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RESEARCH AND DEVELOPMENT ACTIVITIES IN SUPPORT OF HANFORD RIVER PROTECTION PROJECT PRIVATIZATION – SRTC PROGRAM (u)

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ABSTRACT

A team led by BNFL, Inc. was awarded the contract to remediate and immobilize the Hanford radioactive tank waste in support of the Hanford River Protection Program (RPP). BNFL, Inc. is teamed with BNFL Engineering, LTD., Bechtel National, GTS Duratek, and Science Application International Corporation to develop and design integrated facilities for pretreatment and vitrification in support of the RPP mission. This facility will pretreat and immobilize approximately 0.375 MT/day of high level waste (HLW, producing 1.5 MT/day of HLW glass) and approximately 4.5 MT/day of low activity waste (LAW, producing 30 MT/day of LAW glass). During the initial phase of the project (FY98 – FY00), the technology will be validated and optimized to the point that it can be used as the basis for final design, construction, and operation of a vitrification facility in Hanford, Washington.

As part of the overall Hanford River Protection Project, BNFL, Inc. has contracted DOE-Westinghouse Savannah River Company's Savannah River Technology Center (SRTC) to provide research and development services in characterization, pretreatment, and immobilization of actual Hanford tank wastes. SRTC is conducting tests, radioactive and non-radioactive, to confirm all major processing steps for the pretreatment flowsheet. During this testing, SRTC has identified and developed alternate or additional processing steps to address significant processing concerns. Additionally, SRTC is developing design basis data using simulants of Hanford tank wastes in areas of ion exchange, filtration, precipitation, glass former blending, evaporation, and slurry mixing. This paper will provide an overview of SRTC activities completed during the initial phase of the project, flowsheet modifications resulting from SRTC's identification and development of alternate or modified processing steps, as well as a description of the SRTC development program for the next phase of the project.

INTRODUCTION

In August 1998 the U.S. Department of Energy and BNFL, Inc. signed a historic contract that will provide a safe path forward for the pretreatment and immobilization of Hanford's radioactive tank waste [1]. This contract will work in two parts: Part B1 and B2. During the initial two-year period (Part B1), BNFL will complete approximately 30 percent of the facility design, prepare to start construction, and obtain financing to proceed with Part B2. DOE will reimburse BNFL the full cost (\$300 million) of the Part B1 contract including a maximum fee of \$50 million depending on BNFL's performance. The expected cost of the Part B2 contract is currently estimated at \$6.9 billion dollars. During Part B2, the facilities constructed for the BNFL RPP project are expected to produce 600 HLW canisters^a and 6000 units of immobilized LAW. Construction is expected to start late in FY01. HLW Hot Start is expected in FY07 with LAW Hot Start expected in FY08 [2].

The following discussion is a plausible feed sequence based upon the current contract. As the project progresses, BNFL and DOE/RL will jointly establish the sequence of waste tank feed to the BNFL facility.

During the initial two years of actual waste treatment operations, BNFL expects to receive a combined Envelope B/D feed for processing. Envelope B/D waste resulted from neutralizing acidic Purex waste with NaOH and allowing the waste to settle and cool in storage tanks. The neutralized waste was allowed to precipitate and separate into a supernate (Envelope B) and a sludge (Envelope D) fraction^b. The DOE/RL and the primary Hanford site management contractor are expected to transfer the combined Envelope B/D feed from tanks 241-AZ101 and 241-AZ102 to BNFL receipt tanks in the BNFL waste treatment facilities. BNFL plans to process the received waste through a set of cross flow filters that will separate the liquid fraction from the solid sludge fraction. Figure 1 contains a flow sheet of the proposed BNFL process.

