
**Pacific Northwest
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Final Report – Gas Generation Testing of Uranium Metal in Simulated K Basin Sludge and in Grouted Sludge Waste Forms

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August 2004



Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The evolving plan for the majority of the sludge being removed from the Hanford K Basins is to treat it for disposal to the Waste Isolation Pilot Plant (WIPP) as remote handled transuranic waste (RH-TRU). One challenge that must be addressed during removal and disposition is the reaction of the uranium metal component of the sludge with water to form hydrogen gas ($U + 2 H_2O \rightarrow UO_2 + 2 H_2$) in the sealed transportation drums. Because the hydrogen gas concentration in the 55-gallon RH-TRU drums is limited by flammability safety, the number of containers and shipments to WIPP likely will be driven by the rate of hydrogen generated by the uranium metal-water reaction in combination with the hydrogen generated from water and organic radiolysis. To prepare the sludge to meet WIPP transportation and acceptance criteria, it must be solidified or drained to eliminate the associated free liquid. In the study discussed here, grout-type solidification matrices were evaluated for their potential to solidify drainable liquid and inhibit the reaction of water with uranium metal in the sludge, thereby permitting higher sludge loading to the disposed waste form.

Grout solidification matrices, which can be prepared with only a few simple ambient temperature operations, potentially can decrease the uranium metal-water reaction rate by limiting water film or vapor access to the uranium metal by:

- coating the reactive uranium metal surface
- impeding water diffusion to the uranium metal
- chemically sequestering or binding the water.

Gas generation testing with uranium metal particles of known surface area, in simulated K West (KW) Basin canister sludge and immobilized in candidate grout solidification matrices, was used to measure the effectiveness of this approach.

The KW canister sludge was chosen as the basis for the simulant because it is the most reactive sludge being considered for direct disposal in grout. Non-irradiated uranium metal beads (~200-1100 μm diameter spheres) of natural enrichment provided the uranium metal used in the simulated KW canister sludge. The tests were designed to understand the long-term behavior of the sludge-grout mixtures for onsite storage and shipping offsite to WIPP. Four grout formulations (designated BNFL, Bentonite, Weakley, and Cast Stone), based on Portland cement, and two formulations (designated Tectonite and Tectonite-Bentonite), based on magnesium phosphate cement were tested. Parallel tests (reference tests) of uranium metal in water and of uranium metal in simulated KW canister sludge provided comparative data.

Gas generation testing began at 60°C to duplicate the maximum temperature a WIPP-bound waste package might experience in transit. In most cases, the 60°C interval was followed by intervals at approximately 80°C, 95°C, and 40°C to understand the dependence of uranium metal corrosion rate on temperature and to correlate these findings with published uranium metal corrosion rates. The test temperatures then were adjusted to 60°C and completed at about 95°C to react the remaining uranium metal to extinction and allow closure of material balances based on total hydrogen gas formation.

The reference tests with uranium metal in water and in simulated KW canister sludge confirmed prior observations with actual K Basin sludge that sludge overburden acts to decrease the rate of uranium metal corrosion. In addition, the experimental corrosion rates and activation energies of non-irradiated uranium

metal in simulated sludge, in the present testing, are similar to, and thus confirm, those in prior tests of irradiated uranium metal fuel particles from K Basins.

The following table summarizes the hydrogen generation rates from uranium metal corrosion at 60°C for the grout formulations and reference tests. The rates are for hypothetical RH-TRU 55-gallon drums loaded with 14.6 liters of KW canister sludge in the respective reference sludge or grouted sludge waste form. This amount of sludge is at the 200-gram ²³⁹Pu fissile gram equivalent (FGE) limit mandated by WIPP. The hydrogen generation rates at the FGE-limited loadings are compared with the maximum 3.65×10^{-8} moles/second hydrogen generation rate tolerated in a WIPP RH-TRU drum.

Case	Drum Hydrogen Generation Rate (moles H ₂ /sec) ^(a)	Factor Improvement Needed for WIPP
<i>Reference Tests</i>		
Uranium Metal	1.80×10^{-5}	493
Uranium Metal in Simulated Sludge	5.71×10^{-6}	156
<i>Portland Cement</i>		
BNFL	8.57×10^{-6}	235
Bentonite	4.00×10^{-6}	110
Weakley	9.43×10^{-6}	258
Cast Stone	7.37×10^{-6}	202
<i>Magnesium Phosphate Cement</i>		
Tectonite	1.71×10^{-5}	470
Tectonite-Bentonite	7.57×10^{-6}	207
<i>Drum Hydrogen Generation Rate Limit</i>	3.65×10^{-8}	1
(a) Drum H ₂ generation rate based on the uranium metal surface area in 14.6 liters of nominal KW canister sludge $\frac{1.46 \times 10^4 \text{ ml sludge}}{\text{RH-TRU drum}} \times \frac{4 \text{ g sludge}}{\text{ml sludge}} \times \frac{0.05 \text{ g U metal}}{\text{g sludge}} \times \frac{500 - \mu\text{m U particle}}{1.247 \times 10^{-3} \text{ g U}} \times \frac{7.854 \times 10^{-7} \text{ m}^2 \text{ area}}{500 - \mu\text{m U particle}} = \frac{1.84 \text{ m}^2 \text{ U surface}}{\text{RH-TRU drum}}$ and the uranium corrosion rates observed in the present reference and cement waste form testing.		

As evidenced in the table, none of the tested grout formulations radically decreased the uranium metal corrosion rate. Even the best of these formulations produced hydrogen at rates that exceeded the WIPP limit by a factor of 110 for hypothetical drums loaded to the 200-gram ²³⁹Pu FGE limit. The lowest overall hydrogen generation rate observed in any of the grouted tests was found for Portland cement containing bentonite clay. Although the corrosion rate in the Bentonite grout was about 22% of that observed for uranium metal-alone in water, the rate was not appreciably lower than that observed for the starting simulated sludge. Bentonite also decreased the uranium metal corrosion rate in magnesium phosphate grout. The failure of the tested grouts to significantly decrease uranium metal corrosion rates likely results because the grouts are poor desiccants and are unable to diminish the water vapor pressure enough to prevent water condensation or adsorption on the reactive uranium metal/oxide surface.

The gas generation testing shows that grouting alone is not sufficient to treat the K Basin sludge designated as RH-TRU to reach ²³⁹Pu FGE limited loading. Before the sludge can be packaged for disposition to WIPP, additional or alternative treatments will be required in order to meet the disposal criterion for the rate of hydrogen gas generation.

Approaches to inhibit or eliminate either the uranium metal or water reactant, and thus decrease the hydrogen generation rate, include:

- Reacting (oxidizing) the metallic uranium, possibly with a preliminary uranium metal separation/concentration step.
- Removing the water from the sludge by decanting and drying.
- Solidifying the sludge with WIPP-acceptable agents to coat the reactive uranium metal surfaces.

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1.0 Introduction and Background

Since the mid-1970s, more than 2100 metric tons of Zircaloy-clad irradiated uranium metal fuel from the Hanford N Reactor have been stored underwater at the K East (KE) and K West (KW) Basins, two water-filled concrete pools in the 100K Area. This fuel is now being removed for separate dry storage. During the time the fuel has been stored, about 52 m³ of heterogeneous solid material (sludge) has accumulated in the canisters, on the floor, and in the associated pits of the basins. This sludge consists of fuel, fuel corrosion products, fuel cladding, structural corrosion products, windblown material, sloughed concrete from the basin walls and floors, commercial sand used for sand filters, and miscellaneous constituents such as ion exchange material (both organic and inorganic) and paint chips in various proportions. In the Spent Nuclear Fuel (SNF) Project, sludge is defined as any material in the K Basins, including fuel fragments, that is less than or equal to 6350 μm (0.25 in.) in diameter.

Past sampling and analysis campaigns (Makenas et al. 1996-99) characterized the bulk of the sludge, while a more recent study has focused on the ~6.3 m³ of less radioactive, KE North Loadout Pit (NLOP) sludge (Mellinger et al. 2004a). Pearce (2001) summarized the inventory and compositions of all K Basin sludge materials. The evolving plan for all but the KE NLOP sludge is disposition to the Waste Isolation Pilot Plant (WIPP) as remote handled transuranic waste (RH-TRU). The plan for KE NLOP sludge is retrieval and solidification as contact handled (CH)-TRU waste in FY 2004 and 2005, with the intent of ultimate disposition to WIPP.

The uranium metal component in the sludge can corrode and react with water ($U + 2 H_2O \rightarrow UO_2 + 2 H_2$) to generate hydrogen in the sealed transportation drums. Because the hydrogen gas concentration in the drum is limited by flammability safety, the number of containers and shipments to WIPP likely will be driven by the rate of hydrogen generated by the uranium metal and water reaction in combination with the hydrogen generated from water and organic radiolysis. Consequently, immobilization media, such as grout and other solidification agents, are being evaluated for their potential to reduce the rate of uranium metal corrosion.

Gas generation testing was conducted by Pacific Northwest National Laboratory (PNNL) using uranium metal particles of known surface area, in simulated KW canister sludge and immobilized in candidate grout solidification matrices, to determine the effectiveness of this approach for inhibiting the rate of the uranium metal-water reaction and to understand the long-term behavior of the sludge-grout mixtures for onsite storage and shipping to WIPP. Two grout types, based on Portland and magnesium phosphate cements, were tested in formulations containing various additives. Parallel tests of uranium metal in water and of uranium metal in simulated KW canister sludge were performed. This report summarizes results from earlier experiments (Delegard et al. 2004) and provides additional results from completed and follow-on testing. The testing followed PNNL Test Instructions approved through PNNL and Fluor Hanford authorities. The work was performed under contract for the Fluor Hanford Sludge Retrieval and Disposition Project.

Prior experimental measurements of uranium corrosion rates in actual sludge have been used to determine uranium metal concentration, particle size, and reaction rate enhancement factor values in sludge for purposes of sludge removal, transportation, and storage. These measurements were based on hydrogen gas generation and release of krypton and xenon fission product gases from the corroding irradiated uranium metal. The experimental measurements were conducted in three series of gas generation experiments. The first test series (Series I; Delegard et al. 2000) focused on gas generation from

KE Basin floor and canister sludge (size-fractionated and non-fractionated samples collected using a consolidated sampling technique; Baker et al. 2000). The second series (Series II; Bryan et al. 2004) examined the gas generation behavior of KE Basin floor, pit, and canister sludge. Tests were conducted on mixed and unmixed and fractionated KE canister sludge and floor and pit sludge from areas in the KE Basin not previously sampled. The third series (Series III; Schmidt et al. 2003) examined the corrosion and gas generation behavior of irradiated metallic uranium particles with and without sludge addition. Another set of gas generation tests were conducted as part of studies on the KE NLOP sludge (Mellinger et al. 2004a).

In the four test series, sludge samples and irradiated metallic uranium fuel particles were introduced into 850-ml, 220-ml, 60-ml, or 30-ml capacity vessels and connected to gas-tight systems designed to monitor gas pressures and allow gas sampling for analysis. Sludge samples were held at various controlled temperatures and often ended at high temperatures to completely oxidize the contained uranium metal. Analyses of the product gas concentrations and quantities led to a better understanding of the underlying reactions, which, if run to extinction, were used to determine the uranium metal concentration in the sludge and irradiation exposure (burn-up) of the uranium metal fuel.

Because the focus of the SNF Sludge project is changing from interim storage to near-term disposition to WIPP, further gas generation tests, specific to potential WIPP waste forms, were conducted, as discussed here. In general, KE and KW Basin sludge will contain much higher uranium metal concentrations than found in the KE NLOP sludge. To prepare the sludge to meet WIPP transportation criteria, it must be stabilized in a grout or other suitable solidification matrix or be drained to eliminate the associated free liquid, which is not allowed in WIPP waste forms. Because of the higher uranium metal concentrations in most KE and KW sludge, it also would be beneficial for the solidification matrix to inhibit the reaction of water with any residual uranium metal present.

Near-term disposition of the KE NLOP sludge is predicated upon the sludge exhibiting a very low hydrogen gas generation rate from the reaction of uranium metal with water. Gas generation testing (Bryan et al. 2004) conducted with a single consolidated KE NLOP sludge sample collected in 1999 indicated that this sludge contained very little uranium metal (i.e., 0.013 wt% uranium metal based on $H_2/O_2/N_2$ and <0.0088 wt% based on ^{136}Xe). Additional gas generation testing (Mellinger et al. 2004a) was performed to gain confidence in the low uranium metal content of the KE NLOP sludge with samples collected in December 2003. According to ^{136}Xe fission product gas release detection limits, <0.018 wt% uranium metal is present in the December 2003 sludge samples. The effects of draining of water and of solidification agents on the treated KE NLOP sludge gas generation quantity and rate also were examined.

Grout potentially can decrease the uranium metal-water reaction rate by limiting water film or vapor access to the uranium metal by:

- coating the reactive uranium metal surface
- impeding water diffusion to the uranium metal
- chemically sequestering or binding the water.

Based on how effectively the reaction is inhibited by the waste form, additional process steps may be required to significantly diminish or eliminate one or the other of the two reactants—uranium and water:

- React (oxidize) the metallic uranium with an optional preliminary uranium metal concentration step to decrease the sludge quantity requiring the oxidation conditions.
- Remove the water by decanting and drying the sludge.
- Coat the reactive uranium metal surfaces with WIPP-acceptable agents to prevent contact with water.

The need to diminish the reaction of uranium metal with water to produce hydrogen gas can be demonstrated by the following evaluation. The maximum hydrogen generation rate tolerated in a RH-TRU 55-gallon drum is 3.65×10^{-8} moles/second.^(a) The effective uranium metal size observed in KE canister sludge in the Series I testing is 640-970 μm (Delegard et al. 2000). Based on critically reviewed uranium corrosion rates provided in the SNF Databook (Duncan 2001), the 3.65×10^{-8} moles H_2 /second rate is met with only 13.06 grams of 739- μm diameter uranium reacting at 60°C, the maximum temperature anticipated in transit to WIPP. The 739- μm uranium metal particle diameter is representative of that observed in much of the actual sludge and is the effective size of the uranium metal beads that were used to prepare the simulated KW canister sludge in the present testing. The 3.65×10^{-8} moles H_2 /second rate from corrosion leaves no margin for hydrogen generation from radiolysis.

At this hydrogen gas generation rate, only ~65 ml (261 g) of *simulated* KW canister sludge (739- μm -diameter uranium metal particles) containing 13.06 grams of uranium metal could be accommodated in a single RH-TRU drum. For *actual* KW canister sludge, which contains nominally 500- μm -diameter uranium metal particles (Table 4-5a of Schmidt 2004), only 8.84 grams of uranium metal in ~44 ml (or ~177 g) of sludge, could be accommodated in a single RH-TRU drum. For actual size-segregated KW canister sludge collected in the settler tubes (passing a 500- μm screen and taken to be 375- μm -diameter uranium metal particles; Table 4-5b of Schmidt 2004), only 6.63 grams of uranium metal in ~33 ml (or ~132 g) of sludge could be held in a single RH-TRU drum.

Besides drainable liquid and hydrogen gas generation rate limits, packages containing KW canister sludge prepared for shipment to WIPP as RH-TRU will be subject to the ^{239}Pu fissile gram equivalent (FGE)^(b) loading limit of 200 grams per RH-TRU 55-gallon drum. Unlike the drainable liquid or hydrogen gas generation rate limits, the FGE limit cannot be remedied by treatment and thus constitutes a firm upper limit to waste loading. The 1010 liters of KW canister sludge (Schmidt 2004; see Table 4-16) contain 1.38×10^4 g FGE. Thus, 14.6 liters of sludge can be held per RH-TRU drum:

$$(1010 \text{ liters} / 1.38 \times 10^4 \text{ g FGE}) \times (200 \text{ g FGE} / \text{RH-TRU drum}) = 14.6 \text{ liters of KW canister sludge.}$$

With a nominal drum capacity of 177 liters (15% head space in 208 liters total volume), KW canister sludge loading at the RH-TRU limit in the final waste form is ~8.3 volume percent. The FGE limit thus is $14600/44 = 330$ times higher than the loading afforded by the hydrogen gas generation rate in KW canister sludge with 500- μm -diameter uranium metal particles.

The present testing showed that the corrosion rates and reaction activation energies of uranium metal corrosion in water and in simulated sludge are similar to, and thus confirm, those observed in prior tests

(a) The value of 3.65×10^{-8} moles H_2 per second was obtained per guidance provided by David DeRosa, Fluor Hanford. A similar value of 3.8391×10^{-8} moles per second for RH-TRU drum is provided in Table 5.2 of Mellinger et al. (2004b).

