

SPENT FUEL AS A WASTE FORM - DATA NEEDS TO ALLOW LONG TERM
PERFORMANCE ASSESSMENT UNDER REPOSITORY DISPOSAL CONDITIONS.

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ABSTRACT

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Performance assessment calculations are required for high level waste repositories for a period of 10,000 years under NRC and EPA regulations. In addition, the Siting Guidelines (10CFR960) require a comparison of sites following site characterization and prior to final site selection to be made over a 100,000 year period. In order to perform the required calculations, a detailed knowledge of the physical and chemical processes that affect waste form performance will be needed for each site. While bounding calculations might be sufficient to show compliance with the requirements of 10CFR60 and 40CFR191, the site comparison for 100,000 years will need to be based on expected performance under site specific conditions. The only case where detailed knowledge of waste form characteristics in the repository would not be needed would be where radionuclide travel times to the accessible environment can be shown to exceed 100,000 years. This paper will review the factors that affect the release of radionuclides from spent fuel under repository conditions, summarize our present state of knowledge, and suggest areas where more work is needed in order to support the performance assessment calculations.

INTRODUCTION

High level waste disposal in the United States is controlled by several sets of regulations. The Environmental Protection Agency (EPA) has established environmental standards for the disposal of high level waste in geologic repositories [1]. The EPA standards set limits on the cumulative release of radionuclides to the accessible environment for a period of ten thousand years. Release limits are set for individual radionuclides and for the total activity released. The applicant for a repository construction and operation license must demonstrate that there will be a likelihood of less than 0.1 for releases to exceed the limits given in Table 1 of 40 CFR 191 and a likelihood of less than 0.001 for the releases to exceed 10 times those values.

The Nuclear Regulatory Commission has established a rule that implements the EPA standards [2]. In actuality, the NRC rule was published in final form while the EPA standard was still in draft form. Draft amendments to the NRC rule (10 CFR 60) have been prepared to implement those portions of the EPA rule that were not contained in the original version of 10 CFR 60. The NRC rule contains requirements for the total repository system; the only aspects of the rule that will be considered in this paper are the portions governing the long term control of the release rate of radionuclides from the engineered barrier system and the demonstration of performance of the total repository system with respect to controlling releases to the accessible environment.

The final regulation that requires a long range performance assessment of the repository is the Siting Guidelines, 10 CFR 960 [3]. While the screening guidelines were intended primarily for use in the screening and selection of potential repository sites for detailed characterization, they contain a requirement that the sites that have been characterized be compared prior to selection of a final repository site. The comparison is to be based on two calculations of the performance of the repository system for a period of 100,000 years using (1) a specified high value for the release of radionuclides from the engineered barrier system and (2) using a realistic, site-specific value. These calculations will require predictions of

performance of the waste form and engineered barrier system under anticipated processes and events for 10 times longer than the NRC rule.

This paper presents an analysis of the NRC and EPA regulations and derives from that analysis a ranking of the radionuclides in spent fuel. The ranking is based on the relative degree of difficulty anticipated in showing compliance with the regulations. The radionuclides are then grouped by chemical element based on the isotope of the element for which the greatest control is required. The location of the chemical elements in the spent fuel waste form - fuel pellets, cladding, and assembly components - is then discussed. The release characteristics of each of the waste form components for which data are available are reviewed, as are the variables known or suspected to influence the release rates. Finally, the effects of experimental conditions used in examining spent fuel on the data derived from the experiments are discussed and recommendations are made for the areas where data are most needed.

COMPARISON OF THE EPA AND NRC REGULATIONS

The NRC rule contains a requirement that the release rate of any radionuclide from the engineered barrier system following the 300 to 1000 year containment period be controlled to less than 1 part in 100,000 of the inventory of that radionuclide present 1000 years after repository closure. Radionuclides that are released at less than 0.1 percent of the calculated release rate limit, which is 1 part in 100,000 of the total inventory originally emplaced that remains after 1000 years of decay, are exempt from the requirement. Thus, the most stringent control that must be demonstrated is 1 part in 10^5 of an individual radionuclide's inventory at 1000 years after closure or 1 part in 10^8 of the total inventory present 1000 years after emplacement, whichever is greater.

