Processing and Disposition of Remote-Handled Transuranic Liquid Waste Generated at Oak Ridge National Laboratory – 15113

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ABSTRACT

Oak Ridge National Laboratory (ORNL) produces transuranic (TRU) isotopes for the US Department of Energy's (US DOE's) heavy-element research program and other programs for medical and industrial applications. As a result, the research facilities generate remote-handled TRU liquid low-level waste (LLLW). This LLLW is presently collected and mixed with larger volumes of legacy and environmental management waste streams for future treatment. Once the legacy waste is disposed of as part of the US DOE Environmental Management program, the large-scale waste treatment processes will be decommissioned, and new capabilities will be needed to characterize, treat, package, and dispose of the newly generated LLLW at ORNL. Various approaches are being considered for addressing treatment and disposal of the future LLLW streams. A variety of processing methods and final waste forms is under consideration. The impacts of the chemical and radionuclide compositions of the waste stream are being evaluated.

INTRODUCTION

Since the 1980s, ORNL has been collecting, concentrating, and storing LLLW in underground storage tanks for future treatment. Since that time, the LLLW system has accumulated large quantities of relatively low-activity waste from environmental management activities and small volumes of newly generated mission waste that contain high levels of radioactivity. During storage, the concentrated LLLW has segregated into a sludge containing the TRU constituents and a supernatant layer primarily containing cesium and some strontium. In 2003, the US DOE Office of Environmental Management constructed the Transuranic Waste Processing Center (TWPC) facility to treat this large volume of accumulated legacy LLLW as well as the legacy inventory of solid TRU waste. Most of the supernate has been removed from the underground storage tanks, solidified, and disposed of at the Nevada National Security Site (NNSS). The TWPC site is now being upgraded to process the legacy sludge for disposal at NNSS. After treatment of the legacy sludge, the existing collection and treatment systems are planned for shutdown and D&D. Studies are under way to evaluate treatment options for ORNL's future mission-generated LLLW for disposal at the Waste Isolation Pilot Plant (WIPP). Impacts of waste composition and radioisotopic decay on the ability of various waste forms to meet the WIPP waste acceptance criteria (WAC) and/or transportation criteria are being examined.

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DESCRIPTION OF THE WASTE STREAM

ORNL is the production, storage, and distribution center for the heavy-element research program of the US DOE. One of ORNL's main missions is the production of transuranic isotopes. The facilities that support the production of transuranic isotopes will be the primary sources of LLLW generation in the future at ORNL. The stream is expected to contain approximately ~580,000 nCi/g containing ~ 12,000 nCi/g of TRU and will require treatment and disposal at WIPP. The estimated average concentration of select isotopes in future ORNL LLLW is given in Table I.

TABLE I. Expected composition of future ORNL LLLW

Example Isotopes	Concentration (Bq/L)	Chemical Component	Concentration (M)
Sr-90	3E08	Na_2CO_3	0.13
Cs-137	1E09	NaOH	0.19
Ru-103	2E09	NaCl	0.10
Ru-106	4E09	$NaNO_3$	0.49
Ce-144	4E09	$NaAlO_2$	0.03
Eu-154	3E07		
Pu-238	4E08		
Cm-244	1E07		
Zr-95	3E09		
Total	**2E10**		**0.94**

The ORNL LLLW in inventory today consists of large quantities of relatively low-activity waste from environmental management activities and small volumes of newly generated mission waste that contain much higher levels of radioactivity. Once the underground storage tanks are emptied of the existing inventory and environmental management waste streams are reduced/eliminated by ongoing remediation activities, high-activity mission wastes such as those shown in Table I are expected to dominate ORNL's LLLW generation.

DESCRIPTION OF WASTE TREATMENT OPTIONS

Three flow sheets are being evaluated for treatment of ORNL future mission-generated LLLW, as shown in Fig. 1:

a. evaporation and solidification in a grout matrix with disposal of the solidified waste form at WIPP,
b. evaporation to a solid salt cake waste form for disposal at WIPP, and
c. separation of the TRU and high-gamma isotopes before solidification of the bulk waste stream in a grout matrix for disposal at NNSS. The concentrated gamma waste stream would also be treated for disposal at NNSS, and the concentrated TRU stream would be solidified for disposal at WIPP.

