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Pacific Northwest National Laboratory
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Disposition Options for Hanford Site K-Basin Spent Nuclear Fuel Sludge

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Executive Summary

This report provides summary-level information about a group of options that have been identified for the disposition of spent-nuclear-fuel sludge in the K-Basins at the Hanford Site. This study builds upon a review performed in CY1999 which established the current baseline for sludge retrieval and storage from K Basin.[a] Building upon this study, an expert review team was assembled to consider expert knowledge and project progress which has evolved since that time. The membership of this team is provided in Appendix C. This team outlined a revised set of potentially feasible alternatives which could be broadly classified as ambient and elevated temperature treatment methods. In considering the breadth of these methods, the team concluded that the presence of a high uranium metal content fraction was limiting the feasibility of several candidate methods. In other words, if some mechanism were available to eliminate or significantly reduce the uranium metal content, the range and efficacy of feasible treatment methods would be enhanced.

Given these preliminary findings by the team, additional discussions were held with Flour Hanford senior project members to explore both the feasibility of separating a uranium metal stream and the congruence of potentially feasible treatment methods with other program interfaces and objectives.

The selection of alternatives given in this report for disposition of the sludge is derived for this team effort. The product of each treatment option would be treated sludge that would meet waste-acceptance requirements for disposal as transuranic waste at the Waste Isolation Pilot Plant. The separated concentrated uranium stream would be treated by one of several methods identified by the team, which are beyond the scope of this report.

K-Basin sludge is made up of degraded fuel, corrosion products, dirt, and other material that has accumulated in the basins through the 30-year fuel-storage mission. Sludge can be categorized by its location into pit sludge, floor sludge, canister sludge, knockout pot (KOP) sludge, and settler sludge. Pit sludge can be further categorized in accordance with the specific pit in which it resides. Key characteristics of this sludge that shape the selection of a path forward are:

- U-metal[b] content ranging up to 5% for canister sludge (and greater than 50% for KOP sludge)
- Plutonium content greater than 100 nci/gm, requiring controls for airborne alpha
- Dose rates up to approximately 5 rem/h (higher for KOP sludge)
- Fissile content requiring controls for the prevention of nuclear criticality.

The treatment options that were considered can be divided into two groups—those that would be performed at ambient temperature and those that require elevated temperatures. The two

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[a] Sludge Treatment Analysis HNF-4097, Rev. 0, K. L. Pearce, NUMATEC Hanford, 4/27/99.

[b] The term “U-metal” is used to distinguish uranium in the mettallic form from uranium that will be present, as, for example, an oxide or hydride.

ambient-temperature treatment options that were considered were Cementation and Polymer Sorbent Solidification. From the standpoint of process complexity, an ambient-temperature process would be preferable, although using these processes would produce approximately four to eight times as many waste packages as would be produced using the elevated temperature processes. However, to use these ambient temperature processes for the majority of the sludge, H_2 generation from the U-metal-water reaction must be minimized ($U + 2H_2O \rightarrow UO_2 + 2H_2$). Minimizing the U-metal-water reaction will require either 1) demonstrating that the cement or sorbent solidification matrix essentially eliminates the reaction between the U-metal and water that will be present in the treated sludge or 2) demonstrating that the U-metal water reaction in the cement or sorbent solidification products is substantially lower than the rate of reaction in oxygen-free water (perhaps as much as a factor of 20 or greater) and eliminating the majority of the U-metal present in the sludge as a preconditioning step before treatment (perhaps as much as 90% or greater—likely by a physical separation process).

The elevated-temperature treatment options included Drying or Calcining and Bulk Vitrification. These processes will cause the U-metal present in the sludge to be oxidized, which will prevent H_2 generation from U-metal corrosion. These processes also eliminate all (or essentially all) of the water present in the sludge, which will essentially prevent H_2 generation from radiolysis. These two options produce the fewest number of waste packages of any sludge type.

Although it may not be viable to utilize ambient-temperature treatment, such as Cementation or Polymer Sorbent Solidification, to immobilize all of the sludge types without first removing the majority of the U-metal, the anticipated sludge from the KE North Loadout Pit (NLOP) contains U-metal concentrations that are much lower than for the remainder of the sludge. As a consequence, either Cementation or Sorbent Solidification may be a viable option for this sludge fraction.

If Fluor wishes to pursue ambient-temperature treatment for the bulk of the sludge, a number of technical uncertainties must be resolved. These include:

- The nature of the U-metal-water reaction in the cementation product and the amount of U-metal that could be accommodated in the product while achieving acceptable H_2 generation limits.

- The nature of the U-metal-water reaction in the Polymer Sorbent Solidification product and the amount of U-metal that could be accommodated in the product while achieving acceptable H_2 generation limits. Also, the radiation stability and G value for this material should be verified (radiolytic H_2 generation is directly proportional to the G value).

- The extent of U-metal separation that would be required as a sludge preconditioning step to allow Cementation or Polymer Sorbent Solidification to be used, how this preconditioning would be accomplished, and whether implementing this preconditioning step would be feasible and cost effective.

Acronyms

AUC	ammonium uranyl carbonate
CH	contact handled
CONREC	Contaminant Recovery Systems, Inc.
CORECO	College Research Corporation
CSB	Canister Storage Building
CVD	Cold Vacuum Drying Facility
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy-Richland Operations
DST	double shell tank
FGE	^{239}Pu fissile gram equivalent
HLW	high-level waste
INEEL	Idaho National Engineering and Environmental Laboratory
INIS	International Nuclear Information System
KE	K-East
KOP	knockout pot
KW	K-West
LAW	low-activity waste
LDC	large diameter container
MCO	multi-canister overpack
NLO	National Lead Company of Ohio
NLOP	North Loadout Pit
ORNL	Oak Ridge National Laboratory
PCB	polychlorinated biphenyl
PFP	Plutonium Finishing Plant
RCRA	Resource Conservation and Recovery Act
RH	remote-handled
RMIS	Records Management Information System (Hanford)
SAR	Safety Analysis Report
SWB	standard waste box
TRU	transuranic
TSCA	Toxic Substances Control Act

UNC	United Nuclear Corporation
UNH	uranyl nitrate hexahydrate
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant
WTP	Waste Treatment and Immobilization Plant

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1.0 Introduction

This report provides summary-level information about a group of options that have been identified for the disposition of spent-nuclear-fuel sludge in the K-Basins at the Hanford Site. These options are representative of the range of likely candidates that may be considered for disposition of the sludge. The product of each treatment option would be treated sludge that would meet waste acceptance requirements for disposal as transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP).

1.1 Background

K-Basin sludge is made up of degraded fuel, corrosion products, dirt, and other material that has accumulated in the basins through the 30-year fuel-storage mission. Sludge can be categorized by its location into pit sludge, floor sludge, canister sludge, knockout pot (KOP) sludge, and settler tank sludge. Pit sludge can be further categorized in accordance with the specific pit in which it resides. Key characteristics of this sludge that shape the selection of a path forward are:

- U-metal content ranging up to 5% for canister sludge (and greater than 50% for KOP sludge)
- Plutonium content greater than 100 nci/gm requiring controls for airborne alpha
- Dose rates up to approximately 5 rem/h (higher for KOP sludge)
- Fissile content requiring controls for the prevention of nuclear criticality.

Under the baseline approach for processing of the spent fuel and sludge in K-basin, fuel elements and pieces (scrap) larger than 6350 μm (1/4 inch) would be loaded into multi-canister overpacks (MCOs), dried in the Cold Vacuum Drying Facility (CVD), and stored in the Canister Storage Building (CSB), pending disposal at the high-level waste (HLW) repository. The K-Basin sludge would be wet loaded into containers and stored in the 221 T Building until treatment capability is available. A number of treatment options have been considered for such treatment (Pearce et al. 1999).

The sludge found in the North Loadout Pits (NLOPs) in both K-East (KE) and K-West (KW) basins makes up about 20% of the sludge volume. Based on sampling and analysis of the KE NLOP sludge, this stream is lower in U-metal(a) and transuranics than other sludge and is low enough in dose that process operations and waste forms can be engineered to be contact handled. KW NLOP will be sampled in FY 2004 to confirm the assumption that the composition of KE and KW NLOP sludge is roughly the same.

At the other end of the spectrum, KW KOP Sludge has as its principal component U-metal pieces that range in size from 500 to 6350 μm. KOP sludge constitutes only about 1% of the sludge volume but is highly radioactive material that is projected to contain about 25% of all

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(a) The term “U-metal” is used to distinguish uranium in the metallic form from uranium that will be present as, for example, an oxide or hydride.

curies and 87 wt% of all U-metal in the total sludge inventory. This material could be loaded into MCOs, vacuum dried, and stored at CSB as fuel. This path for this material would require that:

- The U-metal be cleaned of fine particulates to ensure effectiveness of the drying process
- Water bearing compounds, such as hydrates, that are mixed with the metal be removed to meet MCO bound-water limits
- Concurrence be obtained from the repository and regulators
- Development of a safety basis for this process.

While interim storage and disposal as fuel appears to be a technically viable option for KOP sludge, this sludge could also be grouped with all the sludge other than NLOP sludge and disposed of as waste.

Sludge other than that held in the NLOP makes up about 80% of the sludge volume. This sludge, which includes the KOP sludge, meets all of the anticipated acceptance criteria for transport to and disposal at WIPP as remote-handled transuranics (RH-TRU), except for free water content, pyrophoric metal content, and hydrogen-generation rate. Hydrogen generation from the decomposition of water from U-metal corrosion ($U + 2H_2O \rightarrow UO_2 + 2H_2$) or from radiolysis could exceed acceptable levels for TRU packages for much of the sludge. To meet requirements for transport and disposal of this waste at WIPP, this sludge must be treated to reduce hydrogen generation from U-metal corrosion.

The review team which engaged in the downselect process resulting in the options discussed within this report recognized that a significant percentage of the uranium metal present in this remaining fraction could be removed by conventional means often employed in the mining industry and elsewhere. The initial screening, already being employed in the KW sludge operations would be to remove all metal particles down to 500 microns. Below this approximate size threshold, other particles besides uranium metal are present and further separation could be achieved by differential specific gravity (uranium being considerably more dense than other constituents.)

Processes that would achieve water removal, such as bulk vitrification or drying/calcining, would reduce hydrogen generation from both corrosion and radiolysis. Immobilization processes that do not remove water, such as Cementation, would not reduce hydrogen generated by radiolysis. Also, the capability of these latter waste forms to inhibit the rate at which hydrogen is generated by uranium corrosion has not been fully demonstrated; if the corrosion rate is not sufficiently inhibited, preconditioning of the sludge to remove or oxidize a substantial fraction of the U-metal would be required before solidification.

1.2 Sludge Inventory

To evaluate the treatment requirements for the various sludge fractions, three sets of K-Basin sludge compositions were considered: safety-basis composition (parameter values and composition at credible extremes), design-basis composition (technically defensible nominal/average values for representative sludge sources), and anticipated composition (projected nominal parameter values and compositions for each individual sludge source, in some cases based on limited data). Safety and design-basis values were taken from the sludge technical data book (Schmidt and Plys 2003). Anticipated values for some the KW KOP and Settler Tank sludge streams were determined by summing the appropriate substreams given in Pearce 2001. Anticipated values for the KE and KW NLOP sludge were based on the analysis of a single sample (composite from several locations) from the KE NLOP. The inventory information is summarized in Table 6.1, Table 6.5, and Table 6.7 that accompany the descriptions of the treatment options in Section 6 of this report.

1.3 Sludge-Treatment Options

Five sludge-treatment options were considered in completing this evaluation. These options were not intended to address all possible alternatives; instead, they were selected to be representative of the range of mature technologies that might be selected for sludge treatment. They include

- Bulk vitrification
- Cementation
- Solidification of the sludge using a polymer sorbent
- Drying or calcining
- Treatment in the River Protection Project Waste Treatment and Immobilization Plant.

Section 6 of this report provides a summary description of each treatment option that addresses:

- The sequence of operations that would need to be performed to implement this option
- Considerations related to storage and transportation of the waste packages that would be produced by this option
- An estimate of the number of waste packages that would be produced
- Uncertainties and potential advantages and disadvantages associated with the option.

2.0 Objective and Scope

The objective of the work documented in this report was to identify and evaluate options for treating the spent-nuclear-fuel sludge in the K Basins at the Hanford Site. These options were selected based on their potential to provide opportunities for accelerated treatment and disposal of this sludge compared to the current baseline.

A group of options was selected for consideration. In making these selections, we did not endeavor to include all potential treatment alternatives. Instead, the selection was intended to be representative of the range of likely candidates that may be considered for disposition of the sludge. Using combinations of these treatment options for the various sludge types was also considered.

The product of each treatment option would be treated sludge that would meet waste -acceptance requirements for disposal as TRU waste at the WIPP. Because the majority of the treated sludge will be remote handled (RH), and waste acceptance criteria (WAC) have not been established by WIPP for RH-TRU, the anticipated WAC for the RH-TRU were developed as a basis for identifying likely treatment requirements and numbers of waste packages to be produced for each treatment option.

3.0 Summary of Results

This section discusses treatment options and disposition strategy.

3.1 Treatment Options

Only one of the treatment options was determined to be non-viable. This option was "Treatment in River Protection Project Waste Treatment and Immobilization Plant (WTP)." Under this option, the sludge would be pretreated to meet double shell tank (DST) storage requirements, and stored in one or more DSTs before treatment in the WTP. This option was judged to be non-viable due to

- Complexity of sludge conditioning required to meet DST acceptance criteria
- Potential requirement to construct, operate, and decontaminate and decommission a new facility for sludge conditioning
- Anticipated time required to bring sludge conditioning capability on-line
- DST space/capacity limitations.

The differences between the remaining four treatment options center on whether treatment would be done at ambient or elevated temperature and the number of packages that would need to be produced to ensure compliance with the anticipated RH-TRU WIPP waste-acceptance requirements. These results are summarized in Table 3.1.

Table 3.1. Summary Comparison of Treatment Options

Treatment Option	**Treatment Temperature**	**Number of Packages[a]**		
		RH 55-Gallon Drums	**RH Canisters**	**CH Standard Waste Boxes**
Ambient Temperature				
Cementation[b]	ambient	2634 – 7593[c]	N/A	N/A
Polymer Sorbent[b]	ambient	3410 – 13,113[d]	N/A	N/A
Elevated Temperature				
Dry or Calcine	~100 to 1100°C	588 - 2280	282 - 1403	N/A
Bulk Vitrification	~1150 to 1250°C	594 - 2280	299 - 1403	1223 - 1409

(a) Value dependent on composition values: Safety Basis, Design Basis, or Anticipated Sludge.

(b) Based on removal of 90% of U-metal and 20× decrease in rate of U-metal-water reaction compared to reaction in oxygen-free water. If U-metal is not removed and the reaction-rate decrease is not realized, the total number of drums could be as high as 300,000 to 600,000.

(c) If KE NLOP sludge is cemented without U-metal removal, the estimated number of 55-gallon drums is 199. This value is based on the Anticipated Sludge composition and is driven by H_2 generation.

(d) If KE NLOP sludge is solidified without U-metal removal, the estimated number of 55-gallon drums is 203. This value is based on the Anticipated Sludge composition and is driven by H_2 generation.

3.2 Disposition Strategy

A disposition strategy for the K-Basin sludge, based on the evaluation of sludge disposition options presented in this report, is shown in. As the figure shows, this strategy provides separate disposition pathways for NLOP sludge; Floor, Canister, and Settler sludge; and KOP sludge.

The NLOP sludge meets all requirements for acceptance for disposal at WIPP as contact-handled TRU (CH-TRU) except for free-water content. This sludge could be treated to eliminate the free water using a Cementation or Polymer Sorbent process. This treatment could be achieved with readily available process systems that could be deployed promptly. Floor, canister, and settler sludge requires treatment to address free-water content, pyrophoric metal content, and hydrogen-generation rate. This might be accomplished by drying/calcining the sludge, immobilizing it in cement (subsequent to removal of the majority of the metal), or immobilizing it in a polymer waste form (if this waste form effectively prevents corrosion of the U-metal present in the sludge). The treated sludge would be disposed of at WIPP as RH-TRU. As discussed in Section 6 of this report, it may be possible to produce CH-TRU through the use of shielded waste packages (e.g., lead-lined 55-gallon drums). If this is done, the waste would be disposed at WIPP as CH-TRU.

The KOP material might be processed for disposal as spent fuel at the HLW repository or processed with the floor, canister, and settler sludge.

Treatment capability will not be available for the bulk of the sludge until well after sludge retrieval is scheduled to start. Therefore, integration of the treatment schedule to the baseline will require interim storage of sludge before treatment or a significant adjustment to the current baseline. One possible exception is the NLOP sludge. If immobilization capability to treat NLOP sludge were acquired on an expedited schedule, then the treatment of this specific sludge could be accelerated. The capability to treat NLOP sludge may have only limited applicability to higher-dose-rate sludge.

Near-term actions for proceeding with an accelerated sludge treatment are as follows:

- Prompt initiation of technical effort to establish a complete technical basis for selected treatment process will be required for any treatment option. This technical effort will include waste-form development and conceptual engineering.
- Laboratory testing to more accurately determine hydrogen generation rates for immobilized K Basin sludge
- Dialogue with HLW Repository Project to determine path forward for pursuing disposal of KOP material as fuel
- Preparation of performance specifications for use in acquiring immobilization process capability.

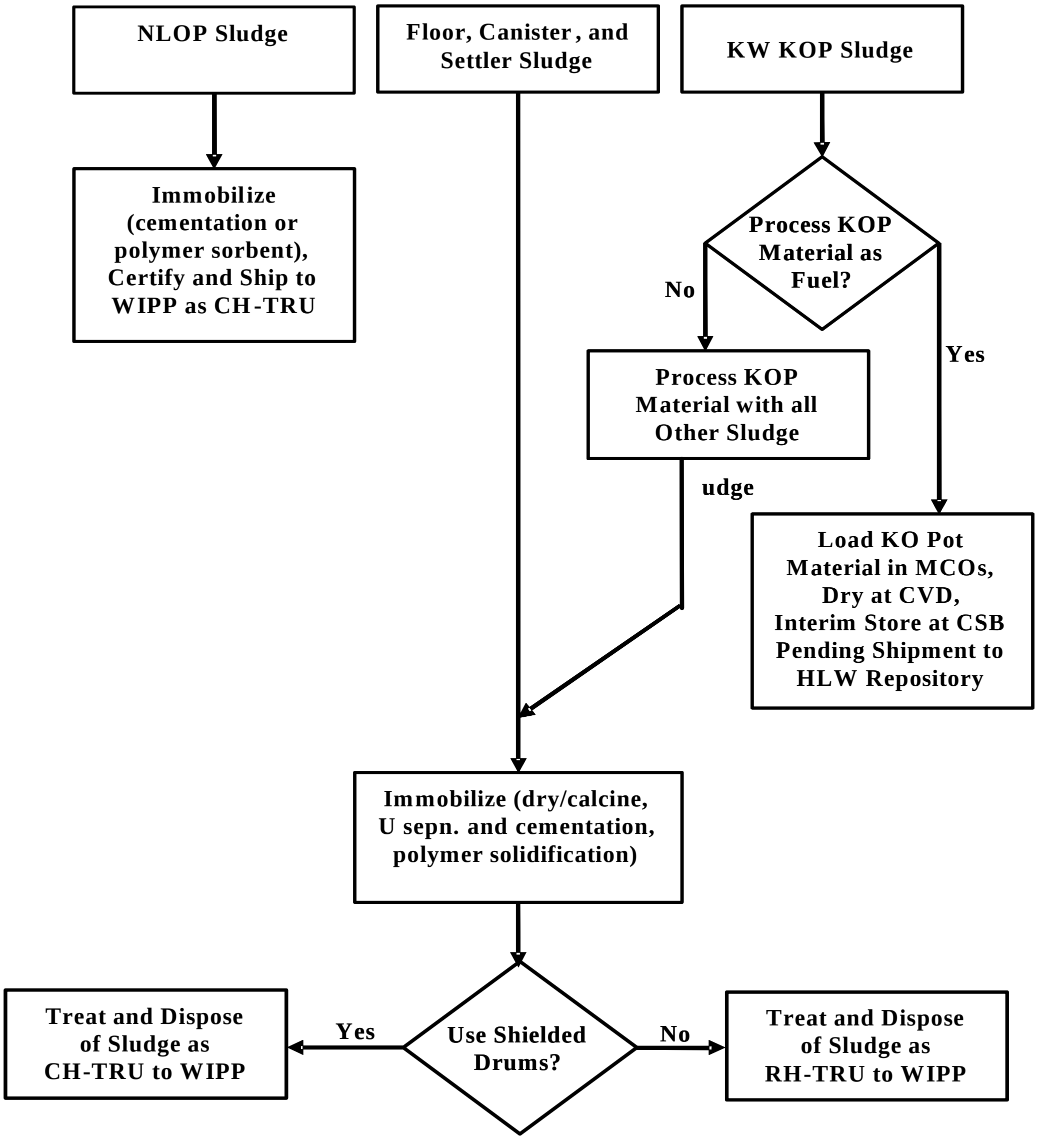

Figure 3.1. Sludge-Disposition Strategy

4.0 Findings and Conclusions

This section covers general findings regarding sludge-disposition alternatives, the various treatment options, the treatment of NLOP sludge, and uncertainties.

