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Gas Generation Testing of Uranium Metal in Simulated K Basins Sludge and Grouted Sludge Waste Forms

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

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1.0 Introduction and Summary

The evolving plan for most of the KE and KW Basin sludges is disposition to WIPP as remote handled (RH) TRU. Because the hydrogen gas concentration in the sealed transportation cask destined for WIPP 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 contained uranium metal's reaction with water ($U + 2 H_2O \rightarrow UO_2 + 2 H_2$) in combination with the hydrogen generated from water and organic radiolysis.

Prior experimental measurements of sludge reaction rates, based largely on hydrogen gas generation and krypton and xenon fission product gas generation, were used to determine uranium metal concentration, particle size, and reaction rate enhancement factor values in sludge for purposes of sludge removal, transportation, and storage. Three series of gas generation experiments were conducted to learn about the properties of K Basin sludge with respect to its contained uranium metal. The first test series (Series I; Delegard et al. 2000) focused on gas generation from KE basin floor and canister sludge (size-fractionated and unfractionated 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. Tested sludges included 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.

In the three test series, sludge samples and irradiated metallic uranium fuel particles were introduced into 850-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 controlled temperatures and often ended at high temperatures to completely oxidize the contained uranium metal. Analysis of the product gas concentrations and quantities allowed understanding of the underlying reactions and, if run to extinction, were used to determine the uranium metal concentration in the sludge.

Because the focus of the SNF Sludge project is changing from interim storage to near-term disposition to WIPP, additional gas generation tests specific to the proposed WIPP waste forms are necessary. Current plans call for the retrieval and solidification of KE North Load Pit (NLOP) sludge as Contact Handled (CH) Transuranic (TRU) waste in FYs 2004 and 2005 with the intent of ultimate disposition to WIPP. 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 NLOP sludge sample collected in 1999 indicated that this sludge contained very little uranium metal (i.e., 0.013 wt% settled sludge based on $H_2/O_2/N_2$ and <0.0088 wt% based on ^{136}Xe). Additional gas generation testing was undertaken to gain confidence on the low uranium metal content of the 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 application of solidification agents (grout, Nochar®) on the treated NLOP sludge gas generation quantity and rate also were examined in this gas generation testing.¹

In general, the KE and KW Basin sludges will contain much higher uranium metal concentrations than found in the KE NLOP sludge. To prepare the sludge to meet WIPP transportation criteria, the sludge

¹ Fulton, J. T. 2004. "Final Revision of Appendix E for January 19, 2004 Deliverable 46897-RPT01, 'Evaluation and Recommendation of Waste Form and Packaging for Disposition of the K East Basin North Loadout Pit Sludge'." Letter report 46857-L27 to S. M. Sax, Pacific Northwest National Laboratory, Richland, WA (May 21, 2004).

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. Depending on how effectively the reaction is inhibited, additional process steps to remove uranium metal from the sludge and then to react the uranium metal also may become necessary.

The need to diminish the reaction of uranium metal with water to produce hydrogen gas can be appreciated by the following evaluation. According to guidance provided by Fluor Hanford,² the maximum hydrogen generation rate tolerated in a RH-TRU drum is 3.65×10^{-8} moles/second. Based on critically reviewed uranium corrosion rates provided in the SNF Databook (Duncan 2001), the 3.65×10^{-8} moles H_2 /sec rate is met with only 13.06 grams of 739- μ m diameter uranium reacting at 60°C. Note that uranium metal beads of effective 739- μ m diameter were used to prepare the simulated KW canister sludge in the present testing and correspond to the effective uranium metal size (640-970 μ m) observed in KE canister sludge in the Series I testing. This rate of chemical production of hydrogen gas leaves no margin for hydrogen generation from radiolysis. At this hydrogen gas generation rate, only ~65 ml (261 g) of nominal KW canister sludge (containing 13.06 grams of uranium) could be accommodated in a single RH-TRU drum.

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 metal
- chemically sequestering or binding the water.

Gas generation testing with uranium metal particles of known surface area and immobilized in candidate (grout) solidification matrices was used to identify the effectiveness of various candidate solidification matrices to inhibit the rate of the uranium metal-water reaction.

Table 1.1 outlines the gas generation study test conditions undertaken to determine the effectiveness of the grout matrices on inhibiting the uranium metal reaction and understanding the long-term behavior of the sludge-grout mixtures for on-site storage and shipping to WIPP. The testing was performed according to PNNL-prepared Test Instructions approved through PNNL and FH authorities.

Testing began at 60°C and was followed by intervals at approximately 80°C, 95°C, and 40°C for Tests 1-6. Tests numbered 7, 8, and 9 have not yet begun. Tests have run approximately 450 hours as of May 24, 2004. The experiments, described more completely in the subsequent discussions, show that grouting decreases the rate of reaction of uranium metal with water.

² The value of 3.65×10^{-8} moles hydrogen gas per second was obtained per guidance provided by David DeRosa of Fluor Hanford. A similar value of 3.8391×10^{-8} moles per second is provided in Table 5.2 of Mellinger et al. (2004).

Table 1.1. Uranium-Water Reaction Test Matrix

Test No.	Test ID	Sludge Simulant Mass, g			Grout Mix, g ^b	Est. Sludge Load, vol% ^c	Target Duration, hr
		Water ^a	Sand/VO ₂	U Metal			
1	U-Control	30	0	1.5	0	NA	1000
2	U-Sludge	30	2.32/21.3	1.5	0	NA	1000
3	BNFL Grout	30	2.32/21.3	1.5	129.5	8.1	1000
4	Bentonite Grout	30	2.32/21.3	1.5	66.2	12.4	1000
5	Weakley Grout	30	2.32/21.3	1.5	54.5	13.7	1000
6	Cast Stone Grout	30	2.32/21.3	1.5	100.6	9.6	1000
7	U-Sludge Dup	30	2.32/21.3	1.5	0	NA	1000
8	Tectonite	30	2.32/21.3	1.5	193.3	6.0	1000
9	Tectonite-Ben	30	2.32/21.3	1.5	178.8	6.4	1000

^a Water amount comprised of 4.9 g for sludge and 25.1 g for grout make-up (see subsequent discussions).

^b Sum grout mix components (cement, blast furnace slag, superplasticizer, bentonite, calcite, gypsum, “neat” Tectonite).

^c Based on final grout form density of 2.0 g/cm³ and sludge feed volume of 7.5 ml (sludge density 4.0 g/cm³).

