PNNL-14741

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Evaluation and Recommendation of Waste Form and Packaging for Disposition of the K East Basin North Loadout Pit Sludge

G. B. Mellinger
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January 2004

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

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Pacific Northwest National Laboratory
Richland, Washington 99352

Preface

This report discusses an evaluation and recommendations on waste forms and packaging configurations considered for disposition of the sludge accumulated in the Hanford K East (KE) Basin North Loadout Pit (NLOP). The final disposition of the waste will be as contact-handled transuranic waste at the Waste Isolation Pilot Plant in New Mexico. These recommendations were supported in part by characterization and testing results performed on a sample of the KE NLOP sludge collected by Fluor Hanford and provided to Pacific Northwest National Laboratory in December 2003.

The original report describing the work conducted and recommended option was written in January 2004. Revised versions of Tables 5.4 through 5.8 (alternatives comparison tables) and Appendix D (chemical/radiochemical characterization of the KE NLOP sludge) were issued in February 2004. These revisions provided additional radiochemical characterization and X-ray diffractometry information not available earlier. A revised version of Appendix E, an assessment of the uranium metal contents of the KE NLOP sludge based on the gas generation behavior, was issued in May 2004. The January report only covered the first 111 hours of gas generation testing and did not provide an estimate of the uranium metal concentration; however, further testing continued for approximately 1000 hours.

Therefore, to provide complete documentation of the recommendations and characterization/testing performed on the KE NLOP sludge sample collected in December 2003, this document includes the updated information and is divided into three parts:

- January 2004 Evaluation and Recommendations Report
- Attachment 1, February 2004 Updated Alternatives Comparison Tables and Revised Appendix D (KE NLOP Chemical/Radiochemical Characterization)
- Attachment 2, May 2004 Revised Appendix E (Gas Generation/Uranium Metal Determination Testing)

Summary

This report documents an evaluation and recommendations provided by Pacific Northwest National Laboratory (PNNL) to Fluor Hanford regarding the treatment of Hanford K East Basin North Loadout Pit (KE NLOP) sludge to produce contact-handled transuranic waste (CH-TRU) for disposal at the Waste Isolation Pilot Plant (WIPP). These recommendations are supported, in part, by testing results performed on KE NLOP sludge collected by Fluor and provided to PNNL in December 2003.

The KE NLOP contains approximately 6.3 m^3 of material (as-settled) that consists primarily of sand from backflushing the KE Basin water treatment system sand filter, with some contamination from spent nuclear fuel corrosion products. Based on the results of this study, PNNL recommends that this material be treated using Nochar Acid Bond® (Nochar, Inc., Indianapolis, IN). The treated waste would be packaged in steel billet cans with slip lids using a “cross tape” closure. These cans would be placed in filtered plastic bags that would be loaded into Standard Pipe Overpacks (WIPP “Authorized Payload Containers” that consist of 12-in.-diameter “pipe components” loaded into 55-gallon drums). Two billet cans would be loaded into each Standard Pipe Overpack.

Of the options considered that would meet all requirements, this option would result in the production of approximately 35 to 60 percent more packages than if the sludge were grouted. However, treatment with Nochar would also result in a robust process that is less sensitive to processing variations than grout. This option also facilitates WIPP certification by Fluor, as well as rework or repackaging of the treated waste by Fluor in the unlikely event that this is required subsequent to delivery of the treated waste to Fluor. Also, Nochar has already been accepted for use by WIPP.

The KE NLOP samples were characterized and tested in accordance with the Fluor-approved “Bench-Scale Testing Plan to Demonstrate Production of WIPP-Acceptable KE NLOP Sludge Waste Forms at the 325 Building.” The characterization and testing completed in support of this study included measurements of physical properties such as sludge density and water content, radiochemical characterization, and limited gas-generation testing. Per the Test Plan, additional reports were issued that provided further characterization and testing data. These updated data provided “Acceptable Knowledge” for use by Fluor in the WIPP certification process, but did not impact the recommendations for waste treatment/waste packaging configuration.

Three potential waste forms for treated KE NLOP sludge were considered:

- grout
- Nochar
- dewatered sludge.

Four waste-package configurations were considered:

- direct loading of the treated waste in 55-gallon drums

- direct loading of the treated waste in Standard Pipe Overpacks

- loading of the treated waste in billet cans that would be placed in vented plastic bags and then loaded in Standard Pipe Overpacks

- direct loading of the treated sludge in S200-B Shielded Pipe Overpacks

An essential element of the study was to identify the constraints that any recommended option would need to meet. These constraints were based on the WIPP CH-TRU waste-acceptance criteria, as well as requirements for acceptance of the treated waste by the Hanford Central Waste Complex. The key constraint was the requirement that the waste packages have a surface dose rate $\leq$200 mrem/h. Options that met the constraints were then evaluated based on four criteria:

- numbers of packages produced

- ease of rework

- schedule viability

- cost.

This report includes the updated/revised information (February 2004) for the alternatives comparison tables and KE NLOP chemical/radiochemical characterization (Attachment 1) and further results (May 2004) from gas generation/uranium metal determination testing (Attachment 2).

Acronyms

AEA	Alpha Energy Analysis
ASO	Analytical Services Operations
CH	contact handled
CWC	Central Waste Complex
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
FGE	fissile gram equivalent
GEA	gamma energy analysis
ICV	Inner Containment Vessel
IXM	ion exchange module
KE	K East Basin
LDC	large diameter container
LEPS	low-energy photon spectrometry
NLOP	North Loadout Pit
PNNL	Pacific Northwest National Laboratory
SPO	Standard Pipe Overpack
STP	standard temperature and pressure
SWB	Standard Waste Box
TDOP	Ten-Drum Overpack
TMU	Total Measurement Uncertainty
TRU	transuranic
TRUPACT-II	Transuranic Packaging Transporter-II
USQ	unreviewed safety question
VOC	volatile organic carbon
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant
WSB	standard waste box

Acknowledgments

Staff from Duratec Federal Services Northwest, Fluor Hanford, and Pacific Northwest National Laboratory (PNNL) comprised the K East Basin North Loadout Pit sludge sample collection team. At PNNL, they include R. E. Thornhill, P. J. MacFarlan, C. L. O'Laughlin, and T. Moreno, Jr. We would also like to thank R. B. Baker (FH) and J. A. Series (DFSNW) for preparing Appendix A, "Sample Collection."

The following PNNL scientists and technical specialists supported sample compositing, physical testing, and gas-generation testing: S. A. Bryan, J. W. Chenault, F. V. Hoopes, W. B. Larson, T. G. Levitskaia, R. L. Sell, B. J. Goecke, and S. I. Sinkov.

B. Schenter (PNNL) performed numerous dose modeling simulations.

The following PNNL scientists and technical specialists provided chemical and radiochemical analyses of the sludge samples: K. N. Pool, L. R. Greenwood, C. Z. Soderquist, L. P. Darnell, K. J. Carson, T.L.T. Trang-Le, and K. K. Thomas.

We thank W. C. Cosby for his diligent editorial and document-production support.

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Attachment 2 – May 2004 Revised Appendix E, Results of Gas-Generation Testing

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1.0 Introduction

The purpose and scope of this report are provided below. Background information is included that is associated with the sludge accumulated in the North Loadout Pit (NLOP) in the K East (KE) Basin and the impetus for its near-term treatment for disposition.

1.1 Purpose

This report documents the alternative waste forms and packaging configurations considered for disposition of the sludge accumulated in the KE Basin NLOP. The recommended option is documented, including the bases for its selection. The final disposition of the waste will be as contact-handled (CH) transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP) located near Carlsbad, New Mexico.

1.2 Scope

The scope of material considered under this report is limited to the sludge present within the KE NLOP main pit and transfer channel. The volume of sludge in this location, based on direct measurements of sludge depths made in 1994, is estimated to be 5.2 m^3 in the main pit and 1.1 m^3 in the transfer channel (Baker 2001). The estimated upper-bound volume of the sludge is 6.2 m^3 in the main pit and 1.3 m^3 in the transfer channel (Baker 2001). During sludge sampling in this pit in 1999, the depths of sludge were noted on the sampling tubes inserted into the sludge in both the main pit and transfer channel. Measurements in 1999 indicated good agreement with sludge depths measured in 1994 (Baker 2001).

The scope of this report includes the identification of constraints that must be met by any of the alternatives examined. A listing of the alternatives considered and justification for removal of specific alternatives from consideration is provided. A shortened list of alternatives is examined against criteria used to evaluate the benefits and detriments of each of these alternatives. Data from testing the considered waste forms are included as part of the evaluation of the alternatives. Conclusions and a preferred recommendation are presented.

1.3 Background

1.3.1 Facility and Sludge Information

The K Basins, built in the early 1950s, have been used to store irradiated reactor spent nuclear fuel underwater for over 30 years. Associated with the spent nuclear fuel is an accumulation of particulate debris referred to as sludge. Sludge is defined as any solid material in the basin that will pass through a screen with 0.64-cm (0.25-in.) openings. Sludge is found on the basin floors, in canisters, and in other areas of the K Basins, i.e., pits. Sludge is composed of irradiated nuclear fuel particles, fuel corrosion products, cladding, storage canister corrosion products, corrosion products from features in the basin pools (e.g., racks, pipes, sloughed-off concrete), beads lost from ion exchange modules, environmental debris (e.g., windblown sand, insects, pieces of vegetation), and various materials (e.g., sand filter media, hardware, plastic) accumulated through operation of the basins over the past 30 years.

One of the locations where sludge has accumulated is the NLOP in the KE Basin. The KE NLOP, also known as the Sandfilter Backwash Pit, is estimated to contain 6.3 m^3 of sludge (Baker 2001). This pit is isolated from the main-basin pool and contains backwash material from the original sandfilter added to the KE Basin for N Reactor fuel storage (the KE Reactor was active from the 1950s to the 1970s and then deactivated, and in 1975, the water-filled storage basin was converted for storage of spent N Reactor fuel). The source of the water filtered through this sandfilter is the skimmers located in each of the three bays of the main basin pool; under normal operation, water passes through the sandfilters and then into an ion exchange module (IXM) and back to the basin. Unlike the K West Basin, which was cleaned of sludge (Wahlen 1980), some unspecified amount of historic sludge remains in the KE Basin from its prior use before being converted for N Reactor spent-fuel storage.

1.3.2 Previous Sludge Characterization Data

Sludge in the KE NLOP has been sampled for characterization purposes twice in the past 10 years. These sampling campaigns (1993 and 1999) used methods that resulted in representative samples of the accumulated sludge material:

- 1993 Campaign. This campaign included a series of 13 core samples taken at random locations across the pit. The cores extended from the top surface of the sludge to the floor surface. These samples were taken in response to unreviewed safety question (USQ)/Safety concerns related to criticality questions over Pu buildup in the pit. Although the primary concern of this sampling was to address criticality, the general composition of the sludge was also measured (analyses were performed at both the 222-S and the Pacific Northwest National Laboratory [PNNL] 325 Building laboratories [Bechtold 1994; Warner and Harris 1994]). The depth of the accumulated sludge was also measured at that time for many positions, mapped, and the corresponding overall sludge volume in the pit estimated (Baker 2001). Selected results from the 1993 campaign are provided in Table 1.1. These results show that there is minimal difference in the composition of the sludge core samples taken at various locations in the NLOP.

- 1999 Campaign. This campaign included two core samples taken as part of an overall characterization effort performed for most of the stream sources for KE Basin sludge (Pitner 1999). The cores extended from the top surface of the sludge to the floor surface. These two core samples were taken from the deeper areas of sludge in the NLOP, one in the main pit and one in the transfer channel. The two samples were then combined in the laboratory to form one large composite sample (Sample FE-3). Full laboratory analyses were performed at the 222-S and PNNL 325 Building laboratories, and the results are provided in Table 1.2 and Table 1.3.[a]

- Gas-generation testing was performed using approximately 20 g of sample FE-3 to quantify the concentration of metallic uranium (Bryan et al. 2004). Based on this testing, FE-3 was estimated to contain 0.013 wt% uranium metal (settled sludge basis). No quantifiable levels of fission-product gases were detected during the gas generation, which provides good assurance that the FE-3 sludge sample contained essentially no uranium metal.

(a) RB Baker and TL Welsh. "Laboratory Data from the Consolidated and Single Pull Core Sludge Sampling Campaigns" (Internal Fluor Hanford Memo, 01-SNF/RBB-004, May 10, 2001).

Table 1.1. 1993 NLOP Sample Data from 222-S and PNNL 325 Laboratories, Key Radionuclides, Aluminum, and Iron (Source of data: Warner and Harris, 1994)

Sample ID	Sample Type	Sample Location	Density 222-S g/mL	U-Laser 222-S mg/mL	Am-241 222-S µCi/mL (GEA)	Pu-239/240 222-S µCi/mL (AEA)	Cs-137 222-S µCi/mL (GEA)	Co-60 222-S µCi/mL (GEA)	Al 222-S mg/mL (ICP-AES)	Fe 222-S mg/mL (ICP-AES)	U Laser PNNL mg/mL	Am-241 PNNL µCi/mL (GEA)	Pu-239/240 PNNL µCi/mL (AEA)	Cs-137 PNNL µCi/mL (GEA)	Co-60 PNNL µCi/mL (GEA)	Al PNNL mg/mL (ICP-MS)	Fe PNNL mg/mL (ICP-MS)
03 S3059	Core	Main Floor	1.08	4.60		0.929			3.2	8.86	4.64	0.849		2.56	0.0972	3.13	8.83
04 S3059	Core	Main Floor	1.3	5.26	1.521	1.696	7.803	0.203	5.43	21.1	6.28	1.48		7.53	0.208	5.05	20.7
11 S3059	Core	Main Floor	1.31	5.95	0.856	1.019	22.06	0.192	7.49	19.1	6.45	0.805	1.00	21.6	0.181	7.47	20.1
02 S3062	Core	Main Floor	1.18	9.95	0.832	0.928	9.899	0.201	4.15	9.33	7.02	0.829		9.89	0.204	4	2.31
03 S3062	Core	Main Floor	1.23	8.25	0.876	1.046	7.06	0.236	4.48	11.4	6.04	0.867	1.15	6.71	0.23	4.39	2.7
04 S3062	Core	Main Floor	1.25	15.00	1.314	1.684	12.513	0.299	5.17	11.9	9.19	1.4		12.3	0.297	4.79	3.48
05 S3062	Core	Main Floor	1.48	7.92	0.866	1.307	8.966	0.192	4.02	6.79	4.57	0.897		8.67	0.189	3.8	1.32
06 S3062	Core	Main Floor	1.53	4.93	0.66	0.769	9.948	0.265	5.2	16	3.48	0.649		9.65	0.255	5.32	3.85
07 S3062	Up-Layer	Main Floor	1.06	7.39	1.689	1.885	6.639	0.148	3.6	6.59	6.38	1.85	2.11	6.44	0.149	3.58	2.51
08 S3062	Low-Layer	Main Floor	1.37	12.30	1.223	1.525	5.026	0.274	3.64	10.7	6.48	1.29	1.77	4.86	0.274	3.67	3.92
05 S3059	Core	Trans Chan	1.08	7.15	1.824	2.24	5.345	0.257	3.29	7.11	7.91	1.83		5.19	0.245	3.22	7.56
06 S3059	Core	Trans Chan	1.2	6.08	1.046	1.259	4.202	0.192	3.01	58.2	6.79	1.06	1.40	4.14	0.194	3.34	57.1
07 S3059	Core	Trans Chan	1.42	6.18	1.245	1.451	12.489		5.08	47.1	6.18	1.22		12.1	0.157	5.38	46.4
08 S3059	Core	Trans Chan	1.31	6.02	1.27	2.96	10.623	0.288	4.7	13.2	5.98	1.23		10.5	0.295	5.16	15.5
Mean - All Samples			1.27	7.64	1.17	1.48	9.43	0.23	4.46	17.67	6.24	1.16	1.49	8.72	0.21	4.45	14.02
Stnd Dev - All Samples			0.15	2.96	0.36	0.60	4.65	0.05	1.19	15.61	1.40	0.38	0.45	4.74	0.06	1.18	17.39
Rel % Stnd Dev - All Samples			11.53	38.80	30.46	40.31	49.37	20.68	26.65	88.32	22.48	32.65	30.59	54.37	27.15	26.59	124.05
Mean - Core Samples			1.28	7.27	1.12	1.44	10.08	0.23	4.60	19.17	6.21	1.09	1.18	9.24	0.21	4.59	15.82
Stnd Dev - Core Samples			0.14	2.87	0.35	0.63	4.78	0.04	1.23	16.43	1.52	0.35	0.20	4.95	0.06	1.23	18.24
Rel % Stnd Dev - Core Samples			11.14	39.52	31.29	44.06	47.37	18.11	26.80	85.67	24.52	31.72	17.08	53.56	26.70	26.79	115.28
Mean - All Main Floor			1.28	8.16	1.09	1.28	9.99	0.22	4.64	12.18	6.05	1.09	1.51	9.02	0.21	4.52	6.97
Stnd Dev - All Main Floor			0.15	3.40	0.36	0.39	5.03	0.05	1.25	4.99	1.57	0.39	0.52	5.20	0.06	1.25	7.36
Rel % Stnd Dev - All Main Floor			12.05	41.72	32.58	30.78	50.34	21.67	27.03	41.00	25.88	35.54	34.62	57.66	28.53	27.63	105.55
Mean - Transfer Channel			1.25	6.36	1.35	1.98	8.16	0.25	4.02	31.40	6.72	1.34	1.40	7.98	0.22	4.28	31.64
Stnd Dev - Transfer Channel			0.15	0.53	0.33	0.78	4.02	0.05	1.02	25.07	0.87	0.34	--	3.91	0.06	1.15	23.85
Rel % Stnd Dev - Transfer Channel			11.65	8.37	24.80	39.47	49.19	19.94	25.45	79.84	12.93	25.40	--	48.98	27.02	26.98	75.38

Table 1.2. Radionuclide Inventory in KE NLOP Sludge Sample FE-3 (Source: RB Baker and TL Welsh. "Laboratory Data from the Consolidated and Single Pull Core Sludge Sampling Campaigns" (Internal Fluor Hanford Memo, 01-SNF/RBB-004, May 10, 2001).)

Isotope	Settled Sludge μCi/mL	Dry Sludge μCi/g
^{241}Am	2.78E+00	4.73E+00
^{237}Np	5.90E-04	1.00-03
^{238}Pu	5.40E-01	9.18E-01
^{239}Pu	2.27E+00	3.85E+00
^{240}Pu	1.24E+00	2.12E+00
^{241}Pu	6.68E+01	1.14E+02
^{242}Pu	6.00E-04	1.02E-03
^{60}Co	1.99E-01	3.38E-01
^{137}Cs	1.10E+01	1.87E+01
^{154}Eu	2.50E-01	4.25E-01
^{155}Eu	1.02E-01	1.73E-01
^{90}Sr	3.90E+00	6.63E+00
^{99}Tc	2.44E-03	4.14E-03
^{137m}Ba	9.90E+00	1.68E+01
^{90}Y	3.90E+00	6.63E+00
^{234}U	3.82E-03	6.49E-03
^{235}U	1.44E-04	2.45E-04
^{236}U	5.41E-04	9.21E-04
^{238}U	3.11E-03	5.29E-03

Table 1.3. Chemical Composition of KE NLOP Sludge Sample FE-3 (Source: RB Baker and TL Welsh. "Laboratory Data from the Consolidated and Single Pull Core Sludge Sampling Campaigns" (Internal Fluor Hanford Memo, 01-SNF/RBB-004, May 10, 2001).

Analyte	**µg/mL Settled Sludge**	**µg/g Dry Sludge**
Al-icp.a	5.81E+03	9.88E+03
Ba-icp.a	3.93E+01	6.68E+01
Be-icp.a	7.12E+01	1.21E+02
Ca-icp.a	4.82E+03	8.20E+03
Cd-icp.a	5.79E+01	9.85E+01
Cr-icp.a	6.15E+01	1.05E+02
Cu-icp.a	1.58E+02	2.69E+02
Fe-icp.a	1.98E+04	3.37E+04
Mg-icp.a	4.47E+02	7.60E+02
Mn-icp.a	2.37E+02	4.03E+02
Ni-icp.a	2.05E+01	3.49E+01
P.icp.a	1.83E+02	3.11E+02
Pb.icp.a	6.94E+01	1.18E+02
Pu-239.icpms	3.53E+01	6.00E+01
S.icp.a	1.33E+02	2.26E+02
Si.icp.a	9.03E+02	1.54E+03
Sr.icp.a	8.79E+00	1.50E+01
TIC	1.53E+03	2.60E+03
TOC	2.52E+03	4.29E+03
Ti.icp.a	7.70E+01	1.31E+02
U.phos	9.88E+03	1.68E+04
Zn.icp.a	2.06E+02	3.50E+02
Zr.icp.a	2.48E+01	4.22E+01
pH	8.34	
Density, g/cc	1.23	
g-dry/g-settled	0.478	

2.0 Constraints

Constraints are considered the requirements that must be met for each alternative waste-form and packaging configuration considered for disposition of the sludge accumulated in the KE Basin NLOP. Any alternative, in order to be evaluated as a viable option, must first be shown to meet specified constraints. The constraints are based on waste-acceptance criteria for storage at the Central Waste Complex (CWC), payload requirements for shipment in the Transuranic Packaging Transporter-II (TRUPACT-II), and waste-acceptance criteria for disposition of CH waste at the WIPP. The criteria listed in this section are not the complete set of criteria required for total compliance with each of these source documents. Only those criteria from each of these sources that were considered to potentially impact one or more of the alternatives considered are described below. For example, all containers must be appropriately labeled so that this criterion was not included; however, package weight limitations exist that could constrain one or more alternatives so that this criterion was included.

It is recognized that these criteria undergo change and could be modified to allow for acceptance of materials previously not included. However, this is generally a lengthy process relative to the time frame in which a decision will be made to select a recommended approach. Therefore, for the purpose of this evaluation, it was considered that these criteria apply as they currently exist.

The treated KE NLOP sludge waste-form and packaging configuration must comply with all requirements associated with storage at the CWC, transport in the TRUPACT-II, and disposal at WIPP (WIPP 2003a, 2003b). Table 2.1 identifies those requirements that are considered to constrain one or more of the alternatives considered.

Table 2.1. Constraints Affecting KE NLOP Sludge Disposition Alternatives

Constraint		
Container/Packaging Properties		
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four directly loaded 55-gallon drums, or containing one bin • TDOPs, either containing up to 10 directly loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: Container Weights • 547 pounds per standard pipe overpack (SPO) with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers were allowed.	TRAMPAC
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC

Table 2.1 (Contd)

Constraint		
Physical Properties		
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 1 inch or 2.5 cm in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC
Chemical Properties		
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC
Radiological/Nuclear Properties		
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063

Table 2.1 (Contd)

Constraint		
Radiological/Nuclear Properties		
	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 g for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063
	S200 pipe overpack payloads shall meet the package specific curie limits in the TRAMPAC (see Appendices 2.3 and 2.4, respectively).	TRAMPAC
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the Total Measurement Uncertainty (TMU), the TRU alpha-activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤ 80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq 1{,}800$ ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤ 80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063

Table 2.1 (Contd)

Constraint		
Gas-Generation Properties		
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 g-moles/ft^3 at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on both the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits).	TRAMPAC
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable (gas/volatile organic carbons [VOCs]) VOCs is also limited along with hydrogen to ensure the absence of flammable VOC mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC

Table 2.1 (Contd)

Constraint		
Gas-Generation Properties		
Pressure	The gases generated in the payload and released into the Inner Containment Vessel (ICV) cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.
TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.
WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

3.0 Alternatives Considered

The alternatives considered are based on a combination of the possible waste form for the KE NLOP sludge and the final packaging configuration for that waste form.

3.1 Preparations and Properties of Waste Forms

Based on assessments given in the Test Plan ("Bench-Scale Test Plan to Demonstrate Production of WIPP-Acceptable KE-NLOP Sludge Waste Forms at the 325 Building," December 2003), three KE NLOP waste forms were prepared to evaluate waste-form preparation methods and to understand the waste forms' performance and qualities. The names and general descriptions of the three waste forms are shown in Table 3.1.

Table 3.1. KE NLOP Waste Forms

Waste Form Name	Description
NLOP-Moist	~50 g of as-settled sludge, drained of liquid
NLOP-Gt	~50 g of as-settled sludge and ~25 g of supernatant solution, blended and cured in grout
NLOP-Nochar	~50 g of as-settled sludge and ~25 g of supernatant solution, blended with Nochar Acid Bond 660.

In the design of preparation methods for any KE NLOP waste form, consideration must be given to the physical and chemical properties of the KE NLOP sludge and its associated supernatant solution. These feed-waste properties are described in more detail in Appendices B, C, and D. The qualities of the feed waste bearing most strongly on waste-form preparation are summarized by the following observations:

- The sludge consists of quickly settling sand, a rusty-brown slow-settling floc, and interstitial and supernatant solution.

- In the sample collection and laboratory testing with liter-scale material quantities, the sand was observed to settle to the container bottom within 1 minute. In contrast, settling the floc to a steady final volume required days.

- In limited testing and observation, and consistent with expectation, the compaction of the floc increases with the floc depth. This means that the floc compaction, and hence settled-sludge density, expected in the 1.5-m-deep LDC (large diameter container) may be greater than the density of 1.24 g/mL observed in laboratory tests with settled sludge about 0.12 m deep.

- The uranium and the analyzed radionuclides (primarily consisting of ^{60}Co, ^{137}Cs, ^{239,240}Pu, and ^{241}Am) partition overwhelmingly to the solid phase. Therefore, the low-activity interstitial and supernatant solution may practically be considered a pure diluent, contributing negligible activity to the total sludge. As a consequence, the addition or removal of the supernatant solution during sludge processing will correspondingly decrease or increase the activity concentrations in the total sludge.

Retrieval of the sludge (particularly the sand) from the LDC likely will require additional solution. As a starting point to model this situation for grouted and Nochar waste-form development, sludge and supernatant solution mixtures were tested using the settled sludge prepared from the composited KE NLOP samples (density 1.24 g/mL) and supernatant solution in an amount corresponding to 50 wt% of the settled-sludge mass. This produced a diluted sludge with a volume about 1.3 times higher than the starting settled sludge (and radionuclide concentration about 1.3 times lower). The diluted sludge therefore had a density of about 1.15 g/mL. In process application, the amount of additional water may be adjusted to accommodate material behavior or target waste-product loadings.

Descriptions of the tested waste-form preparation ratios and physical properties are shown in Table 3.2. For example, the volume increases or decreases (expansion factors) incurred in going from the settled sludge to the prepared waste form are given in Table 3.2. For example, the tests show that the drained sludge product, NLOP-Moist, is only about half (0.47) of the volume of the starting sludge. In contrast, the grouted and Nochar waste forms, which also included additional supernatant solution, added to the final waste-form volumes such that the grouted and Nochar product expansion factors were 2.45 and 1.82, respectively.

Table 3.2. KE NLOP Waste Form Properties

Parameter	Waste Form		
	NLOP-Moist	**NLOP-Gt**	**NLOP-Nochar**
Waste Composition			
KE NLOP settled sludge mass, g	52.87	50.40	53.83
KE NLOP settled sludge volume, mL	42.6	40.6	43.4
KE Basin supernatant solution, g	0	24.73	24.35
Total feed waste mass, g	52.87	75.13	78.18
Total feed waste volume, mL	42.6	65.4	67.8
Additive			
Portland Type I/II cement, g	--	112.00	--
Bentonite, g	--	6.60	--
Nochar Acid Bond 660, g	--	--	2.95
Property			
Final waste-form volume, mL	20	99.3	79 (packed) / 120 (loose)
Final waste-form mass, g	28.92	193.73	81.13
Final waste-form density, g/mL	1.45	1.95	1.03 (packed) / 0.68 (loose)
Expansion factor, settled sludge → final waste form	0.47	2.45[(a)]	1.82 (packed)[(b)] / 2.76 (loose)[(b)]
Expansion factor, sludge and supernate → final waste form	--	1.52	1.17 (packed) / 1.77 (loose)

(a) The expansion factors apply to the feed settled sludge for sludge plus supernatant water formulations; water (e.g., from supernatant solution) still required for grouted waste formulation.
(b) The expansion factors apply to the feed settled sludge for sludge plus supernatant water formulations; the actual expansion factors for sludge-only (supernatant-free) formulations likely are lower and approach 1.17 (packed) / 1.77 (loose). Testing is required to confirm this behavior.

The properties of the individual waste forms are described in the following sections of this report. Section 3.1.1 describes the properties of NLOP-Moist, the sludge form simply drained of associated liquid. Section 3.1.2 describes the grouted waste form NLOP-Gt. Section 3.1.3 describes the waste-form NLOP-Nochar prepared using the Nochar "Acid Bond 660" water absorbent. Further detailed descriptions of the preparation and properties of the waste forms are provided in Appendix F.

3.1.1 Drained Waste-Form NLOP-Moist

The waste-form NLOP-Moist was prepared with the aim to obtain a concentrated (low-volume) waste that had no drainable liquid. In practice, a continuous cross-flow filter, batch-wise filter press, or screened well pump within a final waste package might be used to draw the drainable liquid from the KE NLOP sludge.

The waste form was prepared in the laboratory by weighing a representative aliquot of the KE NLOP settled sludge into a 50-mL plastic centrifuge cone, inverting the cone on a stack of filter papers, and allowing the free liquid to drain through the papers.

The filter papers prevented sludge solids from leaving the cone while acting as a wick to draw solution from the sludge where it could evaporate from the margins of the papers. The boat/filter/cone was kept in the inverted position for 2 days but seemed to be well-drained after 1 day. The centrifuge cone with drained solids was re-weighed after 2 days, and the volume of the tapped solids was measured to determine the final form density of 1.45 g/mL. The drained sludge waste-form NLOP-Moist is undergoing gas-generation testing.

3.1.2 Grouted Waste-Form NLOP-Gt

Consultation with technical experts, review of technical literature, and testing using simulated KE NLOP sludge and supernatant solution were done to develop grouted-waste formulations. The goals were to find a simple formulation producing a "workable" (e.g., readily mixed) slurry that would set under air-tight conditions and produce a solid form yielding no "bleed water" (free liquid) upon curing.

It was found that Portland Type I, II, or I/II cement is suitable as the cement component and that bleed water can be controlled with bentonite or attapulgite clay additives. Bentonite was selected for testing with KE NLOP sludge because it has been used in other waste formulations for WIPP.

Based on experience, a cement/water weight ratio of about 0.5 produces an easily mixed slurry in construction applications. However, this blend produces significant bleed water. Increasing the cement fraction produces slurries that are increasingly difficult to mix and still yield appreciable bleed water (note—the WIPP waste form must have no free liquid). Bentonite additions to 0.5 ratio water/cement slurries were tested for workability and free liquid in the set product. Consistencies that would hold a peak when the mixer was withdrawn, but were not so thick that they would ball-up, produced grouts that set under closed conditions and yielded no bleed water. The amount of bentonite added proved to be about 9 wt% of the Portland cement used.

The NLOP-Gt waste form was prepared by mixing KE NLOP settled sludge, supernatant solution in the amount of half of the weight of settled sludge, and Portland Type I/II cement in an amount equal to twice the mass of the water contained in the combined sludge and supernate. The cement/sludge/supernatant ingredients were mixed thoroughly until the mixture was homogeneous. While stirring continued, dry-powder bentonite was added with stirring. The amount of bentonite added in preparing the NLOP-Gt waste form was 6 wt% of the added cement, somewhat less than the 9 wt% used in simulant testing. Less bentonite was used because the mixture had reached the desired thickness, and further addition would have been less workable. The mixture was thick and would not pour but had to be transferred by spatula. In full-scale application, the Portland cement/bentonite dry ingredients would be dry blended beforehand, and the dry blend mixed with the KE NLOP sludge and supernatant.

The sealed NLOP-Gt product was cast into two vessels (the larger quantity for gas-generation testing). Neither showed any bleed water after mixing or after setting. The waste forms set to hardness within 1 day.

The grouted sludge waste form from NLOP-Gt is undergoing gas-generation testing.

3.1.3 Adsorbent Waste-Form NLOP-Nochar

Nochar Acid Bond 660 is a polyacrylic water sorbent in a dry fine granular powder form. Among other applications, it has been used to absorb aqueous solutions in wastes destined for WIPP. The dry Nochar granules, when added to water with stirring, are observed to swell over a period of 1 to 2 minutes. The volumetric swelling of the particles is dramatic and within the 1- to 2-minute period; the Nochar/water product becomes a gelled mass containing fine (~1-mm-diameter) lumps. A similar product based on low cross-linked polyacrylates used for moisture absorption in rad waste disposal includes "Quik-Solid," a similarly textured dry granular solid offered by Cetco (http://www.cetco.com/groups/ww/TDS/QuikSolid.pdf). Besides their applications in rad-waste disposal, polyacrylate granule/powders are used in disposable diapers.

Based on vendor literature (Nochar, Inc., www.nochar.com), Nochar solidification agents have been tested and proven in over 150 waste streams (including stabilization of TRU-containing aqueous/sludge waste streams for ultimate disposal to WIPP). Stability tests performed on Nochar include paint filter testing, freeze/thaw testing, vibration testing, and radiation stability testing (90 Mrad—gamma/cobalt source). Due to project time constraints (i.e., insufficient time for independent testing), the vendor information on Nochar stability and its acceptance by WIPP serve as the technical basis for judging the long-term stability for the Nochar/KE NLOP sludge waste form.

The Nochar addition absorbs the free liquid and allows the waste to achieve the criterion of having no drainable liquid. The Nochar capacity to absorb water is pH-dependent, according to manufacturer's guidance, with higher absorption found at higher pH. The pH of the KE NLOP settled sludge is about 8.3 and that of the supernatant liquid is about 7.5, well within the range of optimum applicability of Nochar Acid Bond 660.

Preliminary tests with simulated KE NLOP sludge having 50 wt% additional water (a sand-water mixture containing 21 wt% sand) were performed to understand Nochar behavior and judge the quantity of

Nochar required to eliminate drainable liquid. The addition of about 6 wt% Nochar, with respect to water, or about 4.5 wt% Nochar, with respect to the total sludge-plus-water mass, was sufficient to form a gelled semi-solid of cooked Cream-of-Wheat consistency. The product had a bulk density of 1.03 g/mL.

The NLOP-Nochar waste form was prepared by mixing KE NLOP settled sludge, supernatant solution in the amount of half of the weight of settled sludge, and Nochar Acid Bond 660 in an amount equal to about 3.8 wt% of the sludge-plus-water mass. The ingredients were mixed by shaking. After shaking, the bottle was opened and the product observed. No free liquid was seen, and the contents had a gelled springy consistency but with much open volume (air space) caused by the mode of mixing that could not be decreased by tapping. The product was left overnight and no free liquid was seen. A further day of storage still showed no free liquid. The distribution of solids throughout the Nochar-bearing product seemed to be uniform, judging by the relatively even brown color. The total volume bulk density of the void-filled product was about 0.68 g/mL.

The mode of mixing of the Nochar with the KE NLOP sludge and supernatant thus strongly influences the density of the product waste form. The preferred mode of mixing will require further development. However, adding the sludge/supernatant mixture directly to a pre-measured dose Nochar Acid Bond 660 sorbent (or equivalent) seems to be the simplest method. The rate of addition and mixing must be balanced by the rate of water uptake by the sorbent to help ensure that the distribution of radioactivity in the sludge (present almost exclusively on the sludge solids) is uniform in the product matrix.

The product of the laboratory test mixture with genuine KE NLOP sludge, NLOP-Nochar, is undergoing gas-generation testing.

3.2 Waste-Package Configuration

Three waste-package configurations were considered in this study: 55-gallon drums, standard pipe overpacks (SPOs), and S200B Pipe Overpacks. All three of these waste-package configurations are Authorized Payload Containers for transport of CH-TRU to WIPP in the TRUPACT-II or HalfPACT transport cask. Summary descriptions of these packages are provided below. Additional detail is provided in Appendices 2.1, 2.2, and 2.4 of WIPP (2003a). General arrangement drawings for these packages are provided in Appendix 1.3.2 of WIPP (2003b).

3.2.1 55-Gallon Drum

The 55-gallon-drum body, lid, and bolt ring are constructed of steel. A gasket of tubular or foam styrenebutadiene is required for drum lid closure. The approximate dimensions of the 55-gallon drum are given in Table 3.3.

Table 3.3. 55-Gallon Drum Dimensions

Dimension	Approximate Measurement (inches)	
	Inside Dimension	**Outside Dimension (OD)**
Height	33 1/4	35
Diameter	22 ½	24

The drum must have a minimum of one filter vent. An optional, rigid, polyethylene liner and lid may be used inside the drum. If a lid is used with the liner, the liner lid must contain a 0.3-in. minimum diameter hole, or a filter with hydrogen release rates equivalent to or greater than the 0.3-in. minimum diameter hole. A double-lid drum with a filtered inner lid will be considered the same as a drum with a filtered inner confinement layer. Table 3.4 presents the 55-gallon drum construction materials. Figure 3.1 is a drawing of the 55-gallon drum. Table 3.5 specifies the weights associated with the 55-gallon drum.