(b) The ^{239}Pu FGE calculation applies varying quality factors to quantities of listed fissile isotopes ($^{233,235}\text{U}$, ^{237}Np , $^{238,239,240,241,242}\text{Pu}$, $^{241,242\text{m},243}\text{Am}$, $^{243,244,245,247}\text{Cm}$, and $^{249,251}\text{Cf}$) to arrive at a combined loading for criticality safety.

of irradiated uranium metal fuel in water and in actual sludge. The results presented in this report for the grouted waste forms show, at best, a ~fourfold decrease in uranium corrosion rate is attained for grouted simulated KW canister sludge compared with the rates for the reaction of uranium metal with water. The corrosion rates observed in the grouted waste forms were only marginally lower than the rates observed for the original simulated sludge containing uranium dioxide and silica sand in addition to uranium metal and water. As a result, this study concludes that grouting alone will not be a suitable process for treatment of the balance of the K Basin sludges. Alternative treatment approaches will be required to significantly diminish or eliminate either the uranium or water reactant, or their interaction, before the sludge can be packaged for WIPP disposal. These approaches might include:

- Reacting (oxidizing) the metallic uranium, possibly combined with a preliminary uranium metal removal step.
- Removing the water from the sludge by decanting and drying.
- Solidifying the sludge with WIPP-acceptable agents to coat the reactive uranium metal surfaces.

These conclusions and the results of testing and analyses are presented in this report, along with the overall objectives, the materials evaluated, and the experimental conditions and methods. The appendix provides a more detailed discussion of the materials considered and used in the study.

2.0 Test Objectives and Materials

The tests discussed here were conducted to better understand of the effects of temperature, sludge overburden, and, especially, immobilization matrices on the reaction rate of uranium metal with water to produce hydrogen gas. In particular, the testing surveyed candidate grouting media selected to inhibit the reaction of uranium metal with water while producing waste forms meeting the WIPP disposal criterion of having no drainable liquid. The experimental work included controlled gas generation tests with K Basin sludge surrogates spiked with uranium metal particles. All tests used non-irradiated uranium metal particles of known starting particle size distribution representative of the uranium metal particle size present in actual sludge.

The sludge component proportions followed the composition described for the KW canister sludge (Tables 4-1 through 4-4a, Schmidt 2004), the most reactive sludge envisioned for immobilization treatment. The KW canister sludge is considered representative of other streams, such as the KW settler tube sludge, coming from the KW Basin. According to the defined KW canister sludge parameters, the sludge should have a 4.00 g/cm^3 density and contain 65 volume percent water and 2.7 g/cm^3 total uranium, 0.2 g/cm^3 of which would be uranium metal (i.e., the sludge would contain 5 wt% uranium metal). The sludge quantity for the testing was selected based on the capacity of the test vessels to accept the hydrogen gas created by complete corrosion of the uranium metal. As will be shown (see Section 3.4), the corresponding quantity is 1.5 grams of uranium metal in a 220-ml test vessel, with a portion of that total volume excluded by the waste form itself.

For simplicity to assist in making and interpreting calculations related to the other complex mechanisms possible in sludge, the selected sludge simulant ingredients were limited to uranium dioxide (UO_2) powder and uranium metal in water, with fine silica (quartz) sand as the stable component. The KW canister sludge phase distribution (with slightly different starting parameters) is described in a separate analysis (see Appendix B of Schmidt and Delegard 2003).

Several types of experiments were considered:

- Reference test to determine hydrogen generation rate of uranium metal particles in water
- Reference test to determine hydrogen generation rate of uranium metal particles, with simulated sludge, in water
- Hydrogen generation rate tests of uranium metal particles with simulated sludge in water immobilized in candidate agents
 - Hydraulic grout, based on experience in
 - Grouting of active metals (including uranium) by British Nuclear Fuels, Limited (BNFL) and others in the United Kingdom (UK).
 - Grouting of KE NLOP sludge using formulations with clay (i.e., bentonite; attapulgite also was tested with sludge simulant) meant to absorb free or “bleed” liquid.
 - Grouting of uranium metal fuel fabrication turnings and chips in past Hanford operations, as described in Weakley (1980).

- Grout formulations (Perma-Fix) created to immobilize uranium metal fabrication turnings and chips found in barrels recently excavated at Hanford.
 - Uranium metal immobilization in Hanford Cast Stone.
 - Grouting with Tectonite™,^(a) an all-season repair and anchoring inorganic magnesium oxyphosphate cement, typical of a class of cements that have been suggested for use for nuclear waste immobilization.
- Organic-bearing solidification/encapsulation agents (e.g., Nochar®; VES® – vinyl ester styrene; SPC – sulfur polymer cement; OrganoPlex or PetroSet®).^(b)

The compositions and descriptions of the materials are provided in the appendix. Ultimately, testing was confined to grouts based on Portland and magnesium phosphate cements. Immobilization agents containing organic constituents (except for superplasticizers) were not included in the testing. In most instances, the tests were conducted to complete reaction of the contained uranium metal. The experimental conditions and methods are given in Section 3.0.

Three series of tests were conducted: reference; Portland cement grouts; and magnesium phosphate grouts. The reference consisted of two tests, U-Control, containing uranium metal and water, and U-Sludge, containing uranium metal, UO₂, quartz sand, and water. The Portland cement grouts were designated BNFL, Bentonite, Weakley, and Cast Stone; and the magnesium phosphate grouts examined Tectonite and Tectonite-Bentonite formulations.

The U-Control test served as a control to understand the gas generation rate of the uranium particles (beads) with water and in the absence of other sludge surrogate constituents (e.g., UO₂, SiO₂). The behavior of this test also could be compared with observations made under similar test conditions in the Series III experiments with crushed irradiated uranium metal fuel (Schmidt et al. 2003) and with the large body of technical literature on the corrosion of uranium metal by water.

The U-Sludge test served as a control to understand the gas generation rate of the uranium metal beads by water in the presence of other (UO₂ and SiO₂) sludge components. In the Series III testing (Schmidt et al. 2003), it was found that a sludge layer placed over actual uranium metal fuel fragments reduced the gas generation rate relative to fuel fragments with no sludge overburden. Results from the U-Sludge test provided baseline data to compare with tests with immobilization agents and also could be compared with the Series III test findings on the effects of sludge overburden. A duplicate U-Sludge test (U-Sludge Dup) was performed to learn more about the induction time to onset of reaction at 60°C and to confirm the observations of the original U-Sludge test.

The Portland cement grout tests examined the effects of Portland cement grout matrices on hydrogen generation rate of uranium metal-spiked sludge. By comparing these results with the results from the reference tests, quantitative data were obtained to estimate the extent to which the reaction of uranium

(a) Tectonics International, Warm Springs, OR.

(b) Nochar Acid Bond 660 is a polyacrylic water sorbent produced as a dry fine granular powder. Nochar, Inc., Indianapolis, IN. Vinyl ester styrene (VES) polymer immobilization was originally developed by Dow Chemical Company and marketed as Derakane. Its chemistry and one potential Hanford application are described by Burbank (1993). Application of sulfur polymer cement (SPC) is described by the ASTM (2003a) and by Kalb (2001). Use of SPC requires preliminary sludge drying. OrganoPlex and PetroSet (Fluid Tech Corporation) are products that have been applied by TPG Applied Technology, Knoxville, TN, to stabilize uranium metal turnings/chips/fines present in mixed mineral/diesel oil at the Los Alamos National Laboratory.

metal with water is inhibited in grout media. The four compositions tested were all based on prior experience with grouting of uranium metal-bearing materials.

Formulations using the magnesium phosphate cement, Tectonite, were tested based on the perceived potential of a matrix that could chemically combine all of the sludge water as a compound hydrate (i.e., $MgHPO_4 \cdot 6H_2O$) and thus prevent the water from interacting with uranium metal to form hydrogen gas. Two formulations were tested, one using Tectonite alone and the second adding bentonite clay (Tectonite-Bentonite), based on the promising results obtained in tests with Portland cement grout containing bentonite.

Table 2.1 shows the test matrix. The sludge loadings in the various grouted waste forms are near the 8.3 volume percent sludge loading dictated by the ^{239}Pu FGE limit for KW canister sludge.

Table 2.1. Uranium-Water Reaction Test Matrix

Test ID	Sludge Simulant Mass, g			Grout Mix, g ^(b)	Est. Simulated Sludge Load, vol% ^(c)
	Water ^(a)	Sand/UO ₂	U Metal		
<i>Reference Tests</i>					
U-Control	30	0	1.5	0	NA
U-Sludge & U-Sludge Duplicate	30	2.32/21.3	1.5	0	NA
<i>Portland Cement Grouts</i>					
BNFL	30	2.32/21.3	1.5	129.5	8.1
Bentonite	30	2.32/21.3	1.5	66.2	12.4
Weakley	30	2.32/21.3	1.5	54.5	13.7
Cast Stone	30	2.32/21.3	1.5	100.6	9.6
<i>Magnesium Phosphate Grouts</i>					
Tectonite	30	2.32/21.3	1.5	193.3	6.0
Tectonite-Bentonite	30	2.32/21.3	1.5	178.8	6.4
(a) Water amount consists of 4.9 g for sludge and 25.1 g for grout make-up (see text).					
(b) Sum of grout mix components (cement, blast furnace slag, superplasticizer, bentonite, calcite, gypsum, “neat” Tectonite, Cast Stone formulation) constituted to make thick but mixable slurries.					
(c) Based on final grout form density of 2.0 g/cm ³ and sludge feed volume of 7.5 ml (sludge density 4.00 g/cm ³).					

The results from these tests with non-irradiated uranium are discussed in Section 4.0. Subsequent testing with actual sludge, if warranted, would not only validate the tests performed with simulants but would use the release of fission product gases (isotopes of krypton and xenon) to monitor the corrosion of the irradiated uranium metal as a second indicator of uranium metal-water reaction. The fission product gas release from the uranium metal fuel matrix provides definitive and kinetically responsive evidence of irradiated uranium metal corrosion, whereas hydrogen release potentially can be delayed by retention at lower temperatures as uranium hydride or be compromised by other reactions, that produce or consume hydrogen.

3.0 Experimental Conditions and Methods

The experiments were conducted by measuring gas quantities generated from uranium metal reaction in water and in simulated sludge (reference tests), in simulated sludge blended with Portland cement grouts, and in simulated sludge blended with magnesium phosphate (Tectonite) grouts as functions of time. The reference and grout compositions tested are shown in Table 3.1.

Table 3.1. Test Sludge and Waste Form Compositions

Test Name	Sludge Component Mass, g				Grout Component Mass
	U	UO ₂	SiO ₂	H ₂ O	
<i>Reference Tests</i>					
U-Control	1.534	NA	NA	30.00	NA
U-Sludge	1.480	21.30	2.32	30.00	NA
U-Sludge Dup	1.475	21.285	2.299	30.103	NA
<i>Portland Cement Grouts</i>					
BNFL	1.507	21.329	2.339	30.379	25.682 g Type I/II Portland cement; 102.692 g Grade 120 ground granulated blast furnace slag; 1.402 g ADVA Cast 500 superplasticizer
Bentonite	1.458	21.294	2.319	30.187	61.211 g Type I/II Portland cement; 5.011 g bentonite
Weakley	1.523	21.305	2.335	30.230	27.318 g Type I/II Portland cement; 25.630 g CaCO ₃ ; 1.613 g CaSO ₄ ·2H ₂ O
Cast Stone	1.532	21.322	2.291	30.058	100.850 g Cast Stone dry mix (10 wt% Type I/II Portland cement, 46 wt% grade 120 ground granulated blast furnace slag, 44 wt% Class F fly ash)
<i>Magnesium Phosphate Grouts</i>					
Tectonite	1.571	21.263	2.312	30.089	187.550 g Tectonite neat; 6.038 g set retarder
Tectonite-Bentonite	1.491	21.273	2.309	30.010	157.999 g Tectonite neat; 5.080 g set retarder; 15.841 g bentonite

3.1 Reference Test Sludge and Grouted Waste Form Preparation

The properties and sources of the materials used to prepare the test sludge and grouted waste forms are summarized in Table 3.2.

The reference tests were prepared by adding the uranium metal and dry sludge constituents (UO₂ and SiO₂) directly to the ~220-ml-capacity gas generation vessels and then adding the water. The grouted waste forms were prepared by blending the dry simulated sludge and grout constituents in a beaker, adding the water (and in the case of the BNFL grout, the ADVA Cast superplasticizer), and stirring thoroughly for at least 5 minutes. The thick slurries were cast into 41-mm-diameter plastic cylinders and a ~3-mm close-bottomed glass tube set axially in the center of the loose slurry to act as a thermocouple well. The castings were covered with wax film to prevent water evaporation while curing.

Table 3.2. Properties of Test Constituents

Material	Description and Source	Quality
<i>Sludge Constituents</i>		
U metal beads	Natural uranium metal; item H-DP-0405-401; can U59003	See appendix
UO ₂	Uranium dioxide; item 410-2	See appendix
SiO ₂	Sand, white quartz, SiO ₂ ; Aldrich part #274739	-50+70 mesh
H ₂ O	Distilled and deionized	
<i>Grout Constituents</i>		
Portland cement	Oldcastle 94; Oldcastle Materials, Inc., Washington, DC	ASTM C150 Type I/II, premium quality (ASTM 2004a)
Blast furnace slag	Aucem slag; sample ID M-1276; Buzzi Unicem USA; New Orleans Slag Facility	ASTM C989 Grade 120 (ASTM 2004b)
Bentonite	Laboratory Supplies Company, Seattle, WA; stock 35031	Technical powder
CaCO ₃ ; calcite	Calcium carbonate; Baker-analyzed Reagent (J.T. Baker); stock 35058	Reagent grade
CaSO ₄ ·2H ₂ O; gypsum	Alfa Aesar; #36700; lot #F27E30; stock 86247	Reagent grade
Superplasticizer	ADVA Cast 500; Grace Construction Products	As-received from vendor; see footnote describing BNFL test (appendix)
Cast Stone	DRF-KB1; 3/26/04; received from G. A. Cooke, Fluor Hanford	See appendix; Hanford Cast Stone formulation 10 wt% ASTM C150 Type I/II Portland cement (ASTM 2004a), 46 wt% ASTM C989 Grade 120 ground granulated blast furnace slag (ASTM 2004b), 44 wt% ASTM C618 Class F fly ash (ASTM 2003b)
Tectonite	“Neat” Tectonite (i.e., with low silicate filler); Tectonics, International, Warm Springs, OR	See appendix
Set retarder	Sodium tetraborate pentahydrate, Na ₂ B ₄ O ₇ ·5H ₂ O, for Tectonite tests; Tectonics, International, Warm Springs, OR	As-received from vendor
H ₂ O	Distilled and deionized	

The Portland cement grouts were allowed to cure for 4 days before being removed from the casting molds and being loaded into the gas generation vessels. The magnesium phosphate Tectonite grout also cured for 4 days, while the Tectonite-Bentonite grout cured for 10 days, because no gas generation test station was available earlier.

The weights and dimensions of the right circular castings were measured and the densities calculated (Table 3.3). The grouted waste forms based on Portland cement are depicted in Figure 3.1. The Tectonite magnesium phosphate waste form is shown in Figure 3.2; the Tectonite-Bentonite waste form was not photographed but had a similar appearance.

Table 3.3. Grouted Waste Form Properties

Property	Grouted Waste Form					
	BNFL	Bentonite	Weakley	Cast Stone	Tectonite	Tectonite-Bentonite
Mass, g	178.9	118.6	103.7	153.2	239.5	230.1
Height, mm	57	40	35	54	85	82.2
Diameter, mm	41	41	41	41	41	41
Volume, ml	75.3	52.8	46.2	71.3	112.2	108.5
Density, g/ml	2.38	2.25	2.25	2.15	2.13	2.12
Water/Grout Solids ^(a) Mass Ratio	0.237	0.456	0.554	0.298	0.160	0.173
Wt% H ₂ O ^(b)	16.4	24.8	27.5	19.3	12.1	13.0

(a) Grout solids are grouting agents (Portland cement, blast furnace slag, pulverized fuel ash, bentonite, calcite, gypsum, Tectonite; see Tables 3.1 and 3.2).
 (b) $100\% \times (\text{weight water})/(\text{total weight})$.



