequent exposure in the solution, some secondary phase formed that had a lower steady-state [U] than that found in the initial sample. In later testing, care was taken to keep a small amount of solution covering the samples when they were transferred to new reaction vessels. When this was done, the initial test sample had lower [U] than subsequent samples. These results were interpreted to be caused by the formation of an oxidized layer on the spent fuel samples when they were in direct contact with air. Covering the samples with a small amount of solution limited the access of oxygen to the samples and so limited the extent of possible oxidation during sample handling.

Based on the results discussed above, we designed a pretreatment for our samples to remove any layer of oxidized material that might have formed on the samples during storage and handling prior to the start of the isotope dilution experiments. The steady-state surface of UO_2 in dilute bicarbonate solutions exposed to air is slightly oxidized and is characterized by the formula UO_{2+x}. /Shoesmith, 2000/ identified the phase as $UO_{2.33}$, one of the known stoichiometric oxides of uranium. The data from XPS (X-ray Photoelectron Spectroscopy) spectra that were used to identify the phase are also consistent with $UO_{2.25}$, or even with a non-stoichiometric value for x /Shoesmith, personal communication, 2003/. The ion released to solution contains U(VI), which lowers the average oxidation state of the solid surface. The steady-state condition is restored by incorporation of oyxgen dissolved in the solution into the solid phase, returning the surface to its steady-state value of UO_{2+x}. Oxygen that is removed from solution must be replace by transfer of oxygen molecules from the atmosphere above the solution across the atmosphere/solution boundary. Wilson's results suggest that this transfer of oxygen across the solution/atmosphere boundary and subsequent oxidation of the surface is slower than the rate of oxidation of the solid surface when exposed to an air atmosphere /Wilson, 1990/. The pretreatment steps consisted of a series of exposures of the solid to test solutions with the same composition as intended for the isotope dilution tests, with exposure times of 1 to a few days. Details of the pretreatment are given in Appendix A.

For the isotope dilution method to function, the original test solution must contain U with an isotopic composition that is different from the solid samples to be tested. For the tests using air atmosphere, we used depleted U as the solution spike. We selected three different initial concentrations of U – 0.5, 1.0, and 2.0 ppm. Tests were conducted in a synthetic dilute sodium bicarbonate groundwater, "modified Allard groundwater", the composition of which is given in Appendix B. The modification of the groundwater from the original Allard recipe was to ensure thermodynamic stability of the solution under the conditions of the tests.

The solid samples used were commercial fuel pellets; those used at AEA Technology were purchased from BNFL and contained 4.5% ^{235}U, while those used at VTT came from ABB and contained 2.8% ^{235}U. Since spent fuel testing had not shown any indication of differences due to the manufacturer of the fuel, we did not expect any differences in the behavior of these materials.

Samples were gently crushed to produce as much of the material as possible in the size range 1.4 to 4 mm. This is the predominant size of fragments that spent fuel spontaneous separates into when removed from cladding after normal irradiation times and conditions. AEA Technology prepared samples from three different pellets (pellet numbers 5, 6, and 7). VTT prepared fragments from several pellets and also used whole pellets as samples. Tests used 1 gram of fragments of solid in 25 ml of modified Allard groundwater; tests using pellets contained 2 pellets in 71 ml of liquid. All tests were conducted with nominal solid surface area to solution volume ratio (SA/V) of 10 m^{-1} based on geometric surface area. After the tests were started, samples were taken at increasing time intervals to follow the dissolution process. Details of the test procedure are given in Appendix A. Results for the AEA Technology tests for solutions started with 2 ppm U are shown in Figure 2-1. Data for tests started in 0.5 and 1.0 ppm U showed similar dissolution rates. These data have been reported in the first 2 annual reports of the project.

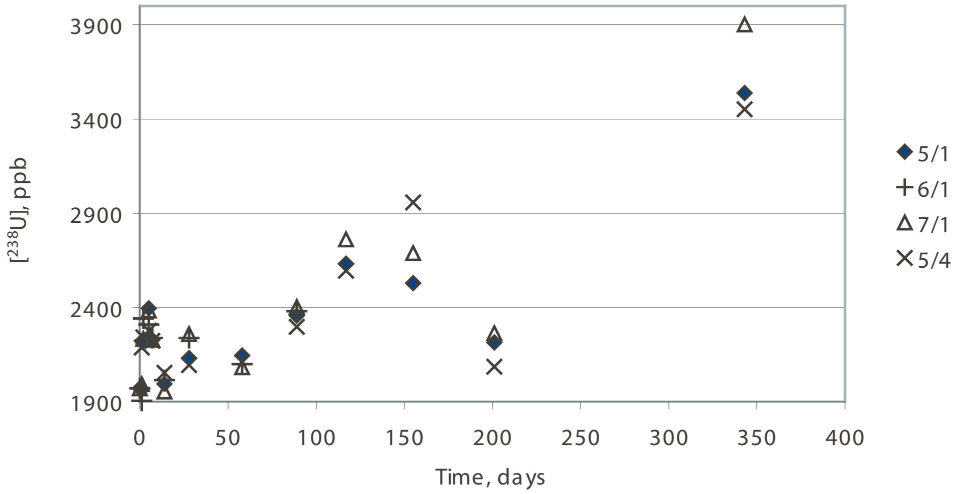

Figure 2-1. Results of testing of fuel pellet fragments in modified Allard groundwater in contact with air atmosphere. Test conducted at AEAT, Harwell.

In the early stages of testing at AEA Technology it became clear that the analytical laboratory that was analyzing the uranium samples was having difficulty in producing reliable results. After several consultations, the quality of the analyses improved (samples taken at days 58 through 117) and the measured [U] was in good agreement with that calculated from the isotope dilution method (see Appendix C). The last three sampling periods showed a wide spread in [U] measured and in one case showed much less U in the reported [U] than was predicted from the isotope dissolution calculation. This was initially interpreted as precipitation; however, at the next sampling the [U] was much higher and agreed with the results of the isotope dilution calculation. This suggested that problems with analytical quality had returned. When test termination data showed that precipitation from the solutions had been minimal, it was concluded that the data from day 201 contained a large, systematic analytical error. Despite these analytical problems, we can see that the solutions after 343 days of testing had reached about 4 ppm in total [U] and that there was not a great deal of difference in results between the 3 pellets that were used. That means that pellets of unirradiated UO_2 taken from the same fabrication batch can be expected to behave in a similar fashion.

VTT conducted 5 tests at each initial [U] in solution; three tests were 1 gm of fragments in 25 ml modified Allard groundwater and 2 tests contained 2 intact pellets in 71 ml of groundwater. Data for tests started with 2.0 ppm depleted U in the groundwater are given in Appendix C. The quality of the analytical data was much better at VTT. There was only one data set that showed suspicious results that indicated a systematic error. That was the data for $^{235}U/^{238}U$ for day 130. These data show indications of interference in the ^{235}U signal leading to a ratio measurement that is too high by about 10%. In subsequent data treatment, these data are not included.

Data for the first cycle of testing (Figure 2-2) showed a much faster rate of dissolution for the VTT solids than had been found for the Harwell solids. After 2 to 3 months all of the VTT samples had reached higher solution concentrations than the Harwell samples had reached after more than 11 months. This meant that the solution isotopic composition for the VTT samples had become close to that of the solid sample and the isotope dilution calculation was very sensitive to small analytical errors or uncertainties. Because of this, the tests were terminated and three tests were restarted with higher initial [U] in the solution: one test each of pellets and fragments was started with 6.6 ppm ^{238}U and one test with pellets was started with 9.3 ppm ^{238}U.

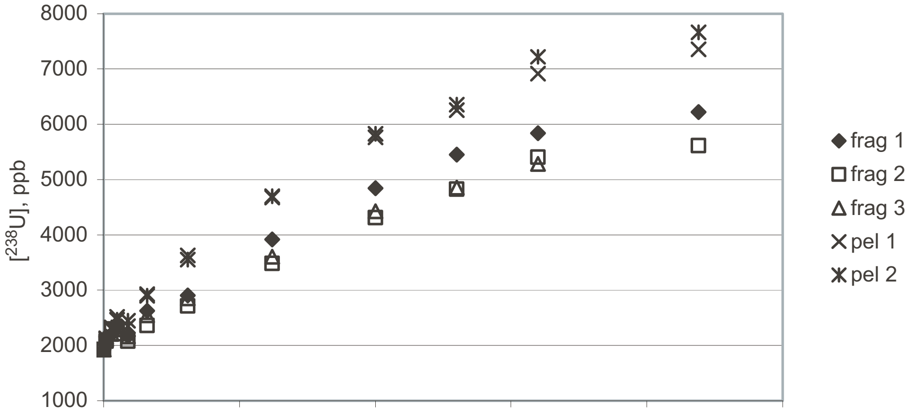

***Figure 2-2.** Results from testing of unirradiated fuel pellets and pellet fragments in modified Allard groundwater. Tests conducted at VTT.*

The tests using intact pellets showed higher dissolution rates than the tests using fragments, despite the fact that the geometric SA/V for all tests was the same. Agreement between results for each type of test was very close, suggesting that the differences in dissolution rates must have something to do with active surface sites that were more effectively removed during pretreatment of the fragments as compared to the pellets. /Shoesmith, 2000/ has suggested that enhanced non-stoichiometry of UO_2 samples, due to incomplete sintering of pellets during manufacture, can change the kinetics of reaction of the solid with dissolved oxygen. The incomplete sintering would leave defect sites in the lattice that might be more reactive than normal lattice sites. For the pellets, the travel path length for water and dissolved oxygen to reach the defect sites would be longer than for the pellet fragments, and the effect of these defects might be expected to last longer. If we assume the samples with more defect sites react faster, then the difference between the VTT and AEAT samples would be explained by a higher amount of defect sites in the VTT samples. Tests at VTT with starting [U] at 0.5 and 1.0 ppm U in solution showed similar results to those started at 2.0 ppm, with comparable differences between the results for pellets and fragments. Details of these tests were published in the annual progress reports of the project.

Data for the three tests that were restarted at higher concentrations are shown in Figure 2-3. The results for the pellet and fragment tests started at 6.6 ppm are now very similar and, if anything, the fragments are dissolving faster than the pellets. The pellets that were restarted at 9.3 ppm [U] in solution are continuing to dissolve at a relatively rapid rate, much greater than that for the 6.6 ppm restart.

Data showing the comparison between the measured [^{238}U] and the calculated [^{238}U] for the restarted pellet tests are shown in Figure 2-4.

In general, there is very good agreement between the concentration in solution predicted by the change in isotopic composition of the solutions and the [^{238}U] measured by ICP-MS up to 337 days. For subsequent samples the measured concentration in solution of ^{238}U becomes nearly constant, with no trend in the measured concentrations for P2, and with a decrease in [^{238}U] for the final sample of P1. There is a continual increase in the $^{235}U/^{238}U$ ratio in solution, indicating that the sample is continuing to dissolve. Thus, U must be precipitating to form a secondary phase. At this time, the three samples all have different steady-state [U]. We anticipate that in the long term, the measured concentration for all three samples should be the same. We will continue these tests to attempt to reach a consistent steady-state [U] for all samples.

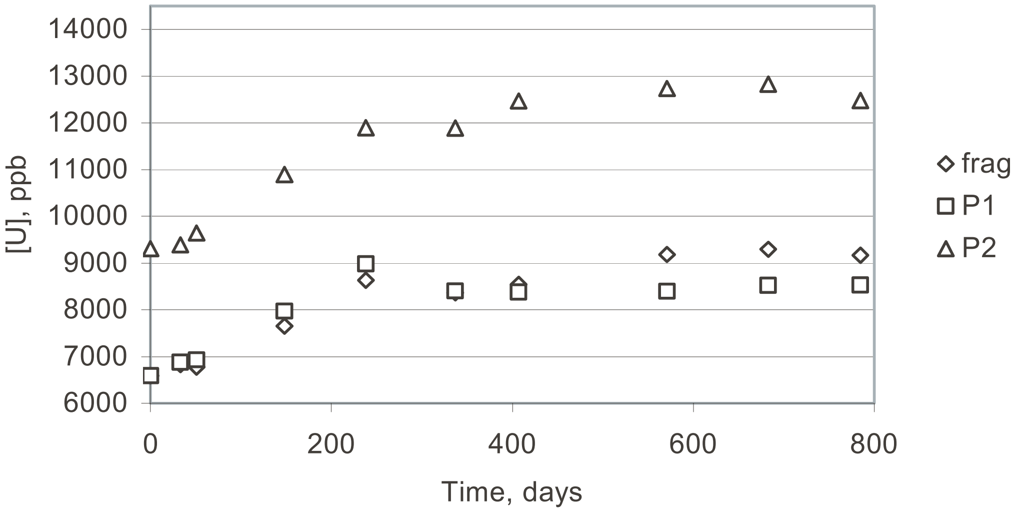

Figure 2-3. Data for restarted VTT tests with pellets and fragments for solutions in contact with air.

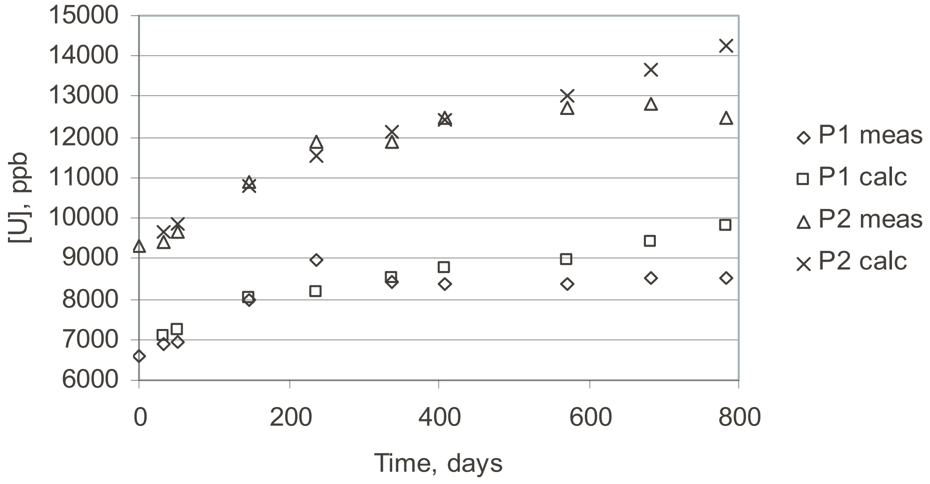

Figure 2-4. *Comparison of measured [^{238}U] and [^{238}U] calculated from the isotopic ratio changes.*

The data in Appendix C for the restated samples can be used to calculate a dissolution rate for the samples at steady-state [U]. The average dissolution rate (and precipitation rate for the secondary phase) is 80 ng/per day for the fragments for times after 337 days, and 210 ng/d for P1 and 320 ng/d for P2. There is no indication that the dissolution rate is decreasing with time during that period. This confirms that the pellets are dissolving faster than the fragments even at steady-state [U].

2.2 Tests under reducing conditions

We had originally planned to carry out tests under reducing conditions at both VTT and AEA Technology, Harwell. Results from pretreatment of solids under reducing conditions at Harwell did not show any dramatic effect on [U] when an iron strip was added to solution. This was surprising. Subsequent testing with a spike containing a ^{235}U/^{238}U ratio of 16.2 showed that the samples had become contaminated with natural or depleted uranium. It is most likely that this occurred in the laboratory that performed the ICP-MS analyses. This difficulty, combined with the imminent closing of facilities at Harwell that were needed to carry out the work, led us to cancel the tests planned for that facility. All results discussed in this section refer to tests conducted at VTT.

Following termination of the first cycle of testing under air atmosphere, several of the samples were used in a trial test under reducing conditions. The samples were transferred to an inert atmosphere (N_2) glovebox and placed in new test vessels. The samples were then immersed in modified Allard groundwater (anoxic composition – see Appendix B) and allowed to equilibrate for periods of 1 to 3 days with changes of solution at the end of each equilibration time. The [U] measured in the solutions was 6 to 7 ppb for fragments and 37 to 38 ppb for pellets after the first day of exposure. After the 6th exposure period (1 day) the [U] was 1.3 ppb for fragments and 8 ppb for pellets. A strip of pure Fe was then added to the vessels together with new solutions. Measurement of [U] (without changes of solutions) gave about 0.1 ppb for fragments after 5 days of equilibration, reducing to < 0.02 to 0.07 ppb after 20 days exposure. The solutions in contact with pellets contained 0.9 ppb U after 5 days and 0.03 ppb after 20 days. These data indicated that the iron strip was very effective in producing reducing conditions in the tests. A preliminary isotope dilution test with these materials showed an initial small pulse of U – 0.5 to 0.6 ppb for fragments and 2.3 ppb for pellets, followed by decreases in the [U] in all cases. At the end of the test the solutions in contact with fragments showed < 0.02 ppb U, while the pellets showed 0.33 ppb U.

We were unsure whether the testing that had been done under air atmosphere conditions might have affected the interior of the pellets and fragments in a way that would take a long time to overcome. For example, the interior surfaces of pores in the materials might have been oxidized during the tests and might now require a long time to become reduced through exposure to the reducing solutions via diffusion through the pore network. For this reason, we decided to use freshly prepared solids for the tests under reducing conditions. A pretreatment process for conditioning the solids and removing any oxidized material on the surface similar to that described above was used. Details of the procedure and results of solution analyses are given in Appendix D. The results from the pretreatment solutions were essentially the same as those found in the treatment of samples following the air atmosphere tests. Most of the U that was recovered in the pretreatment stages was found in the solution samples for steps conducted without iron and in the acid strip solutions for stages conducted with iron. The total recovery of U after the second pretreatment with Fe was very low – 0.05 to 0.2 μg total U recovered and less than 2 ng U recovered in solution samples. We were convinced that this level of pretreatment of the solids was adequate to insure that the surface of the materials was close to $UO_{2.0}$.

A group of 14 day batch tests with samples taken after 1 day, 7 days, and at the end of the test period were started. The spike used had equal amounts of ^{235}U and ^{238}U; some samples were started with 0.08 ppb total U and some with 0.12 ppb total U. Results from these tests are given in Appendix D. After 1 day of testing the samples showed [^{238}U] similar to or slightly higher than the [^{238}U] added as spike and a change in the $^{235}U/^{238}U$ ratio that indicated that some small amount of dissolution had occurred. After 7 days of exposure, the [U] in all samples except one (M7) had dropped below detection limits (< 0.02 ppb). After 14 days of exposure, all samples had [U] < 0.02 ppb. Samples from rinsing the reaction vessels and from the acid strip of the vessels produced much more U than had been seen in the day 1 solution samples. In addition, these samples had an isotopic composition that was essentially the same as the solid samples and showed no influence of the spike. The acid strip was repeated and allowed to equilibrate for a longer time. These samples showed higher [U] than the initial acid strip, suggesting that they contained small particles of UO_2 that were slowly dissolving. See Appendix D for detailed data tables.

To improve the sensitivity of the tests, future tests used a spike solution with $^{235}U/^{238}U = 10.354$. A series of tests using the same samples was started using two spiking levels – 0.05 and 0.10 ppb initial U in solution. In addition, some tests were done without the iron strip to see what difference this caused. See Appendix D for test conditions and results. The tests were allowed to equilibrate for 47 days before sampling. All tests that contained Fe strips had [U] < 0.02 ppb except for M 6, which showed 0.03 ppb U. Tests that did not contain Fe showed higher levels of U, ranging between 0.1 and 0.85 ppb U and had $^{235}U/^{238}U$ ratios that were distinctly different from that of the solid sample. From the data for M7 at day 47 we can calculate that [^{235}U] = 0.085 ppb in the solution and that 0.038 ppb of this came from dissolution of the solid. Since the original spiking level was 0.091 ppb ^{235}U, 34% of the spike must have precipitated, even in the absence of the Fe strip.