Table 3.4. 55-Gallon Drum Materials of Construction

55-Gallon Drum Component	Material
Body, lid, and bolt ring	Steel
Rigid liner and liner lid (optional)	High-density polyethylene
Closure	Bolted ring
Gasket	Type I—Tubular styrene-butadiene, or equivalent
	Type II—Foam styrene-butadiene, or equivalent
Rolling hoops	3-rolled or swedged types

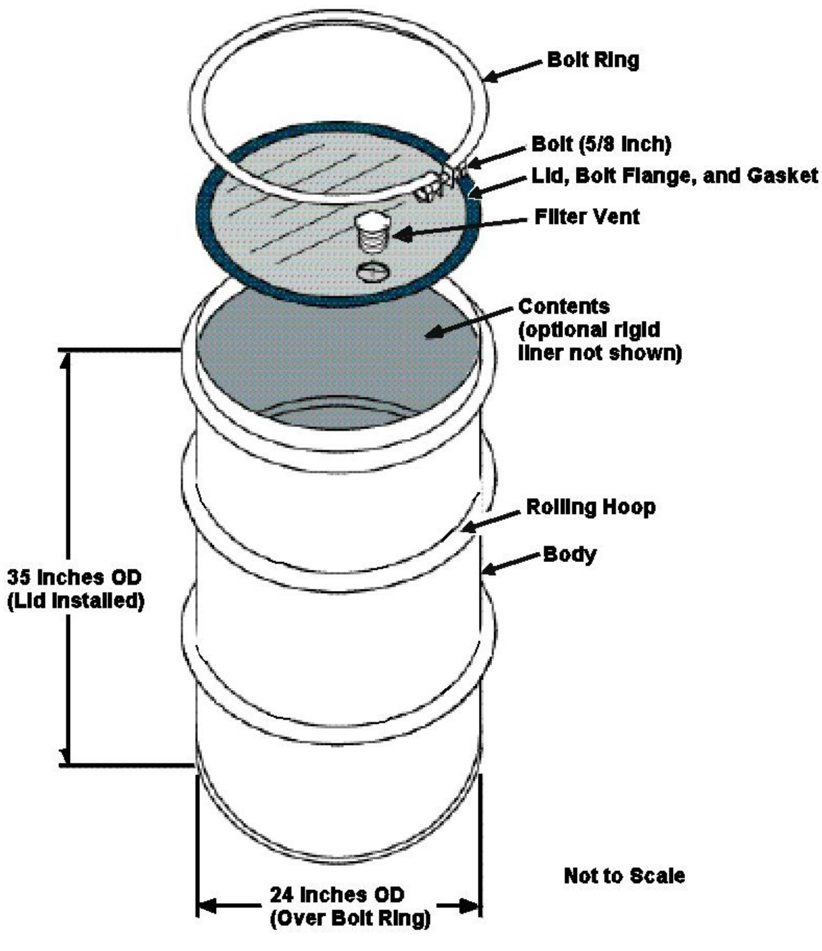

Figure 3.1. 55-Gallon Drum

Table 3.5. 55-Gallon Drum Weights

Component	Weight (lbs)	
	Approximate Empty	Maximum Gross
55-gallon drum	60	1,000
55-gallon drum with rigid liner and liner lid	77	1,000

CH-TRU waste may be directly loaded into a 55-gallon drum or may be loaded into a pipe component, which is then overpacked in a 55-gallon drum. The latter configuration constitutes an SPO, S100 pipe overpack, or S200 pipe overpack.

3.2.2 Standard Pipe Overpack

The SPO consists of a pipe component positioned by fiberboard/plywood dunnage within a 55-gallon drum with a rigid liner and lid (Figure 3.2). The pipe component is available in two sizes as specified in Table 3.6. The size considered in this analysis is the 12-inch pipe component.

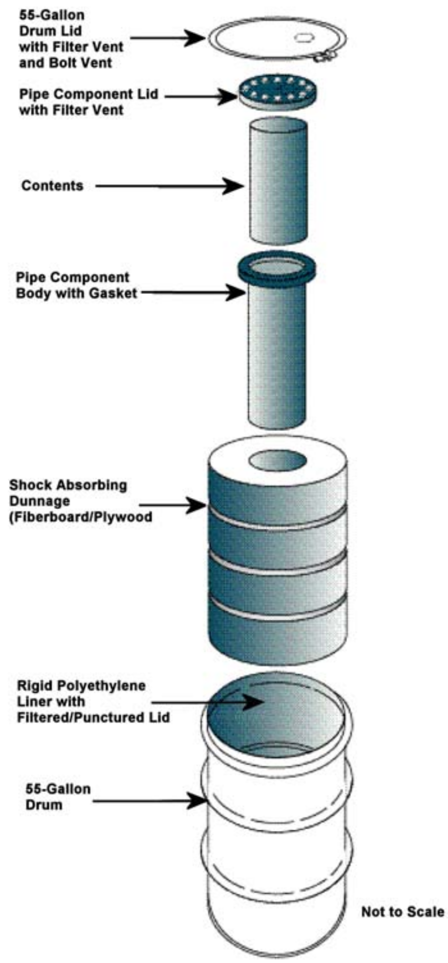

Figure 3.2. Standard Pipe Overpack

Table 3.6. Pipe-Component Dimensions

Pipe-Component Size	Dimension	Maximum Measurement (in.)	Bolt Size (in.)	Number of Bolts	Minimum Bolted Flange Diameter (in.)
6-inch	Diameter	6.7 Outside Diameter	3/4	8	11
	Height	27.5 Overall			
12-inch	Diameter	12.8 Outside Diameter	7/8	12	16.3
	Height	27.5 Overall			

The pipe-component body, lid, and bolt flange are constructed of stainless steel. A butyl rubber or ethylene propylene O-ring is required for pipe-component closure. One or more bolts may have tamper-resistant heads and/or may have a thread-locking compound applied to the threads. As specified in Appendix 2.5, the pipe component and the overpacking 55-gallon drum each must have a minimum of one filter vent. Table 3.7 presents the pipe-component construction materials.

Table 3.8 specifies the weights associated with the pipe components. Table 3.9 specifies the weights associated with the SPO.

Two applications of the SPO were considered in this analysis. One was direct loading of the treated waste in the SPO. The second was loading of the treated waste into "billet can" type containers that would then be loaded into the SPO. Steel billet cans with slip-fit lids would be used that would be placed in bags equipped with WIPP-compliant filters. The bagged cans containing the treated sludge would be loaded into the SPOs (two billet cans per SPO). The billet cans would be approximately 11 in. diameter by approximately 12 in. tall and have an internal volume of approximately 18 L.

Table 3.7. Pipe-Component Materials of Construction

Component	Material
Body, lid, and bolt flange	Stainless steel
Closure	Bolted flange
Gasket	Butyl rubber or ethylene propylene O-ring

Table 3.8. Pipe-Component Weights

Pipe-Component Size	Pipe-Component Weight (lbs)	
	Maximum Contents	Maximum Gross
6-in.-diameter pipe component only	66	153
12-in.-diameter pipe component only	225	407

Table 3.9. Standard Pipe Overpack Weights

Size of Pipe Component Overpacked	Maximum Gross Weight (lbs)
6-in.-diameter pipe component overpacked in a 55-gallon drum	328
12-in.-diameter pipe component overpacked in a 55-gallon drum	547

3.2.3 S200-B Pipe Overpack

The S200 pipe overpack is a shielded version of the SPO described in Section 2.1.2. It consists of a gamma-shield insert located by rigid polyurethane foam dunnage inside a 12-in.-diameter pipe component positioned within a 55-gallon drum by means of fiberboard/plywood dunnage. A schematic of the S200 pipe overpack is shown in Figure 3.3. The 12-in.-diameter pipe component used in the S200 pipe overpack is identical to the 12-in.-diameter pipe component described for the SPO in Section 2.1.2. The 6-in.-diameter pipe component is not used in the S200 pipe overpack. The 12-in.-diameter pipe-component dimensions and materials of construction are specified in Table 3.10 and Table 3.11, respectively. The gamma-shield insert is a lead two-component assembly consisting of a cylindrical body with an integral bottom cap and a detachable lid. The shield insert is available in two sizes as specified in Table 3.10. The S200-B is the S200 pipe overpack considered in this analysis.

The shield-insert body, lid, and dunnage materials of construction are specified in Table 3.11.

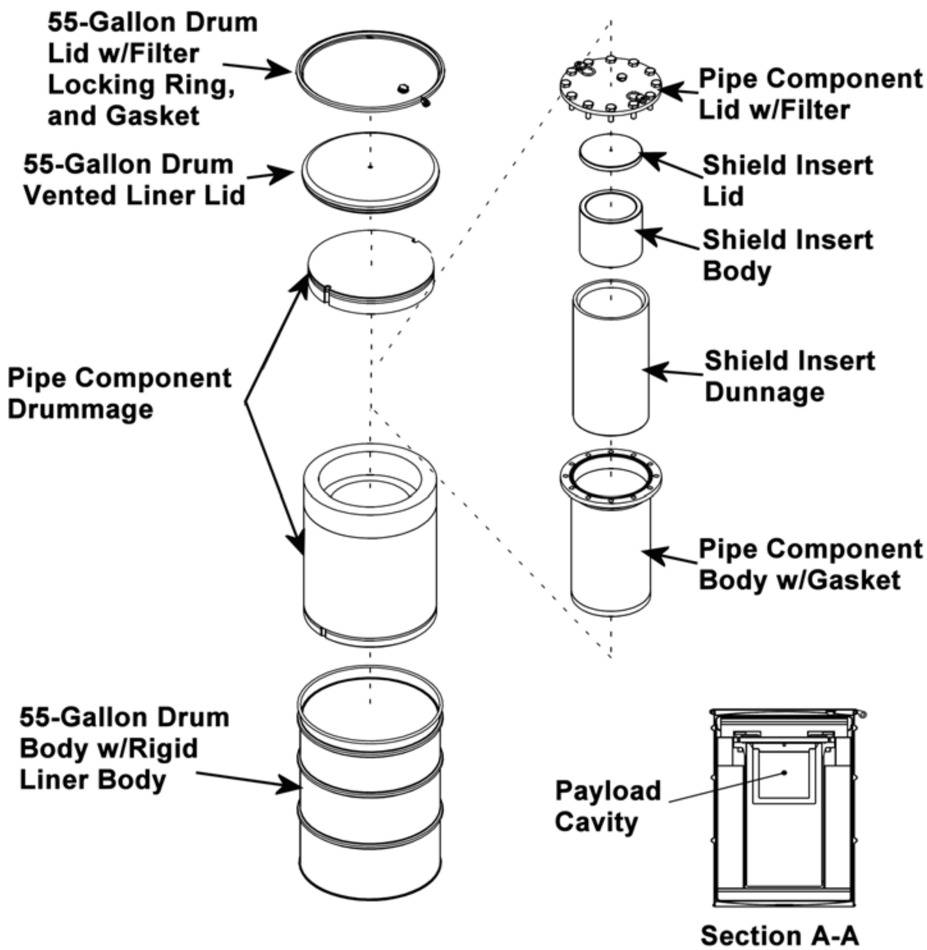

Figure 3.3. S200 Pipe Overpack

Table 3.10. Shield-Insert Nominal Dimensions

Size	Thickness (in.)	Inside Diameter (in.)	Inside Height (in.)	Outside Diameter (in.)	Outside Height (in.)
S200-A	1.000	8.125	8.125	10.125	10.625
S200-B	0.600	8.125	16.125	9.325	17.825

Table 3.11. Shield-Insert Materials of Construction

Item	Material
Body, lid	Lead
Dunnage	Rigid polyurethane foam

The maximum allowable weight of 12-in.-diameter pipe-component contents (shield insert assembly plus payload) is 225 lbs, and the maximum gross weight of the loaded 12-in.-diameter pipe component is 407 lbs, which are consistent with the specified 12-in.-diameter pipe-component weights. The maximum allowable gross weight of the loaded S200 pipe overpack is 547 lbs. Table 3.12 summarizes the nominal individual and maximum total weights associated with the shield-insert assembly components.

Table 3.12. 12-in. Pipe-Component Content Nominal Weights

Item	S200-A (lbs)	S200-B (lbs)
Shield-Insert Body	134	129
Shield-Insert Lid	43	27
Shield-Insert Dunnage	18	15
Payload	25	50
Total (Maximum)	225	225

4.0 Evaluation Criteria

The waste-form and waste-package configurations that are considered in this report are described in Section 3 of this report. All potential combinations of these waste-form and waste-package configurations must meet the acceptance criteria documented in Section 2 of this report to be considered for evaluation. Those combinations that meet the acceptance criteria have been evaluated and ranked based on the evaluation criteria provided below.

4.1 Number of Packages Produced

This criterion considers the estimated number of packages that would be produced for each combination of waste-form and package configuration that meet the acceptance criteria. Creating fewer packages requires acquiring, certifying, and shipping fewer containers to WIPP. A waste-form/waste-package alternative will rank higher if fewer waste packages would be produced.

4.2 Ease of Rework

Final certification of the packaged waste for acceptance at WIPP requires assaying every container of waste. Until a final waste-form and waste-package configuration is selected, it is not possible to determine the preferred method of performing assay of the containers. By allowing inner containers to be removed from the waste packages, it will allow greater flexibility in the approach to assaying the waste packages. Additionally, if individual waste forms or packages cannot meet certification requirements, it is advantageous to provide waste in a form that can be retrieved from the packaging in a contamination-controlled manner. This criterion considers the degree of difficulty associated with retrieving and/or reworking each of the waste-form/waste-package alternatives. A waste-form/waste-package alternative will rank higher if such retrieval or rework would be easier.

4.3 Schedule Viability

This criterion considers the impact that selection of a particular waste-form/waste-package configuration would have on the schedule for completing treatment of the KE NLOP sludge. Schedule impacts may include delays in the start of processing (due, for example, to procurement lead-time requirements), or delays in the completion of processing. The schedule viability will consider, for the waste-form/waste-packaging configurations, both the duration from authorization by Fluor Hanford to proceed until operations can be started and the duration of actual operations. Specifically, each waste-form/waste-packaging configuration will need to be able to demonstrate 1) compliance with 325 Building approval to start operations no later than March 15, 2004, 2) a minimum of 30 packages can be processed, packaged, and shipped to CWC no later than May 1, 2004, and 3) the balance of KE NLOP sludge processed and packaged no later than December 31, 2004. A waste-form/waste-package alternative will rank higher if it is more likely to achieve the listed dates above, which would make it less likely to encounter delays in being able to start processing and less likely to encounter delays during processing.

4.4 Cost

This criterion considers the cost to produce WIPP-acceptable waste forms at the 325 Building. The costs of the various waste-form/waste-package alternatives will be ranked relative to one-another. The costs developed are rough order-of-magnitude costs for relative comparison and should not be detailed estimates, nor should they be considered the total project costs. Costs examined do not consider retrieval of the KE NLOP sludge at K Basins because this cost is independent of the waste-form/waste-package alternative considered. Costs also do not consider the operational startup cost, which is estimated to be roughly equivalent, regardless of the packaging, and the waste-form alternative selected. Costs examined include 1) acquisition of equipment to perform the operation within the 325 Building, 2) acquisition of packaging systems for the waste, 3) acquisition of consumables including waste-former materials, 4) operational costs to create the packaged waste systems, and 5) the cost of demobilization and disposal of the system used to create the waste packages. A waste-form/waste-package alternative will rank higher if its cost is lower compared to the other alternatives.

5.0 Comparison of Alternatives

The alternative waste-form and waste-packaging options are shown in Table 5.1. This table also shows the settled sludge waste loadings, expressed as volume percent, that were considered for the KE NLOP sludge. These sludge waste loadings were based on radiochemical characterization of the sludge performed in support of this evaluation, shielding calculations, and the constraint that the surface dose rate of each package must not exceed 200 mrem/h. A simplified packaging configuration was used for the dose-rate calculation, but the simplifications will not significantly impact the shielding calculations.

Table 5.1. Waste-Form and Waste-Packaging Alternatives for KE NLOP

Packaging Alternatives	Waste Forms		
	Grout	**Nochar**	**Dewatering**
55-Gallon Drum	8%	7%	Not considered
Shielded Pipe Overpack	37%	23%	Not considered
Shielded Pipe Overpack with two billet cans	37%	29%	Not considered
S200-B Shielded Pipe Overpack	Not considered	Not considered	200%[(a)]

(a) The volume of a given quantity of dewatered sludge is half that of settled sludge. As a result, a container filled with dewatered sludge would contain twice the amount of sludge solids compared to the same container filled with settled sludge.

Some of the potential options were eliminated because dose-rate calculations showed that the dose rates would be too high; this applied to dewatered sludge packaged in drums or SPOs. Other potential options were eliminated because the limited internal volume of the package would result in an excessive number of packages; this applied to grout or Nochar packaged in S200-B Shielded Pipe Overpacks.

The following sections discuss how each of the remaining alternatives compares with the constraints presented in Section 2.0 and will also evaluate the alternatives with respect to the evaluation criteria presented in Section 3.0. A summary of the dose rates and WIPP drums produced for the alternatives above is shown in Table 5.2. The volumes of the packaging alternatives that were considered in this study are provided in Table 5.3.

Table 5.2. Summary of Dose Rates and Waste Packages Produced for Waste Form/Waste Package Alternatives

Vol% Settled Sludge (Percent)	Volume of Settled Sludge (Liters)	Density (g/cm^3)	Container Type	Estimated Maximum Dose Rate at Side of Package (m rem/h)	WIPP Process (#)	Form to Achieve Waste Loadings
200	22	1.5	S200-B	55	286	Dewatered
8	14	1.9	55-gal drum	180	445	Grout
5	8.8	1	55-gal drum	192	713	Nochar
37	16	1.9	SPO	150	396	Grout
37	13	1.9	SPO + two billet cans	120	473	Grout
23	10	1	SPO	160	630	Nochar
29	10	1	SPO + two billet cans	160	630	Nochar

Table 5.3. Volumes of Packaging Alternatives

	55-Gallon Drum	Standard Pipe Overpack	Standard Pipe Overpack with 2 billet cans	S200-B Shielded Pipe Overpack
Internal Volume	208	51	42	13.7
Working Volume	177	43	36	11

5.1 Grouted Waste Form Within 55-Gallon Drum

5.1.1 Description of Alternative

This waste form consists of a WIPP-certified drum and liner completely filled with grouted sludge. The grout formulation used was the same as the one demonstrated in the laboratory consisting of Portland cement, bentonite clay, water, and settled sludge. The settled sludge was assumed to be combined with an additional 50 volume percent water, and no additional dewatering steps were used in the process. The sludge and additives would be added directly to the container, mixed, and allowed to solidify.

A comparison of this alternative with the constraints presented in Section 2.0 is provided in Table 5.4. As the table shows, this alternative complies with all of the constraints for which information is currently available.

5.1.2 Evaluation with Respect to Evaluation Criteria

5.1.2.1 Number of Packages Produced

The estimated number of packages for a grouted drum is limited by dose rate and is estimated to be 445 with 14 L of settled sludge per drum. The dose rate target is 150 mrem/h, and the quantity of settled sludge per drum was adjusted to obtain a calculated dose rate of approximately 150 mrem/h. The WIPP limit is 200 mrem/h minus the uncertainties in the measurements. With only 14 L of sludge in the drum, the package does not approach any of the other WIPP limits, except the total weight. The density observed in the laboratory was slightly above 1.9, so the grouted drum weight is about 370 kg and does not exceed the WIPP limit of 454 kg.

5.1.2.2 Ease of Rework

A grouted drum would be very difficult to rework.

5.1.2.3 Schedule Viability

The additional number of containers over other options increases the risk to the solidification schedule, although the schedule viability is not significantly affected by any of the packaging alternatives

Table 5.4. Comparison of Grouted Waste Form Within 55-Gallon Drum with Treated-Waste Constraints (8 vol% settled sludge loading)

Constraint			Value for TBD alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	55-Gallon Drum with rigid liner and liner lid
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: Container Weights • 547 pounds per standard pipe overpack (SPO) with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack. • 1,000 pounds per 55-gallon drum.	TRAMPAC	820 lb (includes 77 lbs for drum and liner)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and liner.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly-generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.4 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 inch) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E)
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.011 W/drum (Based on KE NLOP Safety Basis Composition)[(a)]

Table 5.4 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	3.7 g FGE/drum Based on KE NLOP Safety Basis Composition[a]
	A payload container shall be acceptable for transport only if the ^{239}Pu FGE plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	190 nCi/g [Based on total alpha analysis of KE NLOP Comp] [Safety Basis KE NLOP composition will give 3X higher value.]

Table 5.4 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Curie Content	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to ≤1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 cm (1 ft) from the waste package.	HNF-EP-0063	
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	180 mrem/h [Based on modeling.]
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, a determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package	TRAMPAC	0.011 W/drum (Based on KE NLOP Safety Basis Composition)[a] [Appendix E discusses hydrogen generation from chemical reactions.]

Table 5.4 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Hydrogen Generation	It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits).	TRAMPAC	0.011 W/drum (Based on KE NLOP Safety Basis Composition)[(a)] Appendix E discusses hydrogen generation from chemical reactions.
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay-heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC	
Pressure	The gases generated in the payload and released into the Inner Containment Vessel (ICV) cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC	

(a) Schmidt, A.J. and R.B. Baker. "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Slaughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.
TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.
WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

5.1.2.4 Cost

Grout materials are inexpensive, and the equipment needed to produce the waste would not add significantly to the overall cost. The grout required and the number of containers required would be similar for the filling grouted overpack containers and therefore is considered to have a slightly lower cost since the overpacks themselves will add cost to the grouted overpacks.

5.2 Grouted Waste Form in Standard Pipe Overpack Container Packaged Within 55-Gallon Drum

5.2.1 Description of Alternative

This waste form consists of a WIPP-certified overpack completely filled with grouted sludge. As an alternative, inner billet containers would be filled, bagged, and placed within the overpack container and the accompanying drum. The billet cans would be sized to allow two in a standard pipe overpack. The grout formulation used was the same as the one demonstrated in the laboratory, consisting of Portland cement, bentonite clay, water, and settled sludge. The settled sludge was assumed to be combined with an additional 50 volume percent water, and no additional dewatering steps were used in the process. The sludge and additives would be added directly to the overpack or billet can, mixed, and allowed to solidify.

A comparison of this alternative with the constraints presented in Section 2.0 is provided in Table 5.5. As the table shows, this alternative complies with all of the constraints for which information is currently available.

5.2.2 Evaluation with Respect to Evaluation Criteria

5.2.2.1 Number of Packages Produced

The estimated number of packages for a grouted overpack is slightly more than the grouted drums, based on the waste loading and grout formulation tested in the laboratory. The calculated dose rate is 90 mrem/h at the side of the drum. This is less than the WIPP dose-rate limit and less than the 55-gallon drum grouted directly. The waste loading of 37% results in 16 L of sludge per drum and the production of 396 drums to solidify all the NLOP sludge. If billet cans are used, the number of drums increases to 473 because space is lost and the quantity of sludge per volume of grout was limited by the formulation tested in the laboratory. The dose rate for the billet cans was not calculated directly but would be reduced to approximately 73 mrem/h based on the curie loading.

The number of drums for filling overpacks is based on the waste loading produced in the laboratory that assumed a 50 volume percent increase in water based on the settled sludge weight for sludge-retrieval purposes. It is probable that the waste loading could be increased by using less water to retrieve the sludge and modifying the grout formulation slightly. This form would be recommended over grouting the entire drum.

Table 5.5. Comparison of Grouted Waste Form Within Pipe Overpack Container Packaged Within 55-Gallon Drum with Treated-Waste Constraints (37 vol% settled sludge loading)

Constraint			Value for TBD alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	SPO within a 55-gallon drum
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four direct loaded 55-gallon drums, or containing one bin • TDOPs, either containing up to 10 directly loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC	
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC	500 lb (includes 332 lb for pipe component and drum)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; waste material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and pipe component. For suboptions using billet cans, the can will be cross-taped and placed in vented (filtered) bags.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from the waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 in.) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E)
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC	
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.012 W/drum (Based on KE NLOP Safety Basis Composition)[a]
Fissile Content	The fissile and fissionable-material content of a package is limited dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	4.2 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 g for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	4.2 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	900 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	Information related to this item will be provided in 2/2/04 report.
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	150 mrem/h (Based on modeling.)

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, a determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32°F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.012 W/drum (Based on KE NLOP Safety Basis Composition)[(a)] [Appendix E discusses hydrogen generation from chemical reactions.]

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a one-year period.	TRAMPAC	

(a) A.J. Schmidt and R.B. Baker. "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Slaughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.

TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.

WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

5.2.2.2 Ease of Rework

A grouted overpack would have about the same difficulty of rework as a grouted drum. Ease of rework would be improved if billet cans were used, but grout removal from the billet cans would still be difficult. It should be noted that if there were a hot spot from improperly mixed grout or unusually high concentration of Cs in the sludge, the inner packages could be unloaded, but rearrangement would not likely provide any benefit.

5.2.2.3 Schedule Viability

The additional number of containers relative to Nochar options increases the risk to the solidification schedule, although the schedule viability is not significantly affected by any of the packaging alternatives.

5.2.2.4 Cost

Grout materials are inexpensive, and the equipment needed to produce the waste would not add significantly to the overall cost. The grout required would be less, but the number of containers required would be higher than for filling grouted drums unless the waste loading was increased. Therefore, the cost is higher for this alternative than for filling 55-gallon drums.

5.3 Polymer Sorbent Solidification Waste Form Within 55-Gallon Drum

5.3.1 Description of Alternative

This waste form consists of a WIPP-certified drum and liner completely filled with sludge and Nochar adsorbent. The formulation used in the table has a much lower waste loading than the one used in the laboratory because of high dose rates. The maximum loading could only be used if additional shielding from a billet can or internal aggregate were used. The laboratory formulation used settled sludge combined with an additional 50-volume percent water, and no additional dewatering steps. The actual batch would have additional water added to create a 23% waste loading that complies with the dose-rates requirements. The sludge and additives would be added directly to the container, mixed, and allowed to solidify.

A comparison of this alternative with the constraints presented in Section 2.0 is provided in Table 5.6. As the table shows, this alternative complies with all of the constraints for which information is currently available. The sludge concentration in the waste container could be increased to match the laboratory formulation by adding aggregate to the Nochar mixture to increase the density or utilize a thickwalled billet canister.

5.3.2 Evaluation with Respect to Evaluation Criteria

5.3.2.1 Number of Packages Produced

The waste loading per 55-gallon drum is limited by dose rate. The estimated number of packages for a polymer sorbent waste form in a 55-gallon drum is much higher than for a 55-gallon grouted drum since

Table 5.6. Comparison of Polymer Sorbent Solidified Waste Form Within 55-Gallon Drum with Treated-Waste Constraints (5 vol% settled-sludge loading)

Constraint			Value for TBD alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	55-gallon drum with rigid liner and liner lid.
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: Container Weights • 547 pounds per SPO with 12-inch diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum	TRAMPAC	470 lb (includes 77 lbs for drum and liner)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and liner.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly-generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 in.) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate settled sludge contains << 1% U metal (Appendix E).
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.0068 W/drum (Based on KE NLOP Safety Basis Composition)[a]
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGE). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	2.3 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	2.3 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	230 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	Information related to this item will be provided in 2/2/04 report.
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	190 mrem/h (Based on modeling).

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.0068 W/drum (Based on KE NLOP Safety Basis Composition)[(a)] (Appendix E discusses hydrogen generation from chemical reactions.)

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible).	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a one-year period.	TRAMPAC	
(a) A.J. Schmidt and R.B. Baker. "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Slaughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.			

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.

TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.

WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

the lower density of the Nochar provides less shielding and so can accommodate less sludge while achieving the specified surface dose rate. The number of packages is estimated to be 630 drums with a dose rate less than 160 mrem/h.

5.3.2.2 Ease of Rework

A polymer sorbent waste form could be reworked much more easily than a grouted waste form if the material required retrieval from the primary container.

5.3.2.3 Schedule Viability

The additional number of containers over the overpack option increases the risk to the solidification schedule, although the schedule viability is not significantly affected by any of the packaging alternatives except the S200-B.

5.3.2.4 Cost

The Polymer waste form increases cost because of the additional number of containers.

5.4 Polymer Sorbent Solidification Waste Form in Standard Pipe Overpack Packaged in 55-Gallon Drum

5.4.1 Description of Alternative

This waste form consists of a WIPP-certified overpack completely filled with Nochar adsorbent, or inner billet containers would be filled, bagged, and placed within the overpack container and the accompanying drum. The billet cans would be sized to allow two in an SPO. The formulation used was the same as the one demonstrated in the laboratory, consisting of Nochar, water, and settled sludge. The settled sludge was assumed to be combined with additional water to maintain the dose-rate criteria.. The sludge and additives would be added directly to the overpack or billet cans, mixed, and allowed to solidify.

A comparison of this alternative with the constraints presented in Section 2.0 is provided in Table 5.7. As the table shows, this alternative complies with all of the constraints for which information is currently available.

5.4.2 Evaluation with Respect to Evaluation Criteria

5.4.2.1 Number of Packages Produced

The number of packages is limited by dose rate for the SPOs in a 55-gallon drum, based on a waste loading of 29%, which is lower than achieved in the laboratory. Additional water would be used to dilute the mixture from the minimal amount assumed for retrieval. The estimated number of packages for a polymer sorbent waste form in an overpack is 630 with a waste loading of 29% and a dose rate of 160 mrem/h. This alternative produces a higher lowest number of waste packages, except for Nochar in a 55-gallon drum as discussed in Section 5.5.

Table 5.7. Comparison of Polymer Sorbent Solidified Waste Form Within Pipe Overpack Container Packaged Within 55-Gallon Drum with Treated-Waste Constraints (23 vol% settled-sludge loading)

Constraint			Value for TBD alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	SPO within a 55-gallon drum.
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four direct loaded 55-gallon drums, or containing one bin. • TDOPs, either containing up to ten direct loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC	
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC	420 lb (includes 332 lb for pipe component and drum)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and pipe component (and bags if billet cans are used).
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly-generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 1 inch or 2.5 cm in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E).
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC	
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.0076 W/drum (Based on KE NLOP Safety Basis Composition)[(a)]
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	2.6 g FGE/drum (Based on KE NLOP Safety Basis Composition)[(a)]

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	1,100 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	Information related to this item will be provided in 2/2/04 report.
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	160 mrem/h (Based on modeling.)

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, a determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.0076 W/drum (Based on KE NLOP Safety Basis Composition)[a] (Appendix E discusses hydrogen generation from chemical reactions.)

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC	Information related to this item will be provided in 3/31/04 report.
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC	Information related to this item will be provided in 3/31/04 report.

(a) A.J. Schmidt and R.B. Baker. "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Slaughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.

TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.

WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

Using two billet cans inside the overpack would likely decrease the number of drums if the billet cans provide some significant shielding. In this analysis, the shielding affect of the billet cans was not included.

An increase in waste loading may be possible after production is underway and dose-rate projections are verified, which would reduce the number of drums produced.

5.4.2.2 Ease of Rework

A polymer sorbent waste form could be reworked much more easily than a grouted waste form if the material required retrieval from the primary container.

5.4.2.3 Schedule Viability

With the exception of dewatered sludge packaged in S200-B SPOs, this option produces the fewest containers and is the simplest process to implement. Dose-rate variations from inadequate mixing are the largest process risk that could affect schedule.

5.4.2.4 Cost

Unless the waste loading could be increased, the cost for this alternative is greater than for grouted containers because of the additional number of drums produced. Polymer materials are also more expensive than grout additives per container, even though less material is used. Material costs are not significant in the overall cost.

5.5 Dewatered Sludge in S200B shielded Pipe Overpack Container Packaged Within 55-Gallon Drum

This waste form consists of a WIPP-certified drum, liner, and S200-B SPO. The S200-B package would be completely filled with dewatered sludge with some small amount of Nochar used as void space filler. The concentration formulated for the dewatered sludge was based on laboratory demonstrations that decreased the total volume by a factor of 2 for a unit volume of settled sludge.

The dewatering would take place in the S200-B container that would be filled to approximately 85% of the maximum volume. The total weight of the dewatered sludge per container would be near the payload weight allowable for the S200-B package (50 lbs).

A comparison of this alternative with the constraints presented in Section 2.0 is provided in Table 5.8. As the table shows, this alternative complies with all of the constraints for which information is currently available.

Table 5.8. Comparison of Dewatered Sludge in S200-B Shielded Pipe Overpack Container Packaged Within 55-Gallon Drum with Treated-Waste Constraints (200 vol% settled sludge loading)

Constraint			Value for TBD alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	S200-B shielded pipe overpack container within 55-gallon drum.
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four direct loaded 55-gallon drums, or containing one bin. • TDOPs, either containing up to ten direct loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC	
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-inch diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC	530 lb (includes 497 lb for pipe components, shielding, dunnage, and drum)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and shield assembly.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 in.) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E).
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC	
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.017 W/drum (Based on KE NLOP Safety Basis Composition)[(a)]
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGE). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	5.7 g FGE/drum (Based on KE NLOP Safety Basis Composition)[(a)]

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	5.7 g FGE/drum (Based on KE NLOP Safety Basis Composition)[(a)]
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	S200 pipe overpack payloads shall meet the package specific curie limits in the TRAMPAC (see Appendices 2.3 and 2.4, respectively).	TRAMPAC	Information related to this item will be provided in 2/2/04 report.
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	6,200 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤ 80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq 1{,}800$ ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤ 80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	Information related to this item will be provided in 2/2/04 report.

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 cm (1 ft) from the waste package.	HNF-EP-0063	Information related to this item will be provided in 2/2/04 report.
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	55 mrem/h (Based on modeling.)
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32°F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.017 W/drum (Based on KE NLOP Safety Basis Composition)[a] (Appendix E discusses hydrogen generation from chemical reactions.)

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible).	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC	
(a) A.J. Schmidt and R.B. Baker. “Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit,” PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Slaughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.			

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.
TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.
WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

5.5.1 Evaluation with Respect to Evaluation Criteria

5.5.1.1 Number of Packages Produced

The estimated number of packages for dewatered sludge in a S200-B package is limited by the volume of the container and the dewatering ability of the process. Assuming the container can be filled to ~80% of its maximum volume of about 14 L, approximately 22 L of dewatered sludge could be placed inside the S200-B. Based on this volume, 286 WIPP packages would be produced. No other WIPP limits are approached except for the weight limit on the S200-B package, which could cause a 10% increase in the number of drums to meet the weight limits. The small amount of material in the container and the significant internal shielding allows the dose rate to be less than 55 mrem/h. Polymer absorbent could be added to the top head space to ensure that no free water exists, but no increase in the amount of sludge per container could be made.

5.5.1.2 Ease of Rework

Dewatered sludge would be the relatively easy to rework because there are no hard immobile or organic chemicals in the package; however, the material would be dispersible, and the contact dose rate of the material would be very high and would probably require a shielded location.

5.5.1.3 Schedule Viability

The dewatering process is not thoroughly developed, which provides the greatest risk to the schedule viability. Also, it is unlikely that the S200-B SPOs could be procured on a schedule that is consistent with the project schedule, particularly the requirement that Fluor receive the first 30 packages by March 1, 2004.

5.5.1.4 Cost

The dewatering process in an S200-B would be expensive since the process is more difficult to implement than the other processes, and the waste package is expected to cost more per package, although the number of waste packages is lower than the other options. Waste package cost alone would be less expensive then the other options because there would be significantly fewer drums.

6.0 Conclusions and Recommendations

6.1 Conclusions

6.1.1 Waste Form

Three waste forms for treated KE NLOP sludge were considered in this study:

- grout
- Nochar
- dewatered sludge.

Based on the results of this study, all three of these waste forms could be used to produce CH-TRU that would meet the constraints identified in Section 3 of this report. However, it would be more difficult to ensure that the free-water restriction would be met with dewatered sludge than with either grout or Nochar.

From a processing standpoint, either of the solidification options (grout or Nochar) would be simpler than dewatering. Also, treating of the sludge with Nochar would be somewhat simpler than using grout because only one additive to the sludge would be required (Nochar) compared to grout (Portland cement and bentonite clay); and compared to grout, Nochar would be able to accommodate a larger range of solidification agent/water/sludge ratios, which would enhance the robustness of the process except for the dose-rate limits.

6.1.2 Waste-Package Configuration

Four waste-package configurations were considered in this study:

- direct loading of the treated waste in 55-gallon drums
- direct loading of the treated waste in SPOs
- loading of the treated waste in billet cans that would be placed in vented plastic bags and then loaded in SPOs
- direct loading of the treated sludge in S200-B SPO.

All four of these waste-package configurations could be used to produce CH-TRU that would meet the constraints identified in Section 3 of this report. However, due to the dose rate associated with the dewatered sludge, the use of the S200-B would be required for this waste form. Conversely, the shielding provided by the S200-B would not be required for grout and Nochar, and the limited volume of this package would drive up the number of packages produced. For grout and Nochar, the use of drums or SPOs (either direct loaded or using billet cans) could be considered.

It should be noted that S200-B SPOs are not frequently used, and the lead-time associated with procurement of these packages would likely prevent the May 1 deadline for production of the first 30 packages to be met.

6.1.3 Number of Waste Packages

For the dewatered sludge loaded into S200-B Shielded Pipe Overpacks, the number of waste packages was driven by the waste package and sludge volumes. For all other options, the requirement that the surface dose rate be ≤200 mrem/h drove the estimated number of packages to be produced. All other requirements that are impacted by sludge characteristics, such as the package limitations on FGE and decay heat, will be met if the surface dose-rate limitation is achieved.

It is estimated that the fewest number of packages (approximately 286) would be produced if dewatered sludge were packaged in S200-B Shielded Pipe Overpacks. The next fewest number of packages (approximately 396) would be produced using grout as the waste form and packaging the treated waste in SPOs directly.

6.2 Recommendations

It is recommended that the KE NLOP sludge be treated using Nochar and that the treated waste be packaged in billet cans that would be placed in vented plastic bags and then loaded in SPOs. This recommendation is based on a number of considerations that are summarized below:

- Treatment of the sludge with Nochar would result in a robust process that is not sensitive to variations in processing conditions.

- The use of billet cans would facilitate rework and/or repackaging of the treated sludge by Fluor in the unlikely event that this becomes necessary; the use of Nochar would facilitate rework of the waste form itself.

- The use of billet cans and the low density of the Nochar waste form will facilitate that assay process that Fluor will complete as part of WIPP certification.

- Nochar has already been accepted for use by WIPP (its use is identified in TRUPACT-II Content Code RF-127 ("the waste form is produced by combining the inorganic aqueous liquid/sludge waste material with a polymer-based solidification agent [e.g., Nochar Acid bond, Water Works Crystals, etc.]…").