Figure 3.1. Portland Cement Grouted Waste Forms
 Top, BNFL; Bentonite
 Bottom, Weakley; Cast Stone

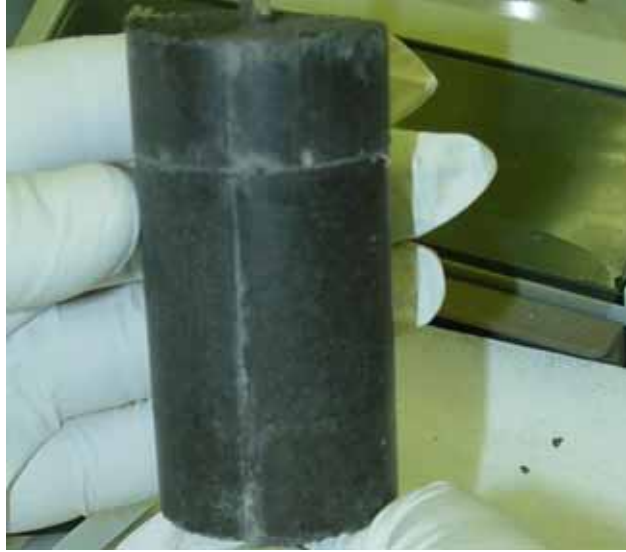


Figure 3.2. Tectonite Grouted Waste Form

3.2 Gas Generation Apparatus

The reaction vessels and the gas manifold system (Figure 3.3) used for the gas generation tests are similar to those described in the Series I-III and KE NLOP gas generation tests with K Basin Sludge (Delegard et al. 2000; Bryan et al. 2004; Schmidt et al. 2003; and Mellinger et al. 2004a). Each vessel was provided

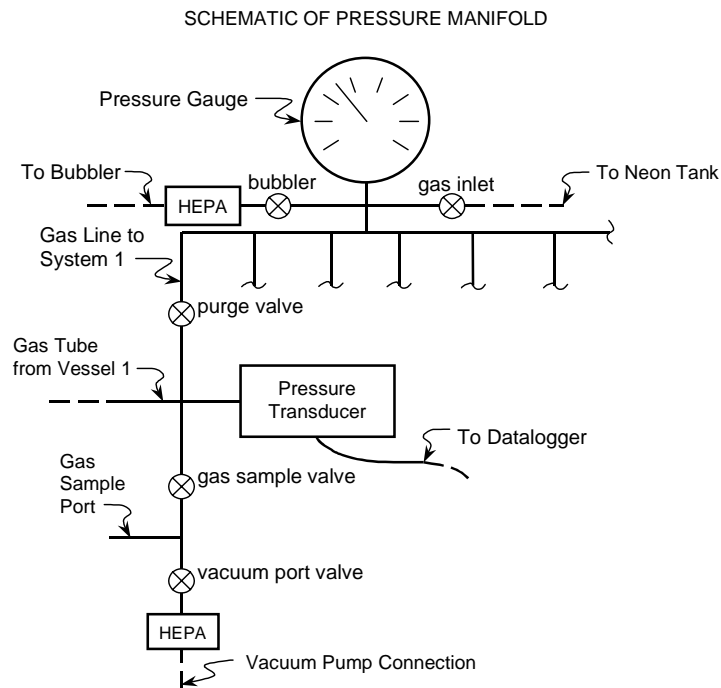


Figure 3.3. Layout of Gas Pressure Measurement and Gas Sample Manifold Used in Gas Generation Tests (Includes Details for One of Six Systems)

with a separate dedicated pressure transducer on the gas manifold line. The entire inner surface of the reaction system exposed to the sludge and grouted sample is stainless steel; the surfaces exposed to the gases also are stainless steel, except for a copper gasket seal between the flange and the top of the reaction vessel. Temperatures and pressures are recorded every 10 seconds on a Campbell Scientific CR10 data logger. The temperature and pressure data are averaged every 20 minutes and saved in a computer file and also manually logged once each working day.

Figure 3.4 illustrates a reaction vessel and shows where the thermocouples are placed inside and outside the vessel. For the gas generation testing, each vessel is wrapped in heating tape and insulated. Two thermocouples are attached to the external body, one for temperature control and one to guard against over-temperature excursions. Two thermocouples are inserted through the vessel top, which is fastened to the vessel bottom with six bolts tightened to uniform (180 inch-pound) torque. The lower thermocouple monitors the temperature of the test material phase (sludge or waste form casting). The upper thermocouple was used to monitor the gas phase temperature within the reaction vessel. The reaction vessels are placed in a fume hood and connected by a thin (0.050-cm inside diameter) stainless steel tube to the gas manifold also in the hood. A stainless steel filter protects the tubing and manifold from particulate contamination. A thermocouple is attached to this filter as well.

An atmospheric pressure gauge is attached to the data logger. The pressure in each system is the sum of atmospheric pressure and the differential pressure between the system internal and external (atmospheric)

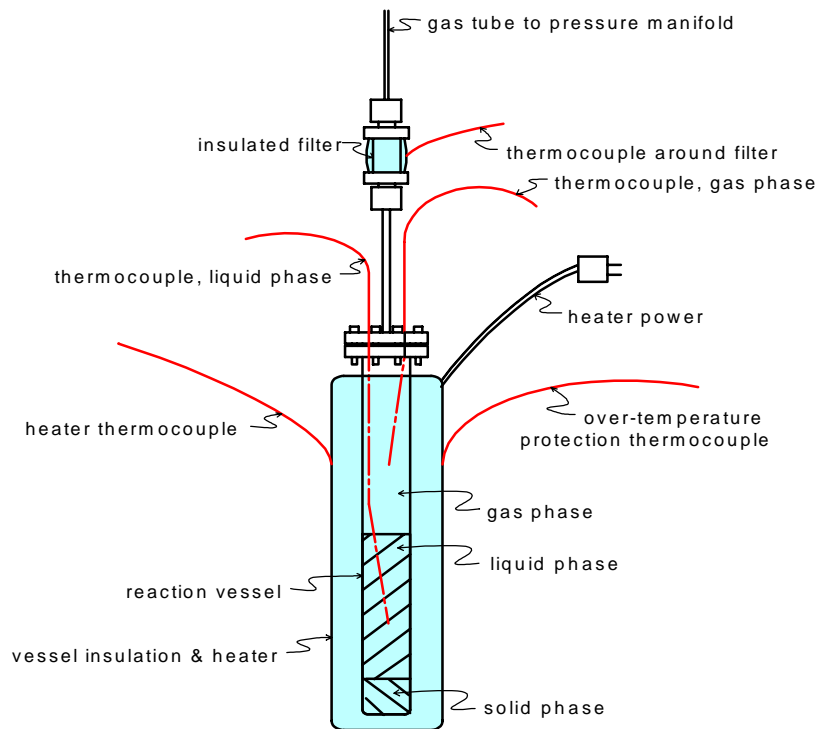


Figure 3.4. Schematic of Reaction Vessel [The diagram shows solid and liquid phases as for the U-Control and U-Sludge tests; each waste form test was a single solid casting that fit with ~4-mm annular clearance from the vessel walls and had no liquid phase.]

pressures. Mass spectrometric analyses of the final product gases were performed. However, the product gas was expected to be hydrogen only. Use of the inert starting cover gas (neon) allowed ready identification of product gases and interpretation of the chemical reactions occurring in the sludge or waste form. The same neon gas was used in prior tests; was analyzed independently by mass spectrometry; and was determined to contain no impurities in concentrations significant enough to warrant correction.

After the reaction vessels were loaded, they were pressurized to ~4 atmospheres and vented to atmospheric pressure 10 times with neon (99.999% purity). Neon cover gas, and this pressurization/venting technique, was used in the previous K Basin sludge testing (Series I-III and KE NLOP). A benefit of using neon cover gas is it allows argon to be employed as a trace on atmospheric contamination. Oxygen and nitrogen reactions can be monitored by evaluating the O₂/Ar and N₂/Ar ratios, respectively, in the gas samples.

The neon-flushed systems started at atmospheric pressure, about 750 Torr, when sealed. The vessels then were heated, and the temperature set points adjusted to keep the material within 1°C of the desired sludge or grout form temperature. At the end of each reaction sequence, the vessels were cooled to ambient temperature, and a sample of the gas taken from the head space for mass spectrometry analysis. Gases in the reaction system were assumed to be well mixed. The stainless steel gas collection bottles were ~75 ml volume. Before sampling, the gas sample bottles were evacuated overnight at high vacuum and then attached to the gas sample port. The gas sample compositions during gas samplings were analyzed using approved analytical procedures.

3.3 Reaction Atmosphere

Inert (i.e., oxygen free) neon atmospheres were used for all gas generation tests. Use of an oxygen-free atmosphere provided conditions that favor the uranium metal-water reaction (i.e., hydrogen generation rates from this testing are expected to be conservative).

The effect of introducing air into a Portland cement grout test (Weakley) that had already achieved anoxic uranium metal corrosion was also studied. For this test, the gas sample was taken after the air introduction and subsequent thermal reaction of the grouted simulant sludge.

3.4 Reaction Vessels

The tests used 220-ml-capacity reaction vessels. The minimum free gas space (after deducting the maximum test material volume) was approximately 100 ml. According to the stoichiometry of the uranium metal corrosion reaction in water ($U + 2 H_2O \rightarrow UO_2 + 2 H_2$), 1.5 grams of uranium produces 0.0126 moles of hydrogen gas (~300 ml at room temperature/pressure) to generate ~2890 Torr additional pressure^(a) above the starting pressure of ~750 Torr, or ~3640 Torr total, in the minimum ~100-ml vessel head space at 95°C for the largest test sample (Tectonite). This is just above the upper threshold of the pressure gauges in the test apparatus (~3200 Torr), so the final gas generation profile as the uranium was being completely reacted could not be followed for this single experiment. However, the total gas generated was determined by cooling the vessels to room temperature, measuring gas temperature and pressure, and by sampling and mass spectrometric analysis of the gas composition.

(a) $1.5 \text{ g U} \times \frac{\text{mole U}}{238.03 \text{ g U}} \times \frac{2 \text{ mole H}_2}{\text{mole U}} \times \frac{0.082057 \text{ liter} \cdot \text{atm}}{\text{mole} \cdot \text{deg K}} \times \frac{368 \text{ K}}{0.1 \text{ liter}} \times \frac{760 \text{ Torr}}{\text{atm}} = 2892 \text{ Torr}$

Progress of the uranium metal corrosion reactions was followed by monitoring the gas pressure, volume, and temperature (PVT) in the test apparatus. A single gas sample was taken at the end of each test to confirm the expected near-100% H₂ product gas composition and to determine, by dilution of the initial 99.999% neon cover gas and by PVD measurements, the quantity of H₂ generated. Gas generation from the grout itself was expected to be low. For instance, gas generation testing at 60°C of the relatively benign (practically metal-free) KE NLOP sludge treated with Bentonite grout showed only ~7.5 micromoles of CO₂ (0.18 ml at room temperature) produced in 1 month from ~138 grams of total grouted waste. This compares with the anticipated 300 ml of room-temperature H₂ from corroding 1.5 grams of uranium metal in water.

3.5 Test Temperatures

To obtain timely data, and consistent with the maximum temperature during waste shipment to WIPP, the target test temperature began at 60°C. Testing at other temperatures (nominally 80°C, 95°C, and 40°C) was performed to discern the temperature dependence of the uranium metal reaction, particularly in the grout matrices. Stepping the tests to higher and lower temperatures provided information on reaction activation energies and the confounding effects of diffusion and the underlying uranium metal-water reaction rates. The effects of varied temperature could be studied to help determine whether the protection afforded by the solidification matrix breaks down, for example, by spallation from the uranium metal surface. Note that although temperatures greater than 60°C accelerate the uranium metal-water reaction, the results may not reflect actual sludge treatment and storage operations.

Beginning the tests at 60°C also shortened the time before onset of the expected rapid anoxic uranium metal corrosion reaction. In Series I gas generation testing with KE canister sludge (Delegard et al. 2000), induction periods before the onset of hydrogen gas generation decreased with increasing temperature. The induction periods were 1340 hours, 205 hours, and 27 hours, at 40°C, 60°C and 80°C, respectively, for hydrogen gas generation, while another test conducted with the same sludge at ~32°C failed to overcome the induction time even after ~10,000 hours (Schmidt et al. 2003). Fission product gas release showed that induction times to onset of reaction of the 40°C, 60°C and 80°C tests actually were 335 hours, 186 hours, and ~0 hours, respectively (Bryan et al. 2004), indicating that hydrogen was sequestered as uranium hydride before being released to the gas phase.

3.6 Test Duration

Previous gas generation tests, using actual K Basin sludge and crushed irradiated uranium metal fuel, have run from 900 to 10,000 hours. The present tests continued for up to 3 months (~2000 hours) to complete extinction of the uranium metal. Note that a 1000-μm uranium metal particle requires 140 to 205 days (i.e., up to ~5000 hours) to corrode to extinction in anoxic 60°C water, based on critical reviews of kinetics data (Duncan 2001; Hilton 2000). Time to extinction of a 1000-μm metal particle in 95°C water (the highest practical temperature for the test apparatus and the highest temperature used in the present testing) is about 20 days.

4.0 Results of Gas Generation Testing with Sludge Simulant and Grouted Waste Forms

The first six tests performed were the U-Control and U-Sludge and the four Portland cement-based grout waste forms, BNFL, Bentonite, Weakley, and Cast Stone. Gas generation measurements began on May 5, 2004. A second U-Sludge test (U-Sludge Dup) began June 4, 2004. The two waste forms based on the Tectonite magnesium phosphate cement began testing June 16, 2004 (Tectonite) and June 22, 2004 (Tectonite-Bentonite). All tests, except Weakley, were run until August 2, 2004. The Weakley test ended June 22, 2004.

The gas generation results for the reference tests (U-Control, U-Sludge, and U-Sludge Dup) are shown in Figure 4.1; results for the Portland cement grouts are shown in Figure 4.2; and results for the magnesium phosphate grouts are shown in Figure 4.3. These plots reflect testing from inception to completion (except Weakley) on August 2, 2004. Data taken during most temperature changes and during an interval of room-temperature pressure checking for the test U-Sludge were removed to provide true plots of the gas generation profile. The y-axes are in units of moles of hydrogen generation per kilogram of uranium metal. Complete reaction of all uranium metal corresponds to 8.4 moles H₂ per kilogram uranium. The gas generation rates decreased to zero in each test, indicating complete consumption of the uranium metal reactant.

Note that undulations were observed in the gas generation plots, particularly in later stages of the testing. The waviness likely arose because of large temperature swings in the room air around the test vessels. Over the span of the present testing, air temperature variations in a single day were as low as 2°C but as large as 10°C during hot weather. Even though the test vessels were insulated and the temperatures of the test materials (sludge and sludge waste form) were held at selected constant temperature by thermostat control, the test vessels themselves were located in an open face hood. The constant high air flow during

