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Revision 3

Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives

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REVISION SUMMARY

<i>Document Name</i>		<i>Unique Identifier</i>		
Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives		WSRC-RP-99-00006		
Summary of Changes				
<i>Revision Number</i>	<i>Date</i>	<i>ECF Number(s)</i>	<i>Affected Sections</i>	<i>Description of Revision</i>
0	10/99	NA	NA	Initial Issue – Decision Phase
1	10/00		All	This is a general revision. Incorporated Solvent Extraction Alternative and <u>some additional</u> R&D <u>results</u> for all alternatives. Grammatical corrections and other minor changes were made.
2	4/01	HLW-SDT-2001-00124	All	This is a general revision. An executive Summary has been added. Technical bases common to all alternatives are consolidated into a single section to eliminate duplication in sections describing alternatives. Duplicate references that appeared in Rev. 1 are eliminated. R&D results from tests resolving uncertainties without impacting bases have been retained, but results having no impact on the bases and assumptions have been deleted.
3	5/01	NA	All	This is a general revision. R&D results impacting bases and assumptions have been updated for all alternatives. Updated salt solution feed blends have been included as Appendix H.

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1.0 EXECUTIVE SUMMARY

The HLW salt waste (salt cake and supernate) now stored at the SRS must be treated to remove insoluble sludge solids and reduce the soluble concentration of radioactive cesium (^{137}Cs), radioactive strontium (^{90}Sr) and transuranic contaminants (principally Pu and Np). These treatments will enable the salt solution to be processed for disposal as saltstone, a solid low-level waste.

A Salt Waste Processing Facility has been proposed to safely treat the HLW salt waste, replacing the In-Tank Precipitation Facility (ITP). Except for safe storage of existing waste, ITP operations have been suspended because of processing uncertainties related to safe operation in its present configuration.

Three process alternatives – Small Tank Tetraphenylborate Precipitation (STTP), Crystalline Silicotitanate Ion Exchange (CSTIX) and Caustic-Side Solvent Extraction (CSSX) – continue to be developed for possible use in the proposed Salt Waste Processing Facility (SWPF) at the Savannah River Site (SRS). The revised technical bases, assumptions and results from continuing research and engineering efforts for STTP, CSTIX and CSSX processes for the proposed Salt Waste Processing Facility are provided. This revision incorporates additional Research and Development (R&D) results that impact the technical bases for the pre-conceptual design phase for each of these processes. This information has been developed to enable the Department of Energy (the DOE) to choose a preferred process for treatment and disposal of HLW salt waste presently stored at the SRS.

Continuing R&D tests are now underway using radioactive waste from the HLW tanks at the SRS. Results from these tests will be incorporated in the next revision to this document prior to the DOE selecting a preferred process alternative.

2.0 ORGANIZATION OF THIS DOCUMENT

Studies leading to the three proposed process alternatives to replace the In-Tank Precipitation Facility for processing HLW salt waste are briefly discussed in Section 3.0. The HLW System configuration prior to suspending operations of the In-Tank Precipitation Facility in 1996 is also briefly described in Section 3.0.

An overview of the proposed HLW System configuration that replaces the ITP facility with a new Salt Waste Processing Facility (SWPF) is provided in Section 4.0. The general functions and interface streams between the eight facilities that comprise the proposed HLW System configuration are discussed in this section. Key limits on influent and effluent streams for the proposed SWPF are also included; these limits define the process requirements for the proposed SWPF.

The engineering approach used to develop the three alternative processes for the SWPF are described in Section 5.0. Technical bases that are common to all three alternatives are included in this section, which are related to operations in upstream and downstream facilities, physical facilities required for the SWPF and the selection of the location for the proposed facility. Information available for operating facilities are used to describe the composition and chemistry of waste processing in the other facilities for use in process models of the HLW System that

would incorporate each of the proposed SWPF alternative processes. The composition and projected variation of the waste to be processed through the SWPF is also described.

Detailed process descriptions and technical bases for STTP, CSTIX and CSSX alternatives are described in Section 6.0. R&D results applicable to each process are included. Process modeling for each of the alternatives is also discussed. Modeling results are included to enable the alternatives to be compared.

Life Cycle Costs for each alternative are summarized in Section 7.

References are consolidated in Section 8.

3.0 INTRODUCTION

The High Level Waste (HLW) Salt Disposition Systems Engineering Team (henceforth referred to as Team) was formed on March 13, 1998, under the sponsorship of the Westinghouse Savannah River Company (WSRC) High Level Waste Vice President and General Manager. The Team is chartered to identify options, evaluate alternatives and recommend a selected alternative(s) for processing HLW salt to a permitted low-level radioactive waste form suitable for disposal at the Savannah River Site. This requirement arises because the existing In-Tank Precipitation (ITP) process, as currently configured, cannot simultaneously meet the HLW production and Authorization Basis safety requirements.

During Phase I (Identification Phase) the Team used multiple approaches to identify alternative processes to meet the production and safety requirements for salt disposition. The resulting list of approximately 140 alternatives was evaluated against a set of minimum screening criteria. The outcome of the exercise was an "initial list" of eighteen alternatives selected for further evaluation, which were grouped in categories including: Crystallization, Electrochemical Separation, Ion Exchange, Precipitation, Solvent Extraction and Vitrification.