- The Nochar, SPO, billet cans, and vented plastic bags are commercially available and could be procured in time to support the project schedule.

It should be noted that the above recommendation is not sensitive to the assumptions that are made about the radiochemical composition of the sludge. The estimated numbers of packages that were determined as part of this study were based on data from characterization of the core samples that were received from Fluor to support this study. If other assumptions regarding source term had been used to estimate the numbers of packages to be produced for each option (e.g., use of Safety Basis values), the package count estimates would likely be different. However, the relative numbers of packages for one option compared to another option would not be expected to change substantially.

It should also be noted that implementation of this recommendation will require approval from the Environmental Protection Agency (EPA) for solidification of wet sludge (this issue is being addressed as part of the *Time Critical CERCLA Regulatory Action* that Fluor is preparing for submission to EPA). It is anticipated that resolution of this issue will be reached by March 1, 2004.

Finally, additional information about the characteristics of the treated waste, such as values for DE-Ci and PE-Ci, are provided in Parts 2 and 3. These additional results do not impact the recommendations provided in this report.

7.0 References

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Appendix A

Sample Collection

Appendix A

Sample Collection Sample Collection from the Sludge in the KE Basin North Loadout Pit

RB Baker and JA Serles

A.1 Sampling Objectives

Sampling of the sludge in the KE NLOP was performed consistent with the controlling Test Plan (C.H. Delegard, "Bench Scale Test Plan to Demonstrate Productivity of WIPP-Acceptable KE NLOP Sludge Waste Forms at the 325 Building." Pacific Northwest National Laboratory, Richland, WA, December 23, 2003). The objective of this sampling campaign was to draw an axial core sample from the sludge in the KE NLOP main pit to recover between 1 and 1.5 L of representative as-settled sludge for disposal process development. The sample was to be taken at the most efficient and accessible position in the main pit area—this position was concluded to be adjacent to the location sampled in the main pit during the 1999 sampling campaign (Baker et al. 1998); this is also the area expected to have one of the deepest accumulations of sludge in the KE NLOP. The sample material was to be delivered to the 325 Building Laboratory by December 24, 2003.

A.2 Acquiring Sludge Core Sample

A.2.1 General Overview

The representative sludge-sample material was drawn using equipment and techniques successfully used in past characterization sampling performed on the KE Basin sludges in 1995 and 1999 (Baker et al. 1998; Baker 1998; Makenas and Baker 1998). As noted in the Sampling and Analysis Plan for the 1999 campaign (Baker et al. 1998), it was expected that there was a minimal difference in sludge composition laterally across the pit and transfer channel because the layers of backwash water and suspended materials would deposit relatively proportionally across the pit; however, it was very likely there was a large difference in sludge composition axially down through the sludge accumulation (e.g., different activities in the basin over the years of operation would result in different material in layers, different settling behavior of the backflushed material [e.g., filter sand, fuel corrosion products] would result in substructure within the layers, and different operations in the pit [e.g., sparging] would influence the bulk layers). These expectations are supported by the overall results from sludge sampling in the pit performed in 1993 (Warner 1994—showing a general consistency laterally across the pit and transfer channel) and 1999 (Pitner 1999—showing a significant difference in material from the top to the floor as indicated by activity of sample bottles).

For the current campaign, a 2-in.-diameter axial (i.e., top surface to floor) core of sludge was taken and shipped in multiple 4-L bottles to the laboratory. These bottles contained varying amounts of sludge solids (all bottles were adjusted after sampling was complete by decanting so when shipped they had 2 L of head space. Six primary sample bottles were required for the core. Combining material from all the bottles provides a sludge sample representative of the average axial material. Because of the way the sampling equipment functions, sequential pairs of primary sample bottles can also, if their solids are analyzed separately, provide insight into the axial layers of material encountered in the core, working down toward the floor.

A.2.2 Sampling Equipment

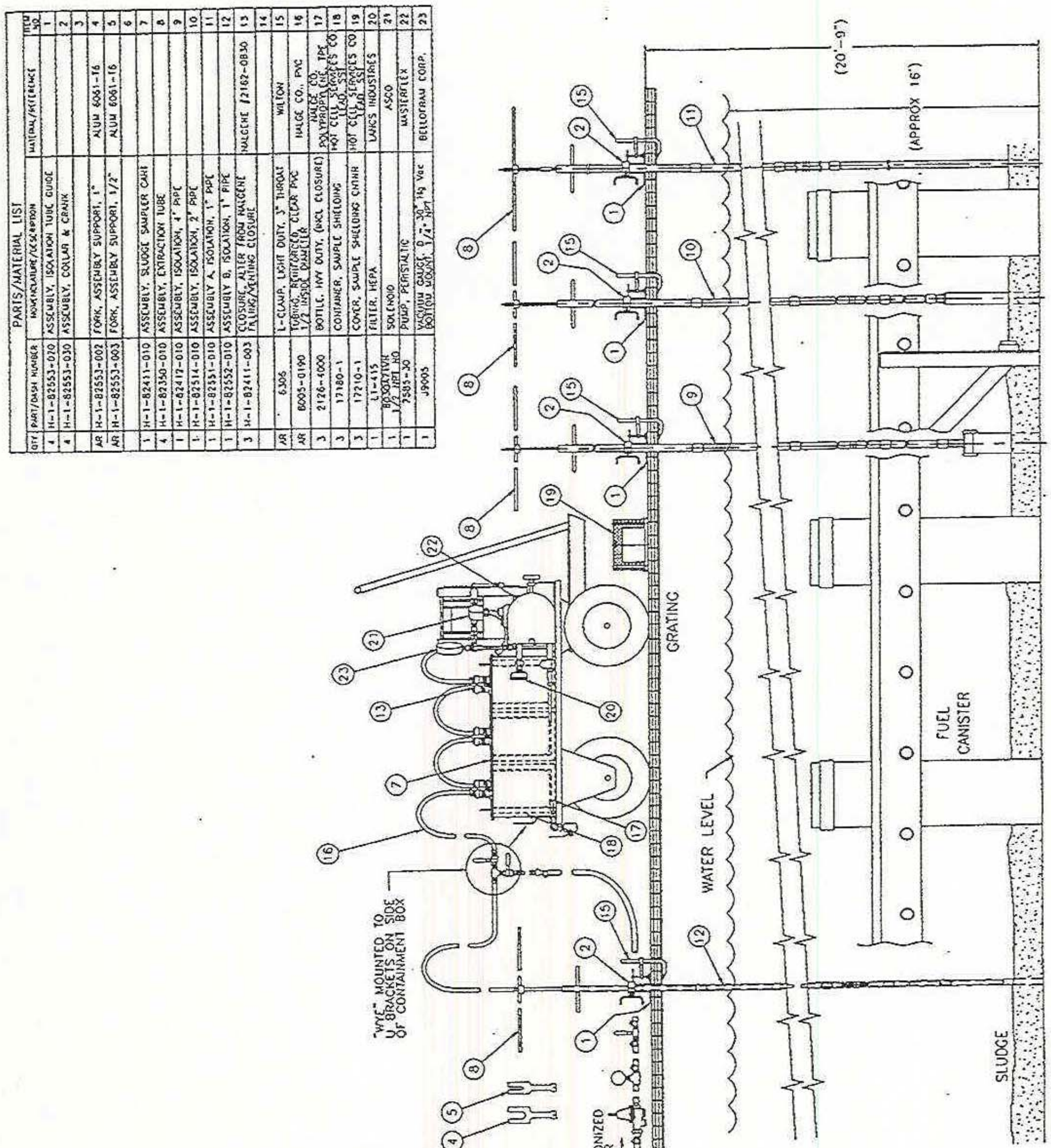
The sampling equipment used (Figure A.1 and A.2) is described in detail in the System Design Description (Baker 1998). The application of this equipment was similar to the 1999 sampling campaign (Pitner 1999) with one exception: there was a requirement that for shipping in the PAS-1 Cask, a 2-L head space must be provided in each shipped bottle—this required transferring (decanting) approximately 2 L of carrier water from each full primary sample bottle to another bottle before shipment. Any time the carrier water was decanted, accommodation was made either to not lose significant fine suspended solids (e.g., wait for the fine material to settle from the carrier water), or the decant water bottle was inspected, and if significant solids were observed, the decant bottle was also shipped to the laboratory to be combined with the other solids. The suspended solids are likely to include fuel-rich material in this case because of the source of the NLOP sludge (i.e., basin skimmer system).

A.2.3 Acquiring the Sample

Isolating the Sludge Core. A 2-in.-diameter isolation tube was inserted into the sludge. At the time of sampling, the KE NLOP had a plywood cover at the deck level for Basin operational safety reasons. The isolation tube was placed through the same slot in this plywood as was used in the 1999 campaign (Pitner 1999). (Since the isolation tube from the 1999 campaign had not been removed, a visual reference was provided to ensure that the December 2003 sample was collected from an undisturbed location.) This location is near the middle of the east side of the main pit where the transfer channel entrance is located. Using the scale marks on the isolation tube, the depth of sludge in this position was ultimately found to be 36.5 inches, similar to what was found in 1999, approximately 37.5 inches. As in the past campaign, as the isolation tube was inserted in the bulk sludge, it was noted that there was significant physical resistance encountered at 13 inches and 10 inches from the floor, indicating that the sludge may have a crusty or hardened nature in this area. With final placement, it was believed that the isolation tube was successfully firmly seated on the pit floor (i.e., the isolation tube has a beveled lower edge to help seat onto the floor surface).

Pulling the Core Sample. With the isolation tube in-place (and with the sampling equipment and basin prepared), the Sampling Team (composed of Duratek, K Basin, and PNNL staff) pulled the core sample over a 2-day period, ultimately working the sampling system extraction tube down the isolation tube from above the sludge surface to the basin floor. It required three pairs of primary sample bottles to pull all the sludge solids. Table A.1 provides a summary of these bottles. The first two pairs were pulled December 13, 2003, and the last pair was pulled December 19, 2003. The period between sampling activities allowed for shipment of a portion of the sample bottles, so needed shielded containers were available for the remaining two primary bottles. The Sampling Team noted that there was some resistance felt on the

Figure 6. Schematic of Floor Sludge Sampler.



PARTS/MATERIAL LIST				
QTY	PART/DASH NUMBER	NOMENCLATURE/DESCRIPTION	MATERIAL/REFERENCE	ITEM NO
4	H-1-82553-020	ASSEMBLY, ISOLATION TUBE GUIDE		1
4	H-1-82553-030	ASSEMBLY, COLLAR & CRANK		2
				3
AR	H-1-82553-002	FORK, ASSEMBLY SUPPORT, 1"	ALUM 6061-T6	4
AR	H-1-82553-003	FORK, ASSEMBLY SUPPORT, 1/2"	ALUM 6061-T6	5
				6
1	H-1-82411-010	ASSEMBLY, SLUDGE SAMPLER CART		7
4	H-1-82350-010	ASSEMBLY, EXTRACTION TUBE		8
1	H-1-82412-010	ASSEMBLY, ISOLATION, 4" PIPE		9
1	H-1-82514-010	ASSEMBLY, ISOLATION, 2" PIPE		10
1	H-1-82551-010	ASSEMBLY A, ISOLATION, 1" PIPE		11
1	H-1-82552-010	ASSEMBLY B, ISOLATION, 1" PIPE		12
3	H-1-82411-003	CLOSURE, ALTER FROM NALGENE FILLING/VENTING CLOSURE	NALGENE #2162-0830	13
				14
AR	6306	L-CLAMP, LIGHT DUTY, 3" THROAT	WILTON	15
AR	6005-0190	TUBING, REINFORCED, CLEAR PVC 1/2 INSIDE DIAMETER	NALGE CO., PVC	16
3	2126-4000	BOTTLE, HVY DUTY, (INCL CLOSURE)	NALGE CO. POLYPROPYLENE, TPE	17
3	17180-1	CONTAINER, SAMPLE SHIELDING	HOT CELL SERVICES CO LEAD, SST	18
3	17210-1	COVER, SAMPLE SHIELDING CNTNR	HOT CELL SERVICES CO LEAD, SST	19
1	L1-415	FILTER, HEPA	LANCS INDUSTRIES	20
1	8030A71VH 1/2 NPT NO	SOLENOID	ASCO	21
1	7585-30	PUMP, PERISTALTIC	MASTERFLEX	22
1	J9005	VACUUM GAUGE, 0 - 30" Hg Vac BOTTOM MOUNT, 1/4" NPT	BELLOFRAM CORP.	23

30

Figure A.1. Overview of Sampling Equipment

Figure A.2. Sampling Cart with Sample Bottles In-Place in Shielded Containers

extraction tube that caused the sampling to go slower through the lower portion of the core sample (where the resistance had been encountered during insertion of the isolation tube).

A.3 Decanting and Shipping Samples

After each pair of primary bottles was filled with carrier water and sludge solids, the bottles were prepared for shipment to the laboratory using the PAS-1 Cask. As noted previously, part of this preparation was the need to decant each primary bottle, providing the required 2-L head space. In each case, the carrier water was decanted from the primary bottle to a similar 4-L "decant" bottle, numbered and handled with similar rigor as the primary bottles. Table A.1 indicates the resulting decant bottles.

Before shipment, each primary and decant bottle was inspected (the polypropylene bottles are semi-transparent) to estimate the level of solids present and to measure for dose rate, Figure A.3. For each decant bottle, a decision was made (as per the Test Plan) if the bottle should be shipped to the laboratory (did the bottle contain significant solids) or discarded (if the bottle contained essentially only carrier water). For the first pair of primary bottles, decanting was done relatively soon (within 20 minutes) after the samples were pulled, which did not allow much time for the fine suspended solids to settle, it was judged that these bottles should be shipped to the laboratory since they appeared to contain solids of

Table A.1. Summary of Primary and Decant Bottles Resulting from Sampling KE NLOP December 2004

Sample Bottle Designation	Date Taken	Minimum Observed Volume of Solids[(a)], mL	Maximum Measured Dose, mr/h on contact (window open measurement includes beta/gamma contribution)	Date Shipped to Lab or Discarded	Comment[(b)]
KE-20-A	Dec 13, 2003	1300	80	Dec 17, 2003	From top ~12" of core sample
KE-20-B	Dec 13, 2003	500	35	Dec 17, 2003	From top ~12" of core sample
KE-20-D	Dec 13, 2003	750	32	Dec 19, 2003	From middle ~12" of core sample
KE-20-E	Dec 13, 2003	200	20	Dec 19, 2003	From middle ~12" of core sample
KE-20–G	Dec 19, 2003	500	220	Dec 21, 2003	From bottom ~12" of core sample
KE-20-H	Dec 19, 2003	250	120	Dec 21, 2003	From bottom ~12" of core sample
KE-20-AD	Dec 13, 2003	200	8	Dec 23, 2003	Two liter decant from KE-20-A
KE-20-BD	Dec 13, 2003	< 50	8	Dec 23, 2003	Two liter decant from KE-20-B
KE-20-DD	Dec 13, 2003	Trace	6	Discarded on 1/14/04	Two liter decant from KE-20-D
KE-20-ED	Dec 13, 2003	Trace	6	Discarded on 1/14/04	Two liter decant from KE-20-E
KE-20-GD	Dec 19, 2003	Trace	7	Discarded on 1/14/04	Two liter decant from KE-20-G
KE-20-HD	Dec 19, 2003	Trace	8	Discarded on 1/14/04	Two liter decant from KE-20-H

(a) Estimates made during observations at K Basins, solids not necessarily fully settled.

(b) The top of the sample extraction tube was clamped 50" above the top of the isolation tube [the lower tip of the extraction tube calculated to be bout 42 1/4" above the floor—sludge depth was ultimately found to be at 36-1/2" at this location]. After collecting samples KE-20-A and KE-20-B, the top of the extraction tube to isolation tube was 32" [the lower tip of the extraction tube calculated to be 24 ¼" from the floor]. After collecting samples KE-20-D and KE-20-E, the new separation was 20" [the lower tip of the extraction tube about 12.25" above the floor]. On December 19, 2003, the sludge depth (which was readily discernible) was observed to be 36 1/2" on the isolation tube scale. After samples KE-20-G and KE-20-H were collected, the final distance between the top of the extraction tube and the top of the isolation tube was 7 ¾". At this point the extraction tube nozzle was resting on the pit floor.

Figure A.3. Decanted Primary Sample Bottle

interest. The decant bottles from the remaining two pairs of primary bottles were inspected and did not contain significant solids to justify additional shipments to the laboratory, but were returned to the basin pool.

Once the sample bottles were decanted and the shipping lids installed, the bottles were placed in a controlled holding area and ultimately placed in special shielded shipping containers. These shielded shipping containers were subsequently loaded in the PAS-1 Cask and shipped two at a time to the 325 Building Laboratory for recovery, consolidation, and analyses.

A.4 Summary Observations

The following are the summary observations from the sampling activity:

- Insertion of the isolation tube into the sludge indicated that there was some physical resistance encountered in the bulk sludge accumulation of the KE NLOP in the region at 13 inches and 10 inches off the floor. This had been generally noted before as a region of crusty sludge material.

- The depth of sludge in the sampled location was measured on the isolation tube scale as 36.5 inches (compared with values in this general area of 37.5 inches measured in 1999 and 33 inches implied from measurements in 1993). The sludge in the KE NLOP required significant time (days) to settle sufficiently to allow measurement of the depth of the sludge surface using the isolation-tube depth scale on the underwater video—initial estimates were on the order of about 40 inches because of a cloudy suspended layer of sludge near the surface.

- Table A.1 provides the observations from the primary and decant sample bottles.

- One day after collecting the initial pairs of primary sample bottles, the apparent volume of the solids layer had consolidated to roughly 50% of the apparent volume on the day of sampling. This consolidation resulted in significant increases to the dose rates measured on contact from the bottom of the bottles. (This observed behavior may in-part explain the lower dose and larger volume of solids noted initially for the 1999 samples from the KE NLOP [Pitner 1999] compared to the volume that was ultimately recovered from the sample bottles in the laboratory.)

- The Sampling Team did an excellent job—successfully obtaining and shipping the sample material as required by the Test Plan, meeting all requirements and safely completing the activity under an extremely short schedule on December 23, 2003.

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Appendix B

Sample Receipt, Inspection, and Compositing

Appendix B

Sample Receipt, Inspection, and Compositing

Sample Receipt

Eight sludge samples were received from the KE Basin in late December 2003. The samples were obtained, pair-wise, from the KE North Load Out Pit (NLOP) in the order KE-20-A and KE-20-B (collected from the top of the NLOP solids layer), KE-20-D and KE-20-E (from the middle of the NLOP solids layer), KE-20-G and KE-20-H (from the bottom), and KE-20-AD and KE-20-BD (which were decantates from KE-20-A and KE-20-B containing appreciable quantities of flocculent solids).

Each 4-L-thick walled sampling bottle originally contained 4-L total volume but had been gravity settled, and the supernatant solution decanted at the KE Basin to a 2-L level were pre-marked on each bottle. The respective decantates collected in similar 4-L bottles were labeled the same as the source bottle but with the addition of the letter D at the end of the sample number (e.g., the decantate from KE-20-A was designated KE-20-AD). Because the decantates from KE-20-D, KE-20-E, KE-20-G, and KE-20-H contained little solid, they were not shipped from the KE Basin to the 325 Laboratory and instead were returned to the KE NLOP waters. Refer to Appendix A for more details on the sampling of the KE NLOP sludge.

The sample receipt dates and estimated settled sludge volumes in each container are shown in Table B.1. As seen in Table B.1, settled sludge comprised no more than 15 volume percent of any sample and, over all eight samples, was only about 9 volume percent of the total received volume.

Table B.1. Sludge Sample Receipt and Compositing

Sample Number	Receipt Date	Side Dose Rate, mrem/h, at Contact / 30 cm[(a)]	Sludge Volume Est., mL	Sample Bottle Weight, g			Sludge Composite	
				Gross	Empty	Net	Weight, g	Volume, mL
KE-20-A	17 Dec 03	80 / 8	250	2767.53	742.71	2024.82	592.93	570
KE-20-B	17 Dec 03	38 / 4.4	200	2753.96	837.69	1916.27		
KE-20-D	19 Dec 03	31 / 3.7	250	2812.54	837.25	1975.29	294.50	355
KE-20-E	19 Dec 03	14 / 1.6	100	2796.02	718.03	2077.99		
KE-20-G	21 Dec 03	110 / 9	300	3056.72	753.87	2302.85	986.30	675
KE-20-H	21 Dec 03	30 / 5	200	2823.27	727.21	2096.06		
KE-20-AD	23 Dec 03	8 / 1.7	100	2796.18	711.27	2084.91	290.16	250
KE-20-BD	23 Dec 03	1.8 [b] / 1.6[(b)]	10	2521.49	713.79	1807.70		
Total sludge composite							2163.89	1850
Decanted sludge composite (density = 1673.93 g/1350 mL = 1.24 g/mL)							1673.93	1350

(a) Window-closed CP readings.
(b) Similar due to background.

The eight sample containers were brought individually into the open-face hood adjacent to the glovebox in Room 528 of the 325 Laboratory. Each container was photographed (Figures B.1 through B.4). The presence of smearable external contamination on containers KE-20-E and KE-20-BD prevented the removal of their plastic bag coverings until their loading into the glovebox and thus prohibited unobstructed views of these two bottles themselves. While in the open-face hood, dose rates were measured from the side at the sludge/water interface. These dose rate data are given in Table B.1. Each as-received sample was closely inspected, but none showed evidence of gassing or bubble formation.

Sample Compositing

The eight sample containers then were loaded into the glovebox and weighed immediately. The composite sludge from the KE NLOP then was prepared. None of the containers showed pressurization (e.g., by gassing or bubbling) when the caps were removed.

To evaluate possible layering of sludge in the KE NLOP, the sludges from the paired samples first were combined according to how they were collected (i.e., KE-20-A and -B were collected, then KE-20-D and -E, KE-20-G and -H, and KE-20-AD and -BD). For example, to do this pair-wise collection for KE-20-A and KE-20-B, the supernatant solution from sample KE-20-A was decanted to the level of the settled solids and the decantate collected. The settled solids in KE-20-A then were slurried by swirling and transferred into the composite receiving container. The composite was collected in a 2-L polypropylene wide-mouth bottle. In a similar manner, the supernatant solution was decanted from KE-20-B and the KE-20-B settled solids slurried and transferred into the same composite container as used for the slurried solids from KE-20-A. The composite KE-20-A and KE-20-B slurried-solids volume and mass were measured and a ~5 mL subsample taken for analysis. The masses of the empty KE-20-A and -B containers then were measured, and the decantates recovered from samples KE-20-A and KE-20-B were combined in container KE-20-A.

The decantation, sludge slurry transfer, and subsampling steps were repeated for the remaining three sample pairs, and the decantates for the pairs were collected, respectively, in containers KE-20-D, KE-20-G, and KE-20-AD. The container gross, tare, and net contents weights, the volumes and masses of the sample pairs, and the overall composite sludge are shown in Table B.1. At this point, the total collected sludge volume was 1850 mL, and the total mass was 2163.89 g.

The composite sludge was allowed to settle overnight (Figure B.5). After overnight settling, 500 mL of clear supernatant solution was decanted to give a final settled sludge volume of 1350 mL (the top ~25 mL being clear) and a total mass of 1673.93 g. The settled-sludge density therefore was 1673.94 g/1350 mL or 1.24 g/mL. These and subsequent manipulations showed that about ⅓ of the settled-sludge volume was sand, and this sand fraction settled rapidly after agitation. The top ⅔ was a brown, easily suspended floc. The 2-L composite container was 115 mm in diameter and the sample depth about 128 mm when holding 1350 mL.

Samples were withdrawn from the well-mixed composite at this point to leave 1210 mL of sludge (i.e., 1350 mL – 1210 mL = 240 mL of settled sludge was withdrawn). The 1210 mL of settled sludge was left undisturbed for another 6 days and was observed to have settled further to show the interface of the settled solid to clear liquid at the 960-mL level (i.e., 1210 mL – 960 mL = 250 mL of clear supernate).

By extension, if the original 1325 mL of settled sludge observed after 1 day of settling had been allowed a further 6 days of settling, the settled sludge volume (assuming negligible additional sludge compression by the added sludge depth) would have been 1070 mL [1350 mL × (960 mL settled/1210 mL total)]. If the supernatant (density of 1.00 g/mL) had been discarded at this point, the remaining settled sludge would have had a bulk density of 1.30 g/mL.

However, to keep the same solid/liquid basis as the original sampling, the sludge and supernatant solution were re-agitated before all subsequent samplings for analysis or testing. The settling observations are summarized in Table B.2.

Table B.2. Settling of KE NLOP Composite Sludge

Time (days)	Total Volume, mL	Settled Sludge Volume, mL
0	1350	1325
6	1210	960
6[a]	1350	1070
(a) Assuming settling of entire sample had occurred.		

The 2-L composite container was 115 mm in diameter, with a 2.0-mm bottom thickness and a 1.5-mm wall thickness. The dose rates on the bottle at contact and at 30-cm distance were measured at the bottom and side of the bottle (centered on the settled sludge) through a 15-mil Hypalon glovebox glove. The bottle contained 1200 mL of settled sludge when the dose-rate measurements were made, the balance having been taken for analytical and gas-generation testing. The settled sludge was about 115 mm deep in the bottle. The dose rates are summarized in Table B.3.

Table B.3. Dose Rate of KE NLOP Sludge Composite

Position	Dose Rate, mrem/h	
	Contact	**30-cm**
Bottom	420	50
Side	350	36
Uncorrected "window-closed" CP readings.		

Figure B.1. Samples KE-20-A and KE-20-B

Figure B.2. Samples KE-20-D and KE-20-E

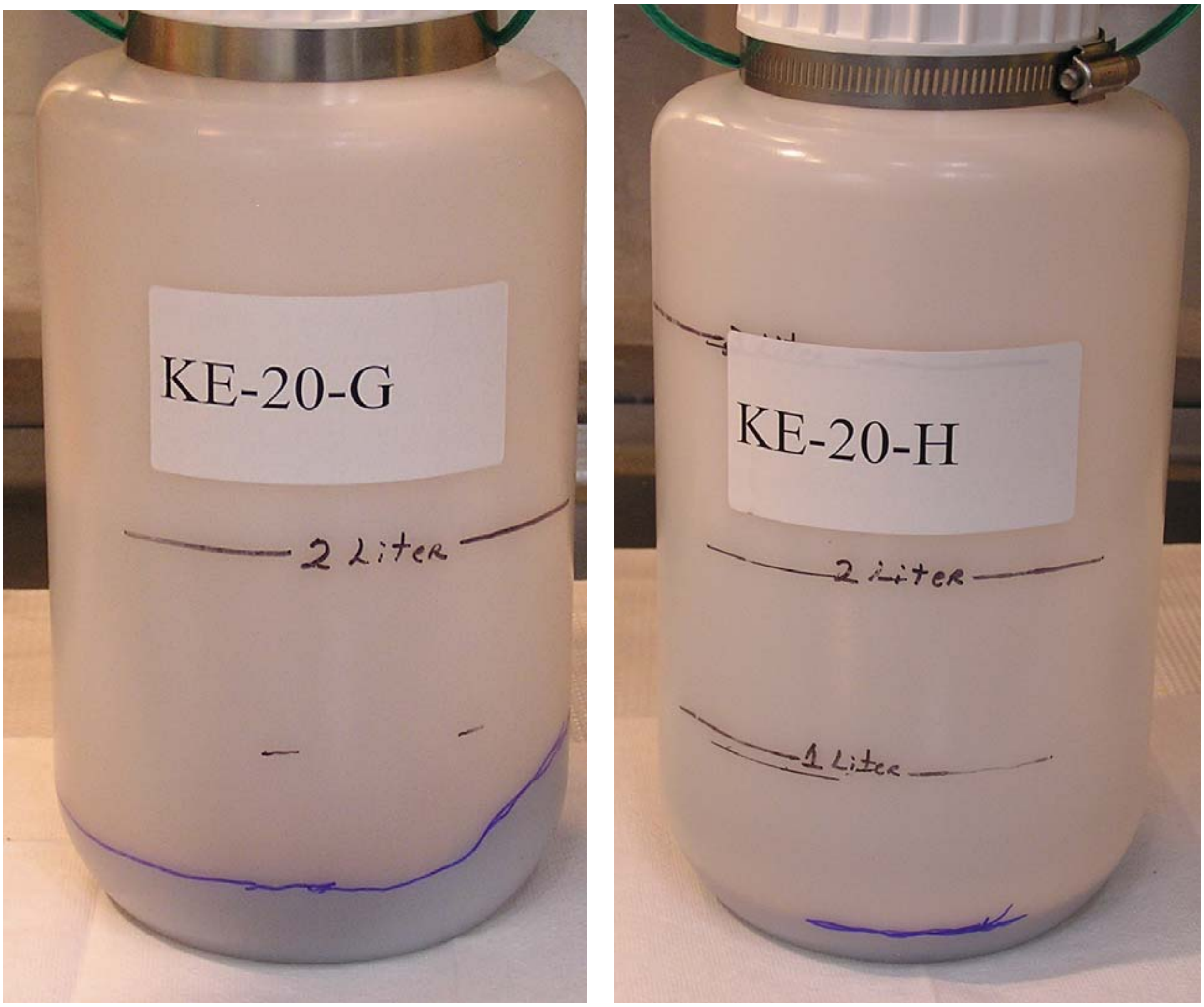

Figure B.3. Samples KE-20-G and KE-20-H

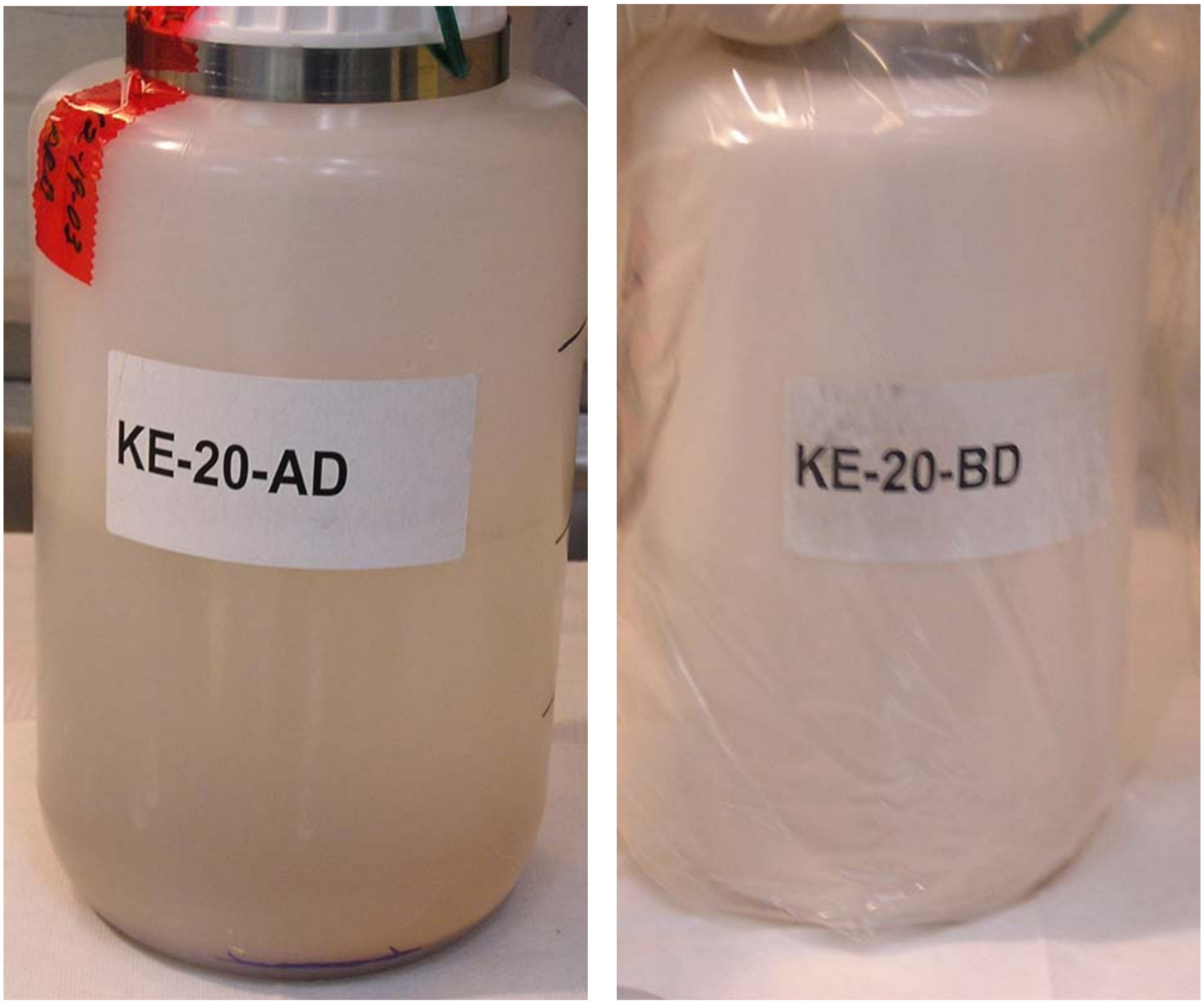

Figure B.4. Samples KE-20-AD and KE-20- BD

Figure B.5. KE NLOP Sludge After Overnight Settling.
Note solution level at red mark (1850 mL) and settled sludge at about 1325 mL.
Level marks in 100-mL increments with top marked level at 2000 mL.

Appendix C

Physical-Property Measurements

Appendix C

Physical-Property Measurements

Physical properties (density and settling rate) of the settled sludge were measured in the glovebox of Room 528 at the 325 Laboratory. This work was conducted under the Test Instruction 46857-TI02, "Preparation of KE NLOP Composites and Samples."

As noted in Appendix B, the density of the settled sludge was found to be 1.24 g/mL. The density was determined by weighing the collected settled sludge in the composite container. The collected composite sludge volume was estimated based on volume level marks drawn on the container. The level marks were made based on adding 100-mL increments of water to the container and marking the levels reached by each successive increment.

The composite sludge density was re-evaluated by weighing 10-mL increments of well-mixed sludge into a plastic 10-mL syringe. The end of the syringe was cut off, and the cut end was beveled to give a smooth edge. The 10-mL level was calibrated by adding 10.0 g of water (density of 1.00 g/mL) to the open-end-up syringe with the plunger withdrawn up the syringe barrel. The plunger was pushed upwards until the water level reached the open end, and the plunger position was marked. The syringe prepared this way functioned as a 10-mL graduated cylinder with the additional capability to discharge all of its contents for density re-measurements and for sampling for subsequent radiochemical analysis.

To make the density determinations, the syringe was tare-weighed, the plunger was withdrawn to the 10-mL mark, the open end was placed upwards, and, using a large transfer pipet, a sludge sample was withdrawn from the composite container while the sludge contents were being aggressively stirred. As seen in Table C.1, the results of the five determinations of the sludge density agree with the 1.24 g/mL sludge density estimated from the mass and volume of the entire collected composite. The variability of the five 10-mL basis density measurements is about 1.2%, relative.

Table C.1. Settled Sludge Density

Measurement	Density, g/mL
1	1.259
2	1.234
3	1.250
4	1.222
5	1.238
Average	1.241
Std. Dev. ($\pm 1\sigma$)	0.014

The settling rate of the dilute sludge also was measured. First, 50 mL of well-mixed composite sludge was added into a 250-mL graduated cylinder. Decant water from KE-20-A then was added to reach a

250-mL total volume. The sludge was mixed thoroughly with the decant water in the graduated cylinder, and then the cylinder was placed on the glovebox floor and the settling behavior assessed as a function of time.

The sand in the sludge settled rapidly (within a few seconds) to the bottom of the graduate. The flocculent brown solids settled more slowly, but even after 6 days had not settled back to the original settled sludge volume (Figure C.1).

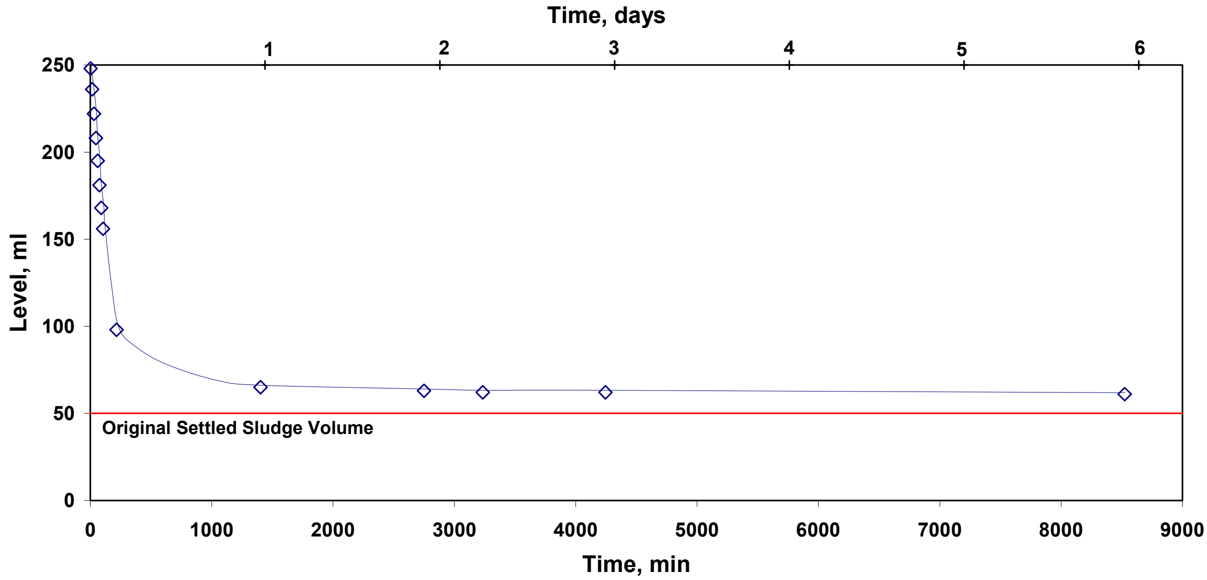

Figure C.1. Settling of Sludge/Supernatant Solution Mixture

Appendix D

Radiochemical Analyses and Data Tables

Appendix D

Radiochemical Analyses and Data Tables

Chemical and radiochemical analyses of the settled sludge and of the supernatant solution were measured in the glovebox of Room 528 and in the Analytical Services Operations (ASO) of the 325 Laboratory. The samplings for analysis and pH measurements were conducted under the Test Instruction 46857-TI02, “Preparation of KE NLOP Composites and Samples.” The sample-preparation digestions and subsequent chemical and radiochemical analyses were performed according to the general directions in the Test Plan (“Bench-Scale Test Plan to demonstrate production of WIPP-Acceptable KE NLOP Sludge Waste Forms at the 325 Building”) and under the specific procedures outlined in Table D.1.