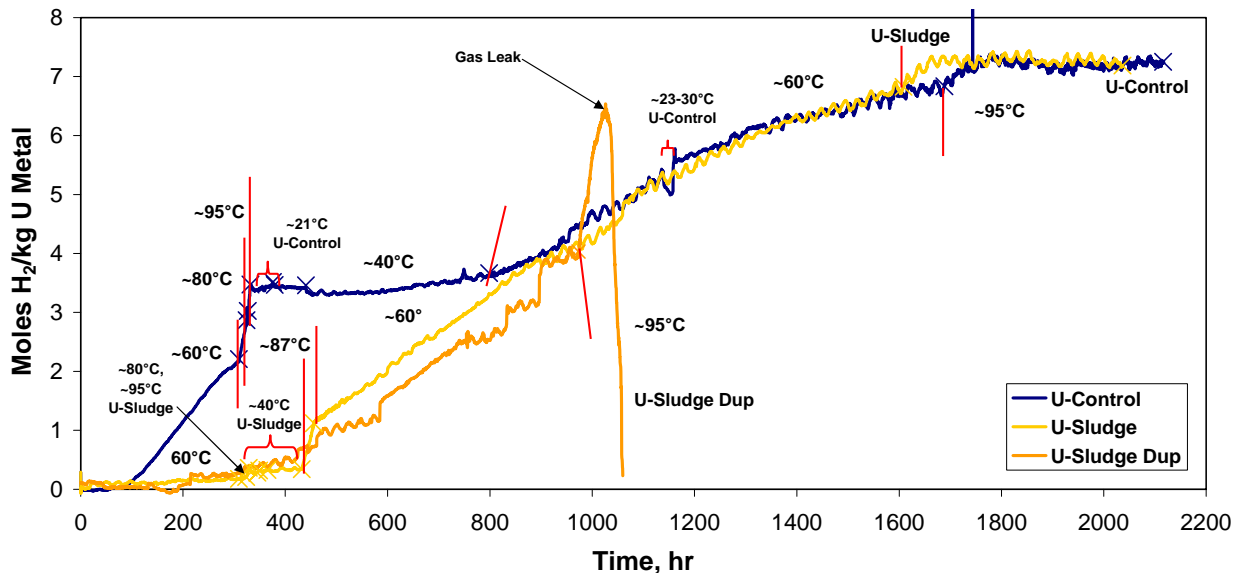


Figure 4.1. Total Gas Generation from U-Control, U-Sludge, and U-Sludge Dup

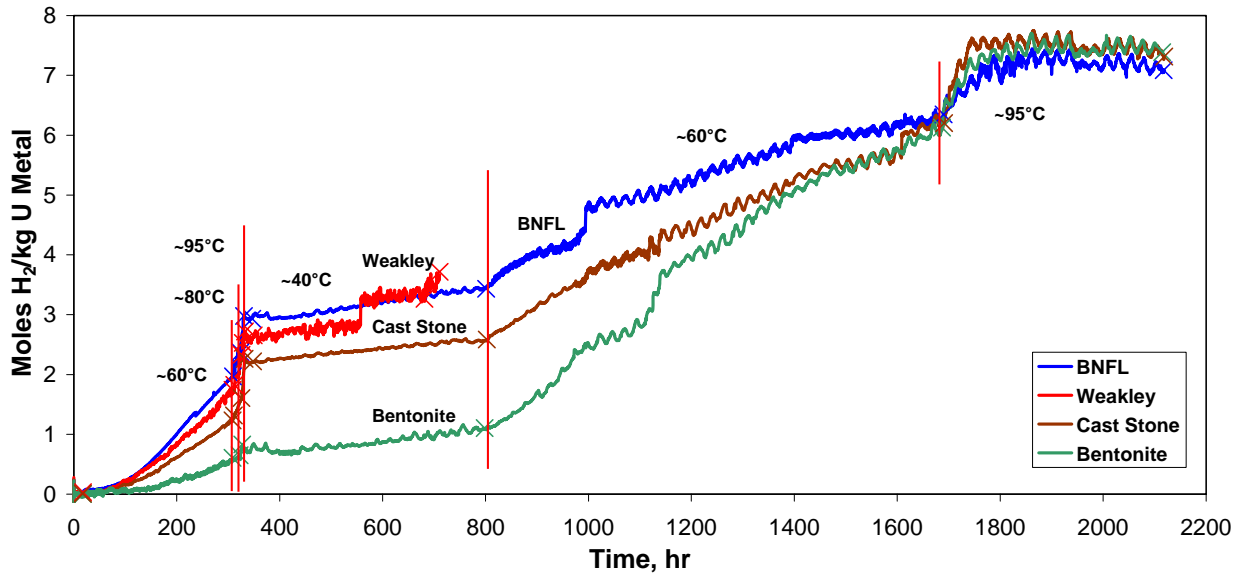


Figure 4.2. Total Gas Generation from Portland Cement Grouts

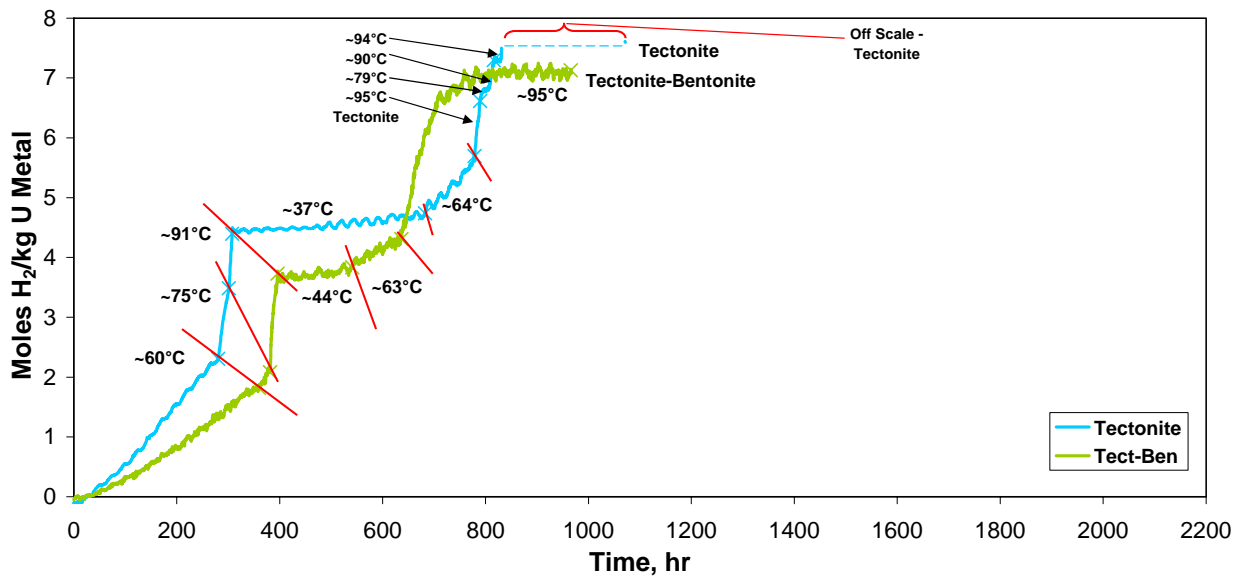


Figure 4.3. Total Gas Generation from Magnesium Phosphate Grouts

warm times of the day caused higher gas temperature in the vessel than was measured by the vapor space thermocouple located at the center of the vessel, increasing the apparent number of moles of gas. This trend was reversed during cool periods and a wavy trace in number of moles with time was observed. The vessels were wrapped with more insulation, but the temperature swings remained. To minimize the effects of the diurnal temperature swings, the rate data were evaluated over several-day periods.

It is seen that a ~50-hour and a ~24-hour room-temperature interval occurred for the U-Control test at approximately 350 hours and 1100 hours, respectively, when the heater unexpectedly tripped off. A gas

leak also occurred shortly after the U-Sludge Dup test temperature was raised to ~95°C, causing this test to terminate before the uranium metal completely reacted.

As shown in Figures 4.1 through 4.3, the gas generation rates increased as temperature increased stepwise from ~60°C, to ~80°C, and then to ~95°C. The gas generation then decreased when the temperature was lowered to ~40°C, increased again when the temperature was returned to 60°C, and then increased for the final excursion to ~95°C. The U-Sludge Dup test was kept at ~60°C for most of its duration to learn about induction time to full onset of reaction.

The gas generation rates appeared to be negative for three of the Portland cement grout tests (BNFL, Weakley, Cast Stone) immediately after lowering the temperature to 40°C, and took some time (~40 hours) to resume evolution. For the fourth Portland cement grout test (Bentonite), gas generation at 40°C resumed after about 100 hours. The two magnesium phosphate grouts (Tectonite and Tectonite-Bentonite) showed no hesitation in gas generation when adjusted to 40°C. The initial negative gas generation rates at 40°C, which followed the testing at 60°C, 80°C, and 95°C, may reflect the contraction of gases trapped in the pores of the grouts (after the ~55°C cooling from 95°C to 40°C) and the consequent slow diffusion of gas from the vessel void space into the grout pores.

Gas generation rates for the tests were determined over selected intervals, which were past the induction times but before 40% uranium consumption had occurred, and during which the temperature was held steady. The rates, which were taken from slopes of the gas generation plots in units of moles H₂ generated per kilogram of uranium per day, were converted to units of grams of uranium corroded per square meter of uranium surface area per day, based on the initial specific surface area of the uranium metal beads (4.28 cm²/g or 0.428 m²/kg) and adjusted based on the fraction of uranium reacted (see Figure A.4 and the footnote in Section A.2).

The temperature and rate values, in terms of grams of uranium corroded per square meter of uranium surface area per day, are shown in Table 4.1. The data may be compared with the SNF Databook (Duncan 2001) rates at similar temperatures also given in Table 4.1.

Table 4.1. Uranium Corrosion Rates in Reference and Grouted Waste Form Tests^(a)

SNF (Duncan 2001)		U-Control		U-Sludge		U-Sludge Dup		BNFL	
T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate
60	6.84E+1	59.80	7.96E+1	60.69	4.67E+1	62.51	5.15E+1	60.98	6.71E+1
80	2.23E+2	80.77	3.60E+2	86.62	2.33E+2	–	–	79.68	2.18E+2
95	4.96E+2	95.57	7.93E+2	95.66	3.01E+2	–	–	95.02	1.11E+3
40	1.81E+1	40.72	3.15E+1	40.33	5.20E+0	–	–	40.10	5.82E+0
20	3.98E+0	–	–	–	–	–	–	–	–
Bentonite		Weakley		Cast Stone		Tectonite		Tectonite-Bentonite	
T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate
60.48	2.34E+1	61.85	4.93E+1	60.98	4.45E+1	59.60	6.00E+1	61.51	4.51E+1
79.59	5.97E+1	80.12	2.30E+2	79.16	1.58E+2	61.09	8.59E+1	75.22	1.40E+2
94.01	3.23E+2	86.19	2.10E+2	94.94	8.88E+2	75.94	4.33E+2	91.49	4.87E+2
41.18	5.45E+0	41.44	1.62E+1	40.02	6.61E+0	90.86	1.75E+3	44.30	1.11E+1
–	–	–	–	–	–	37.02	1.28E+1	–	–

(a) Rates expressed in g/m²·day.

4.1 Induction Time

Induction times before the production of gas were ~50 to 110 hours at 60°C for the Portland cement grout tests (BNFL, Bentonite, Weakley, and Cast Stone) and for the U-Control test (uranium metal in water). This compares with ~205 hours for K Basin sludge sample KC-2/3 P250 tested at 60°C (Delegard et al. 2000).

The magnesium phosphate grouts, Tectonite and Tectonite-Bentonite, showed brief (~10-hour) induction times before gas generation commenced at 60°C. The earlier onset of gas generation may have occurred because the Tectonite grout evolves considerable heat when setting. This heat may have removed dissolved oxygen and been sufficient to overcome at least some of the induction time to onset of the anoxic reaction of uranium metal with water to form hydrogen gas.

Neither the U-Sludge test nor the later U-Sludge Dup test, both containing the simulated KW canister sludge (uranium metal, UO₂, SiO₂, and water; see Table 3.1), began to react at 60°C as early as the test with uranium metal and water only (U-Control) or the six grout tests containing simulated KW canister sludge. The U-Sludge test finally began significant reaction when heated to 95°C, over 310 hours into the test. Once past the induction time, the U-Sludge test showed the expected increase of gas production rate with temperature (Figure 4.1). The U-Sludge Dup test was held at ~60°C for virtually its entire test duration to observe its induction period and subsequent behavior. As seen in Figure 4.1, it began to satisfy the induction time after ~300 hours at 60°C. The rate continued to increase such that after 600 hours it approached the rate observed for U-Sludge at the same temperature. From that point, the rate observed for U-Sludge Dup corresponded to that of the U-Sludge test.

4.2 Portland Cement Grouts

The gas generation rate findings for the four individual tests based on Portland cement grout formulations are summarized individually.

4.2.1 BNFL

The BNFL grout test gas generation profile largely parallels that observed for the U-Control test. While some indication of decreased rate is seen above about 900 hours when compared with U-Control, a gas generation excursion around 1000 hours largely overtook the prior lag. The lag may reflect the expected chemical consumption of water as the dry BNFL grout formulation cured, starving uranium metal of water reactant to form hydrogen gas. However, given the behaviors of other grout tests, showing similar decreases, the decrease may simply indicate depletion of the uranium metal.

4.2.2 Weakley

The Weakley grout test showed relatively high reaction rates through ~710 hours (28 days) of testing. After this point, conditions were altered to study the effects of aeration to possibly poison the anoxic reaction of uranium metal with water. The results of the aeration tests are presented in Section 4.2.3.

An abrupt jump in pressure, and total moles of gas, was observed for the Weakley grout about 557 hours into testing and before aeration. The reason for this jump, which occurred in the span of one 20-minute data-recording interval at 40°C, is not known, but possibly could be due to fracturing of the grouted form,

releasing trapped gas, or due to the relaxation of a stuck pressure transducer. The gas quantity gain rates both before and after this jump, though noisy, are consistent with the remaining data.

4.2.3 Effect of Aeration on the Weakley Test

The Weakley grout test was terminated after about 710 hours under anoxic conditions; the heat turned off; the pressure relieved; and air introduced to the vapor space. Ten cycles of pressurization to about 1.5 atmospheres and venting were used to add air. The vessel was re-connected to the gas measurement manifold; the thermostat set to 60°C; and the heating and gas measurement resumed for ~4 days. The vessel again was cooled; the gas vented; air exchanged in; and heating and gas measurement resumed overnight. Similar such cycles occurred over the next 3 days. The vessel was given a final cooling and venting, and a 7-day gas generation cycle was run. Gas sampling and analysis by mass spectrometry were performed on June 21, 2004, after the final 7-day cycle.

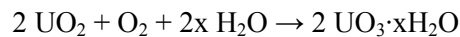
Despite the air purges, mass spectrometric analysis showed that significant neon gas remained from the initial neon-based anoxic test interval (Table 4.2).

Table 4.2. Gas Composition in the Aerated Weakley Test

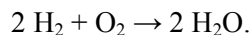
Gas	Composition, mole%	
	Air	Test Vessel
Ar	0.934	0.94
CO ₂	–	0.010
N ₂	78.06	78.8
O ₂	20.97	15.8
H ₂	–	0.58
Ne	–	3.06

As shown in Figure 4.4, net gas consumption occurred after the first and last two air additions and possibly after the intermediate air additions as well. Gas pressure, volume, and temperature measurements at the end of the anoxic period showed that the quantity of hydrogen gas generated was nearly 75% that of the initial neon cover gas. The gas composition results (Table 4.2) showed that after aeration, hydrogen is only about 19% of the neon. Therefore, significant hydrogen gas consumption occurred during the oxic period.

The gas analyses also showed the expected consumption of oxygen. This oxygen consumption is seen by comparing the O₂:Ar ratio normally observed in air (20.96:0.934 = 22.4) with that found in the product gas (15.8:0.94 = 16.8). The oxygen consumption is caused by reactions such as:



and by participation of oxygen in continued uranium metal corrosion, as demonstrated in accounts of uranium metal corrosion in oxygen-water vapor systems (Baker et al. 1966). Alternatively, the hydrogen and oxygen gases could have combined to form water:



Recent studies show that UO₂ can catalyze the hydrogen-oxygen recombination reaction (Ekeroth et al. 2004).

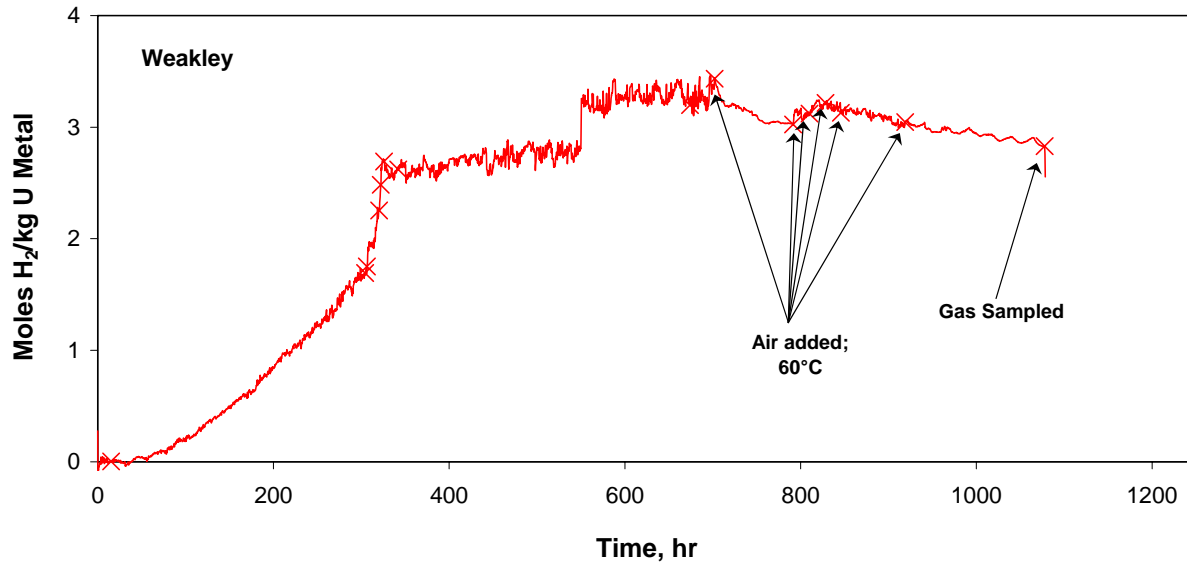


Figure 4.4. Weakley Grout Test Under Anoxic Conditions (to ~710 hours) and Under Aerated Conditions (after ~710 hours)

4.2.4 Cast Stone

The Cast Stone grout test showed somewhat lower rates than either the BNFL or Weakley grout tests. The gas generation rate decreased past about 1000 hours, reflecting consumption of the uranium metal.

