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Waste Acceptance and Waste Loading for Vitrified Oak Ridge Tank Waste

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Waste Acceptance and Waste Loading for Vitrified Oak Ridge Tank Waste

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Abstract

The Office of Science and Technology of the DOE has funded a joint project between the Oak Ridge National Laboratory (ORNL) and the Savannah River Technology Center (SRTC) to evaluate vitrification and grouting for the immobilization of sludge from ORNL tank farms. The radioactive waste is from the Gunite and Associated Tanks (GAAT), the Melton Valley Storage Tanks (MVST), the Bethel Valley Evaporator Service Tanks (BVEST), and the Old Hydrofracture Tanks (OHF). Glass formulation development for sludge from these tanks is discussed in an accompanying article for this conference (Andrews and Workman). The sludges contain transuranic radionuclides at levels which will make the glass waste form (at reasonable waste loadings) TRU. Therefore, one of the objectives for this project was to ensure that the vitrified waste form could be disposed of at the Waste Isolation Pilot Plant (WIPP). In order to accomplish this, the waste form must meet the WIPP Waste Acceptance Criteria (WAC). An alternate pathway is to send the glass waste forms for disposal at the Nevada Test Site (NTS). A sludge waste loading in the feed of ~6 wt% will lead to a waste form which is non-TRU and could potentially be disposed of at NTS. The waste forms would then have to meet the requirements of the NTS WAC. This paper presents SRTC's efforts at demonstrating that the glass waste form produced as a result of vitrification of ORNL sludge will meet all the criteria of the WIPP WAC or NTS WAC.

INTRODUCTION

The waste in the Oak Ridge tanks contains both sludge and supernate (Bayne et al, 1996, Keller et al, 1997, and Francis and Herbes, 1997). This research focuses only on the sludge component of the waste. There are ~ 1,000,000 kg of wet sludge in these tanks containing roughly 50 wt% water. The sludges from these tanks contain transuranic radionuclides at levels which will make the waste Transuranic (TRU) as the sludge loading in the glass is increased. In addition, the sludge contains RCRA metals at levels which could potentially make the waste form characteristically hazardous. One of the objectives for this project was to ensure that the vitrified waste form could be disposed of either at the Waste Isolation Pilot Plant (WIPP) or the Nevada Test Site (NTS).

A major driver which affects the properties of the glass waste form is the waste loading. For this report the waste loading will be expressed as the amount of dry sludge present in the feed that will be delivered to the glass melter. The average weighted sludge composition from all four Oak Ridge Tank Farms contains 47.6 wt% solids and 52.4 wt% water. For example, 63 grams of wet sludge mixed with 70 grams of glass formers would produce a waste loading of 30 wt% dry sludge in the melter feed. During vitrification, this feed will be converted to oxides in the melter to produce a waste oxide loading of ~ 25 wt%.

The chemical composition of the weighted average of all tanks within the four tank farms is provided in a separate report. The weighted average for the radionuclide composition is provided in the Tables of this paper. It is worth noting that the average composition is in reality not achievable. There is not a tank large enough in which to homogeneously blend the contents of every tank. Nevertheless, the average composition provides a starting point from which to develop a glass frit.

There is a large tank-to-tank variation in both chemical and radionuclide composition. There may also be significant in-tank variation in sludge composition both vertically and radially. All samples have been taken from a single riser port and therefore the degree of variation within the tanks has not been determined. The scope of this paper is limited to a fixed composition of the tank waste provided by the weighted average. Frits developed for this task will be evaluated for their capacity to adequately incorporate wastes within the envelope of chemical and radionuclide variations present in the tanks. This work will continue through next year.

It is important in the development of a glass formulation for tank waste, that the resultant glass waste form is acceptable for disposal. For this paper two disposal sites are discussed: the Nevada Test Site (NTS) near Las Vegas, Nevada and the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. The requirements for disposal at the NTS are detailed in the NTS Waste Acceptance Criteria (WAC) (NTS WAC, 1996). The NTS will accept low-level radioactive waste if all of their requirements are met. The WIPP is not yet receiving waste but expects to receive shipments in 1998. To be accepted at WIPP, the waste must be transuranic (TRU) waste and the waste form must meet the WIPP WAC (1996). As will be demonstrated, acceptance at WIPP is dependent upon the waste loading in the glass.