Table D.1. Analytical Procedure Listing

Sample Prep.	Analyte	Procedure Title	Procedure Number
As rec’d.	pH	Test Instruction	TI 46857-TI02
As rec’d.; 2.0-mL aliquots	Density, ρ	Test Instruction	TI 46857-TI02
	GEA	Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)	RPG-CMC-450
As rec’d.; 15-g aliquots	H_2O	Water Determination by Weight Loss on Drying	PNL-ALO-504
Sample residue from H_2O analyses fused and dissolved in acid; Solubilization of Metals from Solids Using Pyrosulfate Fusion (Test Plan) and KOH-KNO_3 Fusion, PNL-ALO-115 Sample supernate, received only a dilution for applicable analyses.	GEA	Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)	RPG-CMC-450
	Pu	Pu and Am/Cm derived from the Alpha Energy Analysis (AEA) results.	RPG-CMC-422
	Am/Cm		
	^{90}Sr/Y	^{90}Sr/Y is inferred based on results of the GEA and Total Beta	N/A
	U by KPA	Uranium by Kinetic Phosphorescence Analysis	RPG-CMC-4014
	AT	Total Alpha and Beta Analysis	RPG-CMC-408
	AEA	Solutions Analysis: Alpha Spectrometry	RPG-CMC-422

<u>pH Measurements</u>

The pH measurements were performed using a Corning wand-type pH meter. The meter was calibrated using fresh buffer solutions, and the check measurements of pH 4.00, 7.00, and 10.00 buffers were within

0.04 pH units of the target value. The pH of the supernatant solutions from combined samples KE-20-A and -B (in Vessel KE-20-A), KE-20-D and -E (in Vessel KE-20-D), KE-20-G and -H (in KE-20-G), and KE-20-AD and -BD (in KE-20-AD) were measured. The pH of the composite KE NLOP sludge also was measured. The pH values, summarized in Table D.2, vary over about 0.8 pH units for the supernatant solutions. The relatively large pH span likely is because ion exchange purification of the supernatant waters removed all buffering ions. The settled sludge pH of 8.31 is similar to the pH 8.34 value observed for FE-3, a prior composite KE NLOP sludge (Table 1.3). In contrast with the unbuffered KE NLOP supernatant solution, the mineral solid-in-water KE NLOP sludge can maintain stable pH-buffered conditions by hydrogen ion (H^+) exchange on the hydrous solids' surfaces.

Table D.2. Solution and Settled Sludge pH

Sample	Measured pH
pH 4.00 buffer	4.03
pH 7.00 buffer	7.01
pH 10.00 buffer	10.04
KE-20-A	7.60
KE-20-D	7.16
KE-20-G	7.95
KE-20-AD	7.36
KE NLOP Sludge	8.31

<u>Sampling for Chemical and Radiochemical Analyses</u>

Four samples were retrieved for priority chemical and radiochemical analyses. Three of the samples were taken from the composited settled KE NLOP sludge, and one sample was supernatant solution taken from Vessel KE-20-A. In addition, duplicate sludge samples were taken from the KE-20-A and -B, -D and -E, -G, and -H, and -AD and -BD interim sludge composites (see Appendix B on the collection of the intermediate sludge layers). The sample sources, subsample names, and subsample quantities are shown in Table D.3. Accurately measured sample volumes (10.0 or 2.0 mL) were delivered to sample vials by adding increments of well-mixed sludge or supernatant solution into tare-weighed plastic volume-calibrated syringes.[(b)] The syringes were discharged into the sample vials, and the syringes were re-weighed to determine, by difference, the delivered weights.

(b) To prepare the measuring syringes, the ends of the barrels of ordinary plastic 10-mL and 5-mL syringes were cut off and the cut ends beveled smooth. The respective 10-mL and 2-mL levels were calibrated by adding 10.0 or 2.00 g of water (density of 1.00 g/mL) to the open-end-up syringes with the plungers withdrawn up the syringe barrel. After adding the precise water mass, the plungers were pushed upwards until the water level reached the open syringe end. The plunger position at that point was marked to show the 10.0- or 2.0-mL levels. The sludge was added to the tare-weighed end-up syringes (with plungers at the set 2.0- or 10.0-mL marks) to the upper level and the syringes re-weighed. The loaded syringes then were discharged into the sample vials. The syringes prepared in this way were capable of discharging nearly all of the sludge contents for subsample preparation and left little residual sludge behind in the syringe. Any residual sludge was measured by re-weighing the emptied syringe.

Table D.3. Chemical and Radiochemical Sample Aliquots

Source	Sample Identification	Sample Quantity	
		mL	g
KE NLOP Composite	KENLOP-1[a]	10.0	12.38
	KENLOP-A[a]	2.0	2.45
	KENLOP-B[a]	2.0	2.40
Supernatant from KE-20-A &-B	KENLOP-Liq[a]	2.0	1.96
Sludge from KE-20-A & -B	KENLOP-AB1	2.0	1.98
	KENLOP-AB2	2.0	2.00
Sludge from KE-20-D & -E	KENLOP-DE1	2.0	2.18
	KENLOP-DE2	2.0	2.21
Sludge from KE-20-G & -H	KENLOP-GH1	2.0	2.39
	KENLOP-GH2	2.0	2.53
Sludge from KE-20-AD & -BD	KENLOP-DS1	2.0	2.00
	KENLOP-DS2	2.0	2.00

(a) Samples for priority analysis.

Chemical and Radiochemical Analyses and Results

Chemical and radiochemical analyses were performed for the subsamples shown in Table D.3. The highest priority was accorded to the KENLOP-1, KENLOP-A, and KENLOP-B composite sludge and KENLOP-Liq supernatant solution subsamples. The results presented here are confined to the findings for these four priority subsamples.

The first step in the analytical sequence was to perform gamma energy analyses (GEA) of the intact subsamples. The as-prepared subsample geometries met the set geometries needed for GEA.

Three accurately weighed ~1-gram portions then were drawn from subsample KENLOP-1 and were dried to constant weight in a 105°C oven. The weight loss at 105°C was ascribed to water. After drying, one portion was reserved for X-ray diffractometry (not yet performed) and the other two portions underwent sequential digestions in acid (mixed nitric/hydrochloric), fusion of the acid digest residue in potassium pyrosulfate, and fusion of the potassium pyrosulfate residue in potassium hydroxide according to established ASO procedures (Table D.1). No residue remained after the final (potassium hydroxide) fusion.

Aliquots from each of the digestates were analyzed for total beta activity, total alpha activity, activity analyses of isotopes by their alpha energies (alpha energy analysis or AEA), and uranium (by kinetic phosphorescence). The primary alpha energy peaks registered by AEA are due to ^{239,240}Pu and ^{238}Pu,^{241}Am with lesser activity due to ^{243,244}Cm. The supernatant solution (KENLOP-Liq) likewise was analyzed for total beta activity, total alpha activity, AEA, and uranium.

The weight-based analyte concentrations in the acid and two fusion digests of the composite settled sludge were summed to determine the total concentrations of the respective analytes. The individual results of the analyses for the acid and two fusion digests, presented in Table D.4, show that the initial acid digest removed 99% or more of the respective analytes.

Table D.4. Analytical Results for KE NLOP Sludge Digests

Analyte	Concentration, µCi/g settled sludge					
	KENLOP-1, Rep-1			KENLOP-1, Rep-2		
	Acid	$K_2S_2O_7$	KOH	Acid	$K_2S_2O_7$	KOH
^{239,240}Pu	1.72E+0	4.98E-4	3.65E-5	1.79E+0	4.15E-4	3.46E-5
^{238}Pu,^{241}Am	1.59E+0	4.74E-5[(a)]	4.11E-6[(a)]	1.74E+0	3.64E-5[(a)]	4.30E-6[(a)]
^{243,244}Cm	3.64E-3			4.22E-3		
Total Alpha	3.75E+0			3.69E+0		
Total Beta	1.13E+1	1.07E-1		1.10E+1	8.54E-2	
^{90}Sr[(b)]	7.81E-1	1.12E-3		9.60E-1	2.95E-3	
Uranium, µg/g	5.68E+3	6.00E-1		5.33E+3	3.60E-1	
^{60}Co	5.80E-2	3.63E-3	1.28E-5	5.66E-2	2.80E-3	1.41E-5
^{137}Cs	7.77E+0	9.94E-2	1.38E-2	7.32E+0	7.54E-2	1.56E-2
^{154}Eu	1.11E-1			1.08E-1		
^{155}Eu	2.84E-2			2.60E-2		
^{241}Am	1.77E+0	4.43E-4		1.57E+0		
^{125}Sb		7.85E-4	4.75E-4		1.30E-3	4.79E-4
Sum gamma	9.74E+0	1.04E-1	1.43E-2	9.08E+0	7.95E-2	1.61E-2

(a) ^{238}Pu only.
(b) ^{90}Sr inferred to be half of the difference between the Total Beta activity and the sum of the gamma activity. The other half of the activity difference is due to ^{90}Y.
Blank spaces are below detection limits.

The overall results of the sample analyses are shown in Table D.5. The following general observations are drawn from these data:

- ^{137}Cs dominates the high energy gamma activity in the sludge; ^{60}Co also provides much of the high energy gamma radiation.
- The settled sludge contains 0.55 wt% total uranium.
- Though the solution comprises nearly ⅔ of the settled sludge mass, it contains very little of the radioactivity or uranium.
- The settled sludge is transuranic with total alpha activity of 3720 nCi/g or 37-times the TRU limit of 100 nCi/g.
- Aside from ^{60}Co and ^{154}Eu (which have half-lives of 5.27 years and 8.59 years, respectively), the concentrations of uranium and radionuclides found in the present KE NLOP dry sludge solids are similar to those reported for the KE NLOP sample FE-3 shown in Tables 1.2 and 1.3.

Table D.5. Analytical Results for KE NLOP Sludge and Supernatant Solution

Analyte	Concentration, µCi/g									Settled Sludge Concentration, µCi/mL[(b)]	% of Analyte in Solids[(c)]
	Settled Sludge					Solution			Dry Sludge Solids[(a)]		
	KENLOP-1		KENLOP-A	KENLOP-B	Avg.	KENLOP-Liq		Avg.			
^{60}Co	7.00E-2		6.83E-2	6.43E-2	6.75E-2	2.33E-5		2.33E-5	1.79E-1	8.37E-2	99.98
^{137}Cs	7.81E+0		5.72E+0	7.07E+0	6.87E+0	4.09E-2		4.09E-2	1.82E+1	8.52E+0	99.63
^{154}Eu	1.32E-1		1.31E-1	1.20E-1	1.28E-1	<3.E-5		3.00E-5	3.39E-1	1.58E-1	99.99
^{155}Eu	3.04E-2		3.37E-2	3.35E-2	3.25E-2	<2.E-4		1.50E-4	8.61E-2	4.03E-2	99.71
^{241}Am	1.77E+0		1.67E+0	1.53E+0	1.66E+0	<4.E-4		4.00E-4	4.40E+0	2.06E+0	99.98
	Rep-1	**Rep-2**			**Avg.**	**Rep-1**	**Rep-2**	**Avg.**			
$^{239,240}Pu$	1.72E+0	1.79E+0			1.76E+0	1.47E-4	1.36E-4	1.42E-04	4.66E+0	2.18E+0	99.99
^{238}Pu,^{241}Am	1.59E+0	1.74E+0			1.67E+0	1.32E-4	1.20E-4	1.26E-04	4.42E+0	2.06E+0	100.00
$^{243,244}Cm$	3.64E-3	4.22E-3			3.93E-3	<5.E-7	<4.E-7	<5.E-7	1.04E-2	4.87E-3	>99.99
Total Alpha	3.75E+0	3.69E+0			3.72E+0	2.92E-4	2.76E-4	2.84E-04	9.87E+0	4.61E+0	100.00
Total Beta	1.14E+1	1.11E+1			1.12E+1	5.27E-2	5.22E-2	5.25E-02	2.97E+1	1.39E+1	99.71
^{90}Sr[(d)]	7.75E-1	9.55E-1			8.65E-1	5.90E-3	5.60E-3	5.75E-03	2.29E+0	1.07E+0	99.59
U, µg/g	5.68E+3	5.33E+3			5.51E+3	1.64E+1	1.66E+1	1.65E+1	1.46E+4	6.83E+3	99.81
Water, wt%	61.71	62.90			62.3						0.00

(a) Analyte concentrations in the sludge solids were determined by deducting the mass and analyte contributions of the solution from the respective settled sludge mass and analyte quantities. For example, there is 6.75×10^{-2} µCi ^{60}Co in one gram of settled sludge. One gram of settled sludge also contains 0.623 g of solution (settled sludge is 62.3 wt% water). The 0.623 g of solution contains ^{60}Co in the amount 0.623 g × 2.33×10^{-5} µCi ^{60}Co/g = 1.45×10^{-5} µCi ^{60}Co. The concentration of ^{60}Co in the sludge solids (0.377 g) in 1 gram of settled sludge is (6.75×10^{-2} µCi - 1.45×10^{-5} µCi) / 0.377 g = 1.79×10^{-5} µCi ^{60}Co/g.

(b) The settled sludge concentration in µCi/mL is calculated by multiplying the concentration, in µCi/g, by the settled sludge density of 1.24 g/mL.

(c) The percentage of analyte in the sludge solids was determined by deducting the contribution of the analyte found in the solution associated with the settled sludge from the total analyte found in the same quantity of settled sludge, dividing by the analyte quantity in the settled sludge, and multiplying by 100%. For example, as shown in footnote [a] above, one gram of settled sludge contains 6.75×10^{-2} µCi ^{60}Co and the associated solution contains 1.45×10^{-5} µCi ^{60}Co. The sludge solids therefore contain 100% × (6.75×10^{-2} µCi ^{60}Co - 1.45×10^{-5} µCi ^{60}Co)/ 6.75×10^{-2} µCi ^{60}Co = 99.98% of the ^{60}Co.

(d) ^{90}Sr inferred to be half of the difference between the Total Beta activity and the sum of the gamma activity. The other half of the activity difference is due to ^{90}Y.

Appendix E

Results of Initial Gas-Generation Testing

Appendix E

Results of Initial Gas-Generation Testing

E.1 Overview

Experimental measurements of sludge reaction rates and gas generation form the technical basis for sludge uranium metal content, uranium metal particle size and reaction enhancement factor values. Three phases, or series of gas-generation experiments, have been conducted and documented. 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. Mixed and unmixed and fractionated KE canister sludge materials were tested, along with 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 from irradiated metallic uranium particles (fuel particles) with and without sludge addition. In the gas-generation testing series, sludge samples and irradiated metallic uranium fuel particles were introduced into reaction vessels, and in most cases, the samples were held at a series of controlled temperatures long enough for essentially complete oxidation of the uranium metal, and gas samples were periodically taken.

Because the focus of the SNF Sludge project has changed from an interim storage mission to near-term disposition to WIPP, additional gas-generation tests with KE North Load Pit (NLOP) are underway, and initial results are summarized here. Current plans call for the retrieval and solidification/stabilization of KE NLOP sludge as Contact Handled (CH) Transuranic (TRU) waste for disposition to WIPP. Near-term disposition of the KE NLOP sludge is predicated upon the sludge being non-pyrophoric and exhibiting a very low hydrogen gas-generation rate (from uranium metal water reaction). Gas-generation testing (Bryan et. al 2004) conducted with a single consolidated NLOP sludge sample collected in 1999 indicated that the sludge contained very little uranium metal (i.e., 0.013 wt% -settled sludge basis). However, to gain additional confidence on the low uranium metal content of the NLOP sludge, additional gas-generation testing is underway, using NLOP sludge collected in December 2003. Additionally, the effects of free/drainable water removal and solidification matrices (e.g., grout and Nochar®) on the gas-generation rate of the NLOP sludge are also being examined. If significant quantities of uranium metal are present, free/drainable water removal and solidification will likely inhibit the reaction between uranium metal and water.

E.2 Test Objectives

The overall goal for this testing is to collect gas-generation rate and composition data under known conditions to better understand the quantity and reactivity of the metallic uranium present in the KE NLOP sludge. Specific objectives for this testing include:

- Verify that the KE NLOP sludge is non-pyrophoric [contains less than 1 wt% pyrophoric material (i.e., uranium metal)]

- Determine the hydrogen generation rate and uranium metal content in KE NLOP sludge

- Determine the effect of free/drainable water removal on the hydrogen generation rate of KE NLOP sludge

- Determine the effect of a grout matrix on the hydrogen generation rate of KE NLOP sludge

- Determine the effect of the Nochar® matrix on the hydrogen (and hydrocarbon) generation rate of KE NLOP sludge

[Note that observation of any effects on the uranium metal-water reaction depends on uranium metal being present in the KE NLOP sludge.]

E.3 Summary of Initial Test Results

Tests to meet these objective were initiated on January 9, 2004 (i.e., tests with sludge and water only). Gas generation has been observed (i.e., pressure in reactor headspaces has increased) and the gas was sampled on January 14, 2004. The gas-generation tests with various waste forms (dewatered sludge, grout, Nochar) were initiated on January 19, 2004. Because the hydrogen gas-generating reaction of uranium metal with water is relatively slow, the full performance of the test specimens will not be known until after January 19, 2004. Ultimately, the tests conducted at 95°C (sludge and water only) will allow estimates of the concentration of uranium metal contained in the sludge.

Based on the results from the initial test interval (11 hours at 95 and 60°C) with the sludge and water only tests, the following observations and conclusion can be made:

- It is highly unlikely that KE NLOP sludge will be designated as being Pyrophoric material (> 1 wt% pyrophoric material). If the KE NLOP sludge contained 1 wt% uranium metal particles (assuming 500 µm diameter spheres), using the SNF Project rate equation (uranium metal in oxygen-free water) with a rate enhancement factor of 1, a hydrogen generation rate of 580 mL-H_2/kg-settled sludge-day would be expected at 95°C. This rate is 290 times greater than the initial measured rate (at 95°C), 2.0 mL-H_2/per kg-settled sludge/day.

- During the initial test interval (111 hours), at 95°C, the total gas-generation rate was 39 mL total gas per kg-settled sludge/day (48 mL total gas per liter-settled sludge-day). Based on the mass spectroscopy analysis, only ~5% of the total gas generated was hydrogen. The balance of the generated gas consists of mostly CO_2 (~95).

- The gas-generation-rate profile (total gas generation vs. time) shows that after about 50 hours at 95°C, the rate dropped to essentially zero, indicating reactants were largely depleted.

- During the initial 111-hour test interval at 60°C, the total gas-generation rate was 6.4 mL total gas per kg-settled sludge/day (8 mL total gas per liter-settled sludge-day). The composition of the gas generated at 60°C was essentially the same as that generated at 95°C.

- With the high CO_2 content in the generated gas, it may be improbable to achieve a gas mixture in any KENLOP sludge processing, transport, or storage operation.

- While the initial gas-generation rates for the 2003 KE NLOP sludge are low, they are significantly greater than those observed for the KE NLOP sludge collected in 1999. For the 1999 KE NLOP sludge sample (FE-3), while at 95°C for 473 hours, the total gas-generation rate was 6.1 mL total gas kg-settled sludge/day (9.7 mL total gas per liter-settled sludge-day) – with greater than 99% of the total gas being carbon dioxide (~0.36% of the total gas generated was hydrogen) (Bryan et. al 2004). The hydrogen gas-generation rate of FE-3 at 95°C for the 473 h test interval was 9.89 E-07 moles per kg-settled sludge/day (0.02 mL/kg-settled sludge/day). [Note the settled density of the FE-3 subsample used for gas-generation testing was 1.6 g/cm^3. Also, the FE-3 sample was stored at hot cell temperatures (32°C) for ~8 months before being used in the gas-generation test. Also note that the FE-3 sample was held at 90°C for about 300 hours before the test temperature was elevated to 95°C.]

- No quantifiable levels of fission product gases were detected during the initial test interval, which provides a preliminary indication that the sludge contains very little no uranium metal. In the previous gas-generation testing, with most K Basin sludges Kr and/or Xe fission product gases were measured, giving quantitative evidence of the corrosion of uranium metal (i.e., fission product gases remain trapped with the solid uranium metal matrix and do not react and are not significantly retained by the corrosion products in the sludge). Of all the sludge types previously subjected to gas-generation testing, Sample FE-3 (1999 KE NLOP sludge) and KC-6 (ion exchange resin beads collected from the floor of the KE Basin) were the only sludge types whose gas samples contained neither Kr nor Xe at detectible levels.

Results from gas-generation tests with dewatered KE NLOP sludge (no drainable liquids) and KE NLOP sludge solidified and grout and Nochar are not available, as these test were started on January 19, 2004.

E.4 Test Matrix, Materials, and Approach

This section describes the overall test approach and methods used for the KE NLOP sludge gas-generation testing.

E.4.1 Test Matrix and Specific Objectives

A total of six gas-generation tests, each with nominally 50 g settled KE NLOP sludge are being conducted. Three tests are being conducted with sludge and water only. In one test, moist sludge (i.e., drainable liquid has been removed) is being used. In the final two tests, the sludge has been solidified in grout and Nochar. After preparing sludge, the samples were placed into 220 mL reaction vessels. The reaction vessels were sealed, connected to the manifold system, and purged with neon gas to remove air.

Next, the vessels were heated to the target conditions, and temperatures and gas pressures were monitored continuously. Initial gas samples from the sludge and water only tests were collected on January 14, 2003. Additional gas samples will be collected as described in the Test Plan. All gas samples will be analyzed via mass spectrometry. These tests are being conducted at PNNL's High-Level Radiochemistry Facility in the 325 Building (325A HLRF), 300 Area, in accordance the Test Plan[(a)] and Test Instruction[(b)] and consistent with the sampling and analysis plan (Baker et al. 2000).

Table E.1 displays the test matrix that identifies test number, test identification, material (target sludge mass) and test conditions (vessel size, target temperature, start data, and target test duration).

Table E.1. Test Matrix for KE NLOP Sludge Gas-Generation Testing

Test No.	Test ID	As-Settled Sludge		Nominal Reaction Vessel Size mL	Matrix	Target Temp, °C	Start Date	Target Duration h
		Type	Mass g					
Tests with KE NLOP Sludge – Collected in 2003								
1	NLOP-U1	NLOP03	50	220	water	95	1-9-04	700
2	NLOP-U2	NLOP03	50	220	water	95	1-9-04	700
3	NLOP-Control	NLOP03	50	220	water	60	1-9-04	1000
4	NLOP-Moist	NLOP03	50	220	moist	60	1-16-04	1000
5	NLOP-Gt	NLOP03	50	220	grout	60	1-16-04	1000
6	NLOP-Nochar	NLOP03	50	220	Nochar	60	1-16-04	1000

Notes:
NLOP03 = KE North Loadout Pit Sludge collected December 2003

E.4.2 Specific Test Description/Objectives

Test 1, NLOP-U1. In this test, a 50 g aliquot of as-settled KE NLOP sludge was added to a reaction vessel. Additional sludge supernatant water was also added to maintain the sludge in a saturated state. The objective of Test 1 is to determine the total uranium metal content as rapidly as possible. Gas generating reactions (including reactions that generated CO_2) will be forced to completion. The results from this test will be used to interpret the results from Tests 2 – 6.

Test 2, NLOP-U2. Test 2 is a duplicate of Test 1. Measurement of the uranium metal content of the KE NLOP sludge is a critical measurement; therefore, a duplicate test is warranted.

Test 3, NLOP-Control. For Test 3, a reaction vessel was loaded in a manner identical to Test 1 and 2. However, whereas Tests 1 and 2 are being conducted at 95°C, Test 3 is being run at 60°C. Test 3 serves as a control to interpret the results of Test 4 to 6 (Test 3 - 6 will be conducted at the same temperature).

(a) CH Delegard. "Bench-Scale Test Plan to Demonstrate Production of WIPP-Acceptable KE-NLOP Sludge Waste Forms at the 325 Building." Pacific Northwest National Laboratory, Richland, WA, December 23, 2003.
(b) AJ Schmidt. "Test Instruction KE NLOP Sludge Gas Generation Testing." 46857-TI04, Rev. 0, Pacific Northwest National Laboratory, Richland, WA, December 23, 2003.

Results from Tests 4 to 6 can be directly compared to the gas-generation rate profile of Test 3 to ascertain the effects of free/drainable water removal and solidification of the sludge.

Test 4, NLOP-Moist. In this test, drainable liquids were removed from a 50 g sample of as-settled KE NLOP sludge before loading the moist material into the reaction vessel. Appendix F provides details on the preparation of this waste form. This test examines the effect of sludge dewatering on the hydrogen generation rate of KE NLOP sludge (i.e., removal of drainable water is expected to inhibit the corrosion of uranium metal). The effect of sludge dewatering on other gas generating/consuming reactions will also be examined.

Test 5, NLOP-Grout. In this test, an aliquot of sludge was immobilized in Portland cement, with bentonite clay added to the matrix. After several days of curing, the grouted sludge was loaded into a reactor vessel. Appendix F provides details on the preparation of this waste form. This test examines the effect of a grout matrix on hydrogen generation rate of KE NLOP sludge. The effect of the grout matrix on other gas generating/consuming reactions will also be examined.

Test 6, NLOP-Nochar. In this test, an aliquot of sludge was immobilized in using a polymer solidification agent, Nochar. After several days of curing, the solidified sludge was loaded into a reactor vessel. Appendix F provides details on the preparation of this waste form. This test will examine the effect of the Nochar matrix on hydrogen generation rate of KE NLOP sludge. The effect of the Nochar on other gas generating/consuming reactions will also be examined.

E.4.3 Test Materials

A full sludge core was collected from the KE NLOP December 2003 (Appendix A), and was composited, homogenized, and subsampled. The mass and volume (as-settled sludge) of subsamples used for gas-generation testing were measured and radiochemical analyses were performed on the subsamples (Appendix B and C). For Tests 4 through 6, waste forms were prepared as described in Appendix F.

E.4.4 Reaction Vessels

Stainless steel reaction vessels were used (approximately 2 in. diameter and 4 7/8 in. tall, 220 mL nominal volume).

E.4.5 Reaction Atmosphere

Neon gas provides an inert atmosphere (i.e., oxygen free) for the gas-generation tests. Use of an oxygen-free atmosphere provides conditions that favor the uranium-metal reaction (i.e., hydrogen generations rates from this testing are expected to be conservative). Argon was not used because it served as an indicator of atmospheric contamination. After loading the reaction vessels and after collecting each gas sample, the vessels are purged multiple times with neon to remove air/oxygen from the system.

E.4.6 Test Temperatures

In the Series I gas-generation testing with KE canister sludge, (Delegard et. al. 2000), induction periods (time at target temperature before the onset of hydrogen gas generation/release) were observed. The induction periods were 1340 h, 205 h, and 27 h, at 40°C, 60°C and 80°C, respectively. Therefore, to obtain timely data, target test temperature in the current work are a minimum of 60°C.

For KE NLOP sludge metal determination (Tests NLOP-U1 and NLOP-U2), the target test temperature is 95°C (consistent with prior uranium metal content determination testing).

For gas-generation rate testing (with and without solidification matrices) the baseline reaction target temperature is 60°C. This temperature (60°C) is consistent with the maximum temperature during shipment to WIPP. While temperatures greater than 60°C may accelerate the testing, the results may not be reflective of expected storage and shipping conditions. However, if after some period of time (e.g., 500 hours) little or no gas generation is observed at 60°C, the test temperature may be increased.

Test temperatures also may be stepped successively to higher values to provide information on activation energies and provide information on the confounding effects of diffusion and underlying uranium-water reaction rates.

E.4.7 Test Duration

Previous gas-generation tests have ranged from 900 to 10,000 hours. It is expect that these test will continue for 1 to 2 months (700 to 1400 hours). Actual test durations will depend upon the gas-generation behavior observed in the individual tests.

E.4.8 Test System Operation

The reaction vessels and the gas manifold system (Figure E.1.) used for the gas-generation tests are similar to those describe in the previous work with K Basins Sludge Delegard et al. (2000) (Series I), Bryan et al. (2004) (Series II), and Schmidt et al. (2003) (Series III). Each vessel has a separate pressure transducer on the gas manifold line. The entire surface of the reaction system exposed to the sludge sample is stainless steel, except for a copper gasket seal between the flange and the top of the reaction vessel. Temperatures and pressures are recorded every 10 s on a Campbell Scientific CR10 data logger; the data are averaged every 20 min and saved in a computer file. Temperature and pressure data are also manually logged once each working day.

Figure E.2 illustrates a reaction vessel and shows where the thermocouples are placed inside and outside the vessel. For the gas-generation testing, each vessel was wrapped in heating tape and insulated. Two thermocouples were attached to the external body, one for temperature control and one for over-temperature protection. Two thermocouples were inserted through the flange. The thermocouple centered in the lower half of the vessel monitored the temperature of the liquid phase; the one centered in the upper half monitored the gas phase temperature within the reaction vessel. The reaction vessels were placed in a hot cell and connected by a thin (0.0058-cm inside diameter) stainless steel tube to the gas

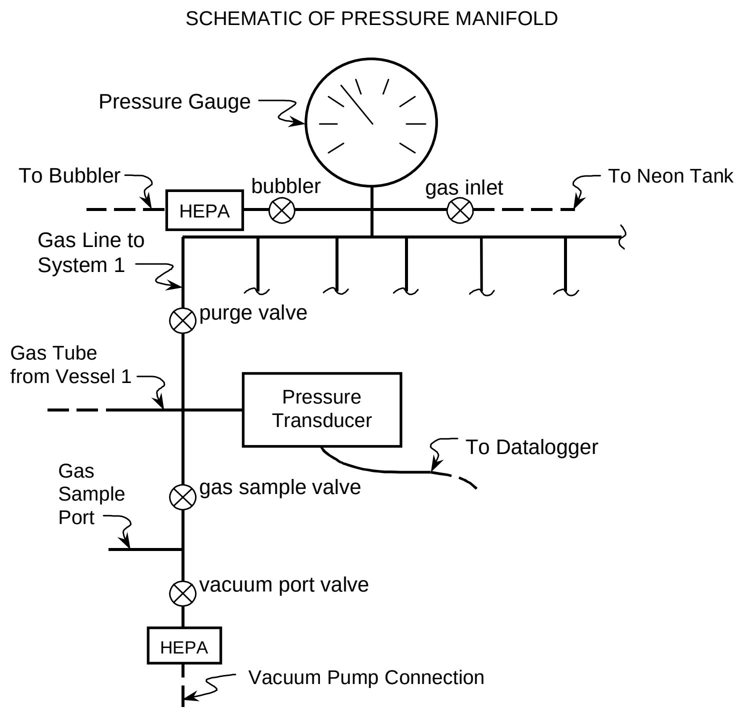

Figure E.1. Layout of Gas Pressure Measurement and Gas Sample Manifold Used in Gas-Generation Tests (includes details for one of 6 systems)

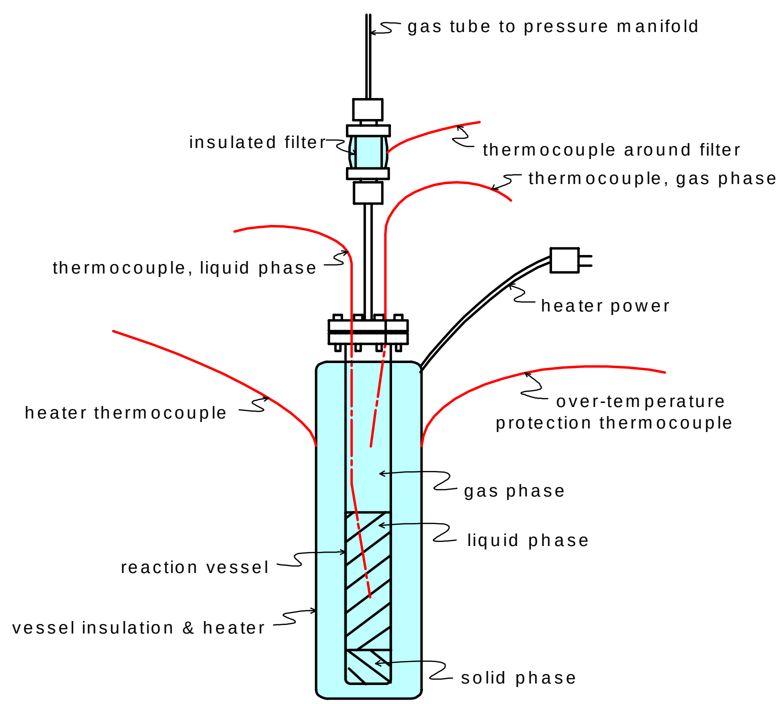

Figure E.2. Schematic of Reaction Vessel manifold outside the hot cell. A stainless steel filter (2-µm pore size, Nupro) protected the tubing and manifold from contamination. A thermocouple was attached to this filter as well.

An atmospheric pressure gauge was attached to the data logger. The pressure in each system was the sum of atmospheric pressure and the differential pressure between the system internal and external (atmospheric) pressures. An inert cover gas (neon) was required to identify product gases and understand the chemical reactions occurring in the settled sludge. The neon gas used was analyzed independently by mass spectrometry and determined to contain no impurities in concentrations significant enough to warrant correction.

At the start of each run, each system was purged by at least eight cycles of pressurizing with neon at 45 psi (310 kPa) and venting to the atmosphere. The systems were at atmospheric pressure, about 745 mm Hg (99.3 kPa), when sealed. The vessels then were heated, and the temperature set points were adjusted to keep the material within 1°C of the desired liquid phase temperatures.

As necessary during the testing and at the end of each reaction sequence, the vessels were allowed to cool to ambient temperature and then a sample of the gas was taken from the headspace for mass spectrometry analysis. Gases in the reaction system were assumed to be well mixed. The metal gas collection bottles were equipped with a valve and had a volume of approximately 75 mL. After the bottle was evacuated overnight at high vacuum, it was attached to the gas sample port. After the sample was collected, the reaction vessel was purged again with neon. The compositions of the gas phase of each reaction vessel during selected gas samplings were analyzed by PNNL using analytical procedure PNNL-98523-284 Rev. 0.

E.5 KE NLOP Gas-Generation Testing Results

In each test, gas-tight reaction vessels were loaded with KE NLOP sludge and waste forms, the gas space purged with neon, and the loaded vessels heated to the selected temperature. Gas samples were taken from the vessels in accordance with the test plan. Gas-generation rates were determined for each gas sample, based on the heating time, the gas composition, the total gas quantity in the system from which the sample was taken, and the sludge mass present in each reaction vessel.

E.5.1 Gas-Generation Profile for Sludge Only Tests

The gas-generation profiles (g-mol of gas generated/kg-settled sludge as a function of reaction time) for the initial test interval of the sludge only tests are provided in Figure E.3. Test 1 and 2, NLOP-U1 and U-2 are duplicate tests conducted at 95°C. Test 3, NLOP-Control, was conducted at 60°C.

E.5.2 Results of Gas Sample Analysis for Sludge Only Tests

Based on the mass spectrometry analysis of the gas sample, carbon dioxide (CO_2), hydrogen (H_2), and methane (CH_4) and higher hydrocarbons were observed and quantified. Detailed descriptions of gas generating (and gas consuming) reactions in K Basin sludge are provided in Delegard et al. (2000), Bryan et al. (2004), and Schmidt et al. (2003).