2.0 Test Objectives

The controlled gas generation tests with K Basin sludge surrogates spiked with uranium metal particles are being undertaken to understand the effects of a number of candidate immobilization matrices on the rate of the uranium-water reaction over short and long terms (i.e., to extinction). The following test conditions were considered:

- Hydrogen generation rate of uranium metal particles in water
- Hydrogen generation rate of uranium metal particles, with simulated sludge, in water
- Hydrogen generation rate of uranium metal particles, with sludge, in water immobilized in candidate agents such as
 - Tailored grout
 - Grout formulation formerly used for Hanford fuel fabrication scrap
 - BNFL/NIREX formulations for uranium (and other active metal)-bearing sludge
 - Perma-Fix formulations applied to Hanford uranium fuel fabrication scrap
 - Portland cement with bentonite additive to be used for KE NLOP sludge
 - Cast Stone
 - Tectonite³

³ Tectonite™ is an all-season repair and anchoring inorganic magnesium oxyphosphate cement. Tectonics International, 4202 Holliday, P.O. Box 959, Warm Springs, OR 97761. Telephone (541) 553-2297; FAX (541) 553-2298; E-Mail: roddaphil@earthlink.net.

- Other solidification/encapsulation agents (e.g., Nochar®; VES® – vinyl ester styrene; SPC – sulfur polymer cement; Organoplex or Petroset)⁴. Note that these agents, which all contain organic constituents, were considered but are not included in the initial tests.

Comparison of the test results improves the understanding of the effects of temperature, sludge overburden, and particularly immobilization matrix on the reaction rate of uranium metal with water to produce hydrogen gas. In particular, the testing surveyed candidate media to inhibit the reaction of uranium metal with water while producing waste forms eligible for WIPP disposal and ultimately will investigate time to extinction (i.e., burn-out) of uranium metal particles having known starting sizes.

Following these screening tests, it is recognized that subsequent testing with genuine sludge may become necessary. Testing with genuine sludge not only will validate the testing performed with simulants but also will have the benefit of utilizing the release of fission product gases (isotopes of krypton and xenon) to monitor the corrosion of the irradiated uranium metal. The fission product gas release provides definitive and kinetically responsive evidence of irradiated uranium metal corrosion whereas hydrogen release can be delayed by retention at lower temperatures as uranium hydride.

3.0 Test Materials

To gain better control of the materials effects, the testing was performed with simulated K Basin sludge of deliberate composition and with various candidate liquid-immobilization agents. Little or no genuine K Basin sludge with significant uranium metal still remains in the Radiochemical Processing Laboratory after prior testing and characterization. The use of sludge surrogates, rather than genuine sludge with its associated fission product content, also allowed the experiments to be conducted more expeditiously and cost effectively in fume hoods instead of in radiologically shielded (hot cell) facilities. The tests use of non-irradiated uranium metal beads of natural enrichment allows re-use of the gas generation vessels and simplifies data interpretation by limiting gas formation to hydrogen and eliminates the possibility of other gas-generating reactions from sludge (e.g., to produce CO₂) observed in prior studies with genuine K Basin sludge.

3.1 K Basin Sludge Simulant

Actual K Basin sludge has been physically, chemically, and radiochemically characterized and the results reported in a number of documents. Though gases other than hydrogen (primarily CO₂) are generated by the reactions within the sludge, the Series III testing (Schmidt et al. 2003) confirmed that the reaction of uranium metal with water to form hydrogen gas dominates the total gas generation at the high uranium metal concentrations targeted for the present testing. Hydrogen gas generation also is the leading technical challenge facing the disposal of the K Basin sludge to the WIPP. Therefore, K Basin sludge simulant may be prepared using the stable inorganic phases which constitute the sludge bulk. Besides uranium oxides, the inorganic phases include Hanford sand (Hanford sand minerals include quartz, anorthite, and mica) and K Basin structural iron and aluminum corrosion products (e.g., hematite,

⁴ Nochar® Acid Bond 660 is a polyacrylic water sorbent produced as a dry fine granular powder. Nochar, Inc., 8650 Commerce Park Place, Suite K, Indianapolis, IN 46268. Telephone: (317) 613-3046; Fax: (317) 613-3052; E-Mail: nochar@in.net.

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 (1992). Sulfur polymer cement (SPC) is described by the ASTM (2003a); use of SPC requires preliminary sludge drying. Petroset and Organoplex are products that have been applied by TPG Applied Technology, Knoxville, TN (Dale Jessop, 865 384-2480) to stabilize uranium metal turnings/chips/fines at the Los Alamos National Laboratory.

goethite, gibbsite). Zirconium metal, as cladding spalled from the corroding fuel, also is found in the sludge. Finally, inorganic ion exchange material (Zeolon 900, based on the zeolite mineral mordenite) is present in the sludge. Organic materials include mixed strong acid / strong base organic ion exchange resin, plastics, and plant and animal debris.

The sludge component proportions follow the composition described for the KW canister sludge (Tables 4-1 through 4-4a, Schmidt 2004), the most reactive sludge envisioned for immobilization treatment. Thus, according to these defined KW canister sludge parameters, the sludge should have 4.0 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., be 5 wt% uranium metal). The sludge quantity for 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, the corresponding uranium quantity is 1.5 grams.

For simplicity, however, to assist in interpreting and making calculations related to the other complex mechanisms being measured, the sludge simulant ingredients were selected to be limited to uranium dioxide (UO₂) 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 more detail in a separate analysis (see Appendix B of Schmidt and Delegard 2003).

For the present situation, it was calculated that to meet all but the 4.0 g/cm³ density criterion requires 0.31 g SiO₂ per cm³ sludge. The resulting sludge composition is outlined in Table 3.1.

Table 3.1. KW Canister Sludge Composition To Meet Water Concentration Criterion

Phase	Density, g/cm ³	Quantity per cm ³		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 3.2), the 65 volume% target water concentration is not met.

Table 3.2. KW Canister Sludge Composition To Meet Density Criterion

Phase	Density, g/cm ³	Quantity per cm ³		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 both are met if a stable sludge solid of density 3.71 g/cm³ is used in place of SiO₂ (Table 3.3).

Table 3.3. KW Canister Sludge Composition With Dense Component To Meet All Criteria

Phase	Density, g/cm ³	Quantity per cm ³		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
??	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 3.2) was selected. The selected formulation contains 0.36 g SiO₂ per cm³ and ~59.6 vol% water to give sludge with density 4.00 g/cm³.

In practice, packages containing KW canister sludge prepared for shipment to WIPP as remote-handled TRU (RH-TRU) will be limited by the ²³⁹Pu fissile gram equivalent (FGE) ⁵ loading of 200 grams per RH-TRU 55-gallon drum. The radionuclide quantities in the 1010 liters of KW canister sludge (Schmidt 2004; see Table 4-16), has 1.38×10⁴ g FGE. Thus, 14.6 liters of sludge can be held per RH-TRU drum.