4.1 General Findings Regarding Sludge-Disposition Alternatives

- A comprehensive systems solution is needed to select the best alternate path for sludge disposition. Selecting the correct technology for sludge treatment is only part of the solution. Each technology choice can impose different levels of risk regarding areas such as regulatory compliance, programmatic and schedule goals, budgetary requirements, and life cycle costs. It is simply not sufficient to assume that these issues will be resolved in the future. They need to be included as part of a systems solution since they can profoundly impact the relative ranking of technologies.

- All radioactive sludge is not the same, and K-Basin sludge represents some of the most difficult material to treat across the complex. This sludge contains a unique combination of alpha source term, high general radiation field, toxic chemical constituent, high metal content, plus a broad variation in particle size, heterogeneity across each basin (east and west), and fundamentally different characterization between the two basins.

- A number of choices for treatment technology appear to be technically feasible. However, none of these has been previously applied by the U.S. Department of Energy for dispositioning sludge of similar composition.

- Application of any alternate technology will impact existing interim program milestones for sludge removal, decontamination and decommissioning, and possibly fuel removal. Most of these program elements are already on the critical path, and little or no float exists.

- The focus of stakeholder interest appears to be to complete the removal of radiological risk to the Columbia River from K Basin, and to ultimately ship all removed materials off the Hanford site. Some willingness among the stakeholders to restructure interim milestones seems feasible, especially if such a restructuring presents a more global solution (e.g., accelerating the ultimate site removal in exchange for some delay in K-Basin closure, especially if this plan includes intermediate risk-reduction measures for the River Corridor).

- The selection of alternate treatment methods should focus on industrially-proven technologies. This might include new applications of existing commercial systems from other industries. However, a number of other promising methods that need additional scientific development simply require too much lead time to be of practical benefit. This same logic may also apply to novel packaging concepts that are still in the conceptual stage.

- The general approach of segregating sludge by location or physical characteristic seems to have merit and seems to be viewed favorably by concerned parties. Much of the conservatism found in the current baseline, and likely to be found in a revised baseline, stems from the large variability in sludge characteristics that impact safety, handling, and transportation (e.g., criticality, heat loading, and hydrogen generation). Within safety space, this requires the overly conservative assumption that the most extreme circumstances of each characteristic appear simultaneously within each batch handled. This conservatism also extends to the efficiency of alternate treatment methods. However, by selectively segregating the sludge characteristics that limit safety compliance, each resultant stream can be handled more easily, and certain candidate technologies that were deemed inappropriate for the entire sludge volume could be employed for one of the segregated streams (e.g., calcinations or cementation).

- Any alternate sludge-disposition path would most likely require some measure of short-term interim storage, either at T-Plant (or alternate Hanford locations) within large-diameter containers (LDCs), alternate containers, or engineered interim storage within K Basin, to allow time for development and regulatory approval of program changes. Simple storage options are best, especially those that are easily recoverable or close to the final waste-acceptance form. One alternative is to store the sludge in the basins themselves over an interim period until final processing measures can be put in place (e.g., a canister sized container that might fit within current fuel storage racks and might additionally involve the transfer of containers from KE for storage in KW.

- Despite its complexity, K Basin sludge represents a relatively small volume of material and is therefore more amenable to "custom handling" than "mass production" treatment methods. Amortization of process costs for elaborate systems is therefore not feasible, but simpler systems, even with lower throughput, become more viable.

- Despite the relatively small volume of sludge, dilution strategies to meet safety constraints do not appear to be effective and typically result in excessively large shipment volumes of treated materials. This especially appears to be of greatest concern for cementation methods.

- Advances in transport containers (e.g., 55-gallon lead-lined drums) and reduced uncertainty over WIPP WAC may allow for more efficient packaging/transportation in the future and possibly the development of CH packages for some or all of the sludge. None of these options appears to be immediately available today, but it might be available by the time alternate treatment methods could be implemented. Therefore, the path forward should not preclude the future inclusion of these improvements.

4.2 Treatment Options

The treatment options that were considered can be divided into two groups – those that would be performed at ambient temperature and those that require elevated temperatures.

- Ambient-Temperature Treatment. The two ambient-temperature treatment options that were considered were Cementation and Polymer Sorbent Solidification. From the standpoint of process complexity, an ambient temperature process would be preferable, although using these processes would produce approximately four to eight times as many waste packages as would be produced using the elevated temperature processes (this package count will be driven by the need to limit the rate of H_2 generation). However, to use these processes for the majority of the sludge, H_2 generation from the U-metal-water reaction must be minimized. If this is not done, the number of packages that would be produced would be large enough that implementation would not be practical. Minimizing the U-metal-water reaction will require either 1) demonstrating that the cement or sorbent solidification matrix essentially eliminates the reaction between the U-metal and water that will be present in the treated sludge or 2) demonstrating that the U-metal water reaction in the cement or sorbent solidification products is substantially lower than the rate of reaction in oxygen-free water (perhaps as much as a factor of 20 or greater) and eliminating the majority of the U-metal present in the sludge as a preconditioning step before treatment (perhaps as much as 90% or greater—likely by a physical separation process).

- Elevated Temperature Treatment. The treatment options included in this group are Drying or Calcining and Bulk Vitrification. These processes will cause the U-metal present in the sludge to be oxidized, which will prevent H_2 generation from U-metal corrosion. These processes also eliminate all (or essentially all) of the water present in the sludge, which will essentially prevent H_2 generation from radiolysis. As a result, the drivers for number of waste packages for these options will be the ^{239}Pu fissile gram equivalent (FGE) limit for higher activity sludge types such as KOP and canister sludge, and the FGE limit and the volume of the final product for lower activity sludge types, such as floor and pit sludge. These two options produce the fewest number of waste packages of any sludge type.

4.3 Treatment of NLOP Sludge

Although it may not be viable to use an ambient-temperature treatment, such as Cementation or Polymer Sorbent Solidification, to immobilize all of the sludge types without first removing the majority of the U-metal, the anticipated sludge from the KE NLOP contains U-metal concentrations that are much lower than for the remainder of the sludge. As a consequence, if the U-metal content of the KE NLOP sludge is equal to or lower than the anticipated value, or if the cement or sorbent matrix moderately inhibits the reaction rate of U-metal, Cementation, or Sorbent Solidification may be a viable option for this sludge fraction.

4.4 Uncertainties

From the standpoint of process complexity, an ambient-temperature process, such as the Polymer Sorbent Solidification or Cementation options, would be preferable. As discussed in the preceding section, these processes appear to be suitable for treating NLOP sludge. However, to use these processes for the majority of the sludge, the H_2 generation from the U-metal-water reaction must be minimized. Key technical uncertainties that must be addressed in the near term related to this source of H_2 generation include:

- The nature of the U-metal-water reaction in the cementation product and the amount of U-metal that could be accommodated in the product while achieving acceptable H_2-generation limits.

- The nature of the U-metal-water reaction in the Polymer Sorbent Solidification product and the amount of U-metal that could be accommodated in the product while achieving acceptable H_2-generation limits.

- The degree of U-metal separation that would be required as a sludge preconditioning step to allow Cementation or Polymer Sorbent Solidification to be used, how this preconditioning would be accomplished, and whether implementing this preconditioning step would be feasible and cost effective.

Initial testing would be performed using simulated sludges. If the results of these initial tests are positive, subsequent testing with actual sludge would be performed.

If the results of the above testing indicate that Polymer Sorbent Solidification is a viable candidate from an H_2 generation standpoint, testing for radiation stability should also be performed. In addition, the G Value for this material should also be verified.

5.0 Product Requirements

The products of sludge treatment will be TRU waste and, as such, they will be disposed of at WIPP. The products of sludge treatment will, in most cases, be classified as remote-handled TRU (RH-TRU); the exception to this is the treated NLOP sludge that may be classified as CH-TRU waste. Although waste acceptance criteria for RH-TRU have not been established by WIPP, it is anticipated that they will be essentially the same as those for CH-TRU waste with the exception of the surface-dose-rate limitation (≤200 mrem/h for CH-TRU vs. ≤1000 rem/h for RH-TRU), and packaging requirements (RH-TRU will be shipped to WIPP in an RH-72B shipping cask; within the shipping case, the waste must be contained in an RH canister or in 55-gallon drums loaded into an RH canister). The anticipated RH-TRU waste acceptance criteria that have the potential to impact sludge treatment are provided in Table 5.1.

Table 5.1. Anticipated Acceptance Criteria[(a)]

Waste-Form Requirement	
Particle Size	Not specified
Pyrophoric Constituents	Radionuclide pyrophorics: <1% Non-radionuclide pyrophorics prohibited
Flammable Gas	Flammable VOCs ≤500 ppm in headspace H_2 concentration in innermost layer of confinement ≤5% by volume
Heat Generation	<300 Watt/RH canister
Fissile Material	Drum: ≤200 FGE RH-TRU Canister or Shipping Container: ≤325 FGE
Surface Dose Rate	≤1000 rem/h (note: 95% of RH-TRU received by WIPP is required to have a dose rate of ≤100 rem/h)
TRU Alpha Activity	≤ 23 Ci/L total activity
RCRA-Regulated Waste	Accepted for specific waste codes identified in Hazardous Waste Facility Permit; wastes exhibiting characteristics of ignitability, corrosivity, and reactivity are specifically excluded
TSCA/PCB-Regulated Waste	<50 ppm PCBs[(b)]
Residual Liquid	< 1% by volume of container
Packaging Requirement	
Container	55-gallon drum RH-TRU Canister (121 in. long × 26 in. diameter)
RH-TRU Canister Weight (max. gross)	8000 lbs (includes canister wt. of 1,760 lbs)

VOC = volatile organic compound; TRU = transuranics; RCRA = Resource Conservation and Recovery Act; TSCA = Toxic Substances Control Act; PCB = polychlorinated biphenyl.

(a) Based on *Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, DOE/WIPP-069 (1996); *Contact Handled Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, DOE/WIPP-02-3122 (2002) (which superceded DOE/WIPP-069); and *Remote Handled Transuranic Waste Study*, DOE/CAO 95-1095 (1995).

(b) Approval granted by EPA, Region 6, on May 15, 2003, of WIPP request to dispose of TRU and TRU-mixed waste containing PCBs (conditional approval for storage and disposal of RH PCB/TRU and PCB/TRU mixed waste was not granted but will consider future requests for approval); WIPP WAC has not been revised to address this approval.

An acceptance criterion that has a significant impact on sludge treatment is the requirement that the H_2 concentration in the innermost layer of confinement not exceed 5% by volume during transportation. Two sources of H_2 generation need to be considered: radiolysis and the corrosion reaction between the U-metal and water present in the treated sludge. For the purpose of this analysis, it was assumed that the cemented sludge, sludge that is solidified using a polymer sorbent, and bulk-vitrified sludge would be packaged within 55-gallon drums; these drums would constitute the "innermost" layer of confinement. Further, it was assumed that dried or calcined sludge would be packaged either into 55-gallon drums or directly into RH Canisters. For the former case, the 55-gallon drums would be the innermost layer of confinement; for the latter, the RH canisters would be innermost layer of confinement.

The safety documentation for the RH-72B shipping cask (for RH-TRU) and TRUPACT II shipping cask (for CH-TRU) specify the methodology for determining the allowable H_2 gas release rate. This methodology assumes a 60-day transportation period and considers how the material is packaged—how many layers of packaging (e.g, bags, drums) there are between the waste and the sealed shipping cask—and the diffusion of the H_2 from the waste through the various layers of packaging. This calculation establishes the maximum rate at which H_2 can be generated. The safety documentation also specifies the methodology for determining the decay-heat limits that ensure that the rate of radiolytic H_2 generation will not exceed the maximum allowable rate of H_2 generation. Finally, the safety documentation provides maximum H_2 generation rate and decay heat limits for numerous waste types and packaging configurations.

For the purpose of this evaluation, the specified methodologies were not used to determine H_2-generation-rate limits. Instead, waste type and packaging configurations in the safety documentation were identified that were similar to treated K-Basin sludge; the H_2-generation-rate limit and decay heat limits for those wastes were assumed to provide a reasonable approximation of the limits that would be determined for the K-Basin sludge. These limits are shown in Table 5.2.

The decay-heat limits were used to determine the number of packages of treated waste that would be produced for each treatment technology based on the need to limit radiolytically generated H_2.

The hydrogen-generation-rate limit for each package was used to determine the number of packages that would be produced for each treatment technology based on the need to limit the rate of total H_2 generation by radiolysis and by U-metal corrosion.

The assumptions that were used in this analysis to assess the impact of U-metal corrosion are shown in Table 5.3. The corrosion-rate values are based on the conservative assumption that the U-metal present in the treated sludge will react with the water present at the same rate as would be found for U-metal corroding in oxygen-free water. The 500-µm value is equal to the Safety Basis and Design Basis value for reactive sludge particle size for non-size-segregated sludge (Schmidt and Plys 2003).

Table 5.2. Hydrogen-Gas-Generation Rate and Decay-Heat Limits for Treated Sludge

Waste Classification	Numeric Payload Shipping Category CH)/ Content Code (RH)	Waste Description	Hydrogen Gas Generation Rate Limit per Package (mole/sec)	Decay Heat Limit per Package (W)
Cemented Sludge				
CH-TRU	10 0130 0190	Sludge mixed with Portland Cement packaged in 55-gallon drums	Drum: 2.643E-08(a)	Drum: 0.1962(a)
RH-TRU	RH 314A	Cemented inorganic process solids packaged in 55-gallon drums	Drum: 3.8391E-08(b)	Drum: 0.6033(b)
Polymer Sorbent Solidified Sludge				
RH-TRU	RH 314A	Cemented inorganic process solids packaged in 55 gallon drums	Drum: 3.8391E-08(b)	Drum: 0.2657(c)
Bulk Vitrified Sludge				
Not applicable – no U-metal will be present, nor will there be any water or hydrocarbon sources for radiolytic H_2 generation.				
Dried or Calcined Sludge				
RH-TRU	RH 322A	Solid inorganic waste	Drum: 3.8391E-08(d) RH Canister: 1.1517E-07(d)	Drum: 18.10(d) RH Canister: 54.30(d)

(a) From Table 5.5-1 of TRUPACT II Authorized Methods for Payload Control [TRAMPAC], Rev 19c, April 2003, for Numeric Payload Shipping Category 10 0130 0190.

(b) From Table 5.1 of the RH-TRU 72-B Cask SAR, Rev 3, June 2002, for content code RH 314A.

(c) From Table 5.1 of the RH-TRU 72-B Cask SAR, Rev 3, June 2002, for content code RH 314A, modified to account for assumed G value of 1.09 compared to G value of 0.48 for RH 314A. Source for G value of 1.09 is Table 5-2 of the "TRUPACT-II Authorized Methods for Payload Control (TRAMPAC) Rev. 19c, April 2003." This is the dose dependent G value for Type III.1 waste with a dose greater than 0.012 watt*year).

(d) From Table 5.1 of the RH-TRU 72-B Cask SAR, Rev 3, June 2002, for content code RH 322A.

Table 5.3. Assumptions Used to Assess Impact of H_2 Generation by U-Metal Corrosion

Form	U Density (g/cm^3)	Surface Area per Unit Mass (cm^2/g-U-metal)	H_2 Generation Rate at 60°C (mL/cm^2-h)	H_2 Generation Rate at 60°C (mL/g/h)
U-metal present as 500-μm diameter spheres	19.05	6.30	0.05261	0.331404

6.0 Treatment-Option Descriptions

This section covers treatment at ambient temperature, treatment at elevated temperatures, and treatment in the River Protection Project Waste Treatment and Immobilization Plant.

6.1 Ambient-Temperature Treatment

Two of the treatment options would be performed at ambient temperature. These include Cementation and Polymer Sorbent Solidification. These treatment options are described in the following sections.

6.1.1 Cementation

In this option, K Basin sludge would be recovered (wet), containerized (or piped), and transported to a facility (modified or new) to characterize and cement the sludge. Alternatively, it is possible that the characterization and cementation operations could be conducted in a skid-mounted or transportable facility adjacent to the K Basins (potentially eliminating the need to containerize and transport the sludge to another facility). The sludge would be mixed with cement formers to produce a mixture that contained 30-vol.% sludge and poured into drums where it would solidify. The cemented sludge would be stored and ultimately transported to WIPP. The steps required to implement this option are shown in Figure 6.1.

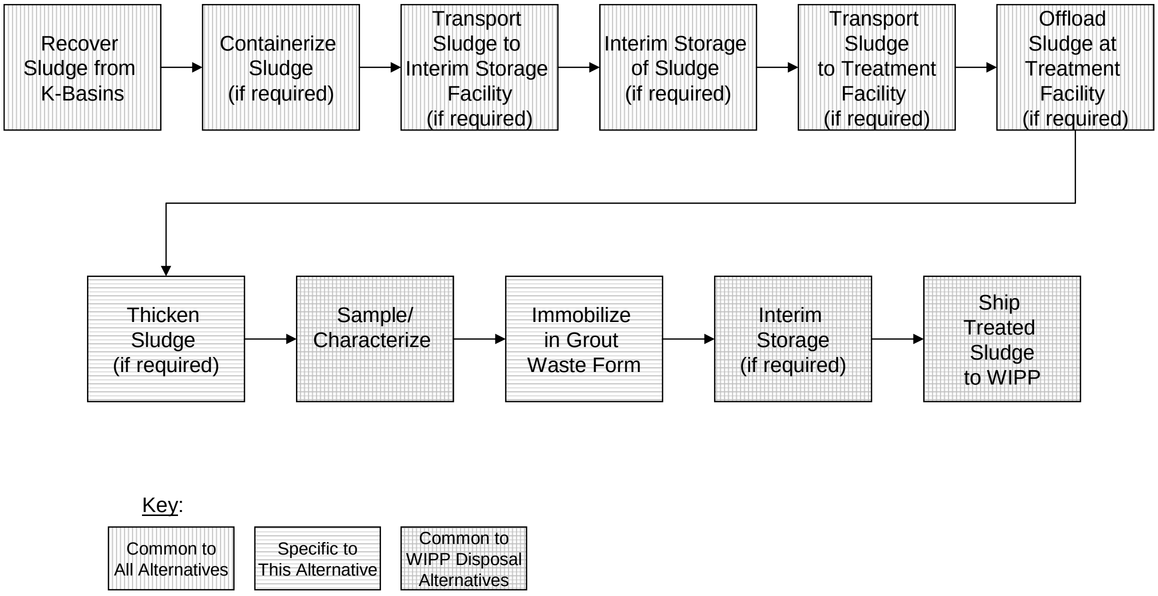

Figure 6.1. Cementation

6.1.1.1 Storage and Transportation of Waste Packages

Hydrogen gas will be generated by the cemented-sludge waste form. This will include some level of H_2 generated by the reaction of U-metal with water ($U + 2H_2O \rightarrow UO_2 + 2 H_2$) as well as H_2 generated by the radiolysis of the entrapped water and water vapor in the cement. The cement would need to be stored in vented containers in a suitable facility. The cemented sludge would be shipped to WIPP in a RU-72B shipping cask.