For sample M8, the [^{235}U] in the solution must be 0.0168 ppb (based on the measured [^{238}U] and the measured $^{235}U/^{238}U$ ratio). This indicates that more than 85% of the original ^{235}U added as spike has disappeared.

At the end of 55 days, the solutions were removed from the test vessels, placed in a new vessel and acidified. (The solids were transferred to new vessels for subsequent testing). Data for these acidified samples are shown in Appendix D. All samples now show measurable [U]. For samples that originally contained an Fe strip, the $^{235}U/^{238}U$ ratio is indistinguishable from that of the solid materials. This strongly suggests that small particles from the solids were dislodged when the solutions were removed from the tests. The total U recovered in each of these samples was (with one exception) on the order of 20 to 50 ng. A grain of UO_2 the size of a cube 10 µm on a side would contain 10 ng; a grain of UO_2 the size of a cube 5 µm on a side would contain 1.25 ng. The amounts of U found are consistent with dissolution of a few individual grains of the solid that were dislodged during sample handling. The results for M7 show a slight increase in [^{238}U] and a decrease in $^{235}U/^{238}U$. Taking the data from day 47, we had 0.85 ppb ^{238}U and 0.085 ppb ^{235}U. Using the measurements for day 47 as a starting point, we can calculate that 1.03 ppb of new U was added to the solution by dissolution between day 47 and day 55. This gives an expected [^{238}U] of 1.85 ppb if no precipitation occurred; however, the measured value was only 0.93 ppb. Thus, the acidified sample at day 55 contains newly dissolved solid, presumably in the form of dislodged particles, but even some of the newly dissolved material seems to have precipitated. The data for M8 show an even more dramatic change in the isotope ratio for the acidified total sample at day 55 as compared to the day 47 sample. The total [^{235}U] in the acidified total sample was only 0.0126 ppb, compared to 0.0168 ppb at day 47, indicating precipitation of about 1/3 of the U from the solution between day 47 and day 55. The change in the total [^{238}U], if adjusted for precipitation of 1/3 of the day 47 amount of 0.1 ppb, would correspond to addition of 0.3 ppb of newly dissolved solid. This amount, again, would correspond to a few grains from the solid being dislodged during solution removal. The vessel rinse and acid strip solutions had total U recovery amounts similar to or somewhat greater than the acidified total solution amounts and isotopic compositions that were very close to or indistinguishable from that of the solid sample.

We conclude, based on the data from the 55-day tests that the Fe strip is very effective in controlling the redox conditions in the tests and results in lower [U] in the test solutions. From the isotopic data for normal solution samples and acidified total solution samples, we conclude that a few individual grains of the solids become dislodged when the last portions of the solution are removed from the test vessels. The data for rinsing and stripping of the test vessels after termination of the tests also are consistent with the dissolution of grains of solid and indicate that the material recovered in these samples was not in solution at any point during the tests.

The next series of tests was designed to investigate the effect of total test length on test results. Duplicate tests of fragment samples (M1 through M8 from previous tests) were tested for periods of 1, 2, 4, or 8 weeks. Tests were started and allowed to run for 2 days before any spike was added. The reason for this was to allow any initial pulse of U dissolution, perhaps caused by a small amount of oxidation of the surface during changing of the test vessels, to precipitate before adding the spike. (The N_2 atmosphere in the glove box contains on the order of 0.1 ppm O_2. This is lower than is usually achieved, but still contains 10^{-7} moles of O_2 in 22.4 L at STP. If even 1 part in 1,000 of this oxygen reacted with the UO_2 surface, 2×10^{-10} moles of U(VI) would be formed. This would amount to 50 ng of U(VI), or 1 ppb [U] in solution at the start of the test.) Solution samples were taken at day 2 of exposure to provide the starting [U] before spike addition. No sample was taken immediately after spike addition. After one day of exposure with the spike, a sample was taken to determine [U] and $^{235}U/^{238}U$. The complete data for these tests are given in Appendix E. Table 2-1 contains some of the data and the results of a calculation of the expected isotopic composition of the solution based on the measured [^{238}U] and the amount of $^{235}U/^{238}U$ added with the spike. The calculations assume for day 2 expected ratio that the amount of ^{238}U measured in the day 2 sample and its associated ^{235}U (based on the isotopic composition of the solid) equilibrated with the spike that was added. If the ratio calculated by the method is lower than the ratio measured on day 3, then some of the U in the day 2 sample was not able to equilibrate with the spike. The most likely reason for this

Table 2-1. Measured versus expected compositions of $^{235}U/^{238}U$ in solution samples for Batch Tests.

Batch test Test	Measured ^{238}U, ppb Day 2	Expected 235/238 Day 2	Measured 235/238 Day 3	Measured ^{238}U, ppb Day 3	Expected 235/238 Day 3
M1	0.10	2.7	5.55	0.06	6.1
M2	0.10	2.7	6.00	0.05	7.3
M3	0.46	0.76	5.53	0.08	4.6
M4	0.07	3.5	7.21	0.05	7.3
M5	0.11	2.5	7.41	0.05	7.3
M6	0.08	3.2	6.66	0.04	9.1
M7	0.02	6.6	7.14	0.04	9.1
M8	0.04	4.9	6.76	0.04	9.1

to happen would be if some of the U was present as colloids in the solution samples. The calculation for expected ratio for day 3 assumes that all of the ^{238}U measured at Day 3 was in true solution, that it includes both the contribution from the added spike and the dissolved solid, and that the ^{235}U from the spike has mixed with this ^{238}U completely – i.e. none of the ^{235}U from the spike has precipitated. If the "expected" ratio is the same as the measured ratio, the assumptions of the calculation are fulfilled and the original colloidal material has completely precipitated. This is the case for samples M1, M2, M4, and M5. If the calculated ratio were less than the measured, it would indicate that some of the original colloidal material remained in the sample. Sample M3 shows this condition. If the calculated ratio is greater than the measured ratio, it indicates that some of the ^{235}U from the spike has precipitated before the day 3 sample was taken. This is the case for samples M6 through M8. (Note: Somewhat erratic count rates during ICP-MS analyses at day 3 and day 5 also suggested the presence of some material that was not completely in solution.)

Comparison of the solution concentration measurements for samples taken at day 3 and day 5 shows that all day 5 samples contained less ^{238}U in solution than day 3 samples, but the isotopic composition remained the same in day 5 samples as it was in day 3 samples. At test termination, after 1 week for M1 and M2, 2 weeks for M3 and M4, 4 weeks for M5 and M6, and 8 weeks for M7 and M8, all samples except M1 had $[^{238}U] < 0.02$ ppb. For M1 and M2, the samples were analyzed 3–4 hours after they were taken. The other samples were acidified and held for 3 to 6 days before analysis. For each sample, a portion of the solution was taken and filtered prior to acidification and analysis. These samples gave the same results as unfiltered samples. The remainder of the solution samples were removed from the solid, acidified, and left for 3 to 6 days prior to analysis in order to allow any solid particles to dissolve. Results are given in Appendix E. For sample M1, we can see that the acidified solution after equilibration contains 0.13 ppb more ^{238}U than the first sample. The isotopic ratio for this sample – $^{235}U/^{238}U = 1.10$ – is consistent with the mixing of the U that was in true solution in the first M1 sample with 0.13 ppb of ^{238}U derived from dissolving particles of the solid after acidification of the solution. The amount of additional U recovered in the acidified solution sample for M1 is 3.25 ng, which is consistent with dissolution of 1 or 2 grains of the solid (assumed grain size 5 to 7 µm). The low $^{235}U/^{238}U$ ratios, together with relatively low solution concentrations for ^{238}U for all of the samples, indicates that the material being measured comes from dissolution of small grains of UO_2 that were dislodged when the solution was removed from the solid. The vessel rinse samples had significant amounts of U only in unfiltered, acidified samples, again indicating that dissolution of solid after acidification of the rinse samples is responsible for the small amounts of U that are found.

The test termination data for the 2, 4, and 8 week exposure periods show no features that indicate that a test period longer than 2 weeks increases the amount of meaningful information for these tests. For tests M3 through M8, the 4 ml unfiltered solution samples that were taken at termination and acidified were held for 3 to 6 days, the same time interval as the 25 ml acidified solution samples were held before analysis. The only difference in sample treatment was that removal of the 25 ml residue of the solution from the solid might have caused grains of the solid to be disturbed and carried over with the solution prior to its acidification. The analyses for the 4 ml samples all showed ^{238}U below the detection limit (<0.02 ppb), while the acidified 25 ml samples all showed small amounts of ^{238}U. This, together with the low $^{235}U/^{238}U$ ratio of the U found in these samples, supports the assignment of the source of this U as dissolution of solid particles following acidification.

All of the tests conducted under reducing conditions to this point had shown their highest concentrations of ^{238}U in the first samples taken after 1 or 2 days of exposure. We believed that this was due to a very small amount of oxidation of the sample surfaces during transfer of samples to new reaction vessels. The very small amount of O_2 (0.1 ppm) in the glove box N_2 atmosphere would be more than enough to cause oxidation of sufficient U to explain the 0.1 to 0.5 ppb [U] found in the day 1 or 2 samples if there had been long enough exposure of the samples to the atmosphere. Since oxygen could more easily reach the sample surface if there was only a thin film of water on the solid, we devised a new test procedure to eliminate as much as possible any U that entered the solution through an initial "puff" of dissolution of oxidized material.

The underlying thought behind the "puff test" procedure was to protect the sample using a relatively thick layer of solution. The samples were transferred to new reaction vessels and 50 ml of conditioned water was added. The tests were allowed to equilibrate for 2 hours, during which time we hoped that any oxidized material would dissolve. After the 2 hours, 30 ml of solution was removed and replaced with new conditioned water. The solution was stirred, covered, and left for 30 minutes. This dilution step was repeated 2 more times. Then the spike was added, as well as an Fe strip, and the test was covered and left for one day before sampling. The details of the test procedure and the results of solution analyses for these steps are given in Appendix E.

We were surprised to find that none of the samples showed any evidence for a rapid pulse of dissolution at the start of the tests. Perhaps this was because only 2 samples were being handled and the sample transfers were more rapid than normal. Samples taken after 1 and 4 days of total exposure to the spike showed measurable U. The concentrations are very low and should be considered as only approximate; the isotopic ratio data for the day 1 samples give a better indication of the [^{238}U] in the samples. A $^{235}U/^{238}U$ ratio of 8, assuming that none of the spike has precipitated, would imply a [^{238}U] = 0.046 ppb, of which 0.035 ppb was added with the spike. Thus, about 0.009 ppb of the measured [^{238}U] came from U that was in solution at the time the spike was added or which dissolved from the sample during the first day of exposure with the spike. The day 4 samples (sample #6) had lower [^{238}U] and lower [^{235}U] as indicated by the lower number of counts recorded by the ICP-MS. This indicates that U that had been in solution after 1 day of exposure is precipitating. The $^{235}U/^{238}U$ for M8, which had the most U left in solution at day 4, is the same as it was at day 1 (within the uncertainties in the analyses), indicating that little or no further contribution of U from the solid occurs during the time the U is precipitating.

Samples taken after 7 days of exposure showed [^{238}U] < 0.02 ppb. At the end of 14 days exposure the tests were terminated. A 5 ml sample of solution was taken, acidified and held 5 days prior to analysis. Another sample (10 ml) was taken, filtered, acidified and stored 5 days before analysis. These samples all had [^{238}U] < 0.02 ppb. The remaining 15 ml of solution was removed from the solid, transferred to a new vessel, acidified (1 M HNO_3)

and held for 11 days with samples taken for analysis at 6 and 11 days. These samples had measurable [^{238}U] – about 0.05 ppb for [^{238}U] in M7, with [^{235}U] < 0.02, and about 0.4 to 0.5 for [^{238}U] in M8, with ^{235}U/^{238}U not far from that of the starting composition of the solid. The amount of ^{235}U found in those samples represents only about 2% of the amount of ^{235}U added as spike. (Total ^{235}U added = 0.365 ppb × 50 ml = 18 ng; ^{235}U recovered in PM8 after 6 days in acid = 0.4 ng). The vessel rinse solutions show the pattern of data consistent with dissolution of grains of the solid. The maximum ^{235}U recovered was 0.3 ng from the acidified rinses after 6 days and 0.2 ng after 11 days.

The data for the 4 acid strip samples all indicate that about 3 ng of the original spike have been recovered during the striping process. This is less than 10% of the added spike. The increase in [^{238}U] between 6 days and 11 days for the strip solutions indicates slow dissolution of particles of the original solid. The ^{235}U/^{238}U ratio in the 11 day strip samples is lower than that in the 6 day samples, which when combined with the higher [^{238}U] results in a constant [^{235}U]. Taken together, these results clearly point to a disappearance of ^{235}U from the parts of the system that were examined, leaving only the surface of the solid UO_2 or the surface of the iron strip as possible locations for the missing U. An attempt was made to remove any U from the iron strip by a quick immersion in acid. The result was a green solution (probably Fe(II) ions) that was difficult to analyze by ICP-MS. The analysis showed little or no U, but because of the condition of the solution, the results are suspect. In future tests a different method for removal of U from the Fe strip will be used.

3 Dissolution of unirradiated UO_2 fuel pellet material doped with ^{233}U

Materials used in these tests were manufactured by BNFL in England, the same company that manufactured the unirradiated fuel pellets that were used by AEA Technology in their tests discussed in section 2. The nominal doping levels for the pellets were 5% and 10% ^{233}U. The pellets were also to contain 4.5% ^{235}U. The nominal composition of the pellets and their density and geometric parameters are given in Appendix F. Two pellets of each composition were made. The measured density of the final products was approximately 96% of theoretical density, which is similar to the density of normal unirradiated fuel pellets.

3.1 Tests under air atmosphere conditions

Tests under air atmosphere conditions were conducted at Chalmers Technical University. The purpose of these tests was to assess the quality of the pellets. No effects of radiation on dissolution rate should be seen under air atmosphere conditions. We had originally planned to do these tests at Harwell, but due to closure of facilities the work had to be moved to Chalmers. We had planned to use as a control sample the same unirradiated fuel pellet materials that had been used in the first series of tests at AEA Technology in this series of tests. This was not possible, so we chose to use a sample of an experimental fuel made from depleted uranium that was available at Chalmers. The details of the fabrication of this material are not available to us.

The ^{233}U-doped materials had been crushed and sieved at AEA Technology before shipment to Chalmers. Fragments of material in the size range 1.4 to 4 mm were chosen for testing. The depleted U fuel was also crushed to give similar size fragments. Triplicate samples of about 1 gram each were prepared for each doping level – 0, 5%, and 10%. Samples were tested in glass bottles with a screw cap using 30 ml of modified Allard groundwater. Before actual testing began, the samples were pretreated by allowing the sample to sit in contact with 30 ml of modified Allard groundwater for 2 days. This solution was discarded and the pretreatment was repeated for a total of 7 times. The isotopic composition and concentration of total U in the final pretreatment solution is given in Appendix F. From these data, we can see that the actual composition of the doped pellets was 4.3% ^{235}U in both samples and 4.8% and 9.6% ^{233}U, respectively for the nominally 5% and 10% ^{233}U samples.

The isotope dilution tests were started by adding modified Allard groundwater to the samples and then taking a small (0.5ml) solution sample. Then a spike of depleted U (0.4% ^{235}U) was added to each test to give a [U] of 1.5 ppm. The samples were then left to dissolve, with samples taken periodically to monitor the dissolution process. Data for testing up to 103 days is given in Appendix F.

The depleted U fuel sample showed rather strange behavior. For the first 41 days there was little or no dissolution. At day 103, the samples all had 3.3 to 3.4 ppm total U in solution, which is about what we would have expected based on our earlier testing of unirradiated fuel materials (section 2). We have no explanation for the delay in initiation of dissolution for this material.

Data for the three 5% ^{233}U-doped samples showed generally more variability between samples than the 10% ^{233}U-doped samples. The results for the 5% samples are shown in Figure 3-1, in which clear differences in total [U] can be seen for the last two sampling times. A similar plot for the 10% would show all three samples plotting on top of each other.

Figure 3-2 shows a comparison of the results for [U] in solution for the three different sample types. At this stage, the samples with 10% ^{233}U-doping seem to be dissolving at a somewhat faster rate than those with the 5% ^{233}U-doping. For testing under an air atmosphere, one would not expect to see any effects from the alpha radiolysis in solution on dissolution rates. We, therefore, suspect that differences in the quality of the pellets – i.e. the level of defects in the materials – may be the cause of the dissolution rate differences. These materials will be studied further in the future. Despite the slight differences in the dissolution rates, the general level of the [U] and the rate of increase of [U] indicates that the pellets are of adequate quality.

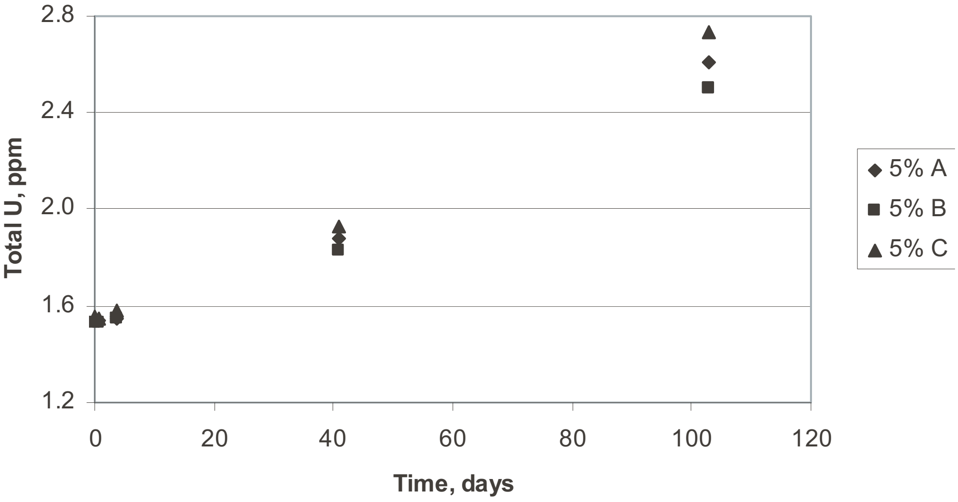

Figure 3-1. Total [U] for samples with 5% ^{233}U-doping tested in modified Allard groundwater in contact with air atmosphere.

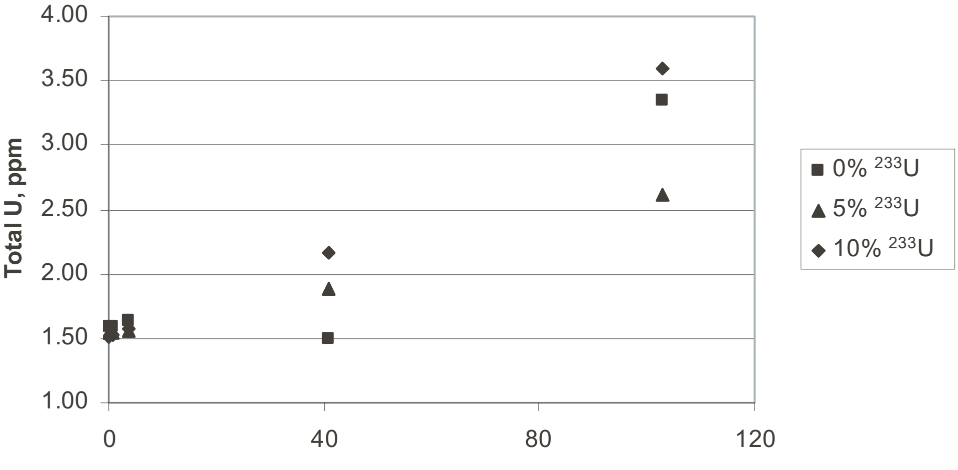

Figure 3-2. Solution concentration for U for the average of three samples at each doping level for tests in modified Allard groundwater in contact with an air atmosphere.