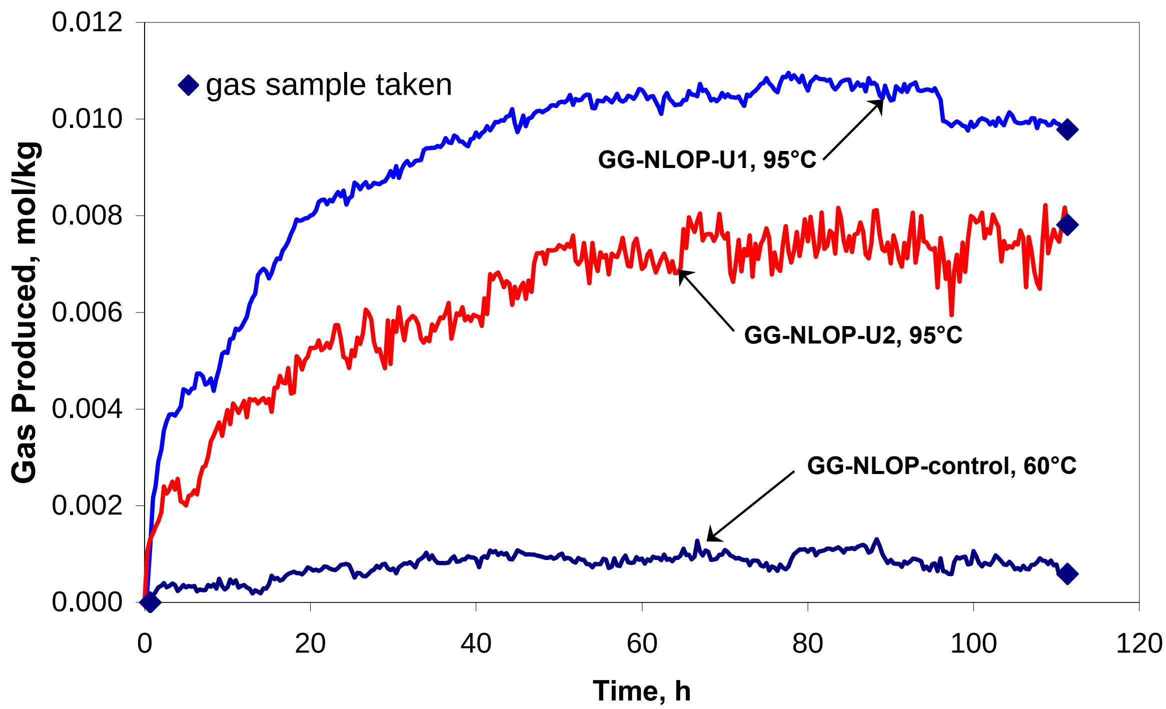

Figure E.3. Total Gas Generation from NLOP-U1 and NLOP-U2 at 95°Cand NLOP-Control at 60°C

The quantities of gas produced and consumed during the initial interval for each test are presented in Table E.2. The gas product was ~95% CO_2 for all three tests. Hydrogen comprised 5.07% 4.17%, and 4.93% of the product gas for NLOP-U1, NLOP-U2, and NLOP-Control tests, respectively. Hydrocarbons comprised the balance of the gas production, and N_2 and O_2 were consumed in all three tests. No indications of the presence of fission product gases were found. For comparison, the quantities of gas produced and consumed for the 1999 sample, FE-3 are provided. While the NLOP-U1, NLOP-U2, and NLOP-Control reaction vessels each contained about 50 g of settled sludge, the FE-3 test was conducted with 21 g of settled sludge.

The gas sample compositions from the NLOP-U1, NLOP-U2, and NLOP-Control tests are given in Tables E.3 through E.5. Gas samples were analyzed by mass spectrometry. The compositions of the generated gases (derived from the compositions of sampled gas by excluding the neon cover gas, argon, and trace nitrogen and oxygen from atmospheric contamination) are presented and are indicated by shading. For example, if analysis found 80% Ne, 5% CO_2, and 15% H_2, the composition of gas formed by excluding Ne would be 25% CO_2 and 75% H_2.

The presence of argon in the gas samples was used to indicate atmospheric contamination (air), since it is not present in the cover gas and is not produced by the sludge. Nitrogen could have been generated or consumed by the sludge or could have come from atmospheric contamination. The percent nitrogen actually generated or consumed is given by the percent nitrogen found minus 83.6 times the percent argon in the sample (the ratio of nitrogen to argon in dry air is 83.6). The percent oxygen actually generated or consumed in the samples may be calculated in a method similar to nitrogen. The sum of all percents for a

Table E.2. Net and Cumulative Quantities of Gas Evolved for FE-3 NLOP-U1, NLOP-U2, and NLOP-Control

Gas	Gas Quantities, moles, at Sampling Times							
	FE-3		GG-NLOP-U1		GG-NLOP-U1		GG-NLOP-Control	
	493.00 h	**970.00 h**	**111.33 h**		**111.33 h**		**111.33 h**	
CO_2	8.52E-05	8.31E-05	4.30E-04		4.22E-04		7.06E-05	
Cumulative	8.52E-05	1.68E-04	4.30E-04		4.22E-04		7.06E-05	
H_2	2.53E-07	3.06E-07	2.30E-05		1.84E-05		3.68E-06	
Cumulative	2.53E-07	5.58E-07	2.30E-05		1.84E-05		3.68E-06	
N_2	-7.11E-06	1.19E-06	-7.16E-06		-1.98E-05		-1.60E-05	
Cumulative	-7.11E-06	-5.92E-06	-7.16E-06		-1.98E-05		-1.60E-05	
O_2	-4.03E-06	-7.81E-07	-7.73E-06		-9.08E-06		-6.97E-06	
Cumulative	-4.03E-06	-4.81E-06	-7.73E-06		-9.08E-06		-6.97E-06	
CH_4	5.42E-08	5.39E-08	3.80E-07		4.34E-07		1.84E-07	
Cumulative	5.42E-08	1.08E-07	3.80E-07		4.34E-07		1.84E-07	
C_2H_x	1.08E-07	8.99E-08	2.53E-07		4.96E-07		2.45E-07	
Cumulative	1.08E-07	1.98E-07	2.53E-07		4.96E-07		2.45E-07	
$\geq C_3H_x$	9.03E-08	8.99E-08	6.33E-08		4.34E-07		6.14E-08	
Cumulative	9.03E-08	1.80E-07	6.33E-08		4.34E-07		6.14E-08	
$\Sigma\ C_yH_x$ C	5.57E-07	5.19E-07	1.09E-06		2.80E-06		8.70E-07	
Cumulative	5.57E-07	1.08E-06	1.09E-06		2.80E-06		8.70E-07	
^{83}Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{84}Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{85}Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{86}Kr								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
Σ Kr	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{130}Xe								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{131}Xe								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{132}Xe								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{134}Xe								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
^{136}Xe								
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
Σ Xe	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	
Cumulative	0.00E+00	0.00E+00	0.00E+00		0.00E+00		0.00E+00	

Table E.3. Gas Analyses for GG-NLOP-U1 at 95°C

Run Sys –3	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	91.8	0.013	0.364	6.8	0.006	0.004	0.001	0.890	0.147	<0.001	<0.0001	111.3
27KE15				5.07	94.77	0.084	0.056	0.014	-1.578	-1.702	<0.014	<0.0014	

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

Table E.4. Gas Analyses for GG-NLOP-U2 at 95°C

Run Sys –4	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	92.5	0.009	0.297	6.8	0.007	0.008	0.007	0.350	0.033	<0.001	<0.0001	111.3
27KE15				4.17	95.52	0.098	0.112	0.098	-4.478	-2.057	<0.014	<0.0014	

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

Table E.5. Gas Analyses for GG-NLOP-Control at 60°C

Run Sys –5	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	60	98.5	0.007	0.060	1.15	0.003	0.004	0.001	0.241	0.021	<0.001	<0.0001	111.3
27KE15				4.93	94.41	0.246	0.328	0.082	-21.397	-9.324	<0.014	<0.0014	

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

test interval in Table E.3 may not be exactly 100%, because the values were rounded. The uncertainties in all the entries in these tables are approximately plus or minus 1 in the last digit.

Individual gas-generation rates are calculated based on the total moles of gas produced (Figure E.3) the generated gas compositions (Tables E.3 through E.5), and the initial test interval time. Tables E.6 through E.8 show the gas-generation rates derived in this manner for the initial test interval.

Table E.6. Gas-Generation Rates from GG-NLOP-U1 at 95°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	8.8E-5	1.6E-3	1.4E-6	9.6E-7	2.4E-7	-2.7E-5	-2.9E-5			111.3

Blank entries are below detection limits.

Table E.7. Gas-Generation Rates from GG-NLOP-U2 at 95°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	7.3E-5	1.7E-3	1.7E-6	2.0E-6	1.7E-6	-7.8E-5	-3.6E-5			111.3

Blank entries are below detection limits.

Table E.8. Gas-Generation Rates from GG-NLOP-Control at 60°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	60	1.4E-5	2.7E-4	7.1E-7	9.5E-7	2.4E-7	-6.2E-5	-2.7E-5			111.3
Blank entries are below detection limits.											

E.6 References

Baker RB, TL Welsh and BJ Makenas. July 2000. "Sampling and Analysis Plan for Sludge from the 105–K Basins to Support Transport to and Storage in T Plant," HNF-6479, Rev. 0, Fluor Hanford Inc.

Bryan SA, CH Delegard, AJ Schmidt, RL Sell, KL Silvers, SR Gano, and BM Thornton. 2004. *Gas Generation from K East Basin Sludges – Series II Testing*. PNNL-13446, Rev. 1, Pacific Northwest National Laboratories, Richland, WA.

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Schmidt AJ, CH Delegard, SA Bryan, MR Elmore, RL Sell, KL Silvers, SR Gano, and BM Thornton. 2003. *Gas Generation from K East Basin Sludges and Irradiated Metallic Uranium Fuel Particles – Series III Testing*. PNNL-14346, Pacific Northwest National Laboratory, Richland, WA.

Appendix F

Waste-Form Preparation and Testing

Appendix F

Waste-Form Preparation and Testing

Waste-form preparation and testing was performed in the 325 Laboratory. Tests with simulated sludge occurred in a non-radioactive laboratory and KE NLOP sludge tests occurred in the glovebox of Room 528. Three waste forms were prepared from KE NLOP settled sludge and KE NLOP supernatant solution to evaluate preparation methods and to understand the waste forms' performance and qualities. The work proceeded according to the Test Instruction "Preparation of KE NLOP Waste Forms," 46857-TI03. After preparation and in-glovebox testing, the waste forms were loaded out of the glovebox for gas-generation testing under the Test Instruction "KE NLOP Sludge Gas Generation Testing," 46857-TI04.

Based on evaluations given in the Test Plan ("Bench-Scale Test Plan to Demonstrate Production of WIPP-Acceptable KE-NLOP Sludge Waste Forms at the 325 Building," December 2003), three waste forms were prepared. The names and general descriptions of the waste forms are shown in Table F.1.

Table F.1. KE NLOP Waste Forms

Waste-Form Name	Description
NLOP-Moist	~50 g of as-settled sludge, drained of liquid
NLOP-Gt	~50 g of as-settled sludge and ~25 g of supernatant solution, blended and cured in grout
NLOP-Nochar	~50 g of as-settled sludge and ~25 g of supernatant solution, blended with Nochar Acid Bond 660

<u>Preparation of the Drained Waste Form NLOP-Moist</u>

The waste form NLOP-Moist was prepared with the aim to obtain a concentrated (low-volume) waste that had no drainable liquid. The waste form was prepared by weighing a representative aliquot of the KE NLOP settled sludge (52.87 g) into a 50-mL plastic centrifuge cone. A stack of two filter papers were placed in a weighing boat and the boat and papers were weighed. The open centrifuge cone was held in the vertical position and the filter papers and boat were placed on the open end of the cone with the papers in contact with the cone. With the boat/filter/cone held tightly together, the assembly was inverted with the cone resting on the filter papers within the boat. The boat was placed on a clean and stable surface and the free liquid allowed to pass through the filter.

The filter papers prevented sludge solids from leaving the cone while acting as a wick to draw solution from the sludge where it could evaporate from the margins of the papers. The boat/filter/cone was kept in the inverted position for two days but seemed to be well drained after one day. The centrifuge cone with drained solids was re-weighed (28.92 g) after two days and the volume of the tapped solids measured (20 mL) to determine final form density (1.45 g/mL).

The drained sludge waste form NLOP-Moist then was ready for transfer to a vessel for gas-generation testing.

Preparation of the Grouted Waste Form NLOP-Gt

Consultation with PNNL technical experts Ryan Lokken and Larry Bagaasen, review of technical literature, and a few preliminary tests using simulated KE NLOP sludge and supernatant solution (21 wt% sand in water) were done to develop grout formulations to solidify KE NLOP settled sludge with 50 wt% (with respect to settled sludge) of accompanying decant water. The goals of the consultation and laboratory work with simulants were to find a formulation producing a "workable" (e.g., readily mixed) slurry that would set under air-tight conditions and produce a solid form yielding no "bleed water" (free liquid). Simple formulations were preferred.

The consultations and findings showed that Portland Type I, II, or I/II cement is suitable as the cement component and that bleed water can be controlled by use of bentonite (mineral name montmorillonite) or attapulgite (mineral name palygorskite) additives. 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 is dispersibility whereas the inter-plate spaces between the bentonite particles collapse in salty environments causing bentonite to lose its ability to hold water.[a] Though both bentonite and attapulgite were tested, bentonite was selected for testing with KE NLOP sludge because the KE NLOP sludge has little salt and because bentonite is an additive familiar to WIPP.

Prior experience and laboratory tests showed that a water/cement ratio of about 0.5 produces an easily-mixed slurry. However, this blend produces significant bleed water. Higher cement fractions in the grout become increasingly difficult to mix and still yield appreciable bleed water (note – the WIPP waste form must have no free liquid). Incremental bentonite additions to 0.5 ratio water/cement slurries were tested for workability and free liquid in the set product. It was found that a consistency that would hold a peak when the mixer was withdrawn but was not so thick that it would ball-up produced a grout that set under closed conditions and yielded no bleed water. The amount of bentonite added proved to be about 9 wt% of the Portland cement used.

Based on these findings, the NLOP-Gt waste form was prepared by adding a weighed amount (50.40 g) of well-mixed KE NLOP settled sludge composite to a plastic mixing beaker, adding supernatant solution (24.73 g) in the amount of half of the weight of settled sludge, and then adding Portland type I/II cement in an amount equal to twice the mass of the water contained in the combined settled sludge (62 wt% water) and supernatant (112.00 g). The cement/sludge/supernatant ingredients were mixed thoroughly until the mixture was homogeneous. While stirring continued, bentonite (a powder) then was slowly sprinkled in. The adding and stirring continued episodically until the mixture was thick but not lumpy. The stirring continued for a full three minutes to ensure homogeneity. The amount of bentonite added was 6.60 g or 6 wt% of the added cement.

The first portion of the sludge/cement/bentonite mixture was cast into a tare-weighed 30-mm diameter by 110-mm long polyethylene container (about 70 mL volume). The remainder was cast into a tare-weighed

(a) Tallard G. 1997. "Self-Hardening Slurries and Stable Grouts from Cement-Bentonite to IMPERMIX®," pp. 142-149. In: *Barrier Technologies for Environmental Management: Summary of a Workshop*, National Academies Press, National Academy of Sciences, Washington, D.C.

50-mL centrifuge cone. The mixture was thick and would not pour but had to be transferred by spatula. Both vessels were capped shut after the grout was transferred and the containers re-weighed. The net amounts of grouted waste were 142.61 g in the polyethylene container and 47.75 g in the centrifuge cone, accounting for 190.36 g of the total 193.73 g of ingredients. The ~3 g of residue was lost on the mixing vessel and tools.

The casting in the centrifuge cone was tapped down to remove voids and allowed to set. The volume of this casting was 24.5 mL (after set though no shrinkage/expansion was observed), yielding a grouted waste-form density of 1.95 g/mL. The other casting, prepared for gas-generation testing, also was tapped down to remove voids. After about one hour, before the cement had set, a ~3-mm diameter hole was pushed axially into the wet grout using a screwdriver shaft. The intention was to form a well in the grouted form to accommodate a thermocouple for the gas-generation test. The grouted forms were examined after one day of curing and found to be solid and to contain no free liquid.

Each grouted form lost only 0.02-0.05 g on curing. The hole in the grouted form evidently had filled-in below about 3-cm depth when the screwdriver was withdrawn from the wet grout. The hole was deepened by use of a twist bit drill after two days of curing. It was observed during the drilling that the grout was hard though not fully cured, but with no muddiness or free moisture. The polyethylene container was cut from the casting and the prepared form NLOP-Gt was ready for gas-generation testing. The net weight of the grouted form after drilling was 138.26 g and contained 71.4% of the settled sludge and supernatant water used in the original mixture.

Preparation of the Nochar Waste Form NLOP-Nochar

The polyacrylic water sorbent Acid Bond 660 offered by Nochar is a dry fine granular powder that has been used to absorb aqueous solutions in wastes destined for WIPP. The Nochar addition absorbs the free liquid and allows the waste to achieve the criterion of having no drainable liquid. The Nochar capacity to absorb water is pH-dependent with higher absorption found at higher pH. The pH of the KE NLOP settled sludge is about 8.3 and that of the supernatant liquid is about 7.5, well within the range of optimum applicability of Nochar Acid Bond 660.

Based on vendor literature (Nochar, Inc., www.nochar.com), Nochar solidification agents have been tested and proven in over 150 waste streams (including stabilization of TRU-containing aqueous/sludge waste streams for ultimate disposal to WIPP). Stability tests performed on Nochar include paint filter testing, freeze/thaw testing, vibration testing, and radiation stability testing (90 Mrad—gamma/cobalt source). Due to project time constraints (i.e., insufficient time for independent testing), the vendor information on Nochar stability and its acceptance by WIPP served as the technical basis for judging the long-term stability for the Nochar/KE NLOP sludge waste form.

Preliminary tests with simulated KE NLOP sludge having 50 wt% additional water (a sand-water mixture containing 21 wt% sand) were performed to understand Nochar behavior and judge the quantity of Nochar required to eliminate drainable liquid. The addition of about 6 wt% Nochar, with respect to water, or about 4.5 wt% Nochar, with respect to the total sludge-plus-water mass, was sufficient to form a gelled semi-solid of cooked Cream-of-Wheat consistency. The water absorption was rapid, occurring in 1 to 2 minutes. The product had a bulk density of 1.03 g/mL.

Based on this information, the waste form NLOP-Nochar was prepared. First, a 53.83 g aliquot of the KE NLOP sludge composite and 24.35 g of supernatant solution (about 68 mL total volume) were combined in a 125-mL bottle. Then, 2.95 g of Nochar Acid Bond 660 was added, the bottle capped, and the contents mixed by shaking. This method of mixing was used to eliminate waste-form losses incurred by use of a stirrer. After shaking, the bottle was opened and the product observed. No free liquid was seen and the contents had a gelled springy consistency but with much open volume (air space), caused by the mode of mixing, that could not be decreased by tapping. The product was left overnight and no free liquid was seen. A further day of storage still showed no free liquid. The total volume of the void-filled product was about 120 mL yielding a bulk density of 0.68 g/mL.

Properties of the Various KE NLOP Waste Forms

The compositional and volumetric properties of the KE NLOP waste forms (NLOP-Moist, NLOP-Gt, and NLOP-Nochar), and the test parameters, are presented and compared in Table F.2. The volume increases or decreases (expansion factors) incurred in going from the settled sludge to the prepared waste form are given in Table F.2. For example, the tests show that the drained sludge product, NLOP-Moist, is only about half (0.47) of the volume of the starting sludge. In contrast, the grouted and Nochar waste forms, which also included additional supernatant solution, added to the final waste-form volumes such that the grouted and Nochar product expansion factors were 2.45 and 1.82, respectively.

Table F.2. KE NLOP Waste-Form Properties

Parameter	Waste Form		
	NLOP-Moist	**NLOP-Gt**	**NLOP-Nochar**
Waste Composition			
KE NLOP settled sludge mass, g	52.87	50.40	53.83
KE NLOP settled sludge volume, mL	42.6	40.6	43.4
KE Basin supernatant solution, g	0	24.73	24.35
Total feed waste mass, g	52.87	75.13	78.18
Total feed waste volume, mL	42.6	65.4	67.8
Additive			
Portland type I/II cement, g	--	112.00	--
Bentonite, g	--	6.60	--
Nochar Acid Bond 660, g	--	--	2.95
Property			
Final waste-form volume, mL	20	99.3	79 (packed) / 120 (loose)
Final waste-form mass, g	28.92	193.73	81.13
Final waste-form density, g/mL	1.45	1.95	1.03 (packed) / 0.68 (loose)
Expansion factor, settled sludge → final waste form	0.47	2.45 [a]	1.82 (packed) [b] / 2.76 (loose) [b]
Expansion factor, sludge & supernate → final waste form	--	1.52	1.17 (packed) / 1.77 (loose)

[a] The expansion factors apply to the feed settled sludge for sludge plus supernatant water formulations; water (e.g., from supernatant solution) still required for grouted waste formulation.
[b] The expansion factors apply to the feed settled sludge for sludge plus supernatant water formulations; the actual expansion factors for sludge-only (supernatant-free) formulations likely are lower and approach 1.17 (packed) / 1.77 (loose). Testing is required to confirm this behavior.

Attachment 1

February 2004
Update to Alternatives Comparison Tables

Revised Appendix D (KE NLOP Chemical/Radiochemical Characterization)

Revised versions of Tables 5.4 through 5.8 and Appendix D provided additional chemical/radiochemical characterization, and analyses and X-ray diffractometry information not available earlier.

Values highlighted in yellow denote changes and/or new information.

Table 5.4. Comparison of Grouted Waste Form Within 55-Gallon Drum with Treated-Waste Constraints (8 vol% settled sludge loading)

Constraint			Value for TBD Alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	55-Gallon Drum with rigid liner and liner lid
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per standard pipe overpack (SPO) with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack. • 1,000 pounds per 55-gallon drum.	TRAMPAC	820 lb (includes 77 lbs for drum and liner)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and liner.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly-generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.4 (Contd)

Constraint			Value for TBD Alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 inch) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E)
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.011 W/drum (Based on KE NLOP Safety Basis Composition)[a]

Table 5.4 (Contd)

Constraint			Value for TBD Alternative
Radiological/Nuclear Properties			
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	3.7 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]
	A payload container shall be acceptable for transport only if the ^{239}Pu FGE plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	0.16 DE-Ci/drum (KE NLOP Safety Basis Composition)[b]
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	190 nCi/g [Based on total alpha analysis of KE NLOP Comp] [Safety Basin KE NLOP composition will give 3X higher value.]

Table 5.4 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Curie Content	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	0.16 PE-Ci/drum (Based on KE NLOP Safety Basis Composition)[b]
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 cm (1 ft) from the waste package.	HNF-EP-0063	
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	180 mrem/h [Based on modeling.]
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, a determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package	TRAMPAC	0.011 W/drum (Based on KE NLOP Safety Basis Composition)[a] [Appendix E discusses hydrogen generation from chemical reactions.]

Table 5.4 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Hydrogen Generation	It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits).	TRAMPAC	0.011 W/drum (Based on KE NLOP Safety Basis Composition)[a] Appendix E discusses hydrogen generation from chemical reactions.
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay-heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC	
Pressure	The gases generated in the payload and released into the Inner Containment Vessel (ICV) cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC	

(a) AJ Schmidt and RB Baker. 2004a "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.

(b) AJ Schmidt and RB Baker. 2004b "Revised Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT03 (January 27, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 27, 2004, via transmittal letter 46497-L04.

Table 5.5. Comparison of Grouted Waste Form Within Pipe Overpack Container Packaged Within 55-Gallon Drum with Treated-Waste Constraints (37 vol% settled sludge loading)

Constraint			Value for TBD alternative
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	SPO within a 55-gallon drum
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four direct loaded 55-gallon drums, or containing one bin • TDOPs, either containing up to 10 directly loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC	
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC	500 lb (includes 332 lb for pipe component and drum)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; waste material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and pipe component. For suboptions using billet cans, the can will be cross-taped and placed in vented (filtered) bags.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from the waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 in.) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E)
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC	
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.012 W/drum (Based on KE NLOP Safety Basis Composition)[a]
Fissile Content	The fissile and fissionable-material content of a package is limited dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	4.2 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 g for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	4.2 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	0.18 DE-Ci/drum (KE NLOP Safety Basis Composition)[b]
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	900 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	0.18 PE-Ci/drum (Based on KE NLOP Safety Basis Composition)[b]

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063	
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	150 mrem/h (Based on modeling.)
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, a determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32°F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.012 W/drum (Based on KE NLOP Safety Basis Composition)[a] [Appendix E discusses hydrogen generation from chemical reactions.]

Table 5.5 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a one-year period.	TRAMPAC	

(a) AJ Schmidt and RB Baker. 2004a "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit." PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.

(b) AJ Schmidt and RB Baker. 2004b "Revised Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit." PNNL letter report 46497-RPT03 (January 27, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 27, 2004, via transmittal letter 46497-L04.

Table 5.6. Comparison of Polymer Sorbent Solidified Waste Form Within 55-Gallon Drum with Treated-Waste Constraints (5 vol% settled-sludge loading)

Constraint			**Value for TBD alternative**
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	55-gallon drum with rigid liner and liner lid.
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-inch diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum	TRAMPAC	470 lb (includes 77 lbs for drum and liner)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and liner.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly-generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 in.) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate settled sludge contains << 1% U metal (Appendix E).
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.0068 W/drum (Based on KE NLOP Safety Basis Composition)[a]
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGE). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	2.3 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	2.3 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	0.10 DE-Ci/drum (KE NLOP Safety Basis Composition)[b]
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	230 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	0.10 PE-Ci/drum (Based on KE NLOP Safety Basis Composition)[b]

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063	
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	190 mrem/h (Based on modeling).
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.0068 W/drum (Based on KE NLOP Safety Basis Composition)[a] (Appendix E discusses hydrogen generation from chemical reactions.)

Table 5.6 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible).	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a one-year period.	TRAMPAC	

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(b) AJ Schmidt and RB Baker. 2004b "Revised Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit." PNNL letter report 46497-RPT03 (January 27, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 27, 2004, via transmittal letter 46497-L04.

Table 5.7. Comparison of Polymer Sorbent Solidified Waste Form Within Pipe Overpack Container Packaged Within 55-Gallon Drum with Treated-Waste Constraints (23 vol% settled-sludge loading)

Constraint			**Value for TBD alternative**
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	SPO within a 55-gallon drum.
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four direct loaded 55-gallon drums, or containing one bin. • TDOPs, either containing up to ten direct loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC	
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-in.-diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC	420 lb (includes 332 lb for pipe component and drum)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and pipe component (and bags if billet cans are used).
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly-generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 1 inch or 2.5 cm in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E).
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC	
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.0076 W/drum (Based on KE NLOP Safety Basis Composition)[a]
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGEs). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	2.6 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	0.11 DE-Ci/drum (KE NLOP Safety Basis Composition)[b]
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	1,100 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to $\leq$1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to $\leq$80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	0.11 PE-Ci/drum (KE NLOP Safety Basis Composition)[b]

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 centimeters (1 foot) from the waste package.	HNF-EP-0063	
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	160 mrem/h (Based on modeling.)
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, a determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32^{o}F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.0076 W/drum (Based on KE NLOP Safety Basis Composition)[a] (Appendix E discusses hydrogen generation from chemical reactions.)

Table 5.7 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible)	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC	

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(b) AJ Schmidt and RB Baker. 2004b "Revised Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit." PNNL letter report 46497-RPT03 (January 27, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 27, 2004, via transmittal letter 46497-L04.

Table 5.8. Comparison of Dewatered Sludge in S200-B Shielded Pipe Overpack Container Packaged Within 55-Gallon Drum with Treated-Waste Constraints (200 vol% settled sludge loading)

Constraint			**Value for TBD alternative**
Container/Packaging Properties			
Container Types	Only the following payload containers are authorized for shipment in the TRUPACT-II (see Appendix 2.1 of the TRAMPAC document): • 55-Gallon Drum • 100-Gallon Drum • Standard Waste Box (SWB) • Ten-Drum Overpack (TDOP).	TRAMPAC	S200-B shielded pipe overpack container within 55-gallon drum.
	Only the following containers are authorized for disposal as CH-TRU at WIPP: • 55-Gallon Drums (either direct loaded or containing a pipe component) • SWBs, either direct loaded, or containing up to four direct loaded 55-gallon drums, or containing one bin. • TDOPs, either containing up to ten direct loaded 55-gallon drums, six 85-gallon drum overpacks, or one SWB.	WIPP CH-TRU WAC	
Container Weights	Each payload container and payload assembly shall comply with the following weight limits: <u>Container Weights</u> • 547 pounds per SPO with 12-inch diameter pipe component • 547 pounds per S200 pipe overpack • 1,000 pounds per 55-gallon drum.	TRAMPAC	530 lb (includes 497 lb for pipe components, shielding, dunnage, and drum)
Sealed Containers	Sealed containers that are greater than 4 L (nominal) are prohibited except for Waste Material Type II.2 packaged in a metal container; Waste Material Type II.2 in metal cans does not generate any flammable gas. For this evaluation, no sealed containers will be allowed.	TRAMPAC	No sealed packages. WIPP-compliant filters will be used on drum and shield assembly.
Filter Vents	Vents or other mechanisms to prevent pressurization of containers or generation of flammable or explosive concentrations of gases shall be installed on containers of newly generated TRU waste at the time the waste is packaged (DOE M 435.1-1, Chapter III, L.1.b.).	HNF-EP-0063	
	Each payload container to be transported in the TRUPACT-II, including all payload containers that are overpacked in other payload containers, shall have one or more filter vents that meet the TRAMPAC specifications. Plastic bags used as confinement layers shall meet the specifications and usage requirements of the TRAMPAC.	TRAMPAC	

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Physical Properties			
Liquid Waste	Liquid waste is prohibited in the payload containers, except for residual amounts in well-drained containers. The total volume of residual liquid in a payload container shall be less than 1 percent (volume) of the payload container.	TRAMPAC	Observations and measurements performed during the bench-scale waste-form testing (Appendix F) demonstrated that no free liquids were released from waste form.
	Liquid waste is prohibited at WIPP. Waste shall contain as little residual liquid as is reasonably achievable by pouring, pumping, and/or aspirating. Internal containers shall also contain no more than 2.5 cm (1 in.) in the bottom of the internal containers. The total residual liquid in any payload container shall not exceed 1 percent by volume of that payload container. If visual examination methods are used in lieu of radiography, then the detection of any liquids in non-transparent internal containers will be addressed by using the total volume of the internal container when determining the total volume of liquids within the payload container.	WIPP CH-TRU WAC	
Chemical Properties			
Pyrophoric Materials	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent [weight]) in payload containers. Radioactive pyrophorics in concentrations greater than 1 percent by weight and all nonradioactive pyrophorics shall be reacted (or oxidized) and/or otherwise rendered nonreactive before placement in the payload container.	TRAMPAC	Initial tests indicate that settled sludge contains <<1% U metal (Appendix E).
	Pyrophoric radioactive materials shall be present only in small residual amounts (<1 percent by weight) in payload containers and shall be generally dispersed in the waste.	WIPP CH-TRU WAC	
Radiological/Nuclear Properties			
Decay Heat	If heat generation from radiological decay in the waste package exceeds 3.5 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers in storage. This evaluation must be provided to and approved by the WMP acceptance organization.	HNF-EP-0063	0.017 W/drum (Based on KE NLOP Safety Basis Composition)[(a)]
Fissile Content	The fissile and fissionable-material content of a package is limited, dependent upon the container and its contents. For 55-gallon or larger steel drums where fissile material is contained in 20% or more of the container volume, the fissionable-material content is limited to 177 fissile gram equivalents (FGE). For 55-gallon or larger steel drums where fissile material is contained in less than 20% of the container volume, the fissionable-material content is limited to 100 FGEs. Limits for other containers are provided in Appendix B of HNF-EP-0063.	HNF-EP-0063	5.7 g FGE/drum (Based on KE NLOP Safety Basis Composition)[(a)]

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Fissile Content	A payload container shall be acceptable for transport only if the ^{239}Pu fissile gram equivalent (FGE) plus two times the measurement error (i.e., two standard deviations) is less than or equal to 200 grams for a 55-gallon drum, a SPO, and an S200 pipe overpack. Note: If a payload container will be overpacked, FGE limits apply only to the outermost payload container of the overpacked configuration.	TRAMPAC	5.7 g FGE/drum (Based on KE NLOP Safety Basis Composition)[a]
Curie Content	Up to 35 DE-Ci per container are acceptable at the CWC as a routine shipment. Quantities up to 150 DE-Ci per container can be accepted, but must be evaluated to ensure compliance with facility inventory limits (HNF-SD-WM-ISB-007).	HNF-EP-0063	0.25 DE-Ci/drum (KE NLOP Safety Basis Composition)[b]
	S200 pipe overpack payloads shall meet the package specific curie limits in the TRAMPAC (see Appendices 2.3 and 2.4, respectively).	TRAMPAC	
	TRU waste payload containers shall contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years. Without taking into consideration the TMU, the TRU alpha activity concentration for a payload container is determined by dividing the TRU alpha activity of the waste by the weight of the waste. The weight of the waste is the weight of the material placed into the payload container (i.e., the net weight of the container). The weight of the waste is typically determined by subtracting the tare weight of the payload container (including the weight of the rigid liner and any shielding external from the waste, if applicable) from the gross weight of the payload container.	WIPP CH-TRU WAC	6,200 nCi/g (Based on total alpha analysis of KE NLOP Comp) (Safety Basis KE NLOP composition will give 3X higher value.)
	Plutonium-239 equivalent curie (PE-Ci) is limited for waste containers and packaging configurations • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤80 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of solidified/vitrified waste forms is limited to ≤1,800 ^{239}Pu PE-Ci. • 55-gallon drum in good condition, direct load of all approved waste forms is limited to ≤80 ^{239}Pu PE-Ci. Other waste containers and packaging configurations have other limits. Refer to WIPP CH-TRU WAC.	WIPP CH-TRU WAC	0.25 PE-Ci/drum (KE NLOP Safety Basis Composition)[b]

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Radiological/Nuclear Properties			
Radiation Dose Equivalent Rate	Waste packages shall not exceed 1 milliSievert per hour (100 millirem per hour) at 30 cm (1 ft) from the waste package.	HNF-EP-0063	
	Waste packages shall not exceed 2 milliSieverts per hour (200 millirem per hour) at any point on the surface of the package.	HNF-EP-0063	55 mrem/h (Based on modeling.)
Gas-Generation Properties			
Hydrogen Generation	For any package containing water and/or organic substances that could radiolytically generate combustible gases, determination must be made by tests and measurements or by analysis of a representative package such that the following criterion is met over a period of time that is twice the expected shipment time: The hydrogen generated must be limited to a molar quantity that would be no more than 5 percent by volume of the innermost layer of confinement (or equivalent limits for other inflammable gases) if present at standard temperature and pressure (STP) (i.e., no more than 0.063 gram-moles/cubic foot at 14.7 pounds per square inch absolute and 32°F). Compliance with this requirement can be achieved by assuring that decay heat limits for each payload container are not exceeded. Per discussions with WIPP personnel during their visit to Hanford on December 16, 2004, the appropriate decay heat limits are as follows: Grout – 0.8800 watt/package Dewatered Sludge – 0.2708 watt/package Nochar – 0.1035 watt/package It should be noted that decay heat limits are dependent on the properties of the waste-form and packaging configuration; the above values are based on treated waste that is packaged in slip-lid cans that are placed within filtered bags in a SPO. These values will bound the decay heat limits for each of the three waste-form options (the other packaging configurations considered in this study—direct loading into a drum, SPO, or S200-B Pipe Overpack—would allow for higher heat limits)	TRAMPAC	0.017 W/drum (Based on KE NLOP Safety Basis Composition)[a] (Appendix E discusses hydrogen generation from chemical reactions.)

Table 5.8 (Contd)

Constraint			Value for TBD alternative
Gas-Generation Properties			
VOCs	TRU wastes to be transported in the TRUPACT-II are restricted so that no flammable mixtures can occur in any layer of confinement during shipment. While the predominant flammable gas of concern is hydrogen, the presence of methane and flammable VOCs is also limited along with hydrogen to ensure the absence of flammable (gas/VOC) mixtures in TRU waste payloads. Only payload containers (analytical category or test category) that meet the flammable (gas/VOC) limits based on the determinations for compliance with the flammable (gas/VOC) limits are eligible for shipment in the TRUPACT-II. Under the analytical category, a conservative analysis is used to impose decay heat limits on individual payload containers to ensure that flammable (gas/VOC) limits are met. Specifically, flammable VOCs are restricted to less than or equal to 500 parts per million (ppm) in the payload container headspace (to ensure that their contribution to flammability is negligible).	TRAMPAC	
Pressure	The gases generated in the payload and released into the ICV cavity shall be controlled to maintain the pressure within the TRUPACT-II ICV cavity below the acceptable design pressure of 50 pounds per square inch gauge (psig). All payloads authorized for transport in the TRUPACT-II will comply with the design pressure limit for a 1-year period.	TRAMPAC	

(a) AJ Schmidt and RB Baker. 2004a "Updated Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT02 (January 12, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 12, 2004, via transmittal letter 46497-L03.

(b) AJ Schmidt and RB Baker. 2004b "Revised Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit," PNNL letter report 46497-RPT03 (January 27, 2004), transmitted to WW Rutherford (FH) and JP Sloughter (NHC) by K. L. Silvers (PNNL) on January 27, 2004, via transmittal letter 46497-L04.

References

HNF-EP-0063, *Hanford Site Solid Waste Acceptance Criteria*, Rev. 9, Fluor Hanford Inc., Richland, Washington, September 2003.

TRAMPAC, *TRUPACT-II Authorized Methods for Payload Control*, Rev. 19c, Washington TRU Solutions, LLC, Carlsbad, New Mexico, April 2003.

WIPP CH-TRU WAC, DOE/WIPP-02-3122, *Contact-Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, Rev 0.1, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico, July 2002.

Appendix D

Revised Appendix D (KE NLOP Chemical/Radiochemical Characterization)

Chemical and radiochemical analyses of the settled sludge and of the supernatant solution were measured in the glovebox of Room 528 and in the Analytical Services Operations (ASO) of the 325 Laboratory. The samplings for analysis and pH measurements were conducted under the Test Instruction 46857-TI02, "Preparation of KE NLOP Composites and Samples." The sample preparation digestions and subsequent chemical and radiochemical analyses were performed according to the general directions in the Test Plan ("Bench-Scale Test Plan to demonstrate production of WIPP-Acceptable KE NLOP Sludge Waste Forms at the 325 Building") and under the specific procedures outlined in Table D.1.