A detailed analysis of the inventories of radionuclides and the NRC regulation has shown that for most radionuclides the total inventory clause is applicable [4]. This is true because the bulk of the activity in spent fuel is dominated in the post-containment time period by americium and plutonium isotopes. As shown in Table I, only 10 radionuclides must be controlled to 1 part in 100,000 of their own inventory, while the remaining 23 nuclides that constitute a significant contribution to the long term activity of spent fuel are covered by the calculated release rate limit clause. For radionuclides that are covered by the calculated release rate limit, the factor by which their release may exceed 1 part in 100,000 of their own inventory is given. For a containment period of 1000 years after repository closure and a total period of 10,000 years for control of releases from the repository, the release rate control period would be 9000 years. Integration of releases for 9000 years at a rate of 11 parts in 100,000 of inventory would cover the entire inventory of a radionuclide. Thus, for any radionuclide listed in Table I with a factor of 11 or greater, the NRC regulation would allow release over time of the entire repository inventory. As we will see later, when the locations of the nuclides in the waste form are considered, releases of this magnitude would be constrained by the properties of the waste form. For radionuclides with a release factor greater than 1 but less than 11, a fractional release of between 9 and 100 percent would be allowed under the NRC rule.

Many chemical elements are represented in Table I by more than one isotope. Since the isotopes of each element should be homogeneously distributed in the spent fuel waste form, the accounting task may be simplified by considering the isotope for which the most stringent control is required and assigning that value to the chemical element. Table II gives the release rate control for each element based on the control for the isotope that requires the most stringent control.

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Table I Release rate control required by 10 CFR 60.

Radionuclides whose release must be controlled to 1 part in 100,000 of their own inventory at 1000 years after repository closure:

Ni-59	Zr-93	Tc-99	U-234	Np-239
Pu-239	Pu-240	Pu-242	Am-241	Am-243

Radionuclides for which the calculated release rate limit applies and the factor by which their release rate may exceed 1 part in 100,000 of their own inventory at 1000 years after repository closure:

Nuclide	Factor	Nuclide	Factor	Nuclide	Factor
C-14	1.3	Cs-135	5.0	Cm-246	17
Nb-94	1.4	U-238	5.5	I-129	54
Pu-238	1.6	U-236	6	U-235	87
Np-237	1.7	Sm-151	11	Pu-241	87
Sn-126	2.3	Pd-107	16	Th-230	102
Se-79	4.3	Cm-242	17	U-233	540
Ni-63	4.6	Am-242	17	Ra-226	558
Cm-245	4.8	Am-242m	17		

Table II Release rate control based on chemical element.

Control of release rate for chemical elements based on the most stringent control required for any isotope of that element, in parts in 100,000 of the 1000 year post-closure inventory of that element.

Element	Control	Element	Control	Element	Control
Zirconium	1.0	Carbon	1.3	Samarium	11
Nickel	1.0	Niobium	1.4	Palladium	16
Technetium	1.0	Tin	2.3	Iodine	54
Uranium	1.0	Selenium	4.3	Thorium	102
Plutonium	1.0	Curium	4.8	Radium	558
Neptunium	1.0	Cesium	5.0		
Americium	1.0				

Table II, when combined with information concerning the location of the elements in the spent fuel waste form, can be used to determine the required control on dissolution rate for each of the waste form components. This assessment will be valid for all elements for which the solubility limit is not exceeded and which are not subject to retardation by ion exchange or other processes before leaving the engineered barrier system. The elements in the first column of Table II, which must be controlled based on their own inventory, contain a matrix element from each of the components of the waste form. Uranium is the major component of the fuel pellets, zirconium (in the case of Zircaloy) or nickel (in the case of stainless steel) are major components of the cladding, and nickel is a major component of the structural components of the fuel assemblies. This means that each of the waste form components must be studied to determine the rate of dissolution under repository relevant conditions. Zirconium generally has very limited solubility and it could be argued that knowledge of the rate of dissolution of

Zircaloy is not necessary; however, carbon-14 occurs as an activation product in the Zircaloy and can be expected to be very soluble under most conditions. Since the carbon-14 control required is only slightly less than the Zirconium control, dissolution rates for the Zircaloy are needed.

The minimum release rate control required by the NRC rule (Table I) can be compared with the requirements of the EPA rule only on a nuclide by nuclide basis unless a simplifying assumption is made. One such assumption is to require that no individual nuclide contribute more than any other to the ratio summation that is required to be less than unity under the EPA standard. The ratio is determined by dividing the actual release at the accessible environment by the allowed release under the EPA standard. If we set a ratio value of 1.0 to be 1 EPA unit, then under this assumption each nuclide would be allowed to contribute 0.035 EPA units to the summation [4]. Two points must be remembered in this comparison: (1) the EPA standard applies at the boundary of the repository with the accessible environment and the comparison to be made here is at the edge of the engineered barrier system, and (2) the assumption that no nuclide contribute more than 0.035 EPA units to the sum is not required by the EPA standard. Despite the limitations noted above, the ratios given in Table III are a useful indication of the portion of the job that remains to be done after the minimum NRC requirement for release rate control is met.