Cemented sludge packaged in 55-gallon drums would have a sufficient surface dose rate to be RH-TRU (1000 rem/h $\geq$surface dose rate $\leq$200 mrem/h).[a] Through the use of shielded (e.g., lead-lined) 55-gallon drums, it may be possible to produce cemented produce from the higher activity sludges that meets the surface-dose-rate requirement for CH-TRU (surface dose rate $\leq$200 mrem/h). However, it should be noted that the TRUPACT-II Authorized Methods of Payload Control (TRAMPAC/Rev. 19c) document specifically proscribes the use of shielding as a means of producing CH-TRU waste packages. Also, the TRUPACT-II Safety Analysis Report (SAR) states that "Since shielding of the radionuclides is not permitted to meet the transportation dose rate limits…" It should also be noted that the use of lead shielding will result in drums that weigh up to ~1800 lbs empty and ~2000 lbs or more when filled with treated sludge; this is substantially more than the 1000-lb limit currently specified by WIPP. As such, the TRUPACT-II SAR and supporting documentation would need to be revised to allow this approach, and relicensing of the cask may be required. Modifications to additional permits and licenses related to receipt and disposal of the waste at WIPP may also be required.

6.1.1.2 Number of Waste Packages

The estimated number of waste packages that would be produced, depending on the sludge composition, is shown in Table 6.1. This information is summarized in Table 6.2.

As can be seen from Table 6.1, if the sludge is cemented without preconditioning to eliminate the U-metal present in the sludge, the numbers of canisters that would be produced will be driven by the requirement to limit H_2 generation by the reaction of U-metal with water. This is a transportation-related requirement that is intended to ensure that H_2 released during transportation does not reach a flammable concentration. The numbers of drums shown in the Table 6.1 "Based on H_2 Generation from U Metal-Water Reaction" are based on the estimated U-metal concentration in the sludge, the assumption that this metal has an average particle size of 500 microns, and the assumption that the U-metal in the cemented sludge will react with the unbound water or water vapor in the cement at the same rate as the U-metal would react with oxygen-free water. Although the reaction-rate assumption is conservative, the reaction rate would have to be lower by a factor of 100 or more for the U-metal-water reaction to no longer drive the package count. It is considered unlikely that this would be demonstrated.

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[a] Cemented KE NLOP sludge packaged in S200 Pipe Overpacks would have a surface dose rate less than the CH-TRU limit of 200 mrem/h.

Table 6.1. Cemented Sludge - Impact of Hydrogen Gas Generation Rates, FGE Limits, and Cemented-Sludge Volume on Number of Drums

Safety Basis													
Sludge Description					**H2 Generation (See Note 1)**						**FGE Limit (See Note 2)**		**Grout Volume (See Note 3)**
					No. 55 Gallon Drums						FGE	No. Drums	No. Drums
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Safety Basis Decay Heat, W/m3	Safety Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on H2 Generation from U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Based on H2 Generation from U Metal - Water Reaction (20X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (20X rxn decrease, 90% U removed)			
KW Basin Sludge Sources													
KOP Sludge	Fuel Piece	0.423	1100	9.4	771	426174	4262	5033	2131	2902	3.46E+04	173	7
Settler Tank Sludge	KW Canister	2.83	256	0.2	1201	60665	607	1808	303	1504	1.56E+05	780	48
Floor Sludge	KW Canister	1.01	256	0.2	429	21651	217	645	108	537	5.55E+04	278	17
NLOP Sludge	KE Floor	3.64	22.4	0.023	135	8973	90	225	45	180	1.18E+04	59	62
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	77	0.125	319	33494	335	654	167	487	6.76E+04	338	43
Floor and Pit Sludge	KE Floor	33.8	22.4	0.023	1255	83323	833	2088	417	1672	1.10E+05	550	578
NLOP Sludge	KE Floor	6.3	22.4	0.023	234	15531	155	389	78	312	2.05E+04	103	108

Design Basis													
Sludge Description					**Hydrogen Generation (See Note 1)**						**FGE Limit (See Note 2)**		**Grout Volume (See Note 3)**
					No. 55 Gallon Drums						FGE	No. Drums	No. Drums
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Design Basis Decay Heat, W/m3	Design Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on H2 Generation from U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Based on H2 Generation from U Metal - Water Reaction (20X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (20X rxn decrease, 90% U removed)			
KW Basin Sludge Sources													
KOP Sludge	Fuel Piece	0.423	689	9.4	483	426174	4262	4745	2131	2614	3.75E+04	188	7
Settler Tank Sludge	KW Canister	2.83	87.2	0.057	409	17289	173	582	86	495	3.91E+04	196	48
Floor Sludge	KW Canister	1.01	87.2	0.057	146	6170	62	208	31	177	1.39E+04	70	17
NLOP Sludge	KE Floor	3.64	3.12	0.004	19	1561	16	34	8	27	1.91E+03	10	62
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	21.7	0.04	90	10718	107	197	54	144	1.61E+04	81	43
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	175	14491	145	320	72	247	1.78E+04	89	578
NLOP Sludge	KE Floor	6.3	3.12	0.004	33	2701	27	60	14	46	3.31E+03	17	108

Table 6.1 (Cont'd)

Anticipated Sludge													
Sludge Description					**Hydrogen Generation (See Note 1)**						**FGE Limit (See Note 2)**		**Grout Volume (See Note 3)**
					No. 55 Gallon Drums						FGE	No. Drums	No. Drums
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Anticipated Decay Heat, W/m3	Anticipated U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on H2 Generation from U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Based on H2 Generation from U Metal - Water Reaction (20X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (20X rxn decrease, 90% U removed)			
KW Basin Sludge Sources													
KOP Sludge	See Note 4	0.52	334	4.21	288	234641	2346	2634	1173	1461	2.26E+04	113	9
Settler Tank Sludge	See Note 5	2.72	50	0.0268	225	7813	78	304	39	264	3.07E+04	154	47
Floor Sludge	KE Floor	1.01	3.12	0.004	5	433	4	10	2	7	5.32E+02	3	17
NLOP Sludge	See Note 6	3.64	0.304	0.0002	2	113	1	3	0	2	3.76E+02	2	62
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	21.7	0.04	90	10718	107	197	54	144	1.61E+04	81	43
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	175	14491	145	320	72	247	1.78E+04	89	578
NLOP Sludge	See Note 6	6.3	0.304	0.0002	3	196	1	5	1	4	6.52E+02	3	108

Note 1: For RH drums, ≤ 3.8391E-08 mole/sec (from Table 5.1 of the RH-TRU 72-B Cask SAR, Rev 3, June 2002, for content code RH 314A, a waste consisting of "Cemented Inorganic Process Solids").

Note 2: Pu-239 Fissile Gram Equivalent (FGE) limit is ≤ 200 for drums.
Note 3: Based on a grout formulation containing 30 volume % sludge

Note 4: Composition base on August 14, 2003 KW Sludge Process Mass Balance. Decay Heat is an approximation
Note 5: Composition base on August 14-03 KW Sludge Process Mass Balance. Decay Heat is an approximation
Note 6. Based on composition of KE NLOP Sludge Sample FE-3. U metal content is 10X valued measured for FE-3

🟩	Number of drums if sludge is preconditiond to remove 90% U, 20X reaction rate decrease.
🟨	Number of drums of cemented KE NLOP sludge based on Anticipated compostion (total is sum of drums based on radiolytic generation plus drums based on U-water reaction).

Table 6.2. Estimated Number of Waste Packages for Cementation Option

Composition	Waste Package	Number of Packages[(a)]	Limiting Requirement(s)
Safety Basis	55-gallon drum	7593	H_2 Generation
Design Basis	55-gallon drum	4178	H_2 Generation, Product Volume
Anticipated Sludge	55-gallon drum	2634[(b)]	H_2 Generation, Product Volume

(a) If the sludge is cemented without preconditioning to eliminate the U-metal present in the sludge, the U-metal-water H_2 generation reaction will likely drive the package count for all compositions and sludge types, and the total number of packages could be as high as 300,000 to 600,000.
(b) If KE NLOP sludge is cemented without U-metal removal, the estimated number of 55-gallon drums is 199. This value is driven by H_2 generation.

If a sufficiently low U-metal-water reaction rate cannot be achieved, an effective means of eliminating the majority of the U-metal from the sludges would be required for Cementation to be a viable option (a potential process for U-metal removal is discussed in Section 6.1.3.2 of this report). Table 6.2 shows the number of 55-gallon drums that would be produced if 90% of the U-metal is eliminated from the sludge, and the U-metal-water reaction rate in the cemented waste form is a factor of 20 lower than the rate in oxygen-free water.

6.1.1.3 Cementation of KE North Loadout Pit Sludge

Although it may not be viable to use Cementation to immobilize all of the sludge types without first removing the majority of the U-metal, the anticipated sludge from the KE NLOP contains U-metal concentrations that are much lower than for the remainder of the sludge. As a consequence, if the U-metal content of the KE NLOP sludge is equal to or lower than the anticipated value, or if the cement matrix moderately inhibits the reaction rate of U-metal, Cementation may be a viable option for this sludge fraction. The estimated package count for this sludge, which accounts for approximately 13% of the total sludge volume, is shown in Footnote (b) of Table 6.2. The steps that might be used to implement this option are shown in Figure 6.2.

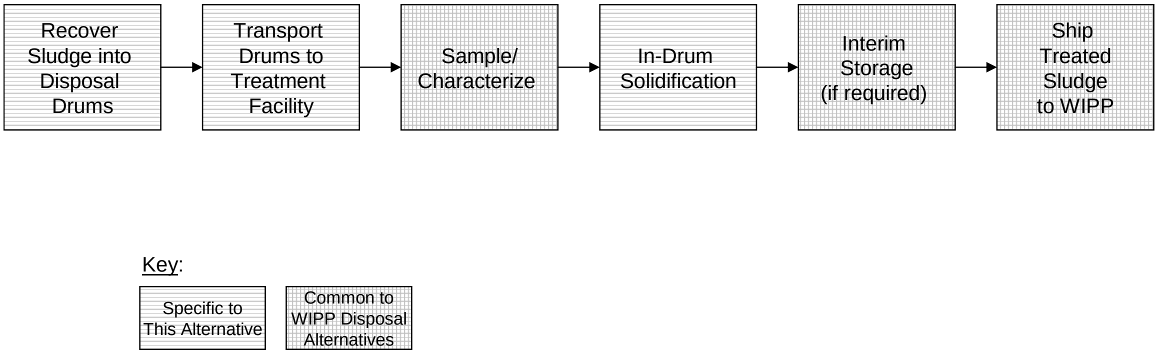

Figure 6.2. NLOP-Sludge Cementation

6.1.1.4 Uncertainties

Before deciding to implement Cementation as the treatment option for sludges other than NLOP sludge, a number of technical uncertainties would need to be addressed. These include:

- Obtaining a better understanding of the U-metal-water reaction in cemented sludge.

- If the U-metal content of the sludge must be substantially reduced or eliminated to allow Cementation, what is the most effective means of accomplishing this (e.g., removal or oxidation of the U-metal), and how would this be accomplished?

- What type of cementation processes are most appropriate for this application and have these processes been proven/demonstrated for high-activity steams?

- If the potential for making CH products through use of shielded 55-gallon drums is to be pursued, it must be determined whether WIPP would certify as CH-TRU waste that achieves the surface-dose-rate limitation through the use of such shielded packages.

6.1.1.5 Advantages and Disadvantages of Cementation

The following items summarize the high-level advantages and disadvantages associated with treating the sludge using Cementation.

Advantages

- Cementation is a technically simple, ambient-temperature process that will produce minimal amounts of secondary waste.
- Could possibly be deployed near-term to solidify NLOP sludge.

Disadvantages

- The process will likely require a preconditioning step to remove or oxidize the U-metal in the sludge to substantially reduce H_2 generated from the reaction of U-metal with entrapped water and water vapor in the cementitious waste form.

6.1.2 Polymer-Sorbent Solidification

In this option, K Basin sludge would be recovered (wet), containerized (or piped), and transported to a facility (modified or new) to characterize and solidify the sludge. Alternatively, it is possible that the characterization and solidification operations could be conducted in a skid-mounted or transportable facility adjacent to the K Basins (potentially eliminating the need to containerize and transport the sludge to another facility). For the solidification operation, drums would be pre-loaded with the solidification agent; sludge, and perhaps additional solidification agent, would be metered into the drums. The solidified material would contain 30 vol.% sludge. This material would be stored and ultimately transported to WIPP. The steps required to implement this option are shown in Figure 6.3.

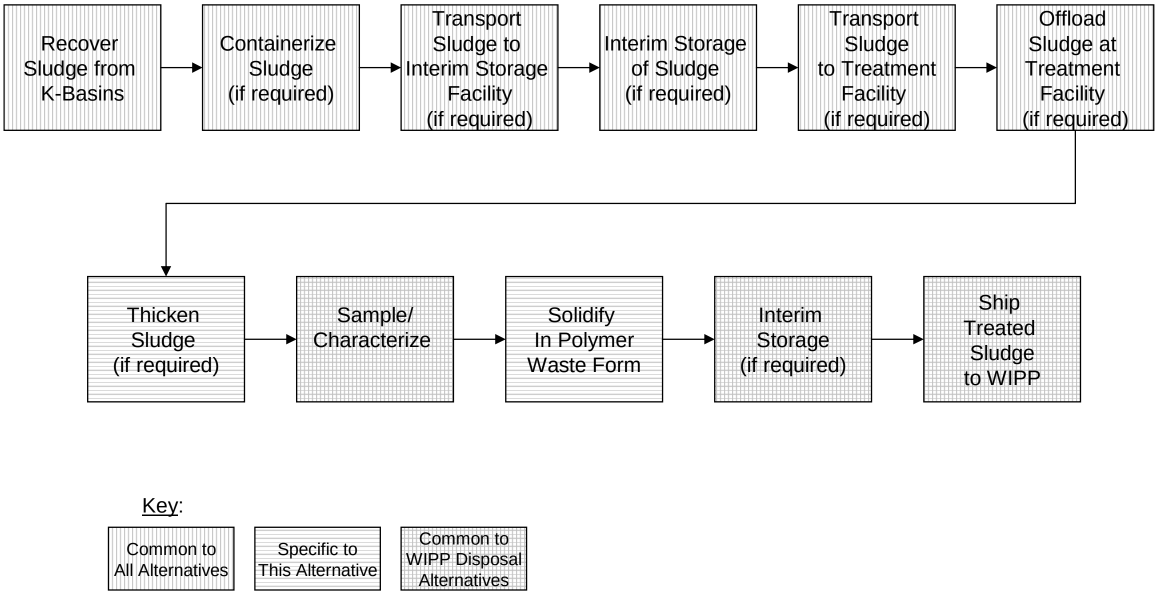

Figure 6.3. Polymer-Sorbent Solidification

6.1.2.1 Storage and Transportation of Waste Packages

Hydrogen gas will be generated by the solidified-sludge waste form. This will include some level of H_2 generated by the reaction of U-metal with water ($U + 2H_2O \rightarrow UO_2 + 2\ H_2$) as well as H_2 generated by the radiolysis of the entrapped water and water vapor in the solidified sludge. The product would need to be stored in vented containers in a suitable facility. The solidified sludge would be shipped to WIPP in a RU-72B shipping cask.

Solidified sludge would have a sufficient surface dose rate to be RH-TRU (1000 rem/h $\geq$ surface dose rate $\leq$200 mrem/h).(a) Through the use of shielded packages (e.g., lead lined) 55-gallon drums, it may be possible to produce a product that meets the surface-dose-rate requirement for CH-TRU (surface dose rate $\leq$ 200 mrem/h). It should be noted that the issues associated with use of shielded drums discussed in Section 6.1.1.1 (use of shielding to achieve the CH surface dose rate, and the higher than allowed weight of the drums) would also apply to packaging of solidified sludge.

6.1.2.2 Number of Waste Packages

The estimated number of waste packages that would be produced, depending on the sludge composition, is shown in Table 6.3. This information is summarized in Table 6.4.

(a) Solidified KE NLOP sludge packaged in S200 Pipe Overpacks would have a surface dose rate less than the CH-TRU limit of 200 mrem/h.

Table 6.3. Polymer Sorbent Solidified Sludge—Impact of Hydrogen Gas Generation Rates, FGE Limits, and Solidified Sludge Volume on Number of Drums

Safety Basis													
Sludge Description					H2 Generation (See Note 1)						FGE Limit (See Note 2)		Solidified Volume (See Note 3)
					No. 55 Gallon Drums						FGE	No. Drums	No. Drums
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Safety Basis Decay Heat, W/m3	Safety Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on H2 Generation from U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Based on H2 Generation from U Metal - Water Reaction (20X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (20X rxn decrease, 90% U removed)			
KW Basin Sludge Sources													
KOP Sludge	Fuel Piece	0.423	1100	9.4	1751	426174	4262	6013	2131	3882	3.46E+04	173	7
Settler Tank Sludge	KW Canister	2.83	256	0.2	2727	60665	607	3334	303	3030	1.56E+05	780	48
Floor Sludge	KW Canister	1.01	256	0.2	973	21651	217	1190	108	1081	5.55E+04	278	17
NLOP Sludge	KE Floor	3.64	22.4	0.023	307	8973	90	397	45	352	1.18E+04	59	62
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	77	0.125	725	33494	335	1060	167	892	6.76E+04	338	43
Floor and Pit Sludge	KE Floor	33.8	22.4	0.023	2850	83323	833	3683	417	3266	1.10E+05	550	578
NLOP Sludge	KE Floor	6.3	22.4	0.023	531	15531	155	686	78	609	2.05E+04	103	108

Design Basis													
Sludge Description					Hydrogen Generation (See Note 1)						FGE Limit (See Note 2)		SolidifiedVolume (See Note 3)
					No. 55 Gallon Drums						FGE	No. Drums	No. Drums
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Design Basis Decay Heat, W/m3	Design Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on H2 Generation from U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Based on H2 Generation from U Metal - Water Reaction (20X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (20X rxn decrease, 90% U removed)			
KW Basin Sludge Sources													
KOP Sludge	Fuel Piece	0.423	689	9.4	1097	426174	4262	5359	2131	3228	3.75E+04	188	7
Settler Tank Sludge	KW Canister	2.83	87.2	0.057	929	17289	173	1102	86	1015	3.91E+04	196	48
Floor Sludge	KW Canister	1.01	87.2	0.057	332	6170	62	393	31	362	1.39E+04	70	17
NLOP Sludge	KE Floor	3.64	3.12	0.004	43	1561	16	58	8	51	1.91E+03	10	62
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	21.7	0.04	204	10718	107	311	54	258	1.61E+04	81	43
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	397	14491	145	542	72	469	1.78E+04	89	578
NLOP Sludge	KE Floor	6.3	3.12	0.004	74	2701	27	101	14	87	3.31E+03	17	108

Table 6.3 (Cont'd)

Anticipated Sludge													
Sludge Description					Hydrogen Generation (See Note 1)						FGE Limit (See Note 2)		SolidifiedVolume (See Note 3)
					No. 55 Gallon Drums						FGE	No. Drums	No. Drums
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Anticipated Decay Heat, W/m3	Anticipated U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on H2 Generation from U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (10X rxn decrease, 90% U removed)	Based on H2 Generation from U Metal - Water Reaction (20X rxn decrease, 90% U removed)	Total H2 Generation - Radolysis plus U Metal - Water Reaction (20X rxn decrease, 90% U removed)			
KW Basin Sludge Sources													
KOP Sludge	See Note 4	0.52	334	4.21	654	234641	2346	3000	1173	1827	2.26E+04	113	9
Settler Tank Sludge	See Note 5	2.72	50	0.0268	512	7813	78	590	39	551	3.07E+04	154	47
Floor Sludge	KE Floor	1.01	3.12	0.004	12	433	4	16	2	14	5.32E+02	3	17
NLOP Sludge	See Note 6	3.64	0.304	0.0002	4	113	1	5	0	5	3.76E+02	2	62
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	21.7	0.04	204	10718	107	311	54	258	1.61E+04	81	43
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	397	14491	145	542	72	469	1.78E+04	89	578
NLOP Sludge	See Note 6	6.3	0.304	0.0002	7	196	1	9	1	8	6.52E+02	3	108

Note 1: For drums, ≤ 3.8391E-08 mole/sec (from Table 5.1 of the RH-TRU 72-B Cask SAR, Rev 3, June 2002, for content code RH 314A, a waste consisting of "Cemented Inorganic Process Solids"). Note - maximum heat load values were adjusted to reflect the estimated G Value of 1.09 for the Nochar product compared to the G Value of 0.48 for RH 314A. The G Value of 1.09 is from Table 5-2 of the "TRUPACT-II Authorized Methods for Payload Control (TRAMPAC) Rev. 19c, April 2003." This is the dose dependent G value for Type III.1 waste with a dose greater than 0.012 watt*year).