Table D.1. Analytical Procedure Listing

Sample Prep.	Analyte	Procedure Title	Procedure Number
As rec'd.	pH	Test Instruction	TI 46857-TI02
As rec'd.; 2.0-ml aliquots	Density, ρ	Test Instruction	TI 46857-TI02
	GEA	Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)	RPG-CMC-450
As rec'd.; 15-g aliquots	H_2O	Water Determination by Weight Loss on Drying	PNL-ALO-504
Sample residue from H_2O analyses fused and dissolved in acid; Solubilization of Metals from Solids Using Pyrosulfate Fusion (Test Plan) and KOH-KNO_3 Fusion, PNL-ALO-115 Sample supernate, received only a dilution for applicable analyses.	GEA	Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)	RPG-CMC-450
	Pu	Pu and Am/Cm derived from the Alpha AEA results.	RPG-CMC-422
	Am/Cm		
	Pu	Separation of Uranium and Plutonium for Isotopic Analysis by Mass Spectrometry	RPG-CMC-455
	$^{90}Sr/Y$	$^{90}Sr/Y$ is inferred based on results of the GEA and Total Beta	N/A
	U by KPA	Uranium by Kinetic Phosphorescence Analysis	RPG-CMC-4014
	AT	Total Alpha and Beta Analysis	RPG-CMC-408
	AEA	Solutions Analysis: Alpha Spectrometry	RPG-CMC-422

<u>pH Measurements</u>

The pH measurements were performed using a Corning wand-type pH meter. The meter was calibrated using fresh buffer solutions and the check measurements of pH 4.00, 7.00, and 10.00 buffers were within 0.04 pH units of the target value. The pH of the supernatant solutions from combined samples KE-20-A and -B (in vessel KE-20-A), KE-20-D and -E (in vessel KE-20-D), KE-20-G and -H (in KE-20-G), and KE-20-AD and -BD (in KE-20-AD) were measured. The pH of the composite KE NLOP sludge also was measured. The pH values, summarized in Table D.2, vary over about 0.8 pH units for the supernatant solutions. The relatively large pH span likely is because ion exchange purification of the supernatant waters removed all buffering ions. The settled sludge pH of 8.31 is similar to the pH 8.3 value observed for FE-3, a prior composite KE NLOP sludge. In contrast with the unbuffered KE NLOP supernatant solution, the mineral solid-in-water KE NLOP sludge can maintain stable pH-buffered conditions by hydrogen ion (H^+) exchange on the hydrous solids' surfaces.

Table D.2. Solution and Settled Sludge pH

Sample	Measured pH
pH 4.00 buffer	4.03
pH 7.00 buffer	7.01
pH 10.00 buffer	10.04
KE-20-A	7.60
KE-20-D	7.16
KE-20-G	7.95
KE-20-AD	7.36
KE NLOP Sludge	8.31

Sampling for Chemical and Radiochemical Analyses

Four samples were retrieved for priority chemical and radiochemical analyses. Three of the samples were taken from the composited settled KE NLOP sludge and one sample was supernatant solution taken from vessel KE-20-A. In addition, duplicate sludge samples were taken from the KE-20-A and -B, -D and -E, -G and -H, and -AD and -BD interim sludge composites (see Appendix B on the collection of the intermediate sludge layers). The sample sources, subsample names, and subsample quantities are shown in Table D.3. Accurately measured sample volumes (10.0 or 2.0 ml) were delivered to sample vials by adding increments of well-mixed sludge or supernatant solution into tare-weighed plastic volume-calibrated syringes.[a] The syringes were discharged into the tare-weighed sample vials and the syringes re-weighed to determine, by difference, the delivered weights. The weights of the sample vials subsequently were reweighed on a more sensitive balance; the latter weights are reported in Table D.3.

[a] To prepare the measuring syringes, the ends of the barrels of ordinary plastic 10-ml and 5-ml syringes were cut off and the cut ends beveled smooth. The respective 10-ml and 2-ml levels were calibrated by adding 10.0 or 2.00 grams of water (density of 1.00 g/ml) to the open end-up syringes with the plungers withdrawn up the syringe barrel. After addition of the precise water mass, the plungers were pushed upwards until the water level reached the open syringe end. The plunger position at that point was marked to show the 10.0 or 2.0 ml levels. The sludge was added to the tare-weighed end-up syringes (with plungers at the set 2.0 or 10.0 ml marks) to the upper level and the syringes re-weighed. The loaded syringes then were discharged into the sample vials. The syringes prepared this way were capable of discharging nearly all of the sludge contents for subsample preparation and left little residual sludge behind in the syringe. Any residual sludge was measured by re-weighing the emptied syringe.

Table D.3. Chemical and Radiochemical Sample Aliquots

Source	Sample Identification	Sample Quantity	
		ml	g
KE NLOP Composite	KENLOP-1 [a]	10.0	12.088
	KENLOP-A [a]	2.0	2.395
	KENLOP-B [a]	2.0	2.426
Supernatant from KE-20-A &-B	KENLOP-Liq [a]	2.0	1.96
Sludge from KE-20-A & -B	KENLOP-AB1	2.0	1.9914
	KENLOP-AB2	2.0	2.0007
Sludge from KE-20-D & -E	KENLOP-DE1	2.0	2.1697
	KENLOP-DE2	2.0	2.1521
Sludge from KE-20-G & -H	KENLOP-GH1	2.0	2.3722
	KENLOP-GH2	2.0	2.5165
Sludge from KE-20-AD & -BD	KENLOP-DS1	2.0	1.9762
	KENLOP-DS2	2.0	1.9886
[a] Samples for priority analysis.			

Chemical and Radiochemical Analyses and Results

Chemical and radiochemical analyses were performed for the subsamples shown in Table D.3. The highest priority was accorded to the KENLOP-1, KENLOP-A, and KENLOP-B composite sludge and KENLOP-Liq supernatant solution subsamples. The results presented here are confined to the findings for these four priority subsamples.

The first step in the analytical sequence was to perform gamma energy analyses (GEA) of the intact subsamples. The as-prepared subsample geometries met the set geometries needed for GEA.

Three accurately weighed ~1-gram portions then were drawn from subsample KENLOP-1 and were dried to constant weight in a 105°C oven. The weight loss at 105°C was ascribed to water. After drying, one portion was reserved for X-ray diffractometry. The XRD analysis found only one identifiable phase, quartz, SiO_2, though several other lines were present. Attempts to fit these lines to uranium phases found previously in K Basin sludge [uraninite, UO_2; U_3O_8; schoepite and metaschoepite, $(UO_2)_8O_2(OH)_{12}(H_2O)_{12}$ and $(UO_2)_8O_2(OH)_{12}(H_2O)_{10}$; becquerelite, $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$; studtite and metastudtite, $UO_4{\cdot}4H_2O$ and $UO_4{\cdot}2H_2O$] were not successful. Likewise, the phases hematite and goethite (Fe_2O_3 and FeOOH), the $Al(OH)_3$ allomorphs (gibbsite, bayerite, or nordstrandite), and calcite ($CaCO_3$) did not fit the unassigned lines.

The other two dried portions underwent sequential digestions in acid (mixed nitric/hydrochloric), fusion of the acid digest residue in potassium pyrosulfate ($K_2S_2O_7$), and fusion of the potassium pyrosulfate residue in potassium hydroxide (KOH) according to established ASO procedures (Table D.1). A small residue remained after the final (KOH) fusion. The residue was counted and found to contain relatively minor remaining activity (Table D.4).

Aliquots from each of the acid digestates were analyzed for total beta activity, total alpha activity, activity analyses of isotopes by their alpha energies (alpha energy analysis or AEA), and uranium (by kinetic phosphorescence). The primary alpha energy peaks registered by AEA are due to $^{239,240}Pu$ and ^{238}Pu,^{241}Am with lesser activity due to $^{243,244}Cm$. Because the digestates from the $K_2S_2O_7$ and KOH fusions are not amenable to direct total alpha and AEA, they were analyzed for plutonium using a plutonium-specific separation followed by AEA counting. The supernatant solution (KENLOP-Liq) was analyzed for total beta activity, total alpha activity, AEA, and uranium.

The weight-based analyte concentrations in the acid and two fusion digests of the composite settled sludge were summed to determine the total concentrations of the respective analytes. Note that the ^{90}Sr results are calculated to be half of the difference between the respective total beta and summed GEA values. This calculation is based on the reasonable assumption that the difference in these two activities for well-aged fuel is due largely to the $^{90}Sr/Y$ couple. However, the calculated difference of these two comparable independently measured values results in intrinsically large relative error for the ^{90}Sr concentrations. More reliable analyses for ^{90}Sr involving preliminary strontium-specific extraction and counting are underway. The results of the individual analyses for the acid and two fusion digests are presented in Table D.4.

Table D.4. Analytical Results for KE NLOP Sludge Digests

Analyte	Concentration, µCi/g settled sludge					
	KENLOP-1, Rep-1			KENLOP-1, Rep-2		
	Acid	$K_2S_2O_7$	KOH	Acid	$K_2S_2O_7$	KOH
$^{239,240}Pu$	1.72E+0	4.98E-4	3.65E-5	1.79E+0	4.15E-4	3.46E-5
^{238}Pu,^{241}Am	1.59E+0	4.74E-5 [a]	4.11E-6 [a]	1.74E+0	3.64E-5 [a]	4.30E-6 [a]
$^{243,244}Cm$	3.64E-3	NA	NA	4.22E-3	NA	NA
Total Alpha	3.75E+0	9.88E-4 [b]	4.06E-5 [b]	3.69E+0	4.51E-4 [b]	3.89E-5 [b]
Total Beta	1.13E+1	1.07E-1	2.87E-2 [c]	1.10E+1	8.54E-2	2.36E-2 [c]
^{90}Sr [c]	7.81E-1	0	7.18E-3	9.60E-1	2.55E-3	3.75E-3
Uranium, µg/g	5.68E+3	6.00E-1	NA	5.33E+3	3.60E-1	NA
^{60}Co	5.80E-2	3.63E-3	1.28E-5 [d]	5.66E-2	2.90E-3	1.41E-5 [d]
^{137}Cs	7.77E+0	1.02E-1	1.38E-2 [d]	7.32E+0	7.66E-2	1.56E-2 [d]
^{154}Eu	1.11E-1	<6E-5	<2E-5 [d]	1.08E-1	<4E-5	<2E-5 [d]
^{155}Eu	2.84E-2	<2E-4	<5E-5 [d]	2.60E-2	<2E-4	<5E-5 [d]
^{241}Am	1.77E+0	6.08E-4	<9E-5 [d]	1.57E+0	<4E-4	<2E-4 [d]
^{125}Sb	<2E-2	9.05E-4	4.75E-4 [d]	<2E-2	8.05E-4	4.79E-4 [d]
Sum gamma	9.74E+0	1.07E-1	1.43E-2	9.08E+0	8.03E-2	1.61E-2

[a] ^{238}Pu only.
[b] Sum of $^{238,239,240}Pu$ and ^{241}Am.
[c] 1.46×10^{-4} and 7.90×10^{-5} µCi beta/g settled sludge in residues of Rep-1 and Rep-2, respectively. ^{90}Sr is inferred to be half of the difference between the total beta activity and the sum of the gamma activities. The other half of the activity difference is taken to be due to ^{90}Y. More reliable analyses for ^{90}Sr are underway.
[d] In $K_2S_2O_7$ fusion residues.
NA indicates fractions that were not analyzed for the given analyte. As shown in the acid digest, $^{243,244}Cm$ is expected to be low in these digestates compared with the other transuranics, Pu and Am. Uranium analyses are forthcoming.

The overall results of the sample analyses are shown in Table D.5. The following general observations may be drawn from these data:

- ^{137}Cs dominates the high energy gamma activity in the sludge; ^{60}Co also provides much of the high energy gamma radiation.

- The dry sludge is 1.46 wt% total uranium; settled sludge contains 0.55 wt% total uranium.

- Though the solution comprises nearly ⅔ of the settled sludge mass, it contains very little of the radioactivity or uranium.

- The settled sludge is transuranic with total alpha activity of 3720 nCi/g or 37-times the TRU limit of 100 nCi/g.

- The uranium and the analyzed radionuclides (which are primarily ^{60}Co, ^{90}Sr, ^{137}Cs, ^{238}Pu, $^{239,240}Pu$, and ^{241}Am) partition overwhelmingly to the solid phase. Therefore, the low-activity interstitial and supernatant solution may practically be considered a pure diluent, contributing negligible activity to the total sludge. As a consequence, the addition or removal of the supernatant solution during sludge processing will correspondingly decrease or increase the activity concentrations in the total sludge.

Minimum detection limits (MDLs) also are reported for ^{95}Nb, $^{106}Ru/Rh$, ^{134}Cs, $^{144}Ce/Pr$, ^{152}Eu, ^{208}Tl, ^{212}Bi, and ^{228}Ra for the as-received KE NLOP sludge, the supernatant liquid, and the digestates. All of these radionuclides are measured by gamma energy analysis. The MDLs are presented in Table D.6.

Table D.5. Analytical Results for KE NLOP Sludge and Supernatant Solution

Analyte	Concentration, µCi/g									Settled Sludge Concentration, µCi/ml [b]	% of Analyte in Solids [c]
	Settled Sludge					Solution			Sludge Solids [a]		
	KENLOP-1		KENLOP-A	KENLOP-B	Avg.	KENLOP-Liq		Avg.			
^{60}Co	7.00E-2		6.83E-2	6.43E-2	6.75E-2	2.33E-5		2.33E-5	1.79E-1	8.37E-2	99.98
^{137}Cs	7.81E+0		5.72E+0	7.07E+0	6.87E+0	4.09E-2		4.09E-2	1.82E+1	8.52E+0	99.63
^{154}Eu	1.32E-1		1.31E-1	1.20E-1	1.28E-1	<3.E-5		3.00E-5	3.39E-1	1.58E-1	>99.99
^{155}Eu	3.04E-2		3.37E-2	3.35E-2	3.25E-2	<2.E-4		1.50E-4	8.61E-2	4.03E-2	>99.71
^{241}Am	1.77E+0		1.67E+0	1.53E+0	1.66E+0	<4.E-4		4.00E-4	4.40E+0	2.06E+0	>99.98
	Rep-1	**Rep-2**			**Avg.**	**Rep-1**	**Rep-2**	**Avg.**			
^{239,240}Pu	1.72E+0	1.79E+0			1.76E+0	1.47E-4	1.36E-4	1.42E-04	4.66E+0	2.18E+0	99.99
^{238}Pu,^{241}Am	1.59E+0	1.74E+0			1.67E+0	1.32E-4	1.20E-4	1.26E-04	4.42E+0	2.06E+0	100.00
^{243,244}Cm	3.64E-3	4.22E-3			3.93E-3	<5.E-7	<4.E-7	<5.E-7	1.04E-2	4.87E-3	>99.99
Total Alpha	3.75E+0	3.69E+0			3.72E+0	2.92E-4	2.76E-4	2.84E-04	9.87E+0	4.61E+0	100.00
Total Beta	1.14E+1	1.11E+1			1.12E+1	5.27E-2	5.22E-2	5.25E-02	2.98E+1	1.40E+1	99.71
^{90}Sr [d]	7.88E-1	9.66E-1			8.77E-1	5.90E-3	5.60E-3	5.75E-03	2.32E+0	1.09E+0	99.59
Other Analytes											
U	5.68E+3, µg/g	5.33E+3, µg/g			5.51E+3, µg/g	1.64E+1, µg/g	1.66E+1, µg/g	1.65E+1, µg/g	1.46E+4, µg/g	6.83E+3, µg/ml	99.81
Water, wt%	61.71	62.90			62.3						0.00

[a] Analyte concentrations in the sludge solids were determined by deducting the mass and analyte contributions of the solution from the respective settled sludge mass and analyte quantities. For example, there is 6.75×10^{-2} µCi ^{60}Co in one gram of settled sludge. One gram of settled sludge also contains 0.623 g of solution (settled sludge is 62.3 wt% water). The 0.623 g of solution contains ^{60}Co in the amount 0.623 g × 2.33×10^{-5} µCi ^{60}Co/g = 1.45×10^{-5} µCi ^{60}Co. The concentration of ^{60}Co in the sludge solids (0.377 g) in 1 gram of settled sludge is (6.75×10^{-2} µCi - 1.45×10^{-5} µCi) / 0.377 g = 1.79×10^{-5} µCi ^{60}Co/g.

[b] The settled sludge concentration in µCi/ml is calculated by multiplying the concentration, in µCi/g, by the settled sludge density of 1.24 g/ml.

[c] The percentage of analyte in the sludge solids was determined by deducting the contribution of the analyte found in the solution associated with the settled sludge from the total analyte found in the same quantity of settled sludge, dividing by the analyte quantity in the settled sludge, and multiplying by 100%. For example, as shown in footnote [a] above, one gram of settled sludge contains 6.75×10^{-2} µCi ^{60}Co and the associated solution contains 1.45×10^{-5} µCi ^{60}Co. The sludge solids therefore contain 100% × (6.75×10^{-2} µCi ^{60}Co - 1.45×10^{-5} µCi ^{60}Co)/ 6.75×10^{-2} µCi ^{60}Co = 99.98% of the ^{60}Co.

[d] ^{90}Sr is inferred to be half of the difference between the total beta activity and the sum of the gamma activity. The other half of the activity difference is taken to be due to ^{90}Y. Because the total beta and sum of gamma activities are of similar magnitude, their difference has a relatively large error. Radiochemical separation and analysis for ^{90}Sr are underway to provide more reliable values.

Table D.6. Analytical Minimum Detection Limits for KE NLOP Sludge and Supernatant Solution

	Concentration, µCi/g [a]											
					KENLOP 1, Rep 1				KENLOP 1, Rep 2			
					Acid		$K_2S_2O_7$		Acid		$K_2S_2O_7$	
Analyte	**KENLOP-1**	**KENLOP-A**	**KENLOP-B**	**KENLOP-Liq**	**Digestate**	**Residue**	**Digestate**	**Residue**	**Digestate**	**Residue**	**Digestate**	**Residue**
^{95}Nb	<2.E-3	<2.E-3	<2.E-3	<8.E-6	<9.E-4	<7.E-5	<8.E-5	<6.E-6	<8.E-4	<1.E-4	<8.E-5	<5.E-6
^{106}Ru/Rh	<3.E-2	<3.E-2	<3.E-2	<3.E-4	<3.E-2	<2.E-3	<2.E-3	<1.E-4	<3.E-2	<2.E-3	<1.E-3	<1.E-4
^{134}Cs	<2.E-3	<2.E-3	<2.E-3	<9.E-6	<1.E-3	<8.E-5	<1.E-4	<7.E-6	<1.E-3	<2.E-4	<9.E-5	<6.E-6
^{144}Ce/Pr	<3.E-2	<3.E-2	<3.E-2	<3.E-4	<2.E-2	<2.E-3	<8.E-4	<8.E-5	<2.E-2	<2.E-3	<9.E-4	<9.E-5
^{152}Eu	<3.E-3	<3.E-3	<3.E-3	<5.E-5	<2.E-3	<3.E-4	<4.E-4	<3.E-5	<2.E-3	<4.E-4	<3.E-4	<3.E-5
^{208}Tl	<1.E-2	<9.E-3	<1.E-2	<1.E-4	<8.E-3	<4.E-4	<4.E-4	<4.E-5	<8.E-3	<5.E-4	<4.E-4	<4.E-5
^{212}Bi	<2.E-2	<2.E-2	<2.E-2	<1.E-4	<2.E-2	<1.E-3	<2.E-3	<9.E-5	<2.E-2	<1.E-3	<1.E-3	<8.E-5
^{226}Ra	<1.E-2	<1.E-2	<2.E-2	<1.E-4	<9.E-3	<5.E-4	<4.E-4	<4.E-5	<8.E-3	<7.E-4	<4.E-4	<4.E-5

[a] Concentration in µCi per gram of starting settled sludge or per gram of liquid for the sample KENLOP-Liq.

Attachment 2

May 2004
Revised Appendix E (Gas Generation/U Metal Determination Testing)

Revised Appendix E provides an updated assessment of the uranium metal contents of the KE NLOP sludge based on the gas generation behavior. The results provided in the January 2004 report covered only the first 111 hours of gas generation testing and did not include an estimate of the uranium metal concentration. The results of further testing, which continued for approximately 1000 hours, are included here, along with the estimated U metal concentration.

Appendix E

Updated

Results of Gas-Generation Testing

E.1 Overview

Experimental measurements of K Basin sludge reaction rates and gas generation form the technical basis for sludge uranium metal content, uranium metal particle size, and reaction enhancement factor values. Three prior series of gas-generation experiments have been conducted and documented. The first test series (Series I; Delegard et al. 2000) focused on gas generation from KE basin floor and canister sludge. The size-fractionated and unfractionated samples were 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. Mixed and unmixed and fractionated KE canister sludge materials were tested, along with 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 from irradiated metallic uranium fuel particles with and without sludge addition. In each series, sludge samples and irradiated metallic uranium fuel particles were introduced into reaction vessels, and in most cases, the samples were held at a series of controlled temperatures long enough to attain essentially complete oxidation of the uranium metal. In all of these tests, gas samples were taken periodically and the gas compositions analyzed by mass spectrometry.

Because the focus of the SNF Sludge project has changed from an interim storage mission to near-term disposition to WIPP, additional gas-generation tests with sludge from the KE North Load Pit (NLOP) were undertaken. Results of these recent studies with the KE NLOP sludge and with samples of sludge in candidate WIPP disposal forms are summarized in this section.

Current plans call for the retrieval and solidification/stabilization of KE NLOP sludge as Contact Handled (CH) Transuranic (TRU) waste for disposition to WIPP. Near-term disposition of the KE NLOP sludge is predicated upon the sludge being non-pyrophoric and 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 the sludge contained very little uranium metal (i.e., 0.013 wt% -settled sludge basis.

To gain confidence on the low uranium metal content of the NLOP sludge, additional gas-generation testing was undertaken using NLOP sludge collected in December 2003. Three tests with NLOP sludge and its contained water were performed. Two of the tests were run at 95°C and the third at 60°C. The effects of free/drainable water removal from the sludge/water mixture and of solidification matrices (e.g., grout and Nochar®[a]) on the gas-generation rate of the NLOP sludge also were examined. In particular, if significant quantities of uranium metal are present in the sludge, free/drainable water removal or sequestration and solidification media, acting to micro-encapsulate the uranium metal particles, may inhibit the reaction of uranium metal with water.

E.2 Test Objectives

The overall goal for this testing was to collect gas-generation rate and composition data under known conditions to better understand the quantity and reactivity of the metallic uranium present in the KE NLOP sludge. Specific objectives for this testing include:

- Verify that the KE NLOP sludge is non-pyrophoric (i.e., contains less than 1 wt% pyrophoric material); the pyrophoric material most likely present in KE NLOP sludge is uranium metal.
- Estimate the hydrogen generation rate and uranium metal content in KE NLOP sludge.
- Determine the effect of temperature (95°C and 60°C) on the rate and quantity of gas generated by the KE NLOP sludge.
- Determine the effect of free/drainable water removal on the hydrogen generation rate of KE NLOP sludge.
- Determine the effect of a grout matrix on the hydrogen generation rate of KE NLOP sludge.
- Determine the effect of the Nochar® matrix on the hydrogen (and hydrocarbon) generation rate of KE NLOP sludge.

Note that observation of any effects on the uranium metal-water reaction depends on uranium metal being present in the KE NLOP sludge.

The gas generation testing of the KE NLOP sludge sampled in December 2003 was undertaken in light of studies of a prior sample (FE-3) of the KE NLOP sludge. In particular, the gas generation testing was done to compare the results from testing of the December 2003 samples of the KE NLOP with the KE NLOP Design and Safety Basis values[b] for uranium metal concentration derived based on analyses of sample FE-3 (Bryan et al. 2004).

The KE NLOP sludge Design Basis value for uranium metal concentration (0.0057 wt%) was conservatively estimated from gas generation testing results with FE-3 by assuming that the combined H_2 generation (Reaction 1) and O_2 depletion (Reaction 2) could be ascribed to uranium metal oxidation.

(a) Nochar, Inc., manufactures the adsorbent Nochar® Acid-Bond 660 used in the present testing. Nochar, Inc., 8650 Commerce Park Place, Suite K, Indianapolis, IN 46268. Telephone: (317) 613-3046; Fax: (317) 613-3052; E-Mail: nochar@in.net.

(b) AJ Schmidt and RB Baker. "Revised Design and Safety Basis Values for Physical Properties, Radionuclides, and Chemical Composition of Sludge in the KE Basin North Loadout Pit." Letter report 46497-RPT03, Rev. 1, February 24, 2004, to Fluor Hanford Inc., from Pacific Northwest National Laboratory, Richland, WA.

$$U + 2\ H_2O \rightarrow UO_2 + 2\ H_2 \qquad \text{(Rxn. 1)}$$

$$U + O_2 \rightarrow UO_2 \qquad \text{(Rxn. 2)}$$

Crediting all oxygen consumption to reaction with uranium metal was stated to be conservative by Schmidt and Baker (2004) in that, besides Reaction 2, a significant fraction of the O_2 depletion could be due to other phenomena including adsorption on solids and reactions with other chemically reduced species (e.g., UO_2 or organic compounds).

Estimates of uranium metal concentration also can be made based on the quantities of fission product gas (krypton and the more abundant xenon) released by the irradiated metal. For FE-3, however, no xenon (Xe) isotopes were detected in the gas generation tests. The estimated uranium metal concentration of <0.0088 wt% in FE-3 was based on the individual Xe isotope detection limit in the gas phase of 0.0001 mole% and detection of ^{136}Xe, the most abundant of the Xe fission product isotopes.

Other KE Basin samples underwent gas generation testing at the same time as FE-3. In testing FE-4/6, a KE Basin sludge sample collected from the dummy elevator and tech view pit, the first of two gas samples was found to contain observable, and thus quantifiable, Xe isotopes at levels below the default 0.0001 mole% detection limit; the second FE-4/6 sample showed <0.0001 mole% Xe for all isotopes. The Xe isotope analysis from the first gas sample from FE-4/6 was found to correspond to a uranium metal concentration of 0.00519 wt% (Bryan et al. 2004).

The test conditions, sampling, and gas analysis performed on sample FE-4/6 were identical to those for FE-3 and the gas analyses were processed in the same batch. The FE-3 test, however, used a larger mass of material (21.22 g) than the FE-4/6 test (15.87 g). Based on the reasonable assumption that the detection limits for FE-3 should be similar to the quantified values observed for FE-4/6 rather than the default 0.0001 mole% and that the FE-3 sample was larger than the FE-4/6 sample, the Xe fission product gases in FE-3 should have been detected at a level corresponding to less than 0.00519 wt% uranium metal. The failure to detect fission product gas in FE-3, the analysis of the quantification limit, and comparison to the detection level of the companion sample (FE-4/6) were viewed as evidence to support the appropriateness of the Design Basis uranium metal concentration in FE-3 of 0.0057 wt% based on Reactions 1 and 2.

The KE NLOP Safety Basis uranium metal concentration was obtained by multiplying the Nominal (Design Basis) concentration value by a factor of 6. The factor of 6 arose from two adjustments. First, because the FE-3 sample was handled and stored at ambient hot cell temperatures for about 7 to 8 months longer than the material used in prior Gas Generation Series I testing (Delegard et al. 2000), it was estimated that about 75% of the initial uranium metal mass could have reacted. Thus, a correction factor of 4 due to prior reaction could be applied to arrive at the Safety Basis value. Note that this factor of 4 also could have been (but was not) applied to the Design Basis uranium metal concentration. Because the factor is based on the conservative assumption that uranium metal in the sample reacted at the oxygen-free rate during hot cell storage, it only was applied to the Safety Basis value. In addition to potential uranium metal reaction during storage, a second adjustment based on the estimated sample variability of the uranium metal concentration was considered. The estimated variability in assessed uranium concentration was ~50%. With the correction factor of 4 and with a sample variability of 50%, an overall factor of 6 (4 × 1.5) was established as the multiplier for the Safety Basis uranium metal concentration.

E.3 Summary of Test Results

Tests to meet the objectives were initiated on January 9, 2004 in experiments with sludge and its contained water only. Gas generation was observed as pressure increase in the reactor headspaces. The first gas samples were taken on January 14, 2004. Further gas-generation tests with dewatered sludge and grouted waste forms were initiated on January 22, 2004. Gas generation testing of the Nochar® waste form commenced on January 27, 2004. Because the hydrogen gas-generating reaction of uranium metal with water is relatively slow, the full performance of the test specimens was not known at the time of the initial report on January 19, 2004. Tests with sludge and water only were conducted at 95°C to allow estimates of the concentration of uranium metal contained in the sludge. Tests of waste forms and a settled sludge-only control were run at 60°C in accord with WIPP shipping criteria.

Based on the results from the initial test interval (111 hours at 95°C and 60°C) with the sludge and water only tests, the following observations and conclusions were made on January 19, 2004:

- The KE NLOP sludge is highly unlikely to be designated as pyrophoric (i.e., contain more than 1 wt% pyrophoric material). If the KE NLOP sludge contained 1 wt% uranium metal particles (assuming 500 μm diameter spheres), using the SNF Project rate equation (uranium metal in oxygen-free water) with a rate enhancement factor of 1, a hydrogen generation rate of 580 mL-H_2/kg-settled sludge-day would be expected at 95°C. This rate is 290 times greater than the initial measured rate (at 95°C) of 2.0 mL-H_2/per kg-settled sludge/day.

- During the initial test interval (111 hours), the total gas-generation rate for the 95°C tests was 39 mL total gas per kg-settled sludge/day (48 mL total gas per liter of settled sludge-day). Based on the mass spectrometry analysis, only ~5% of the total gas generated was hydrogen. Most of the balance of the generated gas was CO_2 (~95%).

- The gas-generation-rate profile (total gas generation vs. time) shows that after about 50 hours at 95°C, the rate dropped to essentially zero, indicating reactants were largely depleted.

- During the initial 111-hour test interval at 60°C, the total gas-generation rate was 6.4 mL total gas per kg-settled sludge/day (8 mL total gas per liter-settled sludge-day). The composition of the gas generated at 60°C was ~5% H_2 and ~95% CO_2, essentially the same as that generated at 95°C.

- With the high CO_2 content in the generated gas, it may be improbable to achieve a flammable gas mixture in any KENLOP sludge processing, transport, or storage operation.

- While the initial total gas generation rates at 95°C for the 2003 KE NLOP sludge are low, they are 5 to 6-times greater than those observed for the KE NLOP sludge collected in 1999. The 1999 KE NLOP sludge sample (FE-3), held at 95°C for 473 hours, produced 6.1 mL of total gas per kg of settled sludge per day (9.7 mL total gas per liter of settled sludge per day). Greater than 99% of the gas was CO_2 while ~0.36% of the gas was H_2 (Bryan et. al 2004). Therefore, in this interval, FE-3 produced 9.89×10^{-7} moles H_2 per kg of settled sludge per day (0.02 mL H_2 per kg settled sludge per day). In comparison, the initial H_2 generation rate for the 2003 KE NLOP sample at 95°C was ~100-times higher. Though the settled density of the FE-3 subsample used for gas-generation testing was 1.6 g/cm^3, somewhat higher than that of the 2003 KE NLOP sample (1.24 g/cm^3), the lower gas generation rates found for the FE-3 sample may have been because it was chemically depleted by storage at hot cell temperatures (27-32°C) for ~13 months prior to testing. Similar rates for both CO_2 and H_2 generation were found for the FE-3 sample during its 300-hour interval at 90°C before the test temperature was elevated to 95°C.

- Despite the H_2 gas generation, no quantifiable levels of fission product gases were detected during any test interval for the 2003 KE NLOP sample. This observation indicates that the sludge contains very little or no uranium metal. Most K Basin sludge samples studied in previous gas-generation testing produced measurable Kr and Xe gas at expected fission product isotopic ratios. The Kr and Xe gases give qualitative and quantitative evidence of the corrosion of uranium metal (i.e., fission product gases remain trapped within the solid uranium metal matrix and are released to the gas space by corrosion). Of all the sludge types previously subjected to gas-generation testing, only samples FE-3 (the 1999 sample of KE NLOP sludge) and KC-6 (ion exchange resin beads collected from the floor of the KE Basin) contained neither Kr nor Xe at detectible levels.

Results from gas-generation tests with dewatered KE NLOP sludge (no drainable liquids; NLOP-Moist) and sludge solidified with grout and Nochar® (tests NLOP-Grout and NLOP-Nochar) were not available at the time of issue of the prior test status report on January 19, 2004.

Gas generation testing continued for the settled sludge, the drained sludge, and the grouted and Nochar®-treated sludge. The progress of the gas generating reactions was followed by gas pressure-volume-temperature measurements and by sampling and analyses of the overlying gases. The following additional conclusions are drawn from the continued experiments with the settled sludge and the waste forms (Moist, Grout, and Nochar):

- The KE NLOP sludge showed no indication of pyrophoricity (i.e., per the WIPP criterion, the sludge contained no more than 1 wt% pyrophoric material).

- The total uranium metal concentration in the settled NLOP sludge samples taken in December 2003, based on hydrogen gas generation and less-than-detectible concentrations of ^{136}Xe (the most abundant fission product gas isotope) in the gas samples, is 0.018 wt% or lower. If the uranium metal concentrations are based on the more conservative combined observed hydrogen generation and oxygen consumption quantities, the average uranium metal concentrations in the NLOP sludge is 0.032 wt% or lower. This compares with 0.0057 wt% (and 0.034 wt% Safety Basis) uranium metal previously estimated for the FE-3 settled sludge sample taken in 1999 from the KE North Load Out Pit (Schmidt and Baker 2004).

- After the first sampling at 111 hours, temperature in the range 25°C to 95°C had little effect on hydrogen generation rate for the settled sludge samples. This is taken to be evidence that the hydrogen production over these periods may be caused by radiolytic rather than thermochemical reactions. Hydrogen gas generation rates after ~700 hours were 1.6×10^{-5} moles H_2/kg settled sludge·day (0.38 ml, at room temperature, of H_2 per kg of settled sludge per day).

- Two of the tested waste forms (NLOP-Moist and NLOP-Grout) had H_2 generation rates after ~700 hours (8×10^{-6} moles H_2, or 0.19 ml H_2 at room temperature, per kg settled sludge per day), about half that of the NLOP-Control sample of settled sludge. However, the H_2 generation rate for the NLOP-Nochar waste form was nine-times lower than the rate observed for the Control [i.e., 2×10^{-6} moles (or 0.048 ml) H_2/kg settled sludge·day].

- The samples of NLOP sludge taken in December 2003 and which underwent the present testing showed higher specific CO_2 and H_2 gas production than similar sludge samples taken in 1999 and tested in 2000. The lower reactivity of the prior sample (FE-3) is ascribed to its being stored for nearly one year at warm (>27°C) hot cell temperatures before gas generation testing.

E.4 Test Matrix, Materials, and Approach

This section describes the overall test approach and methods used for the KE NLOP sludge gas-generation testing.

E.4.1 Test Matrix and Specific Objectives

Six gas-generation tests were conducted, five with ~55 grams of settled KE NLOP sludge and one (the Grout test) with ~36 g of settled sludge. Three tests were conducted with sludge and water only. Moist sludge (i.e., sludge drained of most of its water) was used in the fourth test. In the fifth test, the sludge was solidified in a Portland Type I/II cement grout containing added bentonite clay. The sixth test used Nochar® Acid Bond 660 to absorb the added water and free liquid associated with the NLOP sludge. Table E.1 displays the test program giving test number and description, material quantities, matrix, and conditions (temperature; start, end, and sampling dates; and test duration).

The properties of the moist (drained), grouted, and Nochar®-treated sludge materials, shown in Table E.2, are taken from a larger description of the waste form preparation given in Appendix F of Mellinger et al. (2004).

The settled NLOP sludge samples and the sludge in its tested waste form (moist, grouted, and with Nochar®) were placed into 220 mL reaction vessels for gas generation testing. The reaction vessels were sealed, connected to the gas measurement manifold system, and purged with neon gas to remove air. Next, the vessels were heated to the target conditions. The temperatures and gas pressures were monitored continuously. These tests were conducted at PNNL's High-Level Radiochemistry Facility in the 325 Building (325A HLRF), 300 Area, in accordance the Test Plan[(a)] and Test Instruction[(a)]and are consistent with the sampling and analysis plan (Baker et al. 2000). Initial gas samples from the sludge

(a) CH Delegard. "Bench-Scale Test Plan to Demonstrate Production of WIPP-Acceptable KE-NLOP Sludge Waste Forms at the 325 Building." Pacific Northwest National Laboratory, Richland, WA, December 23, 2003.
(b) AJ Schmidt. "Test Instruction KE NLOP Sludge Gas Generation Testing" 46857-TI04, Rev. 0, Pacific Northwest National Laboratory, Richland, WA, December 23, 2003.

Table E.1. Test Program for KE NLOP Sludge Gas-Generation Testing

Test (Sys) No.[a]	Test ID	Mass, g		Waste Form Vol., ml	Temp, °C	Start Date	Smpl. Date	Time at Temperature, hr	
		Settled Sludge	Added Water					Run Interval	Total
1 (3)	NLOP-U1	57.06	40.44	86.5	95	1/9/04	1/14/04	111.3	111.3
					95	1/14/04	1/26/04	282.7	394.0
					95	1/26/04	2/9/04	329.7	723.7
					25	2/9/04	2/25/04	380.7	1104.3
					95	2/25/04	—		
2 (4)	NLOP-U2	54.47	39.46	83.4	95	1/9/04	1/14/04	111.3	111.3
					95	1/14/04	1/26/04	282.7	394.0
					95	1/26/04	2/9/04	329.7	723.7
					25	2/9/04	2/25/04	380.7	1104.3
					95	2/25/04	—		
3 (5)	NLOP-Control	55.98	36.80	81.9	60	1/9/04	1/14/04	111.3	111.3
					60	1/14/04	1/26/04	282.7	394.0
					60	1/26/04	2/9/04	329.7	723.7
					60	2/9/04	2/25/04	358.3	1082.0
					60	2/25/04	—		
4 (6)	NLOP-Moist	52.87	-23.95[b]	20	60	1/22/04	1/27/04	113.7	113.7
					60	1/27/04	2/9/04	305.7	419.3
					60	2/9/04	2/25/04	358.3	777.7
					60	2/25/04	—		
5 (7)	NLOP-Grout	35.97	17.65	70.9	60	1/22/04	1/27/04	113.7	113.7
					60	1/27/04	2/9/04	305.0	418.7
					60	2/9/04	2/25/04	357.3	776.0
					60	2/25/04	—		
6 (10)	NLOP-Nochar	53.83	24.35	70	60	1/27/04	2/9/04	305.0	305.0
					60	2/9/04	2/25/04	358.0	663.0
					60	2/25/04	—		

[a] Sys is gas generation system number.
[b] Negative water added because water was drained from sludge.

and water only tests were collected on January 14, 2004. Additional gas samples were collected on January 26 and 27 and February 9 and 25, 2004, as shown in Table E.2. The gas samples were analyzed by mass spectrometry.

