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Gas Generation from K East Basin Sludges – Series II Testing

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary and Conclusions

The path forward for the management of Hanford K Basin sludge calls for it to be packaged, shipped, and stored at T Plant until final processing at a future date. An important consideration for the design and cost of retrieval, transportation, and storage systems is the potential for heat and gas generation through oxidation reactions between uranium metal and water. This report, the second in a series [Series II], describes work performed at the Pacific Northwest National Laboratory to examine the gas generation behavior of K Basin sludge materials by using actual K East (KE) Basin floor, pit, and canister sludge. Mixed and unmixed and fractionated KE canister sludge was tested, along with floor and pit sludge from areas in the KE Basin not previously sampled. The first report in this series [Series I] (Delegard et al. 2000) focused on gas generation from KE floor and canister sludge collected using a consolidated sampling technique. The third report [Series III] will present results of gas generation testing of irradiated uranium fuel fragments with and without sludge addition. The work is being conducted under the direction of the Spent Nuclear Fuel Sludge Handling Project managed by Fluor Hanford, Inc., and in accordance with the data quality objectives (Makenas 2000) and the sampling and analysis plan (Baker et al. 2000).

The overall goal for this testing was to collect gas generation rate and composition data under known conditions to better understand the quantity and reactivity of the metallic uranium present in the K Basin sludge. Specific objectives for Series II included:

1. Evaluate the reactivity and determine the quantity of uranium metal present in each sludge type.
2. Provide gas generation data that can be used as design input into sludge transportation and storage systems.
3. Determine whether the reactivity of KE canister sludge is affected by aggressive agitation and sieving.
4. Obtain data on the expected uranium metal fraction and particle size in KE canister sludge to provide a basis for selecting values to be used in analyses.
5. Determine the reactivity of the single-pull (core) KE floor and pit sludge samples.
6. Evaluate the gas generation behavior of KE floor sludge consisting primarily of organic ion exchange material.
7. Evaluate the residual reactivity of archived KE canister sludge collected in 1996 that initially displayed a significant gas generation rate.
8. Compare the gas generation behavior of sludge collected by two different sampling techniques from the same general location.

Tests to meet these objectives were conducted from July through September 2000. The major conclusions are given below:

- Overall, the sludge samples evaluated in the Series II tests were relatively benign and unreactive, as demonstrated by their low gas generation rates. In comparison, the KE canister and floor sludge tested in Series I exhibited a higher uranium metal content than similar sludge tested in Series II. Because the sludge material used in Series II was stored for a longer period of time at slightly elevated temperatures, the Series I results more accurately reflect the uranium metal content of the sludge in the KE Basin.

- For certain sludge samples in Series II, use of fission product gas (Kr and Xe) release data resulted in a higher and more accurate estimation of the uranium metal content in comparison with the corrosion gas (H₂, O₂, N₂) data.
- Canister sludge that had been stored wet in a shielded facility for 14 months at ~32°C, after sample collection, contained about 0.56 wt% uranium metal (based on analysis of the release of fission product gases).
- Testing with canister sludge (stored for 14 months at 32°C) showed that very little metallic uranium is present in the material containing particles less than 500 μm.
- Aggressive agitation and sieving of canister sludge resulted in a 9X increase in the quantity of uranium metal that reacted over the test period (i.e., without agitation, 0.065 wt% of sample reacted; with agitation, 0.56 wt% of sample reacted.)
- The single-pull core floor and pit sludge samples displayed very low chemical reactivity, provided little gas generation, and are estimated to contain 0.0013 to 0.027 wt% metallic uranium (settled sludge basis).
- Sludge that consisted primarily of organic ion exchange resin beads generated very little gas even after 950 hours at temperatures of 90°C and 95°C. It is estimated that this material contains about 0.026 wt% uranium metal.
- Archived canister sludge from the 1996 sampling campaign no longer demonstrated significant reactivity. Based on analysis of the release of fission product gases, this sludge was estimated to contain about 0.9 wt% uranium metal (settled sludge basis).

Consistent with the data quality objectives (Makenas 2000) and the sampling and analysis plan (Baker et al. 2000), this series of tests provides base supporting information for the design and evaluation of the systems being developed to transport and store the K Basin sludge at T Plant. The tests and further interpretation of the results are summarized below.

Test Materials and Description

The sludge materials used in the Series II tests reported here were collected from the KE Basin using single-pull sampling techniques. Ten tests are described in this report. Two other tests were also included in this series (consolidated canister sludge and a fuel fragment), but these tests are ongoing and will be discussed in the Series III report.

Four gas generation tests were conducted using the KE canister sludge sample, KC-1, which contained 37 wt% (settled sludge basis) total uranium. This sample, collected in April 1999, came from a single canister containing highly damaged fuel. For the testing, an agitated (highly mixed) and an unagitated aliquot of KC-1 were used to investigate whether K Basin retrieval operations have the potential to “activate” uranium metal in the sludge. A portion of KC-1 was sieved to separate particles greater than, or “plus,” 500 μm (P500) from particles less than, or “minus,” 500 μm (M500). This separation was made to mimic the separation operations that are planned during the retrieval of certain K Basin sludge types and to gain a better understanding of how uranium metal is distributed in the sludge.

Four other tests were conducted using samples collected from the KE floor and pits between December 1998 and June 1999: main basin floor (FE-1), North Loadout Pit (FE-3), Weasel Pit (FE-5), and Tech View Pit and Dummy Elevator Pit (FE-4/6). These tests were conducted to show how gas generation behavior varies as a function of sludge source location, and to provide further confirmation of the low reactivity of the KE floor and pit sludge. With the exception of FE-1, these tests were conducted using

sludge from areas not sampled during the 1995 KE floor and Weasel Pit sampling campaign (Makenas et al. 1996).

Series II also included a test with a sample collected from the KE floor that was mainly composed of organic ion exchange resin beads (KC-6). This type of sludge is unique, and the test was conducted to gain an understanding of the stability of organic ion exchange resin under T Plant storage conditions. The last test was conducted to determine if the highly reactive sludge, 96-06, collected during the 1996 KE canister sampling campaign (Makenas et al. 1997), still exhibited reactivity and gas generation potential.

For the testing, 14- to 27-gram sludge samples were placed into 60-ml reaction vessels. The vessels were heated to maintain selected temperatures; the gas pressure was monitored continuously; and gas samples were collected twice from each vessel and analyzed via mass spectrometry. The testing was initiated on July 24, 2000, and continued for approximately 950 hours to September 4, 2000. The tests were conducted at elevated temperatures (ranging from 60°C to 90°C) to accelerate the reactions and provide conclusive gas generation data within a reasonable testing period. The temperature in all test vessels was increased to 95°C for a period at the end of the tests to force completion of the reactions. The table below shows the test matrix and the estimated uranium metal content for each sample as determined from the gas generation testing. The technique used to estimate uranium metal content (corrosion gas generation or fission product gas release) is also noted in the table.

Experimental Matrix for Series II Gas Generation Tests and Uranium Metal Estimates

Test Description	Sludge Sample Fraction		Test Temp., °C		Estimated Uranium Metal Content	
	Sample ID	Settled Sludge, g	Start ~300 hr	Final ~650 hr	Wt % U Metal (Settled Sludge Basis)	Estimation Technique
KE Canister Sludge (Consolidated Sampler Used in Single-Pull Mode)						
Unmixed KC-1	KC-1 (whole)	23.8	60	95	0.065	Fission Product Gas
Mixed KC-1	KC-1 (whole)	25.6	60	95	0.56	Fission Product Gas
U Metal in KC-1	Plus 500 µm	14.2	80	95	3.7	Fission Product Gas
U Metal in KC-1	Minus 500 µm	22.3	80	95	0.14	Fission Product Gas
Single-Pull Core KE Floor and Pit Sludge Samples						
Main Floor (FE-1)	FE-1 (whole)	27.0	90	95	0.022	Fission Product Gas
North Loadout Pit (FE-3)	FE-3 (whole)	21.2	90	95	0.0013	Corrosion Gas
Weasel Pit (FE-5)	FE-5 (whole)	20.7	90	95	0.027	Fission Product Gas
Dummy Elevator and Tech View Pit (FE-4 + FE-6)	FE-4 (63%) + FE-6 (37%)	16.1 (10.2/5.9)	90	95	0.0052	Corrosion Gas
Other Tests						
Organic Ion Exchange Resin Sludge	KC-6 (whole)	19.1	90	95	0.026	Corrosion Gas
1996 KE Canister Sludge	96-06	19.5	80	95	0.90	Fission Product Gas

Gas Generation Testing

Gas production observed in the Series II tests with KE Basin sludge was generally lower than observed in similar Series I studies of KE Basin canister and floor sludges (Delegard et al. 2000). The lower gas generation rates can partially be attributed to the longer storage periods at hot cell temperatures experienced by the Series II sludge samples. All tests in Series II (conducted with sludge from samples KC-1, FE-1, FE-3, FE-5, FE-4/6, KC-6, and 96-06) produced CO₂ as the predominant gas product with lower concentrations of H₂, except the KC-1 P500 test, which produced predominantly H₂ gas with lower CO₂ concentrations. Other gases released or produced were Xe, Kr, and hydrocarbons (methane, ethane, and higher hydrocarbons). Trace amounts of O₂ and N₂ present from atmospheric contamination also were consumed in each test. Similar gas generation and consumption was observed in the Series I tests and in gas collection tests from KE canister sludge (Makenas et al. 1997). The release of CO₂ in these tests may be due to the reaction of schoepite with calcite to form becquerelite and CO₂. However, in none of the 10 tests were pHs significantly lowered by reaction. Lowered pHs would be expected unless strong pH buffering was occurring in these sludges.

In the Series I tests, the release of H₂ produced by the reaction of uranium metal with water was shown to lag the release of Xe (and Kr) fission product gas in small-scale vessel tests with the plus 250- μ m consolidated canister sludge composite (KC-2/3 P250). This lag was attributed to the uptake of hydrogen by uranium metal to form the reactive intermediate UH₃. In the present report, data from these Series I experiments were interpreted further to determine the true induction times to onset of the hydride-mediated anoxic corrosion of uranium by water. In agreement with results from tests reported in the technical literature, essentially zero induction time to onset of corrosion was found by analysis of Xe release rates at 80°C, as opposed to about 27 hours as determined by H₂ gas release. Uranium corrosion rates caused by reaction with water were determined by Xe release corrected by the contributions due to reactions with O₂ and N₂. In agreement with previous findings, the rates follow the Arrhenius temperature dependence with a 15.8 kcal/mole activation energy.

Further interpretation of data from the KC-2/3 P250 and other Series I tests confirmed the agreement between the uranium concentration predicted based on the H₂, O₂, and N₂ gases involved in corrosion reactions and the Kr and Xe fission product gases evolved.^(a) The agreement was within a factor of 5 down to about 0.01 wt% uranium in the settled sludge, but deviated below that concentration. Similar comparisons for the results from the Series II tests showed significantly lower uranium concentrations as measured by H₂, O₂, and N₂ than by Kr and Xe. The likely uptake of H₂ by uranium metal to form hydrides and the possible reaction of H₂ with uranium(VI) compounds (such as schoepite) to form chemically reduced U₃O₈ or UO₂ cause the uranium metal concentrations determined by these measurements from corrosion gases to be underestimated. Therefore, estimates of uranium metal concentration based on amounts of fission product gas release are thought to be more reliable and provide a better upper bound when the two estimation techniques vary. It is recognized that uranium concentrations determined by fission product gas release have intrinsic uncertainty because burnup is not known for the uranium in the sludge.

The agitation/aeration tests with the canister sludge, KC-1 [(KC-1 Un (unmixed) and KC-1 Mix (aggressively agitated)], showed that uranium metal corrosion was enhanced by the agitation/aeration treatment. Though the mixed sludge evidently consumed amounts of O₂ and N₂ similar to those of the

^(a) Assuming ~2900 MWd/TeU irradiation.

unmixed sludge, about nine times more corrosion occurred in the mixed test (KC-1 Mix), as shown by fission product gas analyses. Thus, the mixing likely acted to increase corrosion by attrition and exposure of fresh uranium metal surface stripped of protective oxide films. The uranium metal concentration inferred from the KC-1 Mix test is about 0.56 wt%. In comparison, canister sludge sample KC-2/3 in Series I was estimated to contain ~ 1.9 wt% metallic uranium (settled sludge basis). Since the KC-1 sample was stored in a shielded facility at ~32°C for 9½ months longer than KC-2/3, a significant fraction of the uranium metal originally present in KC-1 likely reacted before the Series II testing began. During this storage period, gas bubbles were observed several times in the KC-1 sludge container. Using the rate equation for uranium metal with oxygen-free water given in the *Spent Nuclear Fuel Project Technical Databook, Volume 1* (Reilly 1998), an initial metal particle size of ~800 µm (Delegard et al. 2000), and temperature of 32°C, approximately 75% of the starting uranium metal would be expected to corrode in a 9½-month period. Therefore, the 0.56 wt% metal content of KC-1 is reasonably consistent with KC-2/3 metal content when considering the impact of the storage period and the expected variation of a sample taken from a single canister barrel versus one created from a combination of sludge from 10 barrels (KC-2/3).

The KC-1 P500 sludge was about 3.7 wt% uranium metal, and the KC-1 M500 sludge was about 0.14 wt% uranium metal, based on Kr and Xe release. The higher metal concentration in larger size fraction sludge particles was observed in Series I tests with consolidated canister and floor sludges that were split at 250 µm. Considering the results from both Series I and Series II with fractionated canister sludge, it appears that very little uranium metal exists in canister sludge composed of particles less than 500 µm.

The uranium concentration in the total (combined) KC-1 sludge fractions is 0.57%, in good agreement with the 0.56 wt% concentration found in the KC-1 Mix test. The abrasion experienced by the KC-1 M500 and P500 sludge material during sieving likely provided good exposure of fresh uranium metal, providing results similar to the KC-1 Mix sample. In Series I testing, KC-2/3 P250 was estimated to contain ~7.4 wt% uranium metal. The differences in metal content between KC-2/3 P250 and KC-1 P500 can partially be attributed to corrosion that likely occurred during the storage of the KC-1 sample.

Uranium metal concentrations for the single-pull floor and pit sludges FE-1, FE-3, FE-5, and FE-4/6 are low (0.0013 to 0.027 wt%) and not strongly dependent on the method used (determination based on H₂, O₂, and N₂ reaction gases or fission product gas release). Hydrocarbon gas release from sources other than decomposition of uranium carbide evidently are occurring for these materials, based on the low relative methane concentration in the hydrocarbon fraction and high hydrocarbon amounts in the product gas. The uranium metal content estimated in these samples is consistent with the results from Series I testing with KE floor sludges. From Series I testing, KE Basin floor sludge was estimated to contain less than 0.15 wt% uranium metal.

Uranium metal concentrations in the organic ion exchange resin sludge, KC-6, could not be determined by fission product gas release because of concentrations below the mass spectrometric detection limit. The uranium metal concentration determined from H₂, O₂, and N₂ reaction gases for the KC-6 sludge is 0.026 wt%. The hydrocarbon concentration (primarily due to methane and known carbide concentrations in the uranium metal fuel) was found to be consistent with the uranium metal corrosion estimated from corrosion gases in the KC-6 test. At 95°C, the maximum gas production from KC-6 was 5×10^{-4} mole/kg-day (~11 ml/kg-day).

From the Kr and Xe release, the uranium metal content of the archived canister sludge sample, 96-06, was determined to be ~0.9 wt%. However, the quantity of hydrocarbon gas (generated by decomposition of the uranium carbide) measured during the test was about eight times lower than expected, based on the released fission gas measurements (i.e., hydrocarbon gas data alone would indicate that sample contained ~0.1% uranium metal). During the 4 years at which this sample was stored at ~29°C, an appreciable fraction of uranium metal initially present likely reacted.

References

- Baker, R. B., T. L. Welsh, and B. J. Makenas. 2000. *Sampling and Analysis Plan for Sludge from the 105-K Basins to Support Transport to and Storage in T Plant*. HNF-6479, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Delegard, C. H., S. A. Bryan, A. J. Schmidt, P. R. Bredt, C. M. King, R. L. Sell, L. L. Burger, and K. L. Silvers. 2000. *Gas Generation from K East Basin Sludges – Series I Testing*. PNNL-13320, Pacific Northwest National Laboratory, Richland, Washington.
- Makenas, B. J., T. L. Welsh, R. B. Baker, D. R. Hansen, and G. R. Golcar. 1996. *Analysis of Sludge from Hanford K East Basin Floor and Weasel Pit*. WHC-SP-1182, Westinghouse Hanford Company, Richland, Washington.
- Makenas, B. J., T. L. Welsh, R. B. Baker, E. W. Hoppe, A. J. Schmidt, J. Abrefah, J. M. Tingey, P. R. Bredt, and G. R. Golcar. 1997. *Analysis of Sludge from Hanford K East Basin Canisters*. HNF-SP-1201, DE&S Hanford, Inc., Richland, Washington.
- Makenas, B. J. 2000. *Data Quality Objectives for Analysis of Hanford K Basin Sludge to Support Transport to and Storage in T Plant*. HNF-5345, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Reilly, M. A. 1998. *Spent Nuclear Fuel Project Technical Databook, Volume 1*. HNF-SD-SNF-TI-015, Rev. 6, DE&S Hanford, Inc., Richland, Washington.

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1.0 Introduction

Two water-filled concrete pools [K East (KE) and K West (KW) Basins] in the 100K Area of the Hanford Site contain over 2100 metric tons of N Reactor fuel elements stored in aluminum or stainless steel canisters. During the time the fuel has been stored, approximately 52 m³ of heterogeneous solid material (sludge) have accumulated in the canisters, as well as on the floor and in the associated pits. This sludge consists of various proportions of fuel, structural corrosion products, windblown material, and miscellaneous constituents such as ion exchange material (IXM) (both organic and inorganic) and paint chips (Makenas et al. 1996-99). Pearce and Klimper (2000) describe the inventory and compositions of all K Basin sludge materials in detail. The baseline sludge management plan calls for the sludge to be packaged, shipped, and stored at T Plant in the Hanford 200 Area until final processing at a future date.

Because the sludge produces gas from chemical and, to a more limited extent, radiolytic reactions, gas generation must be considered when developing and evaluating designs for sludge retrieval, transportation, and storage systems. The work discussed in this report is being conducted by Pacific Northwest National Laboratory (PNNL) on actual sludge samples to better understand the reactivity and assess the reaction rates. The work is being performed for the Spent Nuclear Fuel Sludge Handling Project managed by Fluor Hanford, Inc., and is being performed in accordance with the data quality objectives (Makenas 2000) and the sampling and analysis plan (Baker et al. 2000).

This report (Series II) is the second in a series of three, and examines the gas generation behavior of KE canister sludge (mixed and unmixed and fractionated based on particle size) and KE floor and pit sludge from locations not sampled during the 1995 campaign (Makenas et al. 1996). Series I testing (Delegard et al. 2000) focused on gas generation from KE floor and canister sludge collected using a consolidated sampling technique. Series III testing is focused on gas generation from irradiated uranium fuel fragments with and without sludge addition.

The results of Series II testing and analyses conducted from July 2000 through September 2000 are provided here. The overall goal for this testing was to collect gas generation rate and composition data under known conditions to better understand the quantity and reactivity of the metallic uranium present in the K Basin sludge. Specific objectives for Series II testing included:

1. Evaluate the reactivity and determine the quantity of uranium metal present in each sludge type.
2. Provide gas generation data that can be used as design input into sludge transportation and storage systems.
3. Determine whether the reactivity of KE canister sludge is affected by aggressive agitation and sieving.
4. Obtain data on the expected uranium metal fraction and particle size in KE canister sludge to provide a basis for selecting values to be used in analyses.
5. Determine the reactivity of the single-pull (core) KE floor and pit sludge samples.
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7. Evaluate the residual reactivity of archived KE canister sludge collected in 1996 that initially displayed a significant gas generation rate.
8. Compare the gas generation behavior of sludge collected by two different sampling techniques from the same general location.

Ten gas generation tests were conducted with K Basin sludge: four with KE canister sludge sample KC-1; four with KE floor and pit samples FE-1, FE-3, FE-5, and FE-4/6; one with KE floor sample KC-6, which primarily consists of organic ion exchange resin beads; and one with KE canister sample, 96-06, a highly reactive sludge collected in 1996 (see Makenas et al. 1997 for sample composition/details).

Section 2.0 describes the experimental methods and materials for the gas measurements, and Section 3.0 presents the data derived from the testing. During the tests, hydrogen; fission gas products, krypton and xenon; methane and higher hydrocarbons; and carbon dioxide were observed. At the same time, oxygen and nitrogen in the test vessels were consumed (depleted). Section 4.0 details the chemistry of the gas generating (and consuming) reactions and interprets and discusses the test results. Appendix A summarizes the gas composition and generation rates from the gas sampling. Two other tests were also included in this series (a large-scale canister sludge test and a fuel fragment test), but these tests are ongoing and will be discussed in the Series III testing report. Appendix B provides an estimate of the uranium metal content of sample KC-1 on October 7, 1999 (i.e., start date of Gas Generation Series I testing).

A technical data package containing the laboratory bench sheets and raw data (i.e., test instructions, laboratory record book pages, calibrations, temperature and pressure data, gas analysis data, etc.) is available from Fluor Hanford, Inc. (R. B. Baker).

2.0 Test Matrix, Materials, and Approach

This section describes the overall test approach and methods used for the Gas Generation Series II tests. A general description of the testing and the test matrix is provided in Section 2.1. This section also gives the rationale for each test. Section 2.2 provides details on KE sludge samples used in the testing. A summary of the sample collection and handling is given, as well as information on the chemical and radiochemical composition of the samples. The equipment and measurement techniques used for the testing are described in Section 2.3. The test system was the same system (with some upgrades) used in Series I, and details of its verification, reliability, and performance are provided in Appendix A of the Series I report (Delegard et al. 2000).

2.1 Test Matrix

For the gas generation testing, 14- to 27-gram settled sludge samples were placed into 60-ml reaction vessels. The reaction vessels were sealed, connected to the manifold system, and purged with neon gas to remove air. Next, the vessels were heated to the target conditions, and temperatures and gas pressures were monitored continuously. Gas samples were collected twice from each vessel during the testing period and analyzed via mass spectrometry. The testing was initiated on July 24, 2000, and continued for approximately 950 hours to September 4, 2000. The tests were conducted at elevated temperatures (ranging from 60°C to 90°C) to accelerate the reactions and provide conclusive gas generation data within a reasonable testing period. After about 300 hours, the temperatures in all test vessels were increased to 95°C for additional time (~650 hours) to force completion of the reactions.

