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Laboratory Development of Sludge Washing and Alkaline Leaching Processes: Test Plan for FY 1994

Brian M. Rapko
Gregg J. Lumetta

July 1994

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

Summary

The U.S. Department of Energy plans to vitrify (as borosilicate glass) the large volumes of high-level radioactive wastes at the Hanford site. To reduce costs, pretreatment processes will be used to reduce the volume of borosilicate glass required for disposal. Several options are being considered for the pretreatment processes:

1. Sludge washing with water or dilute hydroxide: designed to remove most of the Na from the sludge, thus significantly reducing the volume of waste to be vitrified.

2. Sludge washing plus caustic leaching and/or metathesis (alkaline sludge leaching): designed to dissolve large quantities of certain nonradioactive elements, such as Al, Cr and P, thus reducing the volume of waste even more.

3. Sludge washing, sludge dissolution, and separation of radionuclides from the dissolved sludge solutions (advanced processing): designed to remove all radionuclides for concentration into a minimum waste volume.

This report describes a test plan for work that will be performed in FY 1994 under the Sludge Washing and Caustic Leaching Studies Task (WBS 0402) of the Tank Waste Remediation System (TWRS) Pretreatment Project. The objectives of the work described here are

- to determine the effects of sludge washing and alkaline leaching on sludge composition and the physical properties of the washed sludge

- to evaluate alkaline leaching methods for their impact on the volume of borosilicate glass required to dispose of certain Hanford tank sludges.

The work will be done in accordance with Pacific Northwest Laboratory (PNL) Impact Level III quality assurance (QA) requirements as described in the Good Practices Standard of PNL-MA-70. The work will be conducted in accordance with the TWRS Pretreatment Project QA Plan.

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Laboratory Development of Sludge Washing and Alkaline Leaching Processes: Test Plan for FY 1994

Introduction

During the past few years, the primary mission of the U.S. Department of Energy's Hanford site has changed from producing Pu to restoring the environment. Large volumes of high-level radioactive wastes (HLW) were generated in the past from Pu production. These wastes are stored in underground tanks on site. The current plan for remediating the Hanford tank farms consists of waste retrieval, pretreatment, treatment, and disposal. The HLW will be vitrified as a borosilicate glass; the resulting glass canisters will then be disposed of in a geologic repository. Because of the expected high cost of vitrification and geologic disposal, pretreatment processes will be implemented to reduce the volume of borosilicate glass produced in disposing of the tank wastes.

Various options are being considered for pretreating tank sludges. These options include (in increasing order of complexity) 1) sludge washing with water or dilute hydroxide, 2) sludge washing plus caustic leaching and/or metathesis (alkaline sludge leaching), and 3) sludge washing, sludge dissolution, and separation of radionuclides from the dissolved sludge solutions (advanced processing). Experimental evaluation of these first two options in FY 94 by Pacific Northwest Laboratory (PNL)[a] is the subject of this test plan. Work in this area is expected to continue into later fiscal years: the test plan will be updated as the scope and goals of the project are further refined.

The minimum pretreatment that will be performed is simple sludge washing. Washing the sludge with water or dilute NaOH is expected to remove most of the Na from the sludge, significantly decreasing the volume of glass produced as compared to vitrifying the sludge directly (Straalsund et. al 1992). Such sludge-washing studies with actual tank waste are covered under this test plan.

A second level of treatment involves leaching the sludge with highly caustic (≈3 M) solutions. Such concentrated hydroxide solutions might be expected to dissolve certain non-radioactive elements, such as Al and P, which are present in large quantities in Hanford tank sludges (Weber 1982). Highly caustic solutions can also metathesize many insoluble phosphates to insoluble hydroxides, which also decreases the phosphate content of the sludge. Efficient removal of Al and P (as PO_4) should greatly decrease the amount of solids required to immobilize the waste. In addition, previous studies on leaching sludges with highly caustic solutions (both in the presence or absence of other Cr-solubilizing agents) suggest that other key, nonradioactive components, such as Cr, may also be dissolved (Lumetta et al. 1994, Lumetta and Swanson, 1993a). Enhanced Cr dissolution has been observed at highly caustic vs. mildly basic solutions and may be due to the increased solubility of Cr at high-hydroxide concentrations (Rai, Sass, and Moore 1987).