TRU Components. In order to dispose of a waste form at the WIPP, it must be TRU waste. The WIPP WAC defines TRU waste as waste that contains alpha-emitting radionuclides with atomic numbers greater than that of Uranium (92) and which have a combined alpha activity level greater than 100 nCi/g. Furthermore, the half life of the TRU radionuclides must be greater than 20 years to be included in the total alpha activity level. Calculations of the activity levels include only the mass of the waste form and can not include the mass of any containers.

The average Oak Ridge tank waste has a TRU level of 784 nCi/g. Table 1 lists the transuranic radionuclides and their associated alpha activity levels for the average waste. This sludge composition contains 52 wt% water and 48 wt% solids. Therefore, the TRU alpha activity for dry sludge is 1,647 nCi/g. Figure 1 presents the TRU alpha activity as a function of dry sludge (wt %) in the melter feed. This plot reveals that the waste becomes TRU at relatively low waste loadings (~6 wt%).

TABLE 1. Transuranic radionuclides and associated alpha activities for the average Oak Ridge tank waste.

	Curies/gram	nCi/g wet	nCi/g dry
Am-241	2.3E-07	228.3	479.6
Cf-252	1.0E-09	1.03	2.16
Cm-243	2.8E-07	279.2	586.5
Np-237	2.2E-10	0.22	0.45
Pu-238	1.7E-07	167.5	352.0
Pu-239	8.2E-08	81.9	172.2
Pu-240	2.6E-08	25.7	53.9
Pu-242	5.4E-11	0.05	0.11
Pu-244	0	0	0
TOTAL	7.8E-07	783.9	1646.9