Table III gives the factor by which each chemical element exceeds the EPA release standard at the edge of the engineered barrier system based on the isotope for which the ratio of NRC to EPA allowed releases was greatest. Samarium is not listed because its NRC allowed release is less than 0.035 EPA units. It is obvious from the factors in Table III that americium and plutonium require the most reduction in release. This could be accomplished in a number of ways, such as lower waste form dissolution rates, demonstration of reduction in transportable species resulting from precipitation reactions, retardation of transport due to ion exchange or other sorption processes, or long groundwater travel times. The latter is especially important for americium, because the isotope that requires the greatest reduction has a half-life of only 455 years.

Table III Comparison of NRC and EPA allowed releases assuming that no nuclide contributes more than 0.035 EPA units to the sum of release ratios. Comparison is made at the edge of the engineered barrier system.

Element	NRC/EPA	Element	NRC/EPA
Americium	18,300	Nickel	13
Plutonium	12,300	Iodine	9
Thorium	457	Cesium	5
Uranium	52	Tin	5
Curium	46	Zirconium	5
Carbon	46	Selenium	5
Neptunium	46	Niobium	5
Radium	38	Technetium	3
		Palladium	3

RELEASE CHARACTERISTICS OF SPENT FUEL AT AMBIENT TEMPERATURE

The majority of studies that have investigated the leaching and dissolution behavior of spent fuel have been done at ambient hot cell

temperature. These studies, although they employed leaching solutions with somewhat different chemistry, show the same general features. To illustrate these features, I will use the results of the Nevada Nuclear Waste Storage Investigations (NNWSI) Series 2 dissolution tests. These tests used (in part) PWR fuel of average burnup from the H.B. Robinson reactor. The tests were run in cycles of approximately six months in the same solution. At the end of each cycle the solution and fuel samples were removed from the quartz vessel in which the test was run and transferred to a new vessel with fresh solution. Solution samples were taken periodically during the cycle, and at the end of the cycle the vessel was rinsed and then acid stripped to recover any material that had precipitated from solution. The detailed results from cycles 1 and 2 are given by Wilson [5]; the results from cycles 3 and 4 will be published in the future. The solution used for all cycles was J-13 well water, a dilute sodium bicarbonate groundwater. A detailed comparison of the NNWSI test results with those obtained by the Canadian and Swedish programs is given in Oversby and Shaw [6].

The concentration of uranium in periodic solution samples taken from the tests using bare fuel (with the cladding hulls also included in the test) for the four cycles of the Series 2 tests is plotted in Figure 1. Cycle 1 showed a peak of 4.5 mg/l of uranium in solution on day 6 of the test followed by a gradual decrease to 1.2 mg/l by the end of the cycle (223 days). Cycles 2 and 3 showed peak concentrations of 2 to 3 mg/l with gradual decreases through the test to reach 1 to 2 mg/l by the end of the cycle. The pattern of the data suggests that the early high concentration is due to supersaturation followed by a slow approach to a lower steady-state or equilibrium concentration. The samples were dry when first contacted with water and were allowed to dry between cycles 1 and 2 and cycles 2 and 3. The first pulse of uranium might be due to the suspension of ultra-fine particles of fuel in the solution. In an attempt to reduce this possibility, the fuel was immediately transferred to fresh leaching solution at the end of cycle 3 without allowing it to dry.

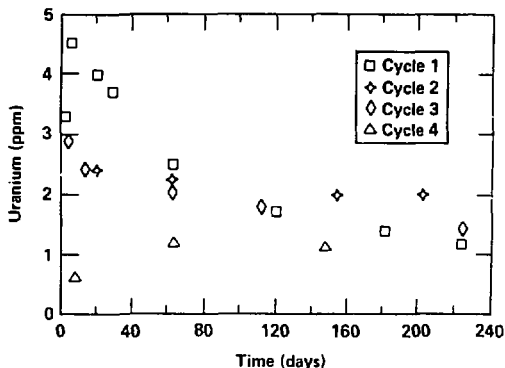


Figure 1. Concentration of uranium in solution for the four cycles of the NNWSI Series 2 dissolution tests. Tests run at ambient hot cell temperature in quartz vessel using bare fuel with split cladding hulls present in the test.

The uranium concentration in cycle 4 does not show an early peak, but starts below 1 mg/l and gradually rises to the value to which the earlier cycles had fallen. The pattern seen in cycles 1 through 3 might also be due to the presence of a very small oxidized layer on the fuel particles, which might have been produced during the drying between cycles and the storage of the fuel in air between sample preparation and test start. In either case, the data have the form expected for a reversed solubility experiment, with cycles 1 through 3 representing the approach from supersaturation and cycle 4 the approach from undersaturation.