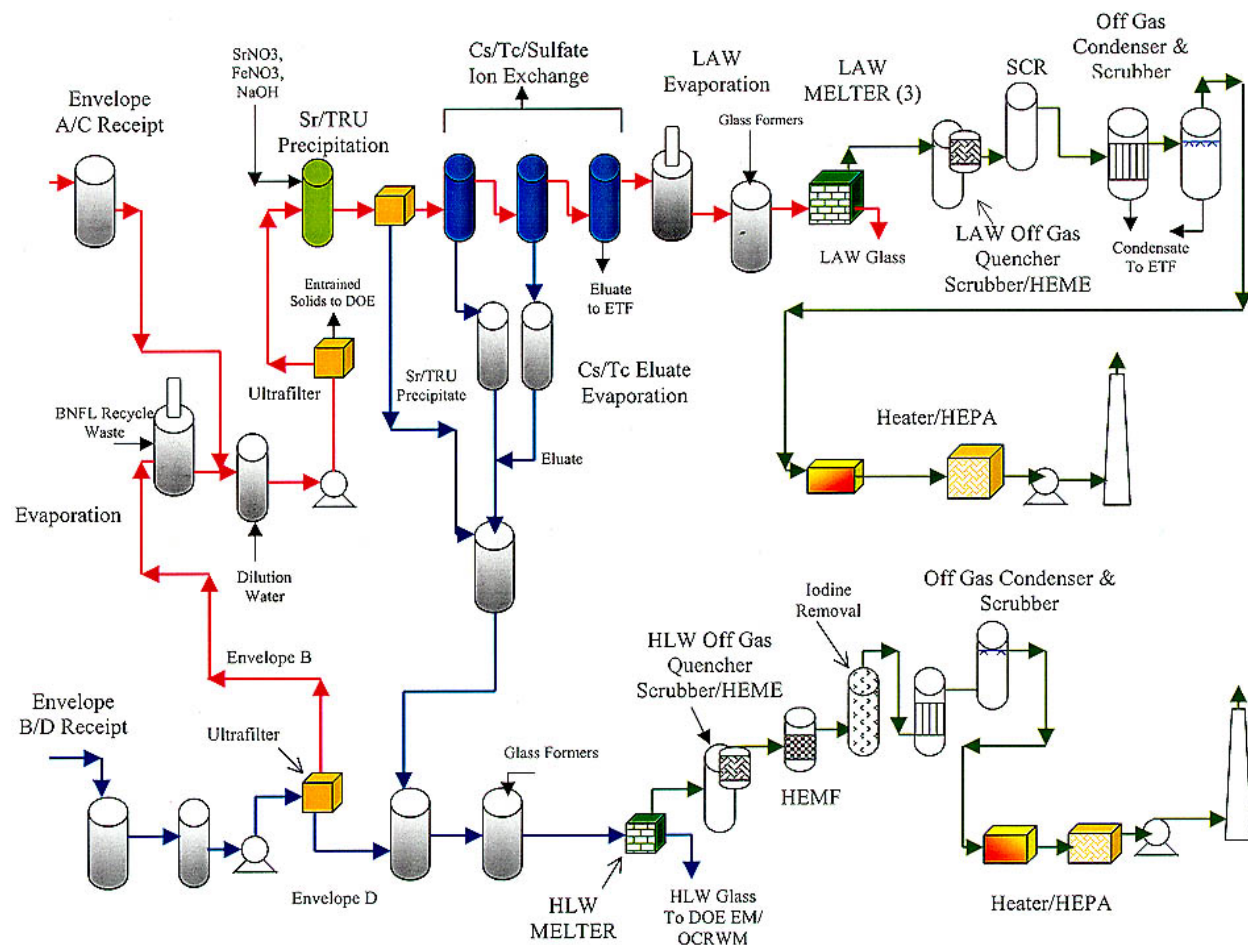


Fig. 1. BNFL TWRS Process.

The liquid fraction from ultra-filtration of Envelope B/D will be forwarded to an evaporator feed tank. BNFL plans to collect the plant recycle waste streams for blending with the Envelope B liquid. The resulting feed will be concentrated through a forced circulation evaporator to approximately 4.5-6 M Na solution. The concentrated liquid will be cooled to 25-30C and processed through a cross flow filter unit to remove solids. The resulting filtrate will be fed through cesium and technetium ion exchange columns (elutable organic based resins) and precipitation process for sulfate removal. The decontaminated low activity waste will be concentrated through a forced circulation evaporator. Depending on the amount of sulfate removed from the initial Envelope B wastes; BNFL and DOE may elect to temporarily store the decontaminated waste before vitrification. If the sulfate content is still too high after sulfate removal then the decontaminated Envelope B waste will be blended with future decontaminated LAW wastes (Envelope A & C^{c,d}) to lower the sulfate content prior to vitrification. If sulfate can be removed to a level that does not impact the vitrification processes, then glass formers will be added to the concentrated LAW and fed to three 10 metric ton per day joule-heated, refractory-lined melters that have been designed to operate at 1150°C (nominal).

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BNFL plans to evaporate, store, sample, and analyze the cesium and technetium eluates generated from pretreating Envelope B through the ion exchange systems. The nitric acid based (Cs) and water based (Tc) eluates will be blended and then mixed with the concentrated Envelope D solids (sludge). Glass formers will be added, and the resulting melter feed will be vitrified as HLW. BNFL plans to use a joule-heated refractory-lined melter that will be operated at 1150°C (nominal). All the waste stored in tanks 241-AZ101 and 241-AZ102 will not be vitrified in the first two years of HLW operations. Therefore, BNFL will pretreat and store the remaining HLW sludge not vitrified during the first two years of plant operations, until vitrification in the later years is accomplished.

During the initial two years of plant operations, BNFL plans to conduct combined pretreatment and vitrification of only HLW feeds. During the next 10 years of operations, BNFL will conduct combined pretreatment and vitrification of both HLW and LAW feeds.

The RPP Privatization contract specifies a LAW feed sequence based on metric tons of sodium in each feed envelope, but does not currently identify a source tank(s) for the LAW feed. BNFL and DOE/RL will jointly establish the sequence of waste tank feed to the BNFL facility. The following discussion is a plausible feed sequence based on the current contract.

The feed to the BNFL LAW/HLW facilities after the first three years of operations will be Envelope A and C feed tanks 241-AN-104 and 241-AN-102. BNFL will process the Envelope C and A feed for two to three years, depending on the quantity of waste actually received. One additional unit of operation is added to the BNFL flow sheet during Envelope C pretreatment. Strontium nitrate and sodium permanganate are added to coprecipitate strontium-90 and transuranic (TRU) radioactive ions in the Envelope C waste. The resulting slurry is filtered using a cross flow filter. The Sr/TRU precipitate slurry is combined with Cs/Tc eluates and HLW sludge and vitrified as HLW. After most of initial feed is processed, the next HEMF ht years of operations will pretreat and vitrify the remaining minimum order quantity feed specified by DOE. The expected feed sequence for the remaining 6-8 years is expected to be the Envelope C feed from 241-AN107 and then the Envelope A feed from tanks 241-AN105, 241-SY101/AP104 blend, 241-AN103, and 241-AW101. The exact feed sequence has not been determined by DOE/RL at this time.

While processing these LAW feeds, BNFL will vitrify the HLW solids stored from pretreatment of the combined B/D feed (241-AZ101 & AZ102), as well as HLW (Envelope D) solids retrieved from tanks 241-C106, 241-AY102, 241-C104 and 241-AY101. Waste from tank 241-C106 is expected to be transferred to 241-AY101 prior to transfer to the BNFL. Additionally, waste from 241-C104 is expected to be transferred to 241-AY101 prior to transfer to the BNFL.

In order to complete the development and initial design of these facilities, BNFL has formed a team that includes BNFL Engineering, LTD., Bechtel National, GTS Duratek, and Science Application International Corporation. BNFL is also working with IBC Advanced Technologies, Inc. to develop ion exchange resins for the pretreatment process.

Additionally, BNFL has contracted the Westinghouse Savannah River Technology Center (SRTC), the Battelle Pacific Northwest National Laboratory, and Catholic University's Vitreous

State Laboratory (VSL) to provide fundamental research and development for the project. In using the DOE or DOE-funded laboratories, BNFL will be able to efficiently transfer the technology developed by DOE to the private sector. Specifically, BNFL will be able to transfer the lessons learned from the West Valley and Defense Waste Processing Facilities to the RPP project. This paper discusses the development program at the Savannah River Technology Center that will be conducted in support of the RPP Part B1 project.