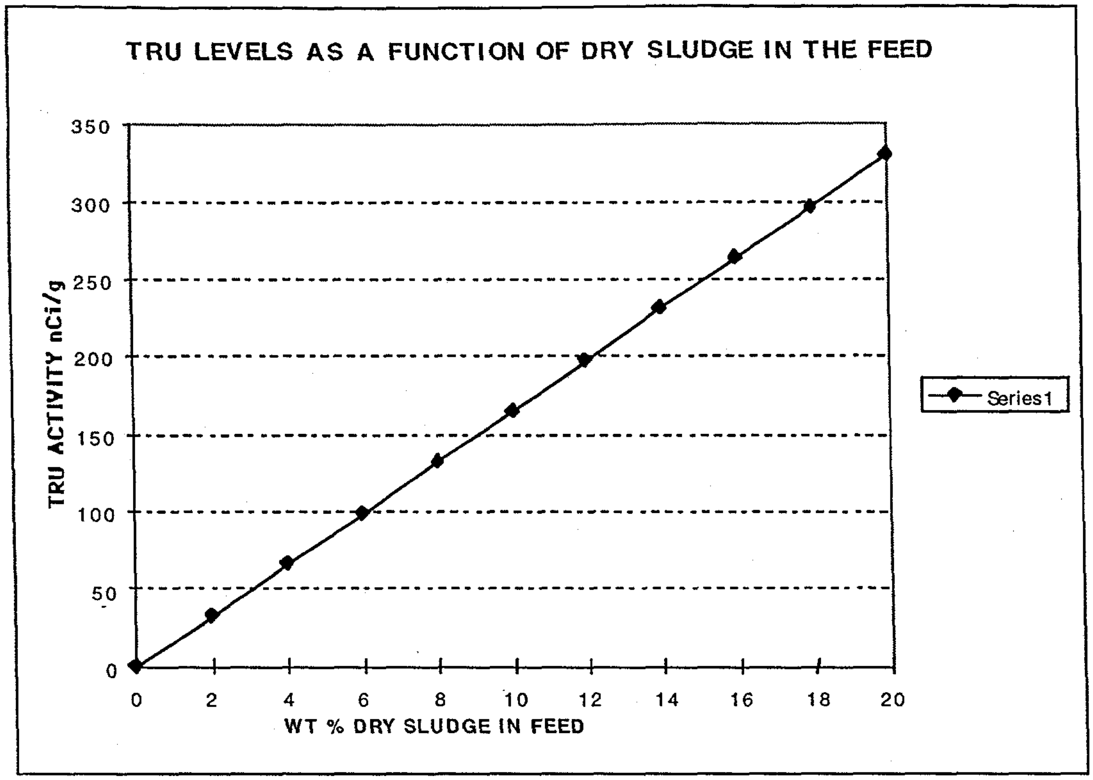

FIGURE 1. TRU Alpha levels as a function of dry sludge loading in the feed.

For disposal of this vitrified waste at NTS, the dry sludge loading in the feed must be low enough that the glass produced contains less than 100 nCi/g of TRU alpha activity (and meets the NTS WAC). Therefore, Figure 1 partitions waste between NTS and WIPP at 100 nCi/g. Since the composite waste is an average of all constituents over the four Oak Ridge tank farms, there will be variation in TRU content with time in the vitrified waste form. Therefore, if WIPP is chosen as the disposal site, it is important that the feed has a higher waste loading to ensure that all of the glass is TRU to meet the requirements of the WIPP. Conversely for disposal of any of the waste at the NTS, a lower loading should be targeted to ensure that none of the waste is TRU.

NTS DISPOSAL

The possibility exists that the vitrified sludge could be shipped to NTS for disposal. For this to occur, the loading of dry sludge in the waste must be below 6 wt% on average to ensure that the waste is not TRU. The waste must also meet the requirements detailed in the NTS WAC.

The NTS does not accept mixed waste from outside the state of Nevada for disposal and the Oak Ridge sludge is not RCRA listed. As discussed below, glass waste forms have transformed and immobilized the sludge. Consequently, the glass waste form removes the concern over ignitable, corrosive and reactive waste. In addition, organics are destroyed due to the high temperatures involved in the vitrification process.

The one area of concern is RCRA regulatory limits for metals based on the EPA TCLP extract. If the metals in the glass are at concentrations less than the RCRA limits, there is no potential for the waste being characteristically hazardous. During the TCLP, a dilution of twenty times the original volume occurs. Therefore, the metals in the glass only need to be lower than twenty times the RCRA limits. Table 2 presents the RCRA metals and their projected concentrations in glass at 6 wt% loading of dry sludge, along with the RCRA limits and twenty times the limits. The only metal which is greater than the 20 times limit is Hg. However, mercury is a volatile element which is removed during the vitrification process and captured in the melter offgas system. Therefore, the waste form at low sludge loadings can not (on average) be characteristically hazardous. No credit is given here for the durability of the glass which certainly would reduce the amount of RCRA metals leached. This resistance to leaching could be used for cases where locally high concentrations of RCRA metals reside (e.g., an individual tank).

Table 2. RCRA metals in the sludge and glass at 6 wt% loading.

Metal	Wet sludge mg/kg	Dry sludge mg/kg	Glass at 6 wt% mg/kg	Limit mg, L	20 x limit
Silver	7.9	16.6	0.99	5	100
Arsenic	17.2	36.1	2.17	5	100
Barium	93.7	196.7	11.80	100	2000
Cadmium	9.2	19.3	1.16	1	20
Chromium	337.4	708.8	42.53	5	100
Mercury	65.6	137.8	8.27	0.2	4
Nickel	63.4	133.2	7.99	50	1000
Lead	462.2	971.1	58.27	5	100

Although shipping the vitrified waste to NTS is possible if lower waste loadings are used, the required reduction in waste loading would result in a greater volume of waste. An analysis is underway to determine costs based on shipment and storage as a function of waste loading for both NTS and WIPP.

WIPP DISPOSAL

Calculations reveal that the vitrified waste form at ~6 wt % loading will produce a dose rate at the surface of a 55 gallon drum in excess of the 200 mrem/hr surface limit.