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

With a nominal drum capacity of 177 liters (15% headspace in 208-liters total volume), sludge loading in the final waste form is ~8.3 volume percent.

At the projected KW 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. This quantity of water produces sludge loadings in the grouted waste forms of 8.1-13.7 volume percent in the present tests (see Table 1.1) and 6.0 and 6.4 volume percent in the proposed tests with Tectonite. The sludge loadings thus bracket the loadings dictated by the FGE limits. Note that at the 1:2 U:H₂O mole ratio required for the corrosion reaction, the U:H₂O stoichiometric weight ratio is 6.61 g U/g H₂O. Therefore, the 1.5 g of U metal will consume 0.22 g or ~0.75% of the available water (i.e., the extent of reaction will be limited by the uranium metal quantity).

3.2 Uranium Metal Particles

Non-irradiated uranium metal shot (~200-1100 μm diameter spheres) of natural enrichment was used for the uranium metal particles. The size brackets the projected size of the uranium metal particles (640-970 μm) thought to be in the KE Basin sludge based on gas generation rates observed in the Series I sludge corrosion tests (Delegard 2000). As will be seen, the uranium metal beads should corrode in a manner similar to that observed in genuine sludge.

The uranium shot is in good metallic condition, free of loose corrosion and dust, with a purplish patina indicating a light interference corrosion layer. Scanning electron microscopy (SEM) showed the beads overall to be spherical. Energy dispersive spectrometry (EDS) obtained during SEM showed small concentrations of iron and aluminum alloying elements. Carbon, another element potentially present in the uranium metal, is not identifiable by EDS.

⁵ The ²³⁹Pu FGE calculation applies varying quality factors to quantities of listed fissile isotopes (^{233,235}U, ²³⁷Np, ^{238,239,240,241,242}Pu, ^{241,242m,243}Am, ^{243,244,245,247}Cm, and ^{249,251}Cf) to arrive at a combined loading for criticality safety.

To understand the surface-limited rate of the uranium reaction with water, the specific surface area of the beads must be known. Measurements of the specific surface area were performed by counting and weighing a ~1.5-gram sample of beads. The 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-g bead samples used in all of the tests were aliquoted in the same manner.

Based on mass measurements of 431 individual spherical beads (1.5339 g), and using the known uranium metal density of 19.05 g/cm^3 , the beads' diameters were found to range from ~200-1100 μm to provide an overall specific surface area of $\sim 4.28 \text{ cm}^2/\text{g}$. A histogram of the particle size distribution is shown in Figure 3.1 and a photograph of beads is given in Figure 3.2.

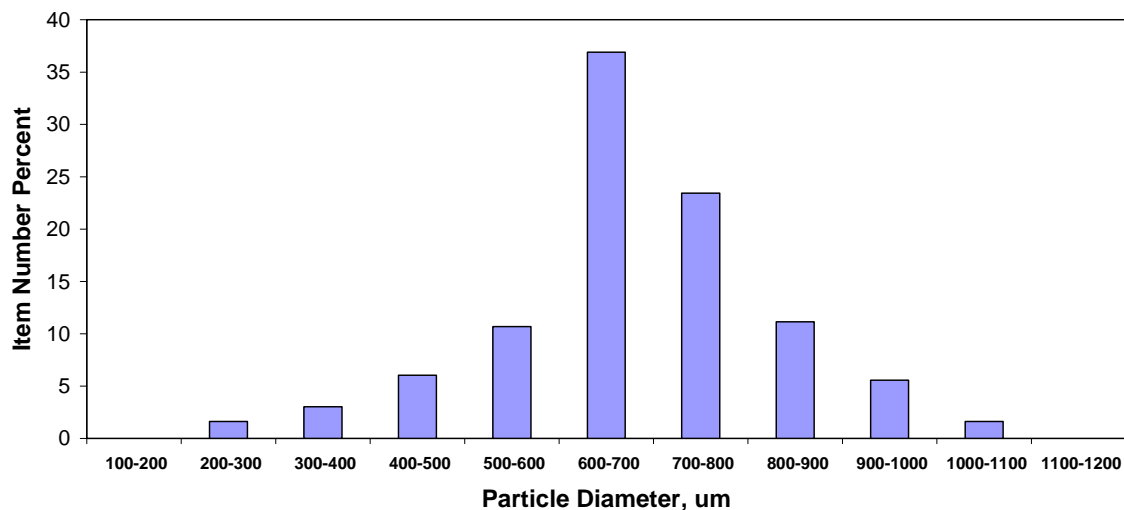


Figure 3.1. Particle Size Distribution of Uranium Metal Beads

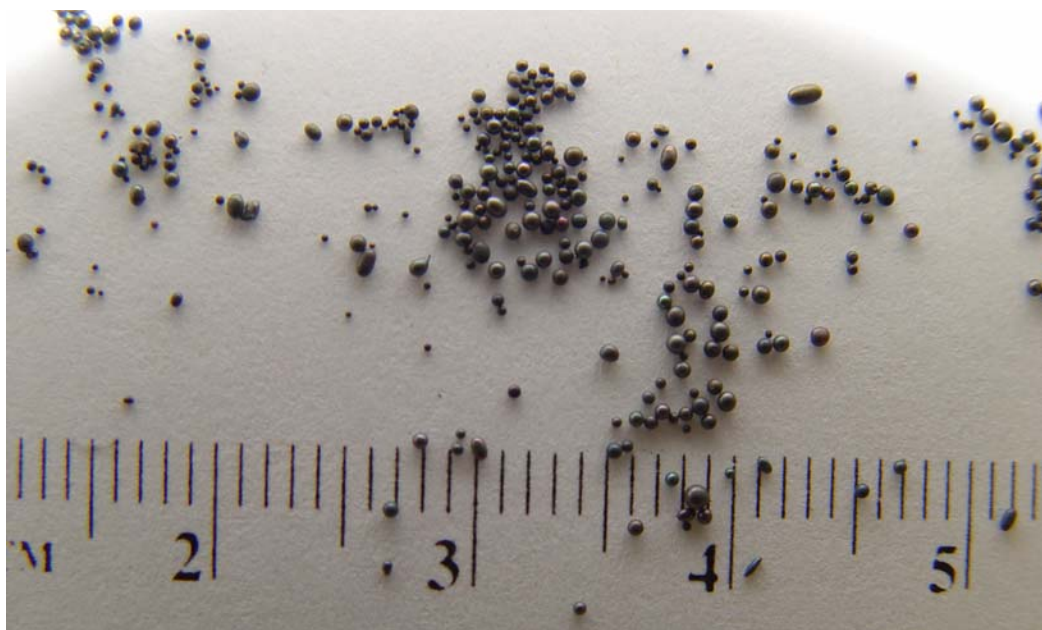


Figure 3.2. Photograph of Uranium Metal Beads (scale in cm)

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 collection of 431 uranium metal beads whose histogram is shown in Figure 3.1. Under these model conditions, the beads should corrode initially as if they were ~740- μm diameter particles (Figure 3.3), in the same range (640-970 μm) as observed in tests with genuine sludge. It is seen that with time, only the larger particles survive and the gas generation “tails out” but deviation from the initial linearity does not occur until $(1-f)^{1/3}$ reaches about 0.6 (i.e., f , the fraction reacted, is about 0.8). This 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).