Table 2.1 contains the general matrix for the gas generation testing and includes the gas sampling schedule. These tests were conducted at PNNL's High-Level Radiochemistry Facility in the 325 Building (325A HLRF), 300 Area, in accordance with the sampling and analysis plan (Baker et al. 2000).

The first four gas generation tests shown in Table 2.1 were conducted using the KE canister sludge sample, KC-1. This sample was collected in April 1999 from a single storage canister barrel containing highly damaged fuel. A single-pull technique was used for sample collection (Pitner 1999). This sample contained 37 wt% (settled sludge basis) total uranium.

For the first two tests in Series II, an agitated (highly mixed) aliquot and an unmixed aliquot of KC-1 were used to investigate whether abrasive actions expected during K Basin retrieval operations have the potential to "activate" uranium metal in the sludge. The tests were also expected to provide insight into whether sieving operations, performed on some sludge samples, could affect the sludge reactivity. These two tests were started at 60°C (compared to initial temperatures of 80°C and 90°C for all other tests). This lower temperature reduced the overall reaction rate, magnifying the potential effect of agitation on induction time. [Note: In contrast with the test temperatures, the temperature for K Basin pool operations ranges from about 10°C to 25°C.]

For the second two tests, a portion of KC-1 was sieved to separate particles greater than, or "plus," 500 µm (P500) from particles less than, or "minus," 500 µm (M500). This separation was made to mimic the separation operations that are planned for the retrieval of certain K Basin sludge types and to gain a better understanding of how uranium metal is distributed in the sludge as a function of particle size.

Table 2.1. K Basin Test Material Masses and Gas Sampling Schedule

Test Identification		Settled Sludge Mass, g	Test Temp., °C	Start Date	Sample Date	Time at Temperature, hr	
						Run Interval ^(b)	Total ^(b)
KE Canister Sludge (collected April 1999)							
1	KC-1 Unmixed	23.75	60	7/24/00	8/7/00 ^(a)	293	293
			95	8/7/00	8/14/00	1. 167 at 95°C	1. 459
			95	8/15/00	9/4/00	2. 477	2. 936
2	KC-1 Mixed (highly agitated)	25.61	60	7/24/00	8/7/00 ^(a)	330	330
			95	8/7/00	8/14/00	1. 167 at 95°C	1. 496
			95	8/15/00	9/4/00	2. 477	2. 973
3	KC-1 P500 (particles greater than 500 µm)	14.15	80	7/24/00	8/7/00 ^(a)	326	326
			95	8/7/00	8/14/00	1. 166 at 95°C	1. 492
			95	8/15/00	9/4/00	2. 477	2. 969
4	KC-1 M500 (particles less than 500 µm)	22.30	80	7/24/00	8/7/00 ^(a)	321	321
			95	8/7/00	8/14/00	1. 166 at 95°C	1. 488
			95	8/15/00	9/4/00	2. 477	2. 965
KE Single-Pull Floor and Pit Sludge (Collected December 1998 – June 1999)							
5	FE-1 Main Floor	27.00	90	7/24/00	8/7/00 ^(a)	329	329
			95	8/7/00	8/14/00	1. 166 at 95°C	1. 495
			95	8/15/00	9/4/00	2. 477	2. 972
6	FE-3 North Loadout Pit	21.22	90	7/24/00	8/7/00 ^(a)	327	327
			95	8/7/00	8/14/00	1. 166 at 95°C	1. 493
			95	8/15/00	9/4/00	2. 477	2. 970
7	FE-5 Weasel Pit	19.93	90	7/24/00	8/7/00 ^(a)	327	327
			95	8/7/00	8/14/00	1. 166 at 95°C	1. 493
			95	8/15/00	9/4/00	2. 476	2. 970
8	FE-4/6 Dummy Elevator and Tech View Pit	15.87	90	7/24/00	8/7/00 ^(a)	326	326
			95	8/7/00	8/14/00	1. 160 at 95°C	1. 486
			95	8/15/00	9/4/00	2. 477	2. 963
Other Tests							
9	KC-6 Organic Ion Exchange Resin (Collected April 1999)	19.10	90	7/24/00	8/7/00 ^(a)	327	327
			95	8/7/00	8/14/00	1. 165 at 95°C	1. 492
			95	8/15/00	9/4/00	2. 477	2. 968
10	96-06 KE Canister Sludge (Collected March 1996)	19.51	80	7/24/00	8/7/00 ^(a)	324	324
			95	8/7/00	8/14/00	1. 147 at 95°C	1. 471
			95	8/15/00	9/4/00	2. 477	2. 947

(a) Dates of temperature transitions without sampling.

(b) Numbers (1 and 2) indicate when first and second gas sample was collected.

Tests 5 through 8 shown in Table 2.1 used samples collected from the KE floor and pits between December 1998 and June 1999: main basin floor (FE-1), North Loadout Pit (FE-3), Weasel Pit (FE-5), and Tech View Pit and Dummy Elevator Pit (FE-4/6). These tests were conducted to show how gas generation behavior varies as a function of sludge source location, and to provide further confirmation of the low reactivity of the KE floor and pit sludge. The North Loadout Pit, the Tech View Pit, and the Dummy Elevator Pit had not been sampled during previous sampling and characterization campaigns. Also, sludge from the South Loadout Pit had been added to the Weasel Pit after it was sampled and characterized in 1995 (Makenas et al. 1996). Therefore, these tests provided the first opportunity to characterize the gas generation behavior of sludge from these pits.

Test 9 was conducted with a sample (KC-6) collected from the KE floor. This sample primarily consisted of organic ion exchange resin beads. This type of sludge is unique, and the test was conducted to gain an understanding of its long-term stability under T Plant storage conditions.

Test 10 was conducted to determine if the highly reactive sludge, 96-06, collected during the 1996 KE canister sampling campaign, still exhibited reactivity and gas generation potential. In the 1996 KE canister sludge characterization campaign, sample 96-06 exhibited a high gas generation rate (up to 150 ml/kg settled sludge-day) at ambient hot cell temperatures (~32°C) (Makenas et al. 1997; Delegard et al. 2000).

2.2 K Basin Sludge Test Materials

The sample collection methods and sample histories for the materials used in the gas generation testing are described below.

2.2.1 Consolidated Sludge Samples: KC-1 and KC-6

Consolidated samples (Baker et al. 2000), including KC-1 and KC-6 (along with four others), were collected from the KE Basin in March and April 1999 by a technique whereby a vacuum is applied and sludge is drawn into 10.3-L sample containers (stainless steel vessels). Sludge was trapped in the container while the excess water returned to the basin through a 5- μ m stainless steel filter. Compared with the single-pull techniques, this consolidated sampling technique collected much larger volumes of sludge from several different sampling locations in the same sample container. However, for sample KC-1, the sampling system was operated in a single-pull mode (i.e., a filter was not used, and the sampling was terminated after the 10.3-L sample container was filled); hence, no material or water was allowed to escape. This technique was used to confirm that the loss of fine sludge material through the filter used for the other samples was insignificant.

Facility records show that the KE Basin water pH ranged from 5.3 to 5.7 and averaged 5.44 during the sampling period. The temperature ranged from 13°C to 17°C. Pitner (1999) provides a detailed description of the sampling equipment and the consolidated sludge sampling campaign.

Sample KC-1 was collected from the east barrel of the canister in Cubicle 4569 in the KE Basin, which contained highly degraded fuel. Sample KC-6 was collected from Cubicle 6758, which contained no fuel canisters. Earlier surveys identified this cubicle as containing a high concentration of organic ion exchange resin beads. Visual observations of this sample confirmed that the sample was almost

exclusively composed of organic ion exchange resin beads. In a previous investigation, the resin beads were identified as Purolite NRW 37 ion exchange resin (Schmidt et al. 1998).

In May 1999, the consolidated samples were transferred from the Postirradiation Testing Laboratory (327 Building) to the 325A HLRF. The sample containers were inspected upon receipt for indications of excessive gas generation during shipment. No explicit evidence was found to indicate gas generation occurred in the sludge during the transport. Table 2.2 summarizes the sampling information and history for KC-1 and KC-6.

The samples that made up the consolidated canister sludge composite (KC-2/3) used in some Series I tests were collected from the KE Basin and transferred to the 325A HLRF at the same time as KC-1 and KC-6. However, KC-2/3 was stored in the hot cell (~32°C) for only 5 months before the start of Series I testing. In comparison, KC-1 and KC-6 were stored for about 14 months at ~32°C before the start of Series II in July 2000. Because the hot cell was 15°C to 20°C warmer than the KE Basin pool, the uranium metal corrosion rate in the samples is calculated to be 2.5 to 3.8 times higher than that experienced by equivalent sludge remaining in the pool.

Table 2.2. Sampling Information for Consolidated Samples in Series II Gas Generation Testing

Container	Material Type	Date Collected from KE Basin	Date Received at 325A HLRF (Storage at ~32°C)
KC-1	Canister Sludge from Highly Damaged Fuel	April 1999	May 7, 1999
KC-6	Floor Sludge Containing High Concentrations of IXM ^(a) Beads	March 1999	May 7, 1999

(a) Ion exchange material.

A subsample of KC-1 was wet-sieved through a Tyler-32 mesh screen (500- μ m openings) to separate the P500 and M500 fractions. A portion of sludge was placed on top of the Tyler-32 sieve. The loaded sieve was then raised and lowered repeatedly into a pan filled with supernatant KE Basin water taken from the respective sample container. As the sieve was raised, particles smaller than 500 μ m drained into the pan. The solids on the Tyler-32 sieve were immediately transferred to a large vessel filled with clean supernatant to keep the sludge wet at all times. On a wet sludge basis, 11.7 wt% of KC-1 material was greater than 500 μ m. In an earlier characterization campaign that used multiple sieves and a more conventional sieving protocol, it was estimated that only 5.5% of KC-1 (wet sample basis) was greater than 500 μ m (Bredt et al. 1999). The different sieving techniques likely affected the water content of the material retained on the sieve(s).

2.2.2 Single-Pull Core KE Floor and Pit Composite Samples: FE-1, FE-3, FE-5, and FE-4/6

In the single-pull core sampling campaign, KE Basin floor and pit sludge samples were collected between December 1998 and June 1999. For this sample collection, single-pull sampling equipment was used in which isolated cores of sludge were suctioned into 4-L bottles. The samples were immediately shipped to the Hanford 222-S Laboratory in the 200 West Area for characterization (Baker et al. 2000) and interim storage. Following receipt at 222-S, six composites were prepared (FE-1, FE-3, FE-4, FE-5, FE-6, and

FE-7) by combining the solids in the sample bottles. During storage at 222-S (11 to 17 months, depending on the sample), the temperature of the sludge samples was approximately 27°C. Details on the single-pull core sampling campaign can be found in Pitner (1999).

In May 2000, portions of five of the composites (FE-1, FE-3, FE-4, FE-5, and FE-6) were transferred to 325A HLRF. Table 2.3 lists the five composites shipped to 325A HLRF and identifies the original sample bottles used for each composite. With the exception of sample FE-4 (Dummy Elevator Pit sludge), all samples received at 325A HLRF contained wet solids with standing liquid. Sample FE-4 was received as moist solids, but with no standing water. Supernatant from other KE floor sludge samples was added to FE-4 to generate a wet slurry with standing liquid. In 325A HLRF, the samples were at a temperature of approximately 32°C for 2 months before the Series II tests were initiated.

Because of higher priority analyses performed at the 222-S Laboratory, the amount of sludge material available from FE-4 and FE-6 was insufficient for the required characterization analyses and the gas generation tests. Consequently, 10.2 g of FE-4 and 5.9 g of FE-6 were combined to form a composite, designated as FE-4/6.

Table 2.3. KE Basin Floor Single-Pull Core Composite Samples
[Shipped to 325A HLRF (May 2000) for Testing]

Composite	Original Sample Bottles	KE Area Represented	Date Collected from KE Basin ^(a)
FE-1 Main Floor	KE-1-A, KE-1-B KE-1-D, KE-1-E	East Bay, Cubicle 0168 South Side, Empty Cubicle	Jan. 1999
	KE-2-A, KE-2-B	East Bay, Cubicle 1065, N. Side	Dec. 1998
FE-3 North Loadout Pit	KE-5-A, KE-5-B, KE-5-D, KE-5-E	North Loadout Pit (NLOP) Center	Jun. 1999
	KE-6-A, KE-6-B	NLOP, Mid Transfer Channel	Jun. 1999
FE-4 Dummy Elevator Pit	KE-7-A, KE-7-B	Dummy Elevator Pit, East	Jan. 1999
	KE-8-A, KE-8-B, KE-8-D	Dummy Elevator Pit, West	Jan. 1999
FE-5 Weasel Pit	KE-9-A, KE-9-B, KE-9-D, KE-9-E	Weasel Pit, Near South Wall, 8 feet from East End	Apr. 1999
	KE-10-A, KE-10-B, KE-10-D, KE-10-E	Weasel Pit, Near Center, 11 feet from West End	Jan. 1999
FE-6 Tech View Pit	KE-11-A, KE-11-B	Just East of Channel to View Pit	Jan. 1999

(a) Within several days of sample collection, the samples were shipped to the 222-S Laboratory, where they were stored at ~27°C. Once sent to the 325A HLRF, the samples were stored at ~32°C.

2.2.3 KE Canister Sludge from 1996 Sampling Campaign: 96-06

KE canister sludge sample 96-06 was collected in April 1996, from the west barrel of the fuel canister in Cubicle 5465, using a sampling technique very similar to that described above for the single-pull samples (Makenas et al. 1997). The fuel in this barrel was highly degraded. In July and August 1996, this sample displayed significant gas generation at the ambient hot cell temperature (~32°C in the 325A HRLF). Further details on the sample collection, characterization, and gas generation behavior are provided in Makenas et al. (1997). Delegard et al. (2000) [Gas Generation Testing Series I report] also includes an analysis of the gas generation behavior of sample 96-06.

When sample characterization was completed in 1996, 96-06 was stored at an average temperature of about 29°C for 4 years until it was retrieved for the gas generation testing. While the sample had been covered with a layer of water when it was put into storage, it was found to be dry when retrieved in July 2000. K Basin canister supernatant water was added to reconstitute the sample to a wet sludge. The reconstituted sludge was aggressively mixed, and a subsample was collected for the gas generation test.

2.2.4 Chemical and Radiochemical Composition of Sludge Samples

The chemical compositions of the samples on a dry and an as-settled sludge basis are shown in Table 2.4. Radiochemical compositions of the sludges are also listed in this table. Details on the analyses performed on KC-1 are given in Elmore et al. (2000). The individual fractions of KC-1 (i.e., KC-1 P500 and KC-1 M500) were not characterized. Steen (2000) describes the analyses performed on the single-pull sludge samples, including FE-1, FE-3, FE-4, FE-5, and FE-6. The chemical and radiochemical characterization information in Table 2.4 for sample 96-06 was taken from Makenas et al. (1997). No analyses were performed on KC-6; however, a similar sample, KES-H-08, containing a high concentration of organic ion exchange resin beads, had already been characterized (Makenas et al. 1996), and those data are included in Table 2.4.

The crystalline phases present in the FE-3, FE-4, FE-5, and FE-6 sludges were determined by X-ray diffractometry (XRD) according to procedure PNNL-RPG-268. Results of the XRD analyses are given in Table 2.5. Quartz, SiO₂, was found in FE-3, FE-4, and FE-5, but was the only Hanford soil mineral identified in any of the single-pull FE samples. Two FeO(OH) phases (lepidocrocite and goethite) were found in both FE-5 and FE-6; lepidocrocite also was found in FE-4. The iron phases likely arise from corrosion of structural steel in the KE Basin. No aluminum corrosion products [e.g., Al(OH)₃ as gibbsite, bayerite, or nordstrandite] were identified in any sample. The only uranium phase found was studtite (UO₄·4H₂O, a uranyl peroxide hydrate phase) observed in FE-6. Zirconium oxide, ZrO₂, may be present in FE-3, but its identification is tentative. Though found in other KE Basin sludges (Makenas et al. 1996), no calcite (CaCO₃) was found in any of the four test samples. Mordenite [(Ca,Na₂,K₂)Al₂Si₁₀O₂₄·7H₂O], an ion exchange mineral used to remove radiocesium from the KE Basin waters, also was not found in any sample by XRD. In sample FE-3, the phase associated with the most intense lines in the XRD pattern was not identified.

The only phases identified by XRD for sludge sample 96-06 are the various uraninites UO₂, U₄O₉, and U₃O₇ (Makenas et al. 1997).

Table 2.4. Chemical Compositions of Sludge Materials

Concentration, dry basis							
Analyte, wt%	KC-1	FE-1	FE-3	FE-5	FE-4/6	KES-H-08^(a)	96-06^(b)
Al	2.04	1.36	0.987	2.65	2.79	1.87	1.45
Ca	0.12	0.138	0.820	1.20	0.17	1.22	<0.02
Fe	0.338	46.8	3.37	30.6	18.3	1.51	0.180
Mg	0.020	0.038	0.076	0.146	0.23	0.225	<0.02
Na	0.237	<0.03	0.025	<0.03	0.01	3.26	0.0441
Si	0.160	0.166	0.154	0.329	0.23	NA	NA
U	69.0	1.15	1.51	6.37	2.51	0.249	74.9
U, phos.	68.6	1.32	1.72	5.32	1.74	0.287	61.1
TIC	NA	NA	0.26	0.18	0.10	0.22	0.0581
TOC	NA	NA	0.43	0.22	0.26	0.88 ^(c)	0.0654
Analyte, $\mu\text{Ci/g}$							
⁶⁰ Co	0.209	0.501	0.339	0.875	0.97	0.185	<0.857
¹³⁷ Cs	392	17.4	18.8	170	38.83	144	320
¹⁵⁴ Eu	8.62	0.245	0.425	0.985	0.26	<0.04	10.7
²⁴¹ Am	122	2.63	4.92	10.2	3.11	0.397	99.5
²³⁸ Pu	21.4	0.562	0.918	2.06	0.61	0.062	18.3
^{239,240} Pu	142	2.88	5.96	13.1	3.89	0.40	104
Concentration, settled sludge basis							
Analyte, wt%	KC-1	FE-1	FE-3	FE-5	FE-4/6	KES-H-08^(a)	96-06^(b)
Al	1.11	0.95	0.472	1.74	2.160	0.854	0.958
Ca	0.065	0.0964	0.392	0.79	0.130	0.558	<0.017
Fe	0.184	32.6	1.61	20.1	14.2	0.692	0.119
Mg	0.011	0.026	0.036	0.096	0.179	0.103	<0.017
Na	0.129	<0.02	0.0121	<0.017	0.010	1.49	0.029
Si	0.087	0.116	0.0734	0.216	0.179	NA	NA
U	37.5	0.801	0.724	4.18	1.95	0.114	49.4
U, phos.	37.2	0.922	0.820	3.49	1.35	0.144	40.3
TIC	NA	NA	0.124	0.115	0.078	0.102	0.0383
TOC	NA	NA	0.204	0.147	0.205	0.403	0.0431
Solids	54.3	69.7	47.8	65.6	77.5	NA	64.8
Analyte, $\mu\text{Ci/g}$							
⁶⁰ Co	0.113	0.349	0.162	0.574	0.748	0.699	<0.57
¹³⁷ Cs	213	12.2	8.96	112	30.1	54.5	211
¹⁵⁴ Eu	4.68	0.171	0.203	0.646	0.201	<0.016	7.05
²⁴¹ Am	66.2	1.83	2.35	6.72	2.41	0.15	53.2
²³⁸ Pu	11.6	0.392	0.439	1.35	0.476	0.0234	12.1
^{239,240} Pu	77.1	2.01	2.85	8.58	3.01	0.152	68.2

(a) Sample KC-6 was not characterized. The data reported are from Sample KES-H-08, a similar sample containing high concentration of organic resin beads. KES-H-08 was collected and analyzed in 1995 (Makenas et al. 1996)

(b) from Makenas et al. (1997) for sample 96-06 M.

(c) Method used for TOC analysis did not measure organic content of polystyrene-based organic ion exchange resin.

TOC, total organic carbon; TIC, total inorganic carbon.

Table 2.5. Crystalline Phases Identified by X-ray Diffractometry in Selected KE Basin Sludges

Crystalline Phase Name and Formula	PDF # ^(a)	Prominence in Sludge ^(b)			
		FE-3	FE-4	FE-5	FE-6
Quartz, SiO ₂	46-1045	H	H	H	N
Lepidocrocite, FeO(OH)	8-098	N	L	M	M
Goethite, FeO(OH)	29-713	N	N	M	M
Studtite, UO ₄ ·4H ₂ O	16-206	N	N	N	M
Zirconium oxide, ZrO ₂	49-1642	Maybe	N	N	N

(a) PDF # = powder diffraction file number.

(b) H – high; M – medium; L – low; N – not observed.

The pH of the settled sludge was measured both before and after the gas generation experiments, using a wand-type pH meter (Piccolo). For each set of measurements, the meter accuracy was verified, and the pH values corrected based on measurements of calibrated buffer solutions. Measurement accuracy is estimated to be ±0.2 pH units. The measured values shown in Table 2.6 indicate that little change in pH occurred during these tests.

Table 2.6. Sludge pH Values Measured Before and After Testing

Sludge Tested	Pre-Test pH	Post-Test pH
KC-1 Un	5.1	5.1
KC-1 Mix	5.1	5.3
KC-1 M500	5.1	5.4
KC-1 P500	5.1	5.3
FE-1	6.8	6.8
FE-3	8.3	7.7
FE-5	7.9	7.8
FE-4/6	Not measured	6.8
KC-6	7.4	7.8
96-06	5.0	5.1

2.3 Test Equipment and Methods

The reaction vessels (Section 2.3.1) and the gas manifold system (Figure 2.1) used for the gas generation tests are similar to those described in previous work with K Basin sludge (Delegard et al. 2000), in earlier studies with simulated Hanford tank waste (Bryan and Pederson 1995), and in work with actual Hanford tank waste (Bryan et al. 1996; King et al. 1997). Each vessel has a separate pressure transducer on the gas manifold line. The entire surface of the reaction system exposed to the sludge sample is stainless steel, except for a gold-plated copper gasket sealing the flange at the top of the reaction vessel. For the tests, temperatures and pressures were recorded every 10 seconds on a Campbell Scientific CR10 datalogger; the data were averaged every 20 minutes and saved in a computer file. Temperature and pressure data were also manually logged once each working day.