E.4.2 Specific Test Description/Objectives

Test 1, NLOP-U1. In this test, an aliquot of as-settled KE NLOP sludge was added to a reaction vessel. Additional sludge supernatant water also was added to maintain the sludge in a saturated state. The objective of Test 1 was to determine the total uranium metal content as rapidly as possible. Gas generating reactions (including reactions that generate H_2 and CO_2) were forced to completion by taking the sludge/supernatant solution to 95°C. The results from this test and test 2, NLOP-U2, may be used to interpret the results from Tests 3 to 6.

Test 2, NLOP-U2. Test 2 is a duplicate of Test 1. Because measurement of the uranium metal content of the KE NLOP sludge is critical, a duplicate test is warranted.

Table E.2. KE NLOP Waste Form Properties

Parameter	Waste Form		
	NLOP-Moist	NLOP-Grout	NLOP-Nochar
Waste Composition			
KE NLOP settled sludge mass, g	52.87	50.40 [a]	53.83
KE NLOP settled sludge volume, mL	42.6	40.6	43.4
KE Basin supernatant solution, g	0	24.73	24.35
Total feed waste mass, g	52.87	75.13	78.18
Total feed waste volume, mL	42.6	65.4	67.8
Additive			
Portland type I/II cement, g	--	112.00	--
Bentonite, g	--	6.60	--
Nochar® Acid Bond 660 [a], g	--	--	2.95
Property			
Final waste-form volume, mL	20	99.3	79 (packed) / 120 (loose)
Final waste-form mass, g	28.92	193.73 [b]	81.13
Final waste-form density, g/mL	1.45	1.95	1.03 (packed) / 0.68 (loose)
Expansion factor, settled sludge → final waste form	0.47	2.45 [c]	1.82 (packed) [d] / 2.76 (loose) [d]
Expansion factor, sludge & supernate → final waste form	--	1.52	1.17 (packed) / 1.77 (loose)

[a] Nochar® Acid Bond 660 is a polyacrylic water sorbent produced as a dry fine granular powder. It has been used to absorb aqueous solutions in wastes destined for WIPP. The Nochar® addition absorbs the free liquid and allows the waste to achieve the criterion of having no drainable liquid. The Nochar® capacity to absorb water is pH-dependent with higher absorption found at higher pH. The pH of the KE NLOP settled sludge is about 8.3 and that of the supernatant liquid is about 7.5, well within the range of optimum applicability of Nochar® Acid Bond 660.

[b] The net weight of the grouted form used in the gas generation testing was 138.26 g and thus contained 71.4% of the settled sludge and supernatant water used in the original mixture or 35.97 g of settled sludge and 17.65 g of supernatant solution.

[c] The expansion factors apply to the feed settled sludge for sludge plus supernatant water formulations; water (e.g., from supernatant solution) still required for grouted waste formulation.

[d] The expansion factors apply to the feed settled sludge for sludge plus supernatant water formulations; the actual expansion factors for sludge-only (supernatant-free) formulations likely are lower and approach 1.17 (packed) / 1.77 (loose). Testing is required to confirm this behavior.

Test 3, NLOP-Control. For Test 3, a reaction vessel was loaded in a manner identical to Test 1 and 2 with settled NLOP sludge and additional supernatant solution. In contrast to Tests 1 and 2 being conducted at 95°C, Test 3 was run at 60°C, the projected highest temperature the waste form might experience in transit to the WIPP. Comparison of the result of Test 3 with Tests 1 and 2 thus helps determine the effects of temperature. Primarily, though, Test 3 serves as a Control to interpret the results of the waste form Tests 4 to 6. Results from Tests 4 to 6 can be directly compared to the gas-generation rate profile of Test 3 to ascertain the effects of free/drainable water removal and solidification of the sludge on the gas generation.

Test 4, NLOP-Moist. In this test, drainable liquids were removed from a ~50-g sample of as-settled KE NLOP sludge before loading the moist material into the reaction vessel. Details on the preparation of this waste form are given in Appendix F of Mellinger et al. (2004) and are summarized in Table E.2. This test examines the effect of sludge dewatering on the hydrogen generation rate of KE NLOP sludge. For example, removal of drainable water might be expected to inhibit the corrosion of uranium metal. The effect of sludge dewatering on other gas generating/consuming reactions also was examined.

Test 5, NLOP-Grout. In this test, an aliquot of NLOP sludge with additional supernatant liquid was immobilized in Portland cement with added bentonite clay. After several days of curing, the grouted sludge was loaded into a reactor vessel. Appendix F of Mellinger et al. (2004) provides details on the preparation of this waste form and the waste form properties are summarized in Table E.2. This test examines the effect of a grout matrix on hydrogen generation rate of KE NLOP sludge. The effect of the grout matrix on other gas generating/consuming reactions also was examined.

Test 6, NLOP-Nochar. In this test, the free liquid in an aliquot of NLOP sludge and supernatant solution was immobilized by using the water-absorbing polymeric solidification agent, Nochar® Acid Bond 660. After several days of curing, the solidified sludge was loaded into a reactor vessel. Appendix F of Mellinger et al. (2004) provides details on the preparation of this waste form. This test examines the effect of the Nochar® matrix on hydrogen generation rate of KE NLOP sludge. The effect of the Nochar® on other gas generating/consuming reactions also was examined.

E.4.3 Test Materials

A full sludge core was collected from the KE NLOP in December 2003. The core samples were composited, homogenized, and subsampled for chemical and radiochemical characterization. The results of these analyses are provided in Appendix D of this report. The masses and volumes of the as-settled sludge and supernatant solution subsamples used for the six gas-generation tests are listed in Table E.1 with details on the preparation of the waste forms for Tests 4 through 6 summarized in Table E.2.

E.4.4 Reaction Vessels

Stainless steel reaction vessels were used. The vessels' inner dimensions were approximately 4.7 cm diameter and 12.7 cm tall with 220 mL nominal volume.

E.4.5 Reaction Atmosphere

The gas space in the apparatus was purged with neon of 99.99% purity at the beginning of each gas-generation test and after each gas sampling event. The neon cover was ensured by multiple cycles of pressurization (to about 3000 Torr) and venting to provide the desired anoxic (i.e., oxygen-free) conditions. Besides providing an inert cover, the neon served to exclude oxygen and thus overcome its poisoning effect on uranium metal reaction with water. The poisoning effect is known to decrease the reaction rate of uranium metal in water by a factor of ~30 (Johnson et al. 1994). Argon is an inert gas that also could have been used as the cover gas. However, because argon is present in air at about 0.932% concentration, its concentration in the gas samples was used instead to indicate atmospheric contamination and monitor the reactions of atmospheric oxygen and nitrogen.

E.4.6 Test Temperatures

Induction periods until the onset of hydrogen gas release were observed in the Series I gas-generation testing with KE canister sludge (Delegard et al. 2000). The induction periods were 1340 h at 40°C, 205 h at 60°C, and 27 h at 80°C. To obtain timely data and to match the maximum temperature in transport to the WIPP, the target temperature for the waste form testing in the current work was 60°C. Test NLOP-Control also was run at 60°C.

For KE NLOP sludge metal determination (Tests NLOP-U1 and NLOP-U2), the target test temperature is 95°C, consistent with prior uranium metal content determination testing, to force the reactions to completion.

Selection of the baseline reaction target temperature of 60°C (with and without solidification matrices) is consistent with the maximum temperature during shipment to WIPP. While temperatures greater than 60°C may accelerate the testing, the results may not reflect expected storage and shipping conditions. However, if after some period of time (e.g., 500 hours) little or no gas generation is observed at 60°C, the option was reserved to increase the test temperature. However, the temperature was maintained at 60°C for the duration of all waste form testing (~700 hours).

The temperatures were dropped to ambient (~25°C) at the end of the two sludge tests begun at 95°C (Tests NLOP-U1 and NLOP-U2) to provide information on activation energies and the possible role of radiolysis on gas generation.

E.4.7 Test Duration

Previous gas-generation tests with K Basin sludge have ranged from 900 to 10,000 hours. The present tests were run at temperatures above ambient from ~700 to 1100 hours.

E.4.8 Test System Operation

The reaction vessels and the gas manifold system (Figure E.1) used for the gas-generation tests are similar to those describe in the previous Series I-III 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 s on a Campbell Scientific CR10 data logger. The temperature and pressure data are averaged every 20 min and saved in a computer file and also manually logged once each working day.

Figure E.2 illustrates a reaction vessel and shows where the thermocouples are placed inside and outside the vessel. For the gas-generation testing, each vessel was wrapped in heating tape and insulated. Two thermocouples were attached to the external body, one for temperature control and one for over-temperature protection. Two thermocouples were inserted through the flange. The thermocouple centered in the lower half of the vessel monitored the temperature of the test material phase (sludge or treated waste form); the one centered in the upper half monitored the gas phase temperature within the

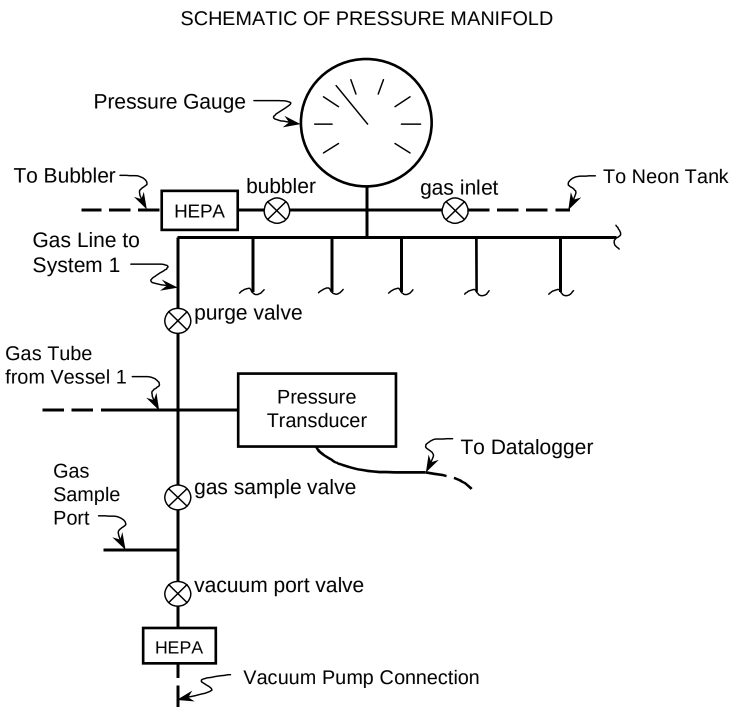

Figure E.1. Layout of Gas Pressure Measurement and Gas Sample Manifold Used in Gas-Generation Tests (includes details for one of 6 systems)

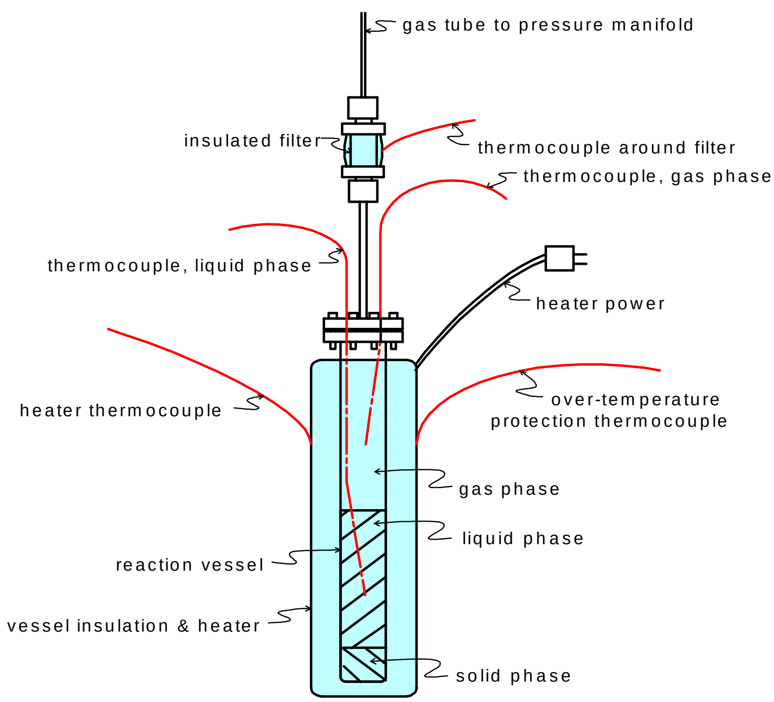

Figure E.2. Schematic of Reaction Vessel reaction vessel. The reaction vessels were placed in a hot cell and connected by a thin (0.102-cm inside diameter) stainless steel tube to the gas manifold outside the hot cell. A stainless steel filter (2-µm pore size, Nupro) protected the tubing and manifold from contamination. A thermocouple was attached to this filter as well.

An atmospheric pressure gauge was attached to the data logger. The pressure in each system was the sum of atmospheric pressure and the differential pressure between the system internal and external (atmospheric) pressures. The inert cover gas (neon) allowed ready identification of product gases and interpretation of the chemical reactions occurring in the settled sludge. The neon gas used was analyzed independently by mass spectrometry and determined to contain no impurities in concentrations significant enough to warrant correction.

At the start of each run, each system was purged by at least eight cycles of pressurizing with neon at 45 psi (310 kPa) and venting to the atmosphere. The systems were at atmospheric pressure, about 745 mm Hg (99.3 kPa), when sealed. The vessels then were heated, and the temperature set points were adjusted to keep the material within 1°C of the desired liquid/slurry/waste form phase temperatures.

As necessary during the testing and at the end of each reaction sequence, the vessels were allowed to cool to ambient temperature and then a sample of the gas was taken from the headspace for mass spectrometry analysis. Gases in the reaction system were assumed to be well mixed. The metal gas collection bottles were equipped with a valve and had a volume of approximately 75 mL. After the bottle was evacuated overnight at high vacuum, it was attached to the gas sample port. After the sample was collected, the reaction vessel was purged again with neon. The compositions of the gas phase of each reaction vessel during all gas samplings were analyzed by mass spectrometry using analytical procedure PNNL-98523-284 Rev. 0.

E.5 KE NLOP Gas-Generation Testing Results

In each test, gas-tight reaction vessels were loaded with KE NLOP sludge and waste forms, the gas space purged with neon, and the loaded vessels heated to the selected temperature. Gas samples were taken from the vessels in accordance with the test plan. Gas-generation rates were determined for each gas sample based on the heating time, the gas composition, the total gas quantity in the system from which the sample was taken, and the sludge mass present in each reaction vessel.

E.5.1 Gas-Generation Profile for the Sludge Only Tests

The gas-generation profiles (moles of gas generated/kg of settled sludge as a function of reaction time) for the sludge only tests are shown in Figure E.3. Tests 1 and 2 (NLOP-U1 and NLOP-U2) are experimental duplicates conducted at 95°C from the start until 723.7 hours and at ambient hot cell temperature (~25°C) until the end of testing. Test 3 (NLOP-Control) was conducted at 60°C over the 1082-hour duration of the experiment.

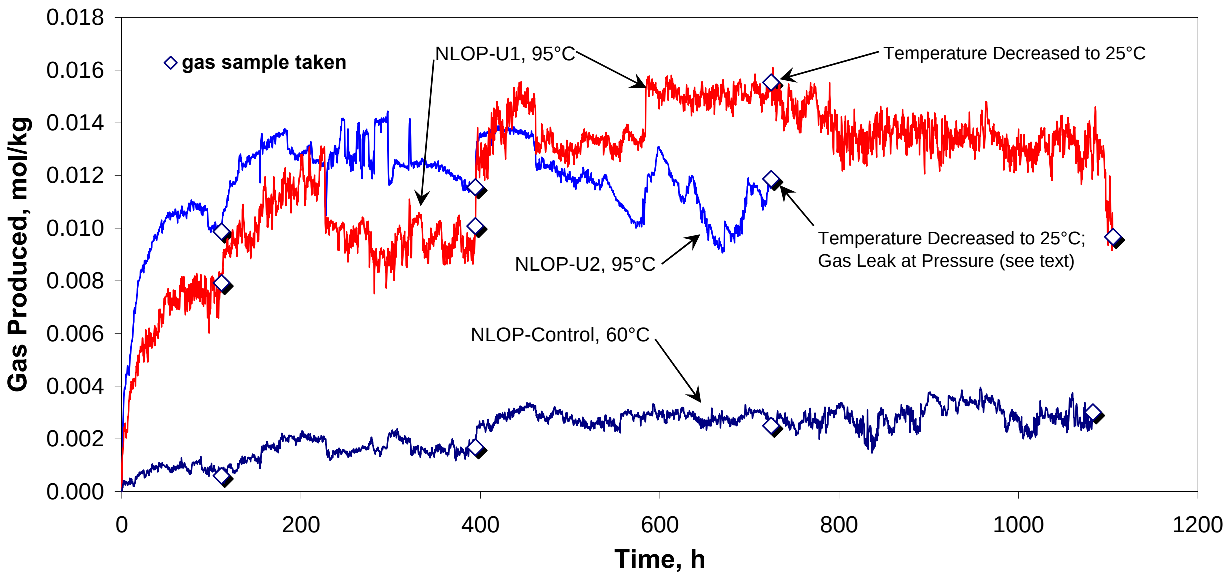

Figure E.3. Total Gas Generation from Tests NLOP-U1, NLOP-U2, and NLOP-Control

A steady decline in the apparent gas production observed in the NLOP-U2 experiment after the temperature decrease to ambient (~25°C) at 723.7 hours was found to be due to inadvertently leaving the vessel pressurized with the neon purge gas after its sampling. The bleed valve was not fully seated, and the pressurized neon slowly leaked over the time of the experiment. This prevented gaining meaningful information from the total gas generation plot past this point.

It is seen that total gas generation for the NLOP-U1 and NLOP-U2 tests was essentially complete by 200 to 300 hours. After that, the noise in the gas generation traces (caused primarily by the sensitivity of the pressure sensors) was similar to any apparent gas generation or loss. The total quantity of gas for both the NLOP-U1 and -U2 experiments was about 0.01 moles per kg of sludge. The NLOP-Control test still seemed to be generating gas at the end of the experiment though trends are difficult to discern at the low observed rates. Better estimates of gas generation rates are obtained by mass spectrometric analyses of the sampled product gases.

E.5.2 Results of Gas Sample Analysis for the Sludge Only Tests

Carbon dioxide (CO_2), hydrogen (H_2), and methane (CH_4) and higher hydrocarbons were observed and quantified by gas sample mass spectrometry analyses. These gases have been observed in many of the past experimental studies of corrosion of irradiated uranium metal from K Basin sludge or from crushed irradiated metal fuel. Detailed descriptions of gas generating and gas consuming reactions in K Basin sludge are provided in prior reports (Delegard et al. 2000, Bryan et al. 2004, and Schmidt et al. 2003). Hydrogen, produced by the reaction of uranium metal with water ($U + 2\ H_2O \rightarrow UO_2 + 2\ H_2$; Reaction 1) and by radiolysis, is of most significance for the present testing because of its impact on treated waste form transport to WIPP.

As discussed in the prior K Basin sludge test reports, the best indicator of the concentration of irradiated uranium metal is measurement of the quantities of the inert fission product gases krypton (^{83}Kr, ^{84}Kr, ^{85}Kr, ^{86}Kr) and xenon (^{130}Xe, ^{131}Xe, ^{132}Xe, ^{134}Xe, or ^{136}Xe) released by metal corrosion. The most abundant of these fission product gas isotopes is ^{136}Xe. However, no measurable quantities of any of these isotopes were detected by mass spectrometry. The detection limit for most gases by the mass spectrometric technique is approximately 1 part per million on a mole basis; the detection limit for the Kr isotopes is about 10 ppm because of hydrocarbon interference.

The quantities of individual gases produced and consumed in each test over the sampling intervals are presented in Table E.3. The gas products were, respectively, 91%, 88%, and 86% CO_2 over the entire test interval for the NLOP-U1, NLOP-U2, and NLOP-Control experiments while hydrogen provided 5.0%, 7.0%, and 13.9% of the product gas. Hydrocarbons comprised the balance of the gas production, and small quantities N_2 and O_2 were consumed and, in fewer intervals, generated. Again, no krypton or xenon fission product gases were detected in any sample.

The quantities of gas produced and consumed for the 1999 KE NLOP sample, FE-3 (Bryan et al. 2004), are shown in Table E.3 for comparison. It is seen that the amount of CO_2 released in the FE-3 testing (1.68×10^{-4} moles after 970 hours at 90-95°C) is about 18% of that released by the NLOP-U1 and -U2 tests (averaging 9.4×10^{-4} moles after 724 hours at 95°C and another 358 hours at 25°C). However, the NLOP-U1 and NLOP-U2 tests each contained about 55 g of settled sludge while the FE-3 test was conducted with 21.22 g of settled sludge. The specific CO_2 generation of the FE-3 settled sludge (8×10^{-3} moles/kg) thus was about half that of the KE NLOP-U1 and -U2 settled sludge samples (1.7×10^{-2} moles/kg). The lower specific quantity of CO_2 produced in the FE-3 experiment likely was because FE-3 sample was stored in the 222-S lab at ~27°C for about 11 months and in the 325A HLRF for 2 months at 32°C after removal from the KE NLOP and before gas generation testing (Bryan et al. 2004). In contrast, the present KE NLOP samples only spent about 20 days at 10 to 15°C (i.e., near the KE Basin water temperature) between sampling and the commencement of gas generation testing. Thus the NLOP-U1 and NLOP-U2 materials had much less time and lower temperatures than the FE-3 sample to lose the CO_2-producing reactants.

The specific hydrogen generation quantities for the FE-3 and NLOP-U1 and -U2 materials also can be compared. For FE-3, H_2 production was about 2.7×10^{-5} moles (0.65 ml at room temperature)/kg sludge. Over similar time periods and temperatures, the NLOP-U1 and -U2 samples produced about 1.13×10^{-3} moles (27 ml at room temperature) H_2/kg sludge, a specific production about 43-times greater than observed for FE-3. The NLOP-Control experiment, run for ~1100 hours at 60°C, produced 7.8×10^{-4} moles (19 ml, room temperature) H_2/kg, about 70% of that of the NLOP-U1 and -U2 samples run for 724 hours at 95°C and another 358 hours at 25°C.

The specific H_2 generation rates for the four sludge-only experiments, displayed in Figure E.4, show that past the first sampling at 111 hours, the hydrogen generation rates are not appreciably different for the NLOP-U1, -U2, and -Control samples even though they are conducted at temperatures ranging from 25°C to 95°C. This suggests that the hydrogen being generated in this interval arises by temperature-independent radiolysis and not thermochemically such as by the reaction of uranium metal with water.

Table E.3. Net and Cumulative Quantities of Gas Evolved for FE-3, NLOP-U1, NLOP-U2, and NLOP-Control

Gas	Gas Quantities, moles, at Sampling Times													
	FE-3		NLOP-U1				NLOP-U2				NLOP-Control			
	493.0 h	970.0 h	111.3 h	394.0 h	723.7 h	1104.3 h	111.3 h	394.0 h	723.7 h	1104.3 h	111.3 h	394.0 h	723.7 h	1082.0 h
CO_2	8.52E-5	8.31E-5	4.36E-4	2.91E-4	1.83E-4	3.63E-5	4.28E-4	2.89E-4	1.84E-4	3.58E-5	7.16E-5	7.96E-5	6.71E-5	5.10E-5
Cumulative	8.52E-5	1.68E-4	4.36E-4	7.28E-4	9.11E-4	9.47E-4	4.28E-4	7.17E-4	9.01E-4	9.37E-4	7.16E-5	1.51E-4	2.18E-4	2.69E-4
H_2	2.53E-7	3.06E-7	2.34E-5	1.29E-5	8.58E-6	6.90E-6	1.87E-5	2.80E-5	1.61E-5	1.18E-5	3.74E-6	1.96E-5	1.19E-5	8.49E-6
Cumulative	2.53E-7	5.58E-7	2.34E-5	3.63E-5	4.49E-5	5.18E-5	1.87E-5	4.67E-5	6.28E-5	7.46E-5	3.74E-6	2.34E-5	3.53E-5	4.37E-5
N_2	-7.11E-6	1.19E-6	-7.27E-6	1.53E-5	1.72E-5	1.96E-5	-2.01E-5	1.56E-6	-3.91E-6	6.86E-6	-1.62E-5	3.23E-6	1.62E-6	1.40E-5
Cumulative	-7.11E-6	-5.92E-6	-7.27E-6	8.05E-6	2.52E-5	4.48E-5	-2.01E-5	-1.85E-5	-2.24E-5	-1.56E-5	-1.62E-5	-1.30E-5	-1.14E-5	2.62E-6
O_2	-4.03E-6	-7.81E-7	-7.84E-6	-3.57E-6	-4.54E-6	-4.45E-5	-9.22E-6	6.62E-7	-6.60E-7	-1.59E-5	-7.08E-6	1.92E-7	4.19E-7	-1.94E-6
Cumulative	-4.03E-6	-4.81E-6	-7.84E-6	-1.14E-5	-1.59E-5	-6.05E-5	-9.22E-6	-8.56E-6	-9.22E-6	-2.51E-5	-7.08E-6	-6.88E-6	-6.46E-6	-8.40E-6
CH_4	5.42E-8	5.39E-8	3.85E-7	3.03E-7	2.29E-7		4.41E-7	4.82E-7	3.47E-7		1.87E-7	1.84E-7	1.20E-7	1.62E-7
Cumulative	5.42E-8	1.08E-7	3.85E-7	6.88E-7	9.17E-7	9.17E-7	4.41E-7	9.22E-7	1.27E-6	1.27E-6	1.87E-7	3.71E-7	4.90E-7	6.52E-7
C_2H_x	1.08E-7	8.99E-8	2.57E-7	3.03E-7	2.86E-7		5.04E-7	4.21E-7	5.20E-7		2.49E-7			
Cumulative	1.08E-7	1.98E-7	2.57E-7	5.60E-7	8.46E-7	8.46E-7	5.04E-7	9.25E-7	1.45E-6	1.45E-6	2.49E-7	2.49E-7	2.49E-7	2.49E-7
$\geq C_3H_x$	9.03E-8	8.99E-8	6.42E-8	1.82E-5	7.43E-7	1.61E-5	4.41E-7	3.01E-5	1.16E-6	9.67E-6	6.23E-8			
Cumulative	9.03E-8	1.80E-7	6.42E-8	1.83E-5	1.90E-5	3.51E-5	4.41E-7	3.05E-5	3.17E-5	4.14E-5	6.23E-8	6.23E-8	6.23E-8	6.23E-8
$\Sigma\ C_yH_x$ C	5.57E-7	5.19E-7	1.10E-6	5.86E-5	3.16E-6	5.10E-5	2.85E-6	9.67E-5	5.05E-6	3.07E-5	8.83E-7	1.84E-7	1.20E-7	1.62E-7
Cumulative	5.57E-7	1.08E-6	1.10E-6	5.97E-5	6.29E-5	1.14E-4	2.85E-6	9.96E-5	1.05E-4	1.35E-4	8.83E-7	1.07E-6	1.19E-6	1.35E-6
^{83}Kr														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{84}Kr														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{85}Kr														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{86}Kr														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Σ Kr	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{130}Xe														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{131}Xe														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{132}Xe														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{134}Xe														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{136}Xe														
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Σ Xe	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Total Gas	8.57E-5	8.36E-5	4.60E-4	3.23E-4	1.93E-4	5.93E-5	4.48E-4	3.48E-4	2.02E-4	5.73E-5	7.59E-5	9.94E-5	7.91E-5	5.94E-5
Cumulative	8.57E-5	1.69E-4	4.60E-4	7.83E-4	9.76E-4	1.04E-3	4.48E-4	7.96E-4	9.98E-4	1.06E-3	7.59E-5	1.75E-4	2.54E-4	3.14E-4

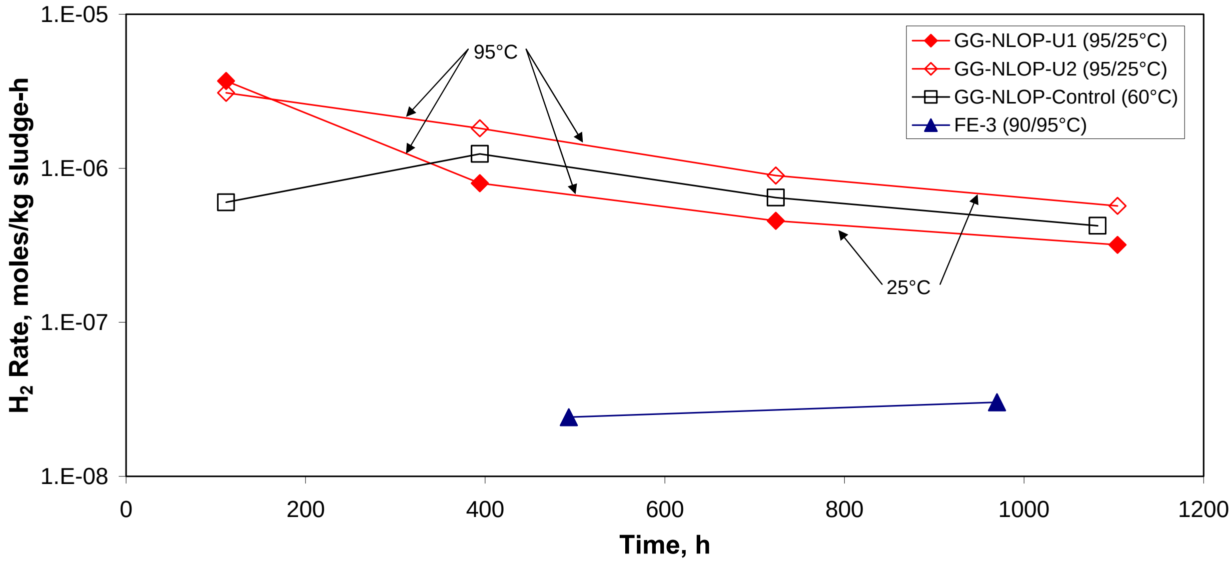

Figure E.4. Specific Hydrogen Generation Rates for Tests FE-3, NLOP-U1, NLOP-U2, and NLOP-Control

The lower, but constant, specific rate observed in the FE-3 test may indicate that FE-3 was subjected to lower radiolytic dose rates than were the present tests. Because the FE-3 and current NLOP-U1, -U2, and -Control samples have approximately the same specific radioactivity, the different dose rates would have to arise from differences in external sources also present in the hot cell during testing. For FE-3, other K Basin sludge samples were present in the gas generation testing carousel. For the recent NLOP tests, tank waste samples were present. However, no radiolytic dose rates were measured in the present or prior (FE-3) testing to validate this hypothesis.

The uranium metal concentration in the KE NLOP sludge is an important parameter in projecting the potential of the sludge to generate hydrogen gas in the waste containers destined for the WIPP. The total uranium metal concentration in the KE NLOP-U1 and -U2 test samples was estimated in three ways based on the gas generation test findings. First, the assumption may be made that all of the hydrogen generated in the tests, including or excluding that which seems to come from background radiolytic reactions, is due to the reaction of water with uranium metal ($U + 2\ H_2O \rightarrow UO_2 + 2\ H_2O$; Reaction 1). The second method would, in addition, attribute all of the oxygen gas consumed from the system to the reaction $U + O_2 \rightarrow UO_2$ (Reaction 2). This is a conservative assumption in that other reactions, including the oxidation of UO_2 to UO_3 hydrates, also may consume oxygen. The third and most accurate method is to estimate an upper limit on uranium metal based on the detection limit for ^{136}Xe, the most abundant fission product gas released in irradiated uranium metal corrosion.

E.5.2.1 Estimating Uranium Metal Based on Hydrogen Gas Generation

To a first approximation, the specific amount of hydrogen generated by uranium metal corrosion in the NLOP sludge is the difference between that observed in the NLOP-U1/-U2 tests (due to corrosion and radiolysis) and the NLOP-Control test (perhaps largely due to radiolysis alone). As shown above, the difference is (1.13×10^{-3} - 7.8×10^{-4}) moles H_2/kg or 3.5×10^{-4} moles H_2/kg settled sludge, equivalent to 1.75×10^{-4} moles uranium/kg settled sludge, 4.2×10^{-5} kg uranium/kg settled sludge, or 0.0042 wt% uranium metal.

If, however, the conservative assumption is made that all of the hydrogen gas (1.13×10^{-3} moles H_2/kg) generated in the ~1100-hour test interval is due to uranium metal corrosion and none due to radiolysis, the uranium metal concentration increases to 0.014 wt%.

E.5.2.2 Estimating Uranium Metal Based on Hydrogen Gas Generation and Oxygen Consumption

As shown in Table E.2, oxygen was consumed overall for each test. However, occasional intervals of oxygen release also occurred. If the net oxygen consumption conservatively is credited to the oxidation of uranium metal to UO_2, the additional increment of uranium metal in the sludge (beyond that estimated based on hydrogen gas generation) is 1.06×10^{-3} moles uranium/kg settled sludge for NLOP-U1 and 4.61×10^{-4} moles uranium/kg settled sludge for NLOP-U2. The uranium concentrations in the FE-3, NLOP-U1, and NLOP-U2 samples, shown in Table E.4, reflect the contributions of the hydrogen

Table E.4. Uranium Metal Quantities Based on Gas Reaction Observations

Reaction	U Metal Quantities Based on H_2 Generation and O_2 and N_2 Consumption							
	FE-3		NLOP-U1		NLOP-U2		NLOP-Control	
	Moles	% of Rxn.	Moles	% of Rxn.	Moles	% of Rxn.	Moles	% of Rxn.
Reaction 1 $U + 2\ H_2O \rightarrow UO_2 + 2\ H_2$	2.79E-7 ±0.10E-7 [a]	5.5	2.59E-5 ±0.02E-5 [a]	30.0	3.73E-5 ±0.02E-5 [a]	59.8	2.19E-5 ±0.02E-5 [a]	72.3
Reaction 2 $U + O_2 \rightarrow UO_2$	4.81E-6 ±0.81E-6 [a]	94.5	6.05E-5 ±0.93E-5 [a]	70.0	2.51E-5 ±0.82E-5 [a]	40.2	8.40E-6 ±4.59E-6 [a]	27.7
Reaction 3 $U + 0.875\ N_2 \rightarrow UN_{1.75}$	6.77E-6	NA	-5.12E-5	NA	1.78E-5	NA	-3.00E-6	NA
Settled Sludge Mass in Test, g	21.22		57.06		54.47		55.98	
U metal, wt% settled sludge, Reaction 1 Only	0.00031 ± 0.00001		0.011		0.016		0.0093	
U metal, wt% settled sludge, Reactions 1 & 2	0.0057 ± 0.0010		0.036 ± 0.004		0.027 ± 0.004		0.013 ± 0.002	
U metal, wt% settled sludge, ^{136}Xe	<0.0088 [b]		<0.018		<0.018		NA	

[a] Error estimated by varying mass-spectrometry analyzed H_2 or Ar gas concentrations by 0.001%. Note that Ar variability (0.934 mole% in air) has a much larger influence on net calculated O_2 consumption than a variability of similar magnitude in O_2 concentration (20.95 mole% in air) because of its 20.95/0.934 = 22.4-fold multiplicative influence in adjusting for air contamination.
[b] Schmidt and Baker 2004.

generation and oxygen consumption reactions. It is seen that attributing all of the hydrogen generation and oxygen consumption to uranium metal corrosion leads to estimated uranium metal concentrations of 0.036 wt% and 0.027 wt%, respectively in NLOP-U1 and –U2, or 0.032 wt% on average.

For completeness, the postulated nitrogen consumption reaction ($U + 0.875\ N_2 \rightarrow UN_{1.75}$) and the NLOP-Control findings also are included in Table E.4. However, based on further consideration of the postulated reaction of uranium metal with nitrogen (Schmidt and Baker 2004), the supplementary contributions of nitrogen consumption have been dismissed as being overly conservative in assessing the total uranium metal concentration in the FE-3 sludge gas generation testing. For the same reasons, the contributions of nitrogen consumption in the present testing likewise were not assessed to estimate uranium metal concentrations in the NLOP samples.

E.5.2.3 Estimating Uranium Metal Based on ^{136}Xe Release

The existence of krypton (Kr) or xenon (Xe) fission products in gases produced by the hydrothermal reactions of sludge with water gives qualitative evidence of the corrosion of irradiated uranium metal. However, no fission product gas isotopes were detected in any of the gas samples obtained in the present tests. Nevertheless, based on the detection limits of these gases, and their expected production in the irradiated uranium metal fuel, estimates can be made of the upper level concentrations of uranium metal in the KE NLOP sludge.

According to burn-up calculations by the ORIGEN code, the Kr and Xe concentrations in irradiated N Reactor metal fuel increase almost linearly with exposure. ORIGEN calculation results for Mark 1A fuel, transcribed into Table E.5, show calculated yields of fission product gas as functions of irradiation at nominal 6, 9, 12, and 16% ^{240}Pu levels. These data were fit to quadratic equations, as shown in Figure E.5, so that values of burnup and Kr and Xe concentrations could be estimated at intermediate irradiation levels. The resulting quadratic equations also are shown in the footnote of Table E.5.

According to Table 4-12b of the Spent Fuel Databook (Duncan 2001), the plutonium inventories in the KE Basin are 3.53 kg ^{238}Pu, 1870 kg ^{239}Pu, 280 kg ^{240}Pu, 33.2 kg ^{241}Pu, and 8.04 kg ^{242}Pu. The inventories and corresponding plutonium isotopic distribution (in wt %) are summarized in Table E.6.