The isotopic composition of the solution samples from the tests with ^{233}U-doped materials can be used to calculate the amount of U from the sample that has been mixed with the added spike. This is the amount of U that has dissolved from the sample. If the total U calculated by adding the result of the isotope dilution calculation to the amount of spike is more than the measured total [U] in solution, precipitation must have occurred. For each sample we can calculate the amount of dissolution using the $^{233}U/^{238}U$ ratio and the $^{235}U/^{238}U$ ratio. If the samples are homogeneous and if we have the correct isotopic composition for the solid, the two results should agree.

The 0.1 hour sample gives the starting [U] and a measure of the isotopic composition of the solid that can be compared with the pretreatment data. For the 5% doping sample, the 0.1 hour sample gives an average composition that is similar to the pretreatment values, but which shows considerable scatter. It is not clear whether this scatter is due to analytical uncertainties or to sample heterogeneity. Further work must be done to clarify this issue. For the time being we will use the values from the pretreatment data as our best assumption for the isotopic composition of the solid phase. An isotope dilution calculation based on the 103 day data and the $^{233}U/^{238}U$ ratio indicated that 1.08 ppm total U has dissolved since the spike was added. This converts to a predicted solution concentration of 2.65 ppm total U, which is in excellent agreement with the average measured value of 2.61 ppm. A similar calculation based on the $^{235}U/^{238}U$ ratio indicates that 1.41 ppm U has dissolved. If the actual composition of the solid was $^{235}U = 4.5\%$, the calculated amount of dissolution would be 1.29 ppm. Both of these values are higher than the dissolution calculated from the $^{233}U/^{238}U$ ratio and may indicate that the solids are inhomogeneous. This will be examined further in the future.

An isotope dilution calculation for the 10% sample based on the 103 day data and the $^{233}U/^{238}U$ ratio indicates that 2.60 ppm U should have dissolved since the addition of the spike. This amount of U together with the spike and the 0.1 hour sample would give an expected [U] of 4.2 ppm. This is considerably higher than the average of the measured values, 3.59 ppm. If the isotopic composition of the solid is estimated using the data from the 0.1 hour sample, the indicated dissolution increases to 2.80 ppm. Thus, the indications for precipitation occurring during the 103 day period are strong. The calculation of dissolution using the $^{235}U/^{238}U$ ratio indicates dissolution of 3.06 ppm total U. Using the data from the 0.1 hour sample to predict the isotopic composition for the solid for ^{235}U (4.15%) would result in a higher calculated value. Using the nominal value of 4.5% gives a calculated dissolution of 2.7 ppm, which is close to the value calculated from the $^{233}U/^{238}U$ ratio. In any case, all calculations indicate that precipitation has occurred from the 10% ^{233}U tests. Before any stronger conclusions can be reached, we must resolve the issue of establishing the isotopic composition of the solids and the degree of heterogeneity of the solids.

3.2 Tests under reducing conditions

Tests under reducing conditions were conducted at VTT using a new, negative pressure anaerobic glove box. The negative pressure feature means that the pressure inside the box is lower than the pressure in the laboratory so that in the case of an accident, the flow of air is into the box. Anaerobic boxes used for low-level radioactive work have a positive pressure, which helps guard against leakage of air into the box. All tests were conducted at ambient glove box temperature.

Samples of the ^{233}U-doped materials were shipped from AEA Technology Harwell to VTT. The samples were prepared for testing by taking approximately 1 g of sample fragments for each planned test and placing the samples on a saucer in 30ml Nalgene bottles. Then, 30 ml of modified Allard groundwater (Appendix B) was added. Leachants were changed on a regular basis every day or two for 5 days. The samples were then changed to new vessels and this procedure was repeated. Then the samples were changed to new saucers and Nalgene bottles, new solution was added, and an Fe strip was placed in the bottle. After 1 week with the Fe strip the samples were changed again to new vessels together with the Fe strip and left for an additional week. Then a third change of vessels was done and the samples were left for 17 days before termination of the pretreatment. Each time vessels were changed, the old vessel was rinsed and acid-stripped. Details of the pretreatment procedure and the results of solution analyses are given in Appendix G.

Two samples of each doping level of ^{233}U-doped materials and two samples of pellet material from the same batch as used in the earlier VTT tests were used in these experiments. The first exposure of the solids to groundwater gave 40 to 86 ppb U in solution. The second exposure gave 7 to 20 ppb and the third gave 1.5 to 4.2 ppb. The acid strip of the vessel from this stage gave 5 to 10 ppb. No trend was seen in the data with respect to sample type. The second cycle without Fe started with most samples giving between 2.5 and 7 ppb, much lower than the first cycle. Sample 1 of the 10% doping level released more U and had 18 ppb in solution in the first sample taken after three days of exposure. This sample continued to have higher [U] throughout this pretreatment cycle. The other samples gave generally decreasing [U] as the pretreatment progressed, ending with [U] between 0.4 and 1.7 ppb (sample 1–10% had 4.4 ppb). These values are actually lower than those achieved during the pretreatment of samples for the first reducing conditions tests (Appendix D), indicating that the glove box was functioning well.

The first pretreatment step with an Fe strip gave low [U] for all samples except 1–10%. Small amounts of U were recovered in the rinse and acid strip samples, indicating that the samples were behaving in an acceptable manner. The second pretreatment cycle with the Fe strip gave [U] < 0.02 ppb for all samples and low values for the rinse and strip samples. The third cycle of pretreatment with the Fe strip again gave [U] < 0.02 ppb for all solution samples, and very low [U] for the acidified total sample, indicating little pick-up of solid grains during solution transfer. The acidified rinse solution and the acid strip solution also had low [U] – 0.02 to 0.63 ppb, indicating few grains of sample had been separated during sample handling. This indicated that the pretreatment had been successful and that the samples should have a secure surface condition with chemical composition of $UO_{2.0}$ and few loose grains that might give erratic results.

Testing of the samples was begun with a two week cycle based on the "puff test" method developed during the previous reducing conditions tests. Details of the method and the data for cycle 1 are given in Appendix H. The first sample taken after 2 hours exposure to modified Allard groundwater showed little or no U in the solutions in contact with the ^{233}U doped samples, but significant amounts – 0.14 and 0.61 ppb ^{238}U in the solutions from the undoped fuel pellet fragments. The samples from the first dilution step, exposed for 30 minutes to the solid, should have [U] = 0.4 of the sample 1 level if the process is simply dilution of dissolved U. One of each of the doped samples showed higher [U] in sample 2, indicating dissolution of U during the 30 minute exposure, while sample 2-0-2 had [^{238}U] consistent with dilution of the sample 1 value. The third sample, taken after a second 60% dilution and 30 minute resting time, showed significant dissolution of both of the 10% ^{233}U-doped materials but no dissolution of the other samples. All of these samples were acidified and held for 2 weeks, with reanalysis after 1 and 2 weeks holding. These analyses had [U] which was generally similar to or lower than the original samples. Since the samples had been acidified to 1M HNO_3, we cannot explain the results by invoking precipitation of U. It seems, rather, that the original samples were very heterogeneous and that they may have included some small grains of solid or colloidal material.

Spike with $^{235}U/^{238}U = 10.35$ was added to give a total [U] = 0.4 ppb of added spike after sample 3 had been taken and the volume had been returned to 50 ml. A sample was then taken to obtain the starting composition and [U] for the tests. The results shown in Appendix H confirm that the 20 ml of solution left after sample 3 had been removed from the 10% ^{233}U-doped samples had a very low [^{238}U] – on the order of 0.01 ppb – before the spike was added. The spike contained 0.035 ppb ^{238}U. This plus the residual U in the solution of 0.01 ppb would give 0.045 ppb ^{238}U, consistent with the measured value of 0.04 – 0.05 for these samples. All samples showed changes in the $^{235}U/^{238}U$ ratio in samples taken at 1 and 3 day intervals, indicating that U was dissolving during the entire testing period. The data suggest that the 10%-^{233}U samples are dissolving faster than the 5% samples, which in turn are dissolving faster than the undoped samples. For sample 7 of the 10% solids, all of the U that dissolved from the sample seems to still be in solution. Calculation of total dissolution from the $^{235}U/^{238}U$ ratio results in predicted dissolution of 0.20 ppb total U, which is close to the average measured value of 0.18 ppb. For the 5% samples, the predicted dissolution is 0.11 ppb, indicating that about 50% of the originally dissolved U has precipitated. For the undoped samples, the fraction of precipitated U is even higher.

After 14 days of total testing, the tests were terminated. The results show no clear trend, with 4 samples at or below 0.02 ppb and two samples with measurable ^{238}U. There is no difference in results for filtered samples and acidified samples that were held to allow further dissolution before analysis, indicating that the U measured in the first sample was in true solution. Mass balance calculations can be used to assess the extent to which the added spike has been recovered in various parts of the system. For samples 2-10 and 1-0, only about 20 to 25% of the added spike was recovered, indicating that the precipitated U must have gone to the UO_2 surfaces or to the surface of the Fe strip. For sample 1-5, about 75% of the spike was recovered, indicating that precipitation in this sample was slower than in the others.

The solids were transferred to new reaction vessels and a new 2-week cycle of testing was started. The method was identical to cycle 1. All tests had about 0.3 ppb U in sample 1. Sample 2, which should be 0.4 of the sample 1 concentration if only dilution occurs was lower than the sample 1 concentration, but only slightly, indicating further dissolution was occurring even in the short 30 minute exposure time. Sample 3, which should be 0.4 of the sample 2 [U] had concentrations that were similar to or higher than sample 2, again indicating further dissolution. Sample 4 was taken after returning the volume to 50 ml and adding the spike. The amount of ^{235}U calculated to be in solution based on the measured [^{238}U] and the $^{235}U/^{238}U$ ratio of the solutions is consistent with the amount of spike added, which contained 0.365 ppb ^{235}U. The measured [^{238}U] in all samples except 1-5-4 was higher than the expected value based on dilution of the residual 20 ml of solution from the sample 3 stage and addition of spike, indicating that even in the time frame of a few minutes, further dissolution was occurring.

Samples taken after 1, 3, and 3 further days of exposure of the solids to modified Allard groundwater showed (by small changes in the $^{235}U/^{238}U$ ratio) that further dissolution was occurring and with a slight indication that the ^{233}U-doped samples were dissolving faster than the undoped samples.

The tests were terminated after 2 weeks total testing. The data, which are in Appendix H, showed that all samples had a measurable amount of U in solution, in contrast to the cycle 1 test in which only 2 samples had significant amounts of U in the final samples. The amounts of material recovered in the rinse and strip samples seem to be similar to those from cycle 1 and, based on the isotopic compisition, are probably small grains from the solid rather than material that has precipitated from solution. In contrast to cycle 1, the calculated amount of ^{235}U in the final samples for the 5 and 10% doping level samples is consistent with the amount added as spike + solid dissolution, indicating that there has been little or no precipitation. For the undoped samples the calculated amount of ^{235}U in solution based on measured [^{238}U] and the isotopic composition is only about 60% of that expected, showing significant precipitation. Again, the spike U was not recovered in the rinse and strip samples, so must be on the U solid or the Fe strip.

The remainder of the solution from cycle 2 (25 ml) was transferred to a new reaction vessel together with the solid samples on their saucers and the Fe strip. The volume was increased to 50 ml and a new dose of spike was added to give an addition of 0.4 ppb total U to the system. The solution was gently mixed and a 5 ml sample taken for analysis. We can use the data from the 14 day test termination and the amount of spike added to calculate the expected results for these analyses. Table 3-1 shows the results of these calculations and the measured values. The agreement between predicted and measured results is excellent.

The tests were left to equilibrate and samples were taken after 1, 3, 3, and 7 days of additional testing. These results are shown in Appendix H with times identified as 14+1, 14+4, 14+7, and 14+14. The 14+1 day samples show the same isotopic composition as the 14+0 samples, indicating that no further dissolution has occurred. In addition, the concentrations of all samples have decreased, indicating active precipitation. At 14+4 days, three samples had ^{238}U less than the detection limit of 0.02 ppb. The other 3 samples had very low ^{238}U and the same isotopic composition (within the limits of uncertainty) as the day 14+1 samples, again showing that precipitation was occurring without further dissolution of the solids.

All samples taken at days 14+7 and 14+14 had [^{238}U] < 0.02 ppb. At day 14+15 a new dose of spike was added to each of the samples and a 5 ml sample was taken. The measured data for day 14+15 in Appendix H confirm that the [^{238}U] at day 14+14 had been low, since the measured amount of ^{238}U at day 14+15 is consistent with the amount added with the spike. The isotopic composition of the solution after spike addition is very close to the spike value. A measured value of 235/238 = 9 after spike addition would correspond to an original [^{238}U] before spike addition of 0.0056 ppb and [^{238}U] = 0.0406 ppb after spike addition.

The samples were left for an additional 7 days and then the tests were terminated. All tests had [^{238}U] < 0.02 ppb, both in an unfiltered acidified sample and in the remainder of the solution, which was analyzed after 10 days equilibration with the acid. Extreme care was taken when the remainder of the solution was removed from the solid not to come in contact with the contents of the sample saucer. This seems to have enabled the solution to be removed without dislodging grains from the sample surfaces. The vessel rinse samples had low [^{238}U] and accounted for recovery of about 1% of the added spike in the highest case (sample 2-0). The acid strip samples all had significant [^{238}U] and isotopic compositions that were different from the starting solid. If the ^{235}U recovered is interpreted as all coming from

Table 3-1. Cycle 2 restart after 14 days with new spike addition, day 14+0 samples.

Sample ID	Predicted ^{238}U, ppb	Measured ^{238}U, ppb	Predicted 235/238	Measured 235/238
1-10	0.25	0.27	2.11	2.18
2-10	0.22	0.22	2.48	2.69
1-5	0.215	0.22	2.53	2.81
2-5	0.30	0.31	1.89	2.06
1-0	0.125	0.15	3.82	3.72
2-0	0.10	0.17	4.10	3.58

precipitation of the spike, the amount in the acid strip amounts to 60% recovery for sample 1-10, 44% for sample 2-10, 50% for sample 1-5, 41% for sample 2-5, 68% for sample 1-0, and 93% for sample 2-0. (Note that this calculation somewhat overestimates the percentage recovery of spike since some of the ^{235}U in solution came from the original pulse of dissolution of the solids, which contain 4.5% ^{235}U for the ^{233}U-doped samples and somewhat less for the undoped samples. Since the amount of the "puff" was small, it would only account for about 1% of the recovered ^{235}U.)

At the end of the test termination, the Fe strips were removed from the glove box and exposed to air for several hours. They were then immersed in 25 ml $NaHCO_3$ solution (250 ppm bicarbonate) in an attempt to remove any U that might be on the strips. This procedure was repeated twice more for a total of 3 successive strippings. Data for analysis of these solutions is in Appendix H. The first stripping of the Fe strips from the ^{233}U-doped samples gave small amounts of U with a 235/238 ratio that was not far from what had been measured in the early stages of the restarted cycle 2 tests. This indicates that the U came from the solution phase and precipitated onto or was reduced onto the surface of the Fe. Sample 1-5 indicates the largest recovery of spike U, corresponding to about 5% of the added spike. The second and third strippings gave [^{238}U] near or below detection limits and ^{235}U < 0.02 ppb in all cases.

The results of the testing of ^{233}U-doped uranium dioxide pellet fragments under reducing conditions show only small effects that might be attributed to the presence of alpha activity in the samples. Further testing is needed to determine whether the effects that are suggested are due to alpha activity or due to differences in the quality of the solids.

4 Dissolution of spent fuel under anaerobic and reducing conditions

The tests using spent fuel were originally planned to be done at AEA Technology, Harwell, using their hot cell facilities. In that location, we could have used the same experimental procedure as was used for tests with unirradiated fuel pellet materials and the alpha-doped materials. When it was announced that the hot cells would be closed before our experiments could be done, we had to relocate the tests. Practical considerations concerning the length of time to get approval from Brussels for a change of test location meant that we needed to start the tests outside of the EU Project if we were to have a chance to get data before the end of the project. Constraints concerning the contract for the project also meant that we, in practice, needed to have the tests done by one of the existing partners in the project. Fortunately, Chalmers was able to do the work, but with a revised experimental procedure that would use steel test vessels to provide some of the shielding needed when working with highly radioactive spent fuel.

The fuel samples used in the experiments at Chalmers came from a fuel pin from the Oskarshamn Nuclear Power Station (fuel pin OI-418-A6). The fuel pin had a burnup of 41 MWd/kgU. The samples were taken about 1 m from the bottom of the fuel pin and were originally used in an experiment involving 200 days of leaching in the presence of bentonite clay. Data from that and related experiments have been published as part of a diffusion study of fission products and actinides in bentonite clay /Albinsson et al, 1990; Ramebäck et al,1994/. The leaching in the bentonite experiments should have removed most of the rapid release fraction of ^{137}Cs. Before use in the present experiments, the samples were removed from their cladding, at which time the samples separated into small fragments. The present experiments use 2 fragments in each test, with a total weight of spent fuel of 0.4 to 0.6 g/test sample. The samples were rinsed and preleached to remove any traces of bentonite from the previous testing.

The spent fuel tests were conducted in steel vessels lined with PEEK (polyether ether ketone), a material that is non-reactive under the conditions used in our tests. The vessels are capable of withstanding significant gas pressures inside them during testing. The fluid phase used for the leaching is the modified Allard groundwater for reducing conditions. Tests were conducted under ambient hot cell temperature (18–25°C). The first cycle of testing used an argon atmosphere of 10 bar in the vessels. Samples were taken after 1, 4, 8, and 21 days of leaching. The atmosphere in the vessels was then changed to H_2 (10 bar) and an additional 20 ml synthetic groundwater was added to return the volume to approximately 30 ml. Samples were again taken after 1, 3, 8, and 21 days. At the end of this cycle, the water was removed and replaced with groundwater that had been equilibrated with an Fe strip and an H_2 (10 bar) atmosphere. This gives a concentration of Fe(II) in the solution of approximately 1–0.1 μM. The change of solution was done in a hot cell with an air atmosphere. Another cycle of samples at 1, 4, 8, and 24 days was taken and the test was terminated.

The spent fuel samples were then transferred to new PEEK vessels for further testing. The vessels from the terminated test series were rinsed with groundwater and then stripped with nitric acid to recover any precipitated material. The test cycle with Fe-equilibrated water and H_2 atmosphere was repeated, including vessel changes, 3 more times. The change of vessel after sample number 20 (110 days total testing) was done in an Argon atmosphere box. The following analyses were done on each sample: ^{90}Sr via solvent extraction followed by Cerenkov counting of Y daughter product /Ramebäck et al, 1995/, Cs and Co using a HPGe-detector for gamma detection, and Fe, Sr, Mo, Tc, Ru, Np, U, Pu, and Zr by ICP-MS. Zr was below detection limits (5×10^{-11}M) in all samples. Measurement of pH shows that the presence of H_2 in the system did not affect the pH.