Impacts of the chemical composition of the newly generated LLLW on potential waste forms are being evaluated. The radiological composition of the LLLW is also being evaluated to determine its impact on the ability of waste forms to meet the transportation requirements and WIPP WAC. In addition, the impact of storage for radiological decay is also being examined. Each of these issues is discussed below.

IMPACT OF CHEMICAL COMPOSITION ON FINAL WASTE FORM

Each of the flow sheets shown in Fig. 1 includes an evaporation step before the solidification step to reduce the volume of final waste from requiring disposal. The preliminary designs for these flow sheets include interim storage of the liquid waste before solidification. The designs also assume that the waste streams would not be concentrated to the point that solids are formed at room temperature. This would allow the waste streams to be stored and processed before the solidification step without the presence of solids. It would reduce plugging and fouling problems in the process equipment and would most likely make waste certification easier.

The aluminum content of newly generated ORNL mission waste is expected to increase from its present value of 0.019 M to 0.034 M. Treatability studies are being performed on the ORNL LLLW stream to assess the impact of the increased aluminum concentration on the proposed treatment flow sheets.

An aluminum solubility correlation [1] has been developed to support development of waste treatment flow sheets at the US DOE Savannah River and Hanford sites using aluminum hydroxide solubility data at 25°C [2]. It is shown in Fig. 2 as the solid blue line and is a function of free hydroxide concentration and the concentration of aluminum in the solution. Operations above this line risk the formation of solids. Data for this solubility curve was collected at varying ionic strengths, including nitrate concentrations ranging from 0 to 8 M.

The green points on Fig. 2 represent initial ORNL LLLW compositions, and the dashed purple lines represent the expected compositions if these waste streams are concentrated by evaporation. The 0.034 M Al and 0.2 M NaOH data point is the expected composition of ORNL LLLW (see Table I). It is above the solubility curve, and evaporation produces a concentrated waste curve that is even further above the solubility curve. If the ORNL LLLW follows the solubility curve developed for Savannah River and Hanford waste, Fig. 2 indicates that precipitation could occur in the future as-generated ORNL LLLW, and additional precipitation of aluminum hydroxide is predicted if the waste stream were to be concentrated by evaporation.

Figure 2 also shows the effect that adding caustic can have on the aluminum precipitation. Increasing the free hydroxide concentration in the initial solution from 0.2 to 0.45 M NaOH shifts the unevaporated waste composition to the right so that it is just below the saturation curve. The increased free hydroxide in the waste also reduces the slope of the evaporation curve,