4.2.5 Bentonite

During the initial stages of testing, the bentonite-containing grout exhibited the lowest gas generation rates of any form over the 40°C-95°C temperature range. However, the rates observed at 60°C for times later in testing (from ~800-1200 hours) were higher than observed during the initial interval at 60°C, between ~150 and 300 hours. The rate after 1000 hours also decreased, and then increased, after 1100 hours. The reasons for these changes in performance are unknown.

4.3 Magnesium Phosphate Grouts

4.3.1 Tectonite

The Tectonite grout gas generation rate at 60°C began at about two-thirds of the rate observed for uranium metal alone in the test U-Control and within the range observed for the BNFL, Weakley, and Cast Stone Portland cement forms at 60°C. With additional time, the rate near 60°C increased to be higher than any of the Portland cement grouts.

4.3.2 Tectonite-Bentonite

The Tectonite-Bentonite test showed significantly lower uranium corrosion rates than the test with Tectonite alone. However, its performance was no better than the Portland cement-based Bentonite test.

4.4 Temperature Dependence of the Uranium Corrosion Reaction

The rate data taken from Table 4.1 for the reference tests, the Portland cement grout tests, and magnesium phosphate grout tests are provided in Arrhenius coordinates in Figures 4.5 through 4.7, respectively. The Arrhenius rate parameters for all tests, presented in these three figures, are summarized in Table 4.3.

4.4.1 Reference Tests

The uranium metal corrosion activation energy observed in the U-Control test conducted with uranium metal beads in water (13.8 kcal/mole) is identical to that predicted in the SNF Database (Duncan 2001) (Figure 4.5), while the observed rate is about 50% higher than predicted by the SNF Database rate. In comparison, the U-Sludge tests containing SiO₂ and UO₂ sludge components have uranium corrosion rates from ~40% to 70% of those predicted by the SNF Database, with higher activation energy, 16.9 kcal/mole, closer to the 15.9 kcal/mole activation energy predicted by the Hilton (2000) correlation.

Present observations of non-irradiated uranium corrosion also may be compared with prior tests of actual K Basin sludge containing crushed irradiated uranium metal fuel (Schmidt et al. 2003), which showed rates about one-third to one-half of those predicted by the SNF Databook and with activation energies closer to those predicted by the Hilton (2000) correlation (15.9 kcal/mole) than the SNF Databook (13.8 kcal/mole; Duncan 2001). The experimental corrosion rates and activation energies for irradiated

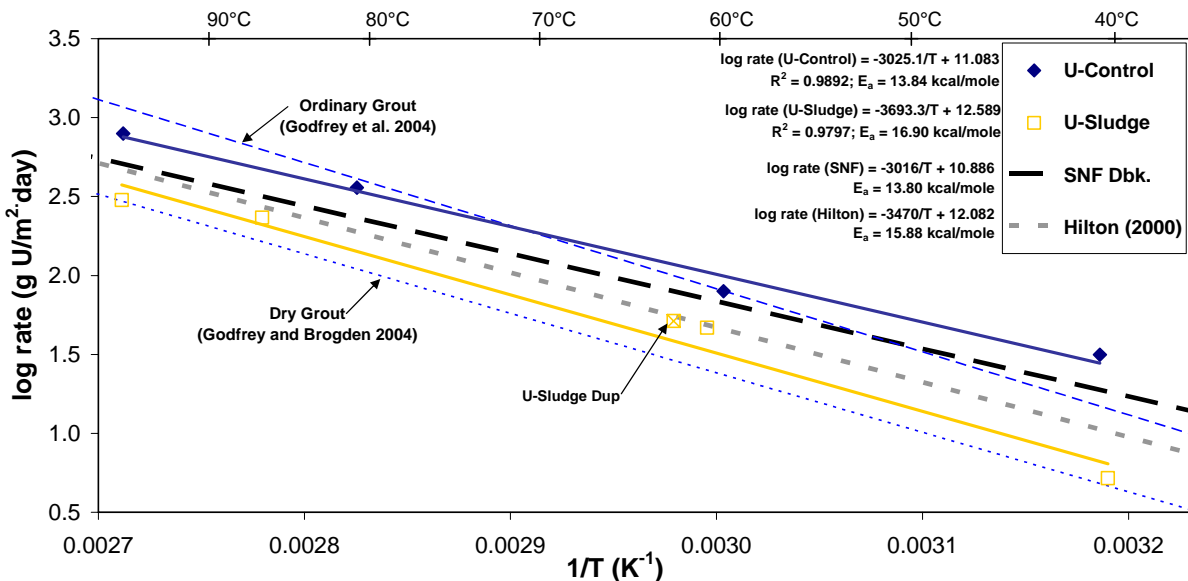


Figure 4.5. Arrhenius Plot of Uranium Corrosion for Reference Tests in Comparison with with SNF Databook (Duncan 2001), Hilton (2000), and Grouted Uranium (Godfrey et al. 2004; Godfrey and Brogden 2004) Correlations

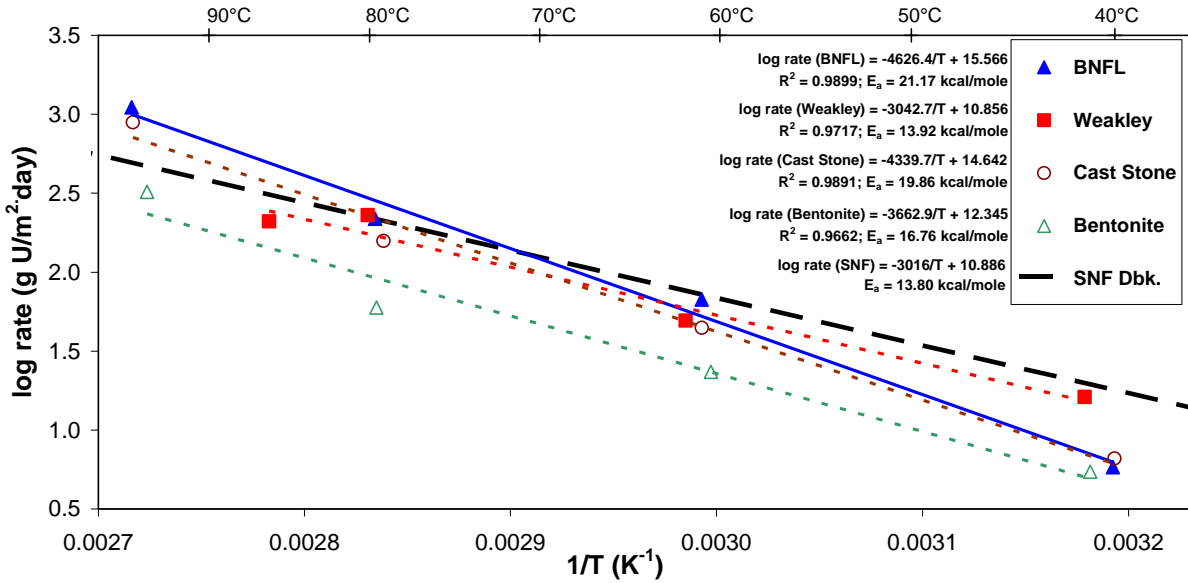


Figure 4.6. Arrhenius Plot of Uranium Corrosion for Portland Cement Grout Tests

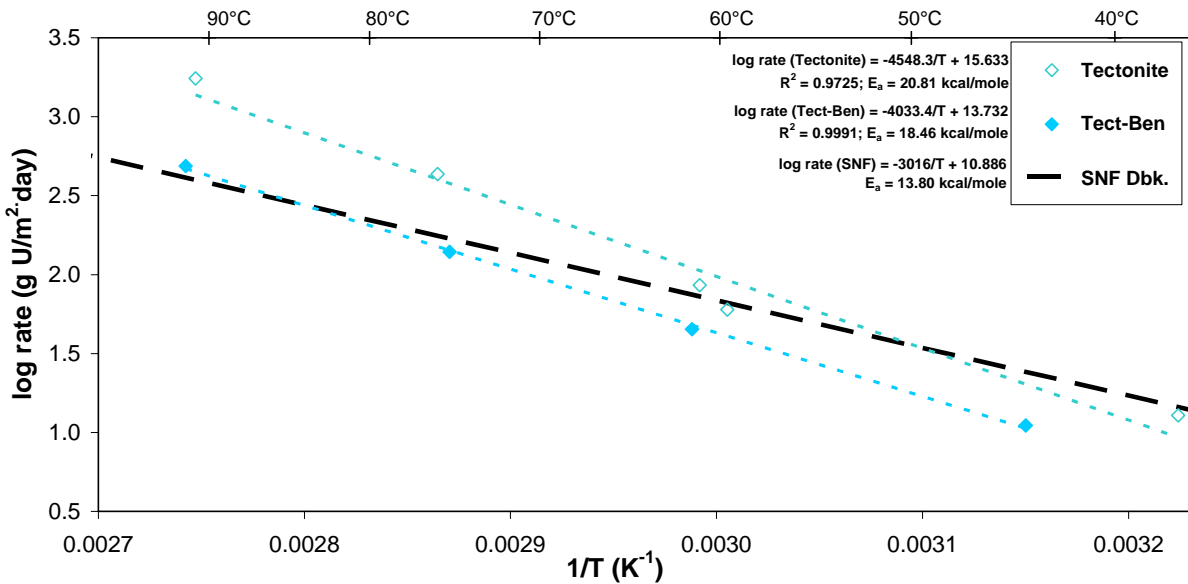


Figure 4.7. Arrhenius Plot of Uranium Corrosion for Magnesium Phosphate Grout Tests

uranium thus are similar to those of non-irradiated uranium in simulated sludge. Together, these observations may be useful in assigning reaction rate safety factors for sludge processing or storage. In contrast, the uranium corrosion rate activation energy for sludge-free, non-irradiated uranium in the test U-Control is identical, and the rate itself 50% higher than that predicted by the SNF Databook values.

Table 4.3. Arrhenius Parameters and Activation Energies for Uranium Metal Corrosion in Reference and Grout Tests Compared with Published Rate Parameters

Test	log rate (g U/m ² ·day = A/T + B)			E _a , kcal/mole
	A	B	R ²	
<i>Technical Literature</i>				
SNF (Duncan 2001)	-3016	10.886	–	13.8
U Metal (Hilton 2000)	-3470	12.082	–	15.9
Ordinary Grout (Godfrey et al. 2004)	-3994.7	13.901	–	18.5
Dry Grout (Godfrey and Brogden 2004)	-3769.6	12.693	–	17.2
<i>Reference</i>				
U-Control	-3025	11.083	0.989	13.8
U-Sludge	-3693	12.589	0.980	16.9
<i>Portland Cement Grouts</i>				
BNFL	-4626	15.566	0.990	21.2
Bentonite	-3663	12.345	0.966	16.8
Weakley	-3043	10.856	0.972	13.9
Cast Stone	-4340	14.642	0.989	19.9
<i>Magnesium Phosphate Grouts</i>				
Tectonite	-4548	15.633	0.972	20.8
Tectonite-Bentonite	-4033	13.732	0.999	18.5

4.4.2 Portland Cement Grout Tests

The activation energies of BNFL, Cast Stone, and Bentonite grouted waste forms (~16.8-21.2 kcal/mole) are closer to those found for the sludge-blanketed uranium metal in the U-Sludge test (16.9 kcal/mole) than to the U-Control test (13.8 kcal/mole) (uranium metal-alone in water). The activation energies in the present Portland cement tests also bracket the rates observed by Godfrey and colleagues for uranium corrosion in Portland cement-based grouts formulated at dry and ordinary water contents (Godfrey and Brogden 2004 and Godfrey et al. 2004, respectively). In contrast, the Weakley grout has an activation energy (13.9 kcal/mole) near that of the uranium metal in water. The higher temperature dependence in grout may indicate that the barrier to corrosion offered by grout is diminished by the improved diffusion and higher vapor pressure of water at higher temperature.

The lowest overall corrosion rates observed in any of the grouted tests were found for the Bentonite grout prepared with Portland cement. Although the corrosion rate in the Bentonite grout at 40°C is about one-fourth that observed for uranium metal alone in water (U-Control), the rate is not appreciably different from that observed for the starting sludge (U-Sludge) in the absence of any grouting agent. The Bentonite grout rate and activation energy closely matches those reported by Godfrey and Brogden (2004) for dry Portland cement.

4.4.3 Magnesium Phosphate Grout Tests

Like the tests with the Portland cement grouts, the tests with grouts formulated with Tectonite showed relatively high activation energies (~18.5-20.8 kcal/mole) compared with uranium metal-alone in water (13.8 kcal/mole). Again, the higher temperature dependence in the magnesium phosphate grout may indicate that the barrier to corrosion is diminished by the improved diffusion of water at higher

temperature. Comparing the two Tectonite tests also shows again that bentonite offers some benefit in decreasing the uranium corrosion rate.

4.5 Gas Analyses

Gas samples were drawn for mass spectrometric analysis at the conclusion of each test. Note, the results for the gas analysis of the aerated Weakley Portland cement grout test were discussed in Section 4.2.3. The remaining tests began with a pure neon cover and were maintained at anoxic conditions. All tests except the Weakley grout were taken to complete oxidation (extinction) of the contained uranium metal, as demonstrated by the flattened gas generation curves.

The gas analysis results are shown in Table 4.4 and compared with the composition of air. As expected, each gas sample contains neon cover gas and hydrogen gas produced by the reaction of uranium metal with water. Despite the multiple neon pressurization/vent cycles at the beginning of the tests, each sample also shows some air contamination, as demonstrated by the presence of argon; nitrogen and oxygen also are present in measurable concentrations. The U-Sludge Dup vessel leaked during testing and shows $(100\% \times 0.043/0.934 =)$ 4.6% air contamination. Air contamination is found to be higher in the grouted waste forms than in the U-Control and U-Sludge tests. The air may have been present in the pores of the grouted waste forms and would have been difficult to remove completely, even by the pressurization and venting technique used in these tests. Finally, methane, C₂ hydrocarbons, and occasionally, higher hydrocarbons are found in each sample.

The individual gas quantities generated or consumed during testing were determined from the final gas compositions and the quantities of total gas present in the vessels, associated tubing, and gas filter at the conclusion of each test (Table 4.4). The total gas quantities were determined from the ideal gas law ($n = PV/RT$, where n is the number of moles of gas and R is the gas constant). The calculation used the

Table 4.4. Gas Compositions and Quantities at the Completion of Testing

Gas	Composition, mole%								
	Air	U-Control	U-Sludge	U-Sludge Dup ^(b)	BNFL	Bentonite	Cast Stone	Tectonite	Tectonite-Bentonite
Ar	0.934	0.002 ^(a)	0.002	0.043	0.011	0.005	0.003	0.005	0.004
N ₂	78.06	0.080 ^(a)	0.078	3.57	0.87	0.329	0.264	0.435	0.367
O ₂	20.97	0.001 ^(a)	0.007	0.60	0.090	0.023	0.012	0.005	0.002
CH ₄	–	0.036 ^(a)	0.033	0.027	0.039	0.025	0.034	0.037	0.028
C ₂ H _x	–	0.0045 ^(a)	0.006	0.005	0.006	0.005	0.006	0.006	0.006
Other HC ^(c)	–	<0.001 ^(a)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
H ₂	–	58.2 ^(a)	47.1	63.2	64.1	58.9	65.0	66.0	64.0
Ne	–	41.6 ^(a)	52.0	32.0	34.8	40.0	34.6	31.5	34.4
Stage	Total Gas, moles								
	Air	U-Control	U-Sludge	U-Sludge Dup	BNFL	Bentonite	Cast Stone	Tectonite	Tectonite-Bentonite
Initial	–	8.20E-3	7.93E-3	8.05E-3	6.31E-3	6.91E-3	6.39E-3	4.82E-3	4.74E-3
Final	–	2.14E-2	2.03E-2	– ^(b)	1.79E-2	1.91E-2	1.70E-2	1.66E-2	1.58E-2

(a) Average of two analyses.
(b) Test apparatus leaked.
(c) HC = hydrocarbon.

final gas pressure, volume, and temperature (PVT) in the test vessels and accounted for the volume occupied by the simulated sludge or solid grouted waste form.

The quantities of nitrogen and oxygen air contamination were calculated from the argon concentration found in the gas samples (Table 4.5). Consequently, the calculations are subject to the high relative error of the argon analyses ($\pm 0.001\%$) in the values presented in Table 4.4). The net amount of nitrogen is found to fluctuate between positive (production) and negative (consumption) values. Oxygen was consumed in each test. The nitrogen and oxygen quantities, ranging from 2.8×10^{-5} moles consumption to 5.2×10^{-6} moles production, are small compared with the $\sim 1 \times 10^{-2}$ moles of hydrogen produced in each test.