As shown in a recent review of uranium metal fuel corrosion (Hilton 2000), unirradiated uranium metal (such as that to be used in the current testing) should corrode at rates similar to those observed for metal fuel irradiated to the relatively low exposures (with resultant low swelling) experienced by the N Reactor fuel.

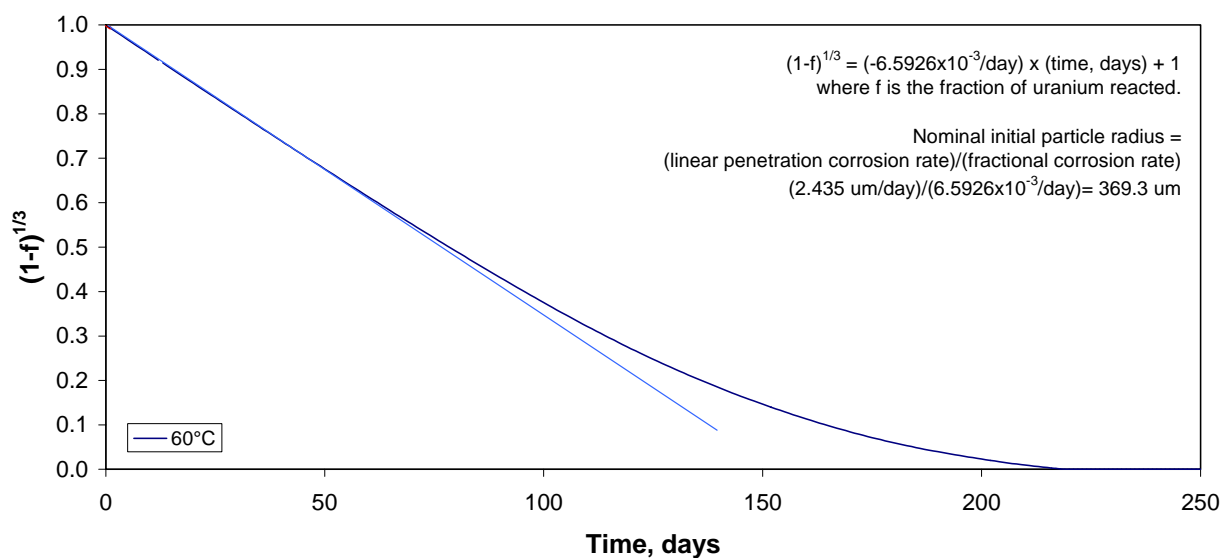


Figure 3.3. Idealized Corrosion of Uranium Metal Beads at 60°C

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 (stated previously to be 900-2700 MWD/metric ton U), which has negligible swelling, is expected to be similar to that of unirradiated U metal. Consistent with this, unirradiated 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).

Note that the corrosion of irradiated uranium immersed in water is not described. However, 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. The uranium in the sludge from

N Reactor fuel stored in the K Basins was irradiated to ~2800 MWD/metric ton 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).

3.3 Grout Compositions for Testing

Grout compositions to be considered for testing are based on prior known application of grouting to materials containing or potentially containing uranium metal. Five alternative applications have been identified in review of the technical literature and recent Hanford experience. These five are based on Portland cement. A sixth candidate hydrothermal grout (Tectonite), based on magnesium phosphate, also is considered based on the promising properties of this material.

- Grouting of active metals (including uranium) in the United Kingdom (UK), by British Nuclear Fuel, Limited (BNFL) or other UK entities.
- Grouting of KE NLOP sludge using grout 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.
- Formulations created to immobilize uranium metal fabrication turnings and chips found in barrels recently excavated at Hanford.
- Cast Stone
- Tectonite.

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 published separately by UK entities suggests that some grout formulations used for active metals are based on 1 part OPC and 3 with an added superplasticizer (ADVA Cast 550) was described in a telecon with BNFL/UK researchers (March 17, 2004). The superplasticizer was added at a dose of 1 ml per 100 grams of cement formers parts pulverized fuel ash, PFA (Wood et al. 1998).⁶ A formulation based on 20 wt% OPC and 80% BFS

⁶ 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 are used in the present testing.

- 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. Type I/II cement, which can be used for either Type I or Type II applications, is used in the present testing (ASTM 2004a).
- 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, is used in the present 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”); Ed Butcher of BNFL notes this is in the same category as Class F fly ash in the US (ASTM C618-03, ASTM 2003a).

(i.e., OPC and BFS).⁷ This grout blend is combined with water in the weight ratio 80:20. The blend reportedly is mixable yet produces a form that sets with no bleed liquid and has relatively low amounts of water (note that a nominal starting point for mixable grout slurries has a cement:water weight ratio of 66.7:33.3).

Bentonite

Testing was performed to immobilize KE NLOP sludge using clay-bearing Portland cement. Portland Type I, II, or I/II cement is suitable as the cement component; Portland Type I/II is used in the present tests. The clay is added to absorb bleed water that arises in the curing of Portland cement under sealed conditions and also used in applications to decrease the hydraulic permeability of grouts for water impoundment or act as barriers to aqueous contaminant dispersal in soils (Tallard 1997). The decreased hydraulic permeability may, in turn, decrease the rate of uranium metal corrosion in the present application. Either bentonite (mineral name montmorillonite) or attapulgite (mineral name palygorskite) clay may be used. Bentonite works by adsorbing water between its plate-like particles. Attapulgite works by adsorbing water between its needle-shaped particles. Attapulgite is preferred for grouts having high salt loading because it maintains its dispersibility whereas the inter-plate spaces between the bentonite particles collapse in salty environments causing bentonite to lose its ability to hold water. Both bentonite and attapulgite were tested with simulant KE NLOP sludge but bentonite was selected for testing with genuine sludge because the sludge has little salt and because bentonite is an additive familiar to WIPP. The grouted KE NLOP sludge formulation tested contained 112.00 g of Portland Type I/II cement, 6.60 g of bentonite clay, 50.40 g of settled sludge (containing 31.40 g water and 19.00 g solids), and 24.73 g of added water. This formulation produced a set product that yielded no bleed water. Further testing showed that formulations with higher bentonite loadings give even better water loadings before onset of bleed liquid.