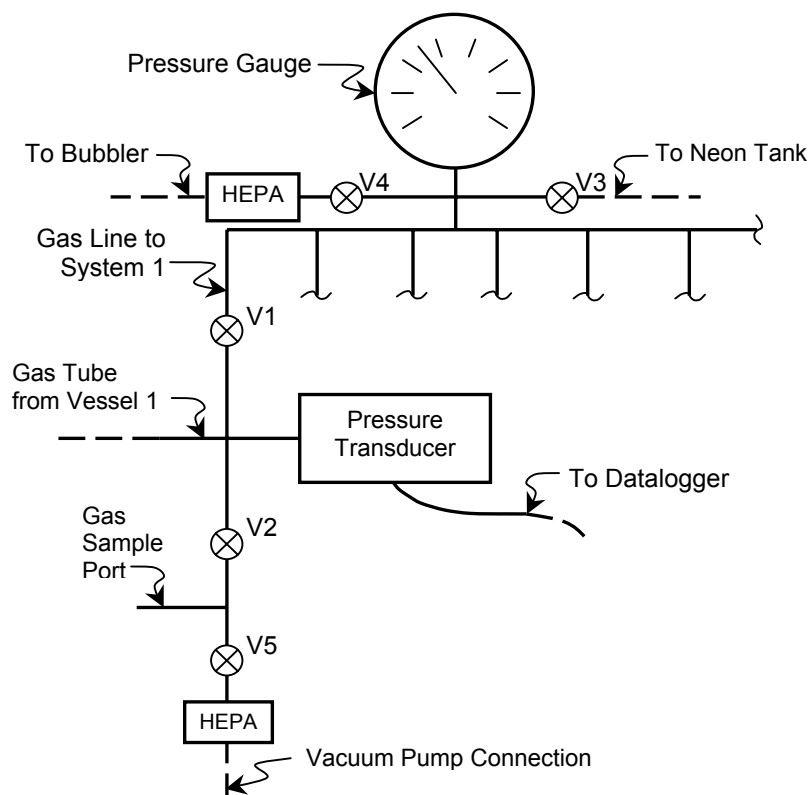


Figure 2.1. Layout of Gas Pressure Measurement and Gas Sampling Manifold Used in Gas Generation Tests (includes details for one of 12 systems)

2.3.1 Reaction Vessel

Figure 2.2 illustrates the 60-ml reaction vessel and shows where the thermocouples are placed inside and outside. The reaction vessels are 304 stainless steel cylinders, each internally ~ 1.75 cm diameter and 27 cm high (internal volume ~ 62 cm³). For the gas generation testing, each vessel was wrapped in heating tape and insulated. Two thermocouples were attached to the external body, one for temperature control and one for over-temperature protection. Two thermocouples were inserted through the cap. The thermocouple centered in the lower half of the vessel monitored the temperature of the liquid phase; the one centered in the upper half monitored the gas phase temperature within the reaction vessel. The reaction vessels were placed in a hot cell and connected by a thin (0.0058-cm inside diameter) stainless steel tube to the gas manifold outside the hot cell. A stainless steel filter (60- μ m pore size, Nupro) protected the tubing and manifold from particulate contamination. A thermocouple was attached to this filter as well.

2.3.2 Volume Determinations of System Components

The total moles of gas in the system were calculated using the Ideal Gas Law from the pressure, temperature, and volume of the parts of the apparatus having different gas phase temperatures:
 $\text{moles}_{\text{total}} = \text{moles}_{\text{vessel}} + \text{moles}_{\text{filter}} + \text{moles}_{\text{manifold and tubing}}$. The manifold and filter volumes were determined from pressure/volume relationships using a calibrated gas manifold system. The manifold volume (the

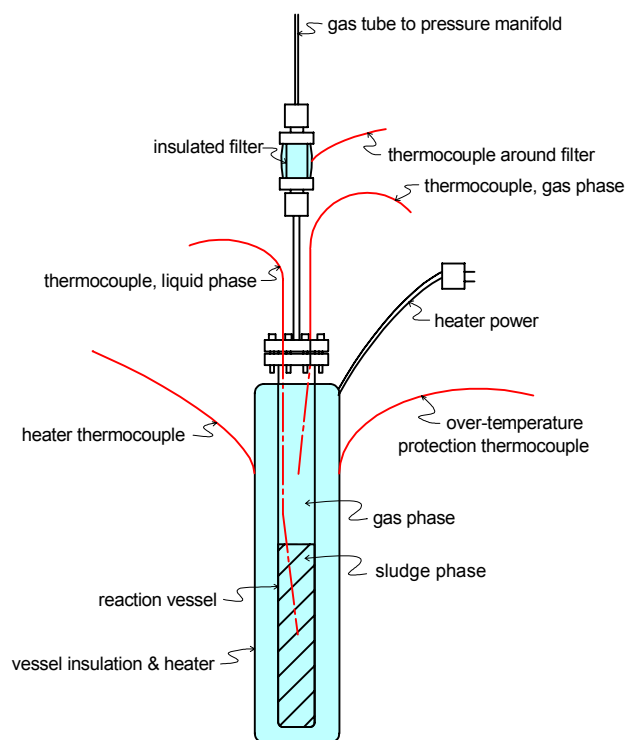


Figure 2.2. Reaction Vessel (60-ml) Used in Series II Gas Generation Tests

pressure sensor, valves, and miscellaneous fittings) was 3.99 ml; the filter volume was 1.34 ml; and the tubing volume was 1.715 ml (by calculation). The cap stem (the tube from vessel to filter) had a volume of 0.20 ml; half of that was added to the filter volume, giving 1.44 ml, and half was added to the vessel volumes. The volume of each vessel was determined gravimetrically by filling it with water. These volumes are recorded in Table 2.7, along with the mass of settled sludge added to each vessel and the gas phase volume in the vessel after the sample was added. The reproducibility of the molar gas determination using this manifold system has been established experimentally, and a detailed discussion can be found in Appendix A of the Series I report. The relative standard deviation for quantitative gas phase measurements conducted over a time frame similar to that of the gas generation tests is typically less than 2%.

An atmospheric pressure gauge was attached to the datalogger. The pressure in each system was the sum of atmospheric pressure and the differential pressure between the system internal and external (atmospheric) pressures. An inert cover gas was required to identify product gases and understand the chemical reactions occurring in the settled sludge. Because neon leaks more slowly than helium from the system, it was used as a cover gas. Argon was not used because it served as an indicator of atmospheric contamination. Nitrogen, as will be discussed later, can react with sludge and thus was not a suitable cover gas. The neon was analyzed independently by mass spectrometry and determined to contain no impurities in concentrations significant enough to warrant correction.

Table 2.7. Masses of Settled Sludge and Vessel Volumes Used in Gas Generation Tests

System	KC-1 Un	KC-1 Mix	KC-1 P500	KC-1 M500	FE-1
Temperature	60°C	60°C	80°C	80°C	90°C
Sample mass, g	23.75	25.61	14.15	22.30	27.00
Gas phase, ml	39.83	42.43	27.70	32.71	32.15
Vessel total, ml	62.40	62.96	62.37	62.45	62.44
System	FE-3	FE-5	FE-4/6	KC-6	96-06
Temperature	90°C	90°C	90°C	90°C	80°C
Sample mass, g	21.22	20.70	16.12	19.10	19.51
Gas phase, ml	38.05	37.17	32.08	36.22	37.29
Vessel total, ml	62.41	61.48	61.42	62.43	62.75

2.3.3 System Startup

At the start of each run, each system was purged by at least eight cycles of pressurizing with neon at 45 psi (310 kPa) and venting to the atmosphere. The systems were at atmospheric pressure, about 745 mm Hg (99.3 kPa), when sealed. The sample portion of the manifold was isolated (valves V1 and V2 closed; see Figure 2.1) for the remainder of the run. The vessels then were heated, and the temperature set points were adjusted to keep the material within 1°C of the desired liquid phase temperatures. The gas phase temperatures were measured to be 5°C to 25°C lower than those of the sample liquid phase.

2.3.4 Gas Sampling and Analysis

As necessary during the testing and at the end of each reaction sequence, the vessels were allowed to cool to ambient temperature and then a sample of the gas was taken for mass spectrometry analysis. Gases in the reaction system were assumed to be well mixed. The 304 or 316 stainless steel gas collection bottles were equipped with a valve (Nupro 4H packless valve with metal seats) and had a volume of approximately 75 ml (about two times the gas phase volume of the reaction vessels). After the bottle was evacuated overnight at high vacuum, it was attached to the gas sample port. Air was removed from the region between valves V2 and V5 (Figure 2.1), using a vacuum pump, and then the gas sample was taken. After the collection bottle was removed, the bottle and sample port were surveyed for radioactive contamination. No contamination was found during these experiments. The reaction vessel was purged again with neon after each sampling event and before the next reaction sequence.

The composition of the gas phase of each reaction vessel during gas sampling was analyzed at the PNNL Mass Spectrometry Facility, using analytical procedure PNNL-98523-284 Rev. 0. The amount of a specific gas formed during heating is given by the mole percent of each gas multiplied by the total moles of gas present in a system. The measured amount of argon in gas samples is an indicator of how much nitrogen and oxygen from air has leaked into the system (the N₂:Ar ratio in air is 83.6:1; the O₂:Ar ratio is 22.4:1). The nitrogen produced or consumed in the vessel is the total nitrogen minus atmospheric nitrogen. A similar calculation is used to correct for oxygen production or consumption.

3.0 Gas Generation from KE Basin Sludge Samples

In each test, gas-tight reaction vessels were loaded with selected KE Basin materials, the gas space purged with neon, and the loaded vessels heated to the selected temperature. Gas samples were taken from the vessels once during the run and again at the end of each run in accordance with the test plan. After the first gas sample was taken from each vessel, the vessel was purged to remove previously generated gases before testing resumed. Gas generation rates were determined for each gas sample, based on the heating time, the gas composition, the total gas quantity in the system from which the sample was taken, and the sludge mass present in each reaction vessel.

Section 3.1 presents the results from the study of the effects of agitation and aeration on the intact (not size-fractionated) KC-1 sludge. Gas generation results for the P500 and M500 (greater than and less than 500 μm , respectively) fractions of the KC-1 sludge are found in Section 3.2. Results of the gas generation studies of the single-pull core samples FE-1, FE-3, FE-5, and FE-4/6 are presented in Section 3.3. The gas generation results for samples KC-6 and 96-06 are presented in Section 3.4.

3.1 Gas Generation Results for Mixed and Unmixed KC-1 Canister Sludge at 60°C and 95°C

Two tests were conducted in which aliquots of KC-1 sludge were heated at 60°C for about 300 hours and subsequently heated to 95°C for an additional ~640 hours. In one test, the sludge was added to the reaction vessel without any agitation (mixing) beyond that required for subsampling and loading the vessel. This test was designated as KC-1 Un. In the second test, the sludge and supernatant liquid were shaken vigorously in a capped vial for 1 minute, the vial and contents allowed to stand 1 minute without agitation, and the vial opened to allow ingress of fresh air. This sequence was repeated four more times before the sludge slurry was transferred to the test vessel. This test was designated as KC-1 Mix.

In both of these tests, the reaction vessel temperature was increased to 95°C to force the reactions to completion so that the quantity of uranium metal present in the initial sludge could be derived. Gas samples were taken after about 470 hours of reaction (including periods at both 60°C and 95°C) and at the end of the test (after a further 477 hours at 95°C). The total amounts of gas produced (e.g., H_2 , CO_2 , CH_4) became constant with time (Figure 3.1), which suggested that the gas-producing reactions went to completion. As expected, the gas generation rates initially increased when the temperature was increased to 95°C. However, no significant induction period was observed before the onset of gas generation in either test. The lack of an induction time is in contrast to the behavior observed in the 60°C Series I test of uranium-bearing sludge KC-2/3 P250, in which a ~200-hour induction period was observed prior to gas generation. The gases produced in the KC-2/3 P250 experiment were predominantly H_2 . However, as shown in Section 4.2, the KC-1 Un and KC-1 Mix gas products were mostly CO_2 and the contribution of H_2 was less than 1% of the total gas evolved.

Note in Figure 3.1 that mixing the KC-1 sludge before it was added to the test vessel had no substantial effect on total gas generation. If anything, sample KC-1 Mix produced slightly less gas than sample KC-1 Un. However, KC-1 Mix produced about 10 times more hydrogen than KC-1 Un. Figure 3.1 also shows that most of the reaction occurred after the temperature was boosted to 95°C. The KC-1 Mix test produced about 0.014 moles of gas per kilogram of settled sludge, and the KC-1 Un test produced about 0.017 moles/kg settled sludge.

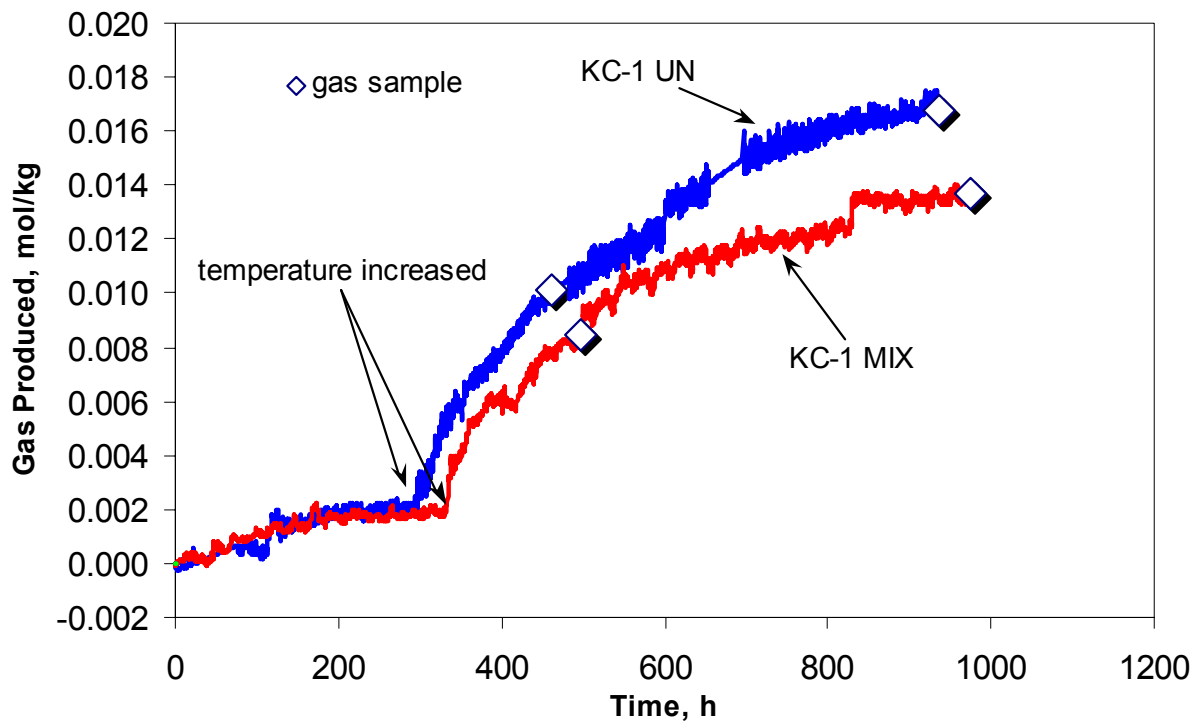


Figure 3.1. Total Gas Generation from KC-1 Mixed (Mix) and Unmixed (Un) Settled Sludge Material at 60°C and Completed at 95°C

The gas sample compositions from the KC-1 Un and KC-1 Mix tests are given in Tables A.1 and A.2 in Appendix A, respectively. Gas samples were analyzed by mass spectrometry. The compositions of the generated gases (derived from the compositions of sampled gas by excluding the neon cover gas, argon, and trace nitrogen and oxygen from atmospheric contamination) are presented and are indicated by shading. For example, if analysis found 80% Ne, 5% CO₂, and 15% H₂, the composition of gas formed by excluding Ne would be 25% CO₂ and 75% H₂.

The presence of argon in the gas samples was used to indicate atmospheric contamination (air), since it is not present in the cover gas and is not produced by the sludge. Nitrogen could have been generated or consumed by the sludge or could have come from atmospheric contamination. The percent nitrogen actually generated or consumed is given by the percent nitrogen found minus 83.6 times the percent argon in the sample (the ratio of nitrogen to argon in dry air is 83.6). The percent oxygen actually generated or consumed in the samples may be calculated in a method similar to nitrogen. The sum of all percents for a run in Tables A.1 and A.2 may not be exactly 100%, because the values were rounded. The uncertainties in all the entries in these tables are approximately plus or minus 1 in the last digit.

Individual gas generation rates are calculated based on the total moles of gas produced (Figure 3.1) and the generated gas compositions (Tables A.1 and A.2). Tables A.3 and A.4 show the gas generation rates derived in this manner for KC-1 Un and KC-1 Mix tests. Because only two gas samples were taken, the rates are averages over extended time periods (i.e., periods including both rapid gas evolution and relative

quiescence). The rates for the first gas sample also include periods at two different temperatures (60°C and 95°C). More detailed consideration of gas composition and generation rates is given in Section 4.2.

3.2 Gas Generation Results for KC-1 P500 and M500 Canister Sludge at 80°C and 95°C

Gas generation tests with the P500 and M500 size fractions of the KC-1 canister sludge were conducted at 80°C for about 320 hours followed by 643 hours of heating at 95°C to force completion of the reactions. The total amount of gas produced became constant at extended heating times (Figure 3.2), indicating that the gas-generating reactions were at, or very near, exhaustion.

Gas samples were taken about 490 hours into the test (gases generated by ~320 hours at 80°C and 166 hours at 95°C) and again at the completion of heating (477 hours at 95°C only). The gas samples were analyzed by mass spectrometry; the analyzed compositions are given in Tables A.5 and A.6. The net compositions of gases generated (and consumed) are presented in shading below each entry. Argon again was used to indicate atmospheric contamination and as a basis to correct for nitrogen and oxygen consumed or generated by the sludge reactions (see Section 3.1). The sums of all percents in Tables A.5 and A.6 for a gas sample may not be exactly 100%, because the values were rounded.

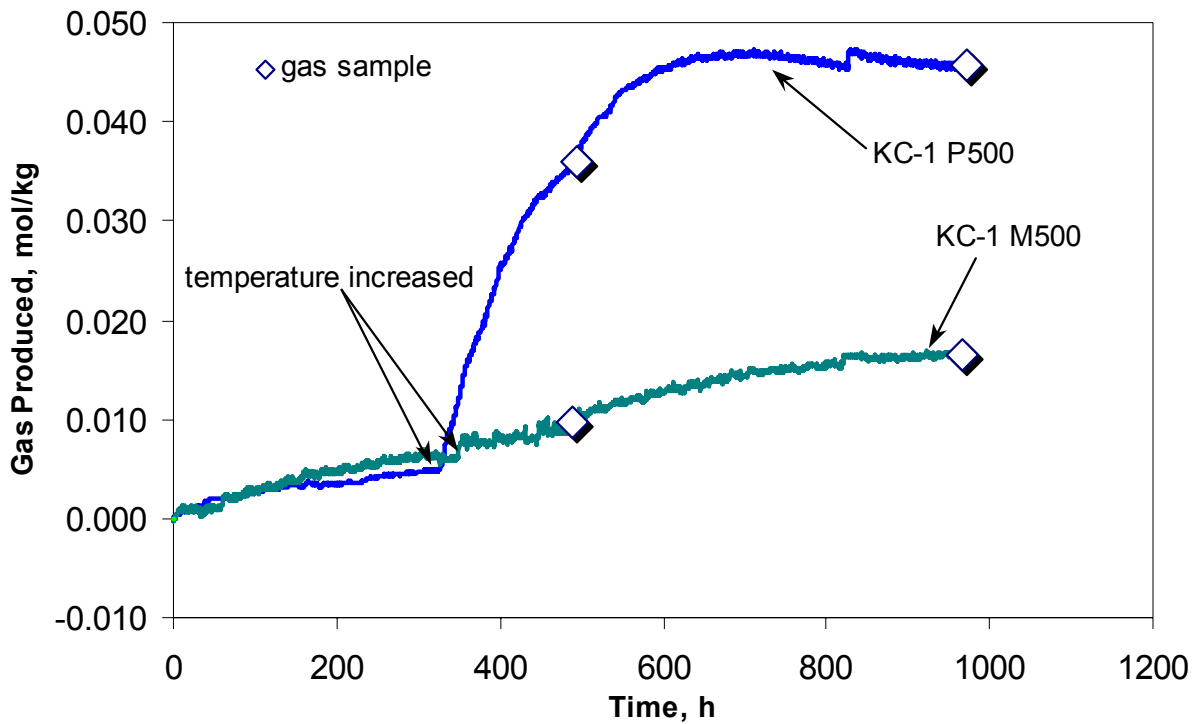


Figure 3.2. Total Gas Generation from KC-1 P500 and M500 (Settled Sludge) at 80°C and Completed at 95°C

The individual gas generation rates calculated based on the total moles of gas produced (Figure 3.2) and the gas compositions (Tables A.5 and A.6) are given in Tables A.7 and A.8 for KC-1 P500 and M500, respectively. Because only two gas samples were taken, the rates are averages over extended time periods and the first sample included time at both 80°C and 95°C temperatures. The specific quantity of gas generated is about three times higher for P500 than for M500. The gas produced by the P500 fraction is about 74% hydrogen, while the M500 fraction only produced about 0.25% hydrogen; the balance in both cases is predominantly carbon dioxide. The compositions of the generated gases are considered in more detail in Section 4.3.

