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Spent Fuel Performance Data: An Analysis of Data Relevant to the NNWSI Project

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1. INTRODUCTION

The spent fuel presently in storage in the United States consists of Boiling Water Reactor (BWR) fuel discharged since 1969 and Pressurized Water Reactor (PWR) fuel discharged since 1970. The characteristics of the fuel have been summarized by Oversby (1984) to provide a reference spent fuel composition for the Nevada Nuclear Waste Storage Investigations (NNWSI) Project testing program. The fuel rods prior to usage consist of a stack of UO_2 pellets encapsulated in a metal tube, which is called the cladding. Most fuel used in the U.S. is clad in Zircaloy; however, four reactors use fuel clad in stainless steel.

The fuel rods are arranged into assemblies for insertion into the reactor. The detailed geometry of the rods and of the assemblies depends on the reactor in which they will be used. Woodley (1983) has described the variation in rod and assembly characteristics, and also the evolution in rod design, to improve performance of the fuel in the reactor. He also has summarized the available literature on the physical and chemical characteristics of spent fuel that are of significance to waste package design. The following discussion is based on his summary, unless otherwise noted.

During irradiation, the physical and chemical nature of the fuel is changed. The chemical changes are caused by the fission of uranium, the production of higher Z (atomic number) actinides by neutron capture reactions, and the production of activation products by neutron capture. The activation products are located in the fuel itself, in the cladding, in deposits on the cladding, and in the assembly parts. Since some of the activation products are in the cladding and assembly parts [such as carbon-14, a radionuclide whose release rate must be controlled to within the U. S. Nuclear Regulatory Commission (NRC) and U. S. Environmental Protection Agency (EPA) specified limits], the waste form for spent fuel is the entire assembly (if disposed of intact) or the clad fuel rods and disassembled nonfuel hardware (if disposed of as consolidated rods).

Oversby (1986) reviewed the constraints on release rates specified by the NRC and EPA regulations and established a list of radionuclides for which data on dissolution rates are necessary. The simplest case, which maximizes the number of such nuclides, results in the identification of 17 chemical elements for which dissolution data are needed for performance assessment. Of these, americium and plutonium are the most important; other actinides, carbon, and nickel are also important.

The abundance and spatial distribution of new chemical species formed during irradiation is dependent on the operating conditions to which the fuel rods are exposed. The abundance of fission products depends principally on the burnup of the fuel, that is, the amount of energy produced per unit weight of initial uranium. Burnup is usually expressed in megawatt-days per metric tons of uranium

(MWd/MTU). The abundance of activation products depends on the composition of the starting materials, particularly with respect to trace impurities such as nitrogen in the fuel and cladding, and on the neutron fluence and spectrum. The transuranic actinide content will depend on burnup and on the neutron fluence and spectral conditions in the fuel (Roddy et al., 1985).

The spatial distribution of fission products in spent fuel depends on the chemical interactions between the matrix and the fission products and on the reactor operating conditions, which can strongly affect the ability of fission products to segregate from the matrix. Fission products that are gaseous (Kr and Xe) accumulate in the matrix as small gas bubbles (Baker, 1977; and Woodley, 1983). If temperatures become high enough, the gases can diffuse to grain boundaries or to the gap between the pellets and the cladding. The degree of migration that has occurred for a given spent fuel rod can be determined by sampling the gas contained in the pellet-cladding gap. This is referred to as fission gas release and is usually expressed as a percentage of the inventory calculated to be present in the rod.

During reactor operation, the centerline temperature of the fuel rods can be between 800 and 1600°C. Some of the fission products that are not gaseous at lower temperatures will be volatile at the higher temperatures. Elements that have been identified as mobile under reactor operating temperatures include cesium and iodine (Johnson et al., 1983a). These elements migrate to grain boundaries and from there to the pellet-cladding gap. Other fission products are metallic under the redox conditions inside the fuel rod and form metallic segregations. These may be located within the grains or at the grain boundaries (Thomas et al., 1986). The degree of fission gas migration was large in early designs that allowed the fuel to reach very high temperatures. Fission gas release of 15 to 25 percent has been measured for spent fuel from several reactors. Improved fuel rod and assembly design has resulted in lower operating temperatures for the fuel and much lower fission gas release. Gas release for modern U.S. fuels is generally less than one percent. Even for burnup as high as 56,000 MWd/MTU, typical fission gas release and cesium migration is less than 4 percent (Peehs et al., 1986).

Migration of fission products can occur by volume and grain boundary diffusion at operating temperatures if they are sufficiently high; however, measurements of internal pressure in an instrumented assembly indicate that most of the migration occurs during reactor power changes, when the rapid temperature changes stress the fuel and induce cracks, thereby allowing enhanced migration of volatile species. Thus, the number of shutdowns and the rates of power changes during operation can influence the gas-release for a fuel rod.

The temperature in the central portion of a fuel rod during irradiation may be high enough for grain growth to occur by a mechanism analogous to sintering. This phenomenon in fuel is referred to as

restructuring and is accompanied by segregation of insoluble fission products such as metals into secondary phases. Operating temperature and starting grain size are both important factors determining the degree of restructuring. Extensive restructuring does not usually occur in light water reactor (LWR) fuels because the majority of the fuel operates with a centerline temperature less than 1300°C. Extensive restructuring is observed above 1500°C and is common in liquid metal fast-breeder reactor (LMFBR) fuels, which have peak center temperatures of approximately 2000°C. Fission product elements that might show larger early releases during the leaching of highly restructured fuels include cesium, iodine, selenium, strontium, and technetium (Wilson, 1985b).

Investigations conducted in Germany on LWR fuels with burnup of less than 36,000 MWd/MTU have shown that tritium is fixed in the cladding and fuel pellets, with only extremely small amounts found in the gas phase. In PWR rods, 63 percent of the tritium inventory is typically in the Zircaloy cladding, while for BWR rods, 50 percent of the tritium is in the cladding (Peehs et al., 1986).

Physical examination of fuel after irradiation shows that the pellets are extensively cracked. If fuel is removed from its cladding, a wide range of particle sizes is obtained, including some very fine fragments (Katayama et al., 1980). Zircaloy cladding develops an oxidized layer on the outer surface during reactor operation. Some materials precipitated from the water during operation might be present on the cladding surface; these deposits are called "crud." Some fuel rods may have small defects such as pinholes or cracks in the cladding. Approximately 1 percent of the rods developed defects in the cladding during reactor operation in the United States from 1969 to 1972. Improvements in fuel rod design and in reactor operating procedures have reduced the rod failure rate for modern fuels to less than 0.1 percent (Woodley, 1983).

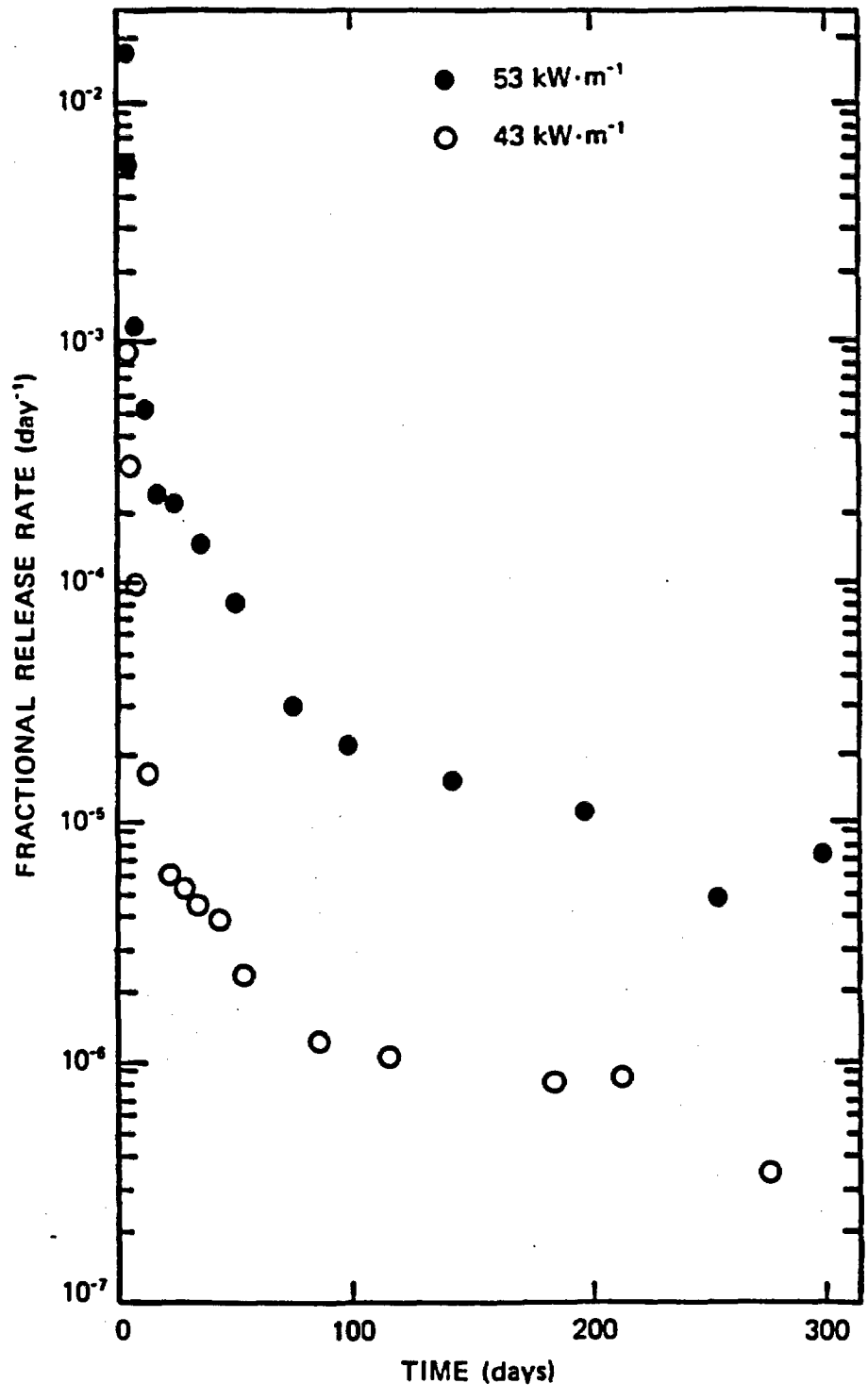
Boehm and Foerch (1985) describe an ultrasonic inspection device to detect water in spent fuel rods without dismantling the fuel assembly. If the rod contains a defect large enough to allow water to enter the rod, water will probably enter through the defect and accumulate in the pellet-cladding gap. The ultrasonic method has been used to examine more than 160,000 fuel rods, mainly in German and Belgian reactors. The authors report detection of water in the fuel rod plenum and fuel region of "more than 300 rods." Assuming that "more than 300" is a number less than 400, we conclude that approximately 0.2 percent of the rods examined contained a defect large enough to admit water. The authors do not state whether the assemblies tested were selected randomly or represent a population that was thought to include an above average number of defects.

Consolidation of spent fuel rods might increase the number of rods with defective cladding. Bailey (1987) states that from a "biased sample of fuel assemblies," handling, examination, reconstitution, and rod consolidation activities resulted in only seven out of 54,000 fuel rods being broken. The author did not state in what way the population was biased. More than 3100 of those rods were involved in rod consolidation activities in the United States (Bailey, 1987). It seems reasonable, based on this evidence, to assume that rod breakage during consolidation activities could be kept to less than 0.5 percent. There are no data presently on the number of defects generated during consolidation that do not lead to immediate rod breakage, but which might result in an enhanced susceptibility to failure at later times.

The information on spent fuel characteristics just described and the data obtained by the Swedish (KBS) and Canadian (AECL) workers on the release of radionuclides from spent fuel in groundwaters of composition similar to J-13 water (the groundwater used in NNWSI testing) were used as the basis for planning the NNWSI Project spent fuel testing program. The results from both the KBS and AECL programs showed that the release rates of some elements from spent fuel pellets in contact with water would be very rapid during the first few months of contact with water (Eklund and Forsyth, 1978; and Johnson et al., 1982). The initial release of cesium from spent fuel correlates with gas release, which itself is a function of linear heat generation rate in the fuel. Figure 1 shows initial release of cesium from CANDU fuel (natural uranium) that had two different power ratings. The data are plotted as the fraction of cesium inventory present in the test that is released to solution per day of solution contact.

Other fission products that migrate to the pellet-cladding gap and/or accumulate on grain boundaries within the fuel, such as iodine-129, might also be expected to show a similar initial release pulse. The release amounts, the rapid nature of the release, and the high solubility of the elements under expected NNWSI Project disposal conditions led to a consideration of the role of the cladding material in providing control of release of radionuclides from the spent fuel pellet and gap inventories. The review by Woodley (1983) indicated that only a small fraction of spent fuel rods delivered to the repository would have defects in their cladding. If the intact condition of the cladding were to continue throughout the disposal period of concern with respect to control of release rates, then the rather large initial cesium release could be controlled easily to a maximum population-averaged release rate of less than 1 part in 10^5 per year. A 1 percent per year release rate of cesium from breached fuel rods could be tolerated, provided that no more than 0.1 percent of rods contained breaches. As shown in Fig. 1, the rapid release fraction of cesium is exhausted after a few months (Johnson et al., 1982; and Forsyth et al.,

Figure 1. Fractional release rates of Cs-137 for fuels of moderate and high power ratings (Johnson et al., 1982).



1985). Thus, the cladding could provide a control on cesium release even if it were to develop defects after disposal, as long as the rate of defect generation is low and cladding failure does not occur nearly simultaneously in all rods.

Based on these considerations, a three-part testing program for spent fuel was established. The heart of the program is a series of fuel dissolution tests that examine the rate of release of radionuclides from bare spent fuel, fuel rod segments with intentionally defected cladding, and rod segments with intact cladding. Details of the test plan can be found in the report by Wilson (1984). Series 1 tests (Wilson, 1985a) used deionized water and ambient hot cell temperature (~25°C). Series 2 tests used J-13 water and ambient hot cell temperature. The test vessel and experimental configuration of the Series 1 and 2 tests are shown in Fig. 2. Results of the Series 1 and 2 tests are given in the reports by Wilson (1985a and 1987). Series 3 tests used J-13 water and sealed stainless steel vessels (shown in Fig. 3) at 85°C. Details of the test plan are described in Wilson (1986). At this time, the Series 3 tests are completed, but the final results are not yet published. Preliminary results are given in Wilson and Shaw (1987).

The second area of testing related to spent fuel is an experimental study of the rate of oxidation of spent fuel under repository disposal conditions. When uranium oxidizes, there is a large volume increase at the stage when U_3O_8 is formed. This has been the cause of large-scale rupture of cladding that originally contained only small defects. The available data on oxidation rates of spent fuel were obtained at higher temperatures than those relevant for long-term disposal conditions. Data are needed at lower temperatures to determine whether the rates extrapolated from the high temperature data are valid at lower temperatures and whether the oxidation mechanism is the same at the lower temperatures. Einziger and Woodley (1985a) have evaluated the potential for oxidation of spent fuel to occur under NNWSI Project disposal conditions. Their evaluation has led to development of a testing program (Einziger, 1985) that combines thermogravimetric analysis (TGA) studies for short periods (Einziger and Woodley, 1985b and 1986) with longer conventional oven-soak oxidation measurements (Einziger, 1986). The TGA studies allow continuous monitoring of weight changes, thereby providing detailed information about the oxidation mechanism and rate. The oven oxidation studies complement the TGA work by allowing longer experimental runs with multiple samples that are larger than those used in the TGA apparatus.

The rate of corrosion and degradation of Zircaloy under disposal conditions will have a profound influence on the ability of the cladding to control the release rate of nuclides from the interior of the fuel rods. An examination of the available information on corrosion of Zircaloy suggested that cladding

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Figure 2. Test apparatus for spent fuel dissolution experiments at 25°C (Wilson, 1985a).