SRTC RPP PART B1 DEVELOPMENT PROGRAM

SRTC supported BNFL during the Part A of the Hanford Privatization contract. SRTC fulfilled critical research and development needs for the Part A deliverables [3, 4]. Pursuant to this, BNFL awarded SRTC a two-year research and development contract to provide critical design basis data in support of the RPP Part B1 project phase. SRTC is supporting BNFL in the areas of characterization, pretreatment, and vitrification. SRTC is developing design basis data using actual and simulated Hanford tank wastes in areas of filtration, ion exchange, precipitation, glass former blending, evaporation, slurry mixing and vitrification. SRTC R&D efforts are being conducted in accordance with DOE Contract DE-AC06-96RL13308 (RPP contract) and BNFL-SRTC contract.

CHARACTERIZATION

SRTC has received the following liquid and solid samples from the Hanford tank farm areas.

Hanford Tank Samples to be processed at SRTC^e

Table I

Sample Name	Tank	Hanford Waste Type	Quantity (liters)
Envelope A	AN103	DSSF	1.25 – 1.5
Envelope A (Denoted as sample AA)	AN104	DSSF	1.25 – 1.5
Envelope B/D	AN102	NCAW	1.25 – 3.5 200-300g sludge solids (dry basis)
Envelope C	AN102	CC	Part of LC 1.25 – 1.5
Envelope LC (LC denotes Large C)	AN102	CC	>15 L

The Hanford tank waste samples have been characterized for chemical and radionuclide content. Additionally, SRTC has obtained density vs. temperature, viscosity vs. temperature, and specific heats for each sample. Ion exchange tests were also conducted using 25 L of Savannah River Purex HLW supernate which is comparable to Envelope A tank wastes at Hanford.

Simulant Development

SRTC has formulated simulants based upon the tank analysis data, literature sources, and the BNFL flow sheet. The simulants will be used to perform non-radioactive experiments and to test

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experimental equipment prior to placing the equipment in radioactive service. The simulants will be characterized for physical and chemical properties. Simulants have been formulated to represent specific tank wastes that are expected to be processed during the initial radioactive operations of the plant. No hypothetical blend recipes will be formulated. Supernate simulants (nominal plus realistic concentration extremes) will be developed to simulate Envelopes A, B, and C. A sludge simulant has been formulated to model the expected NCAW waste. These simulants will be characterized for chemical content, particle size, density, and rheology.

Since BNFL plans to operate with only Envelope D feed combined with eluates during the first two years of HLW vitrification operations, HLW melter feed simulants will be developed on the basis of a sludge/eluate process and on the basis of a sludge/eluate/Sr/TRU precipitate process. Corrosion testing using the Hanford radioactive wastes will also be conducted.

Status

Development of simulants for use in BNFL Part B research has focused on duplicating the compositions of specific, recent Hanford waste samples. The simulants represent all four waste envelopes and were originally chosen to provide information to supplement the active samples processed in Part B research. Currently, the simulants representing the A, B and C waste envelopes have been approved for use and have been used in all phases of inactive testing. Two additional simulants were approved for entrained solids testing in the pilot crossflow filter system.

The first simulant developed was for envelope C research and represented supernate from Hanford waste tanks 241-AN-107. The C envelope waste, also known as complex concentrate, is very high in organic carbon due to the presence of chelating agents from the Hanford processes for recovery of radioactive cesium and strontium isotopes. Successful simulation of AN-107 supernate required the addition of sodium gluconate to complex the iron. The addition of gluconate was based on process knowledge since a method for determining the amount of gluconate in the waste has not been developed. An attempt to simulate the other C envelope tank, 241-AN-102, was not successful due to the complete lack of organic composition for this waste. The C entrained solids simulant contained significant amounts of sodium oxalate.

The A simulant prepared was based on Tank 241-AN-105 and was based in part on the waste characterization from the Part A active sample. The A entrained solids simulant was based on the solids remaining after washing and was high in chromium. Attempts at producing an extreme recipe for the A simulant revealed the complexity of varying any of the waste components to produce an extreme nonexistent waste simulant.

The B simulant represents the supernate from Tank 241-AZ-101 and was based solely upon the Best Basis Inventory since a recent sample analysis was not available. Use of this simulant in the evaporator program has revealed the formation of double salts involving fluoride with phosphate and sulfate anions.

Work continues on developing a D envelope sludge simulant. Current work focuses on maintaining high shear during the sludge preparation to produce sludge particles approaching the size observed in actual Hanford D Sludge.

Additional information obtained from the A and C simulants were an empirical expression relating the sodium concentration to the density and weight percent solids of the simulant. This information was used to support the evaporator, crossflow filter and modeling efforts.

Work continues on realistic simulants which represent partial dissolution of the solids in the A envelope tanks, and on simulants representing the leachates obtained from caustic dissolution of D envelope sludge. These simulants will be used to support the stream mixing studies and modeling efforts.

PRETREATMENT

After characterization, the actual Hanford radioactive tank waste samples will be processed according to the BNFL baseline flow sheet. Figure 2 shows a schematic of how each sample will be processed through the SRTC facilities. SRTC and Battelle collaborated on many of the pretreatment and vitrification process development activities. Battelle's experiences with actual Hanford waste will be applied to the process development activities at SRTC.