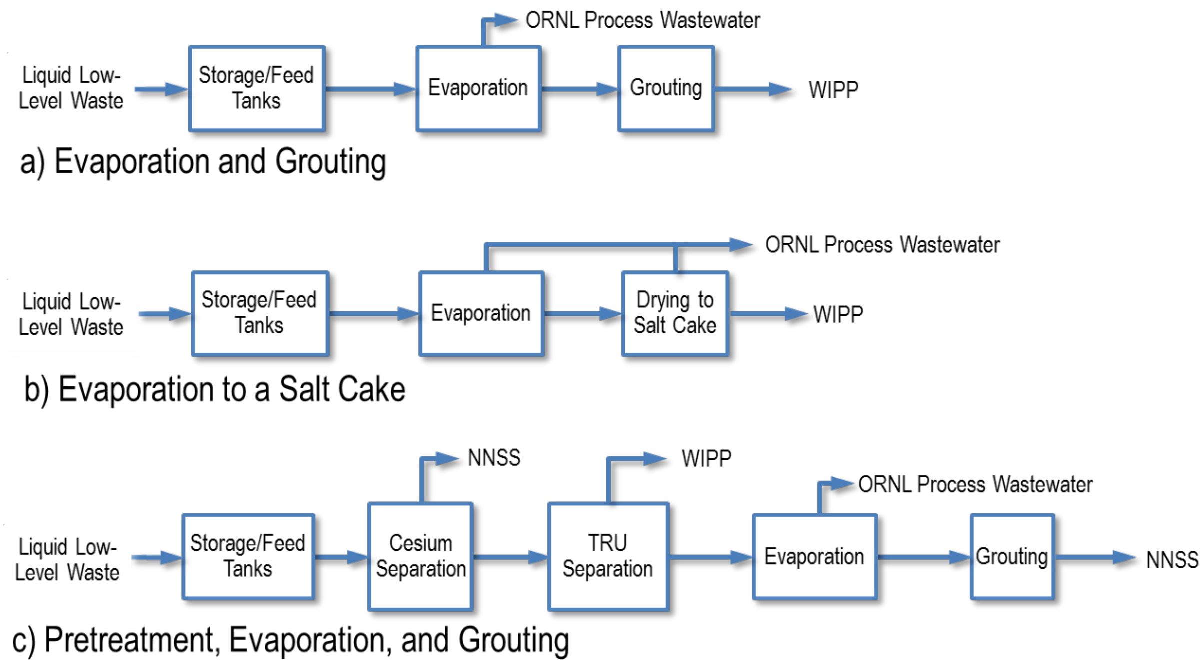

Fig. 1. Proposed Treatment Options for ORNL LLLW.

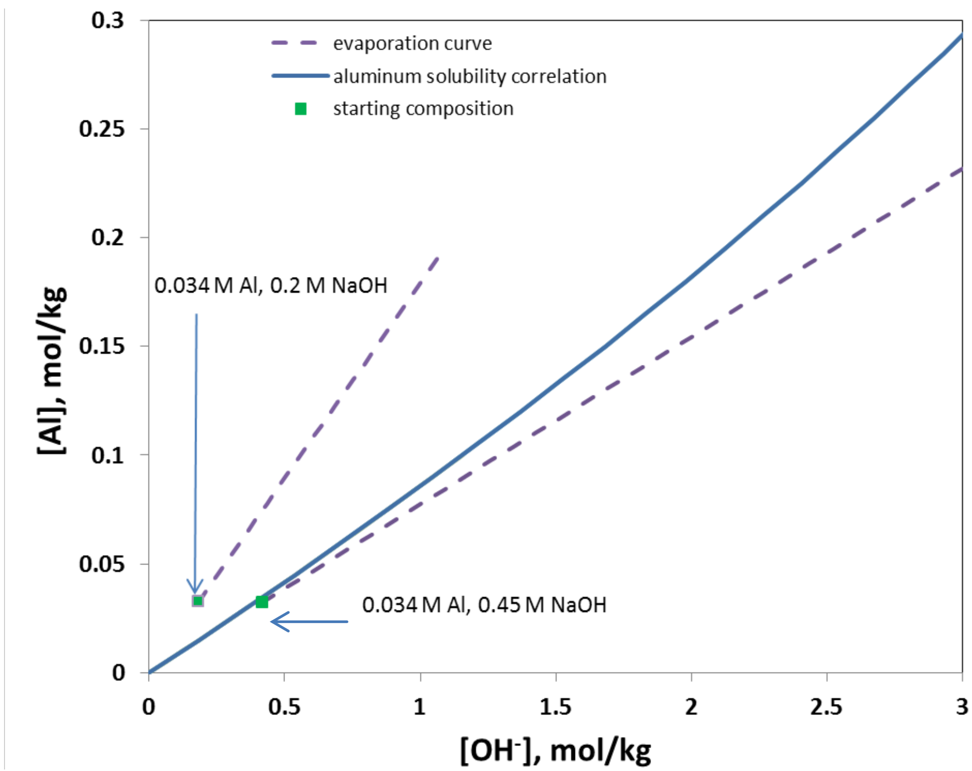

Fig. 2. Solubility of Aluminum in Caustic Solutions.

causing it to stay below the saturation curve. Figure 2 shows that a waste stream with this composition could potentially be evaporated to high volume reduction factors without aluminum precipitation.