3.3 Gas Generation Results for Single-Pull Core Samples FE-1, FE-3, FE-5, and FE-4/6 at 90°C and 95°C

Thermal gas generation data were measured for single-pull sludge samples FE-1, FE-3, FE-5, and a composite of FE-4 and FE-6 (FE-4/6) in tests run for about 327 hours at 90°C and completed at 95°C for an additional 643 hours. The total specific amounts of gas produced versus reaction time were measured for each test and are shown in Figure 3.3. Judging by the flatness of the gas production curves with advanced reaction times, the reactions apparently proceeded to completion for FE-3 and FE-5. Gas samples taken after about 490 hours (reaction at both 90°C and 95°C) and at completion (about 970 hours of reaction time entirely at 95°C) were analyzed by mass spectrometry. The mole percent compositions of the sampled gases are given in Tables A.9 through A.12, respectively. The generated gas compositions

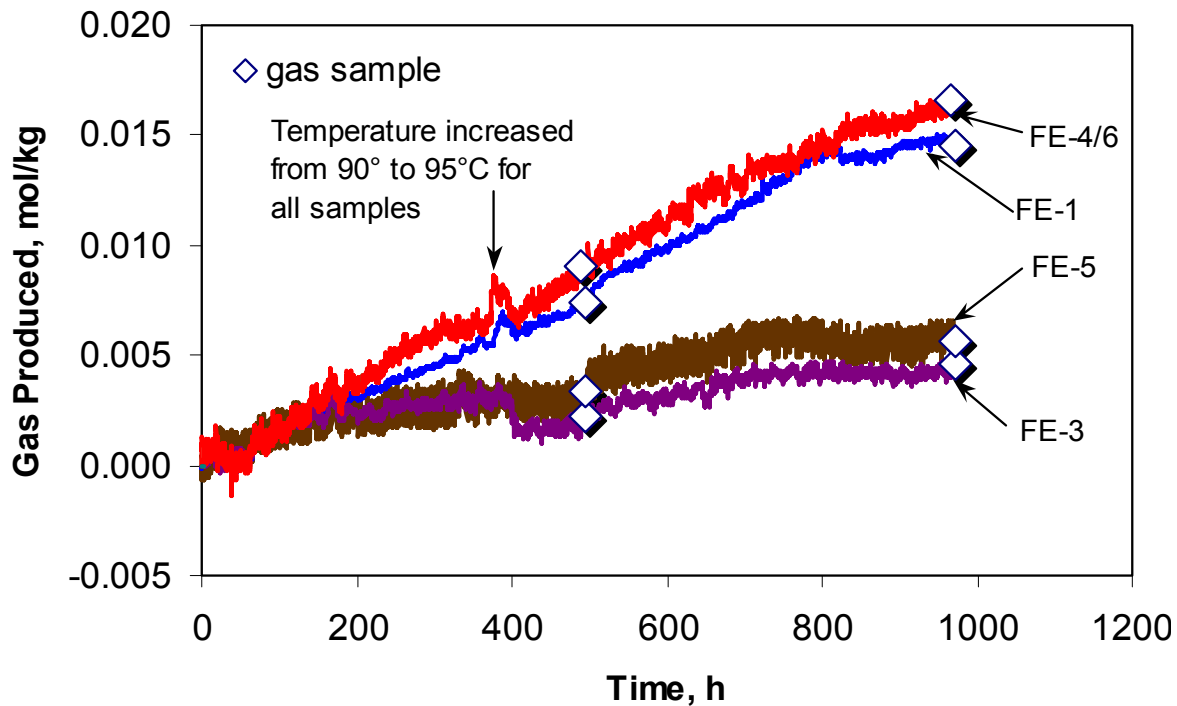


Figure 3.3. Total Gas Generation from FE-1, FE-3, FE-5, and FE-4/6 (Settled Sludge) at 90°C and 95°C

are presented (in shaded areas) below the entry for each run. The individual calculated gas generation rates for FE-1, FE-3, FE-5, and FE-4/6 are given in Tables A.13 through A.16, respectively.

The specific amounts of gas generated for FE-1 and FE-4/6 are about three times higher than the amounts observed for FE-3 and FE-5, and are comparable to the specific amounts found for the KC-1 Un, KC-1 Mix, and KC-1 M500 sludges (see Sections 3.1 and 3.2). In all cases, the evolved gases for the FE single-pull samples are only 0.3% to 3% hydrogen, with the balance predominantly carbon dioxide. The gas compositions are considered further in Section 4.4.

3.4 Gas Generation Results for KC-6, Ion Exchange Material Sludge, at 90°C and 95°C and 96-06 Canister Sludge at 80°C and 95°C

Gas generation experiments were conducted for KC-6 sludge (IXM) and 96-06 canister sludge. The test with the KC-6 sludge was run at 90°C for 327 hours and then completed at 95°C for 642 hours. The test with the 96-06 sludge began with 324 hours of heating at 80°C and finished with 624 hours of heating at 95°C. The total specific quantities of gas produced in these tests are shown as a function of reaction time in Figure 3.4. Gas samples were taken after 492 hours (heating at both 90°C and 95°C) and again at completion (95°C only; 968 hours) for KC-6. Gas samples were taken after 471 hours (heating at 80°C and 95°C) and at completion (95°C; 947 hours) for the 96-06 sludge test. The gas samples were analyzed by mass spectrometry, and the results are tabulated in Tables A.17 and A.18, respectively, with generated

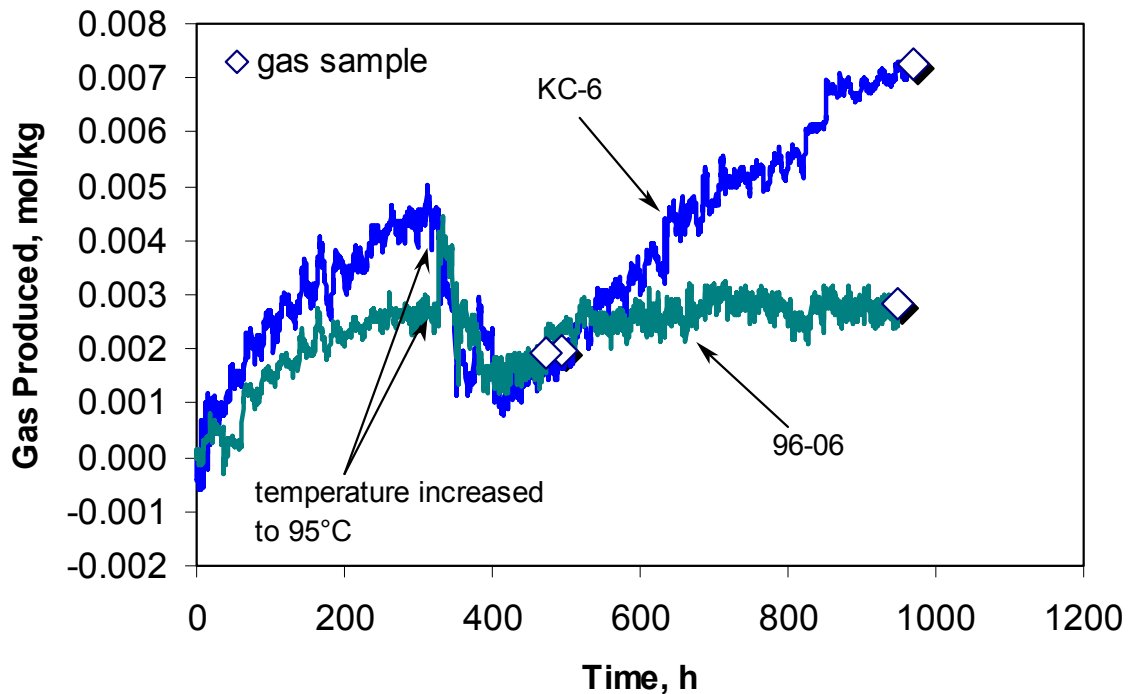


Figure 3.4. Total Gas Generation from KC-6 (Settled Sludge) at 90°C and 95°C and 96-06 (Settled Sludge) at 80°C and 95°C

gas compositions presented in the shaded areas. The individual gas generation rates for KC-6 and 96-06 are provided in Tables A.19 and A.20, respectively.

The specific amounts of gas produced by KC-6 and 96-06 sludges are relatively low and bracket those generated by the tests with the FE-3 and FE-5 sludges. The product gases are 91% and 97% carbon dioxide, respectively, with 8.5% and 2.3% hydrogen. The gas compositions are considered further in Section 4.5.

4.0 Discussion and Interpretation of Series II Results

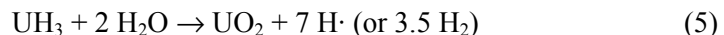
This section presents an evaluation of the results from the gas generation tests performed at various temperatures on samples KC-1, FE-1, FE-3, FE-5, FE-4/6, KC-6, and 96-06, and compares the results with Series I tests (Delegard et al. 2000). Section 4.1 describes the chemical reactions postulated to be responsible for the observed gas generation and consumption phenomenon. Section 4.2 examines in more detail the observations found for the KC-1 unmixed (KC-1 Un) and mixed (KC-1 Mix) tests. The results of the tests with KC-1 P500 and M500 are examined in Section 4.3. Section 4.4 discusses the results from the tests of single-pull core samples FE-1, FE-3, FE-5, and FE-4/6. The results for tests with samples KC-6 and 96-06 are presented in Section 4.5. Section 4.6 gives the overall conclusions drawn from the Series II testing.

4.1 Gas Generating and Gas Consuming Reactions

Hydrogen (H₂); isotopes of the fission product gases, krypton (Kr) and xenon (Xe); methane (CH₄) and higher hydrocarbons; and carbon dioxide (CO₂) were observed in the current tests. The same gases were observed in the 1996 gas collection tests associated with KE canister sludge (Makenas et al. 1997) and in the Series I tests using samples KC-2/3, KC-4, and KC-5 (Delegard et al. 2000). The consumption of oxygen (O₂) and nitrogen (N₂) from trace atmosphere intrusion observed in many of the present tests also was seen in the prior work. The absolute and relative rates of the appearance and disappearance of these gases give evidence of the underlying chemical reactions thought to be occurring in the sludge. These reactions affect the behavior of the sludge in retrieval, transport, and storage conditions. The postulated chemical reactions are discussed in this section and also are described with varying emphasis in the Series I report.

4.1.1 Uranium Corrosion and the Roles of Hydrogen, Oxygen, and Nitrogen

The oxidation of metallic uranium under conditions relevant to K Basin sludge occurs by several reactions that involve the production and depletion of gases:



In aerated waters, uranium metal corrosion occurs largely by Reaction 2 (Montenyohl 1960) and Reaction 3.^(a) However, if the system becomes isolated from the atmosphere (as is the case for the sealed

(a) No explicit mention of the reaction of uranium metal with N₂ in aqueous systems was found in the technical literature. The postulated Reaction 3 is based on the observed depletion of N₂ from the gas phase in the present tests and the observation of a nonstoichiometric UN_{1.75} product from reaction of uranium metal with N₂ at 200°C to 300°C (Cordfunke 1969).

test vessels or in confined layers of settled sludge), the direct reaction of uranium with water dominates and hydrogen gas is evolved (Reaction 1). Significantly, though both Reactions 1 and 2 occur in water to produce UO_2 , the rate of Reaction 2 (in the presence of oxygen) is 30 to 40 times slower than that of the anoxic Reaction 1 (Johnson et al. 1994; Montenyohl 1960). In other words, dissolved oxygen inhibits uranium metal corrosion in water.

Hydrogen accelerates the corrosion of uranium metal in water through the formation, by Reaction 4, of the poorly adherent uranium hydride (UH_3) corrosion product (Montenyohl 1960). The hydride is observed at the metal surface and within cavities and around inclusions in the metal surface (Tyfield 1988). The UH_3 intermediate is unstable in water, forming UO_2 and hydrogen atom radicals (Reaction 5). The released hydrogen atoms then may combine to form H_2 gas. Alternatively, the hydrogen radicals (and the H_2), especially if occluded, can interact with the underlying bulk uranium metal to form more UH_3 by Reaction 4 and continue the corrosion cycle through Reaction 5. Note that the sum of Reactions 4 and 5 is Reaction 1.

The transition in closed experimental vessels to rapid anoxic corrosion dominated by Reactions 4 and 5 usually is preceded by an induction time. The induction times vary unpredictably, even at experimentally identical conditions (Tyfield 1988; Wilkinson 1962). While rapid corrosion by Reactions 4 and 5 is observed in anoxic conditions, Reaction 1 evidently also occurs during the induction time, though at a much lower rate than observed after the induction time, to provide the hydrogen necessary for Reaction 4. Therefore, uranium reaction with water can occur under two regimes. The first is an initial period of low reaction rate (in the absence of significant free hydrogen and hydride hydrogen concentrations) by Reaction 1; with sufficient hydrogen, the second regime is entered in which uranium corrosion by water occurs at the much higher rate afforded by UH_3 mediation (the combined Reactions 4 and 5).

The corrosion rate of uranium by Reactions 4 and 5 is known to follow kinetics that are first order in the uranium metal surface area. An evaluation of data in the technical literature is summarized by the following rate equation:

$$\log \text{rate} \left(U \text{ weight loss, mg / cm}^2 \cdot \text{hr} \right) = 8.505 - \frac{3016}{T} \quad (6)$$

where T is temperature in K (derived from Reilly 1998). The temperature dependence of this rate equation corresponds to a 13.8 kcal/mole activation energy. Another review of the studies of uranium corrosion in water presented kinetic data that can be fit to the equation:

$$\log \text{rate} \left(U \text{ weight loss, mg / cm}^2 \cdot \text{hr} \right) = 9.822 - \frac{3520}{T} \quad (7)$$

The slope of this equation indicates a 16.1-kcal/mole activation energy (derived from Johnson et al. 1994). [The 16.1-kcal/mole activation energy was incorrectly attributed to Pajunen (1999) in the Summary and Conclusions, Section 4.2.1, and Section 4.6 of the Series I report.] No corrosion rate data to describe the initial slow reaction of uranium metal with water have been found in review of the technical literature.

Review of Uranium Corrosions Reactions Observed in Series I Testing: From the discussion above, uranium corrosion in closed vessels by Reactions 2 and 3 (in the presence of residual O_2 and N_2) and the

initially slow Reaction 1 with time give way to corrosion by water (Reaction 1) made rapid by UH_3 mediation through Reactions 4 and 5. Evidence for this sequence is found in the KC-2/3 P250 (canister sludge composite with particles greater than $250\ \mu\text{m}$) tests described in the Series I studies. In these tests, seven to nine gas samples each were taken at the 40°C , 60°C , and 80°C test temperatures. Later, the temperatures were boosted to 95°C to completely corrode all of the uranium metal. Gas analysis data from Series I then were used to calculate and compare uranium metal corrosion as measured by the gases (H_2 , O_2 , and N_2) produced and consumed chemically by Reactions 1-3 with uranium metal corrosion, as inferred by Xe fission product gas release (see Section 4.2.2 of this report).

As seen in Figure 4.1 (generated with data from Series I testing), for each temperature, uranium corrosion, as manifested by the sum of the chemical reactions with H_2O (shown by H_2 release), O_2 , and N_2 (“Corr. Gases”), initially lags the uranium corrosion measured by Xe release (“Xe Total”). This interval is greater at lower reaction temperatures. The amounts of uranium corroded, as determined by Xe release and O_2/N_2 consumption and H_2 production, converge only when about 60% to 80% of the uranium has reacted and sufficient H_2 is released to the gas phase. Because 97% or more of the uranium metal corrosion is caused by reaction with water in the KC-2/3 P250 sludge tests, the corrosion gas delay is almost certainly caused by H_2 uptake in the sludge matrix, such as by Reaction 4 to form UH_3 .

The extent of the combined Reactions 4 and 5 (uranium metal with water to form H_2 through UH_3) may be estimated as the difference between the total uranium reacted as shown by Xe release and the uranium reacted as shown by O_2 and N_2 consumption in Reactions 2 and 3. The amounts of uranium reacted with water estimated in this way are plotted as “Xe from H_2O ” in Figure 4.1 for the Series I tests with KC-2/3 P250 sludge. The dashed line slopes in Figure 4.1 plotted through these points indicate the rates of Reactions 4 and 5 at the three primary test temperatures. The activation energy for uranium metal corrosion by Reactions 4 and 5, based on these rates plotted in Arrhenius coordinates at the three

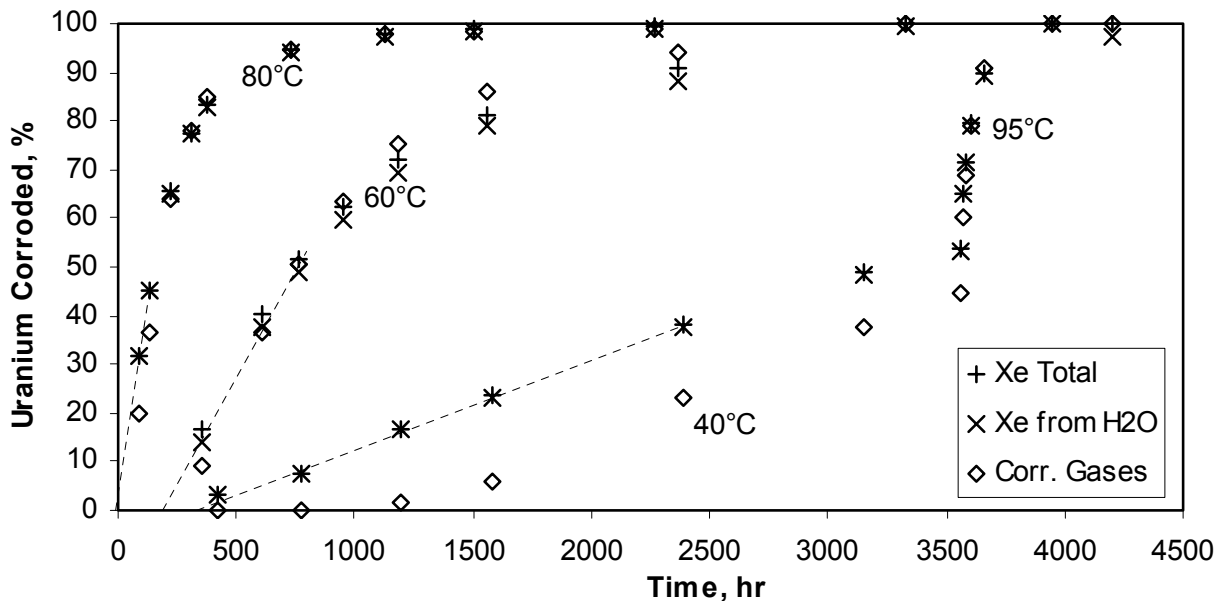


Figure 4.1. Uranium Corrosion in KC-2/3 P250 Series I Small-Scale Tests, as Monitored by Total Xe Release, Xe Released by Uranium Reaction with Water, and Corrosion Gases (H_2 from H_2O ; O_2 ; and N_2)

temperatures, is 15.8 kcal/mole ($R^2 = 1.00$). In comparison, activation energies of 15.1-kcal/mole and 15.8-kcal/mole values were found based on H_2 evolution for the same experiments. The activation energies observed for the KC-2/3 P250 tests thus lie between the 13.8- and 16.1-kcal/mole values for uranium corrosion in water derived by evaluations of the technical literature (Reilly 1998 and Johnson et al. 1994, respectively).

The induction times to onset of the rapid H_2 -mediated corrosion by Reactions 4 and 5 also can be estimated by analysis of the “Xe from H_2O ” data. The induction times are only approximate because the initial rate of Reaction 1 is not known. For example, of all gas samples taken in the Series I KC-2/3 P250 tests, perhaps only the first gas sample in the 40°C test was taken before the full onset of H_2 -mediated corrosion. The induction times, therefore, are measured as the X-axis intercepts of the linear Xe evolution points between about 10% and 50% reaction. The estimated induction times are about 335 hours at 40°C, 186 hours at 60°C, and essentially 0 hours at 80°C. These induction times are lower than the 1340, 205, and 26.9 hours, respectively, estimated from the H_2 gas release rate data (Delegard et al. 2000). The differences again reflect the incorporation of H_2 in the sludge solids as UH_3 or as other species. The negligible induction time for the 80°C test is consistent with tests of uranium corrosion in aerated water conducted at 50°C, 60°C, 70°C, 80°C, and 100°C (Wilkinson 1962, pp. 834-835). In the Wilkinson (1962) tests, induction times were observed at the lower temperatures, but no delays in onset of corrosion (as measured by metal weight loss) were evident in the 80°C and 100°C tests. The induction period has been attributed to the presence of molecular oxygen on the metal surface that blocks the reduction of water to hydrogen (Reaction 1; Tyfield 1988) and to the breakdown of pre-existing protective UO_2 layers on the metal surface (Wilkinson 1962). Saturating the water with H_2 is found to decrease the induction time (Wilkinson 1962).

Growths in H_2 concentration over the experimental periods were not observed in Series II where only two gas samples were taken during each test, and only one test (KC-1 P500) generated significant quantities of H_2 . However, evolution of N_2 and consumption of O_2 in the latter stages of several tests gave evidence that uranium nitride ($UN_{1.75}$), formed by Reaction 2, may have reacted to form uranium dioxide (UO_2).

4.1.2 Release of Fission Product Gases

The existence of the Kr and Xe fission products in the generated gases gives qualitative evidence of the corrosion of irradiated uranium metal. This assertion is based on two reasonable suppositions: 1) that until corrosion occurs, the fission gases remain trapped within the solid uranium metal matrix and 2) that the metal corrosion products (UO_2 , UH_3) and other sludge components cannot react with, and thus retain (except through physical entrapment and dissolution in water), the inert Kr and Xe gases.

According to burnup calculations by the ORIGEN code, the isotopic ratios and the total Kr/total Xe mole ratios remain relatively unaffected by exposure. Thus, the $\Sigma Xe/\Sigma Kr$ mass ratio only increases slightly, from ~11.6 to 13.1 (7.4 to 8.3 mole ratio), as burnup increases from ~1000 to 3600 MWD/TeU. The Kr and Xe production in nominal 2900 MWD/TeU fuel is 0.00016 moles Kr and 0.00134 moles Xe per mole of uranium, and these values increase almost linearly with exposure (burnup). Thus, if exposure is known, the quantity of Kr or Xe released by corrosion of uranium metal can be used to determine the quantity of uranium metal. Conversely, the concentrations of Kr and Xe in the uranium metal (determined by measuring the products of metal corrosion) can be used to calculate burnup (Equations 8 and 9 were empirically derived by fitting output data from the ORIGEN code):

$$\text{Burnup (MWD/TeU)} = -9.94 \times 10^{-5} (\text{Xe, ppmp U})^2 + 4.87 (\text{Xe, ppmp U}) \quad (8)$$

$$\text{Burnup (MWD/TeU)} = 0.154 (\text{Kr, ppmp U})^2 + 54.1 (\text{Kr, ppmp U}) \quad (9)$$

Applying this technique to determine the irradiation exposure of materials in a sludge sample is imprecise, because the sludge can be generated by a number of different fuel elements that may have had different exposures. Furthermore, the irradiation exposure within any given fuel element differs spatially according to its radial and axial locations (e.g., near the cladding versus deep within the fuel element).

As shown above, the quantities of Kr and Xe released by uranium metal corrosion are small. Thus, for sludges with low concentrations of uranium metal, the correspondingly lower quantities of Kr and Xe released by uranium corrosion may not be detectable by mass spectrometry. In this situation, the quantities of Kr and Xe dissolved in solution or present interstitially in the sludge solids also may become significant. For sludges containing miniscule particles of residual uranium metal, a relatively larger fraction of fission product Kr or Xe can diffuse out of the metal matrix. These effects, which act in opposite directions, decrease the reliability of obtaining quantitative uranium metal concentration and burnup data based on Kr and Xe gas analyses from samples having low metal concentrations.

Based on both Kr and Xe analyses, an average burnup of ~2800 MWD/TeU was determined for the ~7.4 wt% uranium KC-2/3 P250 sludge in the Series I small-scale tests. Correspondingly, the correlation between uranium concentration determined by release of Kr and Xe fission product gas and gas formation and consumption by corrosion (Reactions 1-3) for these tests is good. However, other sludge samples tested in Series I were 0.145 wt% uranium metal or lower. As a result, the correlation between uranium metal concentration as determined by Kr and Xe fission product gas release (at nominal 2900 MWD/TeU exposure) and uranium metal concentration determined by corrosion reactions is more scattered (Figure 4.2). Fewer data are shown for Kr than for Xe in Figure 4.2 because the approximately eightfold lower concentration of Kr often is below the mass spectrometric detection limit.