For many sludges, leaching such key components should result in a greatly decreased volume of glass needed, without resorting to more aggressive dissolution and separation methods (Straalsund et al. 1992). For example, removal of Cr from Plutonium Finishing Plant (PFP) sludge alone is estimated to decrease the number of glass canisters from 2500 for washed-only sludge to 500 for Cr-free washed sludge (Lumetta, Swanson, and Barker 1992). This test plan addresses testing and development for pretreating actual Hanford tank sludges through treatment with highly alkaline solutions.

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

The performance of the caustic leaching process might be improved by adding a reagent to enhance dissolution of species whose presence would otherwise limit the amount of sludge that could be incorporated into a given glass volume. Examples of such reagents include 1) oxidants to oxidize Cr(III) to the more soluble Cr(VI) species, and 2) metathesis agents for phosphates other than hydroxide. This test plan addresses testing and development for pretreating actual Hanford tank sludges through contact with alkaline solutions containing simple metathesis agents for phosphates.

The types of sludge to be examined during the work described in this test plan are dictated largely by the tank-waste samples available. The effects of sludge washing and sludge leaching/metathesis already have been determined for several types of tank wastes: a brief summary is provided in Table 1. The types of sludge to be examined this fiscal year include both single-shell tank (SST) and double-shell tank (DST) wastes. These are

- B-201, which primarily contains neutralized concentration waste from the bismuth-phosphate process for Pu purification
- T-107, which contains primarily waste from a process that used tributyl phosphate (TBP) to recover uranium from bismuth-phosphate waste
- BX-107, which contains first-cycle decontamination waste and neutralized aluminum-coating waste from the bismuth-phosphate process for Pu purification, TBP waste and ion-exchange waste from Cs recovery processes
- U-110, which contains first-cycle decontamination waste and neutralized aluminum-coating waste from the bismuth-phosphate process
- AZ-101 and AZ-102 (DST wastes), which contain neutralized current acid waste (NCAW) from the PUREX process.

The scope of this test plan also covers the study of other waste samples as they become available.

Objectives

This test plan specifically describes work that will be performed in FY 1994 under the Sludge Washing and Caustic Leaching Studies Task (WBS 0402) of the Tank Waste Remediation System (TWRS) Pretreatment Project. However, the test approach described in this document can be extended to work scheduled for FY 1995-1998. The scope of work for those later years is not specifically described within this document because of present uncertainties as to the tank samples that will become available during that time. It is also possible that modifications might become necessary as a result of knowledge gained from the work described here. This work is being conducted by PNL at the request of Westinghouse Hanford Company (WHC).

The objectives of the work described here are

- to determine the effects of sludge washing on sludge composition and the physical properties of the washed sludge
- to develop simple leaching procedures that can be used to reduce the volume of borosilicate glass required to dispose of certain Hanford tank sludges.

Table 1. Hanford Tank Wastes Examined for Sludge Washing and Alkaline Leaching

Tank Type	Waste Type(s)	Sludge Washing?	Alkaline Leaching?	Reference
241-B-110	2C[a], FP[b], IX[c]	yes	yes	Lumetta et. al. 1994
241-C-109	TBP[d], FeCN[e], 1C[f], CW[g], IX	yes	yes	Lumetta et. al. 1994
241-C-112	TBP, FeCN, 1C, CW, IX	yes	yes	Lumetta et. al. 1994
241-U-110	1C, CW	yes	yes[l]	Lumetta et al. 1994. Lumetta et al. 1993d.
241-SY-102	PFP[h]	yes	no	Lumetta and Swanson 1993a.
103-AW and 105-AW	NCRW[i]	yes	no	Lumetta and Swanson 1993b. Lumetta and Swanson 1993c.
101-AZ	NCAW[j]	yes[k]	no	Peterson, Scheele and Tingey 1989.

a) Second decontamination cycle bismuth-phosphate waste.
b) Fission product waste.
c) Ion-exchange waste from Cs recovery processes.
d) Waste from the U extraction by TBP process.
e) Waste from Cs precipitation by $Na_2NiFe(CN)_6$.
f) First decontamination cycle bismuth-phosphate waste.
g) Aluminum-cladding-dissolution waste.
h) Plutonium finishing plant process waste.
i) Neutralized Cladding Removal Waste.
j) Neutralized Current Acid Waste.
k) Water and 0.03 M NaOH used.
l) 5 M NaOH at 100°C followed by 1 M K_2CO_3 at 100°C.