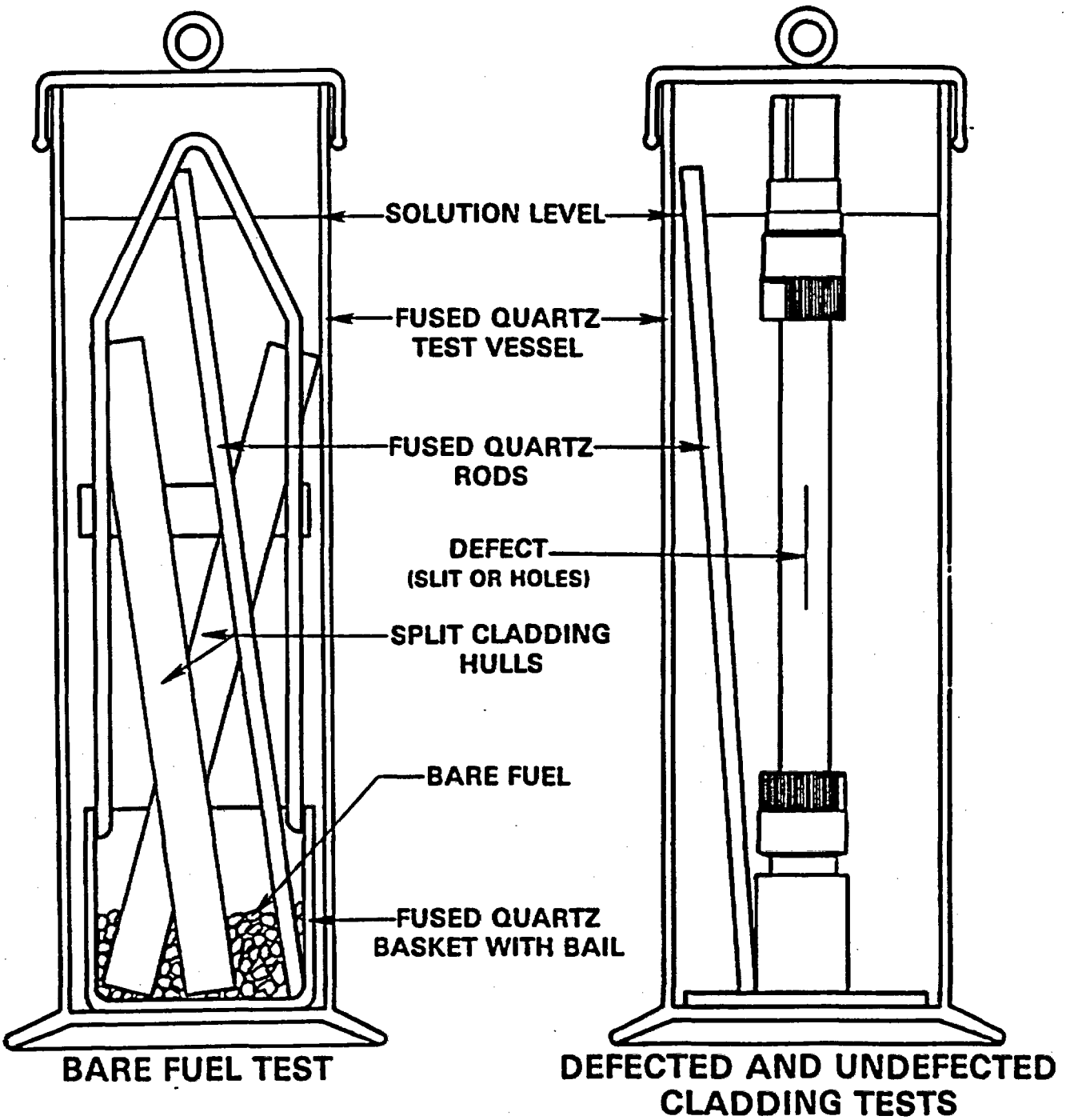

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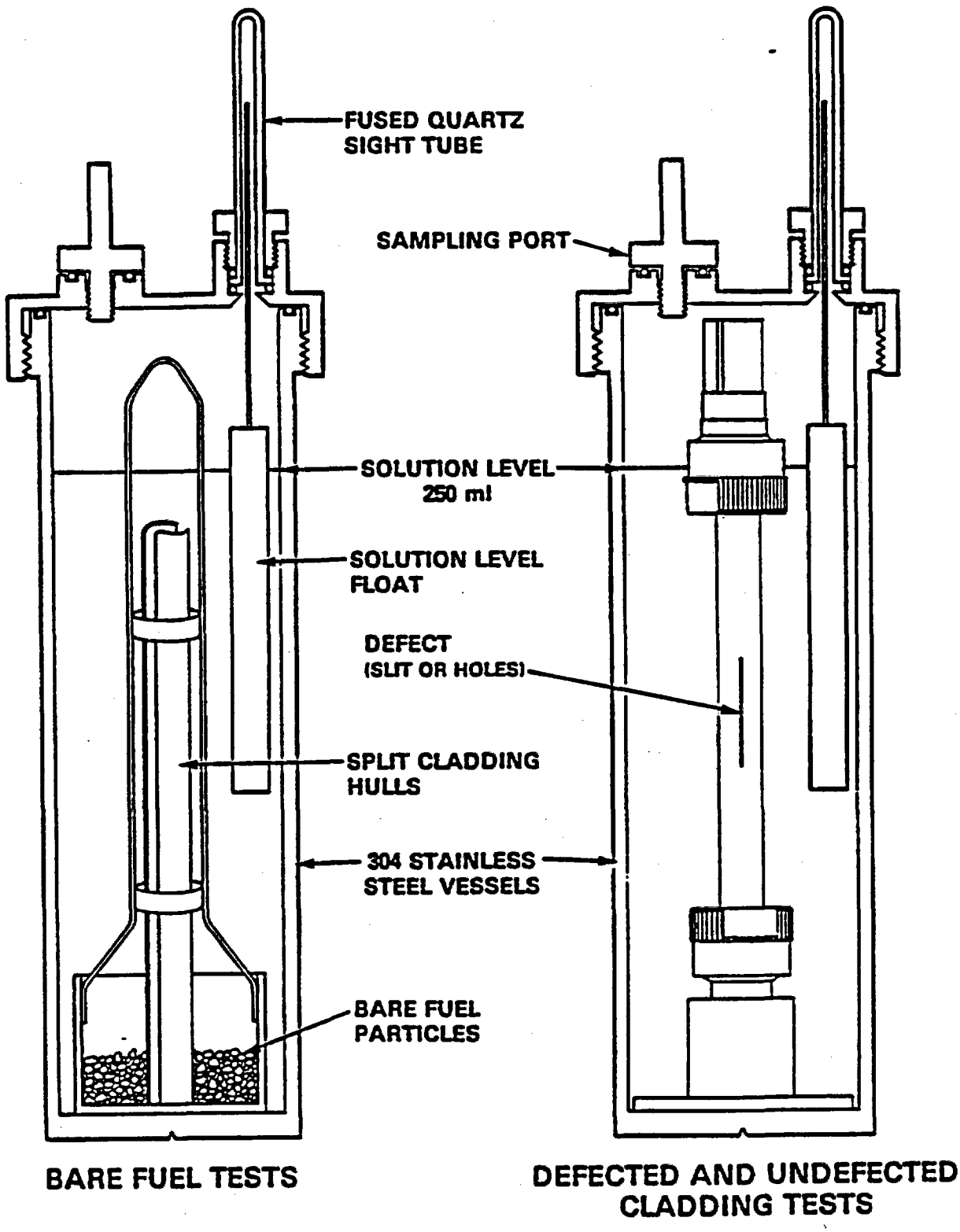
Figure 3. Test apparatus for spent fuel dissolution experiments at 85°C (Wilson, 1986).



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would not develop a large number of defects under NNWSI Project disposal conditions (Rothman, 1984). A few areas were identified where further work on Zircaloy corrosion is needed to determine the expected rate of defect generation under repository conditions. Accordingly, a program of corrosion testing for irradiated Zircaloy cladding was initiated. At present, scoping experiments and tests are being conducted on two potential modes of cladding failure: electrochemical corrosion and stress corrosion cracking. An overview of the planned experiments is given in the report by Smith (1985), and the criteria used in the choice of samples for these experiments are discussed in Smith (1984b). Test plans for the initial electrochemical corrosion scoping experiments at 90°C and 1 atmosphere, and additional tests at 170°C and 0.83 megapascal (120 psia) water, are given in Smith (1984a and 1986a). Preliminary observations from the 90°C corrosion experiments are given in Smith and Oversby (1985). The test plan for the initial scoping experiments on stress corrosion cracking is presented in Smith (1986b).

In the discussion that follows, the work done on spent fuel dissolution by the NNWSI Project is described and the results are compared with those in the published literature. The work on oxidation of spent fuel and corrosion of Zircaloy will be the subject of future publications.

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2. SPENT FUEL DISSOLUTION STUDIES

The purpose of the NNWSI Project testing is to determine the fraction of the sample inventory that is mobilized under test conditions and the physical nature of the mobilized components. That information will then be related to expected release rates at the end of the containment period. These release rates are referenced to the inventory present at 1000 yr after repository closure. Table 1 gives the calculated inventory of radionuclides in PWR spent fuel at 1000 yr for all isotopes with activity greater than or equal to that of iodine-129. The nickel activity is mainly associated with stainless steel and Inconel assembly parts that were not part of the NNWSI Project test samples.

Table 1. PWR spent fuel assembly radionuclide inventories at 1000 yr[a].

Radionuclide[b]	Percent of total 1000-yr activity	Cumulative percent
Am-241	51.84	51.84
Am-243	1.75[c]	53.59
Pu-240	26.87	80.46
Pu-239	17.37	97.83
Pu-242	0.1	97.93
Pu-238	0.06	97.99
Tc-99	0.77	98.76
Ni-59	0.252	—
Ni-63	0.021	—
Zr-93	0.181	—
Nb-94	0.074	—
C-14	0.076[d]	—
U-234	0.113	—
U-238	0.018	—
U-236	0.015	—
Np-237	0.058	—
Sn-126	0.045	—
Se-79	0.023	—
Cs-135	0.022	—
Sm-151	0.013	—
Pd-107	0.006	—
I-129	0.0018	—

[a] Based on ORIGEN data reported in ORNL/TM-6008(2) for 33,000 MWd/MTM burnup PWR assembly.
[b] Radionuclides with 1000-yr activity less than I-129 or half-life less than 1 yr omitted.
[c] Includes activity of Np-239 daughter products.
[d] C-14 activity might vary considerably depending on as-fabricated nitrogen impurities.

The spent fuel samples used in the NNWSI Project testing program to date have come from two PWR reactors: Turkey Point Unit 3 and H. B. Robinson Unit 2. Detailed characterization data are available for sibling rods from the same assemblies from which these materials were obtained in the cases of H. B. Robinson fuel (Barner, 1984) and from the same rods in the case of Turkey Point (Davis and Pasupathi, 1981). The Swedish testing program has used fuel sections from the Oskarshamn I BWR reactor (Forsyth et al., 1983). The Canadian testing program uses CANDU natural uranium spent fuel (Johnson et al., 1982). In the CANDU reactor, where bundles of Zircaloy-clad fuel elements of natural UO_2 are irradiated in an array of process tubes extending through the core, greater variations in fuel rod linear power and fuel operating temperatures occur than in LWR reactors, which use variable uranium-235 enrichments and have more uniform neutron flux across the core. As a result, fission gas release, fuel restructuring, and segregation of fission products from the oxide fuel matrix generally occur to a greater extent and exhibit greater variability in CANDU fuels than in LWR fuels. A summary of the characteristics of the spent fuel samples used in the three testing programs is given in Table 2.

The three testing programs also use different groundwater compositions for the leaching solutions. Although the compositions are similar, differences in some components might affect fuel leaching. The Canadians have used a water composition, referred to by them as KBS groundwater, which is higher in dissolved carbon species than that reported by Forsyth et al. (1983). To distinguish between the two, the Swedish composition will be designated KBS and the Canadian composition will be designated AECL-KBS. The Canadians also use a composition called "granite groundwater," which will be referred to as AECL-GR. The compositions of these three waters are given in Table 3.

As can be seen by inspection of Table 3, the Swedish KBS water and the J-13 water are remarkably similar in composition. The main differences between the two are the presence of small amounts of fluoride and nitrate in J-13 water, higher silicon in J-13 water, and much lower chloride in J-13 water. The KBS water used by the Canadians had 2.5 times as much bicarbonate as the Forsyth et al. (1983) KBS composition. Since uranium (VI) solubility is strongly dependent on the carbonate content of solutions, the higher bicarbonate in the AECL-KBS water can be expected to affect the solution concentrations of uranium under oxidizing conditions. The AECL-GR water is very low in dissolved species and would be expected to show somewhat lower uranium solubilities than the J-13 or KBS waters under oxidizing conditions.

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Table 2. Characteristics of spent fuel samples used in release rate testing. Data from Barner (1984), Johnson et al. (1982 and 1983a), Forsyth et al. (1983), Wilson and Oversby (1985), and Oversby and Wilson (1986).

Characteristic	NNWSI TP	NNWSI HBR	KBS BWR	CANDU
Fuel type	PWR 15 x 15	PWR 15 x 15	BWR	Natural
Cladding	Zircaloy-4	Zircaloy-4	Zircaloy	Zircaloy-4
Sample weight UO_2 (g)	43	80	16	72
Estimated burnup (MWd/kgU)	27	31	42	7.9
Initial enrichment (wt.%)	2.559	2.55	—	natural
Fission gas release (%)	0.3	0.2	0.7	1 to 9
Peak linear heat generation rate (kW/m)	—	32.7	<30	42 to 58
Initial pellet density (% TD)	92	92	—	97
Pellet diameter (cm)	0.9	0.9	—	1.4
Grain size (mm)	~25	~6	—	7-10
Discharge date	11/25/75	5/6/74	—	—

Table 3. Composition of leach solutions in mg/L. Data from Forsyth et al. (1983), Johnson (1982), and Wilson and Oversby (1985).

Component	J-13	KBS	AECL-KBS	AECL-GR
Na	50	65	120	8
K	5	4	2	3
Ca	15	18	6	4
Mg	2	4	3	4
Si	32	6	8	0
Cl	7	70	12	5
F	3	—	—	0.2
NO_3	9	—	—	0.6
SO_4	19	10	12	9
HCO_3	120	123	305	61
pH	7.2	8.1	8.5	6.5–7

The NNWSI Project spent fuel dissolution testing procedure is a semi-static one in which samples of fluid are periodically taken for analysis. The fluid volume is then returned to the starting volume by addition of sufficient fresh leachant to make up for the sample taken. In this repect, the test resembles a slow flow-through test. Evaporative losses are made up using deionized, distilled water. The sampling schedule and test conditions for the three test series are given in Table 4. Each test series consists of several cycles. This is done so that the size of the rapidly released gap and grain boundary

Table 4. Test conditions and sampling schedule for the NNWSI Project spent fuel dissolution tests; Series 1, 2, and 3 (Wilson, 1985a, 1986, 1987, and personal communication).