Corresponding data for the results from the Series II tests, also presented in Figure 4.2, show that uranium concentrations as determined by corrosion reactions are ~0.4 wt% or lower. Though paired Kr and Xe data (where they exist) agree well with each other, it is seen that the fission product gases predict uranium metal concentrations as much as 300 times higher than those determined by corrosion reaction gas analyses. Because, as seen in Section 4.1.1, H₂ is retained in sludge solids, corrosion gas (O₂, N₂, and H₂) consumption and release may understate uranium metal concentrations, particularly for low metal concentrations. Therefore, despite uncertainties in “average” fuel burnup and in analyzing Kr and Xe at low concentrations, determining uranium metal concentration by Kr and Xe release likely is a more accurate measure of uranium metal corrosion, particularly for low apparent uranium metal concentrations in which H₂ absorption or reaction can occur. The interpretation of Kr and Xe fission product gas data in these Series II studies also includes comparisons of their isotopic distributions to ORIGEN calculations, ΣXe/ΣKr ratios, and evaluations of cooling time based on observed ⁸⁵Kr concentration isotopic ratios and decay.

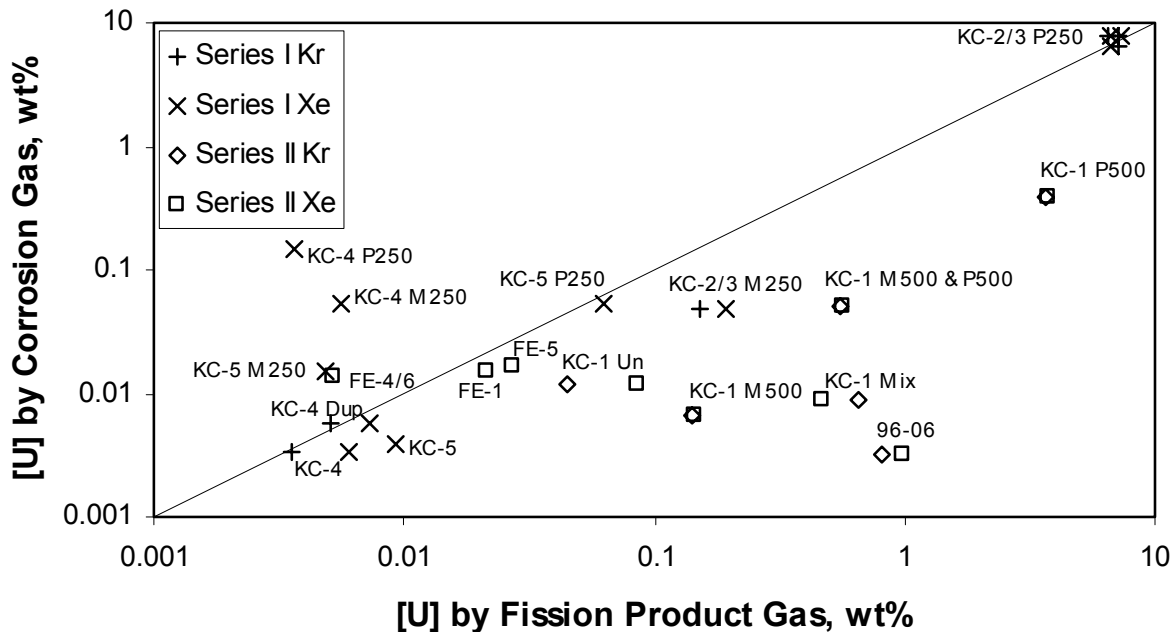
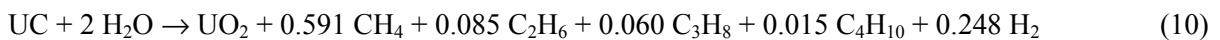


Figure 4.2. Comparison of Uranium Metal Concentrations Determined by Corrosion Reactions and by Release of Kr and Xe Fission Product Gases at Nominal 2900 MWD/TeU Irradiation for Series I and Series II Tests

4.1.3 Creation and Release of Hydrocarbons

Methane, ethane, and higher hydrocarbons, as well as hydrogen, arise from the reaction of water with carbide carbon in the uranium metal fuel. Hydrogen, methane, ethane, propane, butane, pentane, and hexane have been observed in the reaction of mixtures of uranium metal and uranium monocarbide with water at 80°C (Bradley and Ferris 1962, 1964). Methane also was observed in corrosion tests of uranium metal with water at 50°C (Waber 1956). The carbon content in the metallic uranium fuels stored in the K Basins nominally ranges from 365 to 735 ppm (Weakley 1979). At these low carbon concentrations in the uranium-carbon system, the carbon is present as the compound UC (uranium monocarbide) dispersed within metallic uranium (Wilkinson 1962). Uranium carbide inclusions appear as rectangles or parallelograms ~4 μm to ~20 μm on a side in photomicrographs of irradiated N Reactor fuel (Marschman et al. 1997) and unirradiated test fuel (Troutner 1960).

Reaction 10 rationalizes the hydrocarbon product distribution observed in Series I testing that arises when the UC contained in the fuel reacts with water:



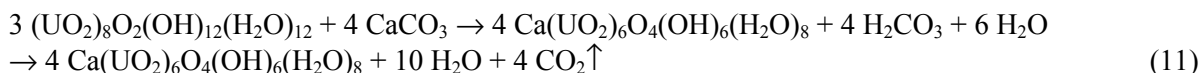
The C₃ and higher hydrocarbons are not discriminated by mass spectrometry in the Series II tests. They are projected to be C_{3,2}H_{8,4} on average, based on the observations of Bradley and Ferris (1962, 1964), and are represented in Reaction 10 by propane and butane in that proportion. The projected 0.248 moles of hydrogen arising per mole of UC is a significant contributor to the total gas generated from UC reaction

with H₂O. However, this quantity is a negligible (~0.14%) addition to the hydrogen generated by reaction of uranium metal with water in nominal 550-ppm carbon fuel.

As in the case of fission product Kr and Xe, however, the relatively low uranium metal concentrations found in the Series II test sludges produce correspondingly low quantities of hydrocarbon from fuel corrosion. The quantities of hydrocarbon gas evolved in the Series II tests, in fact, generally are much higher (by about 3- to 100-fold) than can arise from corrosion of uranium metal measured by evaluation of H₂, O₂, and N₂ data. However, as shown in Sections 4.2 through 4.4, the evolved hydrocarbon quantities are consistent with uranium metal concentrations measured by Xe and Kr fission product gas release. Nevertheless, at low uranium metal concentrations, the fraction of the hydrocarbon arising from degradation of other reduced (noncarbonate) carbon sources in the sludge may become a significant fraction of the total hydrocarbon. Reduced carbon sources might include organic ion exchange resin, plant and animal debris (e.g., twigs, insects), paper and other cellulose, plastic and rubber used in K Basin operations. The carbon concentrations found as evolved hydrocarbon gas in all the Series II tests range from 0.08 to 18 ppm of the settled sludge mass.

4.1.4 Carbon Dioxide Generation

Carbon dioxide is the principal gas generated in 9 of the 10 tests in this series. The CO₂ production may be due to the reaction in water of schoepite, (UO₂)₈O₂(OH)₁₂(H₂O)₁₂ (or 4UO₃·9H₂O), with calcite, CaCO₃, to form the more stable uranium phase, becquerelite, Ca(UO₂)₆O₄(OH)₆(H₂O)₈ (or CaU₆O₁₉·11H₂O) and carbonic acid (H₂CO₃):



Calcite and a calcium uranium oxide hydrate, CaU₆O₁₉·12H₂O, have been observed by XRD in floor sludge from the KE Basin (Makenas et al. 1996); schoepite and metaschoepite [(UO₂)₈O₂(OH)₁₂(H₂O)₁₀] have been found in canister sludge from the KE Basin (Makenas et al. 1997). Several research groups have studied this reaction and published their findings (Vochten and Van Haverbeke 1990; Sandino et al. 1994; Sowder et al. 1996; Wronkiewicz et al. 1996; Sowder et al. 1999). The salient features of these reported studies are described and compared in the Series I report.

Reaction 11 indicates that Ca²⁺ substitutes for 2 H⁺ to form, in this case, H₂CO₃. Therefore, if Reaction 11 proceeds, the solution pH should decrease. As shown in Table 2.6, little pH change was noted for any Series II test. Accordingly, the inorganic carbon concentrations in the various settled sludges tested in Series II experiments, based on analysis of CO₂ gas generation, are low and ranged from about 20 to 120 ppm. Although CO₂ was the principal gas product in 9 of the 10 Series II experiments, the specific amounts of CO₂ production are 0.002 to 0.02 moles/kg settled sludge and below the 0.02 to 0.12 moles/kg observed in the Series I tests with KC-2/3, KC-4, and KC-5 sludges.

4.2 Gas Analysis for the Mixed and Unmixed KC-1 Canister Sludge at 60°C and 95°C

The KC-1 canister sludge tests (mixed and unmixed) that began at 60°C and ended at 95°C produced about 0.017 and 0.014 moles of gas per kg settled sludge, respectively. The initial (and highest) gas

generation rates in each experiment are similar and are about 2.5×10^{-4} moles/kg-day at 60°C and 2.0×10^{-3} moles/kg-day at 95°C (Figure 3.1).

The quantities of gas produced and consumed in each test are presented in Table 4.1. The gas product was 99.8% CO_2 for test KC-1 Un and 95.9% CO_2 for test KC-1 Mix. Hydrogen comprised 0.078% of the KC-1 Un and 0.87% of the KC-1 Mix product gas. Hydrocarbon and fission product gases comprised the balance of the gas production, and N_2 and O_2 were consumed in both tests. While the H_2 evolution was about nine times higher in the KC-1 Mix test than in the KC-1 Un test, the O_2 consumption was about 0.5 times lower. Nitrogen consumptions were about equal for both tests. However, N_2 consumption is observed only in the first sampling, and N_2 was produced in the second sampling. The production of N_2 in the second sampling may have been by conversion of the presumed $\text{UN}_{1.75}$ product to UO_2 by reaction with water or oxygen.

The quantities of uranium metal corroded as determined by Reaction 1, 2, and 3 stoichiometry are shown in Table 4.2. The uranium metal concentrations in each test are low and comparable (about 0.01 wt% each). The concentrations also are lower than found in the Series I tests, which ranged from 0.015 to 7.4 wt% uranium. Agitation and aeration in the KC-1 Mix test resulted in about 20% of the uranium corrosion to occur by reaction with water (Reaction 1); only ~1.7% of the uranium corroded by Reaction 1 in the nonagitated, KC-1 Un test. The reaction of uranium metal with oxygen is complementary; 38 wt% of the uranium is corroded by oxygen in the KC-1 Mix test and 65 wt% in the KC-1 Un test. Nitrogen is responsible for 33 wt% of the uranium corrosion in KC-1 Mix and 42 wt% in the KC-1 Un test.

The uranium metal concentrations predicted based on Kr and Xe release (assuming 2900 MWD/TeU irradiation) are four to seven times higher than predicted based on the corrosion gases for KC-1 Un, and are 50 to 70 times higher for KC-1 Mix. The higher uranium metal concentrations predicted by the fission product gas release may be attributed in small part to error in the assumed burnup. However, if the burnup were doubled to 6000 MWD/TeU (the maximum used in N Reactor power operations), the discrepancies would decrease only about a factor of 2. Another possible explanation is that Kr and Xe were retained and present in the sludge before it was added to the test vessels, and both gases were released by heating during testing. However, the quantities of Kr and Xe were not inordinately higher in the first sampling, when such outgassing would have occurred, as compared to the second sampling. The most likely cause of the difference is that a substantial amount of the H_2 produced by the uranium metal corrosion was not released during the testing despite the prolonged heating. The hydrogen product instead remained in the sludge solids in an unknown form or was consumed by chemically reducing uranium(VI) minerals [e.g., by converting schoepite, $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$, to uranium octoxide, U_3O_8 , or uraninite, UO_2 (Gillies 1958)].

The uranium metal concentrations based on Kr and Xe release also show that agitation substantially increased the uranium metal corrosion. The calculated uranium metal concentrations were about nine times higher, on average, for the KC-1 Mix experiment (~0.56 wt%) compared with the KC-1 Un experiment (~0.065 wt%).

The uranium metal content of KC-1 Mix (0.56 wt%) is considerably lower than the 1.9 wt% uranium metal content of canister sludge composite KC-2/3 measured in Series I testing. However, while KC-1 and KC-2/3 were collected from the KE Basin at approximately the same time, KC-1 was stored in the hot cells (~ 32°C) for about 9½ months between the start of Series I and the start of Series II. During this storage period, gas bubbles were observed several times in the KC-1 sample, indicating that uranium

Table 4.1. Net and Cumulative Quantities of Gas Evolved for KC-1 Un and KC-1 Mix at 60°C and 95°C

Gas	Gas Quantities, moles, at Sampling Times			
	KC-1 Un		KC-1 Mix	
	459.33 hr	936.00 hr	496.33 hr	973.66 hr
CO ₂	2.93E-04	2.20E-04	2.53E-04	1.56E-04
Cumulative	2.93E-04	5.14E-04	2.53E-04	4.09E-04
H ₂	2.24E-07	1.79E-07	1.80E-06	1.93E-06
Cumulative	2.24E-07	4.03E-07	1.80E-06	3.73E-06
N ₂	-4.64E-06	1.17E-06	-4.80E-06	1.34E-06
Cumulative	-4.64E-06	-3.47E-06	-4.80E-06	-3.46E-06
O ₂	-6.00E-06	-1.81E-06	-3.14E-06	-4.88E-07
Cumulative	-6.00E-06	-7.82E-06	-3.14E-06	-3.62E-06
CH ₄	2.04E-07	2.18E-07	5.14E-06	6.99E-06
Cumulative	2.04E-07	4.22E-07	5.14E-06	1.21E-05
C ₂ H _x	6.11E-08		4.93E-07	4.73E-07
Cumulative	6.11E-08	6.11E-08	4.93E-07	9.66E-07
≥C ₃ H _x	1.83E-08		1.07E-07	8.23E-08
Cumulative	1.83E-08	1.83E-08	1.07E-07	1.89E-07
Σ C _y H _x C	3.84E-07		6.46E-06	8.20E-06
Cumulative	3.84E-07	6.02E-07	6.46E-06	1.47E-05
⁸³ Kr	6.11E-10	3.97E-10	1.28E-08	4.11E-09
Cumulative	6.11E-10	1.01E-09	1.28E-08	1.70E-08
⁸⁴ Kr	1.02E-09	7.94E-10	1.71E-08	1.03E-08
Cumulative	1.02E-09	1.81E-09	1.71E-08	2.74E-08
⁸⁵ Kr		5.96E-11	1.28E-09	8.23E-10
Cumulative	0.00E+00	5.96E-11	1.28E-09	2.11E-09
⁸⁶ Kr	1.63E-09	1.39E-09	2.78E-08	1.85E-08
Cumulative	1.63E-09	3.02E-09	2.78E-08	4.64E-08
Σ Kr	3.26E-09	2.64E-09	5.91E-08	3.37E-08
Cumulative	3.26E-09	5.90E-09	5.91E-08	9.28E-08
¹³⁰ Xe				6.17E-11
Cumulative	0.00E+00	0.00E+00	0.00E+00	6.17E-11
¹³¹ Xe	1.02E-08	3.97E-09	4.07E-08	2.06E-08
Cumulative	1.02E-08	1.42E-08	4.07E-08	6.13E-08
¹³² Xe	1.02E-08	5.96E-09	6.21E-08	3.29E-08
Cumulative	1.02E-08	1.61E-08	6.21E-08	9.50E-08
¹³⁴ Xe	1.63E-08	9.93E-09	9.85E-08	5.76E-08
Cumulative	1.63E-08	2.62E-08	9.85E-08	1.56E-07
¹³⁶ Xe	2.04E-08	1.39E-08	1.43E-07	8.23E-08
Cumulative	2.04E-08	3.43E-08	1.43E-07	2.26E-07
Σ Xe	5.70E-08	3.38E-08	3.45E-07	1.93E-07
Cumulative	5.70E-08	9.08E-08	3.45E-07	5.38E-07

Table 4.2. Reacted Metallic Uranium Calculated from Gas Generation and Consumption Reactions in KC-1 Un and KC-1 Mix Tests

Reaction	U Reacted Based on Various Reactions, moles	
	KC-1 Un	KC-1 Mix
Settled Sludge Mass in Test, g	23.75	25.61
Reaction 1 $U + 2 H_2O \rightarrow UO_2 + 2 H_2$	2.01E-7	1.87E-6
Reaction 2 $U + O_2 \rightarrow UO_2$	7.82E-6	3.62E-6
Reaction 3 $U + 0.875 N_2 \rightarrow UN_{1.75}$	3.96E-6	3.95E-6
Total Moles U (Σ Reactions 1-3)	1.20E-5	9.44E-6
U metal, wt% settled sludge, Reactions 1-3	0.012	0.00877
U metal, wt% settled sludge, Kr	0.0446	0.651
U metal, wt% settled sludge, Xe	0.0852	0.468

metal was reacting. To consider the uranium metal content of KC-1 on a similar basis as that of KC-2/3, the uranium metal that corroded during the 9½-month storage period must be accounted for. Assuming that the initial uranium metal particles in KC-1 were the same size as those in KC-2/3, by using Equation 6 (rate equation in Section 4.1.1) it can be shown that KC-1 contained ~2.4 wt% uranium metal at the start of the Series I tests (Appendix B).

The Kr and Xe isotope ratios observed in the product gas are similar to the ratios that are expected based on burnup calculations by the ORIGEN code (Table 4.3). The lower relative quantity of ⁸⁵Kr found in the present tests can be attributed to radioactive decay. The decrease in ⁸⁵Kr abundance indicates a cooling time since discharge of about 17 or 30 years for KC-1 Mix and KC-1 Un, respectively. While these times should be identical because they are derived from Kr gases arising from the same sludge, they are consistent with N Reactor last being at power ~14 years ago (1986). The Xe:Kr mole ratios for the two tests are expected to be about 8.2:1 (13:1 mass ratio), according to ORIGEN calculations, and are relatively insensitive to irradiation dose in the normal N Reactor fuel burnup range of 1000 to 3600 MWD/TeU. The divergent 15.4 and 5.8 mole ratios observed for KC-1 Un and KC-1 Mix, respectively, indicate variability in gas composition perhaps caused by difficulties in measuring near the detection limit.

Methane, ethane, and higher hydrocarbons were found in gases generated during the KC-1 Un and KC-1 Mix tests. As discussed in Section 4.1, because of the low uranium metal concentrations found in the Series II tests, the concentrations of carbon in the uranium metal fuel cannot reliably be determined by comparing the quantity of total carbon in the hydrocarbon gas products (Table 4.1) to the total uranium corroded (Table 4.2). Such calculations show the carbide concentrations in KC-1 Un and KC-1 Mix to be

Table 4.3. Isotope Ratios for KC-1 Un and KC-1 Mix Tests

Gas	Isotopic Composition, atom%		ORIGEN ^(a)
	KC-1 Un	KC-1 Mix	
⁸³ Kr	17.1	18.3	13.3
⁸⁴ Kr	30.7	29.5	28.3
⁸⁵ Kr	1.0	2.3	6.8
⁸⁶ Kr	51.2	49.9	51.5
¹³⁰ Xe	0.0	0.0	0.05
¹³¹ Xe	15.6	11.4	10.7
¹³² Xe	17.8	17.7	18.0
¹³⁴ Xe	28.9	29.0	28.0
¹³⁶ Xe	37.7	41.9	43.2
Xe:Kr	15.4	5.8	8.2

(a) ORIGEN2 calculation for N Reactor MkIV fuel at 2921 MWD/TeU; ratios change <3% relative at lower burnups; ⁸⁵Kr has a 10.76-year half-life.

2540 and 78400 parts per million parts (ppmp) uranium metal (based on Reactions 1-3), respectively, and well above the expected carbon concentration of ~550 ppm uranium (Weakley 1979). However, if the uranium metal concentration is based on the fission product gas analyses, the carbide concentrations, about 520 and 1260 ppmp uranium metal for KC-1 Un and KC-1 Mix, are near expectations.

The carbon evolved as hydrocarbon gases comprises about 0.305 and 6.88 ppm, respectively, of the starting sludge mass; 70 to 80 wt% of the carbon is present as methane. The ~20-fold higher concentration of evolved hydrocarbon gas in the KC-1 Mix test mostly is attributed to the ninefold greater uranium corrosion as shown by Kr and Xe release. The additional factor of 2 higher hydrocarbon concentration suggests that agitation also may have aided the decomposition of the carbonaceous debris in the sludge by attrition. This explanation remains speculative, however.

Carbon dioxide comprises 99.8% and 96% of the gas generated from the KC-1 Un and KC-1 Mix sludge, respectively. The concentrations of inorganic carbon that evolved as carbon dioxide are similar (111 and 73 ppm, settled sludge basis) for KC-1 Un and KC-1 Mix. One potential source of CO₂ is through Reaction 11 to form becquerelite from schoepite and calcite. If so, calcium ion (from calcite or other sources) rather than schoepite is the limiting reagent in these tests, given the high uranium and low calcium concentrations in the KC-1 material (Table 2.4). The solution pH was not appreciably altered by reaction (Table 2.6); in the absence of buffering, a pH decrease would be expected if Reaction 11 occurred. Nevertheless, the inferred inorganic carbon concentrations are consistent with the 5.36- to 1990-ppm inorganic carbon concentrations observed previously in KE floor and Weasel Pit as-settled sludge (Makenas et al. 1996). The inorganic carbon concentration in KC-1 sludge has not been measured directly nor have XRD measurements been made to identify phases participating in Reaction 11.

If the CO₂ arises from the reaction of solid phase calcite and schoepite (Reaction 11), and thus involves the disappearance of these solid phases, the kinetics may be surface-area-dependent and subject to an inverse cubic rate law similar to that described in Section 4.6 of the Series I report for uranium metal

corrosion.^(a) Accordingly, total gas generation data for the KC-1 Un and KC-1 Mix tests at 95°C were plotted in accordance with a shrinking core model. Data from the first several hours following the temperature elevation to 95°C were not used because of exsolution of gas dissolved during the time at the lower hot cell temperature.