Weakley

Weakley (1980) investigated a low-water content 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 prior to 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% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and 50% 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 prior to re-reduction to metal for recycle. It is noted, however, that the grouted uranium metal 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 of this experience).

Perma-Fix

According to Greg Borden of Bechtel Hanford and Ben Crocker, Perma-Fix, barrels of uranium metal turnings and fines recently were excavated near the Hanford 300 Area. The uranium was found to be immersed in oil. The barrels and contents were shipped to Perma-Fix (<http://www.perma-fix.com>) in

⁷ ADVA Cast 550 (Grace Construction Products) is not available in the US but ADVA Cast 500 is. According to Dr. Ara A. Jeknavorian and Robert Hoopes (Robert.J.Hoopes@grace.com) of Grace, ADVA Cast 500 is chemically identical to ADVA Cast 550 but with 6% lower solids content. ADVA Cast 500 was used in the present testing.

Oak Ridge, Tennessee, for remediation. The oil was found to contain polychlorinated biphenyls (PCBs) and the first step in remediation became separation and cleaning of the uranium metal. The cleaned metal was stored in fresh PCB-free oil while the original PCB-bearing oil and detergent used to clean the uranium was disposed. The uranium turnings then were grouted with a formulation containing gypsum to sorb the residual oil. No specific information on the grout formulation, and the bases for its selection, were obtained from Perma-Fix or Bechtel Hanford, the contractor responsible for this action. In the absence of specific formulations, no testing could be performed based on this experience.

Cast Stone

Testing of Cast Stone was undertaken with simulated K Basin sludge containing uranium metal turnings (Lockrem et al. 2003). The existing Hanford Cast Stone formulation consists of 46 wt% blast furnace slag, 44 wt% fly ash, and 10 wt% (Type I/II) Portland cement. For the tests with simulated K Basin sludge, hematite was added for radiolytic shielding to comprise 30 wt% of the Cast Stone solids with blast furnace slag (30 wt%) and fly ash (40 wt%) decreased to accommodate the hematite and the balance (10 wt%) being Portland cement. The waste loading (as dry sand) was 10 wt% of the Cast Stone mix mass and the added water was 33 wt% of the total dry ingredients (sludge/sand plus grout formers). The given blend reportedly mixed well, had good placing characteristics, and gave no bleed water on setting. Tested formulations with a simulant containing uranium metal, UO_2 , $\text{Al}(\text{OH})_3$, Fe_2O_3 , SiO_2 , and Zr metal fines were blended with the Cast Stone mix at amounts such that the sludge simulant solids comprised 11.1 to 25 wt% of the Cast Stone mix mass and water was 40 to 44% of the total dry solids mass.

Tectonite

Tectonite™, a dry-mix grout offered by Tectonics International, is a representative of the class of magnesium phosphate cements formed by the acid-base reaction of dihydrogen phosphate salts with magnesium oxide. The reaction products primarily include $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (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 roads and runway surface repair where the cement's ability to bond to Portland cement (which Portland cement itself cannot do) and its rapid set time are valuable attributes. Such cements also have been tested to microencapsulate plutonium-bearing 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. The test formulations were prepared with the minimum quantity of added water to obtain pastes that were just workable. Similar testing also was performed for the other grout formulations to obtain the driest workable mixes. The qualitative set temperatures were observed and product densities recorded. A test with the neat Tectonite, set retarder, and added bentonite also was run.

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., were water deficient). 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 $\text{MgO} + \text{KH}_2\text{PO}_4 + 5 \text{H}_2\text{O} \rightarrow \text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ 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 water-uranium reaction to overcome the variable induction time.

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 with the KW canister sludge simulant using the last two formulations listed in Table 3.4 are proposed to be performed.

Table 3.4. Tectonite Scoping Test Results

Cement Type	Cement Mass, g	Retarder, g	Water Type	Water Amount, g	Heating	Density, g/cm³
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.						

3.4 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; may be proposed. 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 may preclude some or all of these options.

According to Julia Minton-Hughes of the Los Alamos National Laboratory, 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 peanut butter consistency. The treated Los Alamos metal waste thus is unlike the waterlogged uranium-bearing K Basins sludge.

The present tests did not investigate any organic-bearing options (aside from the small organic constituent provided in the ADVA Cast superplasticizer).

4.0 Test Conditions

4.1 Test Size

The gas generation testing manifold has 12 stations. However, some of the test positions were committed to testing for other projects. Thus, only six stations initially were available and used for the present testing.

4.2 Reaction Vessels

The tests used 220-ml capacity reaction vessels. The free gas space (after deducting the ~95-ml maximum volume of the test materials) was approximately 125 ml.

4.3 Reaction Atmosphere

An inert (i.e., oxygen free) neon atmosphere was used for the gas generation tests. Use of an oxygen-free atmosphere provides conditions that favor the uranium-metal reaction (i.e., hydrogen generation rates from this testing are expected to be conservative). After loading the reaction vessels, the vessels were pressurized (to ~4 atmospheres) and vented (to atmospheric pressure) multiple times with neon of 99.999% purity. Neon cover gas, and this pressurization/venting technique, was used in the previous K Basin sludge testing (Series I, II, and III) and allows use of argon as a trace on atmospheric contamination and a means to monitor oxygen and nitrogen reactions by evaluating the O_2/Ar and N_2/Ar ratios, respectively.

4.4 Test Temperatures

Induction periods before the onset of hydrogen gas generation were observed in Series I gas generation testing with KE canister sludge (Delegard et. al. 2000). The induction periods were 1340 hr, 205 hr, and 27 hr, at 40°C, 60°C and 80°C, respectively, for hydrogen gas generation. However, fission product gas release showed induction times to onset of reaction actually were 335, 186, and ~0 hours, respectively (Bryan et al. 2004) indicating that hydrogen was sequestered as uranium hydride before being released to the gas phase. To obtain timely data, target test temperature in the current work began at 60°C. This temperature also is consistent with the maximum temperature during shipment to WIPP.

While temperatures greater than 60°C accelerate the uranium-water reaction, the results may not reflect actual operations. However, testing at other temperatures is necessary to discern the temperature dependence of the uranium metal reaction, particularly in the grout matrix. Therefore, testing also took place at nominal 80°C, 95°C, and 40°C temperatures. Stepping the tests to higher or lower temperatures provides information on activation energies and the confounding effects of diffusion and the underlying uranium-water reaction rates and may help determine whether the protection afforded by the solidification matrix breaks down by, for example, spallation from the metal surface.