Conditions	Series 1	Series 2		Series 3
Temperature (°C)	25	25		85
Leachant	D.I. water	J-13		J-13
Vessel material	SiO_2	SiO_2		AISI 304
Solution volume (mL)	250	250		250
Sample volume (mL)	10	10-25		10-30
Sampling schedule (days since last restart)				
		TP	HBR	
Cycle 1	1	1	1	1
	5	6	6	7
	15	15	20	14
	30	30	30	33
	60	62	63	62
	90	—	—	—
	120	120	120	119
	150	—	—	147
	180	181	181	174
	202	—	—	—
	250	—	223	—
Cycle 2	1	—	—	1
	5	—	—	7
	15	20	20	14
	30	—	—	34
	60	71	62	62
	90	—	—	—
	120	—	—	120
	150	154	154	—
	210	195	202	181
	250	—	—	—
	271	—	—	—
Cycle 3[a]	—	4	4	—
	—	14	14	20
	—	63	63	55
	—	112	112	97
	—	224	224	—
Cycle 4[a]	—	7	7	—
	—	63	63	—
	—	148	148	—
	—	240	240	—
Cycle 5[a]	—	5	5	—
	—	61	61	—
	—	132	132	—

[a]Bare fuel samples only.

inventory of fission products can be assessed. These nuclides are released very quickly in the first cycle, and the levels attained in subsequent cycles show a progressive decrease. At the end of each cycle, the spent fuel specimens are rinsed and transferred to clean leaching vessels, and the test is restarted for the next cycle, using fresh leachant. After the remaining leach solution is removed at the end of each cycle, the used leaching vessels are rinsed with leachant and stripped with 8M HNO_3 to remove any solid, precipitated, or adsorbed material. Series 1 and 2 tests were conducted in loosely covered, fused quartz vessels at approximately 25°C. The Series 1 tests were conducted using deionized water as the leachant, and the Series 2 tests used J-13 water. These tests also included fused quartz rods, which were removed at intervals to monitor plate-out. Series 3 differs from the previous two series in that the tests were conducted in sealed 304 (cycle 1) or 304L (cycles 2 and 3) stainless steel vessels at a higher temperature (85°C). The leachant used in Series 3 was J-13 water. One bare fuel specimen at 25°C was included in Series 3 so that the results from the Series 2 tests can be compared and so that the effect of changing the experimental vessel on the observed release of radionuclides, exclusive of any temperature effect, can be evaluated.

Each test series includes several types of test specimens, each prepared from a 5-inch segment cut from a full-sized rod: (1) bare fuel with the emptied cladding hulls; (2) fuel rod segments fitted with watertight end caps and with laser-drilled holes through the cladding; (3) fuel rod segments with watertight end caps and with a machined slit through the cladding; and (4) undefected fuel rod segments with watertight end caps. These various specimen types approximate fuel rods with differing degrees of cladding failure. The end caps prevent accidental access of water to the fuel by means other than the induced defect. The exterior surfaces of all specimens are cleaned of radioactive contamination prior to use in a test. Series 1 tests used spent fuel from the Turkey Point Unit 3 reactor. Series 2 and 3 tests used spent fuel from two sources: fuel from the H. B. Robinson Unit 2 reactor obtained from the Pacific Northwest Laboratories' Materials Characterization Center and designated as ATM-101 (Barner, 1984) and fuel from the Turkey Point reactor. The two fuels are similar PWR fuels from the same vendor and are of approximately the same vintage. As can be seen from Table 2, both fuels have low gas release and similar burnup. The grain size of the Turkey Point fuel, however, is significantly larger than that of the H. B. Robinson fuel.

Data were obtained on all samples for americium-241, plutonium isotopes, curium-244, uranium, and cesium isotopes. Cobalt-60 was measured in most test solutions. Selected samples were analyzed for technetium-99, strontium-90, neptunium-237, selenium-79, carbon-14, and iodine-129. In addition, selected samples were analyzed in three fractions: (1) unfiltered, (2) filtered through 0.4-micron filters

(Nucleopore 110407 polycarbonate), and (3) filtered through 1.8-nm filters (Amicon CF-25 membrane cone centrifuge filters).

The following discussion concentrates on the results of the Series 2 tests (Wilson, 1987) because they are more relevant for the conditions in the NNWSI Project proposed repository than are Series 1 data. Significant differences were noted in the behavior of spent fuel in the Series 1 and 2 tests due to the use of J-13 water in Series 2. These differences are discussed when they provide insight into the dissolution process or release mechanism. Complete results for the Series 1 tests are contained in Wilson (1985a).

Figure 4(a) shows the H. B. Robinson uranium data for unfiltered solutions for Series 2, cycles 1 and 2; uranium data for Turkey Point samples are in Fig. 4(b). Data points with a downward pointing arrow are data reported as below detection limits. The line marked 10^{-5} inventory is the solution concentration that would result if 1 part in 10^5 of the test specimen were to dissolve in the leachant. This level is indicated in the figures and tables simply as a convenient reference point for comparing releases of various radionuclides from samples of different sizes and for comparing the releases of radionuclides normalized to their abundance in the fuel. This value cannot be directly related to the NRC release rate limit of 1 part in 10^5 per year of the 1000-yr inventory. Conversion of solution concentrations to release rates requires a model for spent fuel dissolution in the repository setting. Since the mass of the Turkey Point test specimens varied significantly, the 10^{-5} levels are shown for all three defected cladding configurations. Only one reference 10^{-5} line is shown for H. B. Robinson because the fuel mass was nearly equal in all tests.

Solution uranium concentrations reached relatively stable levels after a few days. The H. B. Robinson cycle 1 bare fuel test, which required more than 60 days to reach a stable level, was a notable exception to this. Uranium concentration data for the bare fuel tests are plotted on a linear scale in Fig. 5. Uranium concentration in the H. B. Robinson cycle 1 test peaked at 4.5 μg/mL on day 6 and decreased to 1.2 μg/mL at the termination of cycle 1, as the solution apparently equilibrated with a phase having lower solubility than that initially present on the fuel surface. Uranium in the Turkey Point cycle 1 test began to decrease only after 120 days, dropping from a peak value of 4.9 μg/mL on day 30 to 4.0 μg/mL at the cycle termination, suggesting that a larger amount of a readily soluble phase was init-ially present than in the H. B. Robinson test. The greater amount of a more readily soluble phase in the Turkey Point fuel might be related to this fuel's greater exposure to air prior to testing, which might have resulted in a more extensively oxidized fuel surface. Forsyth et al. (1985) have also seen elevated uranium dissolution for fuel samples stored in air for long periods before testing. During cycle 2, the solution concentration levels of uranium were similar for both fuel types. Uranium concentration dropped from a peak of 2.4 μg/mL in the day 20 sample to 2.0 μg/mL in the H. B. Robinson bare fuel test.

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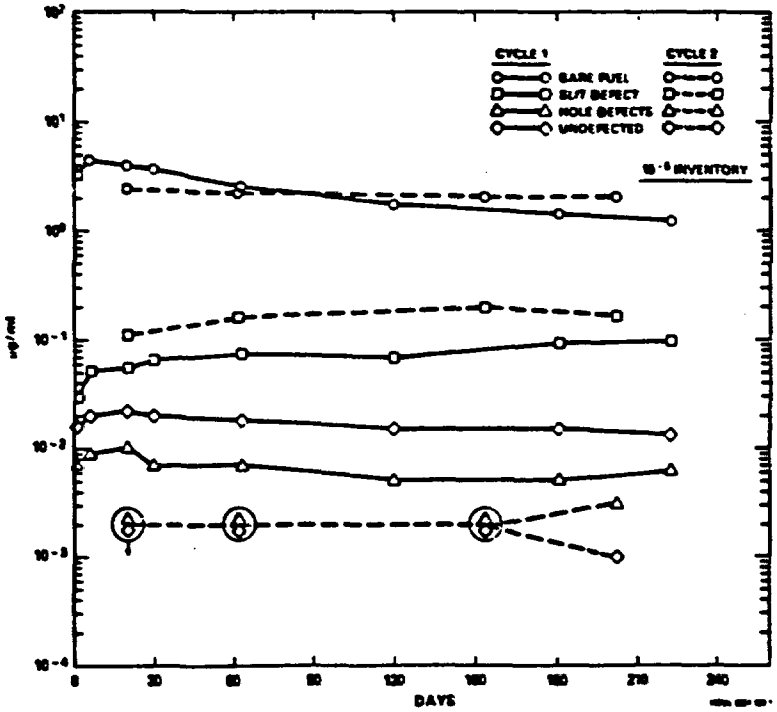
Figure 4. Uranium concentrations in unfiltered solution samples, Series 2, cycles 1 and 2 (25°C, J-13 water) (Wilson, 1987); (a) H. B. Robinson data and (b) Turkey Point data.

URANIUM IN UNFILTERED SOLUTION –
H.B. ROBINSON FUEL IN J-13 WATER



URANIUM IN UNFILTERED SOLUTION –
TURKEY POINT FUEL IN J-13 WATER

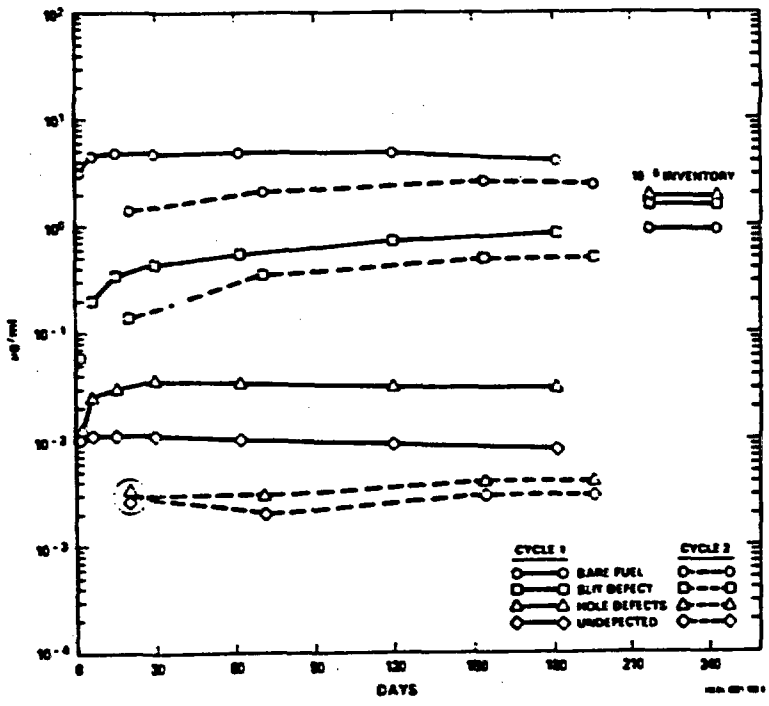
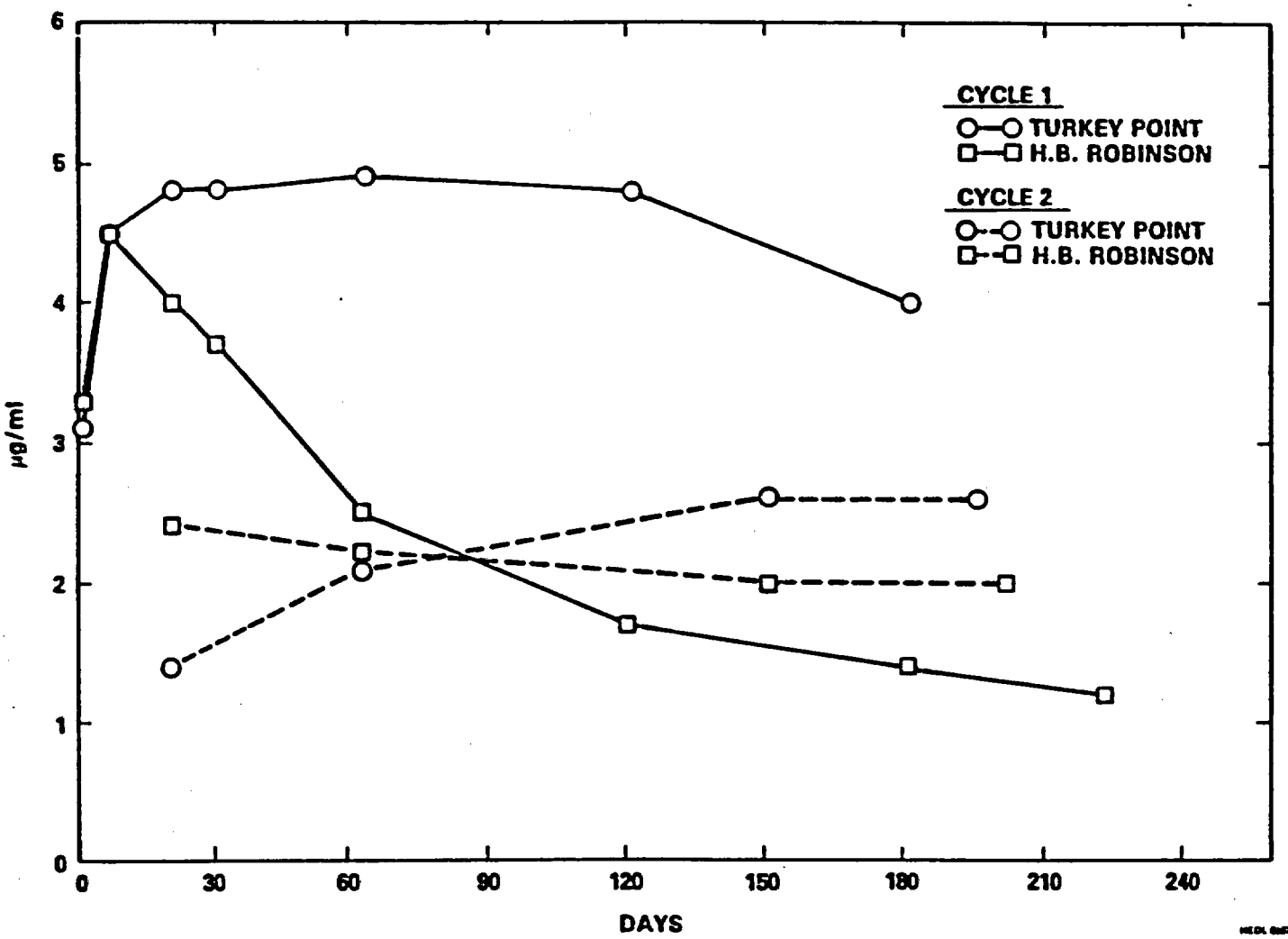


Figure 5. Uranium concentrations for bare fuels in J-13 water, linear scale, Series 2, cycles 1 and 2 (25°C, J-13 water)(Wilson, 1987).



In the Turkey Point test, uranium concentration peaked at 2.6 μg/mL in the day 154 sample and dropped to 2.4 μg/mL in the final sample. Data from the third test cycle for these specimens show uranium concentrations dropping to 1.4 and 1.2 μg/mL for the H. B. Robinson and Turkey Point fuels, respectively, after 224 days (Wilson, 1987).

Table 5 summarizes the uranium release results for Series 2, cycles 1 and 2 of the spent fuel dissolution tests. These data show that the uranium release for the bare fuel specimens was greater than that of any of the defected cladding specimens. The higher fractional release from Turkey Point fuel relative to H. B. Robinson fuel in the three defected cladding configurations might reflect the presence of a more highly oxidized fuel surface on the Turkey Point fuel. Higher uranium concentrations in the undefected test versus the hole defect test for H. B. Robinson cycle 1 specimens is likely due to the presence of residual contamination on the cladding exterior of the undefected specimen; in cycle 2, the uranium concentrations were approximately the same for the hole defect and undefected specimens.

The uranium solubility behavior observed in the Series 2 tests, which used J-13 water, was significantly different from that seen in the Series 1 tests, which used deionized water. In Series 2, essentially all of the uranium measured in the unfiltered solution samples passed through the 0.4-μm and 1.8-nm filters, indicating that the uranium was in true solution. In contrast, in Series 1 much of the uranium was trapped on the 0.4-μm filter, indicating that much of the uranium in the aqueous phase was in a particulate or colloidal state. Uranium solubility in the deionized water used in Series 1 was at or below the detection limit of the technique used to measure uranium in that test (~0.001 μg/mL). The difference between the two test series is attributed to the presence of ~120 μg/mL of HCO_3^- ion in the J-13 water that complexes with uranium in solution and increases its solubility (Wilson, 1985a and 1987).