Note 2: Pu-239 Fissile Gram Equivalent (FGE) limit is ≤ 200 for drums.

Note 3: Based on a Nochar product containing 30 volume % sludge (anecdotal information indicates that volume of final product will be ~3X to 10X initial liquid volume, depending on ratio of Nochar sorbent to liquid volume; sludge will have an average water content of ~70%). Limit for RH Drum fill is 90% of volume (0.1949 m3).

Note 4: Composition base on August 14, 2003 KW Sludge Process Mass Balance. Decay Heat is an approximation

Note 5: Composition base on August 14-03 KW Sludge Process Mass Balance. Decay Heat is an approximation

Note 6. Based on composition of KE NLOP Sludge Sample FE-3. U metal content is 10X valued measured for FE-3

🟩	Number of drums if sludge is preconditiond to remove 90% U, 20X reaction rate decrease.
🟨	Number of drums of solidified KE NLOP sludge based on Anticipated compostion (total is sum of drums based on radiolytic generation plus drums based on U-water reaction).

Table 6.4. Estimated Number of Waste Packages for Polymer Sorbent Solidification Option

Composition	Waste Package	Number of Packages[(a)]	Limiting Requirement(s)
Safety Basis	RH 55-gallon drum	13,113	H_2 Generation
Design Basis	RH 55-gallon drum	5611	H_2 Generation, Product Volume
Anticipated Sludge	RH 55-gallon drum	3410[(b)]	H_2 Generation, Product Volume

(a) If sludge is solidified without preconditioning to eliminate U-metal present in the sludge, the U-metal-water H_2 generation reaction will likely drive the package count for all compositions and sludge types, and the total number of packages could be as high as 300,000 to 600,000 drums.

(b) If KE NLOP sludge is solidified without U-metal removal, the estimated number of 55-gallon drums is 203. This value is driven by H_2 generation.

To develop Table 6.3 assumptions regarding radiolytic H_2 generation were required. A presumption was made that the waste form would be classified by WIPP as Solidified Organic Waste in which water plus organic/carbonaceous material will constitute at least 10 wt% of the solidified matrix (WIPP Waste Category III.1). This waste category has a dose-dependent G value of 1.09 per Table 5.2 of the TRAMPAC document (WIPP 2003). A G value of 1.09 will impose a decay heat limit of approximately 0.80 W/RH canister (or 0.27 W/RH drum), which is approximately 50% of the decay heat limit for cemented inorganic process solids that was assumed for the Cementation option. Based on these assumptions, the package count for higher activity sludges will be driven by the need to limit radiolytic H_2 generation. The relationship between decay heat, radiolytic H_2 generation, and G values is discussed further in Appendix B.

As can be seen from Table 6.3, if the solidification matrix does not greatly inhibit or eliminate the reaction between U-metal and water, the numbers of packages that would be produced will be driven by the requirement to limit H_2 generation from the U-metal-water reaction. However, as noted in Section 6.1.1.2, this could be mitigated if an effective means can be implemented for eliminating the majority of the U-metal from the sludges.
Table 6.4 shows the number of 55-gallon drums that would be produced if 90% of the U-metal is eliminated from the sludge, and the U-metal-water reaction rate in the solidified sludge is a factor of 20 lower than the rate in oxygen-free water.

6.1.2.3 Polymer Sorbent Solidification of KE North Loadout Pit Sludge

In the event that the solidification matrix does not greatly inhibit or eliminate the reaction between U-metal and water, it may not be viable to use the Polymer Sorbent Solidification option to solidify all of the sludge types without first removing the majority of the U-metal. However, the anticipated KE NLOP sludge contains U-metal concentrations that are much lower than for the remainder of the sludge. As a consequence, if the U-metal content of the NLOP sludge is equal to or lower than the anticipated value, or the matrix moderately inhibits the reaction rate of the U-metal, then Polymer Sorbent Solidification may be a viable option for this sludge fraction. The estimated package count for this sludge, which accounts for approximately

13% of the total sludge volume, is shown in Footnote (b) of Table 6.4. The steps that might be used to implement this option would be the same as shown for cementation of NLOP sludge in Figure 6.2.

6.1.2.4 Uncertainties

Before deciding to implement Polymer Sorbent Solidification as the treatment option for sludges other than NLOP sludge, a number of technical uncertainties would need to be addressed. These include the following:

- Obtaining a better understanding of the U-metal-water reaction in the solidified sludge.
- If the U-metal content of the sludge must be substantially reduced or eliminated to allow Polymer Sorbent Solidification, what is the most effective means of accomplishing this (e.g., removal or oxidation of the U-metal), and how would this be accomplished?
- The G Value used in this analysis was based on published WIPP information for an analogous waste type—this value may be conservative

6.1.2.5 Advantages and Disadvantages of Polymer Sorbent Solidification

The following items summarize the high-level advantages and disadvantages associated with treating the sludge using Polymer Sorbent Solidification.

Advantages

- Employs a technically simple, ambient temperature process that will produce minimal amounts of secondary waste.
- Process control is simple and infrastructure support requirements are minimal.
- Process has been proven and is being exercised to stabilize contact-handled organic TRU waste streams for disposal at WIPP.
- Could possibly be deployed near-term to solidify NLOP sludge.

Disadvantages

- Laboratory/bench scale testing will be required to determine the H_2-generation behavior of U-metal in the solidified matrix. If H_2 generation is substantial, it will likely require a preconditioning step (U-metal removal or oxidation).
- While materials stability testing of solidification agents in high radiation fields have been conducted, the process has not been demonstrated for the stabilization of remote-handled waste streams for disposal at WIPP.

- For WIPP applications, the stabilization process has been demonstrated primarily on solutions. Testing may be required to verify that a dense and inhomogeneous sludge will not segregate from the matrix.

6.1.3 Mitigation of U-Metal-Water Reaction

As discussed in Sections 6.1.1 and 6.1.2, H_2 gas will be generated by waste forms that are the product of sludge treated using ambient-temperature processes. If U-metal is not removed as part of this treatment, H_2 generated by the reaction of U-metal with the water present in the product is likely to dominate. It is possible that the rate of H_2 generation in such waste forms may be sufficiently high that achieving acceptable H_2 generation rates may require that the sludge be diluted to the point that ambient-temperature treatment is no longer feasible because of the number of packages that would have to be produced.

Also, difficulties were encountered in prior work related to cementation of U-metal. A white paper that discusses the U-metal-water reaction in grouts/cements is provided in Appendix A. As noted in this paper, when uranium and zirconium metal chips were grouted, the grout would swell and crumble, bursting the steel cans in which this material was cast. The swelling was caused by the reaction of the U-metal to form the more voluminous uranium oxide. Internal heat-of-reaction, begun by the heat of curing of the concrete and accentuated by the oxidation of uranium, likely contributed to the concrete crumbling. It is possible that this type of behavior might be exhibited by cemented sludge if U-metal is not first removed.

As a consequence of the above issues, three concepts for mitigating the presence of the U-metal in the sludge were evaluated. These include chemical treatment to dissolve the U-metal, mechanical separation of the metal, and the use of alternate waste packaging. These concepts are discussed in the following sections.

6.1.3.1 Oxidative Dissolution of U-Metal

One approach to mitigating the presence of U-metal in the K-basin sludge would be to dissolve the U-metal using a simple process at near ambient temperatures and pressures. The process that was examined was oxidative dissolution of the metal using hydrogen peroxide/ammonium carbonate solutions.

Description of Process Chemistry: Laboratory scoping tests were recently performed at PNNL to examine U-metal oxidative dissolution in the presence of hydrogen peroxide (H_2O_2) in ammonium carbonate [$(NH_4)_2CO_3$] solutions to form ammonium uranyl carbonate [$(NH_4)_4UO_2(CO_3)_3$, AUC]:

$$U + 3\ H_2O_2 + 3\ (NH_4)_2CO_3 \rightarrow (NH_4)_4UO_2(CO_3)_3 + 2\ NH_4OH + 2\ H_2O \qquad \text{(Rxn. 6.1)}$$

Six room-temperature tests were conducted with U-metal beads of ~500 to 1000 µm diameter. Over the studied concentration ranges, linear penetration corrosion rates between 5 and 11 µm/h were measured at rates roughly proportional to H_2O_2 concentration. With a linear penetration rate at ~8 µm/h (at ~25ºC and a nominal 1 M H_2O_2), about 400 hours would be required to dissolve to the center of a 6350-μm (¼-inch) diameter metal sphere. In comparison, to achieve a linear penetration rate of ~8 μm/h in an oxygen-free hot-water-oxidation process, a reaction temperature of approximately 140°C would be needed.

Unfortunately, in the presence of carbonate, H_2O_2 auto-decomposition is observed as bubbles forming on UO_2 surfaces at H_2O_2 concentrations above about 0.01 M H_2O_2 (Shoesmith 2000). The disproportionation of H_2O_2 to form H_2O and O_2 also may be catalyzed on surfaces besides UO_2. The iron (hydr)oxides are noted for this effect. The K Basins sludge contains numerous iron (hydr)oxide phases, including hematite (Fe_2O_3), lepidocrocite, and goethite (both FeOOH), and magnetite (Fe_3O_4). Decomposition of H_2O_2 (shown as bubbles) is observed homogeneously in moderately concentrated U(VI) carbonate solutions away from solid surfaces. Finally, low concentrations of transition metal ion catalysts [e.g., 10^{-4} M Cu(II) or Co(II); Krot et al. 1999; Fedoseev et al. 2002] may be effective to enhance the oxidation rate afforded by H_2O_2.

Besides the excess H_2O_2 required to compensate for that lost by disproportionation catalyzed on the sludge particle (UO_2, Fe_2O_3, FeOOH, Fe_3O_4) surfaces or homogeneously from solution, H_2O_2 would be required to oxidize pre-existing UO_2. It is expected that little on no U-metal oxidative dissolution would occur until the more abundant and reactive reduced uranium oxides were themselves oxidized and dissolved to form the same AUC product salt:

$$UO_2 + H_2O_2 + 3\ (NH_4)_2CO_3 \rightarrow (NH_4)_4UO_2(CO_3)_3 + 2\ NH_4OH \qquad \text{(Rxn. 6.2)}$$

The formation of NH_4OH in the U-metal and UO_2 oxidative dissolution reactions 1 and 2 suggests that ammonium bicarbonate (NH_4HCO_3) with NH_4OH in a 3:1 mole ratio is closer to the required reaction stoichiometry and likely a more suitable starting reagent than $(NH_4)_2CO_3$:

$$U + 3\ H_2O_2 + 3\ NH_4HCO_3 + NH_4OH \rightarrow (NH_4)_4UO_2(CO_3)_3 + 5\ H_2O \qquad \text{(Rxn. 6.3)}$$

$$UO_2 + H_2O_2 + 3\ NH_4HCO_3 + NH_4OH \rightarrow (NH_4)_4UO_2(CO_3)_3 + 3\ H_2O \qquad \text{(Rxn. 6.4)}$$

Ammonium bicarbonate also has better thermal stability than ammonium carbonate and a lower ammonia vapor pressure, but, like $(NH_4)_2CO_3$, it still can be decomposed in hot water.

Process-Deployment Configuration: In its simplest configuration, the process would be deployed as a batch operation. Sludge and all reactants would be fed to an agitated batch reactor. Because of the relatively long reaction times (i.e., 400 hours for ¼ inch U-metal particles), a size-segregation operation could be performed to divide the sludge into a small volume plus a 1000-μm stream and a high volume minus 1000 μm. A reaction time of ~65 hours would be required for the minus 1000-μm stream, assuming a ~8-μm/h linear penetration rate.

To achieve a smaller final product volume, it would be necessary to include an evaporator within the system. The process supernatant, which would contain dissolved uranium species, would be concentrated in an evaporator to precipitate AUC salt solids. The evolved ammonia and carbon dioxide fumes could be scrubbed and, if attractive, could be recycled to a subsequent dissolution batch.

Technical Challenges/Uncertainties:

- Will the relatively high initial U-metal dissolution rates be sustained as reaction-product concentrations increase (the PNNL experiments only measured initial rates with minimal reaction products).
- In the actual K Basin sludge matrix, what fraction of H_2O_2 will be lost to disproportionation?
- In the face of disproportionation, can reasonable H_2O_2 concentrations be maintained to achieve suitable U-metal dissolution rates?
- Can transition-metal ion catalysts enhance the dissolution rates?
- Due to the large reactant requirements and the lower uranium-specific concentration of the products, the volume of the dissolved sludge will be significantly greater than the initial sludge volume (i.e., ~ 2.5× to 20× volume increase).
- It is expected that the product $(NH_4)_4UO_2(CO_3)_3$ with excess $(NH_4)_2CO_3/NH_4HCO_3/NH_4OH$ can be mildly heated (~80ºC) to remove the ammonia before the dissolved K Basin sludge is grouted. An offgas treatment system likely will be required to mitigate ammonia emissions, but the fumes could be recycled to subsequent sludge-dissolution batches.

Conceptual Process Description: Sludge would be transported to an agitated reaction vessel (or a series of reaction vessels), and the sludge would be allowed to settle. The excess supernatant would be decanted. Ammonium carbonate (~2 molar stock solution) would be added to the sludge to bring the concentration to ~0.25 M $(NH_4)_2CO_3$. Hydrogen peroxide (30-wt% stock solution; ~10 M) would be added to bring the concentration up to 1 M H_2O_2. Additional H_2O_2 would be supplied as it was consumed in reactions and lost to disproportionation. Depending upon the sludge stream, and assuming that half the H_2O_2 added to the reactor is lost to the disproportionation reaction, the final volume of dissolved solution would be 2.5 to 20 times greater than the starting volume of settled sludge. After completion of the required reaction time (65 to 400 hours—depending upon the particle size of the feed) the reactor contents would be heated to ~80ºC to decompose and volatilize ammonium species. Offgas from the ammonium decomposition step would be routed through an offgas treatment system. The resulting AUC slurry and uranium solution would be solidified with sorbents or by grouting.

6.1.3.2 U-Metal Segregation

A second approach to mitigating the presence of U-metal in the sludge would be the removal of metal from the bulk of the sludge. With off-the-shelf mineral concentration technology (e.g. precious metal/gemstone recovery), it may be possible to remove 85% or more of the U-metal from the sludge. The U-metal depleted stream would be grouted and dispositioned to WIPP as RH-TRU. The metal concentrate stream would be processed to remove tramp material (e.g., aluminum hydroxide nodules, hydrogen/water bearing constituents). If sufficiently cleaned, the resulting concentrated U-metal stream would then be dispositioned to MCOs and dried at CVD. If the hydrogen/water bearing-content of the final concentrate stream could not be reduced to allow the stream to be dispositioned to the MCOs, another treatment process (e.g., hot water oxidation) would be required for this low-volume stream.

Metal Removal/Concentration Process Description:

Sludge mobilization and size reduction: Sludge would be mobilized and pumped to the process feed tank (Figure 6.4). If needed, the feed tank would be mixed (via agitator or slurry mix pump) to maintain the sludge as a mixed slurry. The mixing intensity could potentially be set at a level that would break up large agglomerates and reduce the size of aluminum hydroxide nodules, which are highly friable. Alternatively, the sludge could be processed through a loop that would include an in-line grinder to reduce the non-metallic uranium particulate to less than 2000 µm (less than 10% of the KE Canister and floor sludge is made up of material with a particle size greater than 2000 µm).

U-metal depletion step (primary loop): From the process feed tank, the slurry will be fed to a mineral processing pre-concentration unit operation (Figure 6.4). Two commercially available devices that would be applicable for this operation are 1) a pulsed jigging device (Gekko Inc. In-line Settling Gig, Model IPJ600 and 2) a centrifugal concentrator (Falcon Concentrator's Inc. Model SB250). A thorough vendor search would likely identify other potential systems as candidates for this operation.

The tailings (U-metal depleted stream) from the concentrating device would be recycled back to the feed tank and then back through the concentrating device to achieve a high U-metal removal efficiency. When the batch was completed (after ~30 minutes to 240 minutes of processing), the tailings would be pumped to the grout feed tank.

The concentrate stream (U-metal-rich stream) would be staged in a separate tank for additional processing.

U-metal concentration/tramp material removal step (2nd loop): The uranium-rich concentrate stream (concentrate from U-metal depletion step) will contain some tramp material, including aluminum and iron hydroxides and some uranium oxy-hydrates, that can decompose to release water. Most of the hydroxides/hydrates will need to be removed from the concentrate stream to allow the U-metal to be dispositioned to MCOs. (Temperatures in CVD are not sufficient to decompose/remove the water from the hydroxides and crystal hydrates). The unit operation(s) for refinement of the concentrates is currently not defined; however, a commercial centrifugal concentrator, such as the Gekko ISP02 inline spinner, which is frequently used in tandem with Gekko jigging devices, could potentially be used. For this operation, the feed stream from the concentrated feed tank (Figure 6.4) would be recycled through the inline-spinner (or other device).

The concentrated metal stream from this operation would be loaded into a container for eventual drying in an MCO. The tailings form this process would be recycled back to the process feed tank.

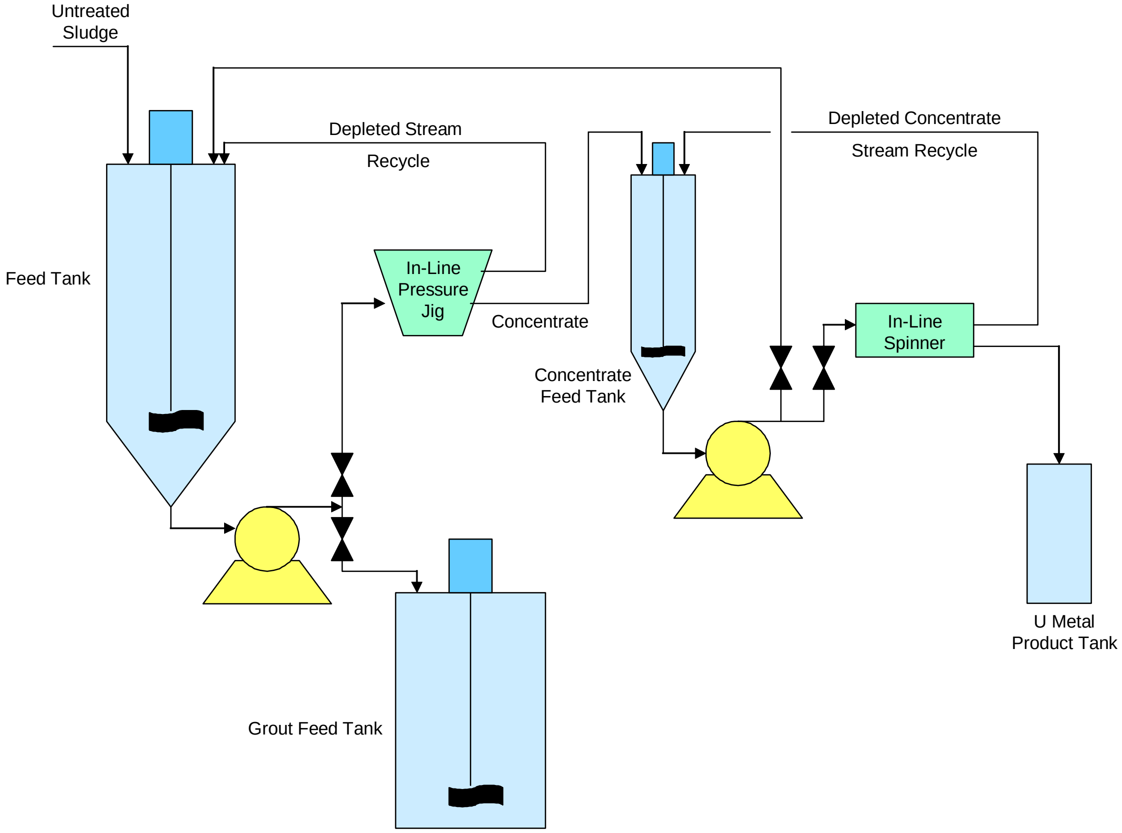

Figure 6.4. Process Flow Diagram for Conceptual K Basin Sludge U-Metal Segregation

Process Viability/Deployment Concept: Although an extensive vendor survey has not been conducted, the viability of this process was assessed by contacting several mineral concentration vendors. The vendors were provided information on the processing objectives, K Basin sludge physical properties (e.g., particle-size distribution, particle densities), and the proposed process flow diagram (Figure 6.4). Based on discussions with vendor technical staff, it was concluded that the use of commercial mineral-concentrating equipment appears to be a promising approach for both achieving a high level of U-metal removal from the bulk of the K Basin sludge and for generating a highly concentrated U-metal concentrate stream. The K Basin sludge application is very similar to some gold recovery operations.