Therefore, the waste forms sent to WIPP will be handled remotely. Remote Handled (RH) waste has requirements which are different than Contact-Handled (CH) waste. The WIPP WAC includes preliminary RH-TRU waste acceptance criteria, requirements, and compliance methods. However, the finalized requirements will not be available until the RH-TRU 72-B Cask SARP is approved. The following discussion is based on the preliminary RH requirements of the WIPP WAC.

Container: The container for RH-TRU waste is a stainless steel canister which can be no larger than 26 inches in diameter and 10 feet, 1 inch in length, and shall include a pintle for axial lifting. Glass can be poured directly into this canister or filled drums can be loaded into this canister.

Shipment to WIPP: The canister will fit into a RH-TRU 72-B Cask which will be transported by truck to WIPP. Each shipment can take one canister in one cask. It may be possible to include up to three 55 gallon drums into a single canister.

Weight of the RH TRU canister: The weight of the loaded canister must be less than 8,000 pounds. The density of glass (~2.5 kg/L) is such that the 8,000 pound limit can not be reached, even for a completely filled canister.

Heat Generation: For remote handled TRU waste the thermal power requirement is a limit of 300 Watts per canister. Calculations have been performed using the average radionuclide concentrations to calculate the wattage per gram of sludge. The result is 5.42 E-07 watt/gram (see Table 3). Assuming that each RH canister will be filled with 1700 Kg of glass, there will be 0.58 watts/canister at melter feed containing 30 wt% dry sludge. Wattage values could range from 0.12 Watt at 6 wt% loading to 0.97 Watts at 50 wt% dry sludge in the melter feed. Thus, the requirement of less than 300 Watts/canister is readily met with this waste stream.

Table 3. Thermal output from a canister filled with 1700 kg of glass at 30 wt% dry sludge in the feed.

	watts/Ci	Bq/gram	Ci/gram	Ci/canister	watts/can	watts/g
Co-60	1.54E-02	3.35E+04	9.06E-07	9.70E-01	1.49E-02	1.40E-08
Sr-90	1.16E-03	1.85E+06	5.00E-05	5.36E+01	6.21E-02	5.80E-08
Y-90	5.54E-03	1.85E+06	5.00E-05	5.36E+01	2.97E-01	2.77E-07
Zr-93	2.90E-04	2.63E+04	7.11E-07	7.60E-01	2.21E-04	2.06E-10
Ru-106	5.90E-04	1.83E+04	4.93E-07	5.30E-01	3.12E-04	2.91E-10
Cs-134	1.02E-02	4.89E+03	1.32E-07	1.40E-01	1.45E-03	1.35E-09
Cs-137	1.11E-03	5.77E+05	1.56E-05	1.67E+01	1.85E-02	1.73E-08
Ba-137	3.94E-03	5.77E+05	1.56E-05	1.67E+01	6.58E-02	6.15E-08
Eu-154	9.08E-03	6.97E+04	1.88E-06	2.02E+00	1.83E-02	1.71E-08
Eu-155	7.59E-04	2.12E+04	5.72E-07	6.10E-01	4.65E-04	4.34E-10
U-234	2.83E-02	9.50E+02	2.57E-08	3.00E-02	7.78E-04	7.27E-10
U-238	2.49E-02	9.44E+02	2.55E-08	3.00E-02	6.80E-04	6.35E-10
Pu-238	3.26E-02	6.20E+03	1.68E-07	1.80E-01	5.85E-03	5.46E-09
Pu-239	3.02E-02	3.03E+03	8.19E-08	9.00E-02	2.65E-03	2.47E-09
Pu-240	3.06E-02	9.50E+02	2.57E-08	3.00E-02	8.41E-04	7.86E-10
Pu-241	3.10E-05	1.07E+04	2.90E-07	3.10E-01	9.62E-06	8.98E-12
Pu-242	2.90E-02	2.00E+00	5.41E-11	5.79E-05	1.68E-06	1.57E-12
Am-241	3.15E-02	8.45E+03	2.28E-07	2.40E-01	7.70E-03	7.19E-09
Am-243	3.44E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Ce-144	6.67E-04	3.64E+04	9.83E-07	1.05E+00	7.02E-04	6.56E-10
Cm-243	3.67E-02	1.03E+04	2.79E-07	3.00E-01	1.10E-02	1.02E-08
Cm-244	3.50E-02	3.64E+04	9.83E-07	1.06E+00	3.68E-02	3.44E-08
Eu-152	7.60E-03	1.32E+05	3.55E-06	3.81E+00	2.89E-02	2.70E-08
Zr-95	5.00E-03	2.63E+04	7.11E-07	7.60E-01	3.81E-03	3.55E-09
U-233	2.91E-02	2.14E+03	5.77E-08	6.00E-02	1.80E-03	1.68E-09
TOTAL					5.81E-01	5.42E-07