Table 6 lists the total fractional release of the actinides measured in the Series 2 tests along with the percentage of the release accounted for by the activity present in the aqueous phase (unfiltered solution activity). Due to the very low activities in solution, reliable neptunium data were not obtained for most of the sample configurations; however, the data that were obtained are consistent with the results for the other actinides.

The H. B. Robinson bare fuel test yielded total fractional releases (summed over both cycles of the test) of approximately 7 to 10 parts in 10^5 of the inventory for all of the actinides, including uranium. The analogous Turkey Point specimen yielded similar releases for the higher (i.e., transuranic) actinides, but had a uranium release approximately twice that of the other actinides. As noted above, this might be due to the presence of a more extensively oxidized surface on the Turkey Point fuel.

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Table 5. Uranium release data, Series 2, cycles 1 and 2 (25°C, J-13 water)(Wilson, 1987). Units are micrograms unless otherwise noted.

	Bare fuel		Slit defect	
	HBR	TP	HBR	TP
Cycle 1				
Solution samples	253	351	6.59	35.8
Final solution	300	1000	23.8	213
[ppm U]	1.2	4	0.09	0.85
Rod samples	36	15	0.31	0.54
Rinse	660	366	1.8	10.2
Acid strip	2700	960	1.5	15.9
Total release	3949	2692	34	274.9
Parts in 10^5 of inventory	5.66	11.67	0.047	0.662
Percent in aqueous phase	14.00	50.19	89.38	90.32
Cycle 2				
Solution samples	142	135	10.2	22.1
Final solution	500	600	40	125
[ppm U]	2	2.4	0.16	0.5
Rod samples	18	3	<0.08	<0.054
Rinse	102	39	1.2	3.6
Acid strip	300	156	1.2	0.3
Total release	1062	933	52.63	151
Parts in 10^5 of inventory	1.54	4.13	0.073	0.363
Percent in aqueous phase	60.45	78.78	95.29	97.42
Summary, cycles 1 and 2				
Total release	5011	3625	86.63	425.9
Parts in 10^5 inventory	7.2	15.8	0.12	1.025

	Holes defect		Undefected	
	HBR	TP	HBR	TP
Cycle 1				
Solution samples	0.63	2.27	1.67	0.76
Final solution	1.5	7.25	3.25	2.00
[ppm U]	0.006	0.029	0.013	0.008
Rod samples	<0.18	<0.19	<0.22	<0.1
Rinse	0.6	<0.6	<0.6	<0.6
Acid strip	0.6	2.7	0.6	<0.3
Total release	3.51	<13	<6.34	<3.76
Parts in 10^5 of inventory	0.005	<0.03	<0.009	<0.009
Percent in aqueous phase	60.86	73.17	77.6	—

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Table 5. Continued

	Holes defect		Undefected	
	HBR	TP	HBR	TP
Cycle 2				
Solution samples	<0.13	0.22	<0.13	0.18
Final solution	0.75	1.00	0.25	0.75
[ppm U]	0.003	0.004	0.001	0.003
Rod samples	<0.06	<0.05	<0.06	<0.05
Rinse	0.6	<0.6	0.6	<0.6
Acid strip	4.5	0.3	—	<0.3
Total release	6.04	<2.17	<1.04	<1.88
Parts in 10^5 of inventory	0.008	<0.005	<0.0015	<0.004
Percent in aqueous phase	14.57	56.22	36.54	—
Summary, cycles 1 and 2				
Total release	9.55	<15.18	<7.38	<5.64
Parts in 10^5 of inventory	0.013	<0.035	<0.010	<0.015

As in the case of uranium, the fractional release of higher actinides in the bare fuel test was much greater than that for any of the other sample configurations. The results listed in Table 6 indicate that for each defected specimen type the release of the higher actinides occurred approximately congruently. The Turkey Point defected specimens have fractional releases in Cycle 1 that are about 10 times higher than observed for the analogous H. B. Robinson specimens. The total fractional uranium release for both of the holes defect specimens is similar to that observed for the other actinides. In the slit defect specimens, the fractional release of uranium was approximately 6 to 10 times the release of the other actinides for both fuel types.

The fractional releases discussed above refer to all of the material mobilized from the test specimens and include material plated out on the quartz rods and on the test vessel walls, recovered by acid stripping the vessel. Of greater interest is the portion of the material present in the aqueous phase, since it is this radioactivity that has the potential to be transported from a failed disposal container by fluid entering and leaving the container. This material can be either in true solution or present as suspended particles or colloids; thus, the entries in Table 6 for the percentage in the aqueous phase are based on unfiltered solution analyses. The percentages of the higher actinides that were in the aqueous phase varied from being approximately congruent for the Cycle 1 bare fuel and slit defect specimens to being very different in the case of the Cycle 2 bare fuel and slit defect specimens. The differences in percent of actinides in the aqueous phase do not appear to be systematically related to either the cladding configuration or the fuel type. In the case of the Cycle 2 H. B. Robinson hole defect

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Table 6. Summary of measured fractional releases of actinides (parts in 10^5); Series 2, cycles 1 and 2; 25°C, J-13 water (Wilson, 1987).

	Bare fuel		Slit defect		Hole defect		Undefected	
	HBR	TP	HBR	TP	HBR	TP	HBR	TP
U								
Fractional release								
Cycle 1	5.66	11.67	0.05	0.66	0.005	<0.03	<0.009	<0.009
Cycle 2	1.54	4.13	0.07	0.36	0.008	<0.005	<0.002	<0.004
Sum	7.20	15.80	0.12	1.02	0.013	<0.035	<0.011	<0.013
Percent in aqueous phase								
Cycle 1	14.00	50.19	89.38	90.32	60.86	73.17	77.60	—
Cycle 2	60.45	78.78	95.29	97.42	14.57	56.22	36.54	—
Pu-239 + Pu-240								
Fractional release								
Cycle 1	7.18	7.31	0.009	0.109	0.002	0.022	0.002	<0.005
Cycle 2	1.28	1.57	0.008	0.015	0.012	0.004	0.001	<0.002
Sum	8.46	8.88	0.017	0.124	0.014	0.026	0.003	<0.007
(Fractional release Pu)/(fractional release U)								
Cycle 1	1.27	0.63	0.18	0.16	0.36	—	—	—
Cycle 2	0.83	0.38	0.11	0.04	1.6	—	—	—
Sum	1.17	0.56	0.14	0.12	1.1	—	—	—
Percent in aqueous phase								
Cycle 1	1.56	12.61	17.10	6.25	48.57	8.01	24.91	~13
Cycle 2	4.12	19.84	11.62	47.31	1.20	17.15	18.55	~22
(Dissolved Pu)/(dissolved U)[a]								
Cycle 1	0.14	0.16	0.04	0.01	0.29	—	—	—
Cycle 2	0.06	0.10	0.01	0.02	0.13	—	—	—

(Continued)

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Table 6. Continued

	Bare fuel		Slit defect		Hole defect		Undefected	
	HBR	TP	HBR	TP	HBR	TP	HBR	TP
Am-241								
Fractional release								
Cycle 1	8.04	6.68	0.009	0.13	<0.002	0.02	—	—
Cycle 2	0.77	1.33	0.005	0.01	0.014	0.004	—	—
Sum	8.81	8.21	0.014	0.14	~0.016	0.03	—	—
(Fractional release Am)/(fractional release U)								
Cycle 1	1.42	0.59	0.19	0.19	<0.4	—	—	—
Cycle 2	0.50	0.32	0.07	0.03	1.8	—	—	—
Sum	1.22	0.52	0.12	0.13	~1.2	—	—	—
Percent in aqueous phase								
Cycle 1	1.57	14.04	20.53	6.16	~48	5.86	—	—
Cycle 2	1.00	5.15	2.00	17.35	—	13.65	—	—
(Dissolved Am)/(dissolved U)[a]								
Cycle 1	0.16	0.16	0.04	0.01	~0.3	—	—	—
Cycle 2	0.01	0.02	<0.01	<0.01	—	—	—	—
Cm-244								
Fractional release								
Cycle 1	8.64	7.79	0.01	0.14	0.002	0.027	0.002	0.004
Cycle 2	1.61	1.42	0.01	0.01	0.017	0.003	0.001	<0.002
Sum	10.25	9.21	0.02	0.15	0.019	0.030	0.003	<0.006
(Fractional release Cm)/(fractional release U)								
Cycle 1	1.53	0.67	0.21	0.21	0.36	—	—	—
Cycle 2	1.05	0.34	0.13	0.03	2.1	—	—	—
Sum	1.42	0.58	0.16	0.14	1.4	—	—	—
Percent in aqueous phase								
Cycle 1	2.29	18.13	19.23	7.34	60.29	5.05	—	—
Cycle 2	1.04	6.73	2.19	24.44	0.19	3.35	—	—
(Dissolved Cm)/(dissolved U)[a]								
Cycle 1	0.25	0.24	0.04	0.02	0.36	—	—	—
Cycle 2	0.02	0.03	<0.01	0.01	0.03	—	—	—

[a] This ratio calculated by taking {(% of actinide X in the aqueous phase) · (fractional release of actinide X)} and dividing by {(% of U in the aqueous phase) · (fractional release of U)}.

test, most of the actinides were recovered in the acid strip, suggesting that the measured release was dominated by a fuel particle dislodged from the specimen. This would also explain the low percentage of actinides found in the aqueous phase in this test. In all cases, the fraction of the uranium that was in the aqueous phase significantly exceeded that of the other actinides. Higher actinide/uranium ratios (normalized to the same ratio in the fuel) in the aqueous phase ranged from less than 0.01 to 0.36. It appears that uranium has the potential to be transported from a failed disposal container preferentially to the other actinides.

Much of the aqueous phase activity due to the higher actinides was also measured in the 0.4 μm-filtered fractions (58 to 96 percent). Much of the plutonium activity also passed through the 1.8-nm filter (30 to 76 percent); however, the majority of the americium and curium was stopped by this filter (only ~1 to 12 percent of the unfiltered activity was found in the 1.8-nm filtrate)(Wilson, 1987). The americium and curium might have been present as large complexes or colloids, preventing them from passing through the finer filter. An alternative explanation may lie in the concentrations of americium and curium, which were only ~100 pg/g and ~3 pg/g, respectively. At such low concentrations, these elements might have been removed from solution by adsorption onto the 1.8-nm filters.

The fission product cesium, which is partially released from the oxide fuel matrix during irradiation, segregates to the grain boundaries and the fuel-cladding gap. This gap and grain boundary inventory dissolves immediately upon contact with water. As shown in Fig. 6, cesium was rapidly released in the NNWSI Project Series 2 dissolution tests. Relatively constant solution levels followed this initial release. Most of the release occurred in cycle 1 (Table 7 and Fig. 6), and the mobilized cesium was retained in solution. For the defected cladding configurations, 97 percent or more of the cesium released was in the aqueous phase. Slightly lower percentages for the bare fuel tests (Table 7) probably reflect the mobilization of small fuel particles that quickly settle. Unlike the case of the actinides, the presence of defected cladding did not act as a significant barrier to the release of cesium. The Turkey Point hole defect test was an exception to this; the fractional release of cesium for this test (<0.01 percent) was much lower than expected and is not currently understood.

Fractional cesium releases for the Turkey Point bare fuel and slit defect tests were 0.3 and 0.2 percent, respectively. This is close to the reported fractional fission gas release for this fuel (Table 2). Fractional releases for the H. B. Robinson bare fuel, slit, and hole defect specimens were 0.8, 0.8, and 0.4 percent, respectively. The reported fractional fission gas release for this fuel is only 0.2 percent (Barner, 1984). The ~250 percent greater fractional cesium release for the H. B. Robinson fuel compared with the Turkey Point fuel is thought to be a reflection of the much smaller grain size of the former.

Figure 6. Cesium-137 activities in unfiltered solution samples, Series 2, cycles 1 and 2 H. B. Robinson fuel (25°C, J-13 water)(Wilson, 1987).

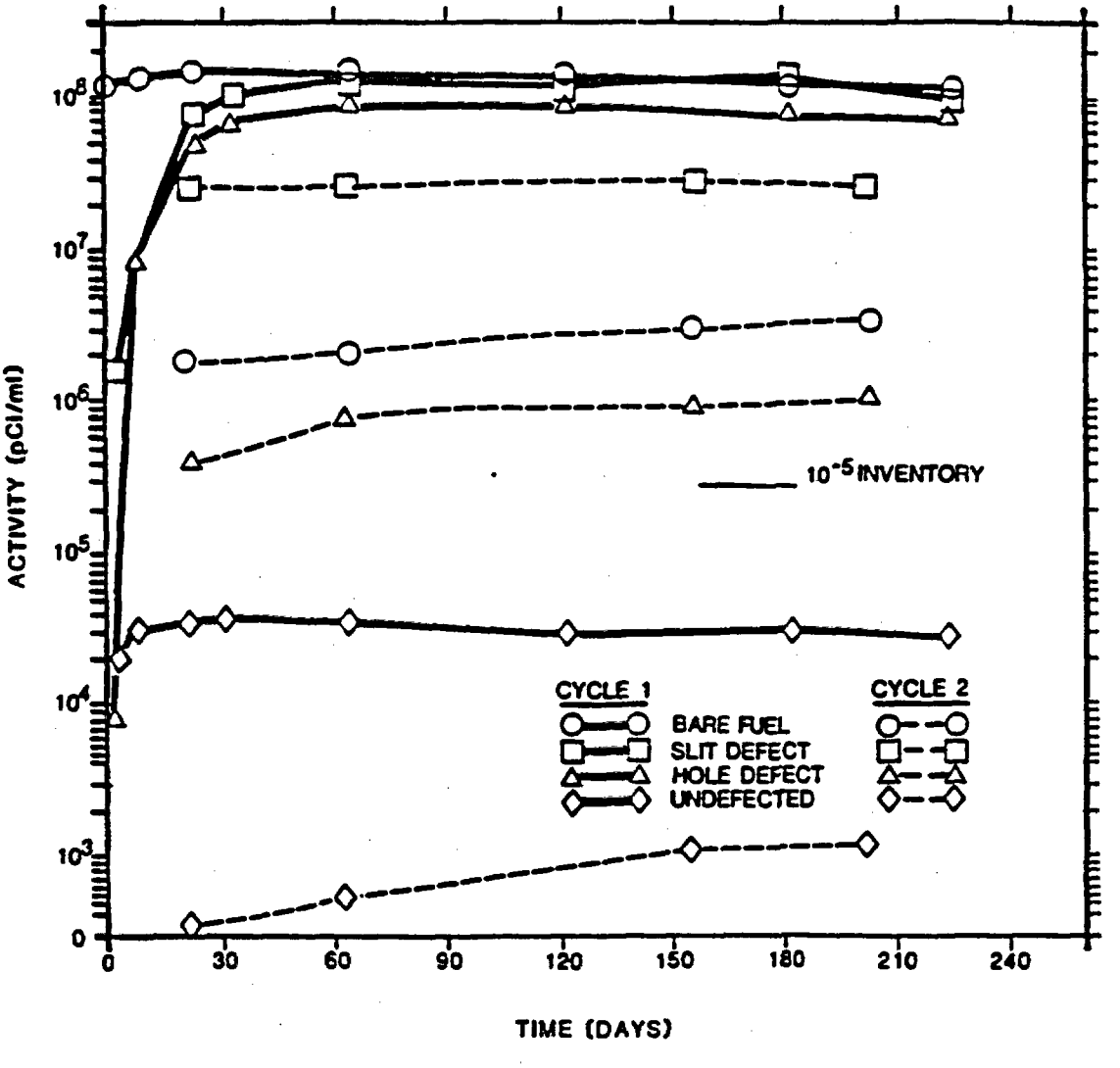

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Table 7. Fractional releases in parts in 10^5 of Cs, Tc, and I; Series 2, cycles 1 and 2; 25°C, J-13 water (Wilson, 1987).