The quantities of uranium metal reacted in each test were determined from the quantities of hydrogen gas produced by $U + 2 H_2O \rightarrow UO_2 + 2 H_2$ and oxygen gas consumed by the reaction $U + O_2 \rightarrow UO_2$, assuming that no other chemical sink for oxygen exists. This assumption is questionable, however, in that UO_2 , which reacts readily with O_2 to form schoepite, was present in all tests as a product of the uranium corrosion reaction in water and was present in abundance in all tests but U-Control as a component of the simulated sludge. Nevertheless, as shown by comparing the uranium metal quantities determined by the hydrogen production and oxygen consumption reactions in Table 4.5, oxygen gas consumption contributes no more than 0.5% to the total number of moles of uranium metal reacted.

Table 4.5. Gas Production and Material Balance at the Completion of Testing

Gas	Production, moles							
	U-Control	U-Sludge	U-Sludge Dup ^(a)	BNFL	Bentonite	Cast Stone	Tectonite	Tectonite-Bentonite
N ₂	-1.85E-5	-1.81E-5	-1.04E-6	-8.81E-6	-1.70E-5	2.26E-6	2.84E-6	5.17E-6
O ₂	-9.60E-6	-7.70E-6	-1.59E-5	-2.80E-5	-1.70E-5	-9.42E-6	-1.78E-5	-1.39E-5
CH ₄	7.70E-6	6.71E-6	1.18E-6	6.97E-6	4.77E-6	5.79E-6	6.14E-6	4.42E-6
C ₂ H _x	9.62E-7	1.22E-6	2.18E-7	1.07E-6	9.54E-7	1.02E-6	9.96E-7	9.48E-7
Other HC ^(b)	–	–	–	–	–	–	–	–
Sum of C in all HC	9.62E-6	9.15E-6	1.61E-6	1.20E-5	6.68E-6	9.46E-6	8.13E-6	8.34E-6
H ₂	1.25E-2	9.57E-3	2.75E-3	9.11E-6	1.12E-2	7.83E-6	1.10E-2	6.32E-6
Value	Material Balance							
	U-Control	U-Sludge	U-Sludge Dup ^(a)	BNFL	Bentonite	Cast Stone	Tectonite	Tectonite-Bentonite
U metal, moles, by $U + 2 H_2O \rightarrow UO_2 + 2 H_2$	6.23E-3	4.79E-3	–	5.73E-3	5.62E-3	5.53E-3	5.48E-3	5.06E-3
U, moles, by $U + O_2 \rightarrow UO_2$	9.60E-6	7.70E-6	–	2.80E-5	1.70E-5	9.42E-6	1.78E-5	1.39E-5
Total U metal, moles by H ₂ and O ₂	6.24E-3	4.78E-3	–	5.75E-3	5.64E-3	5.54E-3	5.49E-3	5.07E-3
Initial U metal, moles	6.44E-3	6.22E-3	–	6.55E-3	6.12E-3	6.43E-3	6.22E-3	6.26E-3
% U Metal Recovery	96.8	77.1	–	87.8	92.1	86.2	88.3	80.9
[C], ppm in U	78	97	59	80	60	71	75	63
(a) Gas leaked.								
(b) HC = hydrocarbon.								

The total number of moles of uranium metal reacted as determined by the gas data may be compared with the quantity of uranium metal added to each test. This comparison, given in the bottom of Table 4.5, shows 96.8% recovery for the U-Control test having only uranium metal in water. However, uranium recoveries in all other tests are lower, ranging from ~77% to 92%, and averaging 85.4%. Each of those tests contained approximately 21.3 grams of UO_2 added as part of the simulated KW canister sludge. The XRD analysis showed UO_2 to be the only crystalline phase present in the UO_2 stock (see appendix). However, amorphous uranium(VI) compounds [e.g., schoepite, $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$] also may have been present as a surface coating on the UO_2 .^(a) For example, schoepite is known to form on the surface of UO_2 in moist air (Buck et al. 1998) and uraninite (the UO_2 mineral) alters to uranium(VI) minerals in natural aerated waters (Finch and Murakami 1999). Schoepite and other uranium(VI) phases are also found in actual K Basin sludge (see Makenas et al. 1996-1999) and necessarily arise from corrosion of uranium metal.

Recent studies have confirmed that H_2 gas can reduce UO_2^{2+} under hydrothermal conditions (Ekeroth et al. 2004). Thus, it is possible that some of the hydrogen gas produced by uranium metal corrosion could have been consumed by uranium(VI) present as a contaminant on the UO_2 used for the simulated sludge. Without further testing, however, this explanation remains speculative.

The potential loss of ~15% of the hydrogen arising from uranium metal corrosion to uranium(VI) reduction or other reactions with simulated sludge components does not affect the conclusions drawn on the relative merits of the various grouted waste forms, because all grout tests used the same simulated sludge composition. The 15% decrease in hydrogen production does, however, offer a slight contribution to the ~threefold decrease in hydrogen generation rate observed from uranium metal corrosion in water in the presence of sludge (the U-Sludge and U-Sludge Dup reference tests) compared with the reference test without sludge (U-Control).

The potential scavenging of trace hydrogen by larger quantities of uranium(VI) may turn out to be an important contributor to achieving the 3.65×10^{-8} moles H_2 /second RH-TRU limit for shipment to WIPP for waste forms having low intrinsic hydrogen gas generation rates. Under these circumstances, the presence of large quantities of uranium(VI) phases may act as significant scavengers of the small fugitive H_2 gas product from uranium metal corrosion or radiolysis.

The methane, C_2 hydrocarbons, and higher hydrocarbons produced during the uranium metal corrosion give evidence for the presence of uranium carbide (UC) in the uranium metal beads. The same gases were observed in tests of K Basin sludge and crushed irradiated metal fuel corrosion in the Series I-III testing. As discussed in those reports, the light hydrocarbons are observed when UC in the metal reacts with water. The carbon concentration in the uranium beads averages 73 ppm. Methane comprises, on average, about 74 mole% of the carbon, consistent with previous observations for actual sludge and crushed fuel.

4.6 Post-Test Examination

Post-test examinations were performed for the uranium metal-water and simulated sludge reference tests and the tests with the grouted waste forms after the vessels were cooled and gas samples were taken. The

(a) The presence of schoepite (72.9 wt% uranium) or other more oxidized uranium compound also would explain the low uranium concentration seen in the stock UO_2 (84.1 wt% versus the expected 88.1 wt%), see appendix.

test vessels first were disconnected from the heater cords, thermocouple leads, and gas tubing, then weighed, opened, and the contents removed and examined.

Water was observed to seep from the gas line fittings when they were disconnected from the tops of each gas generation vessel. The water undoubtedly condensed in the gas lines and gas filters from vapors released during heating of the reference and grout-form test materials. Consequently, the test vessels lost from 0.2 to 3.6 (average 1.6) grams (of water) between the beginning and the end of the test.

The pH of the U-Control, U-Sludge, and U-Sludge Dup slurries was measured and found to be 8.19, 6.08, and 6.00, respectively. The reason for the lower pH of the U-Sludge tests compared with the U-Control tests is not known. The starting or product U-Sludge constituents (U, UO₂, SiO₂, H₂O) could not have reacted to alter the pH unless the SiO₂ itself lowered the pH from the beginning. However, the present observation of higher pH found by corroding uranium metal-alone in water compared with corroding uranium metal in the presence of sludge is similar to that observed for actual crushed irradiated uranium metal fuel corroded in water alone and in water and K Basin sludge (Schmidt et al. 2003). The prior tests with only crushed fuel and no added sludge ended at higher pH (pH 7.9 to 10.9) than tests with crushed irradiated fuel particles and actual sludge (pH 4.9 to 8.6).

Small amounts of liquid water also were observed in the vessels containing the grouted waste forms. Thus, none of the grout materials bound the water sufficiently to keep it from escaping the grout during heating nor were the grouts able to re-sorb the freed water upon cooling. These observations are significant in considering the possible application of grouts to K Basin sludge destined for WIPP. In sufficient quantity, the free water could collect and be considered drainable within the waste drum.

The gas generation testing showed that water, either present as liquid or vapor, was not sufficiently sequestered or chemically bound by the grouts to prevent reaction with the uranium metal. As is known by prior studies, under anoxic conditions, uranium metal corrosion proceeds at essentially the same rate whether immersed in water or simply present in saturated water vapor:

Uranium corrosion in immersed water obeys linear kinetics at temperatures below 300°C and proceeds at a rate similar to the water vapor reaction at saturation pressure. Due to the rate similarity, the same mechanism probably controls water immersion oxidation as well as water vapor oxidation (Hilton 2000, p. 21).

Water absorbed on the uranium metal and uranium oxide surface evidently was sufficient to allow the uranium metal corrosion reaction to continue unabated. The grouts, particularly those with bentonite, if anything, may only help decrease the uranium metal corrosion rate by altering the metal/oxide surface. However, none of the grouts was a powerful enough desiccant to remove water from the vapor phase and thus prevent the uranium metal corrosion reaction.

All grouted waste forms, except the BNFL grout, were found to be fractured and crumbled after testing. It is not known at which temperature, up to ~95°C, the materials fractured or if the fracturing was caused by swelling of the contained uranium metal as it converted to UO₂ or was caused by thermal failure of the grouts themselves. Photographs of the Portland cement and magnesium phosphate grouted waste forms collected after testing are displayed in Figures 4.8 and 4.9.

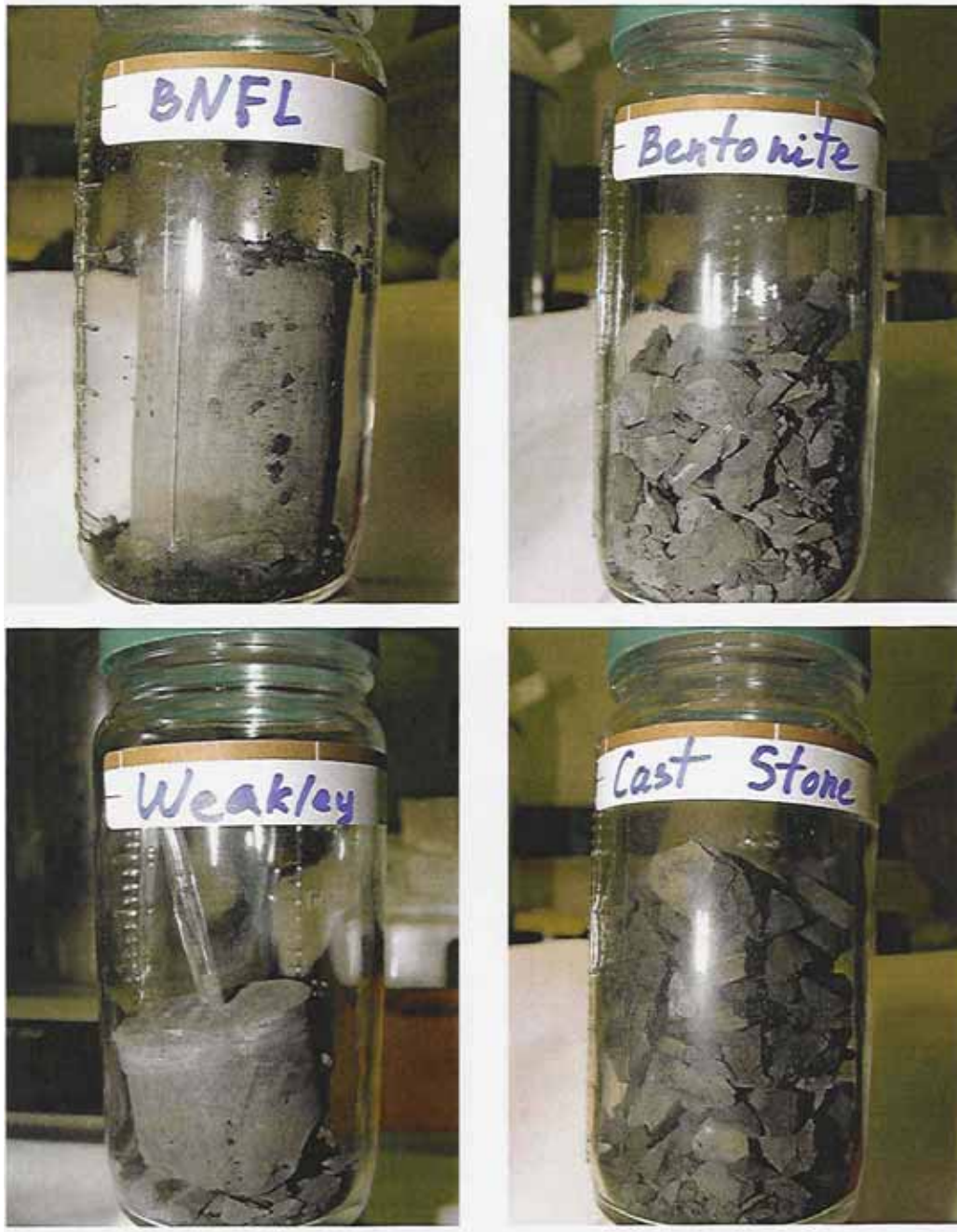


Figure 4.8. Portland Cement Waste Forms After Gas Generation Testing
Top left, BNFL; top right, Bentonite
Bottom left, Weakley; bottom right, Cast Stone



Figure 4.9. Magnesium Phosphate Cement Waste Forms After Gas Generation Testing
Left, Tectonite; right, Tectonite-Bentonite

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Appendix

Evaluation and Characterization of Materials Used in Gas Generation Testing

Appendix

Evaluation and Characterization of Materials Used in Gas Generation Testing

The testing was performed with simulated K Basin sludge of deliberate composition and with various candidate liquid-immobilization agents. The use of sludge surrogates with well-controlled composition, rather than actual sludge, with its associated fission product content, allowed the experiments to be conducted more expeditiously and cost effectively in fume hoods rather than radiologically shielded (hot cell) facilities. The non-irradiated uranium metal beads of natural enrichment allowed re-use of the gas generation vessels and simplified data interpretation by limiting gas formation to hydrogen, eliminating the possibility of other gas-generating reactions from sludge (e.g., to produce CO₂), which have been observed in studies with actual K Basin sludge. Future testing with actual sludge may be necessary to validate the tests with simulated sludge; however, a sampling and analysis campaign would be needed to obtain an adequate amount of sludge material.

A.1 K Basin Sludge Simulant

Actual K Basin sludge has been characterized physically, chemically, and radiochemically, and the results reported in a number of documents. Although gases other than hydrogen (primarily CO₂) are generated by the reactions within the sludge, the Series III gas generation testing (Schmidt et al. 2003) confirmed that it is the reaction of uranium metal with water to form hydrogen gas that dominates the total gas generation at the high uranium metal concentrations targeted for the present testing. Uranium hydride; uranium dioxide (UO₂); and, if oxygen gas is present, more oxidized hexavalent uranium [uranium(VI)] phases arise from this corrosion.

Besides uranium phases, inorganic phases found in actual sludge include Hanford sand (e.g., quartz, anorthite, and mica), sloughed concrete, commercial sand used in sand filters, and K Basin structural iron and aluminum corrosion products (e.g., hematite, goethite, gibbsite). Zirconium metal alloy, as Zircaloy cladding spalled from the corroding fuel, is also found. Inorganic ion exchange material (Zeolon 900, based on the zeolite mineral mordenite) is present as well. Organic materials include mixed strong acid/strong base organic ion exchange resin, plastics, and plant and animal debris.

The sludge composition selected for testing is based on the properties of KW canister sludge, the most reactive sludge being considered for direct disposal in grout. For simplicity to assist in making and interpreting calculations related to the other complex mechanisms being measured, the sludge simulant ingredients selected were limited to uranium dioxide (UO₂) powder and uranium metal in water, with fine silica (quartz) sand as the stable (non-reactive) component. The KW canister sludge phase distribution (with slightly different starting parameters) is described in more detail in a separate analysis (see Appendix B of Schmidt and Delegard 2003).

The fine silica sand was white quartz (SiO₂), ~210-300 μm particle size. The fine blank UO₂ powder was of natural enrichment. A portion of the UO₂ was dissolved in excess nitric acid, heated to dryness, and re-dissolved in nitric acid of known concentration. The absorption spectrum of the product uranium(VI) was recorded over the characteristic uranium(VI) multiplet and the absorbance maximum near 414 nm

measured in a length-calibrated cuvette. Based on the known molar absorptivity of uranium(VI) in this medium, the uranium concentration in the UO₂ powder was found to be 84.1 wt% compared with 88.1 wt% for pure dry UO₂. A separate portion of the UO₂ powder was analyzed by X-ray diffractometry (XRD), and the characteristic powder diffraction pattern for UO₂ was obtained. No other crystalline phases or peaks were found in the XRD scan.