4.5 Test Duration

Previous gas generation tests have ranged from 900 to 10,000 hours. These tests will continue for 1 to 2 months (700 to 1400 hours). To date, the tests have gone for ~450 hours. Some or all tests will be run to complete extinction of the uranium metal. Actual test durations will depend upon the gas generation behavior observed in the individual tests. 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 presented in the technical literature (Duncan 2001 and Hilton 2000, respectively). 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 prior testing) is about 20 days. As shown in the present testing, grout matrices decrease the rate of reaction of uranium with water and thus increase the time to extinction.

4.6 Test Matrix

Table 1.1 outlines the current and proposed (Tectonite and additional U-Sludge) test matrix. The test number, test identification, material (target mass/volume), and test conditions (target temperature, and test duration) are provided.

According to the stoichiometry of uranium metal corrosion reaction in water ($\text{U} + 2 \text{H}_2\text{O} \rightarrow \text{UO}_2 + 2 \text{H}_2$), 1.5 grams of uranium produces 0.0126 moles of hydrogen gas (~300 ml at room temperature/pressure) to generate ~2100 Torr additional pressure⁸ above the starting pressure of ~750 Torr, or ~2850 Torr total, in the ~125-ml vessel head space at 60°C. This is below the upper threshold of the pressure gauge (~3200 Torr) in the test apparatus so the testing can be continued without interruption for gas bleeding or sampling.

Although the progress of the uranium metal corrosion reaction will be followed by monitoring the gas pressure/volume/temperature in the test apparatus, at least one gas sample will be taken at the end of each test to confirm the expected near-100% H₂ gas composition. Gas generation from the grout itself is 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 one month from ~138 grams of grout (see footnote 1). This compares with the anticipated 300 ml of H₂ from corroding 1.5 g of uranium metal in water.

5.0 Test Objectives with Sludge Spiked with Uranium Metal Particles

Test 1, U-Control. This test serves as a control to understand the gas generation rate of the uranium particles (shot) with water and no sludge surrogate addition. The behavior of this test also will be compared with observations made under similar test conditions in the Series III experiments with crushed irradiated uranium metal fuel (Schmidt et al. 2003).

Test 2, U-Sludge. This test serves as a control to understand the gas generation rate of the uranium shot with sludge/surrogate addition. In the Series III testing (Schmidt et al. 2003), it was found that a sludge layer on actual uranium metal fuel fragments reduced the gas generation rate relative to fuel fragments with no sludge overburden. Results from Test 2 provide baseline data to compare with tests with immobilization agents and also may be compared with the Series III test findings on the effects of sludge overburden.

Tests 3-6 BNFL Grout, Bentonite Grout, Weakley Grout, and Cast Stone Grout. These tests examine the effects of grout matrices on hydrogen generation rate of uranium metal-spiked sludge. By comparing the results from Tests 3-6 with the results from Tests 1 and 2, quantitative data are obtained to estimate the

⁸ $1.5 \text{ g U} \times \frac{\text{mole U}}{238.03 \text{ g U}} \times \frac{2 \text{ mole H}_2}{\text{mole U}} \times \frac{0.082057 \text{ liter} \cdot \text{atm}}{\text{mole} \cdot \text{deg K}} \times \frac{333 \text{ K}}{0.125 \text{ liter}} \times \frac{760 \text{ Torr}}{\text{atm}} = 2094 \text{ Torr}$

extent to which the reaction of uranium metal with water is inhibited in grout media. Four different grout compositions are being tested. Other formulations based on Tectonite and Tectonite with bentonite are being considered for subsequent testing.

6.0 Gas Generation Measurements

The reaction vessels and the gas manifold system (Figure 6.1) used for the gas generation tests are similar to those describe in the previous Series I-III gas generation work with K Basins Sludge (Delegard et al. 2000; Bryan et al. 2004; and Schmidt et al. 2003). Each vessel has a separate dedicated pressure transducer on the gas manifold line. The entire surface of the reaction system exposed to the sludge sample is stainless steel, except for a 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.

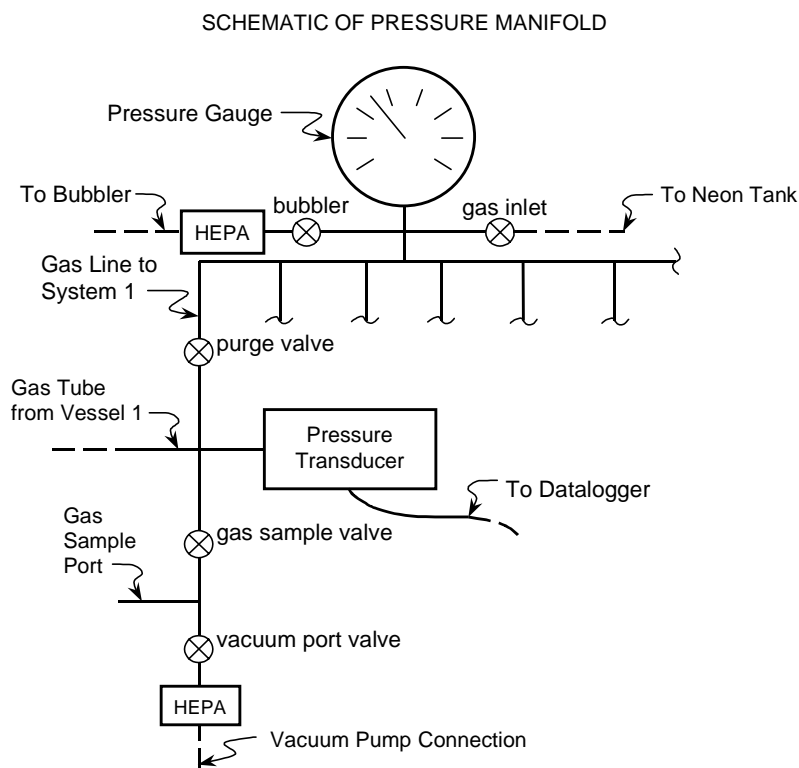


Figure 6.1. Layout of Gas Pressure Measurement and Gas Sample Manifold Used in Gas Generation Tests (includes details for one of 6 systems)

Figure 6.2 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 flange. The lower thermocouple monitors the temperature of the test material phase (sludge or treated waste form); the upper thermocouple monitors the gas phase temperature within the reaction vessel. The reaction vessels