Because it is suspected that the solubility of other chemical compounds in the ORNL LLLW would limit the achievable degree of evaporation, experimental tests were performed with ORNL LLLW simulant having the chemical composition shown in Table I but with the initial aluminum concentration varied from 0.02 to 0.1 M. The room temperature density and suspended solids concentrations for evaporated simulants are shown in Fig. 3. Consistent with the increase in total suspended solids data in Fig. 3, solids began to appear in the cooled concentrate at a volume reduction factor of approximately 5 for a solution initially containing 0.02 M $NaAlO_2$ and ~3 for a solution initially containing 0.1 M $NaAlO_2$. However, precipitation did not occur in the original simulant before evaporation as would have been predicted by the solubility curve in Fig. 2.

The evaluations performed to date indicate that a minimum caustic concentration of 0.45 M may be required to keep the aluminum in the future ORNL LLLW in solution at room temperature, and a volume reduction factor on the order of 2 to 5 should be achievable when processing newly-generated ORNL LLLW. Addition of caustic to and/or evaporation of the ORNL LLLW stream, however, could result in the precipitation of other chemical compounds present in the waste. Therefore, additional testing is recommended to verify these conclusions before completing the detailed flow sheet designs.

To determine the potential impact of the chemical composition on the proposed waste treatment flow sheets, it was assumed that a volume reduction factor of 5 could be achieved for each of the evaporation steps in Fig. 3. Assuming that grouting the LLLW concentrate results in a volume increase of 1.6 and that the salt cake waste form can be further concentrated after evaporation to a specific gravity of 1.5, the final bulk waste forms for the flow sheets shown in Fig. 1 will be:

a. 30% of the original LLLW volume for a grouted waste form for disposal at WIPP,
b. 4% of the original LLLW volume for the salt cake waste form for disposal at WIPP, and
c. 30% of the original LLLW volume for the pretreated grouted for shipment to NNSS if sufficient TRU separations can be achieved to make the bulk waste non-TRU.

IMPACT OF ISOTOPIC COMPOSITION ON FINAL WASTE FORM

The isotopic composition of the future LLLW stream was evaluated for its ability to meet open road transportation limits and the WIPP WAC for three 55-gal drums transported in a 72-B carrier. The parameters evaluated include the hypothetical accident condition limit for the 72-B, the decay heat limit for the 72-B, the surface dose of the 72-B, the surface dose of the unshielded 55-gal drums, the minimum transuranic content of the waste form, and the maximum curie limit of the waste form. Typically, the criterion that limits the concentration of ORNL LLLW in the final waste form is the surface dose for the unshielded 55-gal drum.