The inverse cubic relationship plots for the 95°C data from KC-1 Un and KC-1 Mix tests are shown in Figure 4.3. Also given on the plots are the equations for the best-fit line through the data and the resulting correlation coefficient, R^2 . To the extent of measurement accuracy, the reactions follow the inverse cubic rate law to 90% or greater reaction completion [i.e., $(1-f)^{1/3} < 0.4$].

Similar interpretations of the CO₂ generation data were made in the Series I tests for minus 250- μm canister sludge (KC-2/3 M250), and plus and minus 250- μm floor sludges (KC-4 M250, KC-4 P250, KC-5 M250, and KC-5 P250) reacted at 95°C. As in the prior tests, the variability (“noise”) of the data for both tests in Series II increases with reaction time. This is expected because the absolute rate of gas production decreases at advanced times and becomes more subject to random pressure and temperature fluctuations. The KC-1 Un and KC-1 Mix tests show rates (i.e., k'/r_0 or $k/r_0\rho$) of (1.02 and 1.13) $\times 10^{-3}$ /hour at 95°C that are within the range observed for the Series I tests [(0.74 to 1.22) $\times 10^{-3}$ /hour at 95°C].

Because the rate-determining mineral (calcite or schoepite in the case of Reaction 11), the associated densities of the minerals, and the mass-specific rates k or k' are unknown, the nominal particle size of the rate-determining material cannot be determined. However, the consistency of the slopes suggests that the same material, of essentially the same initial particle size, controls the CO₂-generating reaction rate in the Series II (KC-1) and Series I (KC-2/3, KC-4, and KC-5) tests. Because the original test materials arose from diverse areas of the KE Basin (floor, near the canisters, and within the canisters), the rate-determining reactant is broadly distributed, though with varying concentrations, in the KE Basin.

4.3 Gas Analysis for KC-1 P500 and M500 Canister Sludge at 80°C and 95°C

The KC-1 P500 and M500 canister sludge tests that began at 80°C (about 330 hours) and ended at 95°C (643 hours) produced about 0.045 and 0.016 moles of gas per kg settled sludge, respectively. The latter value is similar to that observed for both the KC-1 Un and KC-1 Mix tests reported in Section 4.2. The initial (and highest) gas generation rates at 80°C in each experiment are about 5.6×10^{-4} moles/kg-day.

^(a) The kinetics of the reaction of a spherical particle or a cube (or collection of equal-sized spherical or cubic particles) may be expressed analytically for reactions whose rates are proportional to the instantaneous surface area of the solid being consumed by reaction. The relevant rate law for spheres or cubes (as derived in Delegard et al. 2000) has the following inverse cubic dependence:

$$(1-f)^{\frac{1}{3}} = 1 - \frac{kt}{r_0\rho} = 1 - \frac{k't}{r_0}$$

in which f is the fraction reacted at time t , r_0 is the initial radius in μm , ρ is the material density in $\mu\text{g}/\mu\text{m}^3$, and k is the areal reaction rate expressed in $\mu\text{g}/\mu\text{m}^2\text{-hour}$. Dividing the areal reaction rate, k , by the material density, ρ , gives k' , the linear penetration rate in $\mu\text{m}/\text{hour}$. A plot of $(1-f)^{1/3}$ versus time (in hours) has a slope of k'/r_0 (or $k/r_0\rho$) and intercept on the vertical axis of 1.

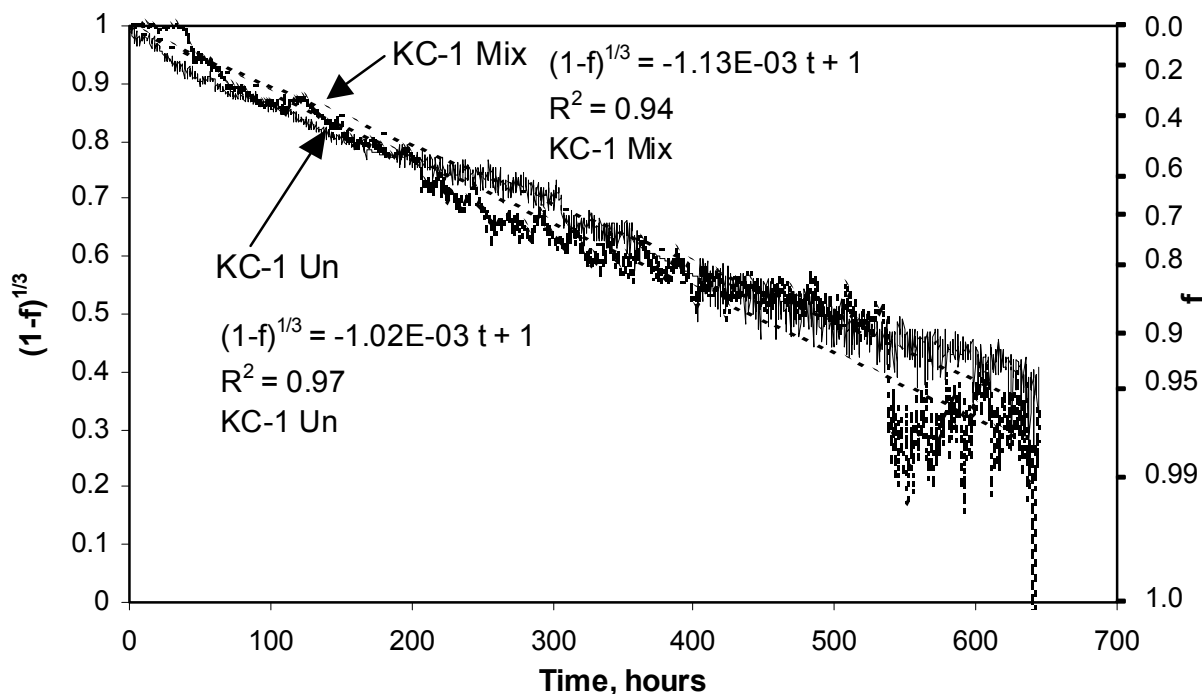


Figure 4.3. Inverse Cubic Function CO₂ Generation Kinetics Plot in the KC-1 Mix and KC-1 Un Tests at 95°C

This compares with 2.5×10^{-4} moles/kg-day observed for the KC-1 Un and KC-1 Mix sludges at 60°C. The KC-1 P500 sludge gas generation rate increased promptly when the temperature was elevated to 95°C and reached a maximum value of about 9.5×10^{-3} moles/kg-day; the KC-1 M500 rate remained relatively unchanged (except for some CO₂ exsolution at the temperature excursion and subsequently at sampling) when the temperature was raised to 95°C (Figure 3.2).^(a) Judging by the flatness in the latter stages of Figure 3.2, the gas generation reactions apparently reached completion in each test.

The quantities of gas generated and consumed in each test are listed in Table 4.4 and show CO₂ to comprise 23% and H₂ 74% of the KC-1 P500 gas (the balance is hydrocarbons, Kr, and Xe). The KC-1 M500 product gas is more like that observed for the KC-1 Un and KC-1 Mix tests – about 99.3% CO₂ and 0.3% H₂. Both N₂ and O₂ are consumed in the KC-1 P500 and M500 tests. A fraction of the N₂ returned to the gas phase during the period covered by the second sampling for both tests. Again, the N₂ production in the second interval may have been caused by conversion of UN_{1.75} to UO₂ by reaction with water or oxygen.

^(a) As shown in Figure 3.2, rapid gas production occurred for each experiment after the first sampling. The surges are postulated to occur by the following mechanism during the gas sampling sequence. During gas sampling, the vessels first are cooled from 80°C to the ~32°C hot cell temperature. Because the predominantly CO₂ product gas has much higher solubility in water at lower temperature, it partially dissolves in the moist sludge. After the vessel has reached hot cell temperature, the vapor space is sampled and the vapor space back-filled with neon. The vessels then are closed and reheated to 80°C. With heating, the CO₂ dissolved during the cooling phase is driven from solution and the gas surge ensues.

Table 4.4. Net and Cumulative Quantities of Gas Evolved for KC-1 P500 and M500 at 80°C and 95°C

Gas	Gas Quantities, moles, at Sampling Times			
	KC-1 P500		KC-1 M500	
	492.00 hr	969.34 hr	487.66 hr	964.66 hr
CO ₂	7.85E-05	6.02E-05	2.54E-04	1.86E-04
Cumulative	7.85E-05	1.39E-04	2.54E-04	4.39E-04
H ₂	3.60E-04	8.36E-05	4.91E-07	7.56E-07
Cumulative	3.60E-04	4.44E-04	4.91E-07	1.25E-06
N ₂	-5.05E-06	6.51E-07	-3.73E-06	9.65E-07
Cumulative	-5.05E-06	-4.40E-06	-3.73E-06	-2.76E-06
O ₂	-4.29E-06	-4.55E-07	-2.27E-06	-1.03E-07
Cumulative	-4.29E-06	-4.74E-06	-2.27E-06	-2.37E-06
CH ₄	1.28E-05	2.79E-06	1.02E-06	6.24E-07
Cumulative	1.28E-05	1.56E-05	1.02E-06	1.64E-06
C ₂ H _x	1.42E-06	4.55E-07	1.18E-07	
Cumulative	1.42E-06	1.88E-06	1.18E-07	1.18E-07
>C ₃ H _x	4.50E-07	1.76E-07	3.38E-08	
Cumulative	4.50E-07	6.26E-07	3.38E-08	3.38E-08
Σ C _y H _x C	1.71E-05	4.26E-06	1.36E-06	
Cumulative	1.71E-05	2.13E-05	1.36E-06	1.98E-06
⁸³ Kr	4.32E-08	7.34E-09		3.29E-10
Cumulative	4.32E-08	5.06E-08	0.00E+00	3.29E-10
⁸⁴ Kr	7.57E-08	1.17E-08	5.08E-09	4.93E-10
Cumulative	7.57E-08	8.74E-08	5.08E-09	5.57E-09
⁸⁵ Kr	1.08E-08	1.47E-09	3.38E-10	4.93E-11
Cumulative	1.08E-08	1.23E-08	3.38E-10	3.88E-10
⁸⁶ Kr	1.26E-07	1.47E-08	1.02E-08	9.86E-10
Cumulative	1.26E-07	1.41E-07	1.02E-08	1.11E-08
Σ Kr	2.56E-07	3.52E-08	1.56E-08	1.86E-09
Cumulative	2.56E-07	2.91E-07	1.56E-08	1.74E-08
¹³⁰ Xe	5.40E-10	5.87E-11		
Cumulative	5.40E-10	5.99E-10	0.00E+00	0.00E+00
¹³¹ Xe	2.34E-07	3.37E-08	1.52E-08	3.29E-09
Cumulative	2.34E-07	2.68E-07	1.52E-08	1.85E-08
¹³² Xe	3.60E-07	5.57E-08	2.20E-08	4.93E-09
Cumulative	3.60E-07	4.16E-07	2.20E-08	2.69E-08
¹³⁴ Xe	5.94E-07	9.39E-08	3.38E-08	6.57E-09
Cumulative	5.94E-07	6.88E-07	3.38E-08	4.04E-08
¹³⁶ Xe	8.83E-07	1.39E-07	4.91E-08	9.86E-09
Cumulative	8.83E-07	1.02E-06	4.91E-08	5.89E-08
Σ Xe	2.07E-06	3.23E-07	1.20E-07	2.46E-08
Cumulative	2.07E-06	2.39E-06	1.20E-07	1.45E-07

The high fraction of H₂ in the gas product and higher specific gas production for the KC-1 P500 sludge as compared with the KC-1 M500 sludge is reflected in the estimated uranium metal concentrations for the two materials. As shown in Table 4.5, the uranium metal concentration in the KC-1 P500 sludge is 0.39 wt%, about 60 times higher than found in the KC-1 M500 sludge (0.0066 wt%). The KC-1 Un and KC-1 Mix tests, derived from the same KC-1 sludge, are 0.0120 and 0.00877 wt% uranium metal, respectively, based on the chemical (H₂, O₂, N₂) data given in Table 4.2. Because the KC-1 P500 fraction represents about 12 wt% of the total KC-1 sludge and the M500 fraction about 88 wt%, the estimated uranium metal content in the combined size fractions is 0.051 wt% [(0.12×0.390%) + (0.88×0.00657%)], about five times higher than that observed for the KC-1 Un and KC-1 Mix tests.

The higher estimated total uranium metal concentration found by combining the results from the P500 and M500 portions of KC-1 sludge compared with the results found in the KC-1 Un and KC-1 Mix tests is unexpected. It is surmised that in the case of the KC-1 P500 test, enough uranium metal existed to produce a sufficiently high nascent hydrogen concentration to initiate the uranium hydride-mediated corrosion through Reactions 4 and 5 (see Section 4.1.1). In contrast, the other three tests (KC-1 Un, KC-1 Mix, and KC-1 M500) may not have generated sufficiently high hydrogen concentrations or pressures to form the active UH₃ intermediate or to dislodge the protective UO₂ coating on the uranium metal particles. In the tests having low hydrogen concentrations, the corrosion reaction of uranium with water by Reaction 1 would have remained at a low rate and not progressed to the rapid hydride-mediated mechanism described by Reactions 4 and 5.

Table 4.5. Reacted Metallic Uranium Calculated from Gas Generation and Consumption Reactions in KC-1 P500 and M500 Tests

Reaction	U Reacted Based on Various Reactions, moles		
	KC-1 P500	KC-1 M500	KC-1 Blend ^(a)
Settled Sludge Mass in Test, g	14.15	22.30	--
Reaction 1 $U + 2 H_2O \rightarrow UO_2 + 2 H_2$	2.22E-4	6.23E-7	--
Reaction 2 $U + O_2 \rightarrow UO_2$	4.74E-6	2.37E-6	--
Reaction 3 $U + 0.875 N_2 \rightarrow UN_{1.75}$	5.03E-6	3.16E-6	--
Total Moles U (Σ Reactions 1-3)	2.32E-4	6.15E-6	--
U metal, wt% settled sludge, Reactions 1-3	0.39	0.00657	0.0514
Settled Sludge Mass in Test, g	14.15	22.30	--
U metal, wt% settled sludge, Kr	3.69	0.140	0.556
U metal, wt% settled sludge, Xe	3.77	0.145	0.569

(a) Weighted combination of KC-1 P500 and KC-1 M500 results:
0.12 × (KC-1 P500 value) + 0.88 × (KC-1 M500 value).

A similar situation may be occurring in the Series I KC-2/3 P250 large-scale (~800-ml vessel volume) test run at ~32°C (Delegard et al. 2000, Section 4.4). That test was projected to have a 145-day induction time based on similar tests conducted in the small-scale (~30 ml) vessels. However, the KC-2/3 P250 large-scale test still has not overcome its induction time, even after ~420 days. In the Series I report it was stated that the longer induction time in the 32°C large-scale test is likely caused by the larger vapor/sludge volume ratio (~10) compared with the small-scale tests (~1). The H₂ concentration in the large-scale test would be more dilute and thus not sufficient to initiate the hydride-mediated corrosion. According to Wilkinson (1962, p. 838):

In aqueous corrosion, no uranium hydride will appear at any temperature below the boiling point unless hydrogen gas is trapped so as to build up the pressure in equilibrium with dissolved hydrogen in the water. The lower the temperature, the higher is the pressure of hydrogen that will be required to provide the activity necessary to form a hydride.

About 96% of the uranium metal corrosion in the KC-1 P500 test is from the reaction with water, judging from the H₂ quantity evolved; about 10% of the uranium corrosion in the KC-1 M500 test is due to reaction with water. The reactions of uranium metal with O₂ and N₂ also are greater in the uranium-rich KC-1 P500 test than in the KC-1 M500 test. The higher uranium metal concentration in the larger size-fraction sludge in these tests with KC-1 P500 (>500 μm) and KC-1 M500 (<500 μm) sludges also was observed in the Series I tests for the KC-2/3, KC-4, and KC-5 sludges segregated at the 250-μm threshold. The classification of uranium metal to larger size fractions was attributed to adherence of the uranium oxide product to the underlying uranium metal and to the formation of oxide/metal particles from larger metal particles arising from fuel fragmentation by moist thermal treatment of fuel. A similar phenomenon also may be operant in the KC-1 P500 and M500 tests.

As seen in Table 4.5, the concentrations of uranium metal predicted based on Kr and Xe release agree well with each other for the KC-1 P500 and M500 fractions and with results for the combined total KC-1 sludge. However, the uranium concentrations predicted by the Kr and Xe release for KC-1 P500 (3.7 wt%), M500 (0.14 wt%), and the combined KC-1 (0.57 wt%) sludge are about 10, 20, and 10 times higher, respectively, than predicted based on the corrosion reactions 1-3. Again, the most plausible explanation of the lower uranium concentration predicted based on the corrosion reactions is that uranium-rich sludge solids consume a substantial fraction of the hydrogen product. The uranium concentration calculated for the total KC-1 (weighted KC-1 P500 and M500) is 0.57 wt%, which agrees with the 0.56 wt% estimated from the KC-1 Mix test data, based in both cases on fission product gas release data.

Estimates of uranium metal concentration from both corrosion gas and fission product gas release show that very little metallic uranium is present in canister sludge made up of particles less than 500 μm. During Series I, sludge was fractionated at 250 μm, so questions remained about the uranium metal content in particles in the 250-μm to 500-μm range. Furthermore, since the KC-1 sample was stored at about 32°C for 14 months, the uranium metal particles in the P500 fraction were probably initially present at a size significantly larger than 500 μm. Using the rate equation for uranium metal with oxygen free water given in the *Spent Nuclear Fuel Project Technical Data Book, Volume 1* (Reilly 1998; Equation 6 in Section 4.1.1 of this report), it is estimated that a spherical uranium metal particle 975 μm in diameter would corrode to about 500 μm after 14 months at 32°C. When considering the 9½-month difference in storage times between the canister sludge used in Series I (KC-2/3) and the canister sludge used in Series II (KC-1), the estimated uranium metal contents are comparable. Canister sludge sample KC-2/3, which

contained ~1.9 wt% uranium metal, was reasonably well modeled by assuming an initial particle size of 800 μm (range was 680 to 970 μm) (Delegard et al. 2000). Using Equation 6, in 9½ months at 32°C, about 75 wt% of an 800- μm uranium metal particle will corrode. That is, sludge initially containing ~1.9 wt% uranium metal is projected to contain ~0.48 wt% uranium metal after the 9½ months at 32°C – which is close to the 0.56 wt% estimated for KC-1.

A similar extrapolation was performed to estimate the uranium metal content of KC-1 P500 at the beginning of the 9½-month storage period (Appendix B). The results from this extrapolation predict that KC-1 P500 contained about 13 wt% uranium metal when placed on the same time basis as KC-2/3 P250, which was shown to contain 7.4 wt% uranium metal. The higher predicted uranium metal for KC-1 P500 may partially be attributed to the fact that the uranium metal was concentrated in a smaller sample mass for KC-1. The P500 fraction of KC-1 comprised about 12% of the KC-1 (whole) sample (Section 2.2.1), while the P250 fraction comprised about 22% of KC-2/3 (whole) (Delegard et al. 2000).

Isotope ratios observed for the Kr and Xe fission product gases are compared with ORIGEN code predictions in Table 4.6. The ^{83}Kr concentration is low in the KC-1 M500 test (at least partially due to a lower-than-detection limit value in the first gas sampling; see Table 4.4), but other isotope concentrations and the final Xe:Kr mole ratios all are consistent with expectations from the ORIGEN code. The ^{85}Kr concentrations in the P500 and M500 tests imply times since discharge of 7.5 and 18 years, respectively. The value for P500 is not credible given the 14-plus years between the last irradiation in N Reactor and when these tests were conducted. The 7.5- and 18-year times compare with 17 and 30 years since discharge predicted from the KC-1 Un and KC-1 Mix sludge tests derived from the same source sludge.

The hydrocarbon gases (primarily methane) generated in the KC-1 P500 and M500 tests represent 18 ppm and 1.1 ppm carbon in the sludge, respectively, and are similar to the 0.30 and 6.9 ppm carbon found in the KC-1 Un and KC-1 Mix tests. The carbide concentrations in the uranium metal (based on Kr and Xe determinations of uranium metal concentrations) are about 480 and 750 ppmp U, respectively, for the KC-1 P500 and M500 tests. These values are similar to those observed in the KC-1 Un and KC-1 Mix tests and also agree with the expected 550 ± 185 ppmp value. About 73% and 83% of the hydrocarbon

Table 4.6. Isotope Ratios for KC-1 P500 and M500 Tests

Gas	Isotopic Composition, atom%		ORIGEN ^(a)
	KC-1 P500	KC-1 M500	
^{83}Kr	17.4	1.9	13.3
^{84}Kr	30.0	32.0	28.3
^{85}Kr	4.2	2.2	6.8
^{86}Kr	48.4	63.9	51.5
^{130}Xe	0.0	0.0	0.05
^{131}Xe	11.2	12.8	10.7
^{132}Xe	17.4	18.6	18.0
^{134}Xe	28.7	27.9	28.0
^{136}Xe	42.7	40.7	43.2
Xe:Kr	8.2	8.3	8.2

(a) ORIGEN2 calculation for N Reactor MkIV fuel at 2921 MWD/TeU; ratios change <3% relative at lower burnups; ^{85}Kr has a 10.76-year half-life.

carbon in the KC-1 P500 and M500 tests, respectively, are from methane. These percentages are similar to those found in the tests with KC-1 Un and KC-1 Mix sludge and with the 59% to 73% observed in the Series I tests with KC-2/3 P250 sludge.

The CO₂ evolved from the KC-1 P500 and M500 tests gives qualitative evidence of the reaction of schoepite with calcite to form becquerelite but, again, little pH change was observed after reaction. The CO₂ quantities correspond to a lower limit of inorganic carbon concentration in the settled sludge of 51 and 100 ppm, respectively. These values are similar to those found in the KC-1 Un and KC-1 Mix tests. The total carbon reporting to the gas phase as hydrocarbon and CO₂ gases in the KC-1 tests is about 111, 80, 69, and 101 ppm for KC-1 Un, KC-1 Mix, KC-1 P500, and KC-1 M500, respectively. No chemical analyses of the KC-1 sludge for organic or inorganic carbon concentrations were performed, however.

4.4 Gas Analysis for FE-1, FE-3, FE-5 and FE-4/6 Single-Pull Sludges at 90°C and 95°C

Samples from FE-1, FE-3, FE-5, and FE-4/6 single-pull KE Basin sludges were run at 90°C for about 490 hours and then at 95°C for a further 477 hours. The FE-3 and FE-5 sludges each produced about 0.005 moles total gas per kg sludge and seemed to have reached exhaustion in gas production, judging by the flatness of the gas production rate beyond about 800 hours. The FE-1 and FE-4/6 sludges each produced about 0.015 moles of gas per kg sludge, but did not appear to be at completion at the end of nearly 1000 hours of heating (Figure 3.3). The gas generation rates for all tests were relatively constant over the first 800 hours of reaction and did not increase significantly when the temperature rose from 90°C to 95°C. The maximum rates were about 5.4×10^{-4} moles/kg-day for the FE-1 and FE-4/6 sludges and about 1.8×10^{-4} moles/kg-day for the FE-3 and FE-5 sludges.