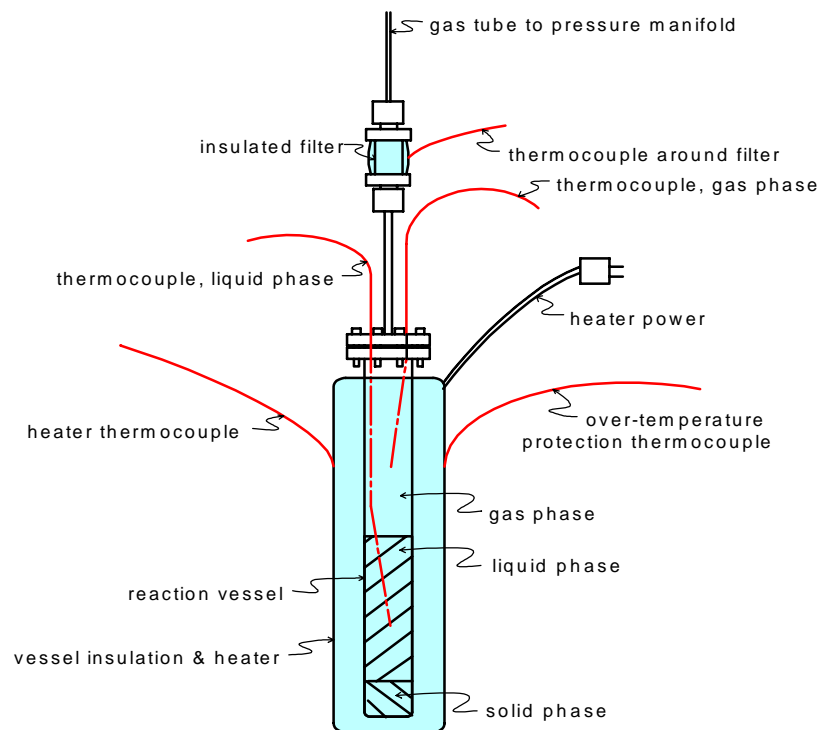


Figure 6.2. Schematic of Reaction Vessel

were 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 (2- μ m pore size, Nupro) 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) pressures. Mass spectrometric analysis of at least the final product gases will be performed. However, the product gas is expected to be only hydrogen. The inert cover gas (neon) will allow ready identification of product gases and interpretation of the chemical reactions occurring in the settled sludge. The neon gas used in prior tests was analyzed independently by mass spectrometry and determined to contain no impurities in concentrations significant enough to warrant correction. Similar neon cover gas will be used in the present tests and its quality measured by mass spectrometry as needed.

At the start of each run, each system was purged by at least eight cycles of pressurizing with neon at 2300 Torr (or higher) and venting to the atmosphere. The systems started at atmospheric pressure, about 745 Torr, when sealed. The vessels then were heated, and the temperature set points adjusted to keep the material within 1°C of the desired condensed phase temperatures.

At the end of each reaction sequence, the vessels will be cooled to ambient temperature and then a sample of the gas taken from the headspace for mass spectrometry analysis. This activity has not yet been done for any of the tests. Gases in the reaction system are assumed to be well mixed. The metal gas collection bottles are equipped with a valve and have volumes of approximately 75 mL. Before sampling, the gas sample bottles are evacuated overnight at high vacuum and then attached to the gas sample port. After the sample collection, the reaction vessel is purged again with neon. The gas sample compositions during selected gas samplings will be analyzed by PNNL using analytical procedure PNNL-98523-284 Rev. 0.

7.0 Results

The gas generation observed over the first 450 hours of Tests 1-6 (Table 1.1) are shown in Figure 7.1. The intervals required for the apparatus to reach temperature, and the gas expansion caused by temperature rise, were excised to provide true plots of the gas generation profile. The y-axis is presented in units of moles of hydrogen generated per kg of uranium metal. Complete reaction of all uranium metal corresponds to 8.4 moles H_2 per kilogram uranium. It is seen that about 44% of the uranium has been reacted in the U-Control test and that the four grout tests (Weakley, BNFL, Cast Stone, and Bentonite) show correspondingly lower gas generation. The gas generation quantities are inexplicably low for the test U-Sludge. This test will be repeated.

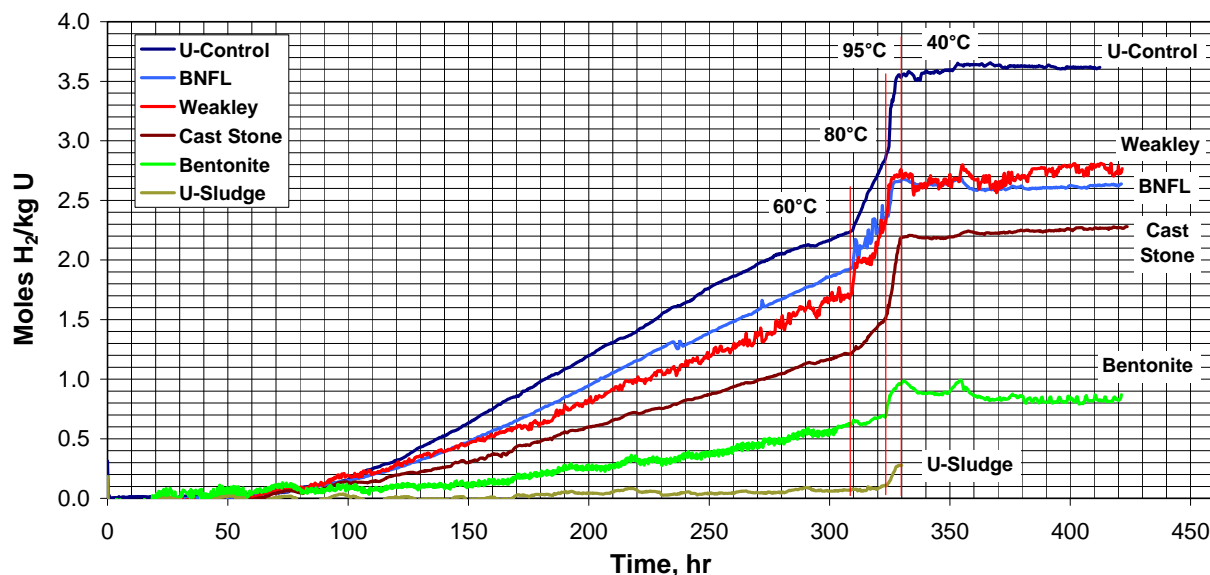


Figure 7.1. Total Gas Generation from U-Control, U-Sludge, and Six Grout Form Tests

Induction times before the production of gas were on the order of 50-110 hours at 60°C for five of the tests. This compares with ~205 hours for K Basin sludge sample KC-2/3 P250 tested at 60°C (Delegard et al. 2000). The test U-Sludge did not begin significant reaction until heated to 95°C, over 310 hours into the test.