Pu-239-FGE: For nuclear criticality concerns, the Pu-239 fissile gram equivalent (FGE) must be less than 325 g per canister. The value calculated from the composite data is 108 g/canister at 30 wt% dry sludge in the melter feed. These data are shown in Table 4. The major contributor to the Pu-239 FGE is U-235. These data show that even higher loadings of waste in the glass will not create a problem with this requirement.

Table 4. Pu-239 Fissile Gram Equivalent for a glass made using 30 wt% dry sludge from the Composite Composition.

Isotope	PU-239 FGE	Specific Activity Ci/g	Activity Bq/g	Activity Ci/g	Activity g	FGE g/g sludge	FGE/canister g
U-233	1.00E+00	9.76E-03	2137	5.78E-08	5.92E-06	5.92E-06	6.337857
U-235	1.00E+00	2.19E-06	7.6	2.05E-10	9.38E-05	9.38E-05	100.4517
Np-237	1.50E-02	7.13E-04	7.77	2.1E-10	2.95E-07	4.42E-09	0.004732
Pu-238	1.13E-01	1.73E+01	6199	1.68E-07	9.68E-09	1.09E-09	0.001172
Pu-239	1.00E+00	6.29E-02	3032	8.19E-08	1.3E-06	1.3E-06	1.395296
Pu-240	2.25E-02	2.30E-01	950	2.57E-08	1.12E-07	2.51E-09	0.00269
Pu-241	2.25E+00	1.04E+02	10717	2.9E-07	2.79E-09	6.27E-09	0.006711
Pu-242	7.50E-03	3.97E-03	2.05	5.54E-11	1.4E-08	1.05E-10	0.000112
Am-241	1.87E-02	3.47E+00	8446	2.28E-07	6.58E-08	1.23E-09	0.001318
Cm-243	5.00E+00	5.22E+01	10330	2.79E-07	5.35E-09	2.67E-08	0.028641
Cm-244	9.00E-02	8.18E+01	36370	9.83E-07	1.2E-08	1.08E-09	0.001158
TOTAL							**108.2314**

Pu-239 Equivalent Activity: The requirement for the Pu-239 equivalent (PE) activity for RH TRU waste in the WIPP WAC is less than 1000 PE-Ci/canister. This requirement is based on inhalation of fine particulates contaminated with radionuclides. It is interesting to note that the limit has been relaxed to 1800 PE Ci for a 55 gallon drum for contact handled TRU waste if the waste has been vitrified. This is due to the fact that the glass waste contains less fines and consequently, inhalation of particulate fines is not as great a concern. The preliminary requirements for the RH waste have not yet relaxed this requirement for vitrified waste. Nevertheless, the calculated PE activity for the composite waste has been calculated assuming a 30 wt% loading of dry sludge in the melter feed. A value of 1.1 Ci (PE) was obtained. This value demonstrates that this requirement can be readily met at reasonable waste loadings. The details of the calculations are shown in Table 5.