The sludge component proportions used in the present testing follow the composition described for the KW canister sludge (Tables 4-1 through 4-4a, Schmidt 2004). The KW canister sludge is considered representative of other streams, such as the KW settler tube sludge, coming from the KW Basin. According to the defined KW canister sludge parameters, the sludge should have 4.00 g/cm³ density and contain 65 volume percent water and 2.7 g/cm³ total uranium, 0.2 g/cm³ of which would be uranium metal (i.e., the sludge would contain 5 wt% uranium metal). The sludge quantity for the present gas generation testing was selected based on the capacity of the test vessels to accept the hydrogen gas created by complete corrosion of the uranium metal. As shown in Section 3.4, the corresponding quantity is 1.5 grams of uranium metal in a 220-ml test vessel, with a portion of that total volume excluded by the waste form itself.

For the present testing, it was calculated that to meet all but the 4.00 g/cm³ density criterion requires 0.31 g SiO₂ per cm³ sludge. The resulting sludge composition is outlined in Table A.1.

Table A.1. KW Canister Sludge Simulant Composition to Meet Water Concentration Criterion

Phase	Density, g/cm ³	Quantity		Quantity per Vessel, g
		Volume, cm ³	Mass, g	
U	19.05	0.0105	0.20	1.5
UO ₂	11.10	0.2559	2.84	21.3
SiO ₂	2.64	0.1174	0.31	2.7
H ₂ O	1.00	0.6500	0.65	4.5
Total	3.87	1.0338	4.00	30.0

Because SiO₂, a relatively low density material, is used as the third solid phase (after U and UO₂), the sludge is below the target 4.00 g/cm³ density. Alternatively, however, if the composition is altered so that the target sludge density is attained (by using 0.36 g SiO₂ per cm³ of sludge; see Table A.2), the 65 volume percent target water concentration is not met.

Table A.2. KW Canister Sludge Simulant Composition to Meet Density Criterion

Phase	Density, g/cm ³	Quantity		Quantity per Vessel, g
		Volume, cm ³	Mass, g	
U	19.05	0.0105	0.20	1.5
UO ₂	11.10	0.2559	2.84	21.3
SiO ₂	2.64	0.1380	0.36	2.3
H ₂ O	1.00	0.5956	0.60	4.9
Total	4.00	1.0000	4.00	30.0 (7.5 ml)

The sludge density and volume percent water targets are met if a stable sludge solid of density 3.71 g/cm³ is used in place of SiO₂ (Table A.3).

Table A.3. KW Canister Sludge Simulant Composition with Dense Component to Meet All Criteria

Phase	Density, g/cm ³	Quantity		Quantity per Vessel, g
		Volume, cm ³	Mass, g	
U	19.05	0.0105	0.20	1.5
UO ₂	11.10	0.2559	2.84	21.3
Unknown	3.71	0.0836	0.31	2.3
H ₂ O	1.00	0.6500	0.65	4.9
Total	4.00	1.0000	4.00	30.0

Because water concentration can be highly variable in settled sludge, the KW canister sludge formulation with SiO₂ that meets the density criterion (Table A.2) was selected. The selected formulation contains 0.36 g SiO₂ per cm³ and ~59.6 volume percent water to give sludge with density 4.00 g/cm³.

At the projected KW canister sludge loadings in grout, water in addition to that contained in the sludge will be required to react with the grout formers. Thirty grams of water (i.e., 30 – 4.9 = 25.1 grams more than the nominal sludge content) was selected for the sludge formulation testing to keep all grout and control tests on the same uranium metal/water reactant ratio. As shown in Table A.4, this quantity of water produces sludge loadings in the grouted waste forms of 8.1 to 13.7 volume percent in the tests with Portland cement grouts and 6.0 and 6.4 volume percent in the tests with magnesium phosphate (Tectonite) grouts. The sludge loadings thus bracket the loadings dictated by the fissile gram equivalent (FGE) limits (see Section 1.0). Note that at the 1:2 U:H₂O mole ratio dictated by the corrosion reaction, the U:H₂O stoichiometric weight ratio is 6.61 g U/g H₂O. Thus, the 1.5 grams of U metal will consume only 0.22 grams or ~0.75% of the available water. The extent of reaction will be limited by the quantity of uranium metal and not the quantity of water unless the water is sequestered or otherwise reacted with the cured grout.

Table A.4. Uranium-Water Reaction Test Matrix

Test ID	Sludge Simulant Mass, g			Grout Mix, g ^(b)	Est. Simulated Sludge Load, vol% ^(c)
	Water ^(a)	Sand/UO ₂	U Metal		
<i>Reference Tests</i>					
U-Control	30	0	1.5	0	NA
U-Sludge & U-Sludge Duplicate	30	2.32/21.3	1.5	0	NA
<i>Portland Cement Grouts</i>					
BNFL	30	2.32/21.3	1.5	129.5	8.1
Bentonite	30	2.32/21.3	1.5	66.2	12.4
Weakley	30	2.32/21.3	1.5	54.5	13.7
Cast Stone	30	2.32/21.3	1.5	100.6	9.6
<i>Magnesium Phosphate Grouts</i>					
Tectonite	30	2.32/21.3	1.5	193.3	6.0
Tectonite-Bentonite	30	2.32/21.3	1.5	178.8	6.4
(a) Water amount is 4.9 g for sludge and 25.1 g for grout make-up (see text).					
(b) Sum of grout mix components (cement, blast furnace slag, superplasticizer, bentonite, calcite, gypsum, “neat” Tectonite, Cast Stone formulation) constituted to make dry but mixable slurries.					
(c) Based on final grout form density of 2.0 g/cm ³ and sludge feed volume of 7.5 ml (sludge density 4.00 g/cm ³).					

A.2 Uranium Metal Particles

Non-irradiated uranium metal beads (~200-1100 μm diameter spheres) of natural enrichment provided the uranium metal particles used in the simulated KW canister sludge. This size distribution brackets the projected size of the uranium metal particles (640-970 μm) observed in the KE Basin sludge, based on gas generation rates observed in the Series I sludge corrosion tests (Delegard et al. 2000), while the Safety and Design Basis uranium metal particle size in KW canister sludge is assumed to be 500 μm (Schmidt 2004). As will be seen, non-irradiated uranium metal should corrode in a manner similar to that of the relatively low-irradiated uranium metal present in actual sludge.

The non-irradiated uranium metal beads were characterized and found to be relatively pure, in good condition, free of loose corrosion products and dust, and with a blue-purplish patina indicating a light interference corrosion layer. Scanning electron microscopy (SEM) and optical photographs showed most beads to be spherical. Energy dispersive spectrometry (EDS) obtained during SEM showed iron and aluminum alloying elements at small, but unquantified, concentrations. Iron (300-400 ppm) and aluminum (700-900 ppm) are the primary alloying elements in N Reactor fuel, while carbon, another potentially present element (365-735 ppm), is not identifiable by EDS. The net uranium concentration in N Reactor fuel is about 99.8 wt% (Weakley 1979). A sample of the uranium metal beads was dissolved in nitric acid; the solution dried and reconstituted in nitric acid of known concentration; and the uranium(VI) absorption spectrum measured at its maximum near 414 nm. The uranium concentration in the metal was found to be 99.7 wt%. The uranium metal beads were used in their original condition without any preliminary treatment (e.g., acid rinsing to remove the surface corrosion layer was not performed).

To understand the surface-limited rate of the uranium reaction with water, the specific surface area of the beads must be known. The specific surface area was measured by counting and weighing individual beads taken from a ~1.5-gram sample. The representative sample was taken from the stock uranium metal by successively dividing the beads through an inverted Y-shaped splitter until the desired ~1.5-gram sample size was obtained. To ensure that the same specific surface area of uranium was available for each experiment, the ~1.5-gram bead samples used in all of the tests were aliquoted from the entire stock of uranium metal beads in the same manner as used to obtain the size distribution sample.

Based on mass measurements of the 431 individual spherical beads in the 1.5339-gram sample, and using the known uranium metal density of 19.05 g/cm^3 , the diameters of the beads were found to range from ~200-1100 μm . The size distribution provides a geometric specific surface area of 4.28 cm^2 per gram of uranium (0.428 m^2/kg U). The particle size distribution histogram is shown in Figure A.1, and the beads themselves are shown in Figure A.2.

The expected corrosion behavior of uranium metal in water was exploited in the prior gas generation test series (I-III) to infer the apparent or effective particle size of uranium metal found in the K Basin sludge. See Section 4.6 and Appendix D of Delegard et al. (2000) for a description of this method. A similar treatment was applied to the size-classified ensemble of 431 uranium metal beads. Under these model conditions, the bead ensemble should corrode initially as if it were a collection of ~740- μm -diameter particles (Figure A.3). Note that this size is in the same range (640-970 μm) as observed in tests with actual sludge. It is seen that with time, only the larger particles survive and the gas generation “tails out.” However, deviation from the initial linearity does not occur until $(1-f)^{1/3}$ reaches about 0.6 (i.e., f , the

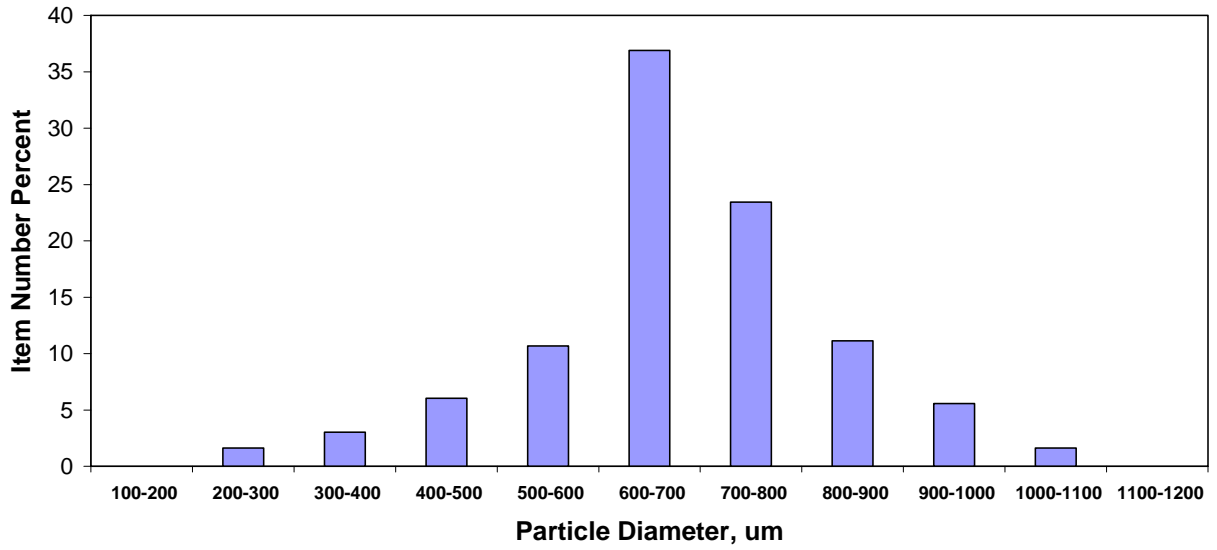


Figure A.1. Particle Size Distribution of Uranium Metal Beads



Figure A.2. Uranium Metal Beads (scale in cm; about 320 beads are in this view)

fraction reacted, is about 0.8; see Figure A.3). This tailing is similar to the behavior observed for uranium metal found in the K Basin sludge (see, for example, Figure 4.10 in the Series I report; Delegard et al. 2000).

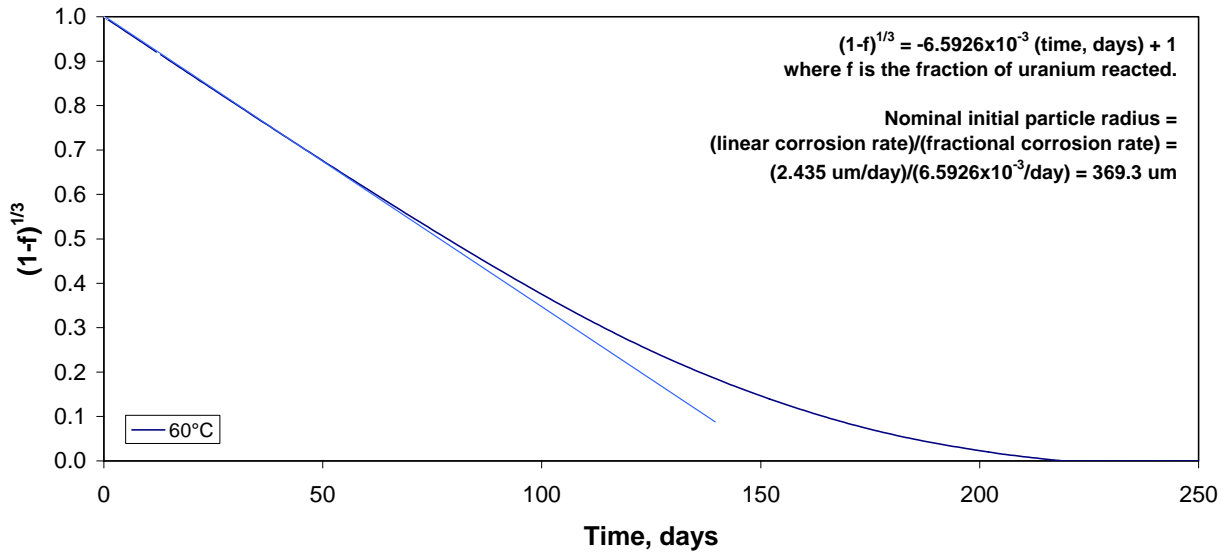


Figure A.3. Idealized Corrosion of Uranium Metal Beads at 60°C

The rate of uranium corrosion in water is proportional to surface area, but the surface area of the uranium metal beads decreases as the reaction proceeds. Therefore, to determine uranium metal corrosion rate over the course of testing with these beads, the uranium metal surface area must be known as a function of the extent of reaction. The dependence of fractional surface area remaining as a function of extent of reaction was determined based on the known isotropic corrosion of uranium metal in water, the spherical shape of the beads, and the particle sizes of the beads. This dependence, shown in Figure A.4, indicates, for example, that about 70% of the starting surface area remains after 40% of the uranium has reacted.

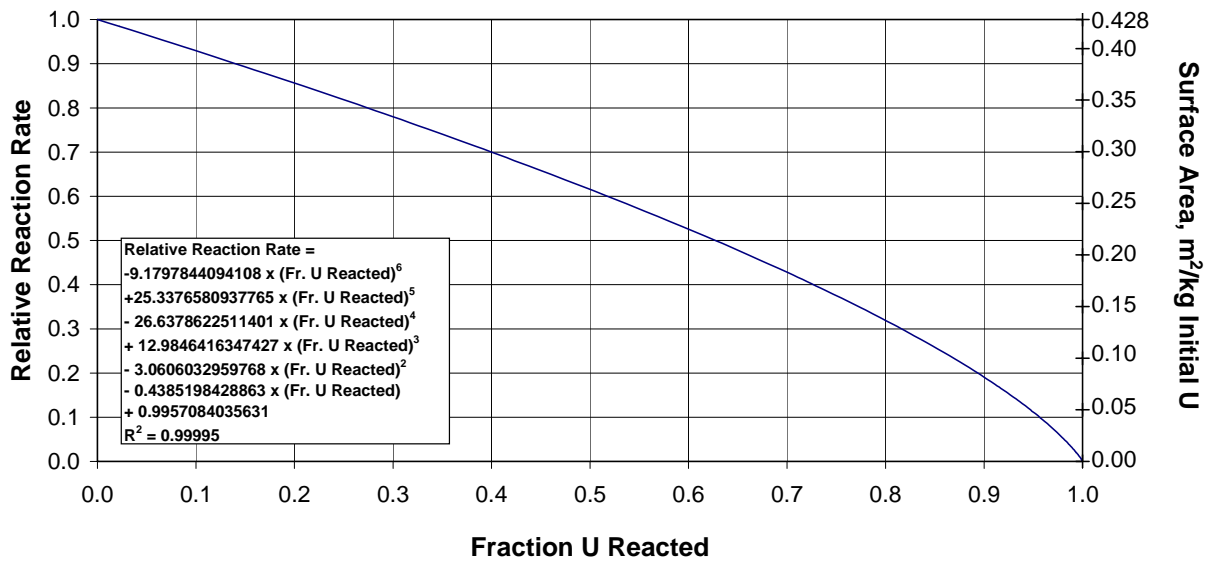


Figure A.4. Uranium Metal Bead Reaction Rate or Surface Area as a Function of Extent of Reaction

The dependence was fit to a sixth-order polynomial, and this equation used to adjust the observed hydrogen gas generation rates by the remaining uranium metal surface areas to obtain uranium corrosion rates in terms of surface area.^(a)

The uranium in the sludge from N Reactor fuel stored in the K Basins was irradiated to ~2800 megawatt-days/metric ton (MWD/MT) uranium based on analyses of fission product gas (Delegard et al. 2000), while the K Basins Safety Analysis Report (SAR) states 3000 MWD/MT irradiation for the fuel inventory (Gibson 2000). As shown in a recent review of uranium metal fuel corrosion (Hilton 2000), non-irradiated uranium metal (such as used here) should corrode at rates similar to those observed for uranium metal fuel irradiated to the relatively low exposures, with resultant low swelling, experienced by the N Reactor fuel.