A large fraction of the total uranium recovered from cycle 1 was found in the vessel rinse and strip samples; only 14% of the uranium was recovered in true solution samples. For plutonium, americium, and curium, the vast majority of the material recovered was in the vessel acid strip. Only 1.6% of the americium and plutonium, and 2.3% of the curium, were recovered as solution species. For neptunium, less than 10% of the recovered material was in solution species. The total amounts of the actinides recovered, as determined by summing the solution, rinse, and acid strip samples, were in proportion to their presence in spent fuel. Total releases for cycle 1 were about 5 times those seen in cycle 2 for the actinides. This suggests that the formation of fine fragments of fuel, perhaps as a result of sample preparation methods, introduces a significant experimental bias in the first cycle of spent fuel dissolution tests. Only by doing several cycles with the same fuel can the effects of this bias be assessed.

In cycle 2 of the test, 60% of the uranium released was recovered in solution samples as was approximately 40% of the neptunium. In contrast, only 1% of the americium and curium, and 4% of the plutonium were recovered as solution species. Again, the total release of each actinide was in proportion to the inventory present in the fuel. Since the uranium release was more than 60% by solution processes, with a maximum of 40% by disaggregation of fine fuel particles, the data indicate congruent dissolution of all of the actinides from the fuel matrix followed by precipitation of the less soluble actinides - curium, americium, and plutonium.

Table IV summarizes the results for uranium, the actinides, and for four fission products that show preferential release patterns. Data for the Turkey Point fuel samples that were also part of Series 2 show similar results. One major difference is that the percent of material recovered as solution samples for the Turkey Point samples was about 5 times higher for the actinides. This is due to the smaller fuel to water ratio for the Turkey Point bare fuel test; solution concentrations for the H.B. Robinson and Turkey Point tests were similar.

Table IV Summary of release data for NNWSI Series 2 H.B. Robinson bare fuel samples, Cycles 1 and 2, conducted at ambient hot cell temperature.

Element	Cycle 1		Cycle 2	
	Total Release parts in 10 ⁵	Percent in Solution	Total Release parts in 10 ⁵	Percent in Solution
Uranium	5.66	14	1.54	60.5
Plutonium	7.18	1.6	1.28	4.1
Americium	8.04	1.6	0.77	1.0
Curium	8.64	2.3	1.61	1.0
Neptunium	<7.0	<10	<1.6	<40
Cesium	776	95	20	93
Technetium	23	77	<8.6	87
Iodine	10.5	nd	7.5	89
Strontium	nd	nd	24.8	88

The largest release observed for any element was for cesium-137 in the first cycle. The fission gas release for this fuel was only 0.2%, so the release of cesium was about 4 times greater than the fission gas content of the pellet-cladding gap. This suggests that a major part of the early cesium release is due to leaching of the grain boundaries of the fuel, where fission products mobilized under reactor operating conditions have been segregated and enriched relative to the average inventory of the fuel. The amount of released cesium not recovered in cycle 1 solution samples was $0.05 \times 776 \times 10^{-5}$ of the inventory of cesium, or 38.8 parts in 100,000 of the total cesium-137 inventory. This is several times the inferred quantity of fuel particles ($0.86 \times 5.66 \times 10^{-5}$ or 4.9 parts in 100,000 based on uranium recovered in rinse and strip samples). Since the fine particles recovered would include mainly those from the surface of the pellets and from the fractures occurring at grain boundaries, this is another indication of enrichment of cesium in the grain boundary regions of the fuel.

Technetium release in cycle 1 was approximately 4 times uranium release, indicating an enrichment of technetium in the gap and grain boundaries regions that is significant but much less pronounced than that of cesium. If we assume that the 23 percent of the technetium recovered in rinse and strip samples represents fuel particles, it would correspond to 5.3 parts in 100,000 of the technetium inventory. This is in good agreement with the estimate based on uranium. Iodine release showed a slight enrichment compared to uranium and the other actinides in cycle 1 and a much larger preferential release in cycle 2. The acid strip solution was not examined for iodine in cycle 1 and may have contained a significant amount, although the cycle 2 strip solution did not.

Figure 2 shows the cesium solution concentrations (in activity units) for cycles 2, 3, and 4, and Figure 3 shows results for technetium for all four cycles. The cycle 1 cesium results are higher than those for cycle 2 by a factor of 40 and would plot far off scale in Figure 2. Cycle 2 cesium results are higher than those for cycles 3 and 4 by a factor of about 4, indicating that an enriched phase or perhaps a phase precipitated from cycle 1 solutions onto the fuel is being preferentially leached. The data for cycles 3 and 4 are in good agreement for cesium, indicating a pseudo-steady state release pattern. The reason for "pseudo" is that the release rate for cesium is still several times higher than that for uranium in cycles 3 and 4. Technetium has reached a pseudo-steady state release rate by the start of cycle 2, as indicated by the agreement of the data for cycles 2, 3, and 4. Again, the technetium release is a higher fraction of the inventory than the uranium release by about a factor of 5.