The quantities of gas generated and consumed in each test are listed in Table 4.7. Carbon dioxide is the predominant gas product in each test and comprises 96.7%, 99.4%, 98.7%, and 99.1% of the FE-1, FE-3, FE-5, and FE-4/6 gas, respectively. Hydrogen constitutes most of the remaining gas at 3.0%, 0.33%, 1.1%, and 0.73% of the respective products. The balance is hydrocarbon (e.g., methane, ethane) and Xe fission product gases. Note, however, that no Kr was detectable in any test, and Xe was also below detection in the test with FE-3 sludge. Both oxygen and nitrogen were consumed in all tests. Similar to the tests with KC-1 sludge, in which N₂ was evolved in the period of the second sampling in all four cases (see Sections 4.2 and 4.3), N₂ evolution was observed in the second sampling in each of the single-pull tests. The conversion of UN_{1.75} to UO₂ by reaction with water or oxygen may be the cause of the N₂ production in the second interval.

Estimated quantities of uranium metal corroded, based on evidence of reaction with water, O₂, and N₂, are given in Table 4.8. The total uranium metal concentrations in the FE single-pull sludges are remarkably consistent (0.013 to 0.017 wt%) and are slightly higher than the ~0.01% uranium metal concentrations found in the same manner for the KC-1 Un and KC-1 Mix sludge tests. The contributions of Reactions 1-3 to uranium metal corrosion vary from test to test, however. For the FE-1 sludge, Reactions 1 and 3 provide about 40% each and Reaction 2 provides 20% of the corrosion. Reactions 2 and 3 provide nearly all the corrosion in the FE-3 and FE-5 tests; nearly 80% is by O₂ alone in the FE-5. Uranium in the FE-4/6 test was corroded 14% by Reaction 1, 55% by Reaction 2, and 31% by Reaction 3.

The Kr isotope concentrations were below detection limits and Xe concentrations were near or below detection limits for all the single-pull tests. However, unlike the tests with the KC-1 sludge, the uranium

Table 4.7. Net and Cumulative Quantities of Gas Evolved for FE-1, FE-3, FE-5, and FE-4/6 at 90°C and 95°C

Gas	Gas Quantities, moles, at Sampling Times							
	FE-1		FE-3		FE-5		FE-4/6	
	495.00 hr	972.00 hr	493.00 hr	970.00 hr	493.33 hr	969.67 hr	486.33 hr	963.00 hr
CO ₂	2.35E-04	2.34E-04	8.52E-05	8.31E-05	7.71E-05	8.02E-05	1.87E-04	1.65E-04
Cumulative	2.35E-04	4.69E-04	8.52E-05	1.68E-04	7.71E-05	1.57E-04	1.87E-04	3.53E-04
H ₂	1.33E-05	1.48E-06	2.53E-07	3.06E-07	7.32E-07	9.82E-07	1.22E-06	1.38E-06
Cumulative	1.33E-05	1.47E-05	2.53E-07	5.58E-07	7.32E-07	1.71E-06	1.22E-06	2.60E-06
N ₂	-5.77E-06	3.09E-07	-7.11E-06	1.19E-06	-2.13E-06	1.89E-07	-2.80E-06	3.63E-07
Cumulative	-5.77E-06	-5.46E-06	-7.11E-06	-5.92E-06	-2.13E-06	-1.94E-06	-2.80E-06	-2.44E-06
O ₂	-3.10E-06	-4.05E-07	-4.03E-06	-7.81E-07	-9.46E-06	-1.52E-06	-4.05E-06	-9.54E-07
Cumulative	-3.10E-06	-3.51E-06	-4.03E-06	-4.81E-06	-9.46E-06	-1.10E-05	-4.05E-06	-5.00E-06
CH ₄	1.05E-07	3.44E-08	5.42E-08	5.39E-08	6.51E-08	8.18E-08	8.14E-08	6.49E-08
Cumulative	1.05E-07	1.39E-07	5.42E-08	1.08E-07	6.51E-08	1.47E-07	8.14E-08	1.46E-07
C ₂ H _x	3.31E-07	3.78E-07	1.08E-07	8.99E-08	4.88E-08	4.91E-08	1.14E-07	9.73E-08
Cumulative	3.31E-07	7.10E-07	1.08E-07	1.98E-07	4.88E-08	9.79E-08	1.14E-07	2.11E-07
>C ₃ H _x	1.05E-07	6.88E-08	9.03E-08	8.99E-08	1.63E-08	4.91E-08	8.14E-08	6.49E-08
Cumulative	1.05E-07	1.73E-07	9.03E-08	1.80E-07	1.63E-08	6.54E-08	8.14E-08	1.46E-07
Σ C _y H _x C	1.10E-06	1.01E-06	5.57E-07	5.19E-07	2.14E-07	3.36E-07	5.68E-07	4.65E-07
Cumulative	1.10E-06	2.11E-06	5.57E-07	1.08E-06	2.14E-07	5.50E-07	5.68E-07	1.03E-06
⁸³ Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
⁸⁴ Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
⁸⁵ Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
⁸⁶ Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Σ Kr	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cumulative	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
¹³⁰ Xe	3.49E-10						9.77E-10	
Cumulative	3.49E-10	3.49E-10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.77E-10	9.77E-10
¹³¹ Xe	2.27E-09	3.44E-10			1.63E-09	9.82E-10	4.89E-10	
Cumulative	2.27E-09	2.61E-09	0.00E+00	0.00E+00	1.63E-09	2.61E-09	4.89E-10	4.89E-10
¹³² Xe	3.49E-09	5.16E-10			3.25E-09	1.47E-09	1.14E-09	
Cumulative	3.49E-09	4.00E-09	0.00E+00	0.00E+00	3.25E-09	4.73E-09	1.14E-09	1.14E-09
¹³⁴ Xe	8.72E-09	6.88E-10			4.88E-09	1.64E-09	6.52E-10	
Cumulative	8.72E-09	9.41E-09	0.00E+00	0.00E+00	4.88E-09	6.52E-09	6.52E-10	6.52E-10
¹³⁶ Xe	8.72E-09	1.03E-09			8.13E-09	3.27E-09	4.89E-10	
Cumulative	8.72E-09	9.75E-09	0.00E+00	0.00E+00	8.13E-09	1.14E-08	4.89E-10	4.89E-10
Σ Xe	2.35E-08	2.58E-09	0.00E+00	0.00E+00	1.79E-08	7.37E-09	3.75E-09	0.00E+00
Cumulative	2.35E-08	2.61E-08	0.00E+00	0.00E+00	1.79E-08	2.53E-08	3.75E-09	3.75E-09

Table 4.8. Reacted Metallic Uranium Calculated from Gas Generation and Consumption Reactions in FE-1, FE-3, FE-5, and FE-4/6 Tests

Reaction	U Reacted Based on Various Reactions, moles			
	FE-1	FE-3	FE-5	FE-4/6
Settled Sludge Mass in Test, g	27.00	21.22	19.93	15.87
Reaction 1 $U + 2 H_2O \rightarrow UO_2 + 2 H_2$	7.37E-6	2.79E-7	8.57E-7	1.30E-6
Reaction 2 $U + O_2 \rightarrow UO_2$	3.51E-6	4.81E-6	1.10E-5	5.00E-6
Reaction 3 $U + 0.875 N_2 \rightarrow UN_{1.75}$	6.24E-6	6.77E-6	2.22E-6	2.79E-6
Total Moles U (Σ Reactions 1-3)	1.71E-5	1.19E-5	1.41E-5	9.09E-6
U metal, wt% settled sludge, Reactions 1-3	0.0151	0.00133	0.0168	0.0136
U metal, wt% settled sludge, Kr	--	--	--	--
U metal, wt% settled sludge, Xe	0.0215	--	0.0272	0.00519

metal concentrations found for the FE-1, FE-3, and FE-4/6 sludge tests, based on Xe fission product gas release, were comparable with the concentrations predicted based on Reactions 1-3.

Because of the low Xe gas concentrations, the Xe isotope percentages correspond poorly with those predicted by ORIGEN, except for the FE-5 results (Table 4.9).

The hydrocarbon concentrations found in FE-1, FE-3, FE-5, and FE-4/6 are 0.94, 0.61, 0.33, and 0.78 ppm, respectively. These concentrations are lower than found for all but one of the KC-1 tests.

Table 4.9. Isotope Ratios for FE-1, FE-3, FE-5, and FE-4/6 Tests

Gas	Isotopic Composition, atom%				ORIGEN ^(a)
	FE-1	FE-3	FE-5	FE-4/6	
⁸³ Kr	--	--	--	--	13.3
⁸⁴ Kr	--	--	--	--	28.3
⁸⁵ Kr	--	--	--	--	6.8
⁸⁶ Kr	--	--	--	--	51.5
¹³⁰ Xe	1.3	--	--	26.1	0.05
¹³¹ Xe	10.0	--	10.3	13.0	10.7
¹³² Xe	15.3	--	18.7	30.4	18.0
¹³⁴ Xe	36.0	--	25.8	17.4	28.0
¹³⁶ Xe	37.3	--	45.2	13.0	43.2
Xe:Kr	--	--	--	--	8.2

(a) ORIGEN2 calculation for N Reactor MkIV fuel at 2921 MWD/TeU; ratios change <3% relative at lower burnups; ⁸⁵Kr has a 10.76-year half-life.

Methane comprises 6.6%, 10%, 27%, and 14% of the carbon in the evolved hydrocarbon as compared with 70% to 80% in the tests with KC-1 sludge. Based on the uranium metal concentrations derived from the Xe results, carbide concentrations of 4400, 1200, and 15000 ppmp in the uranium metal are projected for FE-1, FE-5, and FE-4/6, respectively. These anomalously high values, and the low fraction of methane, suggest that substantial contamination of noncarbide-origin hydrocarbon was present in the gas samples.

Carbon dioxide constitutes most of the gas product in the single-pull floor and pit sludge tests. The CO₂ production found in the FE-1, FE-3, FE-5, and FE-4/6 tests correspond to 104-, 47-, 48-, and 125-ppm lower limits in inorganic carbon concentrations in the respective settled sludges. This range is similar to the 51- to 111-ppm values found for the KC-1 sludge tests. However, the inorganic carbon concentrations found by chemical characterization of these sludges are much higher (1240, 1150, and 480 ppm for FE-3, FE-5, and the FE-4/6 composite, respectively; FE-1 was not analyzed for total inorganic carbon).

The low reactivity and gas generation rate from the single-pull sludge samples is consistent with the results from reaction calorimetry testing. Subsamples of FE-1, FE-3, FE-5, and FE-6 were evaluated for uranium metal content using an acid calorimetry technique at PNNL's Radiochemistry Processing Laboratory in September 2000 (Bredt et al. 2000). The results from this testing indicated that the samples contained little or no uranium metal. Additional calorimetry testing, using the reactive system screening tool (RSST), was performed on subsamples of FE-1, FE-3, FE-5, FE-6, and FE-7 at the 222-S Laboratory in June 2000 (Steen 2000). From the results of the RSST testing, it was concluded that all of these samples exhibited low thermochemical activity and low gas generation.

4.5 Gas Analysis for KC-6 and 96-06 Sludges at 90°C and 95°C

A sample of KC-6 KE Basin sludge was heated at 90°C for 327 hours and then at 95°C for a further 642 hours. An archived sample of KE canister sludge, 96-06, began with 324 hours of heating at 80°C and was completed by 624 hours of heating at 95°C. The KC-6 sludge produced about 0.007 moles of gas per kilogram; the 96-06 sludge only produced about 0.002 moles of gas per kilogram. The KC-6 sludge still seemed to be producing gas after nearly 1000 hours of heating, whereas the 96-06 sludge evidently was at completion in its gas-generating reactions (Figure 3.4). Both tests inexplicably showed sharp downturns in gas generation for about 60 hours, just after the temperature increase to 95°C. After these dips, the KC-6 sludge generated gas at a fairly constant rate through the end of the test, whereas the 96-06 sludge produced gas for about 150 hours and then was quiescent for the final 500 hours of the test. The maximum gas generation rates were about 5×10^{-4} moles/kg-day for the KC-6 sludge and 3×10^{-4} moles/kg-day for the 96-06 sludge.

The quantities of gas generated and consumed in each test are listed in Table 4.10. Carbon dioxide again is the predominant gas product, comprising 91.4% of the KC-6 and 96.4% of the 96-06 output. Hydrogen constitutes most of the remaining gas at 8.5% and 2.3%, with hydrocarbon (e.g., methane, ethane) and fission product gases constituting the balance. However, both Kr and Xe were below detection in the KC-6 test. Both oxygen and nitrogen were consumed in the KC-6 test and oxygen in the 96-06 test. Nitrogen was consumed in the period before the first sampling in both tests and evolved over the period of the second sampling. The amount of N₂ produced in the second period for the 96-06 test was more than that reacted in the first period, however.

Table 4.10. Net and Cumulative Quantities of Gas Evolved for KC-6 at 90°C and 95°C and 96-06 at 80°C and 95°C

Gas	Gas Quantities, moles, at Sampling Times			
	KC-6		96-06	
	491.66 hr	968.33 hr	470.67 hr	947.33 hr
CO ₂	9.60E-05	1.06E-04	6.03E-05	3.32E-05
Cumulative	9.60E-05	2.02E-04	6.03E-05	9.36E-05
H ₂	1.03E-05	8.54E-06	1.59E-06	6.15E-07
Cumulative	1.03E-05	1.89E-05	1.59E-06	2.21E-06
N ₂	-5.22E-06	1.74E-06	-2.55E-06	7.53E-06
Cumulative	-5.22E-06	-3.49E-06	-2.55E-06	4.98E-06
O ₂	-5.22E-06	-1.82E-06	-2.32E-06	-4.93E-06
Cumulative	-5.22E-06	-7.04E-06	-2.32E-06	-7.25E-06
CH ₄	3.62E-08	3.71E-08	8.38E-08	4.55E-08
Cumulative	3.62E-08	7.33E-08	8.38E-08	1.29E-07
C ₂ H _x			8.38E-08	
Cumulative	0.00E+00	0.00E+00	8.38E-08	8.38E-08
≥C ₃ H _x	1.81E-08		5.03E-08	4.55E-08
Cumulative	1.81E-08	1.81E-08	5.03E-08	9.58E-08
Σ C _y H _x C			4.11E-07	
Cumulative	9.36E-08	1.31E-07	4.11E-07	6.01E-07
⁸³ Kr			1.51E-09	1.37E-08
Cumulative	0.00E+00	0.00E+00	1.51E-09	1.52E-08
⁸⁴ Kr			3.35E-09	2.28E-08
Cumulative	0.00E+00	0.00E+00	3.35E-09	2.61E-08
⁸⁵ Kr			1.68E-10	2.28E-09
Cumulative	0.00E+00	0.00E+00	1.68E-10	2.44E-09
⁸⁶ Kr			1.17E-08	3.19E-08
Cumulative	0.00E+00	0.00E+00	1.17E-08	4.36E-08
Σ Kr	0.00E+00	0.00E+00	1.68E-08	7.06E-08
Cumulative	0.00E+00	0.00E+00	1.68E-08	8.73E-08
¹³⁰ Xe				
Cumulative	0.00E+00	0.00E+00	0.00E+00	0.00E+00
¹³¹ Xe			1.68E-08	7.97E-08
Cumulative	0.00E+00	0.00E+00	1.68E-08	9.64E-08
¹³² Xe			2.35E-08	1.34E-07
Cumulative	0.00E+00	0.00E+00	2.35E-08	1.58E-07
¹³⁴ Xe			3.35E-08	2.09E-07
Cumulative	0.00E+00	0.00E+00	3.35E-08	2.43E-07
¹³⁶ Xe			5.03E-08	3.19E-07
Cumulative	0.00E+00	0.00E+00	5.03E-08	3.69E-07
Σ Xe	0.00E+00	0.00E+00	1.24E-07	7.42E-07
Cumulative	0.00E+00	0.00E+00	1.24E-07	8.66E-07

Estimated quantities of uranium metal corroded by Reactions 1-3 given in Table 4.11 are 0.026 wt% and 0.0032 wt% for KC-6 and 96-06, respectively, and are comparable to the uranium metal concentrations estimated for the other tests in Series II, except for KC-1 P500. Reaction 1 (to produce H₂) comprises about 40% of the total uranium metal corrosion in both tests. The net production of N₂ in the 96-06 test negates a substantial fraction of the estimated uranium corroded by reactions with water and O₂.

The Kr and Xe isotope concentrations were below detection limits for the KC-6 test, making it impossible to predict uranium metal concentration based on fission product gas release. The uranium metal concentrations based on Kr and Xe release are similar (each about 0.9 wt%) for the 96-06 sludge and are almost 300 times higher than predicted based on the corrosion gas analyses. Like the situation found for the KC-6 sludge tests, consumption of freed H₂ by reaction with U(VI) compounds in the uranium-rich 96-06 sludge may have been responsible for the apparent shortfall in H₂ gas evolution by uranium reaction with water.

Because of the long sample storage period (~4 years) and the fact that the sample dried out, the original uranium metal content of 96-06, at the time of sampling, cannot be confidently estimated.

Because of the low (undetectable) Kr and Xe gas concentrations, no evaluation of isotopic compositions, cooling time, or uranium metal concentration could be made for the KC-6 sludge. The Kr and Xe isotope distributions for the 96-06 test are similar to those predicted by ORIGEN (Table 4.12). The ⁸⁵Kr decay corresponds to a cooling time of about 14 years or about the last time N Reactor was at power.

The hydrocarbon concentrations in the KC-6 and 96-06 sludges are 0.082 and 0.37 ppm, respectively, and are lower than all other tests in this series except those of KC-1 Un and FE-5 (0.030 and 0.33 ppm). Methane comprises 56% and 21% of the carbon in the evolved hydrocarbon, respectively, in contrast to

Table 4.11. Reacted Metallic Uranium Calculated from Gas Generation and Consumption Reactions in KC-6 and 96-06 Tests

Reaction	U Reacted Based on Various Reactions, moles	
	KC-6	96-06
Settled Sludge Mass in Test, g	19.10	19.51
Reaction 1 $U + 2 H_2O \rightarrow UO_2 + 2 H_2$	9.43E-6	1.10E-6
Reaction 2 $U + O_2 \rightarrow UO_2$	7.04E-6	7.25E-6
Reaction 3 $U + 0.875 N_2 \rightarrow UN_{1.75}$	3.98E-6	-5.69E-6
Total Moles U (Σ Reactions 1-3)	2.05E-5	2.66E-6
U metal, wt% settled sludge, Reactions 1-3	0.0255	0.00325
U metal, wt% settled sludge, Kr	--	0.804
U metal, wt% settled sludge, Xe	--	0.990

Table 4.12. Isotope Ratios for 96-06 Test

Gas	Isotopic Composition, atom%	ORIGEN ^(a)
⁸³ Kr	17.4	13.3
⁸⁴ Kr	29.9	28.3
⁸⁵ Kr	2.8	6.8
⁸⁶ Kr	49.9	51.5
¹³⁰ Xe	0.0	0.05
¹³¹ Xe	11.1	10.7
¹³² Xe	18.2	18.0
¹³⁴ Xe	28.0	28.0
¹³⁶ Xe	42.6	43.2
Xe:Kr	9.9	8.2

(a) ORIGEN2 calculation for N Reactor MkIV fuel at 2921 MWD/TeU; ratios change <3% relative at lower burnups; ⁸⁵Kr has a 10.76-year half-life.

70-80% in the tests with KC-1 sludge. The carbide concentration is apparently 315 ppm uranium metal, based on the reaction gas (H₂, O₂, and N₂) result from the KC-6 sludge, and is consistent with the concentration expected in the fuel. The carbide concentration inferred for the 96-06 sludge is 41 ppm uranium and is unusually low.

Again, CO₂ comprises most of the gas product in the KC-6 and 96-06 sludge tests, corresponding to 66- and 20-ppm lower limits in inorganic carbon concentration, respectively. The inorganic carbon concentrations found by chemical characterization of the 96-06 dry sludge is about 600 ppm (i.e., about 300 ppm for the as-settled sludge), and thus is much higher than found by release of CO₂.

4.6 Conclusions

Several conclusions were drawn from the Series II testing and from analyses of the data derived from the various tests:

- Overall, the sludge samples evaluated in the Series II tests were relatively benign and unreactive, as demonstrated by their low gas generation rates. In comparison, the KE canister and floor sludge tested in Series I exhibited a higher uranium metal content than similar sludge tested in Series II. Because the sludge material used in Series II was stored for a longer period of time at slightly elevated temperatures, the Series I results more accurately reflect the uranium metal content of the sludge in the KE Basin.
- For certain sludge samples in Series II, use of fission product gas (Kr and Xe) release data resulted in a higher and more accurate estimation of the uranium metal content in comparison with the corrosion gas (H₂, O₂, N₂) data.
- Canister sludge that had been stored wet in a shielded facility for 14 months at ~32°C, after sample collection, contained about 0.56 wt% uranium metal (based on analysis of the release of fission product gases).
- Testing with canister sludge (stored for 14 months at 32°C) showed that very little metallic uranium is present in the material containing particles less than 500 μm.

- Aggressive agitation and sieving of canister sludge resulted in a 9X increase in the quantity of uranium metal that reacted over the test period (i.e., without agitation, 0.065 wt% of sample reacted; with agitation, 0.56 wt% of sample reacted.)
- The single-pull core floor and pit sludge samples displayed very low chemical reactivity, provided little gas generation, and are estimated to contain 0.0013 to 0.027 wt% metallic uranium (settled sludge basis).
- Sludge that consisted primarily of organic ion exchange resin beads generated very little gas even after 950 hours at temperatures of 90°C and 95°C. It is estimated that this material contains about 0.026 wt% uranium metal.
- Archived canister sludge from the 1996 sampling campaign no longer demonstrated significant reactivity. Based on analysis of the release of fission product gases, this sludge was estimated to contain about 0.9 wt% uranium metal (settled sludge basis).