Table 5. Pu-239 Equivalent Activity (PE-Ci) for a glass made using 30 wt% dry sludge in the feed

Isotope	Bq/g	Ci/gram	Ci/kg	Ci/can	weighting factor	PE-Ci
U-233	2136	5.77E-08	5.77E-05	0.061829	3.9	0.015853
Pu-238	6199	1.68E-07	0.000168	0.179436	1.1	0.163124
Pu-239	3032	8.19E-08	8.19E-05	0.087764	1	0.087764
Pu-240	950	2.57E-08	2.57E-05	0.027499	1	0.027499
Pu-241	10717	2.9E-07	0.00029	0.310214	52	0.005966
Pu-242	2	5.41E-11	5.41E-08	5.79E-05	1.1	5.26E-05
Am-241	8446	2.28E-07	0.000228	0.244477	1	0.244477
Am-243	0	0	0	0	1	0
Cm-244	36370	9.83E-07	0.000983	1.052764	1.9	0.554086
Cf-252	38	1.03E-09	1.03E-06	0.0011	3.9	0.000282
Np-237	7	1.89E-10	1.89E-07	0.000203	1	0.000203
Total						**1.099307**

Acceptable Knowledge: Several of the requirements in the WIPP WAC can be addressed by acceptable knowledge. In this case the acceptable knowledge comes from the vitrification process. Glass formers are added to the sludge, and the mixture is fed to a melter which normally operates between 1100°C and 1400°C. This high temperature and the relatively long residence time in the melter (the residence time depends on the size of the melter and throughput) provide assurance that the following requirements will be met:

1) **Free liquids.** The intent of the free liquids requirement is to limit liquid waste at the WIPP. The maximum amount of liquid per canister for RH-TRU is 6 liters. The process of vitrification removes all liquids from the feed such that the molten glass is poured into the canister at a temperature exceeding 1000°C. The molten glass flows into the canister and solidifies as it cools. Proper administrative control then ensures that no additional water or other liquid can enter the canister.

2) **Pyrophorics.** The process of vitrification molecularly incorporates the radionuclides and other chemical elements within the glass. Pyrophorics are destroyed in the melter.

3) **Mixed Waste.** The WIPP WAC requires that RH-TRU waste can contain hazardous constituents only as co-contaminants with TRU waste. The glass formers which are added do not contain hazardous components. The WIPP WAC also requires that any corrosive, reactive, or ignitable characteristics shall be treated to remove the hazardous characteristic. The process of vitrification would remove

any corrosive, reactive, or ignitable characteristic, if present, in the feed.

4) **Explosives, Corrosives, and Compressed Gases.** The WIPP WAC requires that there shall be no explosives, corrosives, or compressed gases. Vitrification removes these types of materials.

5) **PCB's.** PCB's, if present in the feed, would be destroyed by the process of vitrification.

6) **Flammable VOC's.** VOC's, if present, would be destroyed at the high melter temperatures. The glass waste form is non-volatile and consequently no additional volatile materials can be released to the canister headspace.

CONCLUSIONS

The development of a glass formulation for sludge immobilization leads to a waste form which is suitable for disposal at either the NTS or WIPP. The waste loading of the sludge determines the classification of the resultant glass waste form. Below a dry sludge feed loading of 6 wt%, the glass will be non-TRU and can be disposed of at the NTS. Above the 6 wt% loading of sludge, the waste will be TRU and can be disposed of at the WIPP.

The process of vitrification provides acceptable knowledge for meeting a number of the WIPP WAC requirements. These include compliance with the requirements of free volume, explosives, RCRA metals, ignitables, corrosives, and PCB's.

The requirements of the WIPP WAC and the average composition of the Oak Ridge tank waste reveal that glass compositions that incorporate significant amounts of waste will be acceptable for disposal at WIPP. This provides more latitude in defining the optimum waste loading if vitrification is chosen as the method of immobilization of the waste. Efforts will continue to (1) determine the robustness of the glass formulation to incorporate variations in the chemical and radionuclide composition of the various tanks, and (2) compare costs of immobilization, storage, shipment, and eventual disposal at both WIPP and NTS based on waste loading in the glass.

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