Data for U are shown in Figure 4-1. In the Ar atmosphere, [U] increased from about 1×10^{-7} M after 1 day of leaching to about 1×10^{-6} M after 21 days of leaching. After changing to the H_2 atmosphere, the [U] began to slowly decrease. Changing the solution at day 42 produced a sharp increase in [U] to 1×10^{-5} M, probably due to some oxygen contacting the sample during the change of solution. By day 3 of the cycle with H_2 atmosphere and Fe(II) in solution, the [U] had dropped dramatically. The [U] continued to decrease during the rest of the cycle and at day 66 it was $\leq 1 \times 10^{-8}$ M. Subsequent changes of vessel and solution produced slightly elevated [U] at the start of the cycle, but none as dramatic as that for the start of cycle 3. The test termination at day 66 included rinsing and stripping of the reaction vessel. In test series 2 and 3, the total U recovered in the rinsing and acid stripping of the PEEK vessels was 2×10^{-9} moles U and 0.6×10^{-9} moles U respectively. The total U in solution at day 1 of the cycle was about 2×10^{-7} moles U. Thus, at most 1% of the uranium that had been in solution was recovered in the cycle termination. This indicates that the U that was precipitated from solution was taken up by the spent fuel sample itself, rather than precipitating or sorbing onto the vessel walls.

Data for ^{137}Cs are shown in Figure 4-2. The small decrease in concentration at the change from Ar to H_2 atmosphere is the result of adding 20 ml of new groundwater to the tests to return the solution volume to near its original value. Each change of solution (day 42) and solution plus reaction vessel (days 66, 89, 110) resulting in exposure of the fuel to a new solution, started a new cycle of ^{137}Cs leaching. The release of ^{137}Cs during the first day of the 4 cycles with Fe(II) solutions seems to be getting lower in subsequent cycles, but there is no clear trend indicating a response to the reducing conditions on the ^{137}Cs release.

Stontium-90 concentrations ranged between 10^{-10} and 2×10^{-9} M (see Figure 4-3), with the low values at the start of the leaching cycles. There is no dependence of [^{90}Sr] on dissolution conditions. There was no spiked release of ^{90}Sr in the sample that showed the high [U]. The ^{90}Sr inventory in the fuel is about 0.04% of the sample by weight, while the ^{137}Cs is about 0.09% by weight.

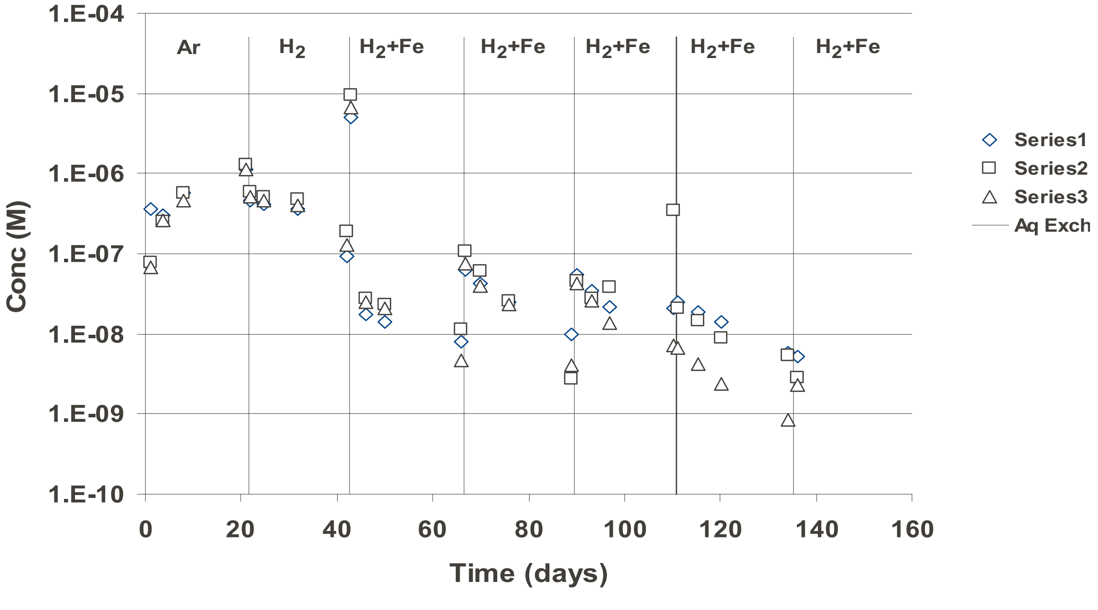

Figure 4-1. Leaching data for U. ICP-MS measurement.

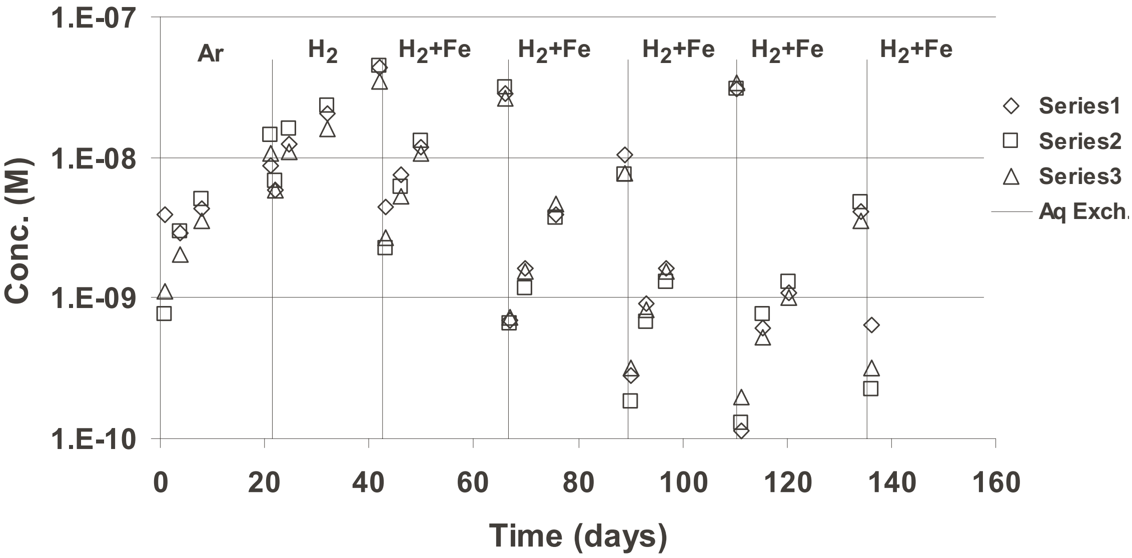

Figure 4-2. *Leaching data for* ^{137}*Cs. Gamma measurements.*

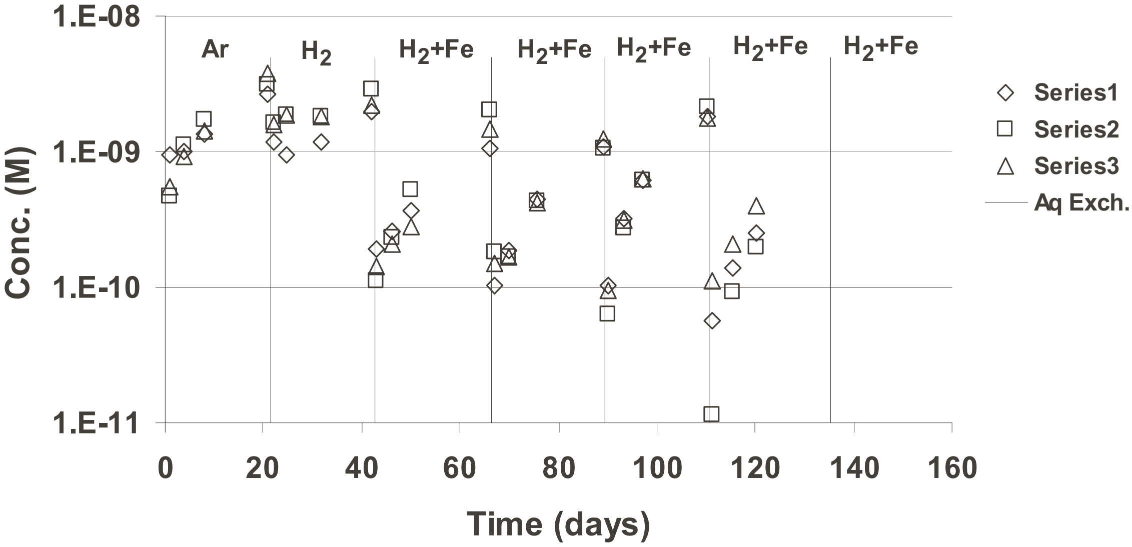

Figure 4-3. *Leaching data for* ^{90}*Sr. Solvent extraction followed by Cerenkov counting of* ^{90}*Y.*

We can use the ^{90}Sr data to calculate how much of the spent fuel U we would expect has been processed through the solution phase. The Sr is thought to be in solid solution in the UO_2 matrix /Kleykamp, 1985/, so release of Sr should indicate dissolution of spent fuel. The first samples of each of cycles 3 to 6 have [^{90}Sr] of about 10^{-10}M. For congruent release of Sr and U, the initial release of U must have been about 2.5×10^{-7}M; however, the [U] measured in the first samples for cycles 4, 5, and 6 are much less than this. This indicates that the U was probably released as a small initial pulse, probably occurring before the vessels were closed. After closing the vessels and applying H_2 gas pressure, the U probably immediately began to precipitate in response to the reducing conditions inside the pressure vessel.

The continued release of Sr during the entire test cycle suggests that continued dissolution and reprecipitation of the the fuel is occurring, resulting in Sr release. This would mean that U is being dissolved and reprecipitated even as the [U] is decreasing towards a solubility limit appropriate to the reducing conditions in the tests.

At the end of this series of experiments the samples were left in their pressure vessels covered by modified Allard groundwater and with an atmosphere of 10 bar H_2 gas. Approximately 6 months later the isotope dilution experiments for the EU Project were started. The solution was removed from each test vessel and replaced with fresh modified Allard groundwater. The vessels were closed, the 10 bar H_2 gas atmosphere was added, and the samples were left for 2 weeks to equilibrate.

One of the difficulties in these tests is to find a way to introduce the spike solution without exposing the solutions to air. We decided to prepare a spike solution inside a pressure vessel so that the solution was under a H_2 gas atmosphere. The spike dose would then be applied by pushing the solution from the spike vessel to the sample vessel using gas pressure. The spike was prepared by placing a 2 ppm solution of the U spike in Allard groundwater into a pressure vessel together with an Fe strip. The vessel was closed and the hydrogen atmosphere was applied. We had hoped that this would give rapid precipitation of excess U and result in a spike solution that had an appropriate concentration for transfer. Unfortunately, the concentrations did not drop rapidly enough and we had to use the spike when it still had a rather high concentration. This led to an overdose of spike. When the spike was added, the test vessel's valve was opened and the gas pressure pushed out most of the solution that the fuel samples were stored in. The test vessel was then connected to a spike vessel and the value to the spike vessel was opened. The pressure in the spike vessel transferred the 30ml solution with the spike over to the test vessel.

The overdose of spike gave a large increase in the total U in the test vessels. A sample was taken immediately after adding the spike (in practice, about 1 hour after spike addition). Further samples were taken after 1, 7, and 18 days of testing. The samples were analyzed for U isotopic composition and concentration by ICP-MS, for ^{90}Sr via solvent extraction followed by Cerenkov counting of Y daughter product /Ramebäck et al, 1995/, and for Cs using a HPGe-detector for gamma detection. Data for the solution analyses are in Appendix I.

The [U] in the first sample (day 0) is dominated by the spike addition. We can calculate the amount of U in solution before the addition of the spike by using the measured amounts for [^{235}U] and [^{238}U]. For Series 1, the addition of 35.35 ppb of ^{235}U would have been accompanied by 3.98 ppb of ^{238}U. The measured [^{238}U] was 4.33 ppb, so the [^{238}U] in solution before spike addition was 0.35 ppb. Since the spent fuel U is 99% ^{238}U, this is essentially the total [U] in solution before spike addition (1.5×10^{-9} M). A similar calculation for series 2 gives a starting concentration of 0.29 ppb and for series 3 gives 0.85 ppb. These starting concentrations are in agreement with measurements that showed less than 1ppb in solution before spike addition.

All three samples show a relatively rapid decrease in [^{235}U] and [^{236}U] and a less rapid decrease in [^{238}U]. This indicates that the spike over-dose is precipitating from solution, but at the same time, the spent fuel is continuing to contribute ^{238}U to the solution phase. We can use the data from day 1, day 7 and day 18 samples to estimate how much additional U has dissolved from the solid while the samples were being tested. The ratio of measured [^{235}U] in the day 1 sample to that in the day 0 sample gives the fraction of U left in solution. For series 1 there is 93% left in solution, for series 2, 92% and for series 3, 92%. If we use these estimates of precipitation to adjust the day 0 value for [^{238}U], we estimate that the series 1 sample at day 1 should have 4.02 ppb for [^{238}U]. The measured value was 4.31 ppb, indicating that 0.29 ppb has been added to solution. Actually, the real addition would be somewhat greater since the sample is probably dissolving at a linear rate and precipitating at the same time, so some of the newly dissolved U has already precipitated when we take the day 1 sample. Since the amount of precipitation between day 0 and day 1 was only about 8%, the correction for the precipitation of newly dissolved U is small. It will be significant, however, for the later samples.

Between day 0 and day 7, the series 1 sample shows a decrease in [^{235}U] from 35.35 ppb to 21.82 ppb. Thus, only 62% of the spike is left in solution. Of the original 4.33 ppb of ^{238}U, only 2.67 ppb should be left. The measured [^{238}U] is 3.80 ppb, so 1.13 ppb of this represents new U that has been added to solution by dissolution. If we assume that the precipitation rate was linear, this would be 80% of the amount that actually dissolved, giving a total amount of U dissolution of about 1.4 ppb, or 0.2 ppb per day. Comparison of the day 7 and day 18 data for [^{235}U] shows that only 22% of the spike U present at day 7 is still in solution at day 18. Adjusting the day 7 [^{238}U] for precipitation gives an expected value of 0.82 ppb if no dissolution occurred. The measured value was 2.14 ppb, indicating 1.32 ppb new U in solution. Comparison of the precipitation rate for day 0 to day 7 with that for day 7 to day 18 suggests that the precipitation rate is somewhat faster than linear. We estimate that the measured increase in [^{238}U] would be about half of what actually dissolved, so total dissolution is about 2.6 ppb. Table 4-1 summarizes calculations for all three sample series. The results are in quite good agreement and indicate an average dissolution rate of 0.2 to 0.3 ppb per day.

Data for ^{137}Cs concentrations are given in Appendix I. The initial concentrations of 2 to 4 x 10^{-10} M are consistent with the data from the first sample for the last three cycles in our earlier series of experiments. The data for the day 18 sample, with values between 6×10^{-10} M and 2×10^{-9} M, are considerably lower than the concentrations measured at the end of the leaching cycle in the previous tests.

The abundance of ^{137}Cs in the spent fuel is about 0.09% of the [^{238}U]. If U were dissolving from the fuel at the same rate as ^{137}Cs, we would expect the dissolution of U between days 7 to 18 to be between $(3 \times 10^{-10})/0.0009$ moles/L (sample 2) and $(1.4 \times 10^{-9})/0.0009$ moles/L (sample 3). This would give a dissolution amount of 3×10^{-7} to 1.5×10^{-6} moles/L. The estimated amount of U dissolution for that time period based on isotopic data was about 3 ppb, or 3 μg/L, corresponding to 1.2×10^{-8} moles/L. This indicates that ^{137}Cs is being released at a rate that is 25 to 125 times faster than the rate of matrix dissolution. This shows that Cs release is not limited by the rate of matrix dissolution at this time.

Data for ^{90}Sr are not yet available. They will be added to the report as soon as the analyses are complete. This will allow us evaluate whether ^{90}Sr can be used as an indicator of matrix dissolution rate in experiments that have not used the isotope dissolution method to get a measured dissolution rate.

Table 4-1. Estimate of dissolution rate for spent fuel samples, ppb U.

Time interval	Series 1	Series 2	Series 3
Day 1 – day 0	0.3	nm	nm
Day 7 – day 0	1.4	0.7	0.07
Day 18 – day 7	2.6	3.6	3

nm = not meaningful

5 Conclusions

The experimental results given in this report allow us to draw the following conclusions.

1) Tests using unirradiated fuel pellet materials from two different manufacturers gave very different dissolution rates under air atmosphere testing. Tests for fragments of pellets from different pellets made by the same manufacturer gave good agreement. This indicates that details of the manufacturing process have a large effect on the behavior of unirradiated UO_2 in dissolution experiments. Care must be taken in interpreting differences in results obtained in different laboratories because the results may be affected by manufacturing effects.

2) Long-term tests under air atmosphere have begun to show the effects of precipitation. Further testing will be needed before the samples reach steady state.

3) Testing of unirradiated UO_2 in systems containing an iron strip to produce reducing conditions gave [U] less than detection limits (<0.02 ppb) after a few days to a few weeks of testing. Uranium recovered from the rinsing of reaction vessels and from acid stripping of vessels was shown to be from dissolution of grains of solid dislodged when the samples were handled after the tests were terminated.

4) Batch tests conducted under reducing conditions showed evidence of colloidal material in the early solution samples.

5) In the batch tests, measurements taken at day 3 and day 5 show that precipitation occurs from day 3 to day 5 without any further dissolution of the solid.

6) At termination of the batch tests, all but one sample had [U] in solution less than detection limits (< 0.02 ppb). Materials recovered in test termination samples showed evidence for recovery of small amounts – amounts corresponding to that expected from a few grains of 5 to 10 µm size – in the acidified solution samples. These are interpreted to have been dislodged during sample handling operations.

7) Batch test data show that increasing test duration beyond 2 weeks does not provide additional meaningful data.

8) A test procedure that used several short exposures of the sample to solution – the puff test procedure – gave results that showed very little recovery of the spike solution at the end of the tests. Only 10% of the ^{235}U added as spike was recovered, indicating that 90% of the spike had precipitated onto the solid sample or the iron strip.

9) Tests of UO_2 pellet materials containing ^{233}U to provide an alpha decay activity similar to that expected for spent fuel 3000 and 10,000 years after disposal showed that the pellet materials behaved as expected under air atmosphere conditions, showing that the manufacturing method was successful.

10) Early testing of the ^{233}U-doped materials under reducing conditions showed relatively rapid (30 minute) dissolution of small amounts of U at the start of the puff test procedure. Results of analyses of an acidified fraction of the same solutions after 1 or 2 weeks holding indicate that the solutions were inhomogeneous, indicating the presence of colloidal material or small grains of solid.

11) Samples from the ^{233}U-doped tests initially indicated dissolution of solid during the first week of testing, with some indication of more rapid dissolution of the material with the higher doping.

12) The second cycle of testing of the ^{233}U-doped materials also showed dissolution occurring during the dilution stages of the puff test. The subsequent week of testing also showed small amounts of further dissolution, with hints that the doped samples were dissolving faster than the undoped samples.

13) At the end of 2 weeks of cycle 2 the remaining solution and solid was transferred to a new reaction vessel, the solution was made up to original volume, and a new dose of spike was added. The results of analyses of [U] and isotopic composition show that the measured U is that expected from dilution of the original solution plus adding the spike.

14) Samples taken during 2 weeks of testing of respiked solution showed precipitation of U without further dissolution of the solids.

15) A new dose of spike was added to the remainder of the respiked cycle 2 solutions. [U] and isotopic composition was measured after spiking. Calculations showed that the [^{238}U] before spiking had been about 0.006 ppb.

16) In the test termination after 7 days, all solution samples were < 0.02 ppb, indicating precipitation of the spike. About 50% of the precipitated spike was recovered in acid stripping of the vessels.