As expected, 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 temperatures were lowered to 40°C. Gas generation rates were determined over selected intervals which were past the induction times, held steady temperature, and provided smooth gas generation. The intervals and corresponding temperature and rate values are shown in Table 7.1. The same observed rates, but expressed in units of g uranium per m² of surface area per day, are shown in Table 7.2. It is seen that the rates observed in the U-Control test are similar to those predicted based on the SNF Databook (Duncan 2001).

Table 7.1. Gas Generation Rates in Terms of Moles H₂/kg U·hr

Interval, hr	U-Control		U-Sludge		BNFL		Bentonite		Weakley		Cast Stone	
	T, °C ^a	Rate ^b	T, °C ^a	Rate ^b	T, °C ^a	Rate ^b	T, °C ^a	Rate ^b	T, °C ^a	Rate ^b	T, °C ^a	Rate ^b
150-200	59.80	1.11E-2	59.89	1.40E-3	60.98	9.37E-3	60.48	3.41E-3	61.85	6.88E-3	60.98	6.11E-3
310-324	80.77	4.40E-2	79.73	2.52E-3	79.68	2.66E-2	79.59	8.53E-3	80.12	2.84E-2	79.16	2.13E-2
327-329	95.57	9.25E-2	95.66	4.39E-2	95.02	1.29E-1	94.01	4.61E-2	86.19	2.47E-2	94.94	1.17E-1
340-360	40.72	3.31E-3										
370-420	21.71				40.10	6.11E-4			41.44	1.87E-3	40.02	8.01E-4

^a Average temperature in the interval.
^b Rate in moles H₂/kg U·hr.

Table 7.2. Gas Generation Rates in Terms of g U/m²·day

SNF (Duncan 2001)		U-Control		U-Sludge		BNFL		Bentonite		Weakley		Cast Stone	
T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate	T, °C	Rate
60	6.81E+1	59.80	7.41E+1	59.89	9.34E+0	60.98	6.25E+1	60.48	2.28E+1	61.85	4.59E+1	60.98	4.08E+1
80	2.22E+2	80.77	2.94E+2	79.73	1.68E+1	79.68	1.78E+2	79.59	5.69E+1	80.12	1.90E+2	79.16	1.42E+2
95	4.94E+2	95.57	6.17E+2	95.66	2.93E+2	95.02	8.61E+2	94.01	3.08E+2	86.19	1.65E+2	94.94	7.81E+2
40	1.80E+1	40.72	2.21E+1			40.1	4.08E+0			41.44	1.25E+1	40.02	5.35E+0

Gas generation rates appeared to be negative for the grout tests immediately after lowering the temperature to 40°C and took some time (~40 hours) to resume evolution. For the bentonite grout, resumption of gas generation at 40°C has not yet occurred. 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 grout (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.

The rate data as functions of temperature can be plotted in Arrhenius coordinates to determine the activation energies and compare with activation energies observed in studies of uranium metal corrosion in liquid water and in grout matrices. The Arrhenius plots in Figure 7.2 show that the grouted uranium forms, except in the case of the Weakley grout, have activation energies higher than those usually reported for non-grouted uranium in water [13.8 kcal/mole (Duncan 2001); 15.9 kcal/mole (Hilton 2000)]. The activation energy reported in recent BNFL studies of grouted uranium, however, is on the same order (77.3 kJ/mole ≈ 18.5 kcal/mole) as observed here for the BNFL, Cast Stone, and Bentonite grouts. The higher temperature dependence in grout may indicate that the barrier to corrosion offered by grout is diminished by the improved diffusion of water at higher temperature.

The testing to-date shows that the grouted forms decrease uranium corrosion to 30% (Bentonite) to 90% (BNFL) of that observed in water at 60°C.

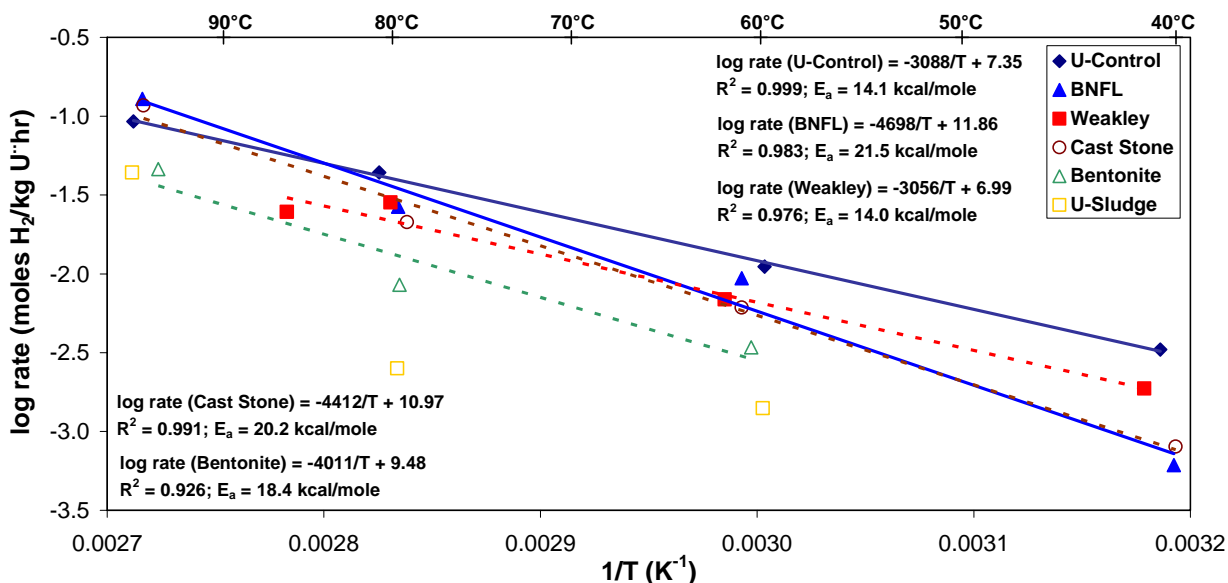


Figure 7.2. Arrhenius Plot of Hydrogen Generation from Uranium Corrosion in Control and Grout Forms

8.0 Future Work

Further testing of the six existing experiments at extended corrosion times is underway. Testing to re-check the behavior of the U-Sludge experiment is in process and further tests with alternative grout forms (Tectonite) are planned.

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