The Pu isotopic distributions of a composite of the recent KE NLOP sludge samples were measured (see the revised Appendix D); the distribution is presented in Table E.6. Adjusted for ^{241}Pu decay and estimated ^{238}Pu (not measured reliably due to uranium interference), the isotopic distribution corresponds with the Databook values (Duncan 2001) and indicates 12.86 wt% ^{240}Pu.

Based on the burnup equation shown at the bottom of Table E.5, it is seen that an exposure of 2698 MWD/TeU is required to produce the 12.86 wt% ^{240}Pu observed in the KE NLOP sludge:

$$\text{Burnup, MWD/TeU} = 5.6145 \times (12.86\%\ ^{240}\text{Pu})^2 + 137.62 \times 12.86\%\ ^{240}\text{Pu} = 2698\ \text{MWD/TeU}$$

The 2698 MWD/TeU burnup derived from the ^{240}Pu concentration is consistent with, though slightly lower than, the ~2800 MWD/TeU exposure estimated for the KC-2/3 P250 sludge in the first Gas Generation test series based on fission product gas yield (page 4.17 of Delegard et al. 2000).

Table E.5. ^{240}Pu Concentrations and Fission Product Gas Isotopic and Element Ratios as Functions of Burnup Based on ORIGEN

Isotope	Kr and Xe Isotopic Wt% Distribution and Product ^{240}Pu Concentration Versus Exposure				
	0 MWD/TeU	1005.2 MWD/TeU	1674.6 MWD/TeU	2512.9 MWD/TeU	3618.6 MWD/TeU
	0% ^{240}Pu	6% ^{240}Pu	9% ^{240}Pu	12% ^{240}Pu	16% ^{240}Pu
^{83}Kr	-	13.76	13.61	13.43	13.18
^{84}Kr	-	27.12	27.44	27.81	28.31
$^{85}Kr^{(a)}$	-	6.91	6.89	6.84	6.78
^{86}Kr	-	52.19	52.03	51.87	51.73
	ΣKr, g/TeU	17.7	28.6	41.6	57.5
^{130}Xe	-	0.01	0.02	0.04	0.05
^{131}Xe	-	10.94	10.92	10.77	10.53
^{132}Xe	-	16.86	17.14	17.47	17.89
^{134}Xe	-	28.72	28.48	28.29	28.08
^{136}Xe	-	43.47	43.43	43.43	43.43
	ΣXe, g/TeU	206	346	523	754
	ΣXe/ΣKr	11.6	12.1	12.6	13.1

(a) t½ = 10.76 years.

Burnup, MWD/TeU = $5.6145\times(^{240}Pu,\%)^2 + 137.62\times(^{240}Pu,\%)$
Xe, g/tonne U = $8.99\times10^{-7}\times(\text{Burnup, MWD/TeU})^2 + 0.205\times(\text{Burnup, MWD/TeU})$
Kr, g/tonne U = $-6.25\times10^{-7}\times(\text{Burnup, MWD/TeU})^2 + 0.0181\times(\text{Burnup, MWD/TeU})$

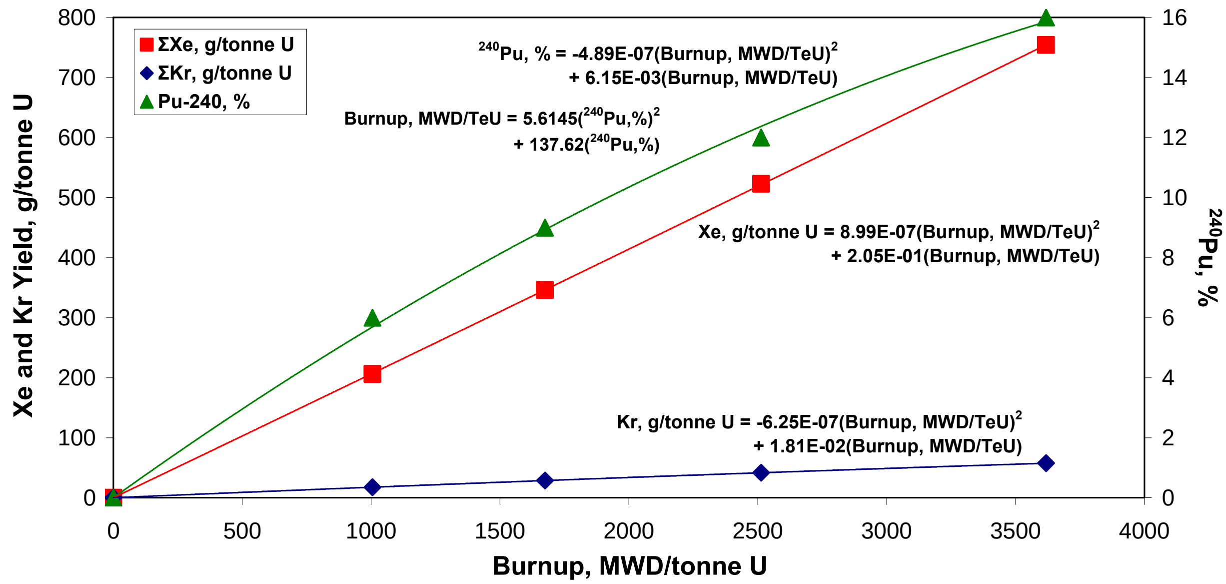

Figure E.5. ^{240}Pu and Fission Product Gas Concentrations as a Function of Burnup

Table E.6. Plutonium Isotopic Distribution

Isotope	Databook (Duncan 2001)		KE NLOP, Mass%	
	Pu, kg	Mass %	TIMS	TIMS-Adj [a]
^{238}Pu	3.53	0.161	NA	0.16
^{239}Pu	1870	85.203	85.70	85.08
^{240}Pu	280	12.758	12.95	12.86
^{241}Pu	33.2	1.513	0.95	1.51
^{242}Pu	8.04	0.366	0.40	0.40

[a] Thermal Ionization Mass Spectrometry (TIMS) result adjusted to include nominal 0.16 wt% ^{238}Pu and 1.51 wt% ^{241}Pu (i.e., less time since separation) based on Databook values.

According to the Xe yield equation (bottom of Table E.5), ~560 g of Xe is produced per tonne of uranium irradiated to 2698 MWD/TeU:

$$\text{Xe, g / TeU} = 8.99 \times 10^{-7} \times (2698 \text{ MWD / TeU})^2 + 0.205 \times 2698 \text{ MWD / TeU} = 559.5 \text{ g Xe / TeU}$$

Of this Xe, 43.43% is ^{136}Xe (Table E.5) or 243 g ^{136}Xe/tonne U. This is equivalent to 0.000425 moles ^{136}Xe per mole of uranium.

The total gas (including Ne) present in the first three sampling intervals of the NLOP-U1 and NLOP-U2 tests, run at 95°C when uranium corrosion was most likely, is ~1.8×10^{-2} moles. If ^{136}Xe were found at the 1 ppm detection limit in each sample, a total of 1.8×10^{-8} moles of ^{136}Xe would be present. This ^{136}Xe is equivalent to 1.8×10^{-8} moles ^{136}Xe × (mole uranium/0.000425 moles ^{136}Xe) = 4.2×10^{-5} moles (0.010 grams) of uranium or 0.018 wt% uranium metal in the ~55 gram settled sludge samples (Table E.4). This calculation thus provides an estimate of the maximum uranium metal concentration in the December 2003 KE NLOP sludge samples.

E.5.3 Evaluation of Uranium Metal Concentration and Comparison of NLOP-U1 and -U2 Test Results to KE NLOP Design and Safety Basis Values

This section provides recommended estimates of the nominal and bounding U metal content values for samples NLOP-U1 and NLOP-U2 and compares these values to the KE NLOP Design and Safety Basis uranium metal content values.

E.5.3.1 Recommended Nominal and Bounding Uranium Metal Values for NLOP-U1 and -U2

As shown in the previous section, the uranium metal concentration is less than 0.018 wt% based on the ^{136}Xe fission product gas release detection limit. The uranium metal concentration in the settled sludge is 0.014 wt% based on the estimation methods using hydrogen gas generation alone. If the uranium metal concentrations are based on the more conservative combined observed hydrogen generation and oxygen consumption quantities, the average uranium metal concentrations in the NLOP-U1 and -U2 tests are about 0.032 wt%.

A conservative nominal interpretation of the NLOP-U1 and -U2 tests is to consider only H_2 gas generation and the ^{136}Xe fission product gas detection limit. The associated deduction of the potential contribution of radiolysis to hydrogen generation (i.e., the difference between the H_2 observed in the NLOP-U1/-U2 tests, due to both corrosion and radiolysis, and the NLOP-Control test, presumed due to radiolysis only) described in the previous section is, however, non-conservative and speculative.[a]

Therefore, the total H_2 generation observed for the NLOP-U1 and -U2 tests, not adjusted for radiolysis, may be used to estimate the uranium metal quantities, and concentrations, present in each test. As shown in Table E.4, the respective uranium concentrations are 0.011 and 0.016 wt% uranium metal in the settled sludge tests, or an average of 0.014 wt%.

The 0.014 wt% value coincidently is similar to the upper limit value, <0.018 wt% uranium metal in settled KE NLOP sludge, based on the ^{136}Xe fission product release detection limit from corroding irradiated uranium fuel. This estimate based on fission product gas release is judged to be more reliable, particularly at the low observed gas generation rates, than the estimate based on H_2 production. This is because the H_2 gas production is not limited to uranium corrosion and can have significant contribution from other processes (e.g., steel corrosion and radiolysis) at the low observed quantities. Hydrogen itself also is reactive and can be consumed or lost (e.g., to hydriding). In contrast, the ^{136}Xe signature is unambiguous because:

- ^{136}Xe arises in significant quantities only from nuclear fission (air contribution is negligible).
- ^{136}Xe only can be released to the gas phase by the corrosion of irradiated uranium metal.
- Xe is chemically inert; i.e., the released Xe will not react or otherwise be lost to detection by gas phase sampling and analysis.

Therefore, the recommended nominal uranium metal concentration for NLOP-U1 and -U2, based on the ^{136}Xe detection limits, is 0.018 wt%.

The KE NLOP sludge sampling campaign in 1993 showed a radionuclide sampling variability of ±35% to give, at two standard deviations, a sampling variability factor of 1.7 (Schmidt and Baker 2004). Applying the variability factor of 1.7 to the ^{136}Xe detection limit-based uranium metal concentration of 0.018 wt% gives a bounding (95% confidence) uranium metal estimate for NLOP-U1 and -U2 of 0.031 wt%.

(a) Also, as will be shown in subsequent discussions, the NLOP-Moist sample, drained to contain only 9.0 grams of water, produced H_2 at nearly the same rate (per gram of settled sludge) as the NLOP-Control sample containing 71.7 grams of water. Both tests were run at 60°C. The lack of correlation of supposedly radiolytic H_2 generation to water quantities in the test vessels calls into question H_2's purely radiolytic origin.

E.5.3.2 Review of KE NLOP Design and Safety Basis Values

The gas generation behavior of the 1999 KE NLOP sludge sample FE-3 (Bryan et al. 2004) was evaluated and design and safety basis uranium metal content values were developed by Schmidt and Baker (2004). The KE NLOP sludge design basis value for uranium metal (0.0057 wt%) was conservatively estimated from the FE-3 gas generation testing results by assuming that all H_2 generation (Reaction 1) and all O_2 depletion (Reaction 2) could be ascribed to uranium metal oxidation. Schmidt and Baker (2004) also pointed out that a significant fraction of the O_2 depletion could be due to other reaction processes including adsorption on solids and reactions with other chemically reduced species such as uranium oxides or organic compounds. However, as with samples NLOP-U1 and -U2, Xe isotopes were not detected in the gas generation tests with FE-3. The estimated uranium metal content based on the xenon detection limit (default 0.0001 mol% detection limit) for the FE-3 test was 0.0088 wt%.

Other samples were gathered from the KE Basin at the same time as FE-3 for analysis and gas generation testing. Among these was FE-4/6, a composite KE sludge samples collected from the dummy elevator and tech view pit. In contrast to the gas analysis findings for sample FE-3, it was found that though the second of two FE-4/6 gas samples showed <0.0001 mol% Xe for all isotopes, the first gas sample contained observable, and thus quantifiable, Xe isotopes at levels below the default 0.0001 mol% detection limit. The Xe isotope analysis from the first gas sample from FE-4/6 corresponded to a uranium metal concentration of 0.00519 wt% (Bryan et al. 2004). The test conditions, sampling, and gas analysis performed on sample FE-4/6 were identical to those for FE-3 (gas analyses were processed in the same batch) even though the test with FE-3 used a larger mass of material (21.22 g) than the test with FE-4/6 (15.87 g). Based on the reasonable assumption that the detection limits for FE-3 were similar to the quantified values observed for FE-4/6 rather than the default 0.0001 mol%, the Xe fission product gases in FE-3 should have been detected at a level corresponding to less than 0.00519 wt% uranium metal. In summary, the failure to detect fission product gases in FE-3, along with the analysis of the quantification limit and comparison to the detection level of the companion sample, FE-4/6, supports the appropriateness of the above nominal/design basis uranium metal content in FE-3 (0.0057 wt%).

The KE NLOP safety basis uranium metal concentration was obtained by multiplying the nominal concentration by a factor of 6 (6 × 0.0057 wt% = 0.034 wt%). The factor of 6 has two contributors, chemical degradation and sampling variability. The FE-3 sample was handled and stored at ambient hot cell temperatures for about 7 to 8 months longer than the material used in prior Gas Generation Series I testing (Delegard et al. 2000). During storage for this period and temperature, about 75% of the initial uranium metal mass could have reacted. Thus, a correction factor of 4 was applied to account for the prior reaction. This factor of 4 could be applied to either the nominal or design basis uranium metal concentration. However, because it is based on the conservative assumption that uranium metal in the sample reacted at the higher oxygen-free (anoxic) rate during hot cell storage, the factor only was applied to the safety basis value. The sample-to-sample variability in uranium metal concentration also was considered and a relative uncertainty of 50% (i.e., the concentration could be 1.5-times higher) was applied. With the reaction factor value of 4 and a sampling variability of 50%, an overall factor of 6 (= 4 × 1.5) was established as the multiplier to arrive at the 6 × 0.0057 = 0.034 wt% safety basis uranium metal concentration.

E.5.3.3 Comparison of U1 and U2 to KE NLOP Design and Safety Basis Values

The recommended nominal uranium metal concentration estimate of NLOP-U1 and -U2, 0.018 wt% based on the analysis of the ^{136}Xe detection level, is about 3.2-times the Design Basis KE NLOP sludge value (0.0057 wt%), but is well bounded by the KE NLOP Safety Basis value. As noted above, the KE NLOP basis document provided a 4× factor in the Safety Basis value to account for the sludge aging incurred by the FE-3 sample before its gas generation testing (Schmidt and Baker 2004). The 4× factor applied to the Safety Basis value therefore also could have been applied to the Design Basis value to be more realistic (i.e., 4 × 0.0057 wt% = 0.023 wt%) whereas the current KE NLOP-U1/U2 samples, suffering negligible loss of reactivity by aging before their gas generation testing, would require no such adjustment for sludge aging. Therefore, the observed <0.018 wt% uranium metal observed in the NLOP-U1 and -U2 tests is within a realistic assessment of the KE NLOP Design Basis value.

In summary, the best interpretation of the uranium metal concentration in the NLOP-U1 and -U2 tests, <0.018 wt%, is based on the analysis of the ^{136}Xe detection limit. This value, adjusted by the sampling variability (95% confidence) to <0.031 wt%, is bounded by the KE NLOP Safety Basis value of 0.034 wt%. The uranium metal concentration based on the ^{136}Xe detection limit coincidently is near the value based on the hydrogen-generating Reaction 1 (0.014 wt%, average of NLOP-U1 and -U2 test results).

The Safety Basis uranium metal concentration also bounds the uranium metal concentration (0.0315 wt%) estimated when both Reactions 1 and 2 are considered for tests NLOP-U1 and -U2. It should be noted, however, that the inclusion of Reaction 2 (uranium metal reacting with oxygen) may be unrealistic given the other potential chemical sinks for oxygen consumption (e.g., UO_2 or organic carbon oxidation).[a]

E.5.4 Gas-Generation Profile for Sludge Waste Form Product Tests

Gas generation testing of a control sample of settled sludge (test NLOP-Control) and sludge in three potential waste forms (tests NLOP-Moist, NLOP-Grout, and NLOP-Nochar) were run at 60°C. The NLOP-Control test was run for 1082 hours and the waste form tests for 663 to 778 hours.

The gas-generation profiles (moles of gas generated/kg of settled sludge as a function of reaction time) for the sludge waste form tests (NLOP-Moist, NLOP-Grout, and NLOP-Nochar) are compared with the NLOP-Control performance in Figure E.6. Though the NLOP-Control experiment seems to have the highest gas generation rate, differences in the total gas generation and gas generation rates for the four experiments are low in all cases. As shown in the following section, better estimates of gas generation rates are obtained by mass spectrometric analyses of the sampled product gases.

(a) Further evaluation of the oxygen depletion data collected during the Series III gas generation tests (Schmidt et al. 2003) did not show a consistent trend with the quantity of uranium metal reacted. The lack of a clear trend with uranium metal reacted is evidence that most of the oxygen depletion measured in the gas generation testing is likely the result of other chemical reactions/interactions or experimental test system sensitivity.

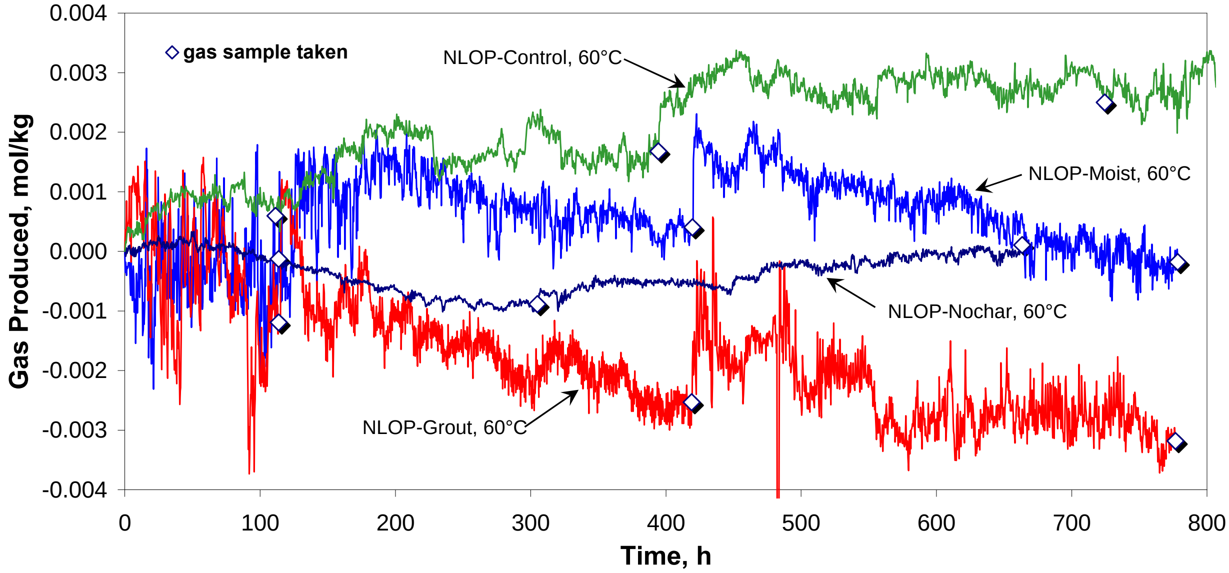

Figure E.6. Total Gas Generation from Tests NLOP-Moist, NLOP-Grout, NLOP-Nochar, and NLOP-Control at 60°C

E.5.5 Results of Gas Sample Analysis for Sludge Waste Form Product Tests

Like the sludge-only tests, carbon dioxide, hydrogen, and hydrocarbons were the primary gases observed and quantified by gas sample mass spectrometry analyses of the NLOP-Control and the three waste form tests. Again, no measurable quantities of any inert fission product gas isotope – krypton (^{83}Kr, ^{84}Kr, ^{85}Kr, ^{86}Kr) and xenon (^{130}Xe, ^{131}Xe, ^{132}Xe, ^{134}Xe, or ^{136}Xe) – were detected.

The quantities of individual gases produced and consumed in each test over the sampling intervals are presented in Table E.7. The gas products were, respectively, 86%, 57%, 30%, and 88% CO_2 over the entire test interval for the NLOP-Control, -Moist, -Grout, and -Nochar experiments. Hydrogen provided 13.9%, 19.7%, 55%, and 10.8%, respectively, of the product gas. Hydrocarbons comprised the balance of the gas production, and small quantities O_2 were consumed and some N_2 generated (for the waste forms). No krypton or xenon was detected in any sample. In addition to gas sample analyses, a separate portion of the NLOP-Grout preparation was found to be pH 11.81 after measurement using soil test methods (ASTM 2001).[a]

(a) According to the methods outlined in the ASTM procedure, ~10 g of crushed NLOP-Grout particles, all less than 2 mm in diameter, were suspended in ~10 ml of distilled/deionized water. The pH of the partially settled slurry was measured to be 11.81 with a pH meter calibrated, in this case, with pH 7.00 and 10.0 buffer solutions.

Table E.7. Net and Cumulative Quantities of Gas Evolved for NLOP-Control, NLOP-Moist, NLOP-Grout, and NLOP-Nochar

Gas	Gas Quantities, moles, at Sampling Times											
	NLOP-Control				NLOP-Moist			NLOP-Grout			NLOP-Nochar	
	111.3 h	394.0 h	723.7 h	1082.0 h	113.7 h	419.3 h	777.7 h	113.7 h	418.7 h	776.0 h	305.0 h	663.0 h
CO_2	7.16E-5	7.96E-5	6.71E-5	5.10E-5	3.75E-5	1.95E-5	1.40E-5	3.71E-6	2.97E-6	8.50E-7	1.79E-5	1.22E-5
Cumulative	7.16E-5	1.51E-4	2.18E-4	2.69E-4	3.75E-5	5.70E-5	7.10E-5	3.71E-6	6.67E-6	7.52E-6	1.79E-5	3.00E-5
H_2	3.74E-6	1.96E-5	1.19E-5	8.49E-6	6.19E-6	1.12E-5	7.19E-6	6.52E-6	3.91E-6	3.27E-6	2.12E-6	1.55E-6
Cumulative	3.74E-6	2.34E-5	3.53E-5	4.37E-5	6.19E-6	1.74E-5	2.46E-5	6.52E-6	1.04E-5	1.37E-5	2.12E-6	3.68E-6
N_2	-1.62E-5	3.23E-6	1.62E-6	1.40E-5	6.99E-6	1.02E-5	9.71E-6	1.01E-5	9.67E-6	6.02E-6	1.81E-6	2.46E-6
Cumulative	-1.62E-5	-1.30E-5	-1.14E-5	2.62E-6	6.99E-6	1.72E-5	2.69E-5	1.01E-5	1.98E-5	2.58E-5	1.81E-6	4.27E-6
O_2	-7.08E-6	1.92E-7	4.19E-7	-1.94E-6	1.00E-6	-1.06E-6	1.18E-6	1.31E-6	-9.82E-7	-1.84E-6	1.25E-6	9.71E-7
Cumulative	-7.08E-6	-6.88E-6	-6.46E-6	-8.40E-6	1.00E-6	-5.87E-8	1.13E-6	1.31E-6	3.24E-7	-1.52E-6	1.25E-6	2.22E-6
CH_4	1.87E-7	1.84E-7	1.20E-7	1.62E-7								
Cumulative	1.87E-7	3.71E-7	4.90E-7	6.52E-7	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
C_2H_x	2.49E-7											
Cumulative	2.49E-7	2.49E-7	2.49E-7	2.49E-7	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
$\geq C_3H_x$	6.23E-8				2.47E-5		5.08E-6	3.84E-6			2.50E-7	
Cumulative	6.23E-8	6.23E-8	6.23E-8	6.23E-8	2.47E-5	2.47E-5	2.98E-5	3.84E-6	3.84E-6	3.84E-6	2.50E-7	2.50E-7
Σ C_yH_x C	8.83E-7	1.84E-7	1.20E-7	1.62E-7	7.84E-5		1.61E-5	1.22E-5			7.91E-7	
Cumulative	8.83E-7	1.07E-6	1.19E-6	1.35E-6	7.84E-5	7.84E-5	9.45E-5	1.22E-5	1.22E-5	1.22E-5	7.91E-7	7.91E-7
^{83}Kr												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{84}Kr												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{85}Kr												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{86}Kr												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Σ Kr	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{130}Xe												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{131}Xe												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{132}Xe												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{134}Xe												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
^{136}Xe												
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Σ Xe	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Cumulative	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0
Total Gas	7.59E-5	9.94E-5	7.91E-5	5.94E-5	6.85E-5	3.07E-5	2.62E-5	1.41E-5	6.88E-6	4.12E-6	2.02E-5	1.37E-5
Cumulative	7.59E-5	1.75E-4	2.54E-4	3.14E-4	6.85E-5	9.91E-5	1.25E-4	1.41E-5	2.09E-5	2.51E-5	2.02E-5	3.40E-5

Because of the high alkalinity of the NLOP-Grout waste form, CO_2 was expected to be at least partially absorbed by reactions such as

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

instead of being released as observed during heating of the untreated sludge. Accordingly, the NLOP-Grout test released only ~5% of the CO_2 released by the NLOP-Control test. However, all treated waste forms were found to release less CO_2 (on a per-kg of settled sludge basis) than the Control test. The respective specific amounts of CO_2 released for the Control and the three waste forms (Moist, Grout, and Nochar) over comparable test intervals (663-778 hours) were 3.9×10^{-3} (100%), 1.3×10^{-3} (33%), 2.1×10^{-4} (5.4%), and 5.6×10^{-4} (14%) moles CO_2/kg settled sludge where the percentages given in parentheses indicate the specific CO_2 amounts compared with the NLOP-Control test.

The specific hydrogen generation quantities for the Control and waste form tests also may be compared over similar test intervals (663-778 hours). For the Control test, H_2 production was about 6.3×10^{-4} moles/kg of settled sludge. All of the waste forms had lower specific H_2 generation. The Moist, Grout, and Nochar samples produced 4.7×10^{-4} (75%), 3.8×10^{-4} (60%), and 6.8×10^{-5} (11%) moles H_2/kg settled sludge, respectively (the percentages again are with respect to the NLOP-Control test).

Although the hydrogen generation rates for the Moist and Grout tests are somewhat smaller than the Control test, the Nochar test yielded a factor of nine less hydrogen than the Control. The reason for the markedly lower hydrogen yield in the Nochar test is not known but may arise from Nochar® acting as a scavenger or recombiner of the hydrogen produced by radiolytic or (less likely) chemical reactions. Like the NLOP-U1 and NLOP-U2 tests (Figure E.4), the specific hydrogen gas generation rates for the Control and three waste form tests are slowly trending lower with time (Figure E.7).

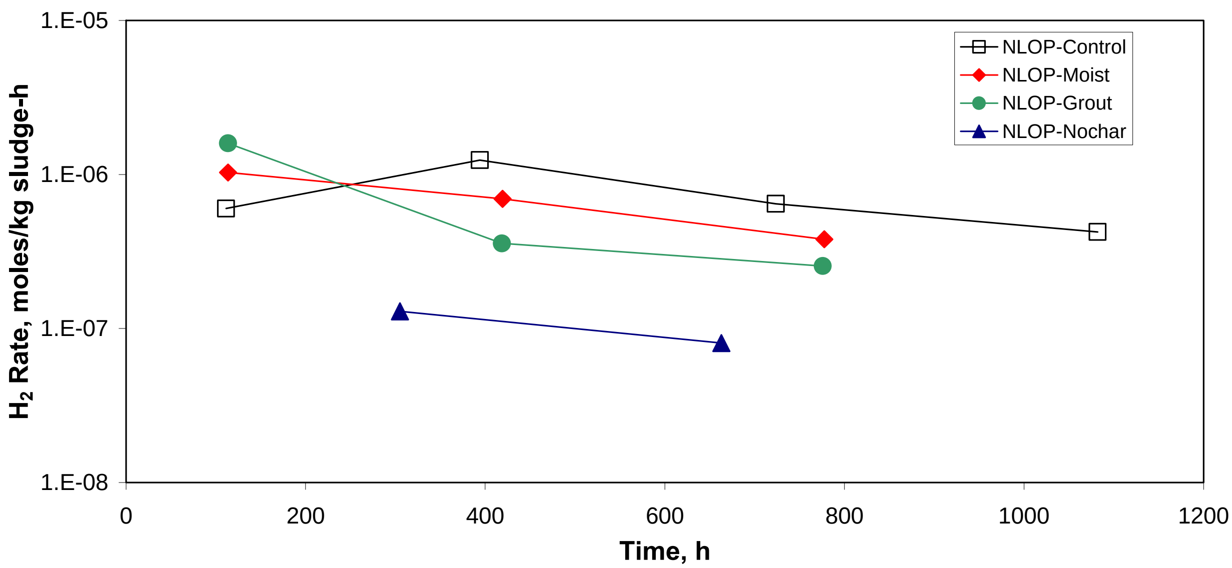

Figure E.7. Specific Hydrogen Generation Rates at 60°C for Tests NLOP-Control, NLOP-Moist, NLOP-Grout, and NLOP-Nochar

E.5.6 Gas Compositions and Generation Rates

The gas sample compositions from the NLOP-U1, NLOP-U2, NLOP-Control, NLOP-Moist, NLOP-Grout, and NLOP-Nochar tests are given in Tables E.8 through E.13, respectively. Gas samples were analyzed by mass spectrometry. The compositions of the generated gases (derived from the compositions of sampled gas by excluding the neon cover gas, argon, and trace nitrogen and oxygen from atmospheric contamination) are presented and are indicated by shading. For example, if analysis found 80% Ne, 5% CO_2, and 15% H_2, the composition of gas formed by excluding Ne would be 25% CO_2 and 75% H_2.

Argon in the gas samples indicates atmospheric (air) contamination, since it is not present in the cover gas and is not produced by the sludge. Nitrogen could be generated or consumed by the sludge or could come from atmospheric contamination. The nitrogen actually generated or consumed is the percent nitrogen found minus 83.6 times the percent argon (the ratio of nitrogen to argon in dry air is 83.6). The percent oxygen generated or consumed in the samples is calculated in a similar manner. The sum of all percents for a test interval may not be exactly 100%, because the values were rounded. The uncertainties in all the entries in these tables are approximately plus or minus 1 in the last digit. However, the low observed gas generation rates and the small absolute quantities of argon from air contamination led, in some cases, to unrealistic projected nitrogen and oxygen consumption and production values for the waste form tests.

Table E.8. Gas Analyses for NLOP-U1 at 95°C and 25°C

Run Sys –3	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1 27KE15	95	91.8	0.013	0.364	6.8	0.006	0.004	0.001	0.89	0.147	<0.001	<0.0001	111.3
				5.1	94.77	0.08	0.06	0.01	-1.58	-1.70	<0.014	<0.0014	
2 27KE20	95	95	91.8	0.213	4.8	0.01	0.005	0.3	1.59	0.3			282.7
				4.0	90.17	0.09	0.09	5.64	4.74	-1.11			
3 27KE24	95	95	92.7	0.15	3.2	0.004	0.005	0.013	2.14	0.414			329.7
				4.4	94.8	0.1	0.1	0.39	8.91	-2.35			
4 27KE26	25	95	94	0.03	0.158			0.07	1.59	0.21			380.7
				11.6	61.2			27.1	33.0	-75.1			

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

Table E.9. Gas Analyses for NLOP-U2 at 95°C and 25°C

Run Sys –4	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1 27KE15	95	92.5	0.009	0.297	6.8	0.007	0.008	0.007	0.35	0.033	<0.001	<0.0001	111.3
				4.17	95.5	0.10	0.11	0.10	-4.48	-2.06	<0.014	<0.0014	
2 27KE20	95	94.2		0.465	4.8	0.01	0.007	0.5	0.026	0.011			282.7
				8.04	83.0	0.14	0.12	8.65	0.4	0.19			
3 27KE24	95	96.5	0.001	0.278	3.18	0.01	0.009	0.02	0.016	0.011			329.7
				7.92	90.6	0.17	0.26	0.57	-1.93	-0.33			
4 27KE26	25	99.2	0.007	0.049	0.148			0.04	0.53	0.069			380.7
				21	62			16.9	12.0	-27.7			

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

Table E.10. Gas Analyses for NLOP-Control at 60°C

Run Sys –5	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	60	98.5	0.007	0.06	1.15	0.003	0.004	0.001	0.241	0.021	<0.001	<0.0001	111.3
27KE15				4.9	94	0.2	0.33	0.1			<0.014	<0.0014	
2	60	98.1	0.003	0.321	1.3	0.00			0.22	0.048			282.7
27KE20				19.8	80	0.2							
3	60	98.6		0.198	1.12	0.00			0.03	0.007			329.7
27KE24				15.0	85	0.2							
4	60	75.2	0.225	0.105	0.63	0.00			18.90	5			358.3
27KE26				14	85	0.3			23.5	-3.2			

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

Table E.11. Gas Analyses for NLOP-Moist at 60°C

Run Sys –6	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	60	98.9	0.003	0.08	0.5		0.3	0.3	0.252	0.057	<0.001	<0.0001	113.7
27KE21				9	55		36.1	36.1			<0.014	<0.0014	
2	60	98.8	0.008	0.14	0.2			0	0.71	0.144			305.7
27KE24				36	64			0					
3	60	98.7	0.008	0.09	0.2		0.06	0.06	0.7	0.171			358.3
27KE26				27	53		19.4	19.4					

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

Table E.12. Gas Analyses for NLOP-Grout at 60°C

Run Sys –7	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	60	99	0.007	0.10	0.1		0.06	0.06	0.66	0.155	<0.001	<0.0001	113.7
27KE21				46.4	26		27.3	27.3			<0.014	<0.0014	
2	60	98.4	0.014	0.06	0.05			0	1.24	0.276			305.0
27KE24				57	43			0					
3	60	99.3	0.006	0.05	0.0			0	0.51	0.084			357.3
27KE26				79	21			0					

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

Table E.13. Gas Analyses for NLOP-Nochar at 60°C

Run Sys –10	Temp. °C	Ne	Ar	H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	60	99.6		0.03	0.286			0.004	0.029	0.02	<0.001	<0.0001	305.0
27KE24				10	88			1.23			<0.014	<0.0014	
2	60	99.5		0.024	0.188				0.04	0.015			358.0
27KE26				11	89								

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

Individual gas-generation rates (Tables E.14 through E.19) are calculated based on the total moles of gas produced (Figure E.3), the generated gas compositions (Tables E.8 through E.13), and the interval times.

Table E.14. Gas-Generation Rates from NLOP-U1 at 95°C and 25°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	8.8E-5	1.6E-3	1.5E-6	9.7E-7	2.4E-7	-2.7E-5	-3.0E-5			111.3
2	95	1.9E-5	4.3E-4	4.5E-7	4.5E-7	2.7E-5	2.3E-5	-5.3E-6			282.7
3	95	1.1E-5	2.3E-4	2.9E-7	3.6E-7	9.5E-7	2.2E-5	-5.8E-6			329.7
4	25	7.6E-6	4.0E-5			1.8E-5	2.2E-5	-4.9E-5			380.7

Blank entries are below detection limits.

Table E.15. Gas-Generation Rates from NLOP-U2 at 95°C and 25°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	7.4E-5	1.7E-3	1.7E-6	2.0E-6	1.7E-6	-7.9E-5	-3.6E-5			111.3
2	95	4.4E-5	4.5E-4	7.5E-7	6.6E-7	4.7E-5	2.4E-6	1.0E-6			282.7
3	95	2.1E-5	2.5E-4	4.6E-7	7.0E-7	1.5E-6	-5.2E-6	-8.8E-7			329.7
4	25	1.4E-5	4.1E-5			1.1E-5	7.9E-6	-1.8E-5			380.7

Blank entries are below detection limits.

Table E.16. Gas-Generation Rates from NLOP-Control at 60°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	1.4E-5	2.8E-4	7.2E-7	9.6E-7	2.4E-7	-6.3E-5	-2.7E-5			111.3
2	95	3.0E-5	1.2E-4	2.8E-7			4.9E-6	2.9E-7			282.7
3	95	1.5E-5	8.7E-5	1.6E-7			2.1E-6	5.5E-7			329.7
4	25	1.0E-5	6.1E-5	1.9E-7			1.7E-5	-2.3E-6			358.3

Blank entries are below detection limits.

Table E.17. Gas-Generation Rates from NLOP-Moist at 60°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	2.5E-5	1.5E-4			9.9E-5	2.8E-5	4.0E-6			113.7
2	95	1.7E-5	2.9E-5				1.5E-5	-1.6E-6			305.7
3	95	9.1E-6	1.8E-5			6.4E-6	1.2E-5	1.5E-6			358.3

Blank entries are below detection limits.

Table E.18. Gas-Generation Rates from NLOP-Grout at 60°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	3.8E-5	2.2E-5			2.3E-5	5.9E-5	7.7E-6			113.7
2	95	8.6E-6	6.5E-6				2.1E-5	-2.1E-6			305.0
3	95	6.1E-6	1.6E-6				1.1E-5	-3.4E-6			357.3

Blank entries are below detection limits.

Table E.19. Gas-Generation Rates from NLOP-Nochar at 60°C

Run	Temp. °C	Gas-Generation Rate, moles/kg-day									
		H_2	CO_2	CH_4	C_2 HC	$C_{>2}$ HC	N_2	O_2	Kr	Xe	Time, h
1	95	3.1E-6	2.6E-5			3.6E-7	2.6E-6	1.8E-6			305.0
2	95	1.9E-6	1.5E-5				3.1E-6	1.2E-6			358.0
Blank entries are below detection limits.											

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