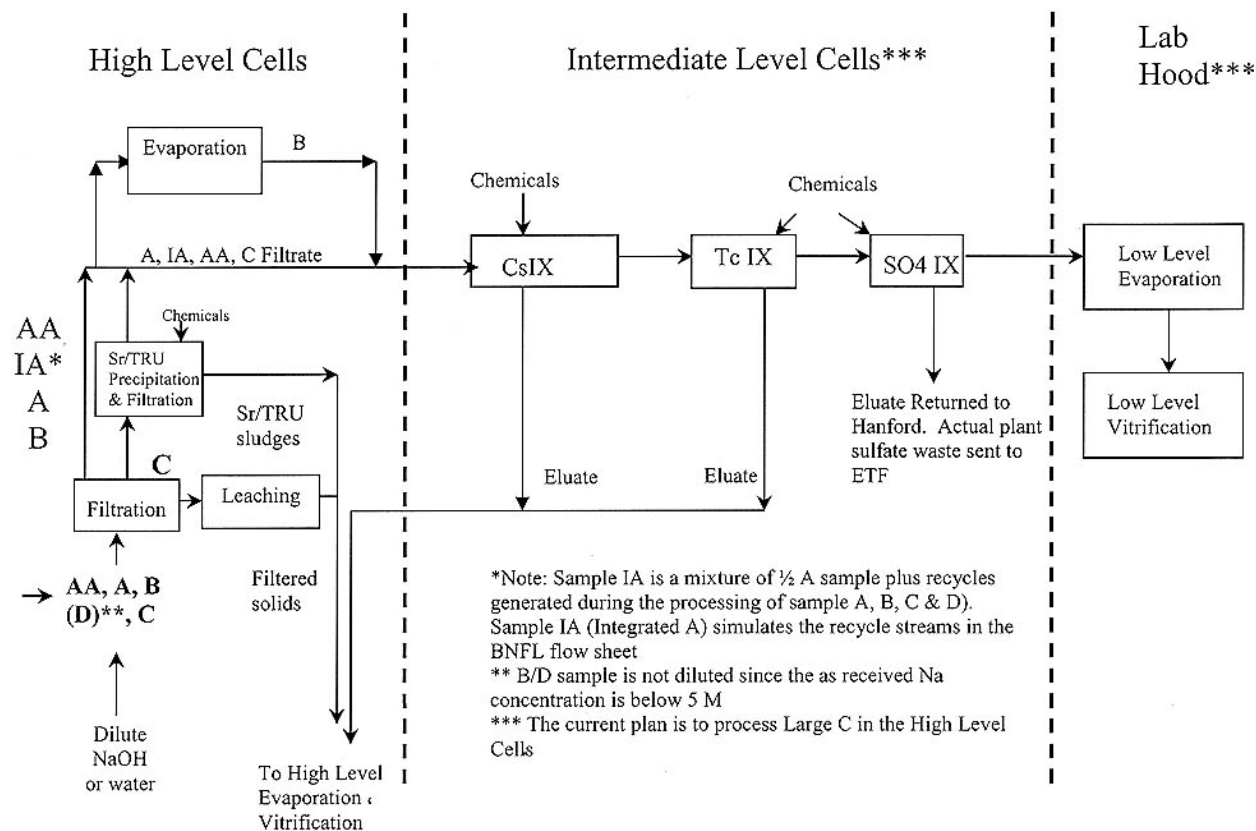


Fig. 2. Flow of Hanford Samples A, B/D, AA & C in SRTC Facilities.

Filtration-Entrained Solids Removal and HLW Sludge Pretreatment

Supernate samples (Envelope A & C) will be diluted to approximately 5.5M Na and then filtered to remove entrained solids using cross flow filtration. The combined Envelope B/D sample will be concentrated using cross flow filtration and the resulting filtrate (Envelope B) will be sent to an evaporator and then to the cesium ion exchange process. The filter concentrate, Envelope D, will be sent to HLW vitrification.

Radioactive filtration testing will be conducted using a cross flow filtration and solids washing system. The testing will be conducted to verify the performance of the cross flow filter during startup, operation, and shutdown sequences (e.g., back pulsing, filter cleaning/washing, permeate flow rates). Solubility versus temperature relations for entrained solids will be determined to estimate the quantity of entrained solids at the expected plant operating temperatures. The Envelope D sludge samples will be concentrated from a nominal 30-g solids/L to 125-g solids/L. Caustic leaching experiments will be conducted using the Envelope D sample. The leaching experiments will be conducted according to Specification 12 of the RPP privatization contract. Each radioactive sample will be processed using an experimental apparatus similar to the filter unit shown in Figure 3 [5]. Simulants will be used to demonstrate multi-tube cross flow filtration and determine conditions such as filtrate flow rates, pressure, and surface area needed to process active solutions. The pilot unit has seven tubes of one-meter length. The unit will be scaled based upon filter area to approximately 1:50 versus the actual plant. Individual tube diameter, tube length and pour size will be full scale.

Status

Initial tests with supernate samples from Envelope C have shown filtration to be extremely difficult. The design basis assumption for filtration of entrained solids could not be obtained via ultrafiltration with a 0.1- μm mott filter element. Subsequent testing at Battelle and SRTC reconfirmed the difficulty in separating entrained solids. Battelle and SRTC also attempted to separate entrained solids using filtration and centrifugation. Dead-end filtration and centrifugation proved to be difficult, time consuming, and impractical for application at plant-scale.