17) Removal of U from the iron strips with sodium bicarbonate solution only recovered 5% of the missing spike. Thus, considerable amounts of the precipitated spike U seem to have gone onto the surface of the test samples.

18) In the final tests with ^{233}U-doped materials there was no evidence of enhanced dissolution due to alpha radiolysis.

19) Testing with spent fuel under 10 bar H_2 atmosphere showed decreasing [U] together with increasing [Cs] indicating that the H_2 was able to act as a reducing agent in the system.

20) Addition of a ^{235}U enriched spike caused larger than desired increases in [U]. Despite the rapid precipitation that subsequently occurred, we were able to calculate a dissolution rate for U from the spent fuel that was occurring even in the presence of precipitation.

21) Further testing is needed using more sensitive analytical techniques to establish the dissolution rate of the ^{233}U-doped materials.

22) Further testing of spent fuel is needed to verify the dissolution rate under H_2 atmosphere conditions and to obtain a dissolution rate in the presence of actively corroding iron.

6 Acknowledgements

The original idea to use isotope dilution for measuring spent fuel dissolution rates was suggested by Henry Shaw. We are grateful that we finally were able to fund a project to use the concept.

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7 References

Albinsson Y, Forsyth R, Skarnemark G, Skålberg M, Torstenfelt B, Werme L, 1990. In Sci. Basis for Nucl.Waste Management XIII, ed. V. M. Oversby and P. W. Brown (Mater. Res. Soc. Proc. 176, Pittsburgh, PA) pp. 559–565.

Forsyth R S, Werme L O, 1992. Spent fuel corrosion and dissolution, Journal of Nuclear Materials 190, 3–19.

Kleykamp H, 1985. J. Nucl. Mater. 131, 221–246.

Ramebäck H, Albinsson Y, Skålberg M, Werme L, 1994. Radiochimica Acta 66/67, 405–408.

Ramebäck H, Albinsson Y, Skålberg M, Sätmark B, Liljenzin J O, 1995. Nuclear Instruments and Methods in Physics research, A357 , 540–545.

Shoesmith D W, 2000. Fuel corrosion processes under waste disposal conditions, Journal of Nuclear Materials 282, 1–31.

Shoesmith D W, personal communication, 2003.

Wilson C N, 1990. Results from the NNWSI Series 2 Bare Fuel Dissolution Tests, Pacific Northwest Laboratory, Richland, WA 99352, September 1990.

Appendix A

Procedures for testing in WP1 and 2

Selection of test vessels

Experience from previous testing

Testing of materials with levels of radiation higher than natural background levels has been conducted in Pyrex, fused quartz, polypropylene, and Teflon vessels. Teflon is unsuitable for tests with elevated radiation levels, even for relatively short periods of time, because the radiation can cause fluoride ion to be released from the container material, resulting in the formation of HF (hydrofluoric acid) in the solution phase.

Pyrex vessels have been used in Studsvik for tests covering may years of total testing in the same vessel. The radiation causes the vessel to discolor, but no other effects due to radiation are seen in the vessel material (i.e. the vessel does not crack or otherwise visibly degrade). Pyrex can contribute significant levels of silica, boron, and sodium to the leaching solution phase due to dissolution of the vessel material.

Fused quartz has been used in testing of spent fuel samples for periods of 7 to 8 months at Westinghouse Hanford Co. No evidence for degradation of the material was observed. Fused quartz can contribute small amounts of silica to leaching solutions, but the amount of silica leached from fused quartz is substantially less than that leached from Pyrex vessels during equal time periods.

Both Pyrex and fused silica are brittle and likely to break if dropped. To limit the potential for contamination in the case of an accident in the glove boxes intended for use in WP1 and 2 it would be desirable to use a less brittle material. It is also desirable to use a material that will not react chemically with the test systems.

Polypropylene vessels were used in a set of tests at Studsvik. The tests used up to 16.6 g of spent fuel in 200 ml groundwater solutions, with a total exposure time of 211 days. Comparison of results of tests in polypropylene with those from tests conducted in Pyrex show no evidence for a difference in behavior attributable to the vessel material. The polypropylene vessels did not show significant degradation due to the radiation from the spent fuel – in particular, they did not crack.

Selection of vessel material

Polyethylene vessels were used by VTT in testing of unirradiated UO_2 in groundwater under air-saturated, anaerobic, and actively reducing conditions. Polyethylene and polypropylene vessels should have similar chemical characteristics under our planned test conditions as well as similar tendency to sorb materials from solution. Polyethylene should have similar resistance to radiation damage as polypropylene.

Based on the information summarized above, we selected polyethylene vessels for WP1 tests and for WP2 anoxic tests. WP2 oxic tests used glass bottles. WP3 tests were performed in pressure vessels lined with PEEK (polyether ether ketone).

Test procedure for WP1 oxic conditions used at VTT

Solid materials

Unirradiated UO_2 pellets obtained from a commercial fuel fabrication company, containing 2.8% ^{235}U, were used.

Pellets were used whole or were gently crushed to provide fragments for testing. The desired size of particles for fragment tests was 2 to 4 mm, which is similar to the size of particles one obtains when spent fuel is separated from its cladding. A percussion mortar was used to reduce a small pellet to fragments with about 60% of the mass in the size range 1.4 to 4.0 mm.

Each test with fragments used approximately 1 g of solid material. The geometric surface area of the particles was approximately 2 cm^2 per g. (This is the surface area of cubes with 3 mm sides and density 10).

Vessels for stock solutions and for testing

Vessels for stock solutions and containers used as test vessels were new high-density polyethylene containers. The vessels were cleaned prior to use by rinsing with high purity water several times. No acid was used in the cleaning process. Cleanliness was tested by filling the containers with high purity water, allowing the vessel to stand for several days, and then removing a water sample for analysis. Analyses included U isotopic composition and concentration and analysis for cations and anions.

The solid sample was placed on a fused silica "saucer" – similar in shape to a watch glass – so that the UO_2 solid did not come into direct contact with the plastic vessels. The purpose of the fused silica saucer is to prevent delivery of a direct radiation dose to the plastic vessel material.

Solutions

The solutions used in these experiments were prepared with high purity water and analytical grade solids (or better). The solutions were prepared and stored in high-density polyethylene bottles. The chemical composition of the solutions – prior to adding U spike – is given in Appendix B. The solution chemistry is the same as that used by Kaija Ollila of VTT during her uranium dioxide solubility studies in the 4th framework programme.

Two solutions of each composition were prepared. A dosage of depleted uranium was to be added to one of the stock solutions after the basic solutions had been equilibrated for a suitable time – a few days for the air saturated solutions. The uranium dosage was added to the stock solution in the form of uranyl nitrate. After addition of the U spike, the concentration and isotopic composition of the solutions – including those without U addition – were measured once a week until the solution concentrations were shown to be stable. Three consecutive determinations that agree within analytical uncertainties at the level of 2σ was the standard required.

Pretreatment of solids prior to the isotope dilution tests

Nine samples of fragments were prepared for testing in triplicate at three different concentration levels for the starting U in solution. Two samples of pellets were also used for each starting concentration. Pellet samples were treated in a manner similar to the fragment samples. The discussion below describes the process for the fragment samples.

The fragments were weighed and transferred, together with their fused silica "saucer", to a high-density polyethylene container in which the tests were done.

All pretreatment steps for the air-saturated set of experiments were done in air atmosphere. The solution that did not contain added uranium spike was used for the pretreatment steps. Approximately 15 to 20 ml of solution was added to the container with the solid. Using a pipette, the solution was swirled around the pellet fragments and then the solution was removed using the pipette. This step was repeated 3 times. The purpose of this step is to remove any loose fine fragments from the sample surface. The solutions from these steps were discarded.

20 to 25 ml of solution was added to the container with the solid and the vessel was covered. The sample was left for one day or longer. The solution was removed (using a pipette) and a sample was taken for analysis of U concentration and isotopic composition. New solution was added and left again for at least one day. This step was done at least 4 times. The purpose of this step is to remove any oxidized material from the sample surface, if present, and to dissolve any fine fragments of solid adhering to the larger particles. When the U concentrations were consistently on the order of 50 ppb, the solid samples were considered to be ready for the isotope dilution experiments. Care was taken that the solids always had a little solution over them to prevent oxidation of the solid above the level of $UO_{2.25}$, the value expected for the surface layer under the conditions of these experiments.

Method for the isotope dilution tests

Solutions containing 0.5, 1 and 2 ppm U were prepared by combining appropriate amounts of stock solutions. 30 ml of solution was prepared for each solid to be tested. 5 ml of solution with the appropriate starting concentration of U was used to rinse the solid and remove any residual solution from the pretreatment steps. (Note: Testing was started immediately after pretreatment was finished, or with a delay of no more than one day, to prevent excessive reaction of the solid with the residual liquid covering the solid.) The 5 ml of rinse solution was removed and saved for analysis. 25 ml of appropriate spiked solution was added to the solid samples and the container was loosely covered. Samples were taken for testing at the intervals given below.

SAMPLE SCHEDULE: 1 ml of solution was taken for analysis at the following times in days after the start of the experiments: 1, 3, 5, 9, 16, 31, 62, 100. It was assumed that the tests would be finished after 3 months. This was not the case, since the [U] was still increasing. Some tests were terminated and restarted in solutions with a higher initial [U] – 7 or 10 ppm; others were continued to longer testing times.

For samples taken during the running of the experiments, the only analyses were U concentration and isotopic composition of U. The solutions were not filtered prior to analysis. At the conclusion of the experiment, the remaining solution was removed and saved for more elaborate analyses. The solid sample was transferred to a new saucer and container and covered with a small amount of unspiked groundwater solution or was restarted in a new test series.

Note that during the tests the SA/V of the test system changed somewhat. After the sample was taken at 16 days into the testing, the SA/V was about 10 m^{-1} based on geometric surface area of the solid. The increase in SA/V during the tests is expected to increase, slightly, the dissolution rate of the solid. Tests using pellets contained 2 intact pellets and an initial volume of 71 ml, which also gave a SA/V of about 10 m^{-1} based on geometric surface area of the solid after the sample at day 16 was taken. Since the proportion of solution taken in a 1 ml sample was less for these tests, the change in SA/V during testing was less for these samples than for the fragment tests.

Test termination

The saucer and the container that were used in the testing was rinsed with unspiked groundwater several times, noting if there were any small solid fragments visible and if there were any signs of precipitated material on the saucer or the vessel surfaces. The rinse solutions were collected in a separate container. A sample of the rinse solutions was taken for U analysis. The remaining rinse solutions was acidified to produce 1M nitric acid solution and allowed to equilibrate for one day. In parallel, 1M nitric acid was added to the test container, with the saucer in it, so that any container surface that was under liquid level during the test was covered by nitric acid. This was left overnight to dissolve any precipitated or sorbed material. The rinse solutions were analyzed – both before and after acidification – and the acid strip solution for U concentration and isotopic composition.

Test procedure for WP1 reducing conditions used at VTT

The solid materials used in preliminary experiments under reducing conditions were samples that had been tested under oxic conditions. Most of the tests under reducing conditions used fresh solid materials, prepared in the same manner as for the oxic tests.

All solids used in reducing conditions tests were pretreated before the start of the reducing conditions tests. The pretreatments were very similar for both the preliminary tests and for the new solid materials. The description here is for the new solids. The vessels used for solution storage and for testing were of the same type as used for the oxic tests.

The solution used in the pretreatment steps was a synthetic modified Allard groundwater especially formulated to be in equilibrium under the anaerobic/reducing conditions expected for the tests and with the pCO_2 to be used in the glove box N_2 atmosphere. See Appendix B for the chemical composition of the solution.

Solid samples were transferred into the glove box placed in test vessels on silica saucers. Synthetic modified Allard groundwater that had been stored in the glove box to ensure that it was free of oxygen was added to the vessels – about 15 to 20 ml for each sample. The vessels were closed securely to avoid contact with the atmosphere in the glove box, which contained trace amounts of oxygen – generally less than 0.1 ppm. The samples were left in contact with the water for a day and then the water was changed. This step was repeated 5 more times, with varying lengths of contact time. The [U] in the solutions at the end of the 6th contact period was 1 to 3 ppb for fragment samples and 7 to 14 ppb for pellet samples (see Appendix D for details). New groundwater was added to each sample together with an Fe strip and the samples were left to equilibrate for 8 days. The water was then changed and the samples were left for 10 days. At the end of this time, the [U] in the solutions was between the detection limit of 0.02 ppb and 0.1 ppb.

The first isotope dilution test under reducing conditions used a U spike with 235/238 = 0.978 and a concentration of 0.08 ppb or 0.12 ppb. The spike was contained in modified Allard groundwater that had been pre-treated with Fe strips to ensure reducing conditions. Samples were taken after 1 day, 1 week and 2 weeks of exposure. Tests were then terminated using a procedure that was essentially the same as that for the oxic tests. The solid samples were transferred into new vessels and covered with conditioned groundwater to ensure that they did not develop an oxidized layer during storage awaiting further testing.

The second set of tests under reducing conditions used the same samples as the first set and was conducted for a long period with sampling only near the end of the tests. Four of the samples were tested without an Fe strip in the system. Tests were terminated after 55 days using the normal termination procedure and sample storage method.

The third and fourth test series used special procedures developed as we learned what was happening in the system. The details of these procedures are given in Appendix E.

Appendix B

Solutions for WP1, 2, and 3

B.1 OXIC: Fresh synthetic groundwater (Modified Allard) (log $pCO_2 = -3.5$)

Table B-1. Composition.

	(mg/L)	(mmol/L)
Na^+	52.5	2.3
Ca_2^+	10.2	0.25
Mg_2^+	2.8	0.11
K^+	3.9	0.10
SiO_2	2.9	0.05
SO_4^{2-}	9.6	0.10
Cl^-	47.5	1.3
HCO_3^-	90.7	1.5
PH theoretical	8.4	

Table B-2. Amounts of chemicals.

	(mg/L)
NaCl	40.95
$CaCl_2 \cdot 2H_2O$	37.54
$MgCl_2 \cdot 6H_2O$	2.88
KCl	7.46
$Na_2SiO_3 \cdot 9H_2O$	13.76
$MgSO_4 \cdot 7H_2O$	24.65
$NaHCO_3$	124.91

B.1.1 Preparation of concentrated stock solutions

The concentration of stock solutions is 200-fold.

Dissolve each chemical in small volumes (50 ml or 100 ml) of high purity water in polyethylene bottles:

Table B-3. Concentrated stock solutions. Amounts of chemicals.

		g/100 ml	g/50 ml
1	NaCl	0.8190	
2	$CaCl_2 \cdot 2H_2O$	0.7508	
3	$MgCl_2 \cdot 6H_2O$	0.0576	
4	KCl	0.1492	
5	$MgSO_4 \cdot 7H_2O$	0.4930	
6	$Na_2SiO_3 \cdot 9H_2O$		0.1376

Add $Na_2SiO_3 \cdot 9H_20$ to a little less than 50 ml water.

Neutralize with ca. 0.4 ml 2 M HCl to pH 8.4. Fill to the mark.

Use a fresh solution each time.

B.1.2 Preparation of oxic modified Allard groundwater (1 l)

1. Add high purity water (ca 800 ml) to a volumetric flask.
2. Add 5 ml conc. stock solutions 1, 2, 3, 4, 5 and 6 (Table B-3).
3. Add 0.1249 g $NaHCO_3$.
4. Add water a little less than to the mark.
5. Allow the solution to equilibrate for one day (or over the weekend) with air. Use magnetic stirring.
6. Adjust pH to 8.4 with 0.1 M NaOH and add water until the final solution volume is obtained.

B.1.3 Preservation

The solution should be stored in contact with air (a cap loosely screwed on).

Reference

Vuorinen U, Snellman M, 1998. Finnish reference waters for solubility, sorption and diffusion studies, Posiva Oy, Helsinki, Finland, Posiva Working Report 98-61, 41 p.

B.2 Fresh synthetic groundwater (modified Allard) ANOXIC (N2 atmosphere) (method 1 using conc. stock solutions)

Table B-4. Composition.

	(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

$pH_{theoretical,\ log\ pCO2=-4}$ 8.8

Table B-5. Chemical amounts.

	(mg/L)
NaCl	56.24
$CaCl_2 \cdot 2H_2O$	18.85
$MgCl_2 \cdot 6H_2O$	5.97
KCl	7.46
$Na_2SiO_3 \cdot 9H_2O$	7.96
Na_2SO_4	14.20
$NaHCO_3$	89.56

B.2.1 Preparation of concentrated stock solutions

The concentration of stock solutions is 200-fold.

Dissolve each chemical in small volumes (50 ml) of high purity water in polyethylene bottles:

Table B-6. Concentrated stock solutions. Amounts of chemicals.

		g/50 ml
1	NaCl	0.5624
2	$CaCl_2 \cdot 2H_2O$	0.1885
3	$MgCl_2 \cdot 6H_2O$	0.0597
4	KCl	0.0746
5	Na_2SO_4	0.1420
6	$Na_2SiO_3 \cdot 9H_2O$	0.0796

Add $Na_2SiO_3 \cdot 9H_2O$ to a little less than 50 ml water.

Neutralize with 1 M HCl to pH 8.8. Fill to the mark.

Use a fresh solution each time.

Place the uncovered bottles containing the concentrated solutions inside a larger container with gas inlets and outlets. Let the solutions deaerate in the container under N_2 flow for one day or overnight. Transfer the container into the glove box. Allow the concentrated stock solutions to equilibrate in the box loosely covered (caps loosely screwed on) for a couple of days before use.

B2.2 Preparation of anoxic modified Allard groundwater (1l)

De-aerate high purity water by bubbling with N_2 in a polyethylene bottle (2 liters: for one day or overnight). Transfer the bottle into the glove box. Continue bubbling with N_2 in the glove box for a couple of hours. Allow the water to equilibrate in the box loosely covered for one week.

1. Add de-aerated high purity water (ca. 800 ml) to a volumetric flask in the glove box.
2. Add 5 ml concentrated stock solutions 1, 2, 3, 4, 5, and 6 (Table B-6).
3. Add 0.0896 g $NaHCO_3$. Fill to the mark.
4. Allow the solution to equilibrate for one day loosely covered.
5. Adjust pH to 8.8 with NaOH (if necessary).

B2.3 Preservation

The solution should be stored in a tightly closed vessel under N_2 atmosphere.

Reference

Vuorinen U, Snellman M, 1998. Finnish reference waters for solubility, sorption and diffusion studies, Posiva Oy, Helsinki, Finland, Posiva Working Report 98-61, 41 p.

B3 ANOXIC (N_2 atmosphere) (method II – without concentrated solutions)

I. Dissolve in small volumes of high purity water:

1) 0.0562 g NaCl
   0.0060 g $MgCl_2 \cdot 6H_2O$
   0.0075 g KCl
   0.0142 g Na_2SO_4

2) 0.0189 g $CaCl_2 \cdot 2H_2O$

3) 0.0080 g $Na_2SiO_3 \cdot 9H_2O$
   Neutralize with 0.1 M HCl to pH 8.8.

II Add high purity water to a volumetric flask.

Add solutions 1), 2) and 3).

Add water a little less than to the mark.

Transfer the solution to a polyethylene bottle with gas inlets and outlets.

De-aerate the solution by bubbling with N_2 for one day.

Transfer the bottle into the glove box.

III Add 0.0896 g $NaHCO_3$ in the glove box.

Fill to the mark in a volumetric flask.

IV Allow the solution to equilibrate loosely covered for one day or over night.

V Adjust pH to 8.8 (if necessary) with NaOH.