	Bare fuel		Slit defect		Hole defect		Undefected	
	HBR	TP	HBR	TP	HBR	TP	HBR	TP
Cs-137								
Fractional release								
Cycle 1	776	308	664	144	425	7.8	0.19	0.11
Cycle 2	19.6	16.1	140	75	5.2	1.5	<0.01	<0.01
Sum	796	324	804	219	430	9.3	0.20	0.12
(Fractional release Cs)/(fractional release U)								
Cycle 1	137	26	1.41×10^4	217	8.5×10^4	—	—	—
Cycle 2	12.7	3.9	1.92×10^3	207	6.5×10^{4} 2	—	—	—
Sum	110	20	6.70×10^3	214	3.3×10^4	—	—	—
Percent in aqueous phase								
Cycle 1	94.9	81.5	99.0	96.9	98.8	98.0	95.9	92.9
Cycle 2	92.8	89.3	98.9	98.0	97.8	98.1	—	54.3
(Dissolved Cs)/(dissolved U)[a]								
Cycle 1	929	42.9	1.56×10^4	233	1.4×10^5	—	—	—
Cycle 2	19.5	4.4	1.99×10^3	208	4.4×10^3	—	—	—
Tc-99								
Fractional release								
Cycle 1	~23.3	~32	~2.8	<15.3	—	—	—	—
Cycle 2	<8.6	<8.3	<2.1	<6.6	—	—	—	—
Sum	<31.9	<41	<4.9	<22	—	—	—	—
(Fractional release Tc)/(fractional release U)								
Cycle 1	~4.1	~2.7	~60	<23.1	—	—	—	—
Cycle 2	<5.6	<2.0	<28.8	<18.2	—	—	—	—
Sum	<4.4	<2.5	<41	<22	—	—	—	—
Percent in aqueous phase								
Cycle 1	~77	~79	~43	—	—	—	—	—
Cycle 2	~87	—	—	—	—	—	—	—
(Dissolved Tc)/(dissolved U)[a]								
Cycle 1	~23	~4.3	~29	—	—	—	—	—
Cycle 2	~8	—	—	—	—	—	—	—

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Table 7. continued.

	Bare fuel		Slit defect		Hole defect		Undefected	
	HBR	TP	HBR	TP	HBR	TP	HBR	TP
I-129								
Fractional release								
Cycle 1	10.5	29.2	5.4	7.9	0.08	0.69	0.09	0.20
Cycle 2	7.5	12.0	0.7	5.7	0.10	0.20	0.12	0.32
Sum	18.0	41.2	6.1	13.6	0.17	0.89	0.21	0.52
(Fractional release I)/(fractional release U)								
Cycle 1	1.9	2.5	114.9	11.9	15.4	—	—	—
Cycle 2	4.9	2.9	9.4	15.7	12.0	—	—	—
Sum	2.5	2.6	50.7	13.3	13.3	—	—	—
Percent in aqueous phase								
Cycle 1	—	—	—	—	—	—	—	—
Cycle 2	89	87	90	96	75	83	—	—
(Dissolved I)/(dissolved U)[a]								
Cycle 1	—	—	—	—	—	—	—	—
Cycle 2	7.2	3.2	8.9	15	62	—	—	—
Sr-90								
Fractional release								
Cycle 1	—	—	—	—	—	—	—	—
Cycle 2	24.8	12.2	26.9	4.4	<0.12	<0.05	—	—
Sum	—	—	—	—	—	—	—	—
(Fractional release Sr)/(fractional release U)								
Cycle 1	—	—	—	—	—	—	—	—
Cycle 2	16.1	3.0	368.5	12.3	<15	<10	—	—
Sum	—	—	—	—	—	—	—	—
Percent in aqueous phase								
Cycle 1	—	—	—	—	—		—	—
Cycle 2	88.5	83.9	98.6	94.4	>75	>30	-	-
(Dissolved Sr)/(dissolved U)[a]								
Cycle 1	—	—	—	—	—	—	—	—
Cycle 2	23.6	3.1	381.3	11.9	—	—	—	—

[a] This ratio calculated by taking {(% of fission product X in the aqueous phase) · (fractional release of fission product X)} and dividing by {(% of U in the aqueous phase) · (fractional release of U)}.

The larger grain boundary area and shorter diffusion path lengths to grain boundaries likely results in a greater grain boundary cesium inventory since cesium is transported to and along grain boundaries during reactor operation. Given the similarities in the fuels (same manufacturer, same vintage, similar burnup, similar gas release), the difference in cesium release clearly shows that more work will be necessary to establish the factors that control cesium distribution in the fuel before general conclusions regarding cesium release can be substantiated.

The release of cesium from the fuel in J-13 water was similar to that observed in deionized water. The main difference in behavior in the two leachants was that no decrease in cesium levels in the aqueous phase occurred in the case of J-13 water. In the Series 1 test, cesium levels over bare fuel began to decrease after 60 days (Wilson, 1985a). This was thought to be due to the precipitation of some cesium salt, possibly $Cs_2U_2O_7$, the cesium analogue of a sodium salt that has been suggested by Johnson (1982) to be the solubility control for uranium in solutions over spent fuel. The J-13 water contains a significant amount of sodium (50 ppm); this might cause sodium uranate to form at the expense of cesium uranate, leaving the cesium in the solution phase. To date, neither of these alkali uranate phases has been identified during post-test examination of the specimens.

The release of technetium is of particular interest since the pertechnate ion is expected to be quite soluble in the mildly oxidizing groundwater at the NNSWI Project candidate repository. Like cesium, technetium tends to separate from the oxide fuel matrix during reactor operation. Technetium should exist as a metal at the oxygen fugacity present in fuel during irradiation. Hence, it is associated with other phase-separated metallic fission products in spent fuel (Thomas et al., 1986).

The detection limit of the radiochemical procedure used for the technetium analyses is adequate to unambiguously detect 10^{-5} of the inventory of an 80-g specimen in solution. Significant activities of technetium-99 were measured in most solution samples that were taken from the bare fuel and slit defect tests (Table 7). As with cesium, most of the technetium release occurred during the early part of cycle 1. More than 75 percent of the technetium mobilized from the bare fuel specimens was in the aqueous phase, consistent with the solubility expectations. The release of technetium from the H. B. Robinson specimens was less than that for the Turkey Point specimens. This implies that the mechanisms involved in distribution of technetium in the fuel and its subsequent release are different than those for cesium. The results may indicate that technetium release is largely controlled by matrix dissolution rather than by a gap and grain boundary inventory.

Iodine-129 was measured on selected solution samples. A summary of the data, given in Table 7, shows that the apparent release of iodine was much less than that of cesium. It is possible, however,

that iodine was lost to the air because these tests were run in unsealed vessels; however, since Johnson et al. (1983b) found high concentrations of iodine in tests conducted under conditions similar to the NNWSI Project tests, it is likely that iodine loss from solution to the air is a minor effect. The Series 3 tests, run in sealed vessels, should provide better constraints on the data for iodine release. If one assumes that iodine loss was negligible, the iodine measured in solution correlates reasonably well with the technetium release. Since iodine should be present in solution as iodide, it should not plate out on the stainless steel vessel. There is evidence from work on CANDU fuel that iodide is sorbed by the Zircaloy cladding present in their tests (Johnson et al., 1985). A check for plate-out components was made at the termination of the second cycle of the NNWSI Series 2 tests by measuring the iodine-129 activity in an acid strip of the test vessel; only ~1.3×10^{-8} of the specimen inventory was recovered in this manner. However, since the vessel strip utilized nitric acid, iodine might have been lost to the atmosphere from the strip solution. Note that only the vessel and basket were stripped; the Zircaloy cladding was not. The data suggest that iodine-129 is being mobilized from the bare fuel at a rate similar to the matrix components and not at the much higher rate exhibited by cesium. The slit defect sample shows a clear enhanced release of iodine relative to the actinides and probably represents a gap inventory release. The amount of release, however, is still two orders of magnitude below the fractional release of cesium from slit defect samples.

The results of carbon-14 analyses of Series 2 test specimens are given in Table 8. There was no correlation between defect severity and release for the H. B. Robinson cycle 1 data, suggesting that the carbon-14 was released from the cladding rather than from the fuel. The cycle 2 data for the undefected cladding specimen are lower, suggesting that in cycle 2, a greater proportion of the carbon-14 was released from the fuel. The data are quite erratic, however, and the significance of the difference in activity is questionable. The lower carbon-14 activity in the Turkey Point undefected tests might be due to the fact that the fuel section used for this specimen came from the bottom end of a fuel rod and therefore might have had a lower carbon-14 inventory (Wilson, 1987).

Carbon-14 was radiochemically separated and measured on fuel and cladding for two samples of the H. B. Robinson fuel rod used for the Series 2 specimens (Wilson, 1987). The average of the analyses was 0.53 μCi/g for the cladding and 0.49 μCi/g for the fuel. In general, 30 to 60 percent of the carbon-14 in the spent fuel waste form is in the nonfuel components such as the cladding. The exact amount depends on the nitrogen impurity levels in the cladding and in the structural materials. By using the measured carbon-14 inventories in H. B. Robinson spent fuel, the carbon-14 release in the H. B. Robinson cycle 1 bare fuel tests was estimated to represent ~1×10^{-3} of the cladding inventory or ~2×10^{-4} of the fuel inventory. For cycle 2, ~1.2×10^{-3} of the cladding inventory or ~2.1×10^{-4} of the fuel inventory is

Table 8. C-14 activities measured in solution samples (pCi/mL). Series 2, cycles 1 and 2 (25°C, J-13 water)(Wilson, 1987).

Solution samples	Bare fuel	Slit	Hole	Undefected
H. B. Robinson				
Cycle 1				
63 day solution	19.8	13.1	5.4	22.5
223 day solution	25.7	55.9	96.4	19.8
Cycle 2				
154 day solution	22.5	75.7	68.0	14.0
202 day solution	24.3	68.9	44.6	7.2
202 day rinse	5.4	3.6	4.9	9.9
Turkey Point				
Cycle 1				
181 day solution	52.7	72.1	16.7	9.0
Cycle 2				
154 day solution	54.1	34.7	32.9	7.7
195 day solution	45.0	35.6	34.2	11.3
195 day rinse	5.9	2.2	2.7	2.7

accounted for by the solution activities. These fractional inventory values are lower limits on the actual release of carbon-14 since the test vessels used were capped with loose-fitting lids that might have allowed loss of carbon as CO_2 to the atmosphere. The Series 3 tests, which used sealed vessels, should yield better estimates of the carbon-14 release.

Additional experiments on the release of carbon-14 are being conducted as part of the Zircaloy degradation investigations of the NNWSI Project. These experiments are aimed at evaluating the potential for gas-phase release and transport of carbon-14 from the spent fuel waste form. Although this work is not part of the dissolution activities, it is discussed here since it involves the release of radionuclides from the spent fuel waste form. The results of an initial experiment, conducted using a spent fuel assembly under an air atmosphere in a sealed container at 275°C, showed that there is an initial release of approximately 0.26 percent of the carbon-14 inventory of the entire assembly (Van Konynenburg et al., 1984). The carbon-14 release occurred as CO_2 gas. Gas analyses of storage tests of spent fuel stored under inert atmospheres (helium and nitrogen) do not show significant releases of carbon-14. These results support the hypothesis that the observed release under oxidizing conditions is

due to the removal of carbon as CO_2 from the outer surface of the Zircaloy cladding by reaction of the carbon with oxygen in the atmosphere (Van Konynenburg et al., 1986).

spent fuel assembly

The experiment was continued, with the air in the container pumped out and replaced several times to measure additional release. During the first part of the experiment, one of the fuel rods ruptured. This occurred after the initial carbon-14 release was measured. Despite the presence of a ruptured rod, the subsequent releases of carbon-14 were found to be much lower than the initial release (Van Konynenburg et al., 1986). These data are still being analyzed; however, the observed carbon-14 release after the initial pulse appears to be consistent with the fuel rod fill gas analyses reported by the Materials Characterization Center on similar fuel (Barner, 1984). Carbon-14 concentrations reported for the fill gas average 0.81 nCi/cm^3 (STP), which is equivalent to an average activity per fuel rod of approximately 0.3 μCi. This is more than three orders of magnitude lower than the observed initial release reported by Van Konynenburg et al. (1984), supporting their conclusion that the initial carbon-14 release came from the cladding or metal components of the assembly rather than from the fuel.

There is presently only one data set for dry oxidative release of carbon-14 from spent fuel (Van Konynenburg et al., 1984 and 1986). Additional experiments are planned to determine the release rate and fraction released under conditions expected at long times. Work is also in progress to determine the spatial distribution of carbon-14 in the cladding by means of controlled etching of the cladding surfaces.

Four types of solids characterization were performed at the end of the first two cycles of Series 2: (1) scanning electron microscope (SEM) examination of small, fractured fuel particles; (2) SEM examination with energy dispersive X-ray (EDX) microanalysis of the filters used to filter the sample solutions; (3) SEM and EDX analyses of residues from bare fuel rinse solutions; and (4) post-test radiometallurgical examination of polished sections from test specimens (Wilson, 1987).

The SEM examination of fuel particles did not reveal any significant change in fuel structure caused by the test. As is typical of spent fuel, the fracture surfaces of the fuel particles tended to follow grain boundaries. This contrasts with the behavior of non-irradiated fuel, which is a hard ceramic material that exhibits transgranular cleavage when fractured. Areas of mixed cleavage and grain boundary fracture were observed in some spent fuel particles thought to be from near the outer radial regions of the fuel pellet. Irradiation temperatures are lower, and less fission product migration to grain boundaries occurs in these areas as compared to the center of the pellet; thus, there is less change in the fracture properties in these regions during irradiation.

An SEM image of one of the larger particles obtained from the H. B. Robinson cycle 1 rinse residues is shown in Fig. 7. The particle is a small fuel fragment, partially coated with a surface layer of material that EDX analyses show to be primarily silicon (or silica; the EDX method does not detect oxygen or other light elements). The layer appears to be composed of silica gel ranging in thickness from 10 to 25 μm. Similar layers were observed on other H. B. Robinson particles as well as on Turkey Point fuel particles. The quantity of silicon involved in the layers appears to be a significant portion of the ~10 mg of silicon contained in the 345 mL of J-13 water used in the tests. The effect of this layer on the dissolution rate of spent fuel is not known but is thought to be small. Forsyth et al. (1985) conducted tests in Pyrex and in polypropylene flasks. They found no differences that could be attributed to the test vessel material. An H. B. Robinson bare fuel specimen was tested at 25°C in a stainless steel vessel in the Series 3 tests (Wilson and Shaw, 1987). This specimen was included to examine the effects, if any, of the test vessel material on the results of the test. The test being conducted in the stainless steel vessel is a closer representation of the repository case.

SEM and EDX analyses of selected filters used in Series 2 commonly revealed extremely small particles composed predominantly of silicon. These probably represent colloidal silica flocs.

Metallographic examination of polished, mounted fuel fragments recovered after the Series 2 tests did not reveal any significant evidence of grain boundary dissolution. Particular attention was given to the examination of the particle edges; however, no unusual features were noted in the post-test samples. These observations differ from those made on the post-test Series 1 fuel fragments. Significant grain boundary dissolution was noted in the H. B. Robinson Series 1 bare fuel particles. This difference may be due to more aggressive action of the deionized water used in the Series 1 tests or to a change in the rinsing procedure used at cycle termination (Wilson, 1987).