Carbon-14 release has been measured in the Series 2 tests, but the results are somewhat ambiguous because the test vessels had loose-fitting lids that allowed equilibration of the air above the solutions with the atmosphere. This could allow some carbon-14 loss due to exchange of $^{14}\text{CO}_2$ from the test solutions with natural carbon dioxide in the atmosphere. The best indication of potential for preferential release of carbon-14 available is that from the air oxidation testing of a full assembly of Turkey Point fuel [7]. This test showed the release of about 0.3% of the inventory of carbon-14 into air at 275°C during the first few weeks of the test. Subsequent data show that this initial release was a pulse of activity and that further releases were orders of magnitude lower [8]. Carbon-14 does not appear to be a significant part of the gas present in the pellet-cladding gap in spent fuel [9].

The release characteristics of carbon-14 present the greatest uncertainty in the present data set, apart from those for nickel isotopes for which no data exist. The reason for the difficulties with carbon-14 are that its inventory is very uncertain. This is because it is an activation product produced by several different mechanisms. The most likely reactions to produce carbon-14 are those involving nitrogen impurities in the fuel pellets, cladding, and assembly components, carbon-13 impurities in all of those components, and reactions involving oxygen-17 in the cooling water of the reactor [8].

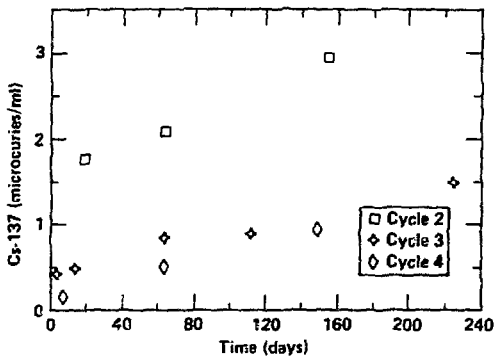


Figure 2. Activity in solution for cesium-137, NNWSI Series 2 tests, cycles 2, 3, and 4. Release for cycle 1 was about 40 times higher than for cycle 2.

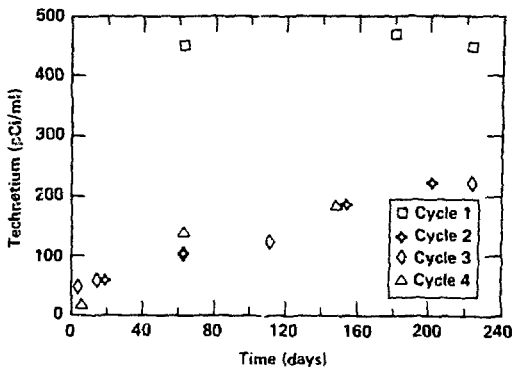


Figure 3. Activity of technetium in solution, NNWSI Series 2 tests.

FACTORS THAT AFFECT THE DISSOLUTION RATE OF SPENT FUEL

There are many factors that are either known to, or are strongly suspected to, influence the dissolution behavior of spent fuel. In some cases the effects may be small, but the importance to repository licensing requires a detailed assessment to be made. In the following paragraphs, I will discuss the factors that I believe will be most relevant to understanding the properties of spent fuel in a repository setting and allowing long-term predictions of its performance to be made.

Reactor type

The type of reactor in which the fuel was used and the burnup to which the fuel was taken could affect the post-irradiation physical and chemical properties of the fuel. Forsyth [10] has suggested that the method of operation of BWR reactors may even lead to differences in fuel dissolution behavior within a single fuel rod. The fuel destined for a repository will consist of a mixture of BWR and PWR fuel with a wide range of burnup for each type. Testing to date in the United States has focussed on two PWR fuels with average burnup. This is due to the difficulty in obtaining spent fuel samples for use in testing. The Swedish program has used a high burnup BWR rod in most of its testing, with limited work on a very low burnup BWR rod [11]. The Canadian reactors use natural uranium and are run under quite different conditions from light water reactors [12]. Where tests have been run in solutions of similar chemistry, the results for all of these fuels have been in good agreement. Differences within nominally equivalent fuels appear to be similar in size to those found between BWR and PWR fuels [6, 11].

Fission product migration - gap and grain boundary inventories

The largest variations in release characteristics for spent fuel occur in the elements that can be volatile under reactor operation conditions or that can be segregated to grain boundaries if restructuring of the fuel occurs during reactor operation. The primary indicator of fission product mobility in spent fuels is the amount of krypton-85 that is released from the fuel pellets and accumulates in the pellet-cladding gap during burnup. This gas can be recovered by puncturing the cladding in a vacuum system, recovering the pressurization gas (if present) and the fission and activation products that are present in the gas. Johnson et al. [12] have shown that preferential release of cesium during the early stages of dissolution tests can be correlated with release of fission gas to the pellet-cladding gap (Figure 4).