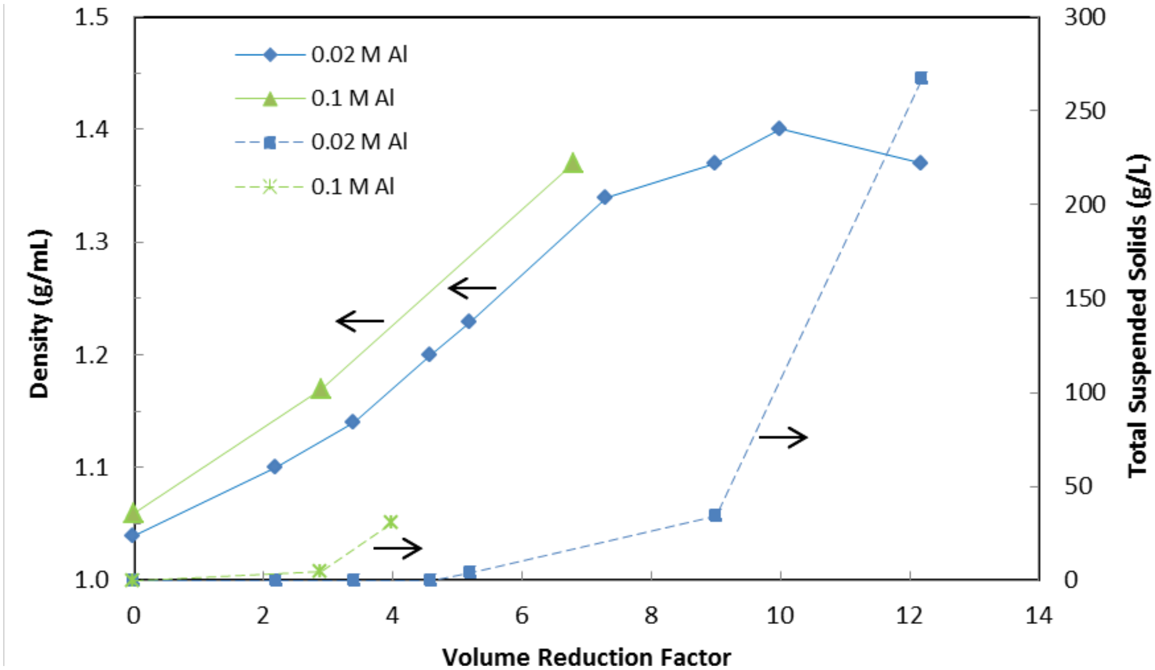

Fig 3. Density and Suspended Solids in Evaporated LLLW Simulants.

The isotopic concentrations of the future LLLW given in Table I are for the waste as it is generated at the ORNL research facilities. This newly generated waste contains short-lived isotopes, such as Zr-95 and Eu-154, that contribute significantly to the surface dose. Their concentrations will decrease fairly rapidly over time. The solid red curve in Fig. 4 shows the impact of storage time for radionuclide decay on the volume of the final waste form required to meet the WIPP WAC. It represents the minimum volume that would be required to meet the WIPP WAC for a waste stream having the composition of the newly generated ORNL LLLW as a function of decay time. It indicates that storage for one year will allow the LLLW to be concentrated more, which will reduce the amount of waste requiring disposal at WIPP by a factor of approximately 6. The dramatic reduction in the final waste form volume occurs during the first 2–3 years of storage; little additional volume reduction is achieved with increased storage time after approximately 6 years. A waste form falling below the red curve (shown in yellow in Fig. 4) would exceed the WIPP WAC and would require additional storage for decay. It should be noted, however, that any waste form that is more concentrated than approximately 20 times the original LLLW volume could not meet the WIPP WAC even with essentially indefinite storage time for decay. Any waste form falling above the red curve would exceed the minimum volume of waste that could be shipped to WIPP, and additional storage time would not be beneficial.

The estimated volumes achievable for the grouted and salt cake waste forms based on chemical composition are shown as dashed lines in Fig. 4. They indicate that the waste would need to be stored approximately 0.5 years for decay for the expected achievable volume for the grouted