Test Approach

For a given sample of actual Hanford tank sludge, sludge washing and alkaline leaching tests will be performed. It is envisioned that the sludge will be subjected to washing with dilute NaOH; then the washed sludge will be treated with 1) strong NaOH followed by 2) $Na_2CO_3(K_2CO_3)$ or $NaOH/Na_2CO_3(K_2CO_3)$. The sludge washing step should remove soluble components, such as simple alkali metal salts, from the sludge; such a step is considered to be the minimal pretreatment that would be performed for tank sludges. The strong caustic-leaching step is being investigated to determine to what extent Al, Cr, P, and Si (and other elements) can be leached from the transuranic (TRU)-contaminated sludge solids. Finally, the carbonate-leaching step may metathesize phosphate from insoluble phosphates, such as $Ca_3(PO_4)_2$, that are not metathesized by hydroxide and so remove P from the remaining undissolved sludge.

A generic procedure for the sludge washing and caustic leaching studies is outlined in Figure 1. It should be stressed that this approach is meant to be a guideline; variations from this procedure will likely occur based on the particular characteristics of each waste.

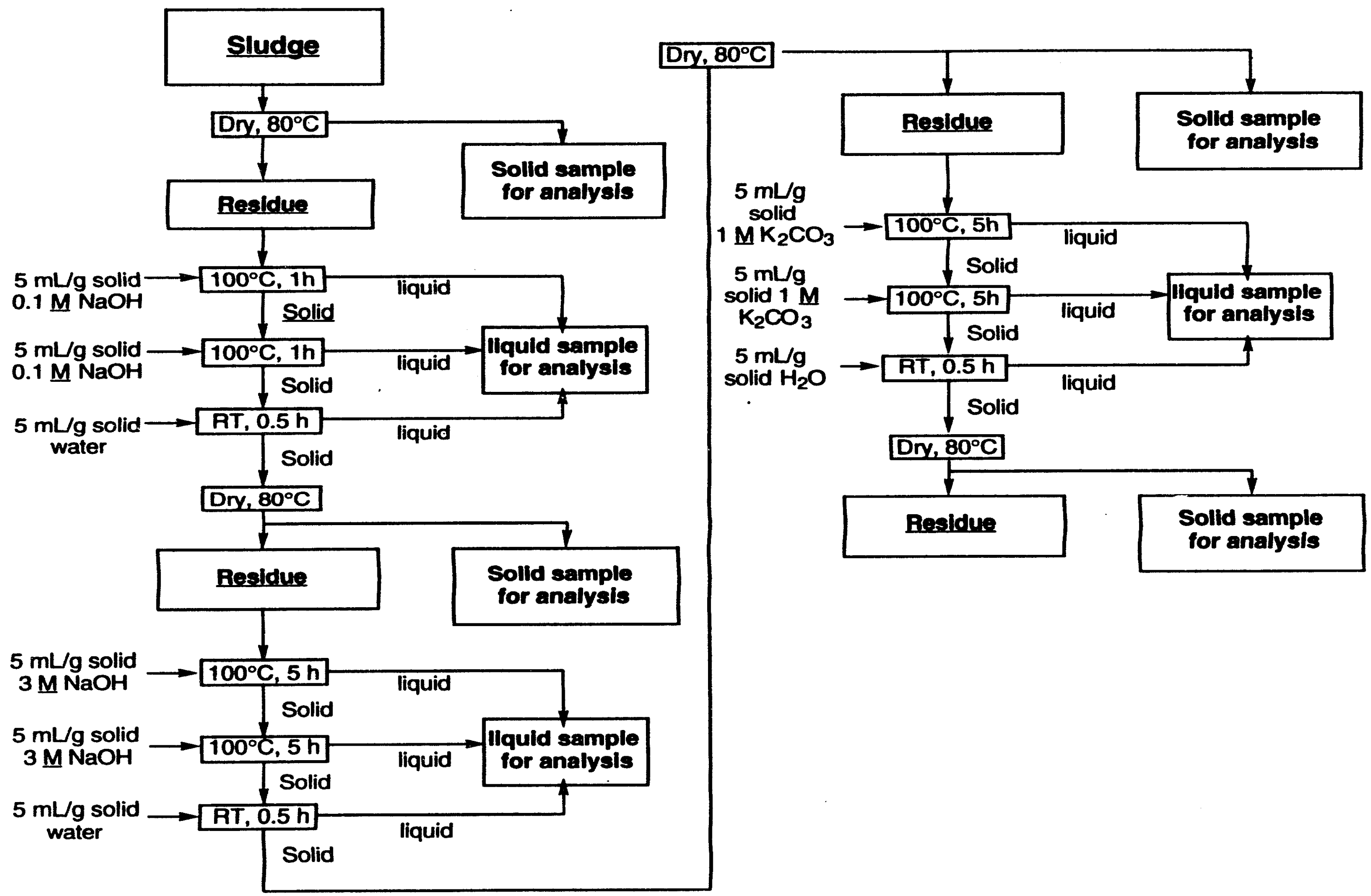
The tank samples presently available for this study have been described above. The same basic steps will be performed on each sludge sample (Figure 1). These steps include