Preservation

The solution should be stored in a tightly closed vessel under N_2 atmosphere.

Reference

Vuorinen U, Snellman M, 1998. Finnish reference waters for solubility, sorption and diffusion studies, Posiva Oy, Helsinki, Finland, Posiva Working Report 98-61, 41 p.

Appendix C

VTT Oxic tests, first cycle

The U-238 concentrations were measured using a U solution with a constant isotope ratio for U-235/U-238 (natural) as a standard.The error caused by U-235 was corrected. Bi-209 was used as an internal standard.

The U-235/U-238 ratios are the mean values of six parallel measurements.

The amounts of the samples for analysis

Day	(ml)	Day	(ml)
1	1.0	62	0.5
3	1.0	100	0.4
5	1.0	130	0.4
9	1.0	160	0.2
16	1.0		
31	1.0		

2000 ppb initial U, Pellet 235/238 = 0.029

UO_2-fragments (1)

(1.0058 g / 25 ml mod. Allard gw.)

SA/V ~ 10 m^{-1}

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	1926	
1	0.0036	2154	1963
3	0.0041	2205	2002
5	0.0051	2328	2086
9	0.0062	2168	2186
16	0.0082	2622	2395
31	0.0113	2903	2811
62	0.0154	3921	3651
100	0.0176	4846	4348
130	0.0223	5449	
160	0.0210	5838	6167
219	0.0222	6217	7236

2000 ppb initial U, Pellet 235/238 = 0.029

UO_2-fragments (2)

(1.0434 g / 25 ml mod. Allard gw.)

SA/V ~ 10 m^{-1}

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	1926	
1	0.0034	2073	1948
3	0.0039	2297	1986
5	0.0048	2282	2060
9	0.0057	2077	2139
16	0.0073	2357	2296
31	0.0098	2713	2593
62	0.0132	3479	3146
100	0.0151	4311	3573
130	0.0191	4826	
160	0.0184	5407	4672
219	0.0200	5615	5491

UO_2-fragments (3)

(1.0791 g / 25 ml mod. Allard gw.)

SA/V ~ 10 m^{-1}

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	1926	
1	0.0035	2158	1955
3	0.0042	2206	2010
5	0.0051	2212	2086
9	0.0062	2159	2186
16	0.0083	2546	2406
31	0.0111	2852	2780
62	0.0150	3600	3547
100	0.0167	4426	4033
130	0.0210	4855	
160	0.0201	5281	5552

2000 ppb initial U Pellet 235/238 = 0.029

UO_2-pellets (1)

(2 pellets / 71 ml mod. Allard gw.)

SA/V= 10 m^{-1} (after five samplings)

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	1926	
1	0.0042	2110	2010
3	0.0059	2292	2157
5	0.0078	2513	2350
9	0.0102	2349	2648
16	0.0133	2922	3166
31	0.0174	3625	4273
62	0.0208	4674	6019
100	0.0214	5761	6487
130	0.0269	6253	
160	0.0245	6914	10835
219	0.0248	7360	11587

UO_2-pellets (2)

(2 pellets / 71 ml mod. Allard gw.)

SA/V= 10 m^{-1} (after five samplings)

Day	U-235/U-238	U-238 ppb meaured	U-238 ppb calculated
0	0.0032	1926	
1	0.0044	2130	2026
3	0.0059	2322	2157
5	0.0075	2462	2317
9	0.0096	2444	2566
16	0.0129	2896	3088
31	0.0172	3548	4202
62	0.0209	4697	6092
100	0.0218	5825	6841
130	0.0278	6352	
160	0.0250	7218	12149
219	0.0254	7666	13453
237	0.0261	7945	16567

VTT restarted oxic tests

UO_2 fragments 1.0791 g/25 ml modified Allard gw. SA/V ≈ 10 m^{-1}

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	6585	
33	0.0041	6826	6822
51	0.0047	6771	6989
148	0.0068	7654	7647
238	0.0090	8631	8483
337	0.0093	8362	8611
407	0.0106	8547	9216
571	0.0119	9181	9911
683	0.0120	9293	9969
785	0.0126	9168	10331

UO_2 pellets # 1 – 2 pellets/71 ml modified Allard gw. SA/V ≈ 10 m^{-1}

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	6585	
33	0.0050	6874	7076
51	0.0055	6927	7226
148	0.0079	7974	8043
238	0.0083	8979	8198
337	0.0091	8402	8525
407	0.0097	8376	8789
571	0.0101	8395	8973
683	0.0110	8524	9419
785	0.0117	8527	9797

UO_2 pellets # 2 – 2 pellets/71 ml modified Allard gw. SA/V ≈ 10 m^{-1}

Day	U-235/U-238	U-238 ppb measured	U-238 ppb calculated
0	0.0032	9306	
33	0.0042	9390	9679
51	0.0046	9642	9837
148	0.0068	10895	10807
238	0.0082	11897	11530
337	0.0092	11889	12108
407	0.0097	12468	12420
571	0.0106	12740	13024
683	0.0115	12826	13689
785	0.0122	12480	14255

VTT Test Termination – first cycle oxic tests

RINSE:	before acidification:	**U-spike**	**U-238 (ppb)**	**U-238/rinse (ug) (15 ml)**	**U-235/ U-238**
R1 – EH	UO_2 fragments (1)	1 ppm	68.2	1.02	0.0268
R2 – EH	UO_2 fragments (2)	”	29.0	0.43	0.0313
R3 – EH	UO_2 fragments (1)	2 ppm	34.1	0.51	0.0270
R4 – EH	UO_2 fragments (2)	”	28.3	0.43	0.0201
R5 – EH	UO_2 fragments (1)	0.5 ppm	23.6	0.35	0.0317
R6 – EH	UO_2 fragments (2)	”	48.3	0.72	0.0315
R7 – EH	UO_2 pellets (2)	1 ppm	52.6	0.79	0.0364
R8 – EH	UO_2 pellets (1)	2 ppm	76.4	1.15	0.0260
	after acidification:				
R1 – H	UO_2 fragments (1)	1 ppm	75.1	1.13	0.0257
R2 – H	UO_2 fragments (2)	”	32.5	0.49	0.0251
R3 – H	UO_2 fragments (1)	2 ppm	36.2	0.54	0.0228
R4 – H	UO_2 fragments (2)	”	26.1	0.39	0.0205
R5 – H	UO_2 fragments (1)	0.5 ppm	24.0	0.36	0.0300
R6 – H	UO_2 fragments (2)	”	45.4	0.68	0.0311
R7 – H	UO_2 pellets (2)	1 ppm	51.7	0.78	0.0298
R8 – H	UO_2 pellets (1)	2 ppm	64.2	0.96	0.0258

ACID STRIP			**U-238 (ppb)**	**U-238/strip (ug) (25 ml)**	**U-235/ U-238**
S1	UO_2 fragments (1)	1 ppm	16.5	0.41	0.0256
S2	UO_2 fragments (2)	”	16.7	0.42	0.0298
S4	UO_2 fragments (1)	2 ppm	5.4	0.13	0.0273
S5	UO_2 fragments (2)	”	2.8	0.07	0.0318
S7	UO_2 fragments (1)	0.5 ppm	4.6	0.11	0.0314
S8	UO_2 fragments (2)	”	3.9	0.10	0.0309
S26	UO_2 pellets (2)	1 ppm	23.9	0.60	0.0324
S27	UO_2 pellets (1)	2 ppm	17.0	0.42	0.0344

AEAT Oxic Tests – Initial U 2ppm

Sample 5/1 – 0.950 g/25 ml modified Allard groundwater

Day	235/238	U238 measured	235/238 caluclated
0	0.0030	1971	
1	0.0032	1968	1975
2	0.0032	2228	1977
5	0.0037	2396	1998
7	0.0039	2228	2008
14	0.0047	1995	2047
28	0.0059	2131	2104
58	0.0084	2146	2238
89	0.0105	2357	2370
117	0.0119	2633	2460
155	0.0160	2530	2787
201	0.0215	2214	3387
343	0.0268	3539	4259

Sample 6/1 – 1.021g/25 ml modified Allard groundwater

Day	235/238	U238 measured	235/238 caluclated
0	0.0030	1971	
1	0.0032	1905	1977
2	0.0035	2342	1987
5	0.0038	2310	2003
7	0.0041	2239	2016
14	0.0050	2016	2059
28	0.0064	2239	2129
58	0.0091	2100	2280
89	0.0112	2381	2417

Sample 7/1 – 1.027g/25 ml modified Allard groundwater

Day	235/238	U238 measured	235/238 caluclated
0	0.0030	1971	
1	0.0033	1994	1980
2	0.0035	2233	1988
5	0.0040	2384	2012
7	0.0042	2229	2023
14	0.0050	1954	2061
28	0.0067	2260	2144
58	0.0100	2082	2338
89	0.0119	2402	2462
117	0.0132	2761	2557
155	0.0151	2688	2713
201	0.0237	2264	3702
343	0.0283	3902	4599

Sample 5/4 – 1.000g/25 ml modified Allard groundwater, no silica glass holder

Day	235/238	U238 measured	235/238 caluclated
0	0.0030	1971	
1	0.0032	2188	1977
2	0.0034	2243	1983
5	0.0039	2277	2005
7	0.0041	2222	2105
14	0.0049	2054	2054
28	0.0063	2095	2123
58	0.0083	1849	2235
89	0.0105	2297	2371
117	0.0117	2596	2248
155	0.0176	2958	2935
201	0.0213	2086	3361
343	0.0254	3452	3985

Reducing conditions tests, VTT
Sample pretreatment – new pellets and fragments

Without Iron

Fragments period	ml	M1 ppb U	M2 ppb U	M3 ppb U	M4 ppb U
1 d	15	5.8	13.1	8.3	7.7
3 d	15	5.7	13.1	8.2	7.7
4 d	15	3.7	12.8	5.4	5.8
1 d	15	1.0	2.8	1.3	1.9
8 d	20	3.1	10.0	5.4	4.8
5 d	20	1.9	5.6	2.7	3.2
2 d	20	0.9	2.1	2.3	1.6

Pellets period	ml	P1 ppb U	P2 ppb U
1 d	15	33.8	33.7
3 d	15	39.1	43.8
4 d	15	29.5	32.3
1 d	15	8.8	10.7
8 d	20	22.9	22.2
5 d	20	12.4	14.1
2 d	20	6.8	6.8

With Iron

Test	First, 8 d 20 ml ppb U	Second, 10 d 30 ml ppb U
M1	0.26	< 0.02
M2	0.18	”
M3	0.74	0.09
M4	0.17	0.02
M5	2.08	0.08
M6	0.13	0.06
M7	0.07	0.07
M8	0.08	< 0.02
P1	0.06	0.10
P2	0.10	0.03

Pretreatment, Total U release

Pretreatment, new pellets and fragments, no iron

Test	Solution* µg U	Rinse µgU/15 ml	Strip µgU/25 ml	Total U, µg
M1	0.36	0.019	0.20	0.57
M2	0.98	0.041	0.37	1.39
M3	0.56	0.022	0.40	0.97
M4	0.54	0.028	0.29	0.86
P1	2.51	0.094	2.08	4.69
P2	2.67	0,086	2.98	5.73

* Total of all solution samples

Note: Samples M5–M8 were pretreated in parallel, but the solutions were not analyzed.

First pretreatment with iron, 8 days

Test	Solution Total U µg U	Rinse Total U µgU/10 ml	Strip Total U µgU/20 ml	Total U µg
M1	0.005	0.012	0.10	0.12
M2	0.004	0.061	0.11	0.17
M3	0.015	0.038	0.10	0.16
M4	0.003	0.026	0.19	0.22
M5	0.042	0.022	0.38	0.44
M6	0.003	0.049	0.25	0.30
M7	0.001	0.023	0.17	0.19
M8	0.002	0.027	0.15	0.18
P1	0.001	0.039	1.40	1.44
P2	0.002	0.059	2.82	2.89

Second pretreatment with iron, 10 days

Test	Solution Total U µg U	Rinse Total U µgU/10 ml	Strip Total U µgU/20 ml	Total U µg
M1	<.0006	0.010	0.04	0.06
M2	<.0006	0.010	0.04	0.05
M3	0.003	0.013	0.06	0.08
M4	0.001	0.011	0.05	0.06
M5	0.002	0.015	0.11	0.13
M6	0.002	0.011	0.04	0.05
M7	0.002	0.009	0.04	0.05
M8	<.0006	0.007	0.04	0.05
P1	0.003	0.005	0.15	0.15
P2	0.001	0.029	0.18	0.21

VTT Reducing conditions isotope dilution trial

14 day test period in U-spiked groundwater

Initial conditions – U-235/U-238 = 0.029 ± 0.003 in the solid

Test	Solid phase	Solution (ml)	U-238 (ppb)	235/238	U-235 (ppb)	total U (ppb)
M1	1 g UO2 fragments	50	0.04	0.978	0.04	0.08
M2	”	50	0.04	0.978	0.04	0.08
M3	”	50	0.04	0.978	0.04	0.08
M4	”	50	0.04	0.978	0.04	0.08
M5	”	50	0.06	0.978	0.06	0.12
M6	”	50	0.06	0.978	0.06	0.12
M7	”	50	0.06	0.978	0.06	0.12
M8	”	50	0.06	0.978	0.06	0.12
P1	1 UO2 pellet	50	0.04	0.978	0.04	0.08
P2	”	50	0.06	0.978	0.06	0.12

Day 1 samples from the solutions

Fine particles in the samples disturbed the isotopic ratios

Test	U-238 (ppb)	235/238	235/238 Std Dev	U-235 (ppb)	total U (ppb)
M1	0.09	0.460	0.158	0.04	0.14
M2	0.20	0.379	0.090	0.08	0.28
M3	0.05	0.457	0.119	0.02	0.07
M4	0.04	0.362	0.148	0.01	0.05
M5	0.06	0.436	–	0.03	0.09
M6	0.07	0.797	0.403	0.05	0.12
M7	0.06	0.730	0.056	0.04	0.10
M8	0.44	0.336	0.113	0.15	0.59
P1	0.04	0.295	0.090	0.01	0.05
P2	0.07	0.379	0.071	0.03	0.10

Day 7 samples from the solutions

All samples less than detection limits (<0.02 ppb) except M7, which had 0.04 ppb U-238.

Day 14 samples from the solutions

All samples less than detection limits (<0.02 ppb)

14 day test termination – rinse samples (15 ml)

Test	Rinse soln U-238 (µg)	235/238	235/238 Std Dev	U-235 (µg)	total U (µg)
M1	0.011	0.029	0.001	0.0003	0.011
M2	0.022	0.030	0.001	0.0007	0.022
M3	0.018	0.030	0.001	0.0005	0.019
M4	0.010	0.029	0.001	0.0003	0.010
M5	0.029	0.030	0.001	0.0009	0.030
M6	0.032	0.030	0.001	0.0010	0.033
M7	0.012	0.030	0.001	0.0004	0.013
M8	0.025	0.029	0.001	0.0007	0.026
P1	0.010	0.029	0.001	0.0003	0.010
P2	0.034	0.030	0.001	0.0010	0.035

14 day test termination – acid strip samples (25 ml except for M1 which was 50 ml)

Test	U-238 (µg)	235/238	235/238 Std Dev	U-235 (µg)	total U (µg)
M1	0.039	0.031	0.004	0.001	0.040
M2	0.138	0.028	0.003	0.004	0.141
M3	0.143	0.028	0.001	0.004	0.147
M4	0.073	0.029	0.002	0.002	0.075
M5	0.215	0.031	0.003	0.007	0.221
M6	0.316	0.029	0.001	0.009	0.325
M7	0.129	0.030	0.001	0.004	0.133
M8	0.219	0.030	0.004	0.007	0.226
P1	0.334	0.032	0.007	0.011	0.344
P2	0.561	0.033	0.007	0.019	0.580

14 day termination – Acid strip reanalyzed – volume adjusted to 40 ml and left for 2 weeks additional stripping

Test	U-238 (µg)	235/238	235/238 Std Dev	U-235 (µg)	total U (µg)
M1	0.23	0.031	0.004	0.007	0.241
M2	0.53	0.028	0.003	0.015	0.541
M3	0.61	0.028	0.001	0.017	0.622
M4	0.31	0.029	0.002	0.009	0.322
M5	0.75	0.031	0.003	0.023	0.769
M6	1.10	0.029	0.001	0.032	1.134
M7	0.58	0.030	0.001	0.017	0.601
M8	0.73	0.030	0.004	0.022	0.756
P1	1.03	0.032	0.007	0.033	1.065
P2	1.66	0.033	0.007	0.055	1.711

Reducing conditions – long test with sampling at day 47 and at the end of the test (day 55) only

Initial conditions: Solid 235/238 = 0.029 ± 0.003

Test	Solid phase	Fe foil	Solution (ml)	U-238 (ppb)	235/238	calculated total U (ppb)
M1	1g fragments	Fe	50	< d. l.	10.354	0.05
M2	”	”	50	< d. l.	10.354	0.05
M3	”	no Fe	50	< d. l.	10.354	0.05
M4	”	”	50	< d. l.	10.354	0.05
M5	”	Fe	50	< d. l.	10.354	0.10
M6	”	”	50	< d. l.	10.354	0.10
M7	”	no Fe	50	< d. l.	10.354	0.10
M8	”	”	50	< d. l.	10.354	0.10
P1	1 UO2 pellet	Fe	50	< d. l.	10.354	0.05
P2	”	”	50	< d. l.	10.354	0.10

Samples taken at day 47

Test	U-238 (ppb)	235/238	235/238 Std Dev
M1	< d. l.	< d. l.	
M2	< d. l.	< d. l.	
M3	0.46	0.067	0.010
M4	0.59	0.071	0.007
M5	< d. l.	< d. l.	
M6	0.03	< d. l.	
M7	0.85	0.100	0.012
M8	0.10	0.168	0.037
P1	< d. l.	< d. l.	
P2	< d. l.	< d. l.	

55 day sampling – total solution acidified (after removal from contact with the solid) – 50 ml

Test	U-238 (ppb)	235/238	235/238 Std Dev	Solution total U (µg)
M1	0.26	0.029	0.003	0.013
M2	0.74	0.030	0.003	0.038
M3	0.73	0.033	0.003	0.038
M4	0.81	0.041	0.003	0.042
M5	0.30	0.030	0.002	0.015
M6	1.92	0.029	0.001	0.099
M7	0.93	0.062	0.003	0.049
M8	0.36	0.035	0.002	0.018
P1	0.43	0.029	0.002	0.022
P2	0.61	0.028	0.003	0.031

55 day termination, rinse solutions (15 ml)

Test	Rinse ppb 238	235/238	235/238 Std Dev	total U (µg)
M1	2.21	0.030	0.004	0.034
M2	2.42	0.034	0.007	0.037
M3	1.32	0.028	0.001	0.072
M4	0.67	0.028	0.009	0.008
M5	2.29	0.036	0.007	0.013
M6	4.57	0.027	0.004	0.038
M7	0.98	0.040	0.004	0.010
M8	2.06	0.035	0.006	0.020
P1	1.48	0.028	0.003	0.024
P2	4.63	0.030	0.003	0.102

Note: M3, M4, M7, and M8 did not contain Fe foils

55 day termination – acid strip of the vessel (50 ml)

Test	Strip 238 (µg)	235/238	235/238 Std Dev	total U (µg)
M1	0.087	0.030	0.003	0.089
M2	0.112	0.031	0.002	0.116
M3	0.066	0.030	0.004	0.068
M4	0.034	0.033	0.004	0.035
M5	0.114	0.036	0.003	0.118
M6	0.228	0.032	0.002	0.236
M7	0.049	0.031	0.003	0.050
M8	0.103	0.029	0.004	0.106
P1	0.074	0.031	0.003	0.076
P2	0.231	0.030	0.002	0.238

Note: M3, M4, M7, and M8 did not contain Fe foils

55 day termination – acid strip of the saucers

Test	U-238 (ppb)	1 M HNO3 (ml)	U-238 (µg)
M1	1.1	25	0.028
M2	4.4	10	0.044
M3	2.3	10	0.023
M4	2.6	10	0.026
M5	2.0	10	0.020
M6	8.6	10	0.086
M7	5.2	10	0.052
M8	2.3	10	0.023
P1	2.8	10	0.028
P2	2.7	10	0.027

55 day termination – acid strip of the Fe coupons

Test	U-238 (ppb)	1 M HNO3 (ml)	U-238 (µg)
M1	0,30	15	0,005
M2	0,79	15	0,012

Appendix E

VTT Reducing conditions batch tests with 1, 2, 4, and 8 week duration

All tests contained Fe foil, used 50 ml of modified Allard groundwater, and a U spike with 235/238 = 10.354.