Metallographic examination of the fuel at the pellet-cladding gap in the slit defect specimens of both fuel types did not reveal any unusual features that could be related to fuel dissolution (Wilson, 1987).

Solution analyses for nonradioactive components were performed on the starting J-13 water and on selected periodic solution samples (Wilson, 1987). The solution chemistry data indicate that there was little change in the composition of the leachant over the course of the tests. As an example, the solution chemistry data for the H. B. Robinson bare fuel test are given in Table 9. The only consistent changes were a shift to more basic pH during both cycles and the formation of a small amount of nitrite due to radiolysis reactions. The barrel of J-13 water used for these tests also shifted in pH during this time, and the change is attributed to equilibration of the J-13 water with the atmosphere. Silicon levels in solution were of interest since the tests were run in fused silica vessels. Except for a 20 to 30

Figure 7. Fuel particle from the H. B. Robinson Series 2 bare fuel test showing remnants of a silica layer deposited on the particle surface during the test. Neg. 8500845-3 (Wilson, 1987).

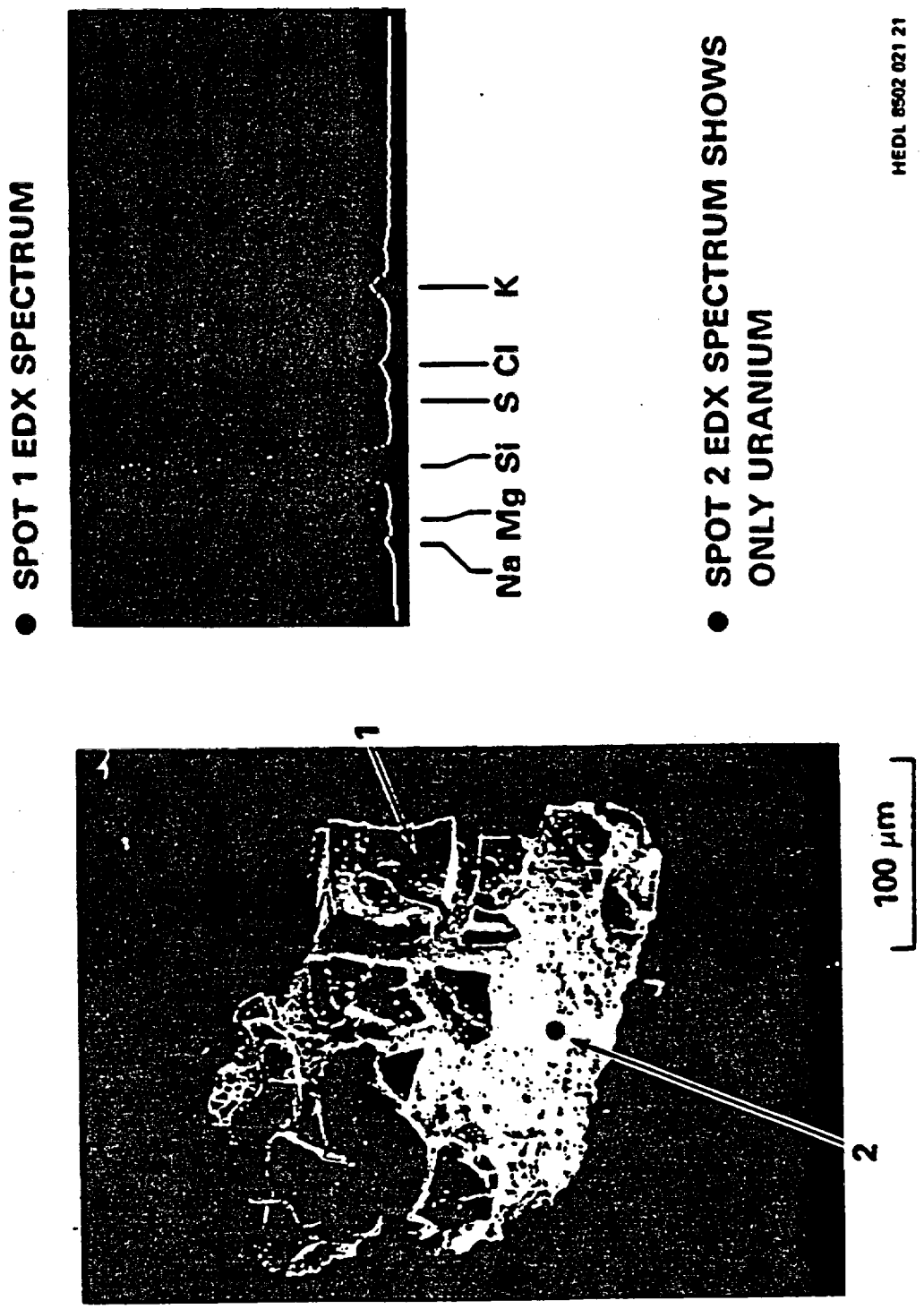

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Table 9. Solution chemistry[a] for the H. B. Robinson bare fuel test, Series 2, cycles 1 and 2 (25°C, J-13 water)(Wilson, 1987).

Cycle 1	Starting J-13 water	30 Days	120 Days	223 Days
pH	7.2	8.2	8.5	8.5
Al	0.11	0.09	0.10	<0.08
B	<0.1	<0.01	0.09	0.26
Ca	15.0	12.7	12.1	12.3
Fe	—	0.21	0.15	0.08
K	5.5	4.5	2.8	2.2
Mg	2.1	1.8	2.1	2.0
Mo	0.08	0.26	0.21	0.20
Na	49.5	41.6	44.5	45.5
Sr	—	—	—	0.06
Si	31.9	24.5	26.2	32.7
Cl	7.3	7.8	7.3	7.6
F	2.7	2.4	2.1	2.2
PO_4	2.8	—	—	—
NO_2	—	~0.5	~0.5	~0.6
NO_3	8.7	7.4	8.1	8.3
SO_4	18.8	18.8	18.6	18.5
CO_3	118.0	—	120.0	118.0

Cycle 2	Starting J-13 water	154 Days	202 Days
pH	8.0	8.2	8.56
Al	<0.08	<0.08	<0.08
B	0.21	0.21	0.23
Ca	11.2	12.6	12.4
Fe	<0.01	<0.01	<0.01
K	1.95[b]	5.46	5.2
Mg	0.93[b]	2.00	2.00
Mo	<0.02	0.08	0.08
Na	43.1	45.1	44.1
Sr	0.04	0.05	0.05
Si	30.6	36.4	36.2
Cl	7.4	7.7	7.5
F	2.3	2.4	2.1
PO_4	—	—	—
NO_2	—	~1.4	~1.7
NO_3	8.3	7.1	6.6
SO_4	18.6	18.6	19.8
CO_3	121.5	112.0	112.0

[a] Units in µg/mL, 0.4 µm filtered.

[b] These values are low compared with other analyses of J-13 water and probably indicate a poor analysis.

percent drop in silicon in the 30- and 120-day H. B. Robinson cycle 1 specimens, the silicon concentrations either remained relatively constant or increased. SEM characterization of residues rinsed from the fuel specimens revealed a deposit of silica on the fuel surface. Apparently, the silica lost by precipitation was replaced at approximately the same rate by dissolution of the vessel; thus, a nearly constant silica concentration was maintained in solution. The only detected change in solution chemistry that could be attributed to radiation effects was the conversion of some of the initial NO^-_3 to NO^-_2. The source of the NO^-_2 is thought to be primarily NO^-_3 rather than dissolved air because the measured concentrations of NO^-_3 and NO^-_2 in solution show an inverse correlation.

The purpose of spent fuel dissolution testing is to provide data on the concentrations of radionuclides that might leave a breached waste container under repository conditions. The testing cannot be done under repository conditions because the expected water flow rates are too low to obtain measurable results in the time period available. To avoid this problem, we conduct tests using a higher ratio of water to fuel than is expected under repository conditions. This provides a system that can be handled experimentally, but introduces the problem of how to relate the results obtained to the repository case.

The link between the laboratory data and the expected repository performance comes through geochemical modeling calculations. The EQ3/6 geochemical modeling code is being utilized for this purpose. For geochemical modeling calculations to be meaningful, the solid phases that control the solution concentrations must be identified (to ensure that they are included in the code's database) and the solubility of those phases under appropriate conditions must be determined. If the thermodynamic properties of all the relevant solids and solution species are known, the solubility data obtained under one set of conditions can be used to calculate solubilities under a range of other conditions of interest. For many of the elements of interest in spent fuel dissolution, however, experimentally determined thermodynamic data are not available for the solids and solution species that are predicted to be important in limiting solution concentrations of radionuclides.

The peak concentration of uranium in cycle 1 of dissolution tests conducted at ambient hot cell temperature in J-13 water was less than 5 ppm, and the solutions for cycle 2 of the tests were 2 to 2.6 ppm. For plutonium, the peak concentration was 5 ppb. These concentrations are much lower than the values of 50 ppm and 430 ppb, respectively, used by Kerrisk (1984) in his calculations of dissolution rates and solubility limits of radionuclides in a tuff repository.

Other data also suggest that the steady-state actinide concentrations in water of similar composition to J-13 are on the order of those measured in the NNWSI Project spent fuel tests rather than the much higher values predicted by calculations done by Kerrisk (1984) using the EQ3/6 geochemical

code. The data obtained by Forsyth et al. (1983 and 1985) have a range of uranium concentrations of 0.1 to 2 ppm, with an average value of 0.8 ppm in KBS water. Forsyth et al. (1985) report a peak plutonium concentration of approximately 3 ppb with the concentration dropping with increased contact time to a plutonium saturation value of less than 1 ppb under the same conditions. Johnson (1982) found uranium concentrations of 1.2 to 4.5 ppm in the AECL-KBS water (higher bicarbonate than Swedish KBS or J-13 waters) and 0.2 to 3 ppm in AECL-GR water. The experimental data were obtained at fuel-weight to water-volume ratios that ranged from a low of 8 g/100mL for the Swedish tests to 72 g/100mL for the Canadian tests. There is no indication of a correlation between solution concentration of uranium and fuel-to-water ratio. There is a weak correlation with bicarbonate content, as might be expected. However, Johnson (1982) acidified solutions in the leach vessel, so those uranium data must be considered as upper limits to the uranium solution concentration because they could include precipitated material and fuel particles that dislodged from the specimen. Some of the variation among the three sets of results might be due to intrinsic differences in the spent fuels. Nevertheless, despite the scatter and uncertainties, there is remarkably good agreement among the maximum solution concentrations in the three data sets.

The agreement among the three data sets with respect to uranium and plutonium solution concentrations suggests that these values represent a better estimate of the solubility of uranium and plutonium over spent fuel than the estimates assumed in Kerrisk's (1984) calculation. This, in turn, suggests either that the phases responsible for limiting the concentration of plutonium and uranium in the system were not represented in the data base used in the calculations or that the thermodynamic properties for the phases were not correct. To extrapolate the results of laboratory testing of spent fuel to the time scales relevant to repository disposal, it is necessary to develop an understanding of the dissolution mechanism for spent fuel. Detailed determination of the mechanism will require the analysis of alteration products on the surface of fuel that has undergone dissolution. Identification of the alteration products on the surface of the fuel and of any secondary phases formed by precipitation from solution will allow the development of a model that will describe both the solid and solution phases during interaction of spent fuel with solutions.

Bruno et al. (1985) and Forsyth et al. (1985) have done thermodynamic modeling calculations to simulate the Swedish fuel tests. They assumed the initial UO_2 fuel surface was partially oxidized to U_3O_8; however, this had no effect on their calculations because the solutions were assumed to be in equilibrium with oxygen in the air above the solutions, thus fixing the oxidation state. Note that the data tabulated in the appendix of Forsyth et al. (1985) are referenced to U_3O_8 as the standard state for U (Bruno, personal communication). They calculated a uranium solubility of 1 to 5 ppm at pH = 8.1 for the KBS groundwater test simulation, in excellent agreement with the experimental data. The results

depend critically on the value chosen for the solubility constant for $UO_2(OH)_2$, the phase that controls uranium solubility in their calculations. [Stroes-Gascoyne et al. (1986) have identified schoepite, $UO_3 \cdot 2H_2O$, or a closely related phase on the surface of a spent fuel specimen leached in distilled water for 7 yr at ambient temperature, and Johnson et al. (1981) found a mixture of partially dehydrated schoepite, $UO_3 \cdot 0.8\ H_2O$ and $UO_2(OH)_2$ on an unirradiated fuel pellet exposed to air-saturated granite groundwater at 150°C for 2 wk. No precipitated phases have been reported in the published work of KBS.] A comparison of the data base for uranium used by Bruno et al. (1985) with that used in the EQ3/6 calculations will be done as part of the geochemical model development for waste form performance prediction.

The methods used by the various workers for reporting the results of leach tests can cause confusion and apparent inconsistencies between data sets, especially when the solution concentrations are limited by the solubility of a sparingly soluble phase. If solution concentrations are constant and data are reported as leach rate per unit time, then the calculated rate will depend on the length of the test. Short tests will give high leach rates and long tests will give low leach rates. The ratio of fuel to liquid will also affect the calculated leach rate since, for concentrations in solution that are controlled by solubility of a phase, the amount of a chemical element in solution depends on the volume of solution and not on the amount of solid in the system. Thus, a fuel-to-water ratio of 10 g/100 mL will give a calculated leach rate that is 10 times higher than a fuel-to-water ratio of 100 g/100 mL if the rates were reported as fractional release per unit time.

To compare release rates determined under different experimental situations, the data must be normalized to a common set of conditions. Unfortunately, published results frequently do not contain all the information that is needed to reduce the data sets to a common basis. Johnson (1982) acidified solutions before he removed them from the leach container; therefore, he measured the sum of the solution plus plate-out component. Forsyth et al. (1983 and 1985) decanted the solutions from the leach vessel, filtered a fraction of the sample to determine colloidal material, rinsed the vessels, and then stripped the leach vessel with acid to measure the plate-out component. It is possible to compare directly the NNWSI Project solution analyses with those of Forsyth et al. (1983 and 1985); but, because Forsyth et al. did not report the amount of material recovered in the rinse or acid strip solutions, total release values cannot be directly compared. [Forsyth et al. (1985) believe that all of the material in the acid-stripping solution was due to fine particles of fuel and that it was inappropriate to include that material in the total release. Their interpretation is probably correct, but because of the possibility of particulate transport in a repository, we believe it is necessary to determine the total amount of material mobilized during the test even if mobilization occurs as very fine solids.]

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The procedures used for testing of spent fuel might also cause differences among the sets of results. Johnson (1982) conducted tests using a modification of the International Atomic Energy Agency (IAEA) test. He used 100 mL of solution in a polypropylene bottle with an open-ended slice of CANDU fuel plus cladding, leaving the fuel sample in the solution for a fixed period of time. He determined that the solution had unimpeded access through the pellet-cladding gap, so his tests are most nearly equivalent to the bare fuel tests conducted in the NNWSI Project studies. After the end of the leaching period, the fuel sample was transferred to a fresh bottle of solution, and the leaching was continued. Leachate solutions were acidified in the bottle prior to removal, so any plated-out material was dissolved and included in the analysis. (This should not matter for uranium in the bicarbonate-rich groundwaters but will have a significant effect on the amount recovered of the other actinides.) Johnson conducted sequential tests for periods ranging from a few days to more than 100 days, with a total leaching time of nearly 3 yr.