5.0 References

- Baker, R. B., T. L. Welsh, and B. J. Makenas. 2000. *Sampling and Analysis Plan for Sludge from the 105-K Basins to Support Transport to and Storage in T Plant*. HNF-6479, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Bradley, M. J., and L. M. Ferris. 1962. "Hydrolysis of Uranium Carbides between 25 and 100°. I. Uranium Monocarbide." *Inorganic Chemistry* 1(3):683-687.
- Bradley, M. J., and L. M. Ferris. 1964. "Hydrolysis of Uranium Carbides between 25 and 100°. II. Uranium Dicarbide, Uranium Metal-Monocarbide Mixtures, and Uranium Monocarbide-Dicarbide Mixtures." *Inorganic Chemistry* 3(2):189-195.
- Bredt, P. R., C. H. Delegard, A. J. Schmidt, and K. L. Silvers. 1999. *Testing and Analysis of Consolidated Sludge Sample from 105K East Basin Floor and Canisters*. PNNL-13341, Pacific Northwest National Laboratory, Richland, Washington.
- Bredt, P. R., C. H. Delegard, A. J. Schmidt, K. L. Silvers, B. M. Thornton, and S. R. Gano. 2000. *Particle Size (Sieving) and Enthalpy (Acid Calorimetry) Analysis of Single-Pull K East Basin Floor and Pit Sludges*. PNNL-13373, Pacific Northwest National Laboratory, Richland, Washington.
- Bryan, S. A., and L. R. Pederson. 1995. *Thermal and Combined Thermal and Radiolytic Reactions Involving Nitrous Oxide, Hydrogen, and Nitrogen in the Gas Phase: Comparison of Gas Generation Rates in Supernate and Solid Fractions of Tank 241-SY-101 Simulated Wastes*. PNL-10490, Pacific Northwest National Laboratory, Richland, Washington.
- Bryan, S. A., L. R. Pederson, C. M. King, S. V. Forbes, and R. L. Sell. 1996. *Gas Generation from Tank 241-SY-103 Waste*. PNL-10798, Pacific Northwest National Laboratory, Richland, Washington.
- Cordfunke, E.H.P. 1969. *The Chemistry of Uranium*, p. 188. Elsevier Publishing Company, Amsterdam, Netherlands.
- Delegard, C. H., S. A. Bryan, A. J. Schmidt, P. R. Bredt, C. M. King, R. L. Sell, L. L. Burger, and K. L. Silvers. 2000. *Gas Generation from K East Basin Sludges – Series I Testing*. PNNL-13320, Pacific Northwest National Laboratory, Richland, Washington.
- Elmore, M. R., A. J. Schmidt, K. L. Silvers, B. M. Thornton, and S. R. Gano. 2000. *Chemical and Radiochemical Analysis of Consolidated Sludge Samples from K East Basin*. PNNL-13360, Pacific Northwest National Laboratory, Richland, Washington.
- Gillies, D. M. 1958. "Some Studies of the Reactions of Uranium Oxides with Hydrogen, Oxygen, and Water." In *Chemistry of Uranium -- Collected Papers*, TID-5290, pp. 746-747, Paper 76, J. J. Katz and E. Rabinowitch, editors. United States Atomic Energy Commission, Oak Ridge, Tennessee.
- Johnson, A. B., R. G. Ballinger, and K. A. Simpson. 1994. "Kinetic and Thermodynamic Bases to Resolve Issues Regarding Conditioning of Uranium Metal Fuels." PNL-SA-24458, Pacific Northwest Laboratory, Richland, Washington.

- King, C. M., L. R. Pederson, and S. A. Bryan. 1997. *Thermal and Radiolytic Gas Generation from Tank 241-S-102 Waste*. PNNL-11600, Pacific Northwest National Laboratory, Richland, Washington.
- Makenas, B. J., T. L. Welsh, R. B. Baker, D. R. Hansen, and G. R. Golcar. 1996. *Analysis of Sludge from Hanford K East Basin Floor and Weasel Pit*. WHC-SP-1182, Westinghouse Hanford Company, Richland, Washington.
- Makenas, B. J., T. L. Welsh, R. B. Baker, E. W. Hoppe, A. J. Schmidt, J. Abrefah, J. M. Tingey, P. R. Bredt, and G. R. Golcar. 1997. *Analysis of Sludge from Hanford K East Basin Canisters*. HNF-SP-1201, DE&S Hanford, Inc., Richland, Washington.
- Makenas, B. J., T. L. Welsh, R. B. Baker, G. R. Golcar, P. R. Bredt, A. J. Schmidt, and J. M. Tingey. 1998. *Analysis of Sludge from Hanford K West Basin Canisters*. HNF-1728, Rev. 0, Fluor Daniel Hanford, Richland, Washington.
- Makenas, B. J., A. J. Schmidt, K. L. Silvers, P. R. Bredt, C. H. Delegard, E. W. Hoppe, J. M. Tingey, A. H. Zacher, T. L. Welsh, R. B. Baker. 1999. *Supplementary Information on K-Basin Sludges*. HNF-2367, Rev. 0, Fluor Daniel Hanford, Richland, Washington.
- Makenas, B. J. 2000. *Data Quality Objectives for Analysis of Hanford K Basin Sludge to Support Transport to and Storage in T Plant*. HNF-5345, Rev. 0, Fluor Hanford, Inc., Richland, Washington.
- Marschman, S. C., T. D. Pyecha, and J. Abrefah. 1997. *Metallographic Examination of Damaged N Reactor Spent Nuclear Fuel Element SFEC5,4378*. PNNL-11438, Pacific Northwest National Laboratory, Richland, Washington.
- Montenyohl, V. I. 1960. "Corrosion of Uranium." Chapter 7, *Reactor Handbook*, 2nd edition, Vol. I, Materials, C. R. Tipton, Jr., editor. Interscience Publishers, Inc., New York.
- Pajunen, A. L. 1999. *Uranium Oxidation Rate Summary for the Spent Nuclear Fuel Project*. HNF-4165, Rev. 0, DE&S Hanford, Inc., Richland, Washington.
- Pearce, K. L., and S. C. Klimper. 2000. *105-K Basin Material Design Basis Feed Description for Spent Nuclear Fuel Project Facilities, Volume 2, Sludge*. HNF-SD-SNF-TI-009, Rev. 3, Fluor Hanford, Inc., Richland, Washington.
- Pitner, A. L. 1999. *K East Basin Sludge/Sampling 1999 Campaigns*. HNF-4746, Rev. 0, Numatec Hanford Corporation, Richland, Washington.
- Reilly, M. A. 1998. *Spent Nuclear Fuel Project Technical Databook, Volume 1*. HNF-SD-SNF-TI-015, Rev. 6, DE&S Hanford, Inc., Richland, Washington.
- Sandino, M., C. Amaia, and B. Grambow. 1994. "Solubility Equilibria in the U(VI)-Ca-K-Cl-H₂O System: Transformation of Schoepite into Becquerelite and Compregnacite." *Radiochimica Acta* 66/67:37-43.

- Schmidt, A. J., G. S. Klinger, and P. R. Bredt. 1998. *Evaluation of Ion Exchange Materials in K Basin Floor Sludge and Potential Solvents for PCB Extraction from Ion Exchange Materials*. PNNL-12108, Pacific Northwest National Laboratory, Richland, Washington.
- Sowder, A. G., S. B. Clark, and R. A. Fjeld. 1996. "The Effect of Silica and Phosphate on the Transformation of Schoepite to Becquerelite and Other Uranyl Phases." *Radiochimica Acta* 74:45-49.
- Sowder, A. G., S. B. Clark, and R. A. Fjeld. 1999. "The Transformation of Uranyl Oxide Hydrates: The Effect of Dehydration on Synthetic Metaschoepite and Its Alteration to Becquerelite." *Environmental Science and Technology* 33:3552-3557.
- Steen, F. H. 2000. *K-East Basin Floor and Pit Composite Sludge Samples, Analytical Results for the Final Report*. HNF-6053, Rev. 0A, Fluor Hanford, Inc., Richland, Washington.
- Troutner, V. H. 1960. *Mechanisms and Kinetics of Uranium Corrosion and Uranium Core Fuel Element Ruptures in Water and Steam*. HW-67370, Hanford Atomic Products Operation, Richland, Washington.
- Tyfield, S. P. 1988. "Corrosion of Reactor Grade Uranium in Aqueous Solutions Relevant to Storage and Transport." *Nuclear Engineering* 27(2):91-98.
- Vochten, R., and L. Van Haverbeke. 1990. "Transformation of Schoepite into the Uranyl Oxide Hydrates: Becquerelite, Billietite and Wölsendorfite." *Mineralogy and Petrology* 43:65-72.
- Waber, J. T. 1956. *A Review of the Corrosion Behavior of Uranium*. LA-2035, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.
- Weakley, E. A. 1979. *Fuels Engineering Technical Handbook*. UNI-M-61, UNC Nuclear Industries, Richland, Washington.
- Wilkinson, W. D. 1962. *Uranium Metallurgy*, Interscience Publishers, New York.
- Wronkiewicz, D. J., J. K. Bates, S. F. Wolf, and E. C. Buck. 1996. "Ten-Year Results from Unsaturated Drip Tests with UO₂ at 90°C: Implications for the Corrosion of Spent Nuclear Fuel." *Journal of Nuclear Materials* 238:78-95.

Appendix A

Gas Analysis and Gas Generation Rate Data

Table A.1. Gas Analyses for Test KC-1 Un at 60°C and 95°C

Run Sys -1	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	60,	84.4	0.017	0.011	14.4	0.01	0.003	0.0009	1.11	0.064	3.0E-05	5.0E-05		8.0E-05		5.0E-04	5.0E-04	8.0E-04	1.0E-03	293
	95			0.1	99.81	0.069	0.02	0.01	-1.578	-2.044	2.1E-04	3.5E-04		5.5E-04		3.5E-03	3.5E-03	5.5E-03	6.9E-03	167
2 22K61	95	87.1	0.018	0.009	11.1	0.01			1.48	0.29	2.0E-05	4.0E-05	3.0E-06	7.0E-05		2.0E-04	3.0E-04	5.0E-04	7.0E-04	477
				0.1	99.80	0.099			0.528	-0.821	1.8E-04	3.6E-04	2.7E-05	6.3E-04		1.8E-03	2.7E-03	4.5E-03	6.3E-03	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.2. Gas Analyses for Test KC-1 Mix at 60°C and 95°C

Run Sys -2	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	60,	86.6	0.016	0.084	11.8	0.24	0.023	0.005	1.03	0.19	6.0E-04	8.0E-04	6.0E-05	1.3E-03		1.9E-03	2.9E-03	4.6E-03	6.7E-03	330
	95			0.7	96.95	1.972	0.19	0.04	-1.84	-1.20	4.9E-03	6.6E-03	4.9E-04	1.1E-02		1.6E-02	2.4E-02	3.8E-02	5.5E-02	167
2 22K61	95	90	0.019	0.094	7.6	0.34	0.023	0.004	1.57	0.38	2.0E-04	5.0E-04	4.0E-05	9.0E-04	3.0E-06	1.0E-03	1.6E-03	2.8E-03	4.0E-03	477
				1.2	94.15	4.21	0.28	0.05	0.81	-0.29	2.5E-03	6.2E-03	5.0E-04	1.1E-02	3.7E-05	1.2E-02	2.0E-02	3.5E-02	5.0E-02	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.3. Gas Generation Rates from KC-1 Un at 60°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1	60,	6.65E-07	8.71E-04	6.0E-07	1.8E-7	5.4E-8	-1.4E-05	-1.8E-05	1.8E-9	3.0E-9		4.8E-9		3.0E-8	3.0E-8	4.8E-8	6.0E-8	293
	95																	167
2	95	5.05E-07	6.23E-04	6.2E-07			3.3E-06	-5.1E-06	1.1E-9	2.2E-9	1.7E-10	3.9E-9		1.1E-8	1.7E-8	2.8E-8	3.9E-8	477

Blank entries are below detection limits.

Table A.4. Gas Generation Rates from KC-1 Mix at 60°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1	60,	4.52E-06	6.36E-04	1.3E-05	1.2E-6	2.7E-7	-1.2E-05	-7.9E-06	3.2E-8	4.3E-8	3.2E-9	7.0E-8		1.0E-7	1.6E-7	2.5E-7	3.6E-7	330
	95																	167
2	95	5.07E-06	4.10E-04	1.8E-05	1.2E-6	2.2E-7	3.5E-06	-1.3E-06	1.1E-8	2.7E-8	2.2E-9	4.9E-8	1.6E-10	5.4E-8	8.6E-8	1.5E-7	2.2E-7	477

Blank entries are below detection limits.

Table A.5. Gas Analyses for Test KC-1 P500 at 80°C and 95°C

Run Sys -3	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	80,	73.7	0.015	20	4.36	0.71	0.079	0.025	0.89	0.076	2.4E-03	4.2E-03	6.0E-04	7.0E-03	3.0E-05	1.3E-02	2.0E-02	3.3E-02	4.9E-02	326
	95			79.04	17.23	2.806	0.312	0.099	-1.108	-0.941	9.5E-03	1.7E-02	2.4E-03	2.8E-02	1.2E-04	5.1E-02	7.9E-02	1.3E-01	1.9E-01	166
2 22K61	95	87.6	0.022	5.7	4.1	0.19	0.031	0.012	1.8	0.44	5.0E-04	8.0E-04	1.0E-04	1.0E-03	4.0E-06	2.3E-03	3.8E-03	6.4E-03	9.5E-03	477
				56.7	40.77	1.889	0.31	0.12	0.441	-0.308	5.0E-03	8.0E-03	9.9E-04	9.9E-03	4.0E-05	2.3E-02	3.8E-02	6.4E-02	9.4E-02	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.6. Gas Analyses for Test KC-1 M500 at 80°C and 95°C

Run Sys -4	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	80,	83.8	0.015	0.029	15	0.06	0.007	0.002	0.95	0.18		3.0E-04	2.0E-05	6.0E-04		9.0E-04	1.3E-03	2.0E-03	2.9E-03	321
	95			0.19	99.3	0.40	0.05	0.01	-1.459	-0.887		2.0E-03	1.3E-04	4.0E-03		6.0E-03	8.6E-03	1.3E-02	1.9E-02	166
2 22K61	95	86.7	0.018	0.046	11.3	0.04			1.48	0.375	2.0E-05	3.0E-05	3.0E-06	6.0E-05		2.0E-04	3.0E-04	4.0E-04	6.0E-04	477
				0.40	99.2	0.33			0.516	-0.055	1.8E-04	2.6E-04	2.6E-05	5.3E-04		1.8E-03	2.6E-03	3.5E-03	5.3E-03	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.7. Gas Generation Rates from KC-1 P500 at 80°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																Time, h
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	
1	80	1.58E-03	3.45E-04	5.6E-05	6.3E-6	2.0E-6	-2.2E-05	-1.9E-05	1.9E-7	3.3E-7	4.7E-8	5.5E-7	2.4E-9	1.0E-6	1.6E-6	2.6E-6	3.9E-6	326
	95																	166
2	95	3.90E-04	2.81E-04	1.3E-05	2.1E-6	8.2E-7	3.0E-06	-2.1E-06	3.4E-8	5.5E-8	6.8E-9	6.8E-8	2.7E-10	1.6E-7	2.6E-7	4.4E-7	6.5E-7	477

Blank entries are below detection limits.

Table A.8. Gas Generation Rates from KC-1 M500 at 80°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																Time, h
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	
1	80	1.49E-06	7.69E-04	3.1E-06	3.6E-7	1.0E-7	-1.1E-05	-6.9E-06		1.5E-8	1.0E-9	3.1E-8		4.6E-8	6.7E-8	1.0E-7	1.5E-7	321
	95																	166
2	95	2.32E-06	5.70E-04	1.9E-06			3.0E-06	-3.2E-07	1.0E-9	1.5E-9	1.5E-10	3.0E-9		1.0E-8	1.5E-8	2.0E-8	3.0E-8	477

Blank entries are below detection limits.

Table A.9. Gas Analyses for Test FE-1 at 90°C and 95°C

Run Sys -5	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	90,	83.2	0.029	0.76	13.50	0.006	0.019	0.006	2.01	0.45					2.0E-05	1.3E-04	2.0E-04	5.0E-04	5.0E-04	329
	95			5.32	94.5	0.04	0.133	0.04							1.4E-04	9.1E-04	1.4E-03	3.5E-03	3.5E-03	166
2 22K61	95	84.1	0.021	0.086	13.6	0.00	0.022	0.004	1.69	0.425						2.0E-05	3.0E-05	4.0E-05	6.0E-05	477
				0.63	99.2	0.01	0.16	0.03								1.5E-04	2.2E-04	2.9E-04	4.4E-04	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.10. Gas Analyses for Test FE-3 at 90°C and 95°C

Run Sys -6	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	90,	93.1	0.027	0.01	4.7	0.003	0.006	0.005	1.78	0.36										327
	95				99	0.06	0.13	0.11												
2 22K61	95	93.7	0.016	0.02	4.6	0.003	0.005	0.005	1.32	0.293										477
					99	0.06	0.11	0.11												

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.11. Gas Analyses for Test FE-5 at 90°C and 95°C

Run Sys -7	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	90,	92.5	0.029	0.05	4.7	0.004	0.003	0.001	2.21	0.046						1.0E-04	2.0E-04	3.0E-04	5.0E-04	327
	95			0.94	99	0.083	0.06	0.02								2.1E-03	4.2E-03	6.3E-03	1.0E-02	166
2 22K61	95	93.1	0.02	0.06	4.9	0.005	0.003	0.003	1.6	0.333						6.0E-05	9.0E-05	1.0E-04	2.0E-04	476
				1.21	99	0.101	0.06	0.06								1.2E-03	1.8E-03	2.0E-03	4.0E-03	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.12. Gas Analyses for Test FE-4/6 at 90°C and 95°C

Run Sys -8	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	90,	86.7	0.021	0.075	11.5	0.01	0.007	0.005	1.50	0.2					6.0E-05	3.0E-05	7.0E-05	4.0E-05	3.0E-05	326
	95			0.65	99.2	0.04	0.06	0.04							5.2E-04	2.6E-04	6.0E-04	3.5E-04	2.6E-04	160
2 22K61	95	88.0	0.017	0.085	10.2	0.00	0.006	0.004	1.36	0.3										477
				0.83	99.0	0.04	0.06	0.04												

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.13. Gas Generation Rates from FE-1 at 90°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1	90	3.13E-05	5.56E-04	2.5E-07	7.8E-7	2.5E-7	-1.4E-05	-7.3E-06					8.2E-10	5.3E-9	8.2E-9	2.1E-8	2.1E-8	329
	95																	166
2	95	3.63E-06	5.74E-04	8.4E-08	9.3E-7	1.7E-7	7.6E-07	-9.9E-07						8.4E-10	1.3E-9	1.7E-9	2.5E-9	477

Blank entries are below detection limits.

Table A.14. Gas Generation Rates from FE-3 at 90°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1	90	7.88E-07	2.66E-04	1.7E-07	3.4E-7	2.8E-7	-2.2E-05	-1.3E-05										327
	95																	166
2	95	9.89E-07	2.69E-04	1.7E-07	2.9E-7	2.9E-7	3.8E-06	-2.5E-06										477

Blank entries are below detection limits.

Table A.15. Gas Generation Rates from FE-5 at 90°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1	90	2.62E-06	2.76E-04	2.3E-07	1.7E-7	5.8E-8	-7.6E-06	-3.4E-05						5.8E-9	1.2E-8	1.7E-8	2.9E-8	327
	95																	166
2	95	3.63E-06	2.96E-04	3.0E-07	1.8E-7	1.8E-7	7.0E-07	-5.6E-06						3.6E-9	5.4E-9	6.0E-9	1.2E-8	476

Blank entries are below detection limits.

Table A.16. Gas Generation Rates from FE-4/6 at 90°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1	90	5.29E-06	8.11E-04	3.5E-07	4.9E-7	3.5E-7	-1.2E-05	-1.8E-05					4.2E-9	2.1E-9	4.9E-9	2.8E-9	2.1E-9	326
	95																	160
2	95	6.09E-06	7.31E-04	2.9E-07	4.3E-7	2.9E-7	1.6E-06	-4.2E-06										477

Blank entries are below detection limits.

Table A.17. Gas Analyses for Test KC-6 at 90°C and 95°C

Run Sys -9	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	90,	92.6	0.02	0.57	5.3	0.002		0.001	1.3	0.138										327
	95			9.71	90.2	0.03		0.02												165
2 22K61	95	91.2	0.025	0.46	5.7	0.00			2.10	0.44										477
				7.47	92.5	0.03														

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.18. Gas Analyses for Test 96-06 at 80°C and 95°C

Run Sys -10	Temp. °C	Ne	Ar	H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136	Time, h
1 22K52	90,	94.4	0.021	0.10	3.6	0.005	0.005	0.003	1.52	0.31	9.0E-05	2.0E-04	1.0E-05	7.0E-04		1.0E-03	1.4E-03	2.0E-03	3.0E-03	324
	95			2.56	96.9	0.13	0.13	0.081			2.4E-03	5.4E-03	2.7E-04	1.9E-02		2.7E-02	3.8E-02	5.4E-02	8.1E-02	147
2 22K61	95	70.8	0.259	0.027	1.5	0.00		0.002	21.90	5.57	6.0E-04	1.0E-03	1.0E-04	1.4E-03		3.5E-03	5.9E-03	9.2E-03	1.4E-02	477
				1.8	95.6	0.13		0.13			3.9E-02	6.6E-02	6.6E-03	9.2E-02		2.3E-01	3.9E-01	6.0E-01	9.2E-01	

Blank entries are below detection limits. Shaded values denote the generated gas composition (i.e., neon cover gas contribution deducted).

Table A.19. Gas Generation Rates from KC-6 at 90°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																Time, h		
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136			
1	90	3.67E-05	3.41E-04	1.3E-07		6.4E-8	-1.9E-05	-1.9E-05												327
	95																			165
2	95	3.11E-05	3.85E-04	1.4E-07			6.3E-06	-6.6E-06												477

Blank entries are below detection limits.

Table A.20. Gas Generation Rates from 96-06 at 80°C and 95°C

Run	Temp. °C	Gas Generation Rate, moles/kg-day																Time, h		
		H ₂	CO ₂	CH ₄	C ₂ HC	C _{>2} HC	N ₂	O ₂	Kr 83	Kr 84	Kr 85	Kr 86	Xe 130	Xe 131	Xe 132	Xe 134	Xe 136			
1	90	5.66E-06	2.14E-04	3.0E-07	3.0E-7	1.8E-7	-9.1E-06	-8.2E-06	5.4E-9	1.2E-8	6.0E-10	4.2E-8		6.0E-8	8.3E-8	1.2E-7	1.8E-7			324
	95																			147
2	95	1.58E-06	8.54E-05	1.2E-07		1.2E-7	1.9E-05	-1.3E-05	3.5E-8	5.9E-8	5.9E-9	8.2E-8		2.0E-7	3.5E-7	5.4E-7	8.2E-7			477

Blank entries are below detection limits.

Appendix B

Estimation of KC-1 Uranium Metal Content on October 7, 1999 (Start of Gas Generation Series I Testing)