All vendors indicated that bench-scale testing (e.g., shaker table tests) would be necessary to confirm the technical viability of this application and to provide estimates of the expected U-metal removal efficiency. Such tests can be performed by the vendor with simulants for costs ranging from $500 to $2000 per test.

If implemented, the metal-concentrating equipment might be deployed using skid-mounted and shielded (via portable shielding) equipment on or near the deck of the KW pool. Feed and product tanks as well as associated pumps, would be located underwater in the pool. No significant air emissions are expected for this process (i.e., no new offgas treatment requirements). While it may be possible to operate the concentration equipment underwater, such a deployment option would require moderate process development. The equipment would be operated using a batch-recycle operating mode processing 1 to 5 m^3 batches. The equipment would be sized to process all of the K Basin sludge that requires metal removal (~44 m^3) in one year or less.

6.1.3.3 Alternate Waste Packaging

A third alternative for mitigating the effects of H_2 generated by U-metal corrosion would be to package the treated sludge in a transportation container analogous to the high-density polyethylene ARROW-PAK transportation container being developed for transport of CH-TRU in the TRUPACT-II shipping cask. It has been determined that the ARROW-PAK is “deflagration proof,” so limits on hydrogen generation no longer apply. Approval from the NRC to ship CH waste in these containers in the TRUPACT-II is expected in 2-3 years.

Although WIPP currently has no plans to pursue the ARROW-PAK concept for RH-TRU, there do not appear to be any technical reasons why this could not be done. Conceptually, the “RH-ARROW-PAK” might be a means to deflagration proof a container that is similar in construction to the ARROW-PAK, but with the same external dimensions as the RH canister (so it would fit in the RH-72B cask). This RH-ARROW-PAK would be loaded with immobilized waste in 35 gallon drums (they would need to be smaller in diameter than the 55-gallon drums since the inside diameter of the high-density polyethylene RH-ARROW-PAK would be smaller than the steel RH canisters).

If this approach were implemented, this would allow the volume of immobilized sludge to be driven solely by the ^{239}Pu fissile gram equivalent limits (for higher activity sludges) or grout volume limits (for lower activity sludges). Hydrogen generation (either by radiolysis or the U-metal reaction) would no longer impact package count, and a U-metal segregation step would not be required.

If Hanford wishes to pursue this for K-Basin sludge that will be RH-TRU, the U.S. Department of Energy-Richland Operations and the Carlsbad Field Office would need to initiate a dialogue.

6.2 Elevated-Temperature Treatment

Two sludge-treatment processes were evaluated that would involve processing the sludge at temperatures above ambient. These two treatment processes, Dry or Calcine and Bulk Vitrification, are discussed in the following sections.

6.2.1 Dry or Calcine

In this option, K Basin sludge would be recovered (wet), containerized, stored, and then transported to a facility (modified or new) to characterize and dry or calcine the sludge. The purpose of the drying or calcining step would be to eliminate the water present in the sludge and oxidize the U-metal present in the sludge. Elimination of the water and U-metal would essentially eliminate the generation of H_2 (either radiolytically or chemically) in the dried/calcined product. The dried/calcined sludge would be containerized in appropriate packages (55-gallon drums or RH canisters), stored, and ultimately transported to WIPP. The steps required to implement this option are shown in Figure 6.5.

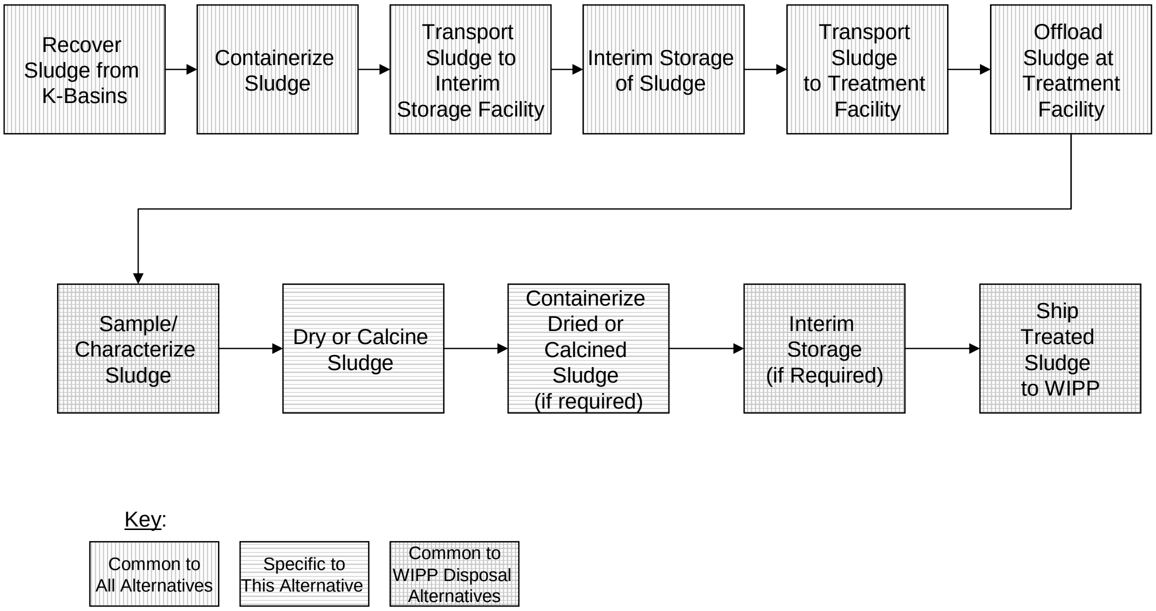

Figure 6.5. Dry or Calcine

The primary difference between a dryer and a calciner is the operating temperature. Most dryers operate a relatively low temperatures (<100°C and under vacuum to perhaps 200°C) to remove physically adsorbed water and loosely bound waters of hydration, but some can operate as high as 400°C by using circulating hot oil as the heat-transfer medium. Calciners operate at higher temperatures (up to about 1100°C) to dehydrate solids and induce other chemical decomposition reactions. The decision about whether to dry or calcine the sludge would be based on considerations such as processing time (which would favor calcining, which is a higher temperature process), and process complexity and regulatory/permitting requirements (which would tend to favor the lower temperature drying process).

The "dry or calcine" step may include multiple sub-steps with different processing conditions. For example, the French STAR Facility uses a three-step process to treat the sludge and fuel pieces that resulted from storage of 20 MT of metallic spent fuel in water. These three steps consist of 1) drying the sludge at 100°C in Ar, 2) heating the dried sludge in Ar at 430°C to drive the UH_3 to U-metal—the H_2 content of the offgas is monitored, and this step is deemed to be complete when H_2 is no longer released, and 3) heating the metal-containing sludge in an Ar-O_2 mixture (starting at 5% O_2 and increasing it to 20% O_2) at 250ºC to oxidize the U—the O_2 content of the offgas is monitored, and this step is deemed to be complete O_2 when it is no longer consumed.

Drying or calcining of the sludge would likely be implemented using a batch process rather than a continuous process. This is because batch processing is more suited to tailoring processing conditions to address the heterogeneity of the particle-size distribution and U-metal content of the sludge. A survey of technologies that are available for drying and calcincing is provided in Appendix B.

6.2.1.1 Storage and Transportation of Waste Packages

As produced, the dried or calcined product would have a sufficient surface dose rate to be RH-TRU (1000 rem/h $\geq$ surface dose rate $\leq$200 mrem/h). Through the use of shielded packages, such as lead-lined 55-gallon drums, it may be possible to produce a product that meets the surface dose-rate requirement for CH-TRU (surface dose rate $\leq$200 mrem/h). It should be noted that the issues associated with use of shielded drums discussed in Section 6.1.1.2 (use of shielding to achieve the CH surface dose rate, and the higher than allowed weight of the drums) would also apply to the packaging of dried or calcined sludge.

6.2.1.2 Number of Waste Packages

The estimated number of waste packages that would be produced, depending on the sludge composition, is shown in Table 6.5. This information is summarized in Table 6.6. At the safety-basis composition, the requirement that the ^{239}Pu FGE be $\leq$200 for drums and $\leq$325 for RH canisters will drive the number of waste packages. For the design basis and anticipated sludge compositions, the FGE requirement will drive the number of packages for the higher activity sludges (such as KOP sludge) while sludge volume will drive the number of packages for lower activity sludges such as the NLOP sludge.

6.2.1.3 Uncertainties

Before deciding to implement drying or calcining as the preferred treatment option, a number of technical uncertainties would need to be addressed. These include

- Optimum processing conditions for drying/calcining (time, temperature, atmosphere)
- Type of dryer or calciner to be used
- Whether organic ion exchange resin beads need to be removed before drying/calcincing

- Whether the presence of grafoil in the sludge will impact the drying/calcining step
- How any secondary wastes from this process will be treated
- The degree to which moisture re-adsorption will occur subsequent to drying or calcining (the dried/calcined material will be stored in vented packages); this water would provide a source of hydrogen for radiolytic H_2 generation.

Table 6.5. Dried or Calcined Sludge—Impact of Hydrogen Gas Generation Rates, FGE Limits, and Dried or Calcined Sludge Volume on Number of Drums/RH Canisters

Safety Basis													
Sludge Description					**Hydrogen Generation (See Note 1)**				**FGE Limit (See Note 2)**			**Product Volume (See Note 3)**	
					No. 55 Gallon Drums		No. of RH Canisters		FGE	No. Drums	No. RH Canisters	No. Drums	No. RH Canisters
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Safety Basis Decay Heat, W/m3	Safety Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction					
KW Basin Sludge Sources													
KOP Sludge	Fuel Piece	0.423	1100	9.4	26	N/A	9	N/A	3.46E+04	173	106	3	1
Settler Tank Sludge	KW Canister	2.83	256	0.2	40	N/A	13	N/A	1.56E+05	780	480	20	4
Floor Sludge	KW Canister	1.01	256	0.2	14	N/A	5	N/A	5.55E+04	278	171	7	2
NLOP Sludge	KE Floor	3.64	22.4	0.023	5	N/A	2	N/A	1.18E+04	59	36	19	4
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	77	0.125	11	N/A	4	N/A	6.76E+04	338	208	18	4
Floor and Pit Sludge	KE Floor	33.8	22.4	0.023	42	N/A	14	N/A	1.10E+05	550	338	180	39
NLOP Sludge	KE Floor	6.3	22.4	0.023	8	N/A	3	N/A	2.05E+04	103	63	34	7

Design Basis													
Sludge Description					**Hydrogen Generation (See Note 1)**				**FGE Limit (See Note 2)**			**Product Volume (See Note 3)**	
					No. 55 Gallon Drums		No. of RH Canisters		FGE	No. Drums	No. RH Canisters	No. Drums	No. RH Canisters
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Design Basis Decay Heat, W/m3	Design Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction					
KW Basin Sludge Sources													
KOP Sludge	Fuel Piece	0.423	689	9.4	16	N/A	5	N/A	3.75E+04	188	115	3	1
Settler Tank Sludge	KW Canister	2.83	87.2	0.057	14	N/A	5	N/A	3.91E+04	196	120	20	4
Floor Sludge	KW Canister	1.01	87.2	0.057	5	N/A	2	N/A	1.39E+04	70	43	7	2
NLOP Sludge	KE Floor	3.64	3.12	0.004	1	N/A	1	N/A	1.91E+03	10	6	19	4
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	21.7	0.04	3	N/A	1	N/A	1.61E+04	81	50	18	4
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	6	N/A	2	N/A	1.78E+04	89	55	180	39
NLOP Sludge	KE Floor	6.3	3.12	0.004	1	N/A	1	N/A	3.31E+03	17	10	34	7

Table 6.5 (Cont'd)

Anticipated Sludge													
Sludge Description					Hydrogen Generation (See Note 1)				FGE Limit (See Note 2)			Product Volume (See Note 3)	
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Anticipated Decay Heat, W/m3	Anticipated U metal Content, g/cm3	No. 55 Gallon Drums		No. of RH Canisters		FGE	No. Drums	No. RH Canisters	No. Drums	No. RH Canisters
					Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction					
KW Basin Sludge Sources													
KOP Sludge	See Note 4	0.52	334	4.21	10	N/A	3	N/A	2.26E+04	113	70	4	1
Settler Tank Sludge	See Note 5	2.72	50	0.0268	8	N/A	3	N/A	3.07E+04	154	94	20	4
Floor Sludge	KE Floor	1.01	3.12	0.004	0	N/A	1	N/A	5.32E+02	3	2	7	2
NLOP Sludge	See Note 6	3.64	0.304	0.0002	0	N/A	1	N/A	3.76E+02	2	1	19	4
KE Basin Sludge Sources													
Canister Sludge	KE Canister	2.5	21.7	0.04	3	N/A	1	N/A	1.61E+04	81	50	18	4
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	6	N/A	2	N/A	1.78E+04	89	55	180	39
NLOP Sludge	See Note 6	6.3	0.304	0.0002	0	N/A	1	N/A	6.52E+02	3	2	34	7

Note 1: For drums, ≤ 3.8391E-08 mole/sec; for RH canisters, ≤ 1.1517E-07 mole/sec (from Table 5.1 of the RH-TRU 72-B Cask SAR, Rev 3, June 2002, for content code RH 322A, a waste consisting of "Solid Inorganic Waste").

Note 2: Pu-239 Fissile Gram Equivalent (FGE) limit is ≤ 200 for drums and ≤ 325 for RH canisters

Note 3: Based on "Corrosion Expansion Factors" from Table 4-6b of HNF-SD-SNF-TI-015, Volume 2, Sludge, Rev. 9. An expansion factor of 1.4 was used for KOP Sludge, Settler Tank Sludge, KW Floor Sludge, and KE Canister Sludge; an expansion factor of 1.04 was used for NLOP Sludge and KE Floor and Pit Sludge. Limit for RH Drum fill is 90% of volume (0.1949 m3); limit for RH Canister is maximum useful volume (0.898 m3).

Note 4: Composition base on August 14, 2003 KW Sludge Process Mass Balance. Decay Heat is an approximation

Note 5: Composition base on August 14-03 KW Sludge Process Mass Balance. Decay Heat is an approximation

Note 6. Based on composition of KE NLOP Sludge Sample FE-3. U metal content is 10X valued measured for FE-3

🟨 Limiting requirement for number of drums

🟩 Limiting requirement for numer of RH canisters

Table 6.6. Estimated Number of Waste Packages for Dry or Calcine Option

Composition	Waste Package	No. of Packages	Limiting Requirement(s)
Safety Basis	RH 55-gallon drum	2280	^{239}Pu Fissile Gram Equivalent
	RH canister	1403	
Design Basis	RH 55-gallon drum	768	^{239}Pu Fissile Gram Equivalent, Product Volume
	RH canister	399	
Anticipated Sludge	RH 55-gallon drum	588	^{239}Pu Fissile Gram Equivalent, Product Volume
	RH canister	282	

6.2.1.4 Advantages and Disadvantages of Drying/Calcining

The following items summarize the high-level advantages and disadvantages associated with treating the sludge using drying or calcining.

Advantages

- Process addresses gas generation, free liquid, energetic-material WIPP criteria.
- Likely to produce smallest number of waste packages compared to other treatment options.

Disadvantages

- Significant potential for dusting and associated spread of contamination.
- Significant potential for remote maintenance/operations issues.
- Offgas and secondary waste-treatment issues.
- May require moderate to high temperatures—may be a permitting challenge.

6.2.2 Bulk Vitrification

In this option, K Basin sludge would be recovered (wet), containerized, stored, and then transported to a facility (modified or new) for bulk vitrification. The sludge would be mixed with glass formers and bulk vitrified at a nominal temperature of ~1200^{o}C in an appropriate container. The bulk vitrified sludge would be stored and ultimately transported to WIPP. The steps required to implement this option are shown in Figure 6.6. It is assumed that the vitrification process will oxidize all U-metal in the sludge and eliminate all water.

Two bulk-vitrification products were considered. One was an RH waste form. These waste forms would consist of right circular cylinders of vitrified sludge, each weighing ~300 kg. The cylinders of vitrified sludge would each be placed in a 55-gallon drum. The nominal composition of this bulk vitrification product would be 40 wt% sludge and 60 wt% glass formers; however, for higher activity sludges, such as KOP sludge, the proportion of sludge would be reduced so that the ^{239}Pu FGE requirement of $\leq$200 FGE per drum would not be exceeded. The second product was a CH waste form. These waste forms would consist of right-circular cylinders of vitrified sludge containing 50 wt% sludge and 50 wt% glass formers. Each cylinder would weigh ~70 kg. Each cylinder of vitrified sludge would be placed in a standard waste box (SWB).

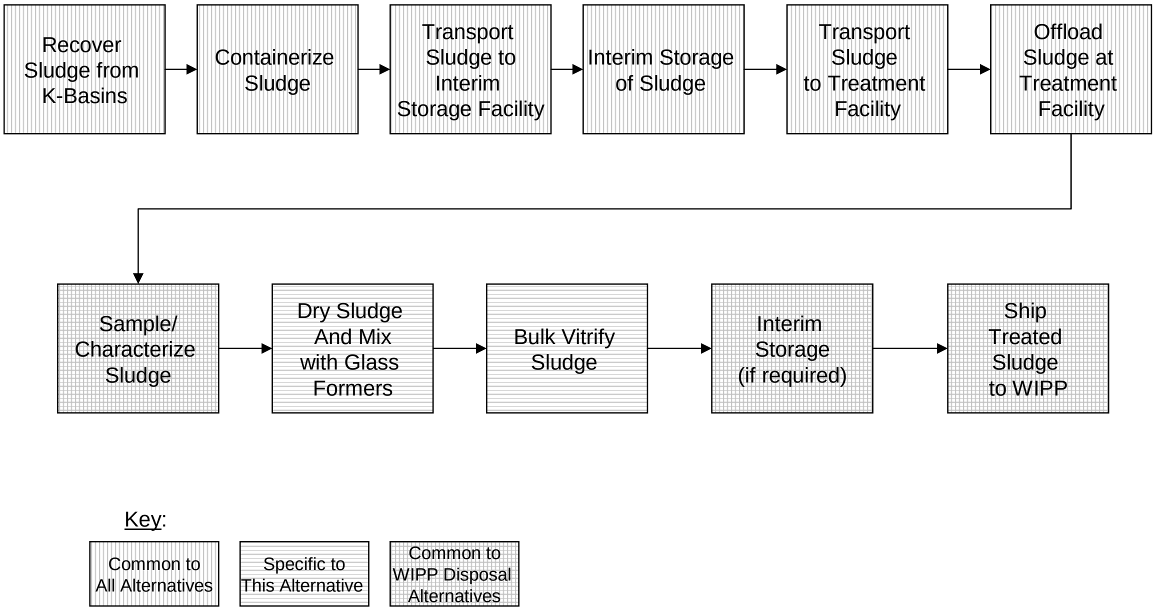

Figure 6.6. Bulk Vitrification

6.2.2.1 Storage and Transportation of Waste Packages

If produced as RH-TRU, the bulk vitrification products would be shipped to WIPP in 55-gallon drums, contained within RH canisters, in a 72-B shipping cask. If produced as shielded packages, the bulk vitrification products would be shipped to WIPP in SWBs contained within TRUPACT-II or HalfPACT shipping casks.

With regard to production of CH-TRU waste forms, the CH bulk vitrified product consists of vitrified sand, surrounded by sand and refractory material; in achieving the CH surface dose rate (≤200 mrem/h), the shielding effect of the sand and refractory is taken into account. It should be noted that the TRUPACT-II SAR states that "Since shielding of the radionuclides is not permitted to meet the transportation dose rate limits…" As such, there is a potential that the TRUPACT-II SAR and supporting documentation would need to be revised to allow this approach, and relicensing of the cask may be required. Modifications to additional permits and licenses related to receipt and disposal of the waste at WIPP might also be required.

6.2.2.2 Number of Bulk-Vitrification Waste Packages

The estimated number of waste packages that would be produced, depending on the sludge composition, is shown in Table 6.7. This information is summarized in Table 6.8.