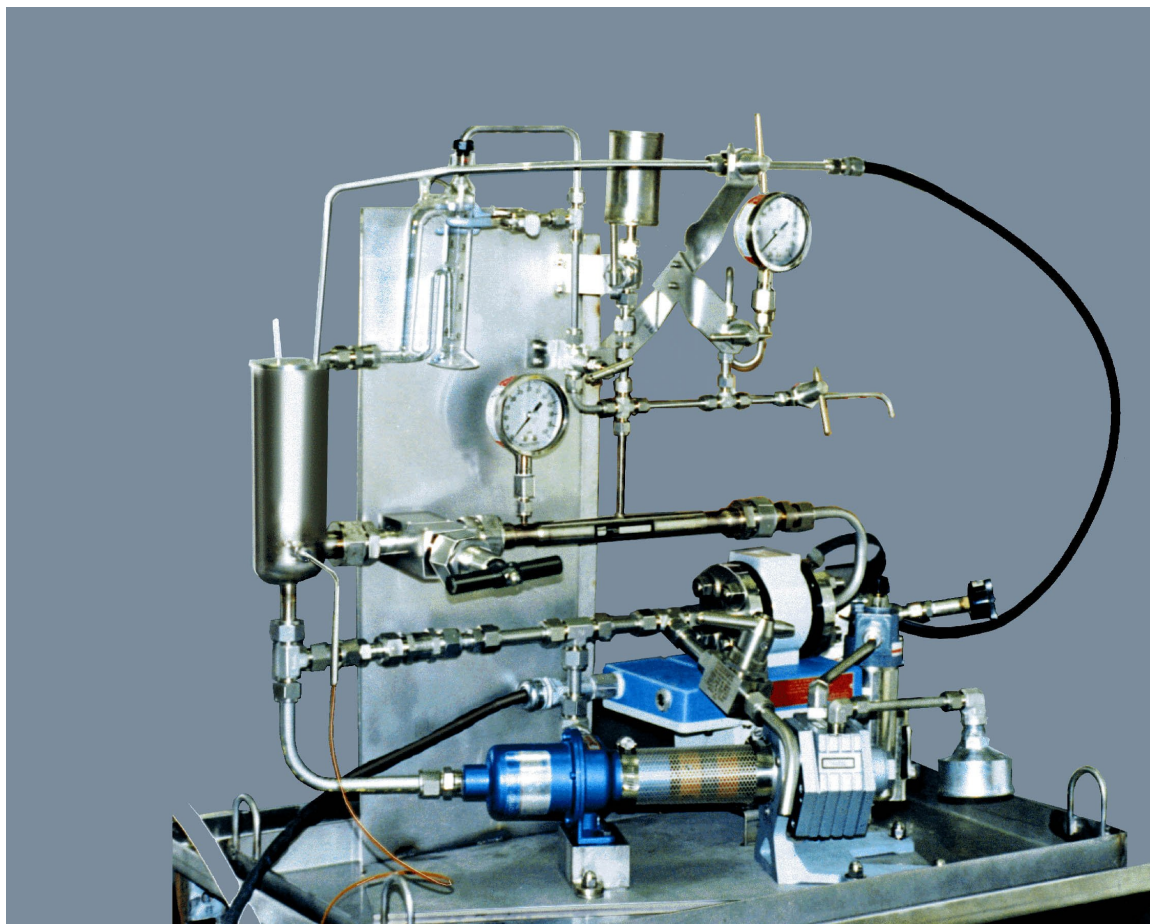


Fig. 3. Remote Cross Flow Filter at SRTC.

During dead-end filtration of the Envelope C sample it was observed that filtration was improved when the Sr/TRU precipitate was used as a filter aid. Cross flow filtration testing demonstrated the feasibility of jointly separating the entrained solids and Sr/TRU precipitate from Envelope C solution. Small-scale radioactive testing (20L) and simulant pilot testing confirmed satisfactory flux for this flowsheet change.

Envelope A and B supernate did not have sufficient entrained solids to proceed with solids filtration. Full depth core samples will be requested during the next phase of testing to ensure adequate solids.

Strontium/TRU Precipitation – Process Verification/Optimization/Adverse Reaction Evaluation

After filtration, Envelope C supernate is sent through the Strontium/TRU precipitation process. Envelope A and B supernates bypass this process and are sent directly to the cesium ion exchange process. Envelope C waste must be processed through the Strontium/TRU

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precipitation process because Sr/TRU radionuclides are more soluble in the waste due to the high levels of organic complexants.

The BNFL process uses strontium nitrate and ferric nitrate to coprecipitate ^{90}Sr and TRU radioactive ions during the pretreatment of Complex Concentrate (Envelope C) waste. Addition of non-radioactive strontium nitrate to the waste causes formation of a precipitate. An exchange of the complexed radioactive ^{90}Sr and the added non-radioactive strontium allow some of the ^{90}Sr to be freed from the complexes and

precipitate. This process is known as “isotopic dilution”. Ferric nitrate is used to precipitate plutonium and americium in a traditional carrier precipitation process. The resulting slurry is filtered using a cross flow filter.

Status

During the initial proof-of-principal testing, SRTC observed difficulty in filtration of the Sr/TRU precipitate. Initial testing of the Envelope C precipitation process during this phase confirmed this observation. The precipitate generated using strontium and ferric nitrate was not filterable.

Small scale testing confirmed that the strontium precipitate by itself provides excellent filter flux while addition of Fe (III) reduces flux to near zero. The Fe (III) in fact forms a gelatinous precipitate that plugs the filter.

As a result of unacceptable filtration, the need for a new precipitation scheme arose. This newly developed scheme implements a strontium isotopic dilution, a sodium permanganate oxidation, and under certain conditions introduction of calcium to the waste stream.

In order to evaluate the newly developed precipitation process further, a series of experiments were statistically designed. This design examined the relationship between the four responses of primary interest and five precipitation parameters. The four responses of interest are precipitate filterability, strontium decontamination, americium decontamination, and plutonium decontamination. The primary precipitation parameters that varied were the initial sodium concentration of the waste, the initial hydroxide level of the waste, and the amounts of calcium, strontium, and permanganate introduced. A limited number of additional experiments were performed to evaluate the impact of other process parameters such as temperature, timing of permanganate addition, and presence of entrained solids on the proposed precipitation scheme.

SRTC has conducted statistical bench simulant tests to optimize the process and develop a model to predict the decontamination factors as a function of temperature, organic constituents, sodium, hydroxide, Al, Sr and MnO_4 ion concentration. Additionally, method of addition and the ability to filter the resulting precipitate is also being studied. Reactor calorimetry experiments will be conducted using Envelope C simulants.

Bench scale radioactive tests were conducted using AN102 samples to verify actual process sequences. Process conditions verified were rate of reagent additions, sequence of reagent addition, temperature, and mixing. Simulant and radioactive experiments were also conducted to

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determine the effects from abnormal operating conditions. Some of the abnormal conditions varied were: elevated reaction temperatures, elevated filtration temperature, insufficient addition of sodium hydroxide, excess addition of ferric nitrate and strontium nitrate, pumping failures, and dissolution of solids with acids (filter cleaning).

The performance of the Strontium/TRU precipitation process was evaluated at pilot scale conditions using simulant solutions. A multi-tube cross flow filtration unit was used to estimate filtrate flow rates, pressure, and required filter surface area. The unit is scaled based upon filter area to approximately 1:50 versus the actual plant. Individual tube diameter, tube length, and pour size will be full scale. Testing with real waste using the Cells Filter Unit confirmed acceptable decontamination and filtration.

Ion Exchange – Cs/Tc/Sulfate Removal

Cesium, technetium, and sulfate will be removed from Envelope A, B, and C waste using elutable organic based ion exchange resins. Each sample received from Hanford, as well as a 25L SRS HLW Purex supernate sample, will be processed through a small-scale version of the BNFL ion exchange process.