The preferential release of cesium, and to a lesser extent technetium, iodine, and strontium, may also depend on the grain size of the initial fuel pellets (prior to irradiation). Wilson [5] found that cesium release during cycle 1 of the Series 2 MWSI test was comparable to fission gas release for Turkey Point fuel but was several times greater for H. B. Robinson fuel. The cesium release characteristics of the two fuels were nearly identical for cycle 2. He attributed the greater release of cesium for the H. B. Robinson fuel to its smaller grain size, which would provide a larger area of grain boundaries relative to the Turkey Point fuel. Neither fuel showed evidence of significant restructuring during irradiation; thus, the greater abundance of cesium available for early release appears to be related to the smaller distance from grain interiors to grain boundaries in the finer grained fuel. The shorter travel path from the interior to the boundary would allow a greater proportion of elements that tend to segregate from the fuel matrix to segregate on grain boundaries rather than form separate phases trapped within the grains. The effect of grain size is suggested by the technetium data, also. The ratio of release of technetium to uranium was also greater in the

H.B. Robinson tests than in the Turkey Point tests.

Oxidation state

Fuel oxidation state is expected to be a significant factor in the dissolution rate of spent fuel. Differences between the release characteristics of uranium for the Turkey Point and H. B. Robinson Series 2 tests have been attributed to the long storage time between preparation of the fuel rod segments and use in the tests [5]. Studies of the dissolution behavior of UO_2 using electrochemical techniques have shown that dissolution proceeds via an oxidized layer on the surface of the pellet [13]. Oxidizing conditions might be produced near the surface of the fuel due to radiolysis of the water, even if the general aqueous conditions were reducing. Differences in oxidation state of the starting materials or the local conditions at the surface of the test specimens might produce differences in test results for spent fuel and unirradiated fuel pellets.

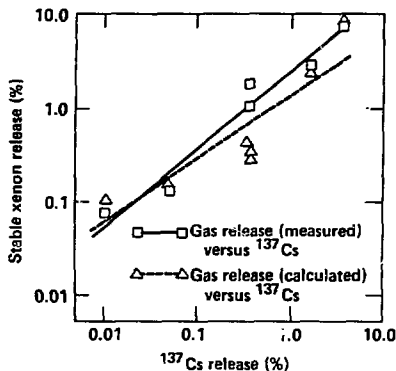


Figure 4. Correlation of fission gas release and rapid release fraction of cesium from CANDU fuel [12].

Cladding condition

The condition of the cladding on fuel can have a dramatic effect on the rate of dissolution of the fuel. Intact cladding prevents the access of water to the fuel and limits radionuclide release to those elements that are present in the cladding or in crud adhering to the cladding. Cladding with rather large defects can still provide an impediment to water flow and may provide a "micro-climate" inside the cladding that causes fuel dissolution to be less than in the case of bare fuel with cladding present but not surrounding the

ue! Figure 5 shows the uranium solution concentrations for tests using H.B. Robinson fuel at 85°C in J-13 water. These tests were run in sealed stainless steel reaction vessels. The labels on the curves indicate the specimen type (UD = undefected cladding, HD = two laser-drilled holes in the cladding, SD = slit machined in the cladding, BF = bare fuel with the cladding hulls included in the test), the fuel type (HBR = H. B. Robinson, TP = Turkey Point), the test series (NNWSI series 2 or 3), and the test temperature (25 or 85°C). The last data point for HBR at 85°C is thought to be low because of incorporation of uranium (and other elements) into corrosion products from the fuel sample basket. The slit and hole defect samples show virtually indistinguishable release from the undefected specimen. Cesium data for these tests showed that the end fittings were water-tight for the undefected specimen, so the uranium release seen is due to external contamination of the cladding. Tests conducted at ambient temperature showed differences between the two defect types and the defected and undefected samples, but the same dramatic difference between bare fuel and fuel with some degree of cladding protection was evident.

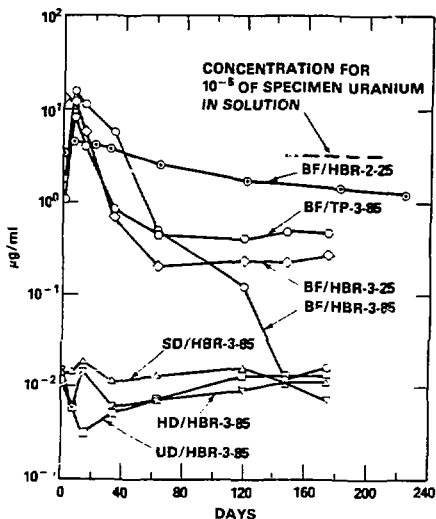


Figure 5. Uranium concentrations in unfiltered solutions for NNWSI Series 3 tests and for the H. B. Robinson Series 2 bare fuel sample [14]. See text for symbol explanation.

Temperature:

The data in Figure 5 show that there is no distinguishable difference between the behavior of the H. B. Robinson fuel in J-13 water at 25 and 85°C in the series 3 tests. There is a difference between the series 2 and series 3 data for 25°C, which may be due to either the vessel material or the use of sealed vessels versus vessels with loose fitting lids. The cause for this difference will be examined in future testing. Further details of the series

3 tests are discussed by Wilson and Shaw [14]. Comparison of results for technetium, a highly soluble element under the test conditions, at the two temperatures confirms the absence of a significant temperature effect. The absence of a strong temperature coefficient for spent fuel dissolution will make the task of long term performance prediction much easier than it would have been if there were a strong temperature dependence.

Water chemistry

Water chemistry is the final factor that needs to be examined. There are few data available where the influence of water chemistry on spent fuel dissolution can be isolated from other effects, such as sample preparation, storage, oxidation state, fuel type. Wilson tested samples of Turkey Point fuel in deionized water [15] and in J-13 water [5] under identical test conditions. The solubility of uranium was lower in deionized water, but the overall release characteristics in the two test series were similar. The most important solution chemistry effect is probably due to carbonate, which can increase the solubility of uranium by complexation [13].

The major effect of water chemistry will probably be to determine the nature of the solid phases that limit the solubility of uranium and the actinides. In deionized water, a uranium oxide or hydroxide phase probably controls the uranium concentration in solution; in a silicate-bearing groundwater, the solubility control may be due to a uranium silicate phase. Identification of the solubility limiting phases and determination of their thermodynamic properties will be needed if theoretical models are to be employed to extrapolate laboratory data to geologic time scales.

ARTIFACTS OF EXPERIMENT DESIGN

In the discussion of factors that affect spent fuel dissolution, mention was made on several occasions of ambiguity that existed because of our inability to distinguish the effects of parameters that have been intentionally varied from effects that arise due to sample preparation methods, sample storage conditions, and experiment design variables. These effects must be understood if we wish to isolate the true repository variables in our efforts to develop a model for spent fuel behavior.

Spent fuel is thermodynamically unstable when in contact with air at one atmosphere and ambient hot cell temperature. The rate of oxidation is a strong function of temperature [16]. While the kinetic data on oxidation rate indicate that the extent of oxidation during storage for several years in air should be small, even minute amounts of oxidation can lead to detectable differences in test results. The Turkey Point test specimens used in the Series 1 and 2 NNWSI tests weighed approximately 50 grams. The amount of "excess" dissolution, estimated by the difference between the maximum solution concentrations for Turkey Point versus H. B. Robinson tests, was about 500 micrograms of uranium. For a 50 gram sample, this amounts to 0.001 percent. The samples had been stored in containers with an air atmosphere for approximately 5 years prior to use in the tests. If we assume that the excess dissolution was due to oxidation and that the rate was linear with time, we can infer that it would take 500,000 years to oxidize the entire sample at the temperature relevant to its storage condition in the hot cell (probably 25 to 30°C). Another way of looking at this effect is that oxidation at that rate for 10,000 years would produce a 2 percent change in the sample. By contrast, the difference in the peak solution concentrations for uranium in cycle 1 of the tests was a factor of 2.

Another difficulty associated with storage of test specimens in air in a condition other than intact cladding is that the temperature at the fuel surface is different from the average hot cell air temperature. This is due to the self-heating associated with radioactive decay. Depending on the age of the fuel, the amount of fuel in a storage container, and the thermal

conduction properties of the fuel and storage medium, quite high temperatures could occur inside the container at the fuel surface while only moderately elevated temperatures would be measured on the external surface of the container. Estimation of the effective thermal conductivity of the de-clad spent fuel would be very difficult because of uncertainties regarding the density of a pile of loose pellets and fragments. Thus, prediction of the extent of oxidation, for storage under an air atmosphere, may be impossible even if the kinetics of the oxidation process were perfectly understood.

The preparation of test specimens of spent fuel necessarily involves mechanical disruption of the fuel rod. The usual methods include cutting a section of rod using a saw or cut-off wheel. Water or other solvents should not be used during the cutting, since they might remove radionuclides of interest, especially cesium. Use of gas as a coolant may remove fine particles of fuel that are relevant to the test specimen; use of no coolant might result in elevated temperatures and fuel oxidation. Since the rod must be cut to obtain the specimen and there is no way to avoid some potential artifact, the best we can do is to document carefully the cutting method used and to try to estimate its effect on the test results.