As shown in Table 6.7, for the RH bulk-vitrification products, the number of packages that would be produced based on the Safety Basis sludge composition will be driven by the requirement that the FGE be ≤200 for RH drums and ≤325 for RH canisters. For the RH products based on Design Basis and Anticipated Sludge compositions, the FGE requirement will

Table 6.7. Bulk Vitrified Sludge—Impact of Hydrogen Gas Generation Rates, FGE Limits, and Vitrified Sludge Volume on Number of RH Drums, RH Canisters, and CH Standard Waste Boxes (SWB)

Safety Basis

Sludge Description					Hydrogen Generation (See Note 1)				FGE Limit (See Note 2)			Product Volume (See Note 3)		
					No. 55 Gallon Drums		No. of RH Canisters		FGE	No. RH Drums	No. RH Canisters	No. RH Drums	No. RH Canisters	No. CH SWB
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Safety Basis Decay Heat, W/m3	Safety Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction						
KW Basin Sludge Sources														
KOP Sludge	Fuel Piece	0.423	1100	9.4	N/A	N/A	N/A	N/A	3.46E+04	173	106	36	12	122
Settler Tank Sludge	KW Canister	2.83	256	0.2	N/A	N/A	N/A	N/A	1.56E+05	780	480	49	16	166
Floor Sludge	KW Canister	1.01	256	0.2	N/A	N/A	N/A	N/A	5.55E+04	278	171	17	6	59
NLOP Sludge	KE Floor	3.64	22.4	0.023	N/A	N/A	N/A	N/A	1.18E+04	59	36	23	8	78
KE Basin Sludge Sources														
Canister Sludge	KE Canister	2.5	77	0.125	N/A	N/A	N/A	N/A	6.76E+04	338	208	37	12	125
Floor and Pit Sludge	KE Floor	33.8	22.4	0.023	N/A	N/A	N/A	N/A	1.10E+05	550	338	214	71	724
NLOP Sludge	KE Floor	6.3	22.4	0.023	N/A	N/A	N/A	N/A	2.05E+04	103	63	40	13	135

Design Basis

Sludge Description					Hydrogen Generation (See Note 1)				FGE Limit (See Note 2)			Product Volume (See Note 3)		
					No. 55 Gallon Drums		No. of RH Canisters		FGE	No. RH Drums	No. RH Canisters	No. RH Drums	No. RH Canisters	No. CH SWB
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Design Basis Decay Heat, W/m3	Design Basis U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction						
KW Basin Sludge Sources														
KOP Sludge	Fuel Piece	0.423	689	9.4	N/A	N/A	N/A	N/A	3.75E+04	188	115	36	12	122
Settler Tank Sludge	KW Canister	2.83	87.2	0.057	N/A	N/A	N/A	N/A	3.91E+04	196	120	49	16	166
Floor Sludge	KW Canister	1.01	87.2	0.057	N/A	N/A	N/A	N/A	1.39E+04	70	43	17	6	59
NLOP Sludge	KE Floor	3.64	3.12	0.004	N/A	N/A	N/A	N/A	1.91E+03	10	6	20	7	68
KE Basin Sludge Sources														
Canister Sludge	KE Canister	2.5	21.7	0.04	N/A	N/A	N/A	N/A	1.61E+04	81	50	24	8	82
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	N/A	N/A	N/A	N/A	1.78E+04	89	55	185	62	628
NLOP Sludge	KE Floor	6.3	3.12	0.004	N/A	N/A	N/A	N/A	3.31E+03	17	10	35	12	117

Table 6.7 (Cont'd)

Anticipated Sludge														
Sludge Description					**Hydrogen Generation (See Note 1)**				**FGE Limit (See Note 2)**			**Product Volume (See Note 3)**		
					No. 55 Gallon Drums		No. of RH Canisters		FGE	No. RH Drums	No. RH Canisters	No. RH Drums	No. RH Canisters	No. CH SV
Sludge Location or Source	Representative Sludge Source	Nominal Sludge Volume m3	Anticipated Decay Heat, W/m3	Anticipated U metal Content, g/cm3	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction	Based on Radiolytic H2 Generation	Based on H2 Generation from U Metal - Water Reaction						
KW Basin Sludge Sources														
KOP Sludge	See Note 4	0.52	334	4.21	N/A	N/A	N/A	N/A	2.26E+04	113	70	44	15	150
Settler Tank Sludge	See Note 5	2.72	50	0.0268	N/A	N/A	N/A	N/A	3.07E+04	154	94	47	16	159
Floor Sludge	KE Floor	1.01	3.12	0.004	N/A	N/A	N/A	N/A	5.32E+02	3	2	6	2	19
NLOP Sludge	See Note 6	3.64	0.304	0.0002	N/A	N/A	N/A	N/A	3.76E+02	2	1	20	7	68
KE Basin Sludge Sources														
Canister Sludge	KE Canister	2.5	21.7	0.04	N/A	N/A	N/A	N/A	1.61E+04	81	50	24	8	82
Floor and Pit Sludge	KE Floor	33.8	3.12	0.004	N/A	N/A	N/A	N/A	1.78E+04	89	55	185	62	628
NLOP Sludge	See Note 6	6.3	0.304	0.0002	N/A	N/A	N/A	N/A	6.52E+02	3	2	35	12	117

Note 1: Assumes that no water or U metal are present in bulk vitrified product.
Note 2: Pu-239 Fissile Gram Equivalent (FGE) limit is $\leq$ 200 for drums and $\leq$ 325 for RH canisters
Note 3: RH drum based on ~300 kg glass per drum containing ~40 wt.% dried sludge. Three RH drums of bulk vitrified product would be loaded into each RH canister. CH Standard Waste Box (SWB) based on 70 kg glass per SWB containing 50% dried sludge. Dried sludge bulk density based on Tables 4-1. *As-Settled Sludge Density*, and 4-2. *Percent Water (vol%)* from HNF-SNF-TI-015, Vol. 2, Sludge, Rev.9.

Note 4: Composition base on August 14, 2003 KW Sludge Process Mass Balance. Decay Heat is an approximation
Note 5: Composition base on August 14-03 KW Sludge Process Mass Balance. Decay Heat is an approximation
Note 6. Based on composition of KE NLOP Sludge Sample FE-3. U metal content is 10X valued measured for FE-3

🟨 - Limiting requirement for number of RH drums.

🟩 - Limiting requirement for number of RH canisters.

Table 6.8. Estimated Number of Waste Packages for Bulk-Vitrification Option

Composition	Waste Package	Number of Packages	Limiting Requirement(s)
Safety Basis	RH drum	2280	^{239}Pu Fissile Gram Equivalent
	RH canister	1403	
	CH SWB	1409	Surface Dose Rate
Design Basis	RH drum	775	^{239}Pu Fissile Gram Equivalent, Product Volume
	RH canister	409	
	CH SWB	1241	Surface Dose Rate
Anticipated Sludge	RH drum	594	^{239}Pu Fissile Gram Equivalent, Product volume
	RH canister	299	
	CH SWB	1223	Surface Dose Rate

drive the number of packages for the higher activity sludges, such as KOP sludge, while the sludge volume will drive the number of packages for lower activity sludges, such as the NLOP sludge. For the CH bulk vitrification products, the number of packages is driven by the assumptions regarding the weight of glass in each package and sludge loading in the bulk vitrification glass. These assumptions were based on the activity of the sludge in the KW Basin. If further consideration is given to the production of CH bulk vitrification products, the impact of the activity of the KE Basin sludges on these assumptions should be determined. In particular, the activity of the KE Basin floor and pit sludge, which accounts for approximately 60% of the sludge volume, is much lower than the average for KW Basin sludge; it is likely that taking the lower activity of this sludge into consideration would allow the weight of glass in each package to be increased, which would lower the package count.

6.2.2.3 Uncertainties

Before deciding to implement bulk vitrification, a number of technical uncertainties would need to be addressed. These include:

- Does bulk vitrification oxidize all of the U-metal? Preliminary data indicate that all of the U-metal oxidizes; this must be confirmed.
- Will the presence of organic ion exchange resin beads and grafoil in the sludge impact the capability to vitrify this material?
- How would secondary wastes from this process be treated?
- If the potential for making CH products is to be pursued, could agreement be reached with WIPP that the candidate CH-TRU waste form would be classified by WIPP as CH-TRU?

6.2.2.4 Advantages and Disadvantages of Bulk Vitrification

The following items summarize the high-level advantages and disadvantages associated with treating the sludge using bulk vitrification.

Advantages

- Process addresses gas generation (radiolysis and U-metal-water reaction), energetic material WIPP criteria.
- Would allow sludge treatment program to benefit from ongoing bulk-vitrification development by CH2M HILL Hanford Group.
- Produces fewer waste packages than ambient-temperature processes.
- May offer potential for production of CH-TRU.

Disadvantages

- Permitting may be more difficult and time consuming compared to other treatment technologies because this is a high temperature process.

- The bulk-vitrification process will produce offgas and secondary wastes that will require treatment.
- Produces a waste form that substantially exceeds acceptance requirements.

Relative complexity of process flowsheet compared to ambient-temperature processes.

6.3 Treatment in River Protection Project Waste Treatment and Immobilization Plant

In this option, K Basin sludge would be recovered (wet), containerized, stored, and then transported to a facility (modified or new) for conditioning to meet DST waste-acceptance criteria. The conditioned sludge would then be transported to a transfer station and pumped into a DST. This could be an existing DST or a new storage tank constructed specifically for this purpose. The sludge would be processed by the WTP Pretreatment Facility to separate the waste into a low-activity waste (LAW) fraction and an HLW fraction. The LAW would be immobilized in the WTP LAW facility or by supplemental treatment for onsite disposal; the high-activity fraction would be immobilized in the WTP HLW Facility and stored onsite at the Canister Storage Building pending transportation to the Federal Repository. It is not anticipated that there would be any extraordinary issues associated with storage and transportation of these waste packages. The steps required to implement this option are shown in Figure 6.7.

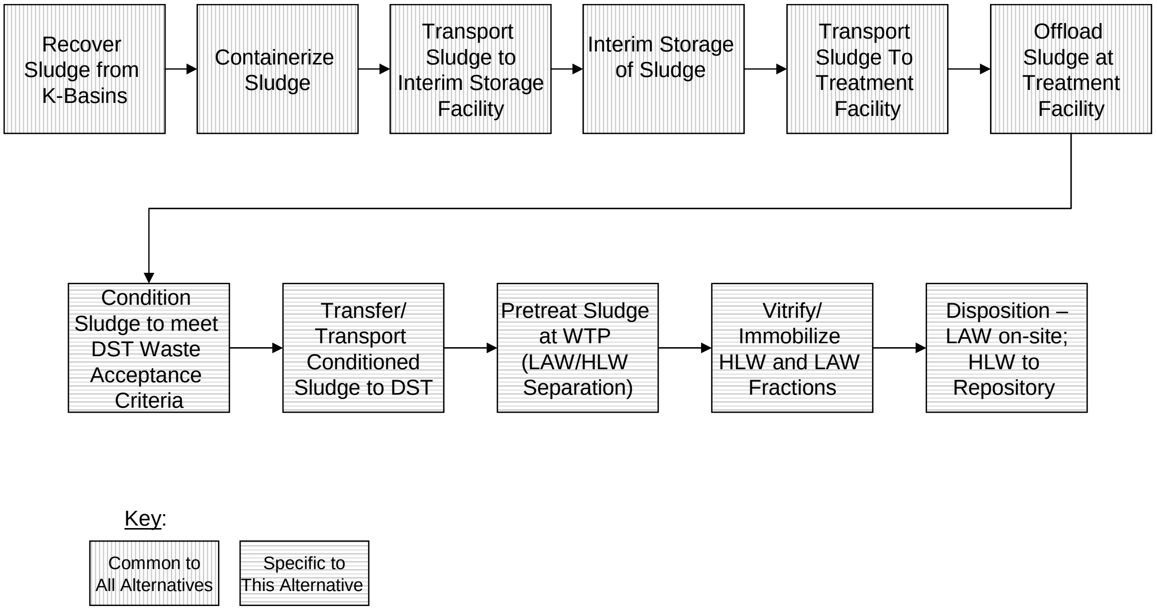

Figure 6.7. Treatment in River Protection Project Waste Treatment and Immobilization Plant

The "Condition Sludge to meet DST Waste Acceptance Criteria" step is unique to this option. In conditioning the sludge, the following requirements must be addressed:

- **Criticality:** The particle size must be less than 10 µm, and the Fe/Pu ratio must be >353.

- **Particle size:** All particles must be less than 177 µm for slurry mobilization/transport.
- **Flammable gas, energetics, and pyrophoric material criteria:** These criteria indicate that non-radiolytic gas generation and pyrophoric material are not acceptable (implying that all U-metal must be reacted before sludge can be introduced to DSTs).
- **Polychlorinated Biphenyls (PCBs)**: The presence of regulated levels of PCBs in the K Basin sludge may require some level of treatment of these compounds.

Based on the above requirements (particularly the criticality requirement), it is likely that a chemical oxidation/dissolution and reprecipitation process would be required for sludge conditioning.

6.3.1 Uncertainties

Before deciding to implement treatment in WTP, a number of technical uncertainties would need to be addressed. These include the following:

- Certain of the Hanford HLW storage tanks contain regulated levels of PCBs; as a result, treatment of the PCBs in the sludge may not be required as part of the preconditioning step.
- Can waste classified as RH-TRU be put into the HLW tanks?

If sludge is to be staged in a purpose-built (rather than existing) DST, the waste-acceptance requirements associated with such a tank may be different from those for existing DSTs. If the storage requirements are different, the preconditioning processes may also be different.

6.3.2 Advantages and Disadvantages of Treatment in WTP

The following items summarize the high-level advantages and disadvantages associated with treatment of the sludge in the WTP.

Advantages

- The processes required to complete the sludge conditioning step are technically mature and demonstrated.
- Immobilization would be completed in the existing onsite WTP facility.
- There is a clear disposal pathway for immobilized material.

Disadvantages

- The complexity of the sludge conditioning required to meet DST acceptance criteria.
- The potential requirement to construct, operate, and decontaminate and decommission a new facility for sludge conditioning.
- The anticipated time required to bring the sludge conditioning capability on-line would require the sludge to be stored for a multi-year period subsequent to retrieval from basins; this storage period would likely be longer than for any of the other treatment options.
- The DST space/capacity is limited.

7.0 References

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Appendix A

Grouting/Cementation of U-Metal: Literature Review and Hanford Experience

Appendix A - Grouting/Cementation of U-Metal: Literature Review and Hanford Experience

A review of the technical literature was performed to collect information on the reaction(s) and reaction rates of U-metal in mixtures with grout, cement, or concrete. The reviews examined the following technical databases:

1. Energy Citations Database, U.S. Department of Energy (DOE) Version—https://www.osti.gov/doeecd/
2. DOE Information Bridge (DOE/DOE Contractor version)—https://www.osti.gov/doebridge/
3. International Nuclear Information System (INIS)—http://inisdb.iaea.or.at/inis/
4. Chemical Abstracts, Compendex, and Energy databases—searched by the Hanford Technical Library.

A search of the first three resources failed to uncover relevant data on the reaction(s) of U-metal in grout, cement, or concrete matrices. The findings from the Chemical Abstracts, Compendex, and Energy searches conducted by an information expert from the Hanford Technical Library similarly yielded no direct information on the corrosion reaction rates of U-metal in grout-like matrices.

However, the search did identify an invention and its application on the Hanford Site to mix uranium and zirconium metal chips and fines with concrete as a means to control the metals' pyrophoricity (Weakley 1972; Toffer and Weakley 1972). Such control allowed the shipment of the collected uranium for its subsequent recovery. The early references pointed to concern with nuclear criticality but did not mention problems with chemical reactivity (Long and Toffer 1971).

Uranium and zircaloy chips and fines were generated during Hanford's N Reactor fuel-fabrication operations. To prevent fires of the flammable metals, the collected chips and fines were stored underwater in 30-gallon drums. The metals react slowly with water to produce hydrogen gas and the corresponding metal oxides. The flammable hydrogen gas evolved slowly enough that it was simply released to the room air and diluted naturally. Before 1971, the collected metals periodically were removed from the barrels and ignited to their oxides in an open-air incinerator under a roof (similar to a carport). From 1971 until 1982, the metal chips and fines were immobilized in concrete. The concreting process was abandoned ~1982, and the ignition and burning of the metals was reinstated until fuel production ceased in the mid 1980s. The burned-metal products, like the concrete-cast product produced from 1971 to 1982, were shipped to National Lead (in Fernald, Ohio) for recycle of the valuable uranium.

The metal-scrap-burning operations were suspended in 1971 due to environmental problems in the metal incinerator, which allowed uranium oxide dusts to settle on the ground surrounding the open incinerator. Safety problems were compounded by the presence of tramp-fission-product technetium in the slightly enriched uranium and the evaporation of technetium oxide (Tc_2O_7) in the burning process (personal communication with Everett Weakley, October 2003). Technetium oxide boils at 310.6°C (Vida 1989).

The concreting technique was applied to U-metal fuel-fabrication operations in 1971 to supplant prior uranium/Zircaloy scrap-burning operations. In the concreting process, the wet collected metals were mixed with masonry cement (47% limestone, 3% gypsum, and 50% Type II Portland cement) and water in a nominal per-charge weight ratio of 18 kg metal/54 kg cement/ 30 kg water (derived from Weakley 1980). The concrete mixtures were cast in ~27-L (~1 ft^3 or ~7 gallon) thin-walled steel cans and were called "billets."

At National Lead, the thin steel cans were peeled from the cast billets, the castings were broken into 6 to 8 chunks, and the chunks were charged to a gas-fired oven where the masonry cement decomposed and crumbled to release carbon dioxide and water vapor while the U-metal and Zircaloy burned to their oxides. The fired product then was removed from the oven and passed through an 8-mesh screen. The materials not passing the 8-mesh screen were crushed further and then re-burned. The crushed and fired materials then were transferred to a facility for acid dissolution and solvent-extraction purification of the dissolved uranium.(a)

Two fires subsequently occurred at Hanford during storage of concreted products. In August 1977, six concreted billets burned when at least one of the billets autoignited in the 304 Building. The concreted products swelled by the burning and heat to burst the steel cans in which they were cast (Figure A.1). The swelling was due to reaction of the U-metal to form the more voluminous uranium oxide and to thermal decomposition of the limestone-rich masonry cement. A second autoignition incident occurred in July 1979 in the 3712 Building warehouse. The wooden shipping boxes in which the billets were packed awaiting shipment ignited to damage or destroy 21 concreted billets. In both cases, the crumbled materials were simply swept up and cast again in concrete. However, concern over the safety of storing and shipping the uranium/Zircaloy-bearing product billets led to suspension of this practice in August 1979.

An experimental program was rapidly implemented to determine the causes of the fires and identify processing techniques to eliminate the risk of autoignition (Weakley 1980). The following summary from the experimental studies report identified processing methods to eliminate the risk of autoignition by implementing a careful drying and curing sequence:

> Through extensive testing and analyses of the concretion process, billets and shipping conditions, it has been determined that properly cured concreted billets can be safely shipped to National Lead Company of Ohio (NLO), Fernald, Ohio. During curing, billets will be dried for 26 days prior to shipment with the last 10 days between 54-66ºC (130-150ºF). Such dried billets can withstand temperatures up to 85ºC (185ºF). The maximum billet temperature that can be expected to occur in shipment is 50ºC (123ºF). Thus, the drying cycle becomes a "burning test" at temperatures which the billets will not reach during shipment to NLO.

(a) EA Weakley. Memo to Daryl T. Jonson, "DUNIR-058 – AEC Case S-39,919 – A Concretion Process for Preparing Pyrophoric Solids and/or Fissile Materials for Shipment, Storage, and/or Disposal," Douglas United Nuclear, Inc. (February 16, 1972).