SRTC is conducting extensive testing using ion exchange resins manufactured by IBC Advanced Technologies, Inc. SRTC will be conducting cesium ion exchange tests using IBC's SuperLig 644 and 632 resin. Tc ion exchange testing will be conducted using IBC's SuperLig 639 resin and sulfate removal will be accomplished with SuperLig 655.

Pilot scale tests (1 liter columns) will be conducted using simulants and Cs/Tc resins to determine relationships for pressure drop, mechanical (i.e., production of fines), chemical and expansion/contraction effects. Fluidization velocities and methods of separating the ion exchange fines from the bulk resin will be investigated. SuperLig 644 is known to decompose slowly in the presence of air and sodium hydroxide. Therefore, the decomposition of the ion exchange resins in the presence of air and caustic solutions under realistic conditions will be investigated. Small-scale batch contact tests will be conducted with actual waste samples and Cs/Tc/Sulfate resins to determine the equilibrium distribution coefficients^f. IBC Advanced Technologies will be performing radiation and chemical degradation studies.

Each supernate sample received will be pretreated using small ion exchange columns. The decontaminated LAW samples will be sent on to LAW vitrification. Small-scale radioactive testing will be conducted to determine system kinetics and separation efficiencies for Cs, Tc, and sulfate. Intermediate scale testing (50-100 ml columns) will be done with both radioactive (LC and SRS Samples) and simulated wastes. System kinetics will be determined by varying the superficial velocity and the column aspect ratio for the intermediate scale columns. The columns will be eluted with nitric acid or water and the composition of the eluates and decontaminated supernates will be determined. The quantity of radionuclides and other elements remaining on the spent ion exchange material will be determined to verify the reference disposal pathway (LAW vitrification) does not violate the contract specifications for LAW glass. Additionally, Tc ion exchange resin testing will be conducted using a 25-liter SRS HLW supernate sample, as this waste is comparable in speciation and composition to Envelope A. In particular, the technetium

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is in the pertechnetate form (TcO_4) and will be removed by the ion exchange resin. This is in contrast to the LC sample, which as a significant fraction of non-pertechnetate.

SRTC is developing models of the ion exchange process that will be integrated into the overall BNFL flow sheet model.

Status

A major concern with the BNFL flowsheet has been sulfate removal in the pretreatment phase of the process to prevent the problem inherent with excessive sulfate in the glass melter feed (i.e., separation, accelerated corrosion, safety concerns). BNFL has three major thrusts underway 1) development of an ion exchange resin, 2) glass formulation development, and 3) alternate removal processes.

SRTC investigated a number of alternate processes for sulfate removal identifying three – precipitation, evaporation/crystallization, and low temperature crystallization for further evaluation. Bench scale testing identified barium precipitation as the only process meeting the required decontamination factor.

Proof-of-principle testing has been completed and work is underway to demonstrate with active samples as well as selection of solid/liquid separation equipment, definition of reaction conditions, physical properties, stream mixing and disposition and vitrification to provide data necessary for a major flowsheet change.

Testing with Cs (SuperLig 644) and Tc (SuperLig 639) ion exchange resins in 5, 15 and 100-ml columns for Envelope A and C have been successfully completed meeting all design basis parameters. In addition a 50-ml column test with Savannah River supernate to evaluate large scale Tc removal was successfully completed.

The SRS supernate sample was selected because its composition is similar to some of the Hanford wastes that will be treated as part of the RPP, and, the sample was readily available. Approximately 28L of cesium-decontaminated sample were processed through a single 50 mL bed of SuperLig 639 resin. The 50% technetium breakthrough point was observed after approximately 540 resin bed volumes (BV) of solution had been processed. The resin performance exceeded expectations, based on preliminary experiments and simple calculations. No problems such as resin floating or channeling were observed during column operation. The technetium was subsequently removed from the resin by eluting with 35 BV of water. This test reconfirms SuperLig 639 resin capability to remove technetium and far exceeds the current BNFL plant design criteria which requires a minimum of 50 BV of feed to be processed prior to column elution and regeneration.

Mixing of Process Heels and Process and Recycle Streams

SRTC will evaluate the effects of mixing various recycle streams using simulants for each feed envelope. The simulants will be used to evaluate the chemical reactions and modifications to solution physical properties (e.g. density, viscosity). Initially, the BNFL recycle streams will be

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modeled using OLI Systems, Inc., Environmental Simulation Program (ESP). ESP will be used to guide the simulant development process and to predict the consequences of internal recycle stream mixing. The following recycle or heel mixing tests will be conducted:

- Heel of Envelope A mixes with C waste
- Heel of Envelope A mixes with B waste
- Heel of Envelope C mixes with B waste
- HLW wash water and leachate mixed with Envelope A feed
- HLW off gas scrubber recycled and mixed D waste
- LAW Entrained solids filter wash water mixed with A waste
- Sr/TRU precipitate wash water mixed with C waste

Actual Radioactive Hanford samples will be used to evaluate the effects of heel mixing in the BNFL TWRS double shell slurry feed tank. Additionally, SRTC will be conducting an integrated process demonstration (Sample IA) using part of Envelope A sample, Envelope A vitrification off gas condensate, Envelope D filtrate, Envelope A filter cleaning solution and possibly caustic leachate. Sample availability will defer this work until the next phase of the project.

Cs/Tc Eluate and LAW Evaporation

Once the Hanford tank samples (Envelope A, B, and C) are decontaminated, each sample will be evaporated to approximately one half its original volume. The samples will be concentrated to approximately 80 percent of the known saturation point. A small bench-scale evaporator will be operated on a continuous basis to approximate the BNFL evaporation process. BNFL has chosen a forced circulation evaporator to evaporate the pretreated supernates prior to sending the waste to vitrification.