- washing the sludge with 0.1 M NaOH at 100°C
- leaching the sludge with 3 M NaOH at 100°C
- leaching the sludge with 1 M K_2CO_3 at 100°C.

The sludge washing and leaching process has been broken down into each of these individual components so as to ascertain the impact of each individual step. As each step requires the introduction of additional materials to the sludge washing process, such a breakdown should allow an evaluation of the minimal amount of pretreatment necessary to achieve particular processing goals. Two additional experiments related to processing are planned. The first experiment involves testing a combined OH^-/CO_3^{2-} leach, which will be investigated to determine if the results of these individual steps above are cumulative if both species are simultaneously present. The second will target sludges where the above-described conditions appear unsuccessful at removing specific target elements (such as Al). In these instances, the impact of variables, such as increased hydroxide concentrations and/or extended contact times, will be explored.

The initial dried sludge, all solutions, and undissolved solids will be analyzed by both chemical and radiochemical methods. The dry weight of the sludge residue will be determined after completing the pretreatment steps. Including a measurement of the initial sludge and dried residues should allow for a check on the mass balance during the test as well as for a better comparison to other tank-characterization data. In selected cases, samples of washed sludge and undissolved solids will be analyzed by X-ray powder diffraction (XRD), transition electron microscopy (TEM), scanning electron microscopy (SEM), and particle size analysis to enhance understanding as to how the types of species and physical properties of the sludge are affected by these various types of pretreatments. The XRD, TEM, and SEM analyses will be conducted under the Tank Waste Treatment/Science Technology Development Task of the TWRS Pretreatment Project.

Figure 1. Schematic of Sludge Washing and Alkaline Leaching Tests



Deliverables and Reporting Requirements

Four quarterly reports will be issued to WHC on sludge washing and caustic leaching. These quarterly reports will be due on the last day of each quarter of the fiscal year. In addition, results of this work will be included in the topical report of the FY 1994 sludge-pretreatment development work, which will be cleared for public release in FY 1995. These reporting requirement are as defined in the PNL TWRS Pretreatment Technology Development FY 1994 Project Work Plan.

Waste Handling

Unused tank samples will be returned to WHC. Wastes generated during this task will also be shipped to WHC for their ultimate disposition.

Quality Assurance (QA)

The work will be done in accordance with PNL Impact Level III QA requirements as described in the Good Practices Standard of PNL-MA-70. The work will be conducted in accordance with the TWRS Pretreatment Technology Development Project QA Plan.

Experimental results will be recorded in dedicated laboratory notebooks, which will be safeguarded according to standard procedures.

The chemical and radiological hazards associated with this project do not exceed those normally encountered in our laboratories, and no special safety considerations are necessary.

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