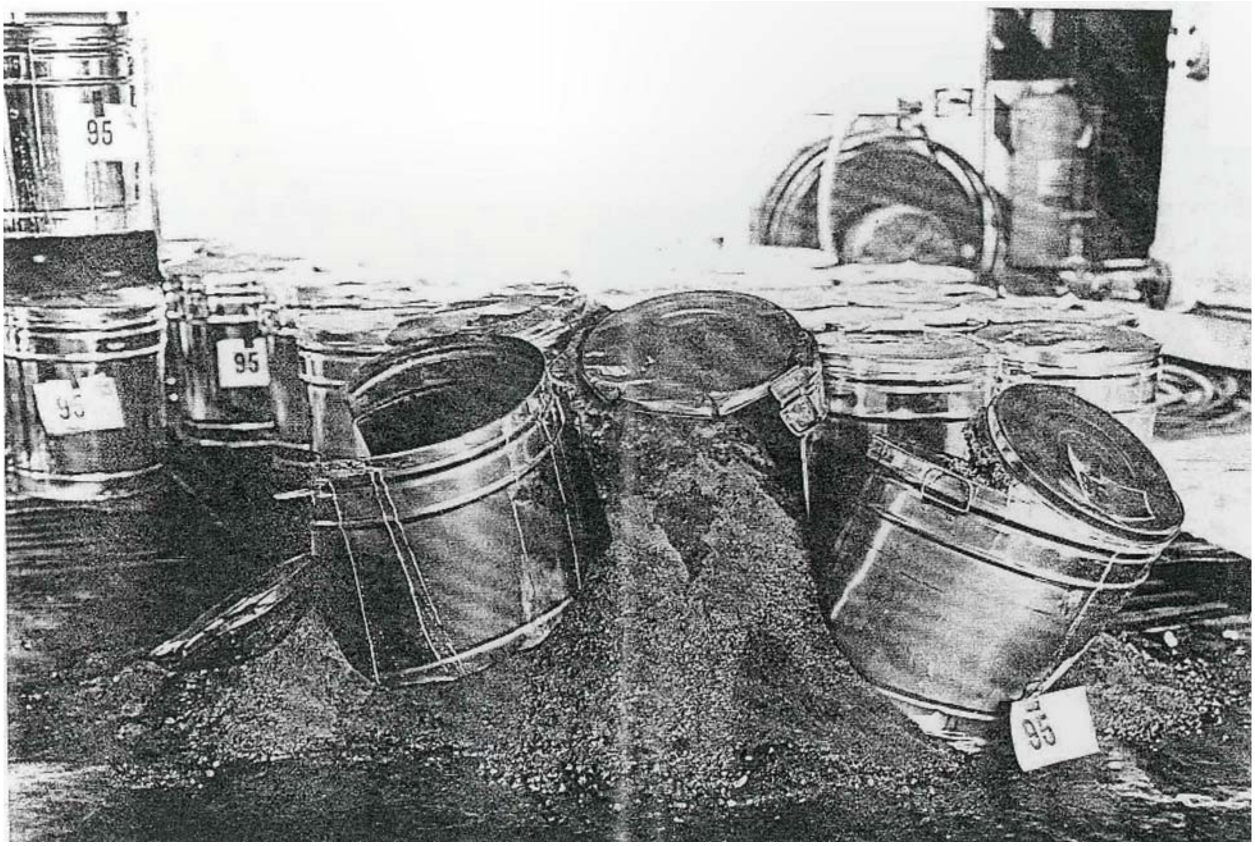

Figure A.1. Concreted Uranium Billets After First Autoignition Incident, August 1977 (Weakley 1980)

Experiments under 22 test conditions (10 with single test specimens, 10 in duplicate, one in triplicate, one with nine test specimens) were conducted. Curing times and temperatures, uranium/Zircaloy granularity and loading, and drying and long-term storage temperatures for the cast billets were varied. The centerline temperatures of the billets were monitored, and the conditions of the billets were observed at the completion of the testing.

The experimental studies showed that hydrogen was released during autoignition events, indicating that the reaction

$$U + 2\,H_2O \rightarrow UO_2 + 2\,H_2$$

occurred and was a key source of heat. The heat generated during curing of a blank masonry cement specimen with no uranium/Zircaloy chips/fines caused centerline temperatures in the ~7-gallon forms to rise from a beginning temperature of 25°C to a maximum 83°C after ~13 hours in a 32 to 38°C room. Abrupt temperature excursions, caused by autoignition and burning, were favored for moist billets having higher metal loadings of finer materials stored at higher temperatures. The rapid temperature excursions associated with the autoignition events seemed to begin near 100°C (Figure A.2), consistent with the U-metal corrosion onset being associated with the availability of saturated-water-vapor partial pressures. The maximum temperature recorded in this test was 803°C, the highest temperature observed in the 14 billet specimens that burned. Centerline temperatures observed for the tests in which burning occurred were 157, 222, 244, 244, 314, 344, 360, 388, 430, 446, 483, 646, and 803°C (one test's temperature not specified).

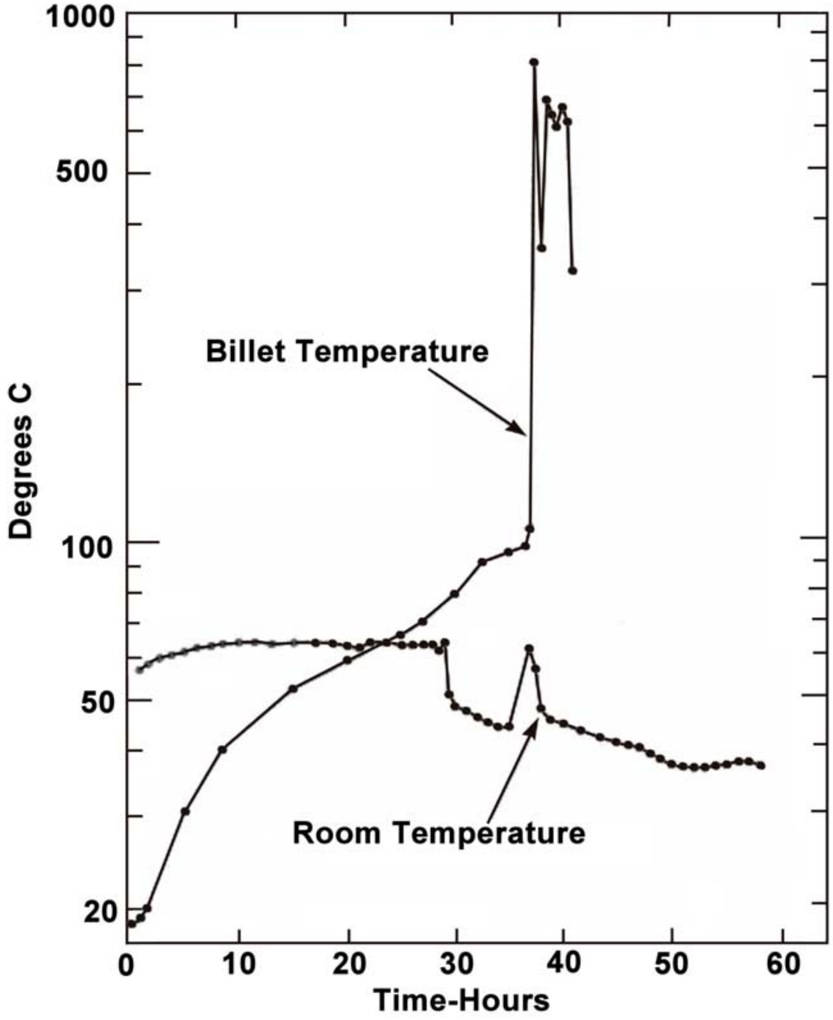

Figure A.2. Temperature Curve for Test Billet Undergoing Autoignition (Weakley 1980)

Note: This curve is for a heavy uranium fines-to-chip ratio concreted billet containing two pounds of unmixed fines in the center of the billet. Water was sprinkled for 3 days before the oven test.

Figure A.3 compares the appearances of concreted test specimens that did and did not burn. The crumbling associated with burning sometimes also occurred with higher curing temperatures (≥63°) in the absence of burning. The high temperature evidently led to simple structural failure of the masonry cement.

Figure A.3. Photographs of Test Concreted Specimens After Curing(a)
Note the burst can and crumbled concreted materials
spilling from the can on the right after the reaction.

The following excerpt from the introduction to the report “Technical Criteria Uranium Chips and Fines Burning Facility” (Weakley 1982) indicates that, despite the modified practices, an autoignition/fire event still occurred during a curing step and that subsequent concerns with traffic-accident scenarios in transporting the billets precipitated abandonment of the concreting process:

> Slightly enriched uranium chips and fines from the fuels fabrication process are currently mixed with masonry cement and water and cast into 7 1/4-gallon metal or polyethylene cans. These cast “billets” are prepared for shipment to NLO, Inc., Fernald, Ohio, by 1) cooling for seven days in cold water to remove the heat of hydration, 2) air cooled for at least 16 days to allow further concrete hydration and hydrolysis, 3) high temperature cured at 123-150ºF for at least 26 days to remove excess water and 4) air cooled for at least 3 days before packaging in wood or metal shipping containers.[1] This elaborate cooling and curing cycle was developed in 1979 and 1980 after two incidents occurred in which concreted billets autoignited during curing or storage at United Nuclear Corporation (UNC).[2, 3]
>
> The U. S. Navy has extensively measured temperatures within loaded vans and the maximum ordnance temperature obtained was only 114ºF in the Mojave Desert and a week of high ambient temperatures (105-111ºF) was required to build up this value.[4] Thus, the high temperature curing cycle with the last ten days at 130-150ºF becomes a

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(a) Hanford Records Management Information System (RMIS). 1980. Accessions N02670755 (right) and N02670757 (left), October 30, 1979; images from the testing available in RMIS are N02670752 to -58, N02681161 to -70, -73, -77, and -80.

> "burning test"; a temperature which the uranium billets will not reach during cross country shipments. One incident occurred in March 1982 in which concreted billet autoignited during the high temperature curing cycle.[5]
>
> Hypothetical accident conditions could result in which an external fire (such as an accident with a gasoline tanker) would ignite the uranium chips and fines in the concreted billets. Therefore, DOE-RL has requested that alternative methods to the concretion process be developed.[6] Three alternative methods of converting the uranium chips and fines into stable non-burning form were considered: 1) chemical conversion to sodium diuranates, 2) water autoclave conversion to uranium oxides and 3) a scrap burner to produce uranium oxides. The chemical conversion method has serious environmental problems with NO and NO_2 gas control and the residual finely divided Zircaloy-2 is pyrophoric and would present a disposal problem. The water autoclave conversion to uranium oxides presents a hydrogen gas disposal problem and a Fe-U eutectic formation problem above 725ºC which could seriously affect the integrity of the autoclave vessel.
>
> References to excerpt of UNI-1864
>
> [1] UNI-1454, "Interim Report on Concreted Uranium Fines and Chips Billets Curing Tests - A Basis for Resuming Shipment of Concreted Scrap Billets", E. A. Weakley, 5-2-80.
>
> [2] Fuels Production Division - Unusual Event Report, UE 77-2, 8-8-77.
>
> [3] Fuels Production Department - Unusual Occurrence Report, UO 79-27, 8-2-79.
>
> [4] NWP TP 4822, "Temperature Profiles of Truck Transported Ordnance", BD Martin and HC Schafer, Navel Weapons Center, June 1970.
>
> [5] Fuels Production Department - Unusual Occurrence Report, UO 82-05, March 13, 1982.
>
> [6] Letter, G. J. Miskho, DOE-RL, to President, UNC, "Resumption of Uranium Concretion and Shipping", dated 6-6-80.

The problems with preparing and transporting the U-metal chips and fines ultimately were addressed at the Hanford fuel-fabrication facility by abandoning the concrete process and instead burning the uranium and zirconium metals to their respective oxides before transportation and recovery of the contained uranium.

The facility for uranium/Zircaloy chips/fines burning was placed in the 303 M building, the "Uranium Oxide Facility," under project H-596. The requirements and features of the new facility are described (Weakley 1982; Gydesen 1982). The chips/fines were burned in water-cooled 30-gallon barrels lying under offgas exhaust hoods. The chips/fines were ignited by a gas torch and self-burned to the oxides.

Conclusions

No references were found in the technical literature to describe quantitatively the reaction rates for U-metal held in concrete, grout, or other cementitious matrices. U-metal reaction with the interstitial pore water or water vapors present in the cement might be expected, but information on any diminution or enhancement of the reaction rate in the cement matrices was not found. However, Hanford has operational experience with the concreting of uranium/Zircaloy chips/fines arising from Zircaloy-clad U-metal fuels. This experience has shown that the reaction of U-metal with water still can occur to such an extent that the concreted form can autoignite. Hydrogen gas was observed in extensive testing conducted to identify conditions leading to ignition and burning of the concreted U-metal castings. The reaction rate seems to increase sharply near 100°C when the gas phase becomes pure water vapor, thus guaranteeing contact of the water and U-metal reactants.

References

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Long JT, and H Toffer. 1971. *Safety Review – Shipping Masonry Cement Billets Containing Scrap Uranium in NLO Boxes*. DUN-7654, Douglas United Nuclear, Richland, WA.

Toffer H, and EA Weakley. 1972. "Criticality Safety of Uranium Metal Scrap in Concrete Billets." *Trans. Amer. Nucl. Soc.* 15(1):310-311.

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Weakley EA. 1972. "Method for Processing Scrap Fissile Material into a Form Suitable for Shipping," US Patent No. 3,779,938, US Patent and Trademark Office. Available at: http://patimg1.uspto.gov/.piw?docid=US003779938&PageNum=1&&IDKey=978B9B8CE5C3&HomeUrl=http://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO1

Weakley EA. 1980. *Interim Report on Concreted Uranium Fines and Chips Billet Curing Tests: A Basis for Resuming Shipment of Concreted Uranium Scrap Billets*. UNI-1454, United Nuclear, Richland, WA.

Weakley EA. 1982. *Technical Criteria Uranium Chips and Fines Burning Facility*. UNI-1864 Rev 1, United Nuclear Industries, Inc., Richland, WA.

Appendix B

Review of Available Drying/Calcining Technologies

Appendix B – Review of Available Drying/Calcining Technologies

This appendix provides a brief review of available technologies as well as those used in the past for processing radioactive materials by drying or calcining. Recommendations are made regarding preferred configurations and issues that need to be considered in selecting a system for treating K-Basin sludge.

Available Technologies

A search of the internet was made to identify potential technologies, and in particular off-the-shelf technologies, that might be suitable for treating the sludge. Technologies considered were dryers, calciners, and ovens.

The concept involving an oven would be to place a large container containing the sludge into a large oven and heat the container, driving off water to produce a dry product. This technique is probably not practical because it would take a very long time to dry the solids, it would be hard to ensure that the interior of the solids in the container were dry, and it would be difficult to achieve good steam-uranium particle reactions at temperatures above the boiling point of water. However, there are ovens available that can handle very large containers. An exhaustive search was not conducted, but examples would be walk-in ovens offered by Quincy Corp. that heat up to 232°C and have a variety of sizes such as 5 ft W × 7 ft H × 6 ft D. Other ovens with similar sizes and temperatures up to 400°C or more are offered by Lewco Inc., Wisconsin Oven, and Surface Combustion, Inc.

The main difference between a dryer and a calciner is the operating temperature. Most dryers operate at relatively low temperatures (<100°C and under vacuum to perhaps 200°C) to remove physically adsorbed water and loosely bound waters of hydration; some can operate as high as 400°C by using circulating hot oil as the heat-transfer medium. Calciners operate at higher temperatures (up to about 1100°C) to dehydrate solids and induce chemical decomposition reactions.

There are several types of dryers, including spray, fluidized bed, vacuum, conduction, flash, and rotary. Likewise there are spray, fluidized bed, and rotary calciners. Fluidized bed, flash and spray systems are directly heated with hot gases. Rotary systems and conduction/vacuum systems are usually indirectly heated but can also be directly heated, or a combination of both.

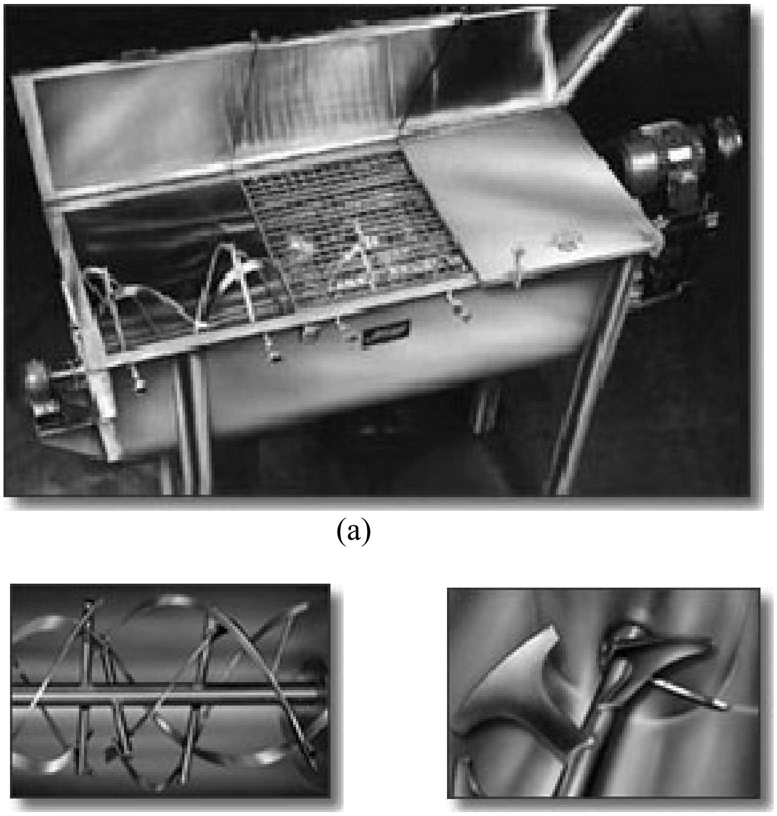
Spray dryers are unsuitable for sludge because it cannot be easily atomized. Fluidized bed dryers are used for drying slurries that coat beads in the fluidized bed and then flake off as dry product. This would not work well with the sludge because of the large variation in particle sizes and density. Flash dryers are generally used for drying wet cakes and powders and would also not be suitable.

Rotary dryers and calciners consist of a rotating cylinder, heated on the outside and containing sludge on the inside. The inside may also contain various kinds of lifters attached to the cylinder wall to make sure the solids do not just slide on the cylinder surface. Figure B.1 shows a picture of a relatively compact rotary calciner offered by College Research Corporation. If there is a tendency for the solids to stick to the cylinder, it is also possible to suspend a heavy chain inside that scrapes against the cylinder wall, thereby removing adhering solids (Perry et al. 1984). Perry's Handbook also mentions recycling solids in rotary systems to increase the solids content of the incoming feed. This effectively creates a dryer feedstock that is more friable. This would need to be considered if rotary dryers or calciners are used.

Figure B.1. Rotary College Research Corporation Calciner with Internal Afterburner

Vacuum dryers are typically used for temperature-sensitive materials, and they would not necessarily apply here because of the need to react the uranium with steam at elevated temperature. However, in some systems, it is possible to operate this type of system at pressures of 1 atmosphere or greater. In this case, certain types of vacuum dryers would be more generally considered as conduction dryers.

Conduction, (and vacuum) dryers are also classified as agitated dryers, where wet material is placed in a trough or cylinder and a rotating set of paddles, plows, screws, or ribbons lift the sludge to break it up and expose new sludge surface to the heated surfaces in the dryer. These heated surfaces include the hollow shaft supporting the paddles or screws and the trough/cylinder walls. The agitating elements (ribbon, screw, plow, and/or paddle) are configured to move the sludge/solids in multiple directions within the vessel. These dryers are also sometimes classified as heated blenders or mixers. Some of the agitated mixers operate in a high intensity mode, producing a mechanically fluidized suspension that facilitates drying. Another type of agitated dryer uses a rotating set of heat-transfer tubes inside a cylinder that lifts and tumbles the material against the heated tubes. Figures B.2 and B.3 are photographs of agitated dryers that use a variety of mixing elements.