Results of the Johnson tests (1982), which were conducted in granite groundwater at ambient hot cell temperature, are plotted in Fig. 8. The data are plotted as leach rates in terms of fractional release rate per day of cesium-137, strontium-90, technetium, uranium, and plutonium. Release rates were found to decrease for the first 6 months of the test and then to level out for all elements, including cesium. The range in release rates is nearly two orders of magnitude for the samples taken at 200 to 800 days into the test, with cesium, strontium, and technetium release all higher by a factor of 5 to 10 than the uranium release rate of a few parts in 10^8 per day. The fuel used in these tests was Pickering bundle A01790. Gas release quoted by Johnson (1982) was a calculated value of 0.45 percent; Johnson et al. (1983a) quote a measured value of 1.8 percent gas release for an outer element from this bundle. The average cesium release after 800 days in the four tests conducted by Johnson (1982) was 0.3 percent. This is substantially lower than the measured fission gas release cited by Johnson et al. (1983a).

Data for uranium were not given for the tests run during the first 6 months of the sequential reaction series. The NNWSI Project work has shown that the release of uranium and actinides is highest for the first contact of the sample with water, perhaps due to release of ultrafine particles of fuel or the dissolution of a readily soluble, partially oxidized surface layer on the fuel. Since Johnson's first data point for uranium was measured after a dozen or more changes of solution, his values should correspond to true solution of fuel only. This might explain why he saw very low solution concentrations of uranium in deionized water, an observation that is in agreement with the "true solution" concentration of uranium obtained in the NNWSI Project deionized water studies (Wilson, 1985a) after subtraction of the particulate component.

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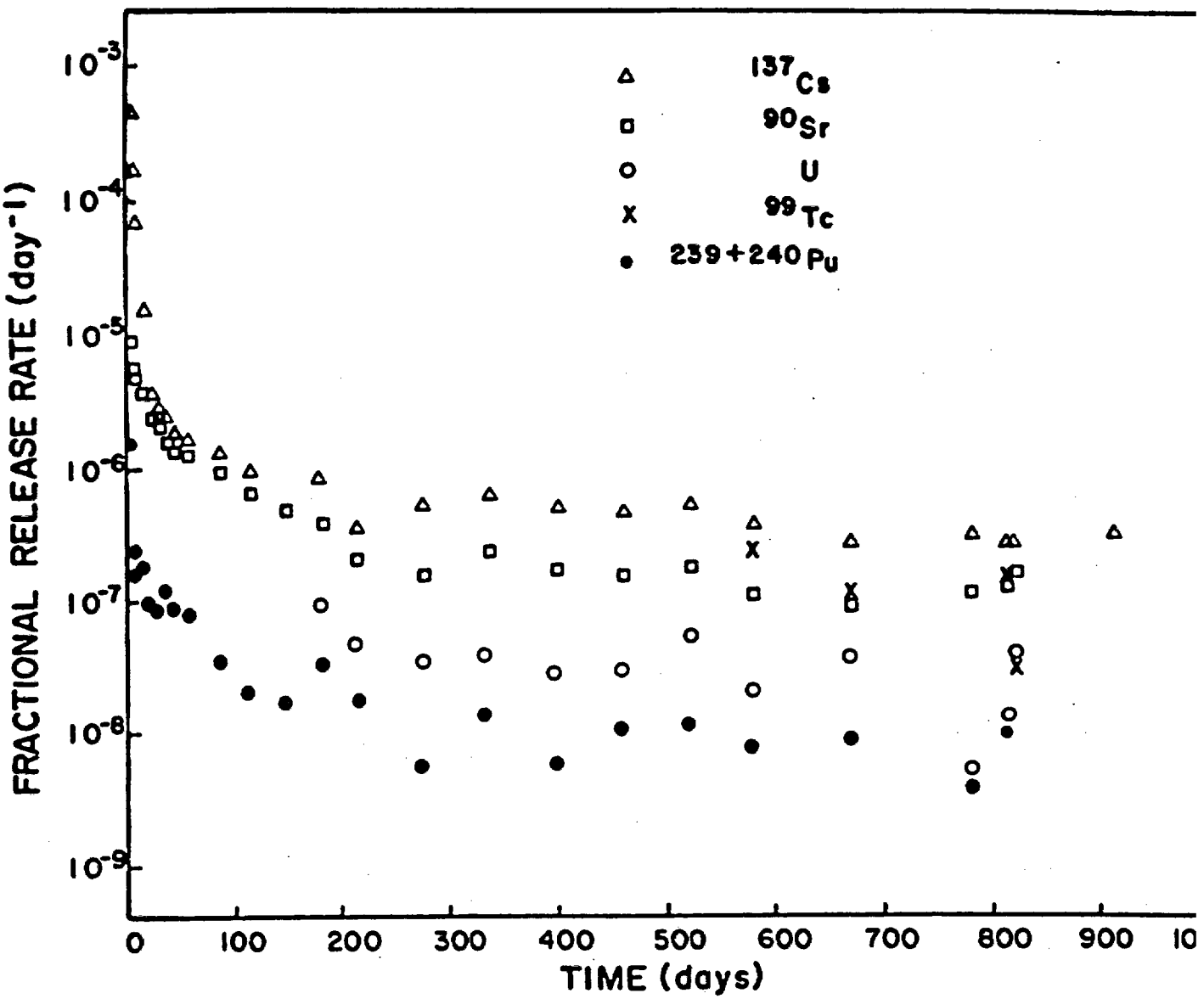
Figure 8. Fractional release rates of radionuclides in granite groundwater (Johnson, 1982).



Katayama et al. (1980) reported results of the leaching of H. B. Robinson spent fuel in deionized water, 0.03M $NaHCO_3$, and three other leachants. They used the same general test procedure as did Johnson (1982), but used bare fuel fragments 2 to 5 mm in size, 15 g of fuel, and 300 mL of solution. This gives a fuel-to-solution ratio of 5 g/100 mL, more than 10 times lower than Johnson's. They acidified the solutions in the leaching vessel, as did Johnson (1982), so they measured the sum of the solution component and the readily soluble plate-out component. They then performed an acid stripping of the vessel and added the amount in the acid-stripping solution to the original solution value. This total was converted into a leach rate in g/cm^2-day. There is sufficient information in the report to back out the original total amount of each element that was mobilized during each sequential leaching step, but because the leach solution and acid-stripping data were added together (and never reported separately), it is difficult to compare their data meaningfully to any other group's data. They reported rather high uranium release in deionized water, which apparently is in conflict with Johnson's (1982) results; however, since the data contain an indeterminate amount of plate-out material and/or fuel particles, there might not be an inconsistency. In the NNWSI Project Series 1 work, 99 percent or more of the uranium release in deionized water was recovered from rinsing the fuel sample (which might dislodge precipitated material) or from acid stripping the vessel or glass plate-out monitors. As mentioned above, the true solution component data for deionized water obtained in the NNWSI Project studies would support Johnson's results. However, the total mobilized uranium during the NNWSI test, recovered mainly in the acid-stripping solutions, is not very different from Katayama's total release into deionized water, including the plate-out component. In the future, it would be desirable to report the complete set of experimental data in a manner that allows others to evaluate the significance of the various components.

Katayama et al. (1980) also reported data for sodium bicarbonate water leaching. The bicarbonate concentration was approximately 1800 ppm, a level much higher than any of the groundwaters used in NNWSI, KBS, or Canadian fuel leaching. The data given on page A-1 of their report can be converted into solution concentrations if it is assumed that the bicarbonate concentration is sufficiently high to ensure that no uranium has plated out. The calculated concentrations range from 1 to 6 ppm uranium, a range that is in excellent agreement with the results for groundwater leaching of spent fuel discussed above.

Forsyth et al. (1983 and 1985) reported their data as the fraction of the inventory in the aqueous phase (FIAP) and based their leach rates on FIAP; in some cases, data are reported as solution concentrations. It is possible, therefore, to compare directly their results for BWR fuel with the NNWSI Project unfiltered solution analysis results for PWR fuel. Forsyth et al. use a fuel-to-water ratio of 8 g/100 mL compared with the ratio of 32 g/100 mL used for the H. B. Robinson tests in J-13

water. Forsyth et al. (1985) found that the fraction of cesium released rapidly in the tests was approximately 1 percent, slightly higher than the 0.7 percent fission gas release. Strontium was released at approximately one-tenth the rate of cesium release, and uranium release was lower than strontium release by a factor of 10. They did tests using both an IAEA type of sequential procedure and a static test procedure and found that the results of the two types of tests for cumulative cesium and strontium release were consistent, which indicates the absence of saturation effects for these two elements in their tests (Forsyth et al., 1985).

During each cycle of the sequential tests, approximately 1 part in 10^5 of the specimen uranium inventory was released to solution in the Forsyth et al. (1983) studies. If only the aqueous phase uranium is considered, for the H. B. Robinson bare fuel test, the FIAP for cycle 1 was 0.8 part in 10^5 and for cycle 2 was 0.9 part in 10^5. By expressing the release in this manner, the results appear to be in excellent agreement; however, the agreement is an illusion. The average solution concentration in the NNWSI tests was approximately 2 ppm uranium, while that for the KBS tests was approximately 0.8 ppm. The differences in fuel to water ratio, when combined with the differences in concentration, cause the fractional release data to be very close. This illustrates the dangers in comparing release rate data if the underlying experiment details are not thoroughly understood.

Johnson (1982) obtained fractional release rates of approximately 5×10^{-8} per day (with considerable scatter) for uranium and approximately 5×10^{-9} per day (with less scatter) for plutonium for leaching periods of 60 to 100 days during the long-term portions of their IAEA-type testing. Forsyth et al. (1983) obtained leach rates of 7×10^{-8} per day for uranium and 3×10^{-9} per day for plutonium for leaching periods of similar length. Forsyth et al. (1983) commented on the agreement of their leach rates with Johnson's (1982). Again, it is probable that this agreement is fortuitous and that there are real and understandable differences between the two data sets. Both sets of data appear to have concentrations controlled by solubility; however, the fuel-to-fluid ratios differ by a factor of nine. Thus, had Johnson done experiments at a fuel-to-fluid ratio of 8 g/100 mL, the expected results expressed as release rate would be 45×10^{-8} per day for uranium and 45×10^{-9} per day for plutonium; i.e., the same concentration of uranium and plutonium should be in solution per milliliter, but there would be more solution per gram of fuel and therefore an apparent higher fractional release. Johnson's solution concentrations of uranium averaged 3 to 4 parts per million for the 60-day leach solutions, and Forsyth et al. (1983 and 1985) reported values that were generally between 0.1 and 1 ppm for contact times up to approximately 3 yr. There appears to be a real difference between the two sets of data, and the difference is probably due to the different concentrations of bicarbonate in the solutions used in the two studies. The bicarbonate content of J-13 water is similar to the KBS water; the uranium concentrations in the NNWSI Project

tests are intermediate between the other two data sets, with the values for long contact times being closer to those of Forsyth et al. (1985).

Stroes-Gascoyne et al. (1987) investigated the behavior of cesium-137 release as a function of the power history of the fuel. They found that fuels that had low peak linear power ratings (<40 kW/m), and thus low peak operating temperatures, had fission gas release to the pellet-cladding gap of less than 0.1 percent. Cesium release for these fuels when tested for 5 days in a solution of 0.2 g/L potassium iodide (KI) in deionized water at 25°C was only approximately 20 percent of the measured fission gas release. For fuels with higher power ratings, and thus higher operating temperatures, gas release was greater and cesium release over a 5-day test was comparable to the gas release. Scanning electron microscope photos show that low power rating fuels exhibit transgranular fracture and high power fuels exhibit intergranular fracture. The intergranular fracture is induced because of gas bubble accumulation at the grain boundaries while the fuel is at high temperature. The authors argue that only 10 percent of the cesium produced is in the form of CsI, which is volatile under reactor operating conditions. Thus, the cesium that is associated with the fission gas in the pellet-cladding gap should be 0.1 of the gas value, while the remaining cesium should be on grain boundaries. In the low power rating fuels, with transgranular fracture, the grain boundaries are not readily accessible for leaching and cesium release might take 90 days or more to reach the value of the gas release. In high power rating fuels, with intergranular fracture, the leaching of grain boundaries is rapid and cesium release is comparable to gas release within a few days (Stroes-Gascoyne et al., 1987).

Wilson (1985b) has shown that H. B. Robinson fuel exhibits intergranular fracture. Thus, according to the Stroes-Gascoyne et al. (1987) model, the cesium release should be comparable to the gas release within a few days. While the rapid release of cesium is essentially complete within a few days, the value released in the H. B. Robinson test is 2.5 times the gas release, which is not accounted for by the model. One of the high gas release CANDU samples also shows cesium release greater than gas release by a factor of two. The authors do not offer an explanation for the data. The BWR high-burnup fuel tested by Forsyth et al. (1983 and 1985) also showed cesium rapid release somewhat in excess of fission gas release.

Johnson et al. (1983b and 1985) and Stroes-Gascoyne et al. (1987) have extended the study of mobile element release from CANDU fuel to include iodine. Iodine and cesium release were measured in distilled water or KI solution at 25°C for up to 5 days. The same possibility of iodine loss to air that applies to the NNWSI Project Series 1 and 2 iodine data also applies to this study because the Canadian tests were also run in unsealed vessels. An example of the release pattern observed is shown in Fig. 9. The test results cited in the 1987 report give different values for samples originally reported

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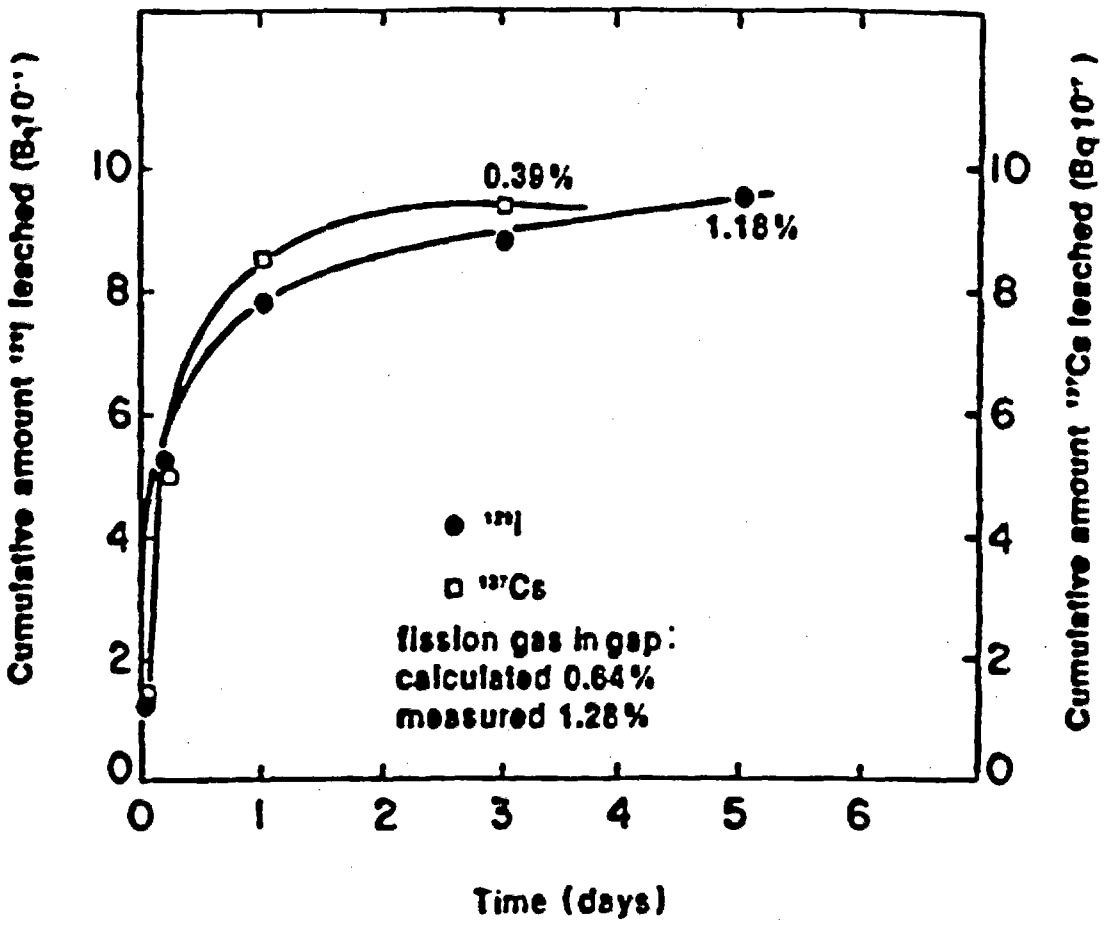
Figure 9. Cumulative amounts of I-129 and Cs-137 leached in KI solution at 25°C from a piece of element #9 of Pickering fuel bundle A13894W as a percentage of total inventory (Johnson et al., 1983b). The referenced work states that distilled water was used as the leachant, but Johnson et al. (1985) state a KI solution was used. Johnson confirmed by personal communication that the leachant was KI.



in 1983. This appears to be due to recalculation of calculated gas release and averaging of two data points. (For example, iodine release for PA13894W, cited as 1.8 ±0.18 percent in the 1987 report, appears to come from the average of 1.18 and 2.36 from the 1983 report. Cesium release was cited as 0.96 percent ±2 percent in 1987, while the 1983 report contained two values, 0.39 percent and 1.52 percent, the average of which is 0.96 percent.) Only one fission gas analysis has been reported, which should be representative of the entire fuel element. There appears to be real and significant heterogeneity in the Cs and I data that is masked by the averaging of two quite different results. It is not possible to determine from either report whether the low Cs and I values came from the same test specimen.