Prior to evaporation of the actual radioactive samples, evaporation studies will be conducted using simulants. The objective of these studies is to develop preliminary operating and corrosion data and expected concentration endpoints using simulants of A, B, and C waste envelopes. Scoping studies will be conducted to determine the concentration at which precipitation first occurs. A small bench scale evaporator has been fabricated and will be used to evaluate scaling and foaming of simulated pretreated LAW. Organics will be spiked into the simulants to determine the distribution of organics in the concentrate, condensate, and evaporator off gas. This will provide a measure of organic entrainment in the LAW evaporator overheads. Analysis for hazardous metals will also be conducted. The concentrate and condensate will be characterized for chemical and physical properties (e.g. viscosity, density). The data developed during the LAW evaporation experiments will be used to validate an OLI ESP evaporation model that is also being developed by SRTC. Corrosion testing will be conducted using simulants and actual Hanford radioactive wastes.

BNFL plans to evaporate the Cs and Tc eluates generated during the ion exchange process prior to sending the eluates to the HLW vitrification process. The nitric acid (or water) eluates will be evaporated in a semi-continuous evaporator and the nitric acid overheads will be recovered and reused during the next elution cycle. SRTC will evaporate the radioactive Cs/Tc eluates prior to

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mixing these streams with Envelope D sludge. A small-scale evaporator will be designed and installed in the SRTC Shielded Cells Facility to evaporate the eluates generated during the ion exchange process. Simulant tests will be conducted to develop a procedure and methodology for evaporating the radioactive eluates.

SRTC is performing extensive OLI ESP modeling of the BNFL eluate evaporation process. The initial modeling efforts will focus on determining the volatility of Cs and Tc at various operating temperatures (e.g. 50C and 100C). The purpose of the modeling is to develop mathematical equations that relate the solubility of eluate solutions to temperature, sodium, potassium, nitric acid, and Cs/Tc concentration. SRTC will also develop mathematical relationships that relate temperature, sodium, potassium, nitric acid, and Cs/Tc concentration to solution density and heat capacity. SRTC will perform bench scale solubility and evaporation experiments to validate the mathematical relationships developed by the OLI ESP models.

Status

SRTC has defined the initial concentration limits for the simulants of the Envelope A (241-AN105), Envelope B (241-AZ101) and Envelope C (241-AN107) for the Pretreated LAW Melter Feed Evaporator. Beaker (125ml) and Bench Scale Evaporation tests (≈ 15 L) coupled with extensive process modeling of the BNFL evaporation process have been completed in support of the BNFL design efforts.

SRTC researchers found that Envelope B simulants of 241-AZ101 formed fluoride-phosphate and fluoride-sulfate double salts upon evaporation of this waste. The double salt, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ was found to be the major precipitating species in the Envelope B evaporation experiments and therefore was found to govern the final evaporation endpoint of this waste. Additionally, Kogarkoite (NaFSO_4) was also observed to form. These results were also confirmed with the OLI ESP Evaporator models.

VITRIFICATION

The goal of BNFL RPP project is to pretreat and immobilize the waste received from the Hanford HLW tanks such that it can be safely stored by DOE at the Yucca Mountain, NV repository (HLW only) or at the Hanford site in a near surface disposal vault (LAW only).

Glass Former Feed Preparation

An important requirement for any chemical process, especially a radioactive waste immobilization process, is to ensure that the product is within specified compositional limits. For vitrified radioactive waste, these limits and the processes that control the limits become part of a "contract" (Waste Form Compliance Plan for HLW) between the producer (BNFL) and the receiver (DOE). Currently BNFL plans to control the vitrified HLW and LAW waste form by controlling and analyzing the composition of the blended glass formers and waste stream. Blended glass formers will be analyzed separately from the waste stream and then mixed with the waste stream and pumped into the melter. Depending on the vitrification process, a mixture of between four and 13 individual glass formers could be used to make up a blended glass former

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batch. It is, therefore, necessary to control the glass former materials, the weighing and mixing process, and the transferring of the blended glass formers to the slurry mix tanks.

In collaboration with the VSL, a glass former raw material selection criterion will be developed and raw materials will be selected. SRTC will characterize the chemical and physical properties of the individual glass formers as well as the expected raw material blends. Physical property measurements include powder flow properties, TRU particle and packed density, and particle size distribution. The individual materials will be characterized for trace impurities that may affect the vitrification process. Glass former sampling systems will also be evaluated. A conceptual design for the glass former feed preparation system will be generated from this effort.

Status

Approximately thirty commercial technical grade, glass former materials, suitable for use in the Hanford LAW vitrification process, were obtained and their physical-chemical properties determined. These property determinations included various physical properties, powder flow properties, and suspension and durability determinations in NaOH solutions. Blends of the glass formers for envelopes A, B, and C were also made from the best candidate glass formers and evaluated.

After the characterizations, glass formers which could cause powder flow problems were identified for further evaluation by a powder flow consultant. These problem glass formers included Kyanite, zircon flour, titania, zinc oxide, and iron oxide. These materials are also the most dense materials which may lead to settling in the feed mix tank whenever stirring is halted. The least durable materials in NaOH were boric acid, lithium carbonate, and zinc oxide.

Blend B was found to clump together after storage for 30 days at room temperature. Additional tests will be performed to see if this happens at shorter time periods. The blends may also cause some powder flow problems.

The process area which may cause the most process problems is the storage and feeding of the blends just before mixing with LAW liquid in the feed mixing tank.

Wet Feed Mixing – Melter Feed Rheology Studies

Once the Hanford supernate samples have been pretreated to remove suspended solids, Sr/TRU (Envelope C only), Cs, Tc, and sulfate, the resulting concentrated wastes are mixed with glass formers and characterized for rheological properties as a function of total solids concentration. The recipes for the glass formers are determined by Catholic University's Vitreous State Laboratory (VSL). The VSL is responsible for all glass formulation efforts on the BNFL RPP project.

Rheological studies are also being conducted with simulants (A, B, C, and D). Simulants, which have been previously evaporated, and glass formers, will be characterized for shear stress vs. shear rate at various solids concentrations. The change in rheological properties versus time will also be measured to determine if the expected melter feeds are stable during plant outage

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conditions. As mentioned previously, HLW melter feed simulants will be developed on the basis of a sludge/eluate process and on the basis of a sludge/eluate/Sr/TRU precipitate process.