The effects of irradiation on uranium metal oxidation are summarized as follows. Irradiation does not increase the intrinsic oxidation rate of uranium metal. The apparent rate (normalized to geometric surface area) increases with irradiation-induced swelling. The enhancement factor due to irradiation is defined as an exponential function of swelling and is attributed to the associated increase in surface area. The oxidation rate of metal fuel irradiated to low burnup [note – stated to be 900-2700 MWD/metric ton U], which has negligible swelling, is expected to be similar to that of non-irradiated U metal. Consistent with this, non-irradiated uranium and irradiated KW SNF (which has a low burnup and negligible swelling) have essentially the same reaction rates in oxygen and water vapor environments, within the variability of the literature data. (Hilton 2000)

Even though the corrosion of irradiated uranium immersed in water is not described, this review and the SNF Databook (Duncan 2001) observe that uranium metal corrosion rates in saturated anoxic water vapor and anoxic liquid water are practically indistinguishable.

A.3 Grout Compositions for Testing

Grout compositions were considered for testing based on prior known application of grouting to materials containing or potentially containing uranium metal. Five alternative applications, based on Portland cement, were identified through a review of the technical literature and recent Hanford experience:

- Grouting of active metals (including uranium) by British Nuclear Fuels, Limited (BNFL) or others in the United Kingdom (UK).
- Grouting of KE NLOP sludge in lab tests using formulations with clay (i.e., bentonite; attapulgite also was tested with sludge simulant) meant to absorb free or “bleed” liquid.
- Grouting of uranium metal fuel fabrication turnings and chips in past Hanford operations (Weakley 1980).
- Grout formulations (Perma-Fix) created to immobilize uranium metal fabrication turnings and chips found in barrels recently excavated at Hanford.
- Laboratory tests of uranium metal immobilization in Hanford Cast Stone.

(a) $\text{Corr. Rate, } \frac{\text{g U}}{\text{m}^2 \cdot \text{day}} = \text{Corr. Rate, } \frac{\text{moles H}_2}{\text{kg U} \cdot \text{hr}} \times \frac{\text{kg U}}{10^3 \text{ g U}} \times \frac{\text{kg U}}{0.428 \text{ m}^2} \times \frac{\text{mole U}}{2 \text{ moles H}_2} \times \frac{238.03 \text{ g U}}{\text{mole U}} \times \frac{1}{\text{Rel. Surf. Area}}$ where the relative surface area (Rel. Surf. Area) remaining is obtained from the equation in Figure A.4.

Also, while not previously applied to uranium metal, magnesium phosphate grouts (prepared using formulations provided by Tectonics International) were tested, based on their application to other radioactive wastes and promising characteristics.

BNFL

Research has been performed in the UK to investigate the immobilization of active metals (e.g., uranium, magnesium, aluminum) in cementitious matrices. BNFL described their experience in grouting various intermediate level wastes in a January 19, 2004, workshop held by Tom Yount and colleagues from BNFL, and alluded to uranium corrosion data available for grouts containing blast furnace slag (BFS) and ordinary Portland cement (OPC). Prior research presented at the workshop and in other work (Wood et al. 1998) suggests that some grout formulations used for active metals are based on 1 part OPC and 3 parts pulverized fuel ash (PFA).^(a) A formulation based on 20 wt% OPC and 80% BFS with an added superplasticizer (ADVA Cast 550^(b)) was described in a March 17, 2004, telecon with BNFL/UK researchers. The superplasticizer was added in the amount of 1 ml per 100 grams of cement formers (i.e., OPC and BFS). This grout blend was to be combined with water in the weight ratio 80:20 (note that a nominal starting point for mixable grout slurries has a cement:water weight ratio of 66.7:33.3). The dry blend reportedly is mixable, yet produces a form that sets with no bleed liquid.

Results of studies by BNFL were published after the present testing was underway. The studies summarized prior BNFL tests on grouting uranium in Portland cement formulations at ordinary water loadings (Godfrey et al. 2004) and recent studies showing lower corrosion rates obtained for drier Portland cement grouts (Godfrey and Brogden 2004). The Arrhenius rate laws summarizing the BNFL work are presented in Figure 4.5 and Table 4.3.

Preliminary tests showed that adequate mixing by hand was barely achievable at the low water additions recommended by BNFL. The present tests were conducted using 80.9:19.1 weight ratio of cement former (OPC and BFS) to water.

-
- (a) The grouting materials (OPC, BFS, PFA) used in the BNFL/UK testing correspond to British standards. To be applicable to Hanford, equivalent US source and standard materials are required and were used in the present testing. The UK and US standards, compared below, have been contrasted by Lawrence (1998).
- BNFL OPC conforms to British Standard BS EN 197-1, "Cement - Part 1: Composition, Specifications and Conformity Criteria for Common Cements"; OPC is known as Type I Portland cement in the US (ASTM 2004a). Type I/II cement, which can be used for either Type I or Type II applications, was used in the testing.
 - BNFL BFS conforms to British Standard BS6699 ("Ground Granulated Blastfurnace Slag for Use with Portland Cement"). The corresponding US standard is ASTM C989-04 (ASTM 2004b); the highest quality, Grade 120, was used in the testing.
 - BNFL PFA conforms to British Standard BS3892 ("Pulverized-Fuel Ash" "Part 1: Specification for Pulverized-Fuel Ash for Use with Portland Cement"; "Part 2: Specification for Pulverized-Fuel Ash to Be Used as a Type I Addition"; "Part 3: Specification for Pulverized-Fuel Ash for Use in Cementitious Grouts"); this is in the same category as Class F fly ash in the US (ASTM C618-03, ASTM 2003a).
- (b) ADVA Cast 500 (Grace Construction Products) is available in the US, and consequently was used in the present testing. According to Dr. Ara A. Jeknavorian and Robert Hoopes of Grace, ADVA Cast 500 is chemically identical to ADVA Cast 550 but with 6% lower solids content.

Bentonite

Testing has been performed to use clay-bearing Portland cement for KE NLOP immobilization (Mellinger et al. 2004). Portland Type I, II, or I/II cement is suitable as the cement component. Portland Type I/II cement and bentonite clay were used in the prior tests and also in the present tests.

In concrete technology, bentonite clay is added to cement to improve its plasticity and decrease sedimentation of particles during setting. However, bentonite also is found to decrease the cement strength (Scrivener and Capmas 1998). Either bentonite (mineral name, montmorillonite) or attapulgite (mineral name, palygorskite) clay may be added to absorb bleed water that arises in the curing of Portland cement under sealed conditions, and both are used to decrease the hydraulic permeability of grouts for water impoundment or to act as barriers to aqueous contaminant dispersal in soils (Bensted 1998, p. 801; Tallard 1997). Because bentonite and attapulgite decrease hydraulic permeability, it was postulated that these clays also may decrease the rate of uranium corrosion in the present application by limiting water transport to the uranium metal surface.

Bentonite acts as a water absorber and diffusion barrier by binding water between its plate-like particles. Attapulgite retains water between its needle-shaped particles. Attapulgite is preferred for grouts having high salt loading because it maintains its dispersibility, whereas bentonite's inter-plate spaces collapse in salty environments, compromising its ability to hold water. Both bentonite and attapulgite were tested with simulatant KE NLOP sludge, but bentonite was selected for testing with actual KE NLOP sludge because the sludge has little salt and because bentonite is an additive familiar to WIPP (Mellinger et al. 2004). Note also that attapulgite use in cement is banned in some countries because of the structural similarity of its fibers to asbestos fibers (Bensted 1998).

The grouted KE NLOP sludge formulation tested contained 112.00 grams of Portland Type I/II cement, 6.60 grams of bentonite clay, 50.40 grams of settled sludge (containing 31.40 grams water and 19.00 grams solids), and 24.73 grams of added water. This formulation produced a set product that yielded no bleed water. Further testing with simulated sludge showed that formulations with higher bentonite loadings give even better water loadings before onset of bleed liquid. According to Bensted (1998), for each 1 wt% bentonite added (with respect to dry cement), water loading in the grout slurry can be increased by ~5.3%. Bentonite loadings from 2 to 12 wt% (or more) of the cement can be used, depending on application. In the present tests, bentonite was about 8.2% of the Portland cement weight and 10.0% of the Tectonite weight.

Weakley

Weakley (1980) investigated a masonry cement grout (0.55 lb water per lb masonry cement) to solidify uranium metal scrap (chips, turnings, fines) arising from Hanford N Reactor fuel fabrication. This process was implemented on a ton scale for several years. The scrap was grouted before its shipment to National Lead in Fernald, Ohio, for the recovery and purification of the contained uranium. The masonry cement used in this application was ~47 wt% limestone (CaCO_3), 3 wt% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and 50 wt% Type II Portland cement.

The grouted uranium metal was cast into thin steel-wall, 7-gallon buckets. At National Lead, the buckets were cut away, the cement fractured into large chunks, and the chunks fired to crumble the cement (limestone thermal decomposition to CaO aided the crumbling). The fired materials were sieved, the

oversize fragments crushed and recycled to the furnace, the fine fraction acid-leached, and the uranium in the product acid solution purified by solvent extraction before re-reduction to uranium metal for recycle.

It is noted, however, that the uranium metal grouted for shipment sometimes ignited and that subsequent testing showed hydrogen gas evolved from the cement (see Appendix A of Mellinger et al. 2004 for a more complete discussion). As a result, the grouting practice was abandoned after a few years. The present tests used a cement formulation based on the Weakley recipe.

Perma-Fix

According to Greg Borden of Bechtel Hanford and Ben Crocker of Perma-Fix, barrels of uranium metal turnings and fines recently excavated near the Hanford 300 Area are being treated and immobilized in grout. The uranium was found to be immersed in oil. The barrels and contents were shipped to Perma-Fix in Oak Ridge, Tennessee, for remediation. The oil was found to contain polychlorinated biphenyls (PCBs), and the first step in remediation was to separate and clean the uranium metal. The cleaned uranium metal was stored in fresh, PCB-free oil. The uranium metal was then grouted with a formulation containing gypsum to sorb the residual oil. Because no specific information on the grout formulation, and the bases for its selection, was available, Perma-Fix formulations were not tested.

Cast Stone

Cast Stone formulations have been tested with simulated K Basin sludge containing uranium metal turnings (Lockrem et al. 2003). The blends reportedly mixed well, had good placing characteristics, and gave no bleed water on setting, but gas generation testing was not performed. The present tests were conducted using the baseline Cast Stone formulation of 46 wt% Grade 120 blast furnace slag, 44 wt% Type F fly ash, and 10 wt% (Type I/II) Portland cement, and were mixed with the simulated KW canister sludge at ratios to give thick, but workable, slurries.

Tectonite

Tectonite is representative of the class of magnesium phosphate cements formed by the acid-base reaction of dihydrogen phosphate salts with magnesium oxide. The primary reaction product using potassium dihydrogen phosphate is $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Wagh et al. 2001). The reaction in such cements initially is endothermic as the phosphate salts dissolve, but becomes exothermic as the acid-base reaction to form magnesium potassium phosphate occurs. The product set times of minutes to hours can be extended by set retarders (borate salts or sodium tripolyphosphate). The cements also include inert fillers such as sand (Bensted 1998). Magnesium phosphate cements are applied to repair roads and runway surfaces, where the ability of these cements to bond to Portland cement (which Portland cement itself cannot do) and their rapid set times are valuable attributes. Such cements also have been tested to microencapsulate plutonium-bearing waste materials (Wagh et al. 1999) and mixed wastes (Wagh et al. 2001).

Samples of Tectonite in a “neat” form, containing a small fraction of inert silicate filler, and in the commercially prepared formulation, having a larger fraction of silicate filler, were provided by the vendor. The vendor also supplied a quantity of borate set retarder (sodium tetraborate pentahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$). Scoping tests were run with the neat and original Tectonite formulations, having varying quantities of set retarder, and with water and with water containing ADVA Cast 500 superplasticizer. A test with the neat Tectonite, set retarder, and added bentonite also was run.

The test formulations were prepared with the minimum quantity of added water to obtain pastes that were just workable, as similar testing was performed for the other grout formulations to obtain the driest workable mixes. The objective of minimizing water addition was to attain products reagent-limited in water (i.e., obtain products having no free water available to react with the uranium metal). Based on vendor information, all tested compositions with the “neat” Tectonite were sub-stoichiometric in water (i.e., water deficient). The qualitative set temperatures were observed and product densities recorded.

The testing showed that addition of ADVA Cast 500 superplasticizer provided little improvement in decreasing the water demand by increasing the fluidity of the mixture. The tests showed that the addition of set retarder successfully extended the set times (from ~10 minutes without set retarder to ~30-40 minutes with the highest set retarder dose rate) to allow sufficient time for the materials to be mixed before hardening occurred. It should be noted that the significant exotherm produced by the nominal reaction $MgO + KH_2PO_4 + 5 H_2O \rightarrow MgKPO_4 \cdot 6H_2O$ accelerates the setting and, in larger vessels, would cause higher temperatures to be reached in shorter times than observed in the test specimens. The higher temperatures also could help initiate the uranium metal-water reaction.

Based on the scoping test observations as related to extended set times and the potential to decrease the reaction rate by limiting water availability and gain the benefits of bentonite, tests were performed with the KW canister sludge simulant and the last two formulations listed in Table A.5.

Table A.5. Tectonite Scoping Test Results

Grout Type	Cement Mass, g	Retarder, g	Water Type	Water Amount, g	Qualitative Heating Observations	Density, g/cm ³
Neat Tectonite	50	-	Plain	8.7	Too hot to hold	1.99
Neat Tectonite	50	-	4% ADVA Cast	8.0	Too hot to hold	1.92
Tectonite	50	-	Plain	5.6	Slight	2.23
Tectonite	50	-	4% ADVA Cast	5.4	Slight	2.24
Neat Tectonite	50	0.8	Plain	8.7	Very warm	1.82
Neat Tectonite	50	0.8	4% ADVA Cast	8.0	Very warm	1.86
Tectonite	50	0.8	Plain	5.7	Slight	2.19
Tectonite	50	0.8	4% ADVA Cast	5.4	Slight	2.14
Neat Tectonite	50	1.6	Plain	8.0	Almost too hot to hold	1.99
Neat Tectonite	50 + 5 g bentonite	1.6	Plain	9.7	Almost too hot to hold	2.01
All tests cast into 35-mm film containers. Neat items set within 15 minutes; others took 30-60 minutes.						

A.4 Other Potential Immobilization Agents for Testing

Other solidification/encapsulation agents, e.g., Nochar, VES–vinyl ester styrene (Burbank 1993), SPC–sulfur polymer cement or polymer modified sulfur, were considered for testing. However, the presence of organic compounds (including the presence of volatile styrene in the VES and bicyclopentadiene for

SPC), the chemical compatibility of the sulfur with uranium (for SPC), and the necessity of preliminary drying for the SPC process precluded investigating these options in this test series.

According to Julia Minton-Hughes of the Los Alamos National Laboratory (telecon March 12, 2004), OrganoPlex and PetroSet were used or are being used at Los Alamos to immobilize, for buried disposal, uranium metal chips, turnings, and fines immersed in diesel oil. The OrganoPlex/PetroSet agents are water-free organic matrices having a “peanut butter” consistency. The treated Los Alamos uranium metal waste, thus, is unlike the waterlogged, uranium metal-bearing K Basin sludge.

The present tests did not pursue any sludge immobilization options using organic-bearing agents, aside from the small organic constituent provided in the ADVA Cast superplasticizer. Instead, the tests were limited to grouts based on Portland and magnesium phosphate cements.

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