Tests were started and allowed to run for 2 days before the spike was added.

The amount of spike added was sufficient to give a total [U] = 0.4 ppb – i.e. $[235]_{add}$ = 0.365 ppb and $[238]_{add}$ = 0.035 ppb.

Test	**Solid phase**	**Day 2 (4ml) ^{238}U ppb**
M1	1 g fragments	0.10
M2	1 g fragments	0.10
M3	1 g fragments	0.46
M4	1 g fragments	0.07
M5	1 g fragments	0.11
M6	1 g fragments	0.08
M7	1 g fragments	0.02
M8	1 g fragments	0.04
P1	1 pellet	0.03
P2	1 pellet	0.09

Day 3 samples (4 ml)

Test	**^{238}U (ppb)**	**^{235}U/^{238}U**	**^{235}U/^{238}U Std Dev**	**^{235}U (ppb)**	**Total U (ppb)**
M1	0.06	5.55	0.25	0.36	0.42
M2	0.05	6.00	0.73	0.32	0.37
M3	0.08	5.52	0.64	0.41	0.48
M4	0.05	7.21	0.64	0.39	0.44
M5	0.05	7.41	1.32	0.40	0.45
M6	0.04	6.66	0.96	0.28	0.32
M7	0.04	7.14	0.63	0.31	0.35
M8	0.04	6.76	1.26	0.29	0.33
P1	0.03	6.49	0.99	0.21	0.24
P2	0.05	5.59	0.48	0.30	0.35

Day 5 samples (4 ml)

Test	^{238}U (ppb)	$^{235}U/^{238}U$	$^{235}U/^{238}U$ Std Dev.	^{235}U (ppb)	Total (ppb)
M1	0.04	5.10	0.74	0.22	0.26
M2	0.03	6.25	0.86	0.20	0.23
M3	0.04	4.77	0.65	0.20	0.25
M4	0.03	6.08	1.01	0.20	0.23
M5	0.03	6.86	1.38	0.22	0.25
M6	0.02	6.35	0.63	0.14	0.16
M7	0.02	7.48	1.17	0.16	0.18
M8	0.02	7.19	0.95	0.15	0.18
P1	< 0.02				
P2	< 0.02	^{235}U > d.l.			

Notes on 235/238 measurements: Ratios given are normally the mean of six parallel measurements. Some measurements on day 3 and day 5 gave different values – typically only one of the six measurements giving high 238 counts. These measurements were excluded. They indicate the presence of very fine particle(s) from the original solid that is slowly dissolving.

Solution samples at test termination, unfiltered 4 ml samples, acidified immediately after sampling. Samp les for M1 and M2 were analyzed 3–4 hours after they were taken; other samples were analyzed after 3 to 6 days.

Test	Duration weeks	238 ppb	235/238	235 ppb	Total U ppb
M1	1	0.03	6.37	0.20	0.24
M2	1	<0.02	^{235}U>d.l.		
M3	2	<0.02	^{235}U>d.l.		
M4	2	<0.02	^{235}U>d.l.		
M5	4	<0.02		<0.02	
M6	4	<0.02		<0.02	
M7	8	<0.02		<0.02	
M8	8	<0.02		<0.02	

Note: 9 or 10ml of solution was also taken and filtered before acidification. Then the acidified samples were held for 3 to 6 days prior to analysis. Results for those samples are identical to the results for unfiltered samples.

Remained of solution (about 25 ml) removed from the solid, transferred to a new vessel and acidified (1M HNO_3). Solutions allowed to rest before analysis.

Test	Rest time days	238 ppb	235/238	Std. Dev.
M1	5	0.16	1.10	0.21
M2	5	0.23	0.32	0.03
M3	3	0.11	0.32	0.08
M4	3	0.09	0.51	0.11
M5	3	0.06	^{235}U<d.l.	
M6	3	0.03	0.22	0.18
M7	6	0.08	0.058	0.007
M8	6	<0.02		

Vessel rinse (3 × 5 ml, solutions combined)

		Filtered	Unfiltered		
Test	Rest time days	238 ppb	235/238	238 ppb	235/238
M1	5	0.03	^{235}U<d.l.	0.22	^{235}U<d.l.
M2	5	0.02	^{235}U<d.l.	0.60	^{235}U<d.l.
M3	3	<0.02	^{235}U<d.l.	0.50	0.07
M4	3	<0.02	^{235}U<d.l.	0.25	0.07
M5	3	0.03	^{235}U<d.l.	0.42	0.07
M6	3	<0.02	^{235}U<d.l.	0.29	0.11
M7	6	<0.02		0.25	0.11
M8	6	<0.02		0.86	0.06

Acid strip

		Vessels	50 ml	Saucers	10 ml
Test	Strip time days	238 ppb	235/238	238 ppb	235/238
M1	5	0.22	^{235}U<d.l.	nd	
M2	5	0.36	^{235}U<d.l.	nd	
M3	3	0.19	0.16	nd	
M4	3	0.06	0.18	nd	
M5	3	0.31	0.08	0.72	0.042
M6	3	0.18	0.43	0.63	0.075
M7	6	0.23	0.14	nd	
M8	6	0.57	0.09	nd	

nd= not determined

Puff test: to eliminate effects of any rapid release due to trace oxygen contact with samples during transfer to new vessles

To follow termination of batch tests

– terminate M7 and M8 and transfer the solids to new vessels. Add 50 ml of conditioned water as quickly as possible, cover, and leave for 2 hours.

After 2 hours: stir the solution gently and remove 30 ml.

This is **Sample 1**.

Add 30 ml to the vessel to return the volume to 50 ml. Stir gently, cover and leave for 30 minutes.

After the 30 minutes are up, stir gently and remove 30 ml.

This is **Sample 2**.

Add 30 ml to the vessel to return the volume to 50 ml. Stir gently, cover and leave for 30 minutes.

After the 30 minutes are up, stir gently and remove 30 ml.

This is **Sample 3**.

Add 30 ml to the vessel to return the volume to 50 ml. Stir gently, take a 5 ml sample.

This is **Sample 4**.

Then add the spike to give 0.4 ppb 235U in solution.

Add the Fe strip, cover and leave for one day.

After 1 day with the spike and Fe strip, take a 5 ml sample.

This is **Sample 5**.

After 3 days

Take **Sample 6** (total time = 4 days).

After 3 days

Take **Sample 7** (total time with the spike is 7 days).

Leave one week more and terminate after 2 weeks total exposure.

Puff test results

Test	Sample	^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std Dev	^{235}U counts
M7	Sample 1	< 0.02	–	–	–
M8	”	< 0.02	–	–	–
M7	Sample 2	< 0.02	–	–	–
M8	”	< 0.02	–	–	–
M7	Sample 3	< 0.02	–	–	–
M8	”	< 0.02	–	–	–
M7	Sample 4	< 0.02	–	–	–
M8	”	< 0.02	–	–	–
M7	Sample 5	0,03	7.805	0.441	1303
M8	”	0,06	8.225	0.249	1961
M7	Sample 6	< 0.02*	4.092	1.234	130
M8	”	0,02	7.599	0.950	768
M7	Sample 7	< 0.02	–	–	73
M8	”	< 0.02	–	–	113

* ^{238}U at detection limit

Test termination at 2 weeks total exposure

Samples of 5 ml from M7 and M8 taken, acidified and measured 5 days later. Total volume was 30 ml before sampling.

Samples of 10 ml each of M7 and M8 were then taken and filtered (0.2 μm) before acidification. Measured 5 days later. Volume remaining after sampling is about 15 ml.

These 4 samples were all below detection limits – < 0.02 ppb ^{238}U.

The remaining solution (15 ml) was removed from the solid, acidified with 1 M HNO_3 and left for 11 days. Samples were taken for analysis at 6 and 11 days.

Acidified solution results

Equilibrate Time	Test	^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std. Dev.
6 days	PM7	0.04	^{235}U<d.l.	
6 days	PM8	0.41	0.07	0.047
11 days	PM7	0.06	^{235}U<d.l.	
11 days	PM8	0.51	0.04	0.004

Rinse and acid strip solutions

A 5 ml sample of the rinse solution was filtered, acidified and analyzed 6 days later. This sample was below detection limits (< 0.02 ppb ^{238}U). The remaining 10 ml of rinse solution was acidified and left for 11 days with samples taken after 6 and 11 days. The acid strip of the vessel was also done for 11 days, with samples at 6 and 11 days.

Acidification Time	Test	^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std. Dev.
Rinse solution				
6 days	PM7	0.87	0.039	0.006
6 days	PM8	0.71	0.048	0.010
11 days	PM7	1.42	0.034	0.001
11 days	PM8	1.23	0.039	0.004
Acid strip				
6 days	PM7	0.45	0.149	0.019
6 days	PM8	0.34	0.182	0.008
11 days	PM7	0.58	0.115	0.017
11 days	PM8	0.55	0.112	0.012

Appendix F

Tests done at Chalmers

Tests with material doped with ^{233}U, air atmosphere

Table F-1. Data for pellets manufactured by BNFL.

Pellet	^{233}U(g)	^{235}U (g)	∑U (g)	^{233}U Bq/g
5–1	0.1970	0.1773	3.940	1.57E+07
5–2	0.1967	0.1770	3.934	
10–1	0.3894	0.1752	3.894	3.14E+07
10–2	0.3895	0.1753	3.895	

Pellet	Immersion Density (g/cm^3)	Density (%TD)	Diameter (mm)	Length (mm)
5-1	10.51	95.86	9.460	6.060
5-2	10.48	95.61	9.460	6.059
10-1	10.58	96.50	9.350	6.085
10-2	10.54	96.13	9.370	6.078

Table F-2. Pretreatment of pellet materials – 7 2-day equilibration times in modified Allard groundwater. Results for 7th period. [U] in ppb.

Sample	Total U	^{233}U/U$_{total}$	^{235}U/U$_{total}$
0%–A	22	<0.1	0.21
0%–B	23	<0.1	0.21
0%–C	20	<0.1	0.20
5%–A	12	4.8	4.3
5%–B	8	4.7	4.2
5%–C	11	4.8	4.3
10%–A	12	9.6	4.3
10%–B	12	9.6	4.3
10%–C	11	9.5	4.3

Table F-3. Air atmosphere testing of pellet fragments containing depleted uranium.

Sample	Time	233%	235%	238%	Total U, ppm
A0	0.1 h	0.00	0.22	99.8	0.14
B0	0.1 h	0.00	0.21	99.8	0.15
C0	0.1 h	0.00	0.21	99.8	0.13
A0	1h	0.00	0.36	99.6	1.60
B0	1h	0.00	0.36	99.6	1.59
C0	1h	0.00	0.36	99.6	1.58
A0	17h	0.00	0.36	99.6	1.60
B0	17h	0.00	0.36	99.6	1.58
C0	17h	0.00	0.36	99.6	1.58
A0	3.7d	0.00	0.35	99.6	1.64
B0	3.7d	0.00	0.35	99.6	1.65
C0	3.7d	0.00	0.35	99.6	1.64
A0	7.7d	0.00	0.45	99.5	nd
B0	7.7d	0.00	0.43	99.6	nd
C0	7.7d	0.00	0.42	99.6	nd
A0	41d	0.00	0.30	99.7	1.52
B0	41d	0.00	0.30	99.7	1.48
C0	41d	0.00	0.31	99.7	1.48
A0	103d	0.00	0.35	99.7	3.40
B0	103d	0.00	0.35	99.6	3.33
C0	103d	0.00	0.35	99.6	3.32

Table F-4. Air atmosphere testing of pellet fragments containing 5% ^{233}U.

Sample	Time	233%	235%	238%	Total U, ppm
A5	0.1 h	4.87	4.38	90.7	0.08
B5	0.1 h	4.60	4.11	91.3	0.05
C5	0.1 h	4.67	4.14	91.2	0.07
A5	1h	0.11	0.46	99.4	1.54
B5	1h	0.14	0.49	99.4	1.53
C5	1h	0.14	0.49	99.4	1.56
A5	17h	0.10	0.45	99.4	1.54
B5	17h	0.13	0.48	99.4	1.53
C5	17h	0.12	0.47	99.4	1.55
A5	3.7d	0.15	0.50	99.3	1.55
B5	3.7d	0.18	0.52	99.3	1.55
C5	3.7d	0.20	0.54	99.3	1.58
A5	7.7d	0.52	0.67	98.8	nd
B5	7.7d	0.87	1.14	98.0	nd
C5	7.7d	1.01	1.26	97.7	nd
A5	41d	0.95	1.18	97.9	1.88
B5	41d	1.28	1.54	97.2	1.83
C5	41d	1.33	1.53	97.1	1.93
A5	103d	2.20	2.30	95.5	2.61
B5	103d	2.14	2.25	95.6	2.50
C5	103d	2.03	2.46	95.5	2.73

Table F-5. Air atmosphere testing of pellet fragments containing 10% ^{233}U.

Sample	Time	233%	235%	238%	Total U, ppm
A10	0.1 h	9.38	4.16	86.5	0.08
B10	0.1 h	9.36	4.14	86.5	0.08
C10	0.1 h	9.25	4.15	86.6	0.07
A10	1h	0.13	0.43	99.4	1.51
B10	1h	0.16	0.44	99.4	1.51
C10	1h	0.14	0.43	99.4	1.50
A10	17h	0.22	0.46	99.3	1.52
B10	17h	0.31	0.50	99.2	1.54
C10	17h	0.21	0.46	99.3	1.52
A10	3.7d	0.45	0.56	99.0	1.57
B10	3.7d	0.54	0.59	98.9	1.58
C10	3.7d	0.44	0.55	99.0	1.55
A10	7.7d	2.15	1.37	96.5	nd
B10	7.7d	2.14	1.33	96.5	nd
C10	7.7d	1.91	1.25	96.8	nd
A10	41d	2.88	1.61	95.5	2.16
B10	41d	3.11	1.71	95.2	2.21
C10	41d	2.89	1.61	95.5	2.14
A10	103d	5.94	2.93	91.1	3.58
B10	103d	6.31	3.10	90.6	3.60
C10	103d	6.22	3.08	90.7	3.60

Appendix G

Tests done at VTT with ^{233}U doped UO_2 under reducing conditions

Pretreatment of samples

Day 1	Solid samples were immersed in 30 ml Allard groundwater (30 ml Nalgene bottles).
Day 2	5 ml samples from the leachant, changing of leachants
Day 4	As for day 2
Day 5	5 ml samples from the leachant, changing of leachants changing of test vessels acid stripping of the used test vessels
Day 8	5 ml samples, changing of leachants
Day 9	As for Day 8
Day 10	As for Day 8
Day 11	As for Day 8
Day 12	10 ml samples from the leachants, equilibration of the rest of the leachant with acid (1 M HNO3) changing of leachants changing of test vessels new saucers Fe strips immersed acid stripping of the used test vessels
Day 19	10 ml samples from the leachants, equilibration of the rest of the leachant with acid (1 M HNO3) changing of leachants changing of test vessels Fe strips immersed rinsing and acid stripping of the used test vessels
Day 26	As for day 19
Day 43	Termination of pretreatment 10 ml samples from the leachants, equilibration of the rest of the leachant with acid (1 M HNO3) rinsing and acid stripping of the used test vessels

Pretreatment without Fe strip

First cycle – 30 ml modified Allard groundwater

		1 day			2 days	
^{233}U (%)	Solid phase (g)	^{238}U (ppb)	^{233}U (ppb)	^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)
10	1.0120	86.29	9.42	10	19.73	2.07
10	0.9125	70.06	7.59	10	12.82	1.46
5	1.0085	50.68	2.57	5	8.51	0.46
5	0.9792	39.94	1.97	5	7.21	0.38
0	1.0995	52.14	–	0	15.26	–
0	1.0558	39.45	–	0	8.96	–

	1 day		Test vessel strip 30 ml 1 M HNO_3	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	3.74	0.41	10.16	1.11
10	2.81	0.30	8.93	0.99
5	2.70	0.15	4.90	0.25
5	1.50	0.08	4.87	0.26
0	4.21	–	7.71	–
0	2.26	–	8.30	–

Second cycle – 30 ml modified Allard groundwater

	3 days		1 day		1 day	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	17.86	1.90	4.61	0.54	1.49	<0.01
10	2.54	0.29	0.57	0.10	0.39	0.04
5	5.33	0.29	1.40	0.07	1.21	0.07
5	2.28	0.12	0.51	0.03	0.49	0.03
0	6.95	–	1.76	–	0.26	–
0	3.58	–	0.95	–	0.89	–

	1 day		1 day		Test vessel strip 30 ml 1 M HNO_3	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	8.01	0.86	4.40	0.54	5.69	0.61
10	0.39	0.05	0.41	0.03	6.06	0.64
5	2.50	0.14	1.73	0.10	4.77	0.24
5	0.58	0.03	0.74	0.06	4.81	0.25
0	1.50	–	1.41	–	13.31	–
0	0.99	–	0.67	–	15.50	–

Pretreatment with Fe, first cycle, 1 week duration

Test	Solution 10 ml		Acidified remainder 20 ml, 3 day hold	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	4.40	0.25	2.25	0.26
10	0.12	0.01	0.15	0.02
5	0.42	0.02	1.18	0.06
5	0.44	0.03	0.51	0.03
0	0.20	–	0.35	–
0	< 0.20	–	1.37	–

	Rinse, 15 ml acidified, 3 day hold		Acid strip, 30 ml, 4 day hold	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	0.26	0.03	1.54	0.17
10	0.19	0.02	1.20	0.13
5	1.39	0.07	5.68	0.26
5	0.50	0.03	1.98	0.10
0	0.59	–	2.18	–
0	11.71	–	5.21	–

Pretreatment with Fe, second cycle, 1 week duration

Test	Solution 10 ml		Acidified remainder 20 ml, 13 day hold	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	< 0.02	< 0.01	0.19	0.02
10	< 0.02	< 0.01	0.33	0.04
5	< 0.02	< 0.01	0.20	0.01
5	< 0.02	< 0.01	0.11	0.01
0	< 0.02	–	0.86	–
0	< 0.02	–	2.41	–

	Rinse, 15 ml acidified, 13 day hold		Acid strip 30 ml 13 day hold	
^{233}U (%)	^{238}U (ppb)	^{233}U (ppb)	^{238}U (ppb)	^{233}U (ppb)
10	0.36	0.03	0.85	0.09
10	0.29	0.02	1.06	0.11
5	0.24	0.07	0.86	0.05
5	0.15	0.03	0.65	0.03
0	0.41	–	0.86	–
0	0.53	–	1.08	–

Pretreatment with Fe, third cycle, 17 days duration

Test ^{233}U (%)	Solution 10 ml ^{238}U (ppb)	^{233}U (ppb)	Acidified remainder 20 ml, 2 day hold ^{238}U (ppb)	^{233}U (ppb)
10	< 0.02	–	< 0.02	–
10	< 0.02	–	0.02	–
5	< 0.02	–	< 0.02	–
5	< 0.02	–	0.10	–
0	< 0.02	–	0.13	–
0	< 0.02	–	0.39	–

^{233}U (%)	Rinse, 15 ml acidified, 2 day hold ^{238}U (ppb)	^{233}U (ppb)	Acid strip, 30 ml, 2 day hold ^{238}U (ppb)	^{233}U (ppb)
10	0.63	–	0.22	–
10	0.02	–	0.09	–
5	0.04	–	0.06	–
5	0.03	–	0.11	–
0	0.15	–	0.38	–
0	0.50	–	0.55	–

Appendix H

Test done at VTT with ^{233}U-doped UO_2 under reducing conditions

Cycle 1 – Puff test method

All steps to be carried out in the N_2 atmosphere glove box.