Vitrification

After mixing the blended glass formers with the pretreated LAW (Envelope A, B, C) and HLW (Envelope D + Cs/Tc Eluates + Sr/TRU precipitates), the melter feed samples will be vitrified in 60-gram batches at a temperature of 1150C. Crucible samples will be cooled according to a design basis canister-cooling schedule. Scanning electron microscopy and x-ray diffraction analysis will be conducted to determine crystallinity. The glass will be characterized for chemical and radionuclide content and durability (Product Consistency Test-PCT at 40 and 90C [LAW glasses] and 90C [HLW glass] and Toxicity Characteristic Leaching Procedure-TCLP). PCT and TCLP testing will be conducted in accordance with national consensus standards and guidelines (ASTM C-1285 and EPA SW-846 Method 1311, respectively). All glasses will be tested to confirm that combustibles, explosives, organics, free liquids, and pyrophoric components are not present in the glass. Organic analysis will be conducted in accordance with the EPA SW-846 procedures. The Washington State Department of Ecology Fish Toxicity Test will be conducted on the LAW glasses.

The large C sample (15 L) will be blended with glass formers and vitrified in a continuously fed melter. The off gases and condensate from the Melter will be characterized for organics according EPA SW-846 procedures. Scanning electron microscopy and x-ray diffraction analysis will be conducted to determine crystallinity. The glass will be characterized for chemical and radionuclide content and durability (ASTM PCT at 40 and 90C and EPA SW-846 TCLP).

ANALYTICAL DEVELOPMENT

The experimental work described above will generate a very large number of samples, both radioactive and non-radioactive, that require chemical analysis. The SRTC Analytical Development Section (ADS) will provide this service using ADS personnel, instrumentation, and procedures. Planning has taken place to estimate the number of samples and analyses required for each sample, along with the date the samples will be generated. This planning helps to assure that adequate SRTC resources will be available to meet the needs of the BNFL program.

In several cases, it will be necessary for SRTC to develop new analytical techniques and/or improvements in existing analytical methods to meet the analysis needs for the BNFL SRTC development program. Specific examples include: 1) developing an improved analysis for sulfate in solutions containing large amounts of salts and/or organic material to provide lower detection limits than possible with the existing methods and 2) developing a new, rapid radiochemical separation method for the determination of actinide isotopes. In addition, SRTC will determine the best means of providing the analyses of an extensive set of analytes for regulatory purposes.

SRTC is coordinating a development effort to identify and test methods for the on-line determination of technetium-99. Existing technologies for Tc monitors will be evaluated and

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tested. The Tc-99 monitor will be used to measure the TC-99 content of the pretreated LAW waste (before and after the technetium removal column operation). The program will identify potential candidate techniques and one or more will be selected for radioactive testing.

CONCLUSIONS

SRTC is supporting BNFL in the development and design of the RPP-WTP LAW & HLW pretreatment and immobilization facilities during the Part B1 phase of the DOE-BNFL contract. This paper provided a programmatic summary of the SRTC research and development efforts.

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REFERENCES

- [1] DOE Press Release, DOE and BNFL Inc. Sign Contract for Hanford Tank Waste Treatment Environment and Local Community to Benefit, 8/24/98.
- [2] DOE Contract DE-AC06-RL13308 Amendment No. A006, TWRS Privatization Contract, Release to Web, 9/10/98.
- [3] C. L. Crawford, D. M. Ferrara, B. C. Ha and H. E. Bibler, "Production of a High-Level Waste Glass from Hanford Waste Samples," Proceedings from Spectrum '98, Vol. 1, Denver, CO, 9/13-9/18, (1998) Sponsored by American Nuclear Society, Inc., pp. 581-588.
- [4] D. M. Ferrara, C. L. Crawford, B. C. Ha and N. E. Bibler, "Vitrification of Three Low-Activity Radioactive Waste Streams from Hanford," Proceedings from Spectrum '98, Vol. 1, Denver, CO, 9/13-9/18, (1998) Sponsored by American Nuclear Society, Inc. pp. 706-713.
- [5] Charles A. Nash, "Apparatus for Crossflow Filtration Testing of High Level Waste Samples," Advances in Filtration and Separation Technology – Proceedings, Vol. 12, of the Advancing Filtration Solutions '98 Conference, May 4-6, 1998, St. Louis, Missouri, pp. 472-478.
- [6] T. Bond Calloway, Jr. et al., "Research and Development Activities in Support of Hanford Privatization-SRTC Program," Proceedings from Spectrum '99, Tucson, AZ, 2/28-3/5, (1999) Sponsored by American Nuclear Society, Inc.

FOOTNOTES

- a. A HLW canister is defined as 4.5-meter tall canister. BNFL will design and test a 4.5-meter canister. The current West Valley and DWPF canister is approximately 3 meters. The

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canister diameter is the same as the West Valley and DWPF canister. A LAW unit is defined as either a rectangular package (1.85 m L x 1.25 m W x 1.25 m H) or square package (1.45 m L x 1.45 m W x 1.45 m H). 1300 – 1600 LAW units are expected from Envelope B waste and with the balance derived from Envelope A, B, or C.

- b. Envelope B/D waste is also known as Neutralized Current Acid Waste (NCAW). HLW generated in the Hanford Purex plant was denitrated with sugar and then neutralized with NaOH. Sodium nitrite was added to minimize corrosion in the tank farms.
- c. Envelope C waste is also known as Complex Concentrate waste. This waste resulted from Cs/Sr separation and encapsulation process which was operated in Hanford B plant. The waste has a high TOC due to the organic complexants that were added during the process.
- d. Envelope A waste is also known as Double Shell Slurry Feed (DSSF) waste and resulted from evaporating salts supernates stored in the original single shell tanks. Additionally, supernate wastes generated from Hanford B plant also are classified as Envelope A wastes.
- e. SRTC processed the following Hanford Tank wastes during Part A: Envelope C 241-AN107 and 241-AN102; Envelope A 241-AW101; Envelope D 241-C106; Envelope B 241-AN105. 241-AN105 is actually an Envelope A tank and was spiked with CsOH and potassium chromate so that it simulated an Envelope B sample.
- f. The equilibrium distribution coefficient (K_D) is defined as the ratio of the concentration of the ionic species on the ion exchange resin and in the solution phase.