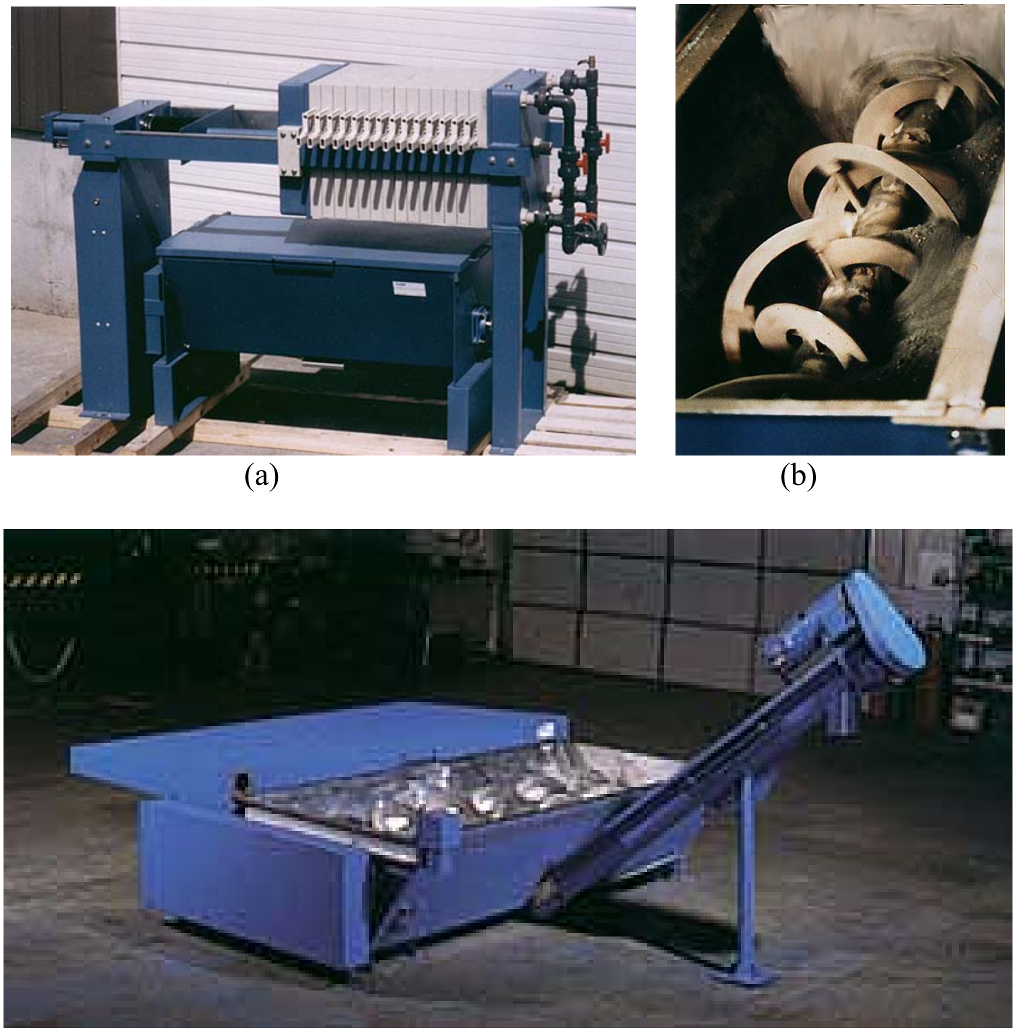


(a)

(b) (c)

Figure B.2. Jaygo Inc. Ribbon Blender (a) and Associated Ribbon (b) and Paddle (c) Mixing Elements

Table B.1 provides a list of venders located on the internet that offer agitated dryers and rotating dryers and calciners that may be applicable to sludge treatment. For the most part, the rotating dryers and calciners appear to be continuously-fed systems while the ribbon and paddle dryers are not. Screw dryers could be either batch or continuously fed.



(a) (b)

(c)

Figure B.3. **Contaminant Recovery Systems, Inc. Sludge Dryer Showing Placement Underneath Filter Press (a), Quad-Screw Mixing Element for Dryer (b), and with Optional Discharge Auger Attached (c)**

Table B.1. Listing of Companies Offering Selected Dryers and Calciners

Company	Products	Comments
Air Preheater Company (Alstom Power Inc.) Wellsville, NY 14895-0372 Telephone: (585) 593-2700 http://www.airpreheatercompany.com/default.asp	Rotary Dryers Rotary Calciners	Indirect and direct heated dryers range from 6 in. to 156 in. diameter × 3 ft to 100 ft. in length. Laboratory-scale dryer is 6 in. diameter × 3 ft length. Indirect heated calciners range from 6 in. to 120 in. diameter × 7 ft to 100 ft. length. Laboratory scale is 6.5 in. diameter × 3 or 6 ft length.
Barr-Rosin, Inc. Oakbrook Terrace, IL Tel: 800-561-8305 http://www.barr-rosin.ca/	Paddle Dryer Rotary Dryer	
Buffalo Technologies Corp. Buffalo NY (888) 529-9925 http://www.thomasregister.com/olc/08872004/	Rotary Vacuum Dryer	Has provision for sprayers to wash down system.
College Research Corporation (CORECO) Germantown, WI Phone: (262) 255-4700 http://www.corecocorp.com/index.html	Rotary Calciner	Indirectly fired to 1100°C. System appears to be fairly compact.
Comessa Strasbourg – France Ph: 03 88 79 41 41 http://www.comessa.fr/pages_uk/sommaire_fr.htm	Rotary Calciner Rotary Dryer Paddle Dryer	
Comline-Sanderson Peapack, NJ Ph: (908) 234-9487 http://www.komline.com/	Paddle Dryer Paddle Calciner	Indirectly heated up to 400°C.
Comp Engineering and Exports Pune - 411 016 India Ph: + 91 20 5658203 /5658205 / 5658206 http://www.compengg.com/	Rotary Calciner Conduction Dryers Rotating Tube Bundle Paddle Dryer	

Table B.1 (Cont'd)

Company	Products	Comments
Contaminant Recovery Systems, Inc. (CONREC) Smithfield, RI Ph: (401) 231-3770 http://www.conrec.net/	Slurry Dryer – Rotating Screw Sludge Dryer – Ribbon (?)	Designed for liquid slurries from metal finishing operations with ppm to several percent solids. Up to 20 ft^3 tank-holding capacity. Sludge Dryer indirectly heated, 2—100 ft^3 capacity. Handles up to 75% moisture in sludge. Can be placed under filter press.
Davenport Machine Phone (563) 322-6201	Rotary Dryer	Directly and indirectly heated system.
H&P Renneburg Division Canonsburg, PA. Ph: (724) 743-1000 http://www.heylpatterson.com/products/calciner	Rotary Calciner Rotary Dryer Multi-Disk Thermal Processor	260 to 1,200°C, indirectly heated (rotary dryer listed as both direct and indirect heating).
Hoffland Environmental Inc. Conroe TX Ph: 936-856-4515 http://www.hoffland.net/	Ribbon dryer – Batch System Ribbon screw – Continuous System	Batch system 4 to 100 ft.^{3} Continuous system at 4 to 20 ft^3/h. Either system can be fed by filter press.
Jaygo Inc. Union, NJ Ph: (908) 688-3600 http://www.jaygoinc.com/saturn.htm	Ribbon/Paddle/Turbulent Blender/Dryer Conical Screw Blender/Dryer	Not clear whether turbulent blender is heated.
Littleford Day Inc. Florence, KY Ph: (859) 525-7600 http://www.littleford.com/	Polyphase high intensity mixer/dryer	Mechanically fluidized mixing. Handles materials efficiently in the paste or pseudoplastic state.
The Met-Chem Group Cleveland, OH (216) 391-7659 http://www.metchem.com/	Ribbon Dryer	Indirectly heated batch system. Sizes range from 1 to 6 ft^3 mini-unit to 6 to 75 ft^3 maxi series. Can be fed by filter-press discharge. Discharges below unit. Drying takes 3 to 6 hours.

Table B.1 (Cont'd)

Mitchell Dryers Ltd Cumbria, England Ph: 44(0)1228 534433 www.mitchell-dryers.co.uk	Rotating Dryer Rotating Calciner	Calciner indirectly heated to 1100°C. Has a rotary dryer specific to handling sludge.
Marion Mixers Inc. Ph: 800-852-8963 http://www.marionmixers.com/contact.htm	Trough type, paddle, ribbon and double reversing agitated mixers,	Capacities range from 1.5 to 600 ft^3. Custom designed inlets, outlets etc.
Patterson Industries Scarborough, ON, CAN Tel: (416) 694-3381 http://www.pattersonindustries.com	Rotary Dryer Jacketed Ribbon/Paddle Mixer	
Paul O. Abbe, Inc. Bensenville, IL Phone: 800-524-2188 Phone: 630-350-2200 http://www.pauloabbe.com	Ribbon and Paddle Mixer Dryers	
Processall Incorporated Cincinnati, OH Ph: 513-771-2266 http://www.processall.com/	Agitated heated mixer	Mechanically induced fluidized bed heated mixers. Also has pressure/vacuum agitated reactor system and pilot plants that are easy to disassemble.
Reliance Industries, Inc. Missouri City, TX Ph: 800-353-0472 http://www.reliancemixers.com/	Medium and high intensity mixers	Self-cleaning mixing tools, 0.1 to 70 ft^3 capacities.
Thermal Processing Solutions, Inc. St. Charles IL. Ph: (630) 587-1977 http://www.tpshome.com	Rotary Calciner	

Table B.1 (Cont'd)

WATROPUR AG Unterseen, Switzerland http://www.watropur.com/ USA Sales: N-Tec Bensalem, PA Ph: 843-832-8931	Rotary Dryer	Appears to be a batch system with a tipping mechanism to empty. It also appears to be compact. Moisture is condensed and recovered from exhaust gas, and dried gas is recycled to dryer.
Winkworth Machinery ltd. Berkshire, UK Ph: 44 (0) 118-988-3551 http://www.mixer.co.uk/	'U' trough, spiral blade, contra flow blade, paddle blade, heated agitated mixers Paddle or plough blade vacuum dryer	Mixers range in size from 10 L to 11,500 L (0.35 to 400 ft^3).

Dryers/Calciners used in Radioactive Materials Applications

A quick internet search was also conducted to identify the types of driers/calciners that have been used in radioactive applications. The information that was found is summarized below.

The following applications were found:

- Fluidized Bed – Idaho National Engineering and Environmental Laboratory (INEEL)
- Unstirred Pots – Hanford Site, UO_3 Plant
- Trough – Hanford Site, UO_3 Plant, Oak Ridge National Laboratory (ORNL), Y-12 Plant
- Stirred bed – Hanford Site, Plutonium Finishing Plant (PFP), plutonium containing solutions treatment
- Screw – Plutonium Finishing Facility at La Hague, France, COGEMA
- Screw – Hanford Site, PFP Plant, oxalate precipitate calcination
- Rotary – La Hague, France – COGEMA.

The calciners used at INEEL were a fluidized bed design and used to treat a liquid waste containing dissolved solids (INEEL Oversight Program 2000). The liquid waste was sprayed as a fine mist into the fluidized bed vessel that contained beads as the fluidizing medium. Solids would form a coating on the beads as the water evaporated in the bed. The constant motion of the beads chipped off the coating, producing flakes that were removed from the vessel and recovered in storage bins.

The Uranium Trioxide (UO_3) Plant at Hanford originally used large indirectly heated pots (The Hanford Site 1999). The calcined material foamed, caked, and stuck in the pots during calcining because of the presence of organic decomposition products in the feed so that the calcine had to be vacuumed and even chopped out. Later process improvements corrected much of this problem.

In 1956, several new continuous-flow calciners were installed at the UO_3 Plant (The Hanford Site 1999). These calciners had large troughs with paddle agitators that turned and mixed the uranyl nitrate hexahydrate (UNH) throughout the process. This design was reported to eliminate caking and clogging problems and to produce a granular product consisting of spheres with an average diameter of 200 µm. According to a design report for this process, the calciners were U-shaped troughs approximately 12 ft long with a height of about 36 in. and an inside diameter of 26 in. for the bottom of the U. The outside of the trough was heated with radiant electric heat using three banks of heating elements to provide 175 kW of power. The solution was continuously fed into the bed of calcined solids at four locations along the longitudinal axis, and accumulated calcined solids were withdrawn from one end of the trough (Ingalls 1955). Nominal average bed temperatures ranged between 250°C and 350°C, the nominal operating pressure was 3 to 5 in. of water vacuum below ambient pressure, and the nominal design throughput was rated at 3.25 t/day. T-shaped bars were installed on a central shaft to agitate the solids.

A trough-type calciner was also used at ORNL's Y-12 plant to calcine UNH solution to UO_3 at 315°C (Defense Nuclear Facilities Safety Board 1995). Presumably, this calciner was similar in design to the one at Hanford.

The PFP at Hanford also used a screw calciner to calcine plutonium oxalate precipitate to plutonium oxide (Sevigny et al. 1995). This unit consisted of a 206-cm-long stainless-steel trough with a 10-cm-diameter stainless-steel conveyer screw running down the center. Three 3500-watt electric resistance heaters strapped to the outside of the trough provided indirect heat to the precipitate. Process throughput for this system was 2500 g/h.

PFP also developed a vertical denitration calciner that was to be used to calcine plutonium-containing solutions (Compton 1999). In the vertical-calciner direct-denitration process, small additions of liquid feed were metered into a continuously heated and stirred bed of previously generated product solids. The liquid feed was rapidly evaporated, and then, more slowly, it underwent drying and denitration and final heat treatment to stabilize the PuO_2. The PuO_2 product was expected to contain some residual sulfate and/or phosphate-derived impurities, but would be substantially free of chloride, fluoride, and other volatile-acid impurities if any were present in the feed. Off-gas condensates were expected to be very low in plutonium content. The process was tested with simulants and was known to work with plutonium, thorium, uranium, and mixtures of those elements in concentrations ranging from 15 to 500 g/L. The process was not particularly energy efficient for very dilute feeds and could not handle feeds high in sodium, potassium, or other constituents that formed nitrates that were molten and refractory at ~1000°C, such as acid solutions that had been neutralized with NaOH or KOH. Organic impurities were largely consumed and only partly reported to the off-gas. This process was later abandoned in favor of a precipitation process, followed by drying and calcining the precipitate in trays, first placed on a hot plate to drive off most of the moisture and then placed in a furnace to calcine the solids.

COGEMA uses calciners in two different applications at La Hague France (Bera et al. 2001; Moncouyoux and Nabot 2002). In one application, a solution of plutonium (typically 30 to 100 g/L) is adjusted to the tetravalent state and fed continuously, together with oxalic acid solution, into a vortex-type stirred-vessel precipitator where plutonium oxalate is formed. The pulp is recovered by overflow and fed into a continuous rotary drum filter (with internal feed). The precipitate is separated from the mother liquor, washed, and dewatered. The suspension then falls into a screw calciner for drying and calcination before sending the oxide to a conditioning step. In the second application, fission-product solutions are evaporated and calcined in a rotating kiln, producing a calcine consisting of elements in the fission product as nitrate and oxide solids. The calcined material is then mixed with glass frit and vitrified.

At the STAR facility in France, degraded and partially degraded fuel elements were dried at 100°C to remove water, calcined at 430°C in an inert gas to decompose uranium hydride to U-metal and hydrogen gas, and finally oxidized at 250°C to produce a stable uranium oxide product.

All but three of the processes discussed above appear to have been designed for continuous feeding (the exceptions being the unstirred pots and vertical calciner at the Hanford Site and the STAR facility in France). However, most of these processes appeared to be part of larger continuous processing schemes and would be more amenable to these applications. All but two of the calciners used some form of stirring (e.g., screw, paddles), the exceptions being the rotary kiln at La Hague and the unstirred pots at Hanford Site. Based on the experience with the unstirred pots, some form of stirring would be highly desirable.

Discussion and Recommendations

The total quantity of K-Basin sludge is relatively small and would be amenable to batch drying/calcining. Furthermore, the batch systems may offer the best system in terms of process control and product quality since the sludge is heterogeneous, and different batches could behave differently, thus requiring different residence times. Any of the agitated systems, either dryers or calciners, are potentially suitable for this application. The process would use steam at between 200°C and 400°C to convert U-metal and uranium hydride to uranium oxide. As an option, oxygen could be subsequently added to the treated uranium to further oxidize the uranium oxides and any remaining unreacted U-metal.

Rotary dryers and calciners are less suitable because they typically operate in a continuously fed mode, with a slight incline to the rotating tube and/or the addition of spiral flights to the tube wall used to move the material from the inlet to the outlet of the system. Batch operation would require some adaptation of this system (adjustable tilt or reverse rotation with spiral flights) to prevent accumulation of solids at the discharge end during drying, but provide for movement of the solids to the discharge end in order to empty the tube.

It is recommended that indirect heating be used as the primary means of drying the sludge and using a minimal gas flow rate through the vessel to carry out water vapor. This should minimize the amount of solids entrainment in the off-gas treatment system. Some of the moisture recovered from the process could be used to recycle captured solids back to the storage tank or to clean solids from the tank walls and mixing elements before refilling the dryer/calciner with a new charge of sludge. The typical methods for indirect heating with commercial dryers are a hot fluid (steam, hot gases, hot water, hot oil) circulated through a jacketed drying vessel or electric heating. Calciners are more typically indirectly fired using natural gas, propane, or fuel oil. Electric heating should be viable in the proposed application, based on the experience with an electrically heated calciner at the UO_3 plant at the Hanford Site.

Several of these systems have the capability of being placed beneath, and possibly attached to, the bottom of a filter press, as shown in Figure B.3a, which may provide an appropriate means for transferring material from the filter press to the dryer. This method would have the benefit of providing a higher solids-content sludge to the dryer, thereby reducing drying time and possibly providing better flow properties. However, this combination also introduces a second unit operation that increases the potential for problems in operating the two pieces of equipment together, as well as overall maintenance.

Several of the ribbon/paddle mixer dryers provide for removing the dried material through the bottom of the dryer. It is not clear whether some of these systems have any provision for sealing the outlet to a container receiving the dried solids. Several companies mention discharging the solids to bags. Figure B.3c shows the addition of a auger discharge for removing solids from the bottom of a screw blender, illustrating an alternate method for removing solids from the dryer to a receiving vessel. Another company, specializing in mixers, offers several discharge valve options, including knife gate, butterfly, and ball valves, as well as a drop-bottom option that provides instantaneous discharge of an entire batch.

One concern for drying sludge with a low solids content (slurry) is that the material could transition from being a soupy material to being a sticky material before becoming dry enough to become friable. Should this occur, it may lead to the formation of large agglomerates that stick to the heated and unheated surfaces and are difficult to dislodge. This possibility needs to be considered in talking with vendors and selecting/designing a system. It is likely that the one of the different agitation methods, ribbon, paddle, or screw, would be preferred for this application or that other design and operating parameters, such as mixing intensity, can address this problem.

Batch dryers/calciners offer an opportunity to combine more than one processing step into the system. For example, the system can be designed to initially operate under vacuum to facilitate final water removal at lower temperatures followed by operation at or near atmospheric pressure with the addition of steam to react with the solids at a higher temperature. Subsequently, the feed gas can be changed to an oxygen gas to facilitate oxidation of the uranium.

A properly designed batch dryer/calciner should be able to dry one to two batches per day. However, additional time may be required to ensure complete oxidation of the U-metal and uranium hydride in the sludge. It is reasonable to expect that a dryer or calciner could be sized to handle 2 m^3/wk. This would translate into a processing time of roughly 6 months, operating 5 days/wk, but not accounting for down time for scheduled maintenance or other reasons. Thus, the expected sludge capacity of dryer/calciner processing one batch/day would be approximately 0.4 m^3 (14 ft^3). If two or more units were used, the size range would be correspondingly lower. Smaller systems may be preferred because they would be easier to decontaminate and dispose of after completing the project. It is also likely that they would be easier to operate remotely. Two or more units could be considered to ensure that at least one system is operable if another is down for maintenance or cleaning.

It is unlikely that an off-the-shelf design will be available that can process the K-Basin sludge in a remote handling environment. The final system will need to be capable of being integrated with a suitable method for receiving sludge and a suitable method to transfer the dried/calcined product to a suitable container for interim storage and final disposal. Issues related to safety and health unique to handling of radioactive materials will also need to be incorporated into the design, as will special requirements for remote operation and maintenance.

In summary, the use of a batch dryer or calciner to remove water from the sludge and to convert U-metal to an oxide appears to be a viable approach for treating the K-Basin sludge for packaging and transportation to WIPP. Batch dryers/calciners are currently used to dry sludge, and some have been used to dry slurries. Continuously fed calciners that use similar methods of mixing have been used successfully in the past to dry and calcine radioactive liquids and solids, although these materials were more homogeneous than the present application. However, batch systems with similar mixing principles should be capable of handling a heterogeneous mixture as would be the case with the K-Basin sludge. By agitating the sludge as it dries, they would ensure good contact between the solids and any reacting gases, such as steam or air, facilitating oxidation of U-metal in the sludge. The anticipated equipment capacity requirements are also well within the range of several types of batch dryers. A custom design will likely be needed to address remote-handing requirements as well as the material-processing requirements of the K-Basin sludge. Testing will be needed to determine process conditions needed to meet product specification and verify suitability of the design for remote operation.

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Appendix C

Spent Nuclear Fuel Sludge Treatment Options Expert Review Team

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