During Phase II (Investigation Phase), the Team focused on the application of screening criteria for performance of a preliminary technical and programmatic risk assessment of the eighteen alternatives to establish a short list for detailed evaluation. As part of this assessment, the Team requested HLW Process Engineering to provide preliminary material balances, cycle times, and HLW system wide impacts for the eighteen alternatives. The results of this effort are documented in the WSRC-RP-98-00166 (Ref. 1).

During Phase III (Recommendation Phase) the Team focused on more detailed screening and risk assessment to develop a Short List of four alternatives. The engineering scope in Phase III was to evaluate the Short List alternatives in a greater level of detail to support life cycle and schedule assessment efforts. The HLW Process Engineering Team completed material balances in addition to any required energy balances. Data were obtained through additional research, literature reviews, calculations, and experiments on the selected alternatives to address some of the uncertainties and assumptions involved in Phase II. The physical components of the Phase III models, such as tanks and ion exchange columns, were defined to a greater level of detail. Equipment sizing was developed and used to develop pre-conceptual facility layouts and process flow configurations. Others used the layouts to develop life cycle cost estimates and project schedules for the facilities. The results of these efforts are documented in WSRC-RP-98-00168 (Ref. 2).

In February of 2000, the DOE accepted the WSRC recommendation to move the precipitate hydrolysis process from the DWPF Salt Cell to the SWPF for the Small Tank Tetraphenylborate Precipitation (STTP) alternative (Ref. 3). Basic data to support the acid hydrolysis process, including the precipitate washing operations previously planned for the Late Wash Facility, has already been developed in conjunction with coupled DWPF operations based on the ITP precipitate slurry product that would have been processed in the DWPF Salt Processing Cell. This information serves as part of the basis for the STTP process alternative described in Section 6.1 (Ref. 4, 5).

The DOE also requested that the work on the Caustic Side Solvent Extraction (CSSX) flowsheet be continued (Ref. 6). Additional R&D was begun to support this alternative. The original solvent extraction flowsheet has now been modified as a result of this work, and is described in Section 6.3.

The engineering scope in Phase IV (Decision Phase) focuses on the technical uncertainties for the remaining three alternatives in a greater level of detail to support a recommendation for the most technically suited alternative. Additional data obtained through continuing research, calculations and experiments on these alternatives are included to address some of the uncertainties and assumptions that remained from Phase III. HLW Process Engineering revised material balances and the Process Flow Diagrams to reflect the new technical information. The physical components of the Phase IV models, such as tanks and ion exchange columns, were resized where new experimental data indicated this was required. Equipment sizing was developed and used to evaluate proposed facility layouts developed as a part of Phase IV.

In addition, the alpha sorption operation for CST Ion Exchange (CSTIX) or Caustic Side Solvent Extraction (CSSX) alternatives has been re-configured as the result of ongoing R&D efforts and a new trade study (Ref. 7, 8, 9, 10).

3.1 Background

The High-Level Waste System consists of seven different interconnected processes (Figure 3.1-1) operated by the High Level Waste and Solid Waste Divisions. These combined processes function as a waste treatment plant that receives, stores, and treats high-level wastes at SRS and converts these wastes and byproduct streams generated during treatment into forms suitable for final disposal or release to the general environment. The three major permitted disposal forms are high-level radioactive waste borosilicate glass (HLW glass), planned for disposal at a Federal Repository; saltstone, disposed as solid low-level radioactive waste (LLW saltstone) in vaults on the SRS site; and treated water effluent, released to the environment. Any liquid organic waste generated by the system will be incinerated. Mercury metal, which is recovered and purified as part of high-level waste vitrification process in the DWPF, is presently being returned to NMSS at the SRS for reuse in fuel reprocessing. Final disposition of purified mercury metal recovered from HLW has not yet been selected by the DOE. Purified mercury will be stored at the SRS until the DOE decides on the most appropriate disposition for this material.

As originally designed, these processes include:

- 1) High-Level Waste Storage and Evaporation (F and H Area Tank Farms)
- 2) Salt Processing (In-Tank Precipitation and Late Wash Facilities)
- 3) Sludge Processing (Extended Sludge Processing Facility)
- 4) Vitrification (Defense Waste Processing Facility)

- 5) Wastewater Treatment (Effluent Treatment Facility)
- 6) Solidification (Saltstone Production and Disposal Facilities)
- 7) Organic Destruction (Consolidated Incineration Facility)

F and H Tank Farms, Extended Sludge Processing, Defense Waste Processing Facility, Effluent Treatment Facility, Saltstone Production and Disposal Facilities and the Consolidated Incineration Facility are all operational. In-Tank Precipitation Facility operations are now limited to safe storage and transfer of materials. The Late Wash Facility has been tested and is in a dry lay-up status. The In-Tank Precipitation Facility (ITP) initiated radioactive operation in Tank 48H in September of 1995. During pump operation in December of 1995, benzene evolved from Tank 48H at higher rates than expected, although the operational safety limit was never approached. The benzene was generated as a byproduct of the process from the catalytic decomposition of sodium tetraphenylborate (NaTPB).