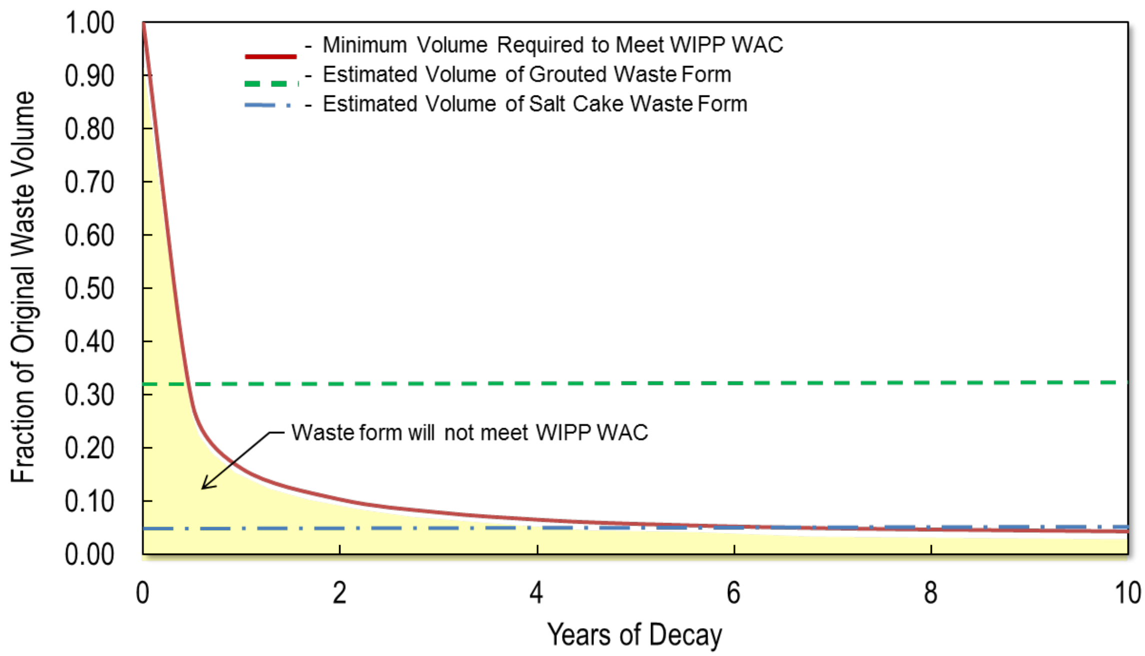

Fig. 4. Proposed Treatment Options for ORNL LLLW.

waste form to meet the dose WIPP WAC and approximately 5 years for the expected salt cake volume to meet the WAC. Any waste form with a volume less than this salt cake form would be challenging for WIPP disposal.

IMPACT OF PRETREATMENT ON FINAL WASTE FORM

Preliminary experimental data [3] shows that approximately 95% of the TRU components, 97% of the rare earths, and 99.9% of the cesium and strontium can potentially be removed by pretreatment. At these removal levels, the bulk pretreated LLLW would still be transuranic and would not be eligible for disposal at NNSS as proposed in the Fig. 1 (c) flow sheet. A TRU removal efficiency of 99.2% would have to be achieved to make the as-generated LLLW a non-TRU waste. The flow sheet shown in Fig. 1 (c) would produce the same volume of the bulk grouted waste stream for disposal at WIPP as the Fig. 1 (a) flow sheet, plus an additional concentrated TRU waste form and a cesium rich waste form would be generated for disposal. The concentrated TRU waste form generated from the pretreatment step is expected to be much more concentrated than the salt cake waste form described above and would exceed essentially all of the WIPP WAC even with long-term storage for radioactive decay. Disposal of this waste at WIPP would be extremely challenging. The cesium rich waste stream could potentially be dispositioned at NNSS.

STATUS OF TREATMENT FLOW SHEET DEVELOPMENT

The grout flow sheet shown in Fig. 1(a) is the most commonly used treatment method for liquid low-level waste streams. It would require the least amount of additional development effort, and it is a commonly accepted waste form at disposal sites. The salt cake flow sheet (Fig. 1[b]) has the advantage of potentially reducing the amount of waste destined for WIPP by a factor of approximately 7, but it would require more development work than the grout flow sheet. Discussions with WIPP would be required to determine whether a sodium nitrate waste form would be acceptable in the future for disposal at WIPP. Initial evaluation of the pretreatment flow sheet (Fig. 1 [c]) has indicated that pretreatment will not meet the original objective of making the bulk of the waste non-TRU, and disposal of the concentrated waste forms from pretreatment will be problematic. Therefore, the grout flow sheet shown in Fig. 1(a) is being considered the baseline option for additional studies.

CONCLUSIONS

Studies are underway to evaluate treatment options for ORNL's future mission generated LLLW for disposal at WIPP. Impacts of chemical and radiological waste composition and decay time on various waste forms and their ability to meet the WIPP WAC and/or transportation criteria are being examined. Evaluations to date indicate that a minimum caustic concentration of approximately 0.45 M may be required to keep the aluminum in the future ORNL LLLW in solution at room temperature, and a volume reduction factor on the order of 2 to 5 should be achievable when processing newly generated ORNL LLLW without the production of solids. Studies show that storage of less than a year for radioactive decay of short-lived radionuclides could reduce the volume of a grout waste requiring disposal at WIPP by half. If a salt cake waste form were to be used, the waste form would require approximately 5 years of storage for decay, and the volume of waste would be reduced by a factor of approximately 7 compared with the grouted waste form. The flow sheet considered for pretreatment to remove TRU and high gamma components from the bulk waste stream to produce a non-TRU waste form appears challenging. Additional testing is recommended to verify these conclusions before completing the detailed flow sheet designs for treatment of ORNL LLLW.

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