Transfer the pretreated samples to new vessels. Add 50 ml of conditioned water as quickly as possible, cover and leave 2 hours.

At the end of the 2 hours, stir the solution gently and remove 30 ml. This is Sample 1. Add 30 ml to the vessel and return the volume to 50 ml total. Stir gently, cover and leave for 30 minutes.

After 30 minutes are up, stir gently and remove 30 ml. This is Sample 2. Add 30 ml to the vessel and return the volume to 50 ml total. Stir gently, cover and leave for 30 minutes.

After 30 minutes are up, stir gently and remove 30 ml. This is Sample 3. Add 30 ml to the vessel and return the volume to 50 ml total. Add U spike so that the spike contribution to the solution is 0.4 ppb – 0.365 ppb ^{235}U and 0.035 ppb ^{238}U. Stir gently and take a 5 ml sample. This is Sample 4 and is the starting concentration measurement for the isotope dilution test. Add the Fe strip, cover and leave one day.

After 1 day with the spike and Fe strip take a 5 ml sample. Sample 5.

After 3 days more take a 5 ml sample. Sample 6 (total time = 4 days).

After 3 days more take a 5 ml sample. Sample 7 (total time = 7 days).

After 1 week more terminate the tests. The sample volume at termination is 30 ml. A 5 ml sample is taken and acidified without filtering. The remainder of the solution is removed from the solid, transferred to a new vessel, acidified and left for 4 days to equilibrate with the acid. The solid is removed and transferred to a new vessel and covered with conditioned water for storage until a new test series will start. The reaction vessels are rinsed 3 times with 5 ml of conditioned water. The rinse solutions are combined and acidified and held for 4 days to equilibrate with the acid. 50 ml of 1 M HNO_3 is added to the test vessel and left for 4 days before analysis. A 5 ml sample of this is the Acid Strip.

Data for cycle 1 puff test. Sample ID is “solid # – % ^{233}U – solution sample #”

Solid sample weights are given in Appendix G

Sample	^{238}U(2 days) (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std Dev	^{238}U(1 week) (ppb)	^{238}U(2 weeks) (ppb)
1-10-1	< 0.02	–	–	0.03	0.04
2-10-1	0.05	–	–	0.09	0.04
1-5-1	0.02			0.04	0.04
2-5-1	0.02			0.04	0.06
1-0-1	0.14			0.07	0.03
2-0-1	0.61			0.05	0.06
1-10-2	0.03	–	–	0.03	0.02
2-10-2	0.02	–	–	0.04	0.04
1-5-2	0.09	–	–	0.02	0.02
2-5-2	0.02	–	–	0.03	0.03
1-0-2	< 0.02	–	–	< 0.02	0.02
2-0-2	0.16	–	–	0.04	0.06
1-10-3	0.11	–	–	< 0.02	< 0.02
2-10-3	0.37	–	–	0.05	0.05
1-5-3	< 0.02	–	–	< 0.02	< 0.02
2-5-3	< 0.02	–	–	0.02	0.03
1-0-3	0.03	–	–	< 0.02	< 0.02
2-0-3	0.03	–	–	0.06	0.09
1-10-4	0.04	6.87	0.85	0.04	
2-10-4	0.05	9.17	1.69	0.05	
1-5-4	0.05	9.00	1.35	0.12	
2-5-4	0.05	7.58	1.47	0.06	
1-0-4	0.05	8.50	1.76	0.05	
2-0-4	0.04	7.63	0.53	0.04	
1-10-5	0.03	8.65	2.13		
2-10-5	0.06	8.69	1.37		
1-5-5	0.06	9.29	2.29		
2-5-5	0.04	7.64	1.02		
1-0-5	0.04	7.65	1.67		
2-0-5	0.05	6.52	1.15		
1-10-6	0.05	5.72	0.77		
2-10-6	0.12	3.84	0.25		
1-5-6	0.03	6.28	1.02		
2-5-6	0.04	6.58	1.34		
1-0-6	0.03	6.51	0.83		
2-0-6	0.03	7.36	1.61		
1-10-7	0.13	2.06	0.29		
2-10-7	0.24	1.41	0.11		
1-5-7	0.06	3.34	0.48		
2-5-7	0.05	3.98	0.51		
1-0-7	0.02	5.19	0.36		
2-0-7	0.02	8.36	0.90		

Cycle 1 termination (total duration 2 weeks)

Test	Solution ^{238}U (ppb)	Unfiltered ^{235}U/^{238}U	^{235}U/^{238}U Std Dev	Acidified remainder ^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std Dev
1 - 10	< 0.02	–	–	< 0.02	–	–
2 - 10	0.30	0.797	0.073	0.33	0.759	0.038
1 - 5	0.24	0.830	0.094	0.26	0.750	0.059
2 - 5	< 0.02	–		0.02	–	–
1 - 0	0.02	2.636	0.614	0.02	1.699	0.493
2 - 0	0.02	3.007	1.253	0.07	0.664	0.113

Test	Rinse ^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std Dev	Acid Strip ^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std Dev
1 - 10	0.14	0.14	0.03	0.21	0.35	0.06
2 - 10	0.33	0.08	0.01	0.05	^{235}U < d.l.	–
1 - 5	0.34	0.14	0.01	0.14	0.13	0.02
2 - 5	0.28	0.08	0.03	0.31	0.24	0.04
1 - 0	0.49	0.05	0.01	0.12	^{235}U < d.l.	–
2 - 0	1.35*	0.034*	0.01	0.42	0.06	0.01

*particles

Cycle 2 Puff test method

All steps to be carried out in the N_2 atmosphere glove box.

Take the stored samples from cycle 1 and transfer to new vessels, using new saucers. Add 50 ml of conditioned water as quickly as possible, cover and leave for 2 hours.

At the end of the 2 hours, stir the solution gently and remove 30 ml. This is Sample 1. Add 30 ml to the vessel and return the volume to 50 ml total. Stir gently, cover and leave for 30 minutes.

After 30 minutes are up, stir gently and remove 30 ml. This is Sample 2. Add 30 ml to the vessel and return the volume to 50 ml total. Stir gently, cover and leave for 30 minutes.

After 30 minutes are up, stir gently and remove 30 ml. This is Sample 3. Add 30 ml to the vessel and return the volume to 50 ml total. Add U spike so that the spike contribution to the solution is 0.4 ppb – 0.365 ppb ^{235}U and 0.035 ppb ^{238}U. Stir gently and take a 5 ml sample. This is Sample 4 and is the starting concentration measurement for the isotope dilution test. Add a new Fe strip, cover and leave one day.

After 1 day with the spike and Fe strip take a 5 ml sample. Sample 5.

After 3 days more take a 5 ml sample. Sample 6 (total time = 4 days).

After 3 days more take a 5 ml sample. Sample 7 (total time = 7 days).

At the end of 2 weeks, take a 5 ml sample. Transfer the rest of the solutions, the saucers with the samples on them, and the Fe strip to new test vessels. Increase the solution to a total volume of 50 ml and add a new dose of spike (20 ng total U added to increase the solution concentration of U by a total of 0.4 ppb.) Mix and take a 5 ml sample (Sample 14 + 0). Rinse and acid strip the old test vessels.

After one day take a 5 ml sample (Sample 14 + 1)

After 3 days more take a 5 ml sample (Sample 14 + 4)

After 3 days more take a 5 ml sample (Sample 14 + 7)

After 1 week more take a 5 ml sample (Sample 14 + 14)

After one day more increase the volume to 50 ml (same vessel). This dilutes the day 14+14 [U] by a factor of 2. Add a new dose of 20 ng of U spike, mix and take a 5 ml sample.

After 7 days take a 5 ml sample. This is 14 + 22 days total testing.

Leave the samples for 65 days. Terminate the tests. Total testing time is 14 + 87 days.

Termination procedure

1) A 10 ml sample was taken from the solution and transferred out of the box. The sample was then acidified to 1M HNO_3.

2) The remainder of the solution (30 ml) was pipetted very carefully from the region outside of the saucer and transferred to a new bottle. The solution was acidified to 1M HNO_3 after transfer from the box.

3) The solid sample in the saucer was transferred to a new test vessel (30 ml), 30 ml of Allard groundwater and an Fe strip were added, the bottle was closed and left in the box.

4) The used test vessel was rinsed with 3 × 5 ml water. The rinse solution was acidified to 1M HNO_3.

5) The used test vessel was filled with 50 ml of 1M HNO_3.

10 days later, 5 ml samples were taken from samples 2, 4, and 5. These were analyzed by ICP-MS 2 days later together with sample 1.

Cycle 2 test data – sample ID as for cycle 1

Test	^{238}U (ppb)	$^{235}U/^{238}U$	$^{235}U/^{238}U$ Std Dev
1-10-1	0.25	–	–
2-10-1	0.26	–	–
1-5-1	0.21		
2-5-1	0.27		
1-0-1	0.28		
2-0-1	0.37		
1-10-2	0.21	–	–
2-10-2	0.25	–	–
1-5-2	0.18	–	–
2-5-2	0.21	–	–
1-0-2	0.24	–	–
2-0-2	0.19	–	–
1-10-3	0.19	–	–
2-10-3	0.21	–	–
1-5-3	0.33	–	–
2-5-3	0.20	–	–
1-0-3	0.32	–	–
2-0-3	0.17	–	–
1-10-4	0.19	1.77	0.12
2-10-4	0.28	1.28	0.18
1-5-4	0.18	1.97	0.12
2-5-4	0.22	1.58	0.13
1-0-4	0.25	1.48	0.11
2-0-4	0.18	1.88	0.15
1-10-5	0.22	1.59	0.09
2-10-5	0.25	1.41	0.12
1-5-5	0.20	1.64	0.09
2-5-5	0.26	1.30	0.08
1-0-5	0.21	1.47	0.12
2-0-5	0.19	1.75	0.16
1-10-6	0.27	1.21	0.12
2-10-6	0.30	1.18	0.09
1-5-6	0.20	1.55	0.20
2-5-6	0.31	1.17	0.09
1-0-6	0.19	1.46	0.18
2-0-6	0.17	1.61	0.15
1-10-7	0.30	1.06	0.10
2-10-7	0.30	1.07	0.10
1-5-7	0.24	1.37	0.20
2-5-7	0.37	0.91	0.10
1-0-7	0.19	1.34	0.03
2-0-7	0.15	1.45	0.06

Cycle 2 – 2 week data plus rinse and strip of old vessels

Test	Solution (5ml) ^{238}U (ppb)	$^{235}U/^{238}U$	$^{235}U/^{238}U$ Std Dev
1 - 10	0.43	0.760	0.045
2 - 10	0.37	0.982	0.099
1 - 5	0.36	0.938	0.096
2 - 5	0.53	0.761	0.035
1 - 0	0.18	1.247	0.096
2 - 0	0.13	1.460	0.119

Rinse, 15 ml

Test	^{238}U (ppb)	$^{235}U/^{238}U$	$^{235}U/^{238}U$ Std Dev
1 - 10	0.24	0.072	0.026
2 - 10	0.54	0.060	0.009
1 - 5	0.10	^{235}U < d.l.	–
2 - 5	0.19	^{235}U < d.l.	–
1 - 0	1.59	0.031	0.005
2 - 0	0.24	^{235}U < d.l.	–

Acid strip 50 ml Test	6 day hold ^{238}U (ppb)	$^{235}U/^{238}U$
1 - 10	0.18	^{235}U < d.l.
2 - 10	0.14	^{235}U < d.l.
1 - 5	0.05	^{235}U < d.l.
2 - 5	0.09	^{235}U < d.l.
1 - 0	0.28	^{235}U < d.l.
2 - 0	0.13	^{235}U < d.l.

Cycle 2 – Second and third spike addition. Times given as 14 + x days because vessels were changed at 14 day. Solution [U] at day 14 + 0 should be 0.5 of that at the end of day 14 (previous table) if no further dilution has occurred.

Test	time (days)	^{238}U (ppb)	^{235}U/^{238}U	^{235}U/^{238}U Std Dev
1-10	14 + 0	0.27	2.18	0.09
2-10	14 + 0	0.22	2.69	0.18
1-5	14 + 0	0.22	2.81	0.28
2-5	14 + 0	0.31	2.06	0.16
1-0	14 + 0	0.15	3.72	0.43
2-0	14 + 0	0.17	3.58	0.30
1-10	14 + 1	0.14	1.95	0.27
2-10	14 + 1	0.16	2.79	0.29
1-5	14 + 1	0.11	2.80	0.43
2-5	14 + 1	0.21	1.98	0.12
1-0	14 + 1	0.10	3.53	0.66
2-0	14 + 1	0.10	3.84	1.07
1-10	14 + 4	0.03	2.09	0.49
2-10	14 + 4	0.03	3.02	0.37
1-5	14 + 4	0.02	^{238}U< d.l.	–
2-5	14 + 4	0.04	2.57	0.47
1-0	14 + 4	0.02	^{238}U< d.l.	–
2-0	14 + 4	0.02	^{238}U< d.l.	–
1-10	14 + 7	<0.02	–	–
2-10	14 + 7	<0.02	–	–
1-5	14 + 7	<0.02	–	–
2-5	14 + 7	<0.02	–	–
1-0	14 + 7	<0.02	–	–
2-0	14 + 7	<0.02	–	–
1-10	14 + 14	<0.02	–	–
2-10	14 + 14	<0.02	–	–
1-5	14 + 14	<0.02	–	–
2-5	14 + 14	<0.02	–	–
1-0	14 + 14	<0.02	–	–
2-0	14 + 14	<0.02	–	–
Add spike				
1-10	14 + 15	0.03	8.70	1.80
2-10	14 + 15	0.03	10.24	0.68
1-5	14 + 15	0.03	9.36	0.84
2-5	14 + 15	0.03	9.17	–
1-0	14 + 15	0.03	9.32	0.97
2-0	14+15	0.05	8.82	1.00

Cycle 2

Test	Time, days	^{238}U, ppb
All samples	14 + 22	< 0.02

Test termination samples

Test ID	Sa.1, ^{238}U, ppb	Sa. 2, ^{238}U, ppb
1-10	< 0.02	< 0.02
2-10	< 0.02	0.02
1-5	< 0.02	< 0.02
2-5	< 0.02	< 0.02
1-0	< 0.02	0.02
1-0	< 0.02	0.25

Rinse Samples

Sample ID	^{238}U, ppb	$^{235}U/^{238}U$	$^{235}U/^{238}U$, std.
1-10	0.11		
2-10	< 0.02		
1-5	0.03	0.33	0.07
2-5	< 0.02	1.20	0.34
1-0	0.21	0.093	0.012
2-0	0.55	0.050	0.006

Acid strip samples

Sample ID	^{238}U, ppb	$^{235}U/^{238}U$	$^{235}U/^{238}U$, std.
1-10	2.70	0.164	0.006
2-10	0.56	0.569	0.015
1-5	1.48	0.248	0.002
2-5	0.51	0.584	0.005
1-0	5.30	0.094	0.002
2-0	14.20	0.048	0.001

Leaching of U from the iron strips with $NaHCO_3$ solution (250 ppm bicarbonate)

1) The iron strips were transferred out of the glove box. They were allowed to stay in air for a couple of hours.

2) Each strip was immersed in $NaHCO_3$ solution (1 strip/25 ml) in Nalgene bottles. The bottles were loosely closed.

3) The Fe strips were allowed to stay in the solutions for one day.

4) The solutions were removed from the bottles and acidified (1M HNO_3).

5) A new dose of $NaHCO_3$ solution (25 ml) was added.

6) The Fe strips were allowed to stay in solutions for two days.

7) The solutions were removed from the bottles and acidified.

8) A new dose of $NaHCO_3$ solution (25 ml) was added.

9) The Fe strips were allowed to stay in solutions for two days.

10) The solutions were removed from the bottles and acidified.

Solutions (4), (7), and (10) were analyzed using 5 ml samples.

The Fe strips from the “undoped” and the “doped” tests seemed to behave differently in $NaHCO_3$ solution. The solutions in contact with the Fe strips from the undoped tests (1-0 and 2-0) had yellowish-brown precipitate in solution and on the surface of the strips. The addition of acid did not dissolve the precipitate entirely. These solutions were filtered before analysis. The solutions in contact with Fe strips from the doped tests looked colorless and did not have any yellowish precipitate. These solutions were not filtered.

Solutions Test ID	from (4) ^{238}U, ppb	$^{235}U/^{238}U$	5/8 Std. Dev.	from (7)* ^{238}U, ppb	from (10)* ^{238}U, ppb
1-10	0.03	1.18	0.12	0.02	0.04
2-10	0.03	1.55	0.12	0.03	0.04
1-5	0.03	2.43	0.18	< 0.02	0.02
2-5	0.04	1.61	0.12	< 0.02	0.02
1-0	< 0.02	–		< 0.02	< 0.02
2-0	< 0.02	–		< 0.02	< 0.02

* ^{235}U below 0.02

Appendix I

Data for isotope dissolution tests of spent fuel

Spike 234: 0.71±0.02%, 235: 84.6±0.1%, 236: 5.14±0.05%, 238: 9.53±0.05%

Fuel sample: 235: 0.35±0.04%, 236: 0.44±0.05%, 238: 99.21±0.07%

time,days	235% Series 1	238%
0	83.90	10.28
1	83.31	10.95
7	80.44	14.00
18	65.80	29.70
time	**Series 2**	
0	84.40	9.73
1	84.46	9.68
7	83.65	10.55
18	72.34	22.63
time	**Series 3**	
0	82.78	11.46
1	83.94	10.24
7	82.59	11.68
18	58.83	37.06

Time	Series 1	U 235 Series 2	ppb Series 3
0	35.35	112.98	32.93
1	32.83	103.43	30.41
7	21.82	43.80	16.48
18	4.73	9.82	3.13

Time	Series 1	U 236 Series 2	ppb Series 3
0	2.15	6.90	2.01
1	1.98	6.30	1.85
7	1.32	2.67	1.00
18	0.29	0.60	0.19

Time	Series 1	U 238 Series 2	ppb Series 3
0	4.33	13.02	4.56
1	4.31	11.85	3.71
7	3.80	5.52	2.33
18	2.14	3.07	1.97

Cesium-137 data

^{137}Cs	Concentration in moles per liter		
Time,days	sample 1	sample 2	sample 3
0.1	3.83E-10	1.70E-10	2.43E-10
1	3.49E-10	1.25E-10	2.87E-10
7	5.81E-10	2.71E-10	4.13E-10
18	1.13E-09	5.79E-10	1.82E-09

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