For tests where bare fuel is to be used, removal of the cladding will change the state of stress on the fuel pellets and may lead to the pellets separating into several pieces. This increases the surface area available for aqueous attack and may also generate some quantity of very fine particles with high surface energy that would behave differently to the main mass of the fuel. Presence of such fine particles would be particularly important in short term tests and in tests where only one cycle of aqueous contact was used.

Some testing has used crushed fuel. This introduces another problem that is closely related to the issue of cladding removal. Crushing causes damage to the surface of the material and creates ultrafine particles that adhere to the surface of materials. Even when extreme measures are taken to remove the fine particles, such as a dozen ultrasonic wash steps followed by slow settling and decanting, the effects of the surface damage to the larger grains cannot be removed. These effects have been well documented in the case of feldspar dissolution kinetics [17] and might be expected to be even more important for a heavily damaged material such as spent fuel. Crushing also increases the exposure of grain boundaries to the aqueous medium, thereby enhancing the effects of grain boundary dissolution on the test results.

Some testing has been done using gold-cell rocking autoclaves. These systems have the advantage of allowing samples of fluid to be extracted without disrupting the main reacting system. The potential disadvantage is that the rocking action may itself disrupt the reacting system. Many corrosion mechanisms involve the formation of protective films on the reacting surface. If test components are loose in the gold-bag, the rocking action would produce collisions between materials, which could knock off these films. Depending on the component for which this occurred, the test could be affected by producing higher or lower apparent dissolution rates for the spent fuel. Fresh Zircaloy is an extremely effective getter for oxygen. It corrodes by forming an oxide film that impedes further access of oxygen to the metal. Tests with cladding hull pieces in rocking autoclaves could produce redox conditions that are lower than real system conditions would be if rocking caused damage to the oxide layer on the Zircaloy.

The necessity to avoid excessive fluid loss during long-term tests introduces another problem in experiment design. For NNWSI conditions, the repository environment will always be in contact with the atmosphere through the porosity of the rock. Tests at elevated temperatures must be conducted in sealed vessels to avoid excessive fluid loss. The effects of depletion of oxygen in the atmosphere over the test solutions must be investigated to ensure that test conditions have the relevant redox conditions.

The final problem in experiment design is perhaps the largest. How can we sample the reacting system without causing a major change in it by the act of taking a sample? Lowering the temperature to open reaction vessels can cause

back-reactions to occur. Sampling at temperature can cause flashing in pressurized systems. Changes in the atmosphere over the test solutions may occur during sampling; if they do, are they desirable or undesirable? Static tests that are sampled once at the end of the test may give results that are different from flow-through tests if solution species are depleted by precipitation early in the static tests. In each case, the experimental design must address the unavoidable artifacts and determine the sampling method most appropriate to the application.

AREAS WHERE DATA ARE MOST NEEDED

There are six areas where little or no data currently exist and for which data will be needed in a repository license application. These areas are

- (1) The effect of reactor type and burnup on dissolution properties of spent fuel.

As discussed above, fuel dissolution is likely not to depend heavily on these parameters, but the population variability must be addressed in the licensing arguments.

- (2) Dissolution studies on stainless steel clad fuel.

Part of the existing inventory of spent fuel is clad in stainless steel and more such fuel is currently in use. No data exist on its behavior in dissolution tests.

- (3) Dissolution studies of oxidized spent fuel.

These studies are needed to understand the effects of oxidation state on spent fuel dissolution rate and solubility. They will help us to assess the potential effects of oxidation in the repository environment and to understand the effects of air storage of test specimens. They are also needed to address the potential for air access to fuel during dry storage, either at the reactor site or at a potential monitored retrievable storage facility.

- (4) Dissolution studies using assembly components.

Some fuel may be disposed of as intact assemblies. Also, the fuel hardware from consolidated rods might be destined for repository disposal. At present, there is no information on the rate of radionuclide release from such components in aqueous solutions.

- (5) The inventory and release characteristics of carbon-14.

Data are needed on both the release in air and the release into aqueous solutions of carbon-14. Good estimates of the actual inventory of carbon-14 and its location in the spent fuel components, as well as the likely variations in the inventory are needed.

- (6) Thermodynamic properties of solids that might limit radionuclide solubility.

For many geologic systems, silicate minerals may limit the solubility of uranium and thereby affect the dissolution properties of spent fuel. Data for uranium silicates are sparse to nonexistent. Data are also needed for the compounds thought to limit the solubility of the actinides. The success of efforts to model the long-term

behavior of geochemical systems depends on the availability of good thermodynamic data for the relevant phases. The success of the repository license application may depend on the use of such models.

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