Johnson et al. (1985) found that iodine release was low if deionized water was used as a leachant. The effect was attributed to sorption of trace iodide onto the Zircaloy cladding. Most of their subsequent experiments used a solution with 0.2 g/L of potassium iodide to act as a carrier. Although this increased the reproducibility of their results, the relevance of the iodine release measured in these experiments to the release in groundwater in the absence of large amounts of iodide in solution is questionable. (The tests with KI do, however, provide a means of determining the location of the iodine-129 inventory within the fuel.) The low iodine-129 release rates observed in the NNWSI Project experiments might reflect either a lower gap inventory of iodine-129 in PWR fuel or the relative immobility of the iodine-129 in the absence of an iodide carrier. Because Johnson et al. (1985) found large amounts of iodine under test conditions open to the atmosphere, it is unlikely that the low iodine results in the NNWSI Project tests are due to loss of iodine from solutions in volatile form.

Some data are available on the dissolution of spent fuel at higher temperatures. Results of testing CANDU fuel at 150°C are contained in the reports by Johnson et al. (1981 and 1982). The experiments were conducted at 150°C in 1-L titanium autoclaves using 500 mL of granite groundwater (Table 3), initially saturated with air. The runs were 8, 21, and 28 days long, with the fuel samples having been preleached at ambient temperature for 100 days to remove the readily soluble cesium fraction. During the course of the run, the free oxygen content of the system was thought to have decreased by a factor of 2 to 3 (i.e., to 50 percent or 33 percent of the original value). Experiments were also conducted using deionized water saturated with air. The results gave similar uranium and plutonium concentrations for deionized water and granite groundwater, with an average concentration of 0.05 to 0.1 ppm for uranium, and 0.1 ppb for plutonium. The uranium concentrations were much lower than those observed at ambient temperature. Rinsing of the autoclaves with acid showed that only 5 to 15 percent of the uranium and 10 to 30 percent of the plutonium mobilized was in the solution phase.

Stroes-Gascoyne et al. (1986) report results of testing CANDU fuel from the Bruce reactor in WN-1 saline solution (Na = 1940 mg/L, Ca = 2190 mg/L, Cl = 6240 mg/L, SO_4 = 1100 mg/L, HCO_3 = 13 mg/L) at 150°C. The fuel had a relatively low linear power rating (35-39 kW/m) and low gas release (~0.1 percent). Two tests were run for 10 days each in a 1-L glass-lined titanium autoclave using 300 mL of air-saturated solution and with air as a cover gas. Results for uranium and technetium were reported as the average solution concentration (excluding the first day results) of several samples taken over the course of the tests. (The authors state that concentrations were relatively constant after the first day.) Experiment W01 gave 0.6 mg/L for uranium and W02 gave 2.1 mg/L. These values are considerably higher than those reported by Johnson et al. (1981 and 1982) for tests using the more dilute granite groundwater. The earlier work was done using unlined titanium autoclaves, which showed a greater tendency for uranium to adsorb onto the vessel. This might account for the difference in apparent solubility.

The NNWSI Project Series 3 dissolution tests were conducted at 85°C (Wilson and Shaw, 1987). Based on the results of Johnson et al. (1981 and 1982) and the preliminary Series 3 results, it is not expected that a substantial increase in matrix solubility over that found at 25°C will be observed in the 85°C tests.

Forsyth et al. (1985) have studied the effect of the intensity of the alpha radiation field on the dissolution rate of spent fuel. It is possible that the dissolution rate of UO_2 could be affected by changes in the redox state of the leachant due to alpha radiolytic decomposition of the water in contact with the fuel. Forsyth et al. conducted leaching experiments using very low-burnup (~0.5 MWd/kgU) fuel that had a fission product activity similar in size (though different in composition) to that of fuel with more typical burnup. Due to the low burnup, the inventory of alpha emitters was much less than for normal fuel. The dissolution behavior of this fuel was significantly different from that of higher burnup fuel, but the observations could not be attributed to the difference in the alpha field. Rather, they believe that differences in microstructure and composition between the types of fuel are the reasons for the observed difference in leaching behavior.

The most detailed studies concerning oxidative dissolution of non-irradiated UO_2 have been done as part of the Canadian program. They have used natural uranium in the form of sintered UO_2, which is the fuel material for the heavy water CANDU reactors. Enriched uranium fuel pellets of the type used in light water reactors generally have a lower density than the unenriched pellets (see Table 2 for comparison). This might affect the depth of penetration of surface oxidation and the surface area readily available for oxidative dissolution but should not significantly alter the mechanism.

Sunder et al. (1981 and 1987) and Shoesmith et al. (1983, 1984, and 1986) report the results of electrochemical studies using an electrode fashioned from fuel pellet material. They used potentiostatic and cyclic voltametric techniques to determine the mechanism for oxidation in solution of the surface of the uranium dioxide electrode. Sunder et al. (1981) used dilute Na_2SO_4 solutions in the pH range 6 to 11, and Shoesmith et al. (1983 and 1984) used aqueous carbonate solutions with a range of 0.0001 to 0.5 mole/L total carbonate. The mechanism of dissolution has been found to be different in the two systems because of the ability of the carbonate ion to complex hexavalent uranium. The more recent studies used 0.1 mole/L $NaClO_4$ to investigate the effects of dissolved oxygen, hydrogen peroxide, and alpha radiolysis on the oxidation and dissolution processes.

In the absence of carbonate, the surface of the fuel oxidizes to U_3O_7 by the addition of oxygen from the solution into interstitial sites in the UO_2 lattice. This addition occurs without major structural rearrangement of the lattice. Further oxidation from U_3O_7 to U_3O_8 involves a large unit cell volume increase and occurs by nucleation and growth. The electrochemical data suggest an oxide of stoichiometry U_2O_5 forms from the U_3O_7 as an intermediate step in the oxidation. This intermediate stage is thought to form via uranyl ions that are adsorbed on the surface of the sample. If sufficiently high potentials are applied to the electrode [E > 0.4 V versus Saturated Calomel Electrode (SCE)], the oxidation proceeds from U_3O_7 to hydrated uranyl trioxide, which precipitates on the surface as $UO_3 \cdot zH_2O$ (Sunder et al., 1981). These studies used a potential applied to the electrode to drive the reaction. In the natural case of repository storage, the potential would be set by reactions taking place in the system.

Shoesmith et al. (1986) investigated the aqueous oxidation of UO_2 using open circuit potential measurements, which are more relevant to the repository case. They found that corrosion of UO_2 in a solution of 0.1 mole/L $NaClO_4$ saturated with air produced a film of U_3O_7 on the UO_2 electrode. (The $NaClO_4$ is a noncomplexing electrolyte used to ensure that a current-carrying species is available in the solutions.) The film thickness was 6 nm and the film composition was determined using x-ray photoelectron spectroscopy (XPS). The film achieved the 6-nm thickness after approximately 10 hr of exposure to the solution. Further exposure showed a slow positive drift in the open circuit potential from +0.03 V to approximately +0.09 V, with no increase in film thickness. This was postulated to be due to a conversion of UO_{2+x} to U_3O_7 in the film.

Oxidation in solutions with 2.66×10^{-4} and 1.27×10^{-3} mole/L of H_2O_2 occurred 200 times faster than oxidation in air-saturated solutions (Shoesmith et al., 1986). The overall process for film formation appeared to be similar for the two cases. Once the film had formed, the predominant reaction on the electrode surface was decomposition of H_2O_2 without any changes in the uranium phases involved.

Further studies of the effects of H_2O_2 concentration on the nature of the film formed by oxidation of UO_2 in 0.1 mole/L $NaClO_4$ showed that for concentrations less than 0.01 mole/L H_2O_2 the extent of oxidation did not exceed U_3O_7 (Sunder et al., 1987). The electrode reaction was postulated by Sunder et al. (1987) to change from peroxide decomposition to oxidative dissolution of UO_2 when the peroxide concentration exceeded 0.01 mole/L. They further determined that pH had no detectable effect on the oxidation of UO_2 by hydrogen peroxide in the range 6 to 10.5.

Studies of the effects of an alpha radiation source on the oxidation of UO_2 show that the radiolysis products in solution due to a polonium-210 source of 0.7 Ci strength give an open circuit potential similar to air-saturated solutions or to 0.001 mole/L H_2O_2 (Sunder et al., 1987). Use of weaker alpha sources (5 and 100 microcuries) produced a corrosion potential similar to that found in nitrogen-purged solutions with a residual dissolved oxygen level of 1 ppb. This suggests that alpha radiolysis is unlikely to be an important process in the oxidizing environment expected at Yucca Mountain.

In the carbonate solutions, dissolution of UO_2 was found by Shoesmith et al. (1983 and 1984) to occur from a layer of U_3O_7 at potentials of 0.1 V or less and from a layer of U_2O_5 at applied potentials of 0.15 and 0.2 V, where the total dissolved carbonate content was less than 0.001 mole/L (60 ppm). The experiments were conducted at pH 9.5, so the dissolved carbonate species should be predominantly carbonate. As the carbonate concentration was increased, dissolution of the electrode was enhanced and the oxide film on the surface became thinner. For total carbonate concentrations greater than 0.01 mole/L (600 ppm carbonate), the oxidation of the layer did not progress beyond U_3O_7 because uranyl ions were complexed by carbonate and taken into solution, thereby being unavailable for incorporation into the oxide layer for the next step in film formation. Further support for these observations is provided by the tests conducted by Johnson et al. (1983b) discussed below.

The mechanism of dissolution has been shown to be a function of both the potential applied to the electrode and the carbonate content of the system (Shoesmith et al., 1983 and 1984). It is probable that for the NNWSI Project tuff repository conditions, the surface from which dissolution occurs would be composed of U_3O_7 because of the combination of mildly oxidizing conditions and moderate bicarbonate concentrations. In addition, at pH 7 to 8, most of the dissolved carbonate should be present as bicarbonate. Thus, one would expect a higher total dissolved carbonate to be necessary to shift the reaction mechanism than was needed at pH 9.5.

The dissolution mechanism proposed by Shoesmith et al. (1984) for a potential of +0.1 V is probably appropriate for Yucca Mountain conditions since the open circuit potential was shown to be +0.09 V in air-saturated solutions (Shoesmith et al., 1986).

The proposed mechanism is:

$$UO_2 + 1/3\,H_2O \xrightarrow{fast} U_3O_7 + 2/3\,H^+ + 2/3\,e^-$$

$$U_3O_7 + H^+ \xrightarrow{slow} (UO_2^{+2})_{ads} + 1/3\,OH^- + 4/3\,e^-$$

$$(UO_2^{+2})_{ads} + 3HCO_3^- \underset{}{\overset{fast}{\rightleftharpoons}} UO_2(CO_3)_3^{-4} + 3H^+$$

At +0.1 V, the dissolution rate of UO_2 was found to be almost independent of carbonate concentration, which suggested the second reaction as rate limiting.

Johnson et al. (1983b) investigated the effect of gamma radiation on the dissolution of unirradiated UO_2. They used 3-mm thick polished pellet segments of UO_2 placed in sealed vitreous silica tubes with 8 mL of synthetic groundwater (Na = 1910 mg/L, Ca = 2130 mg/L, Cl = 6460 mg/L, SO_4 = 1040 mg/L, and HCO_3 = 68 mg/L). One pair of samples was irradiated in a 4.1 Gy/hr gamma field for 485 days at 100°C while a control pair was held at 100°C in an oven for 455 days. Examination of the surface of the wafers after testing showed the unirradiated sample surfaces to be $UO_{2.38}$ and $UO_{2.40}$ while the irradiated surfaces were $UO_{2.46}$ and $UO_{2.49}$. Samples tested with 0.01 mole/L $NaHCO_3$ under the same conditions resulted in $UO_{2.31}$ and $UO_{2.30}$ on the unirradiated sample surfaces and $UO_{2.35}$ and $UO_{2.34}$ on the irradiated samples. Although there was little or no difference in the surface oxidation state, the irradiated $NaHCO_3$ sample showed clear evidence of more extensive dissolution. Further interpretation of these tests was complicated by the dissolution of the silica vessel during the test and precipitation of silica phases onto the samples.

Wang (1981) and Wang and Katayama (1982) reported the results of studies using single crystals of UO_2. They proposed a different mechanism for oxidation than did the Canadians; however, their studies are much less detailed than those discussed above, and their results are correspondingly less certain. Experiments were conducted at 75 and 150°C in systems that were pressurized to give 200 ppm oxygen dissolved in the solutions. This level of dissolved oxygen is very high and might affect the oxidation mechanism for the samples and the nature of the alteration products. The studies done by the Canadians are more relevant to the NNWSI Project tuff repository conditions than is the work referred to in this paragraph.

In summary, the results of the several studies on the oxidative dissolution of UO_2 indicate that the mechanism by which uranium is liberated to solution is a multistage process that depends on both the chemistry of the solution (particularly the thermodynamic activity of CO_2) and the Eh or oxygen fugacity of the system. The effects on the nature of the oxide film formed on the surface of raising the Eh are opposite to the effect of raising the activity of CO_2. At low activities of CO_2, the UO_2 surface oxidizes to U_3O_7, U_2O_5, and UO_3, with the higher oxides only forming at high Eh (high activity of

O_2). Uranium is removed to solution from this oxide surface. At a constant Eh, as the activity of CO_2 increases to the levels comparable to and higher than that present in groundwater at the NNWSI Project candidate repository, the oxidation of the surface does not progress beyond U_3O_7. At these activities of CO_2, uranium appears to be removed directly from the U_3O_7 surface, with no role played by higher uranium oxides in the surface layer.

Plans to develop the thermodynamic data base and additional information to support the fuel dissolution model needed for geochemical code development are discussed in Shaw (1987). The plans include studies to identify fuel-surface alteration products and secondary phases formed by precipitation from solution and experiments to ascertain the effect of the initial oxidation state of the fuel matrix on release rates. The radiation present in the spent fuel interferes with most available surface analysis techniques. Because of the analytical difficulties involved, current program planning is being based on the assumption that the work of others on the dissolution mechanism of unirradiated UO_2 will be relevant to spent fuel and that the work on actual spent fuel can be limited to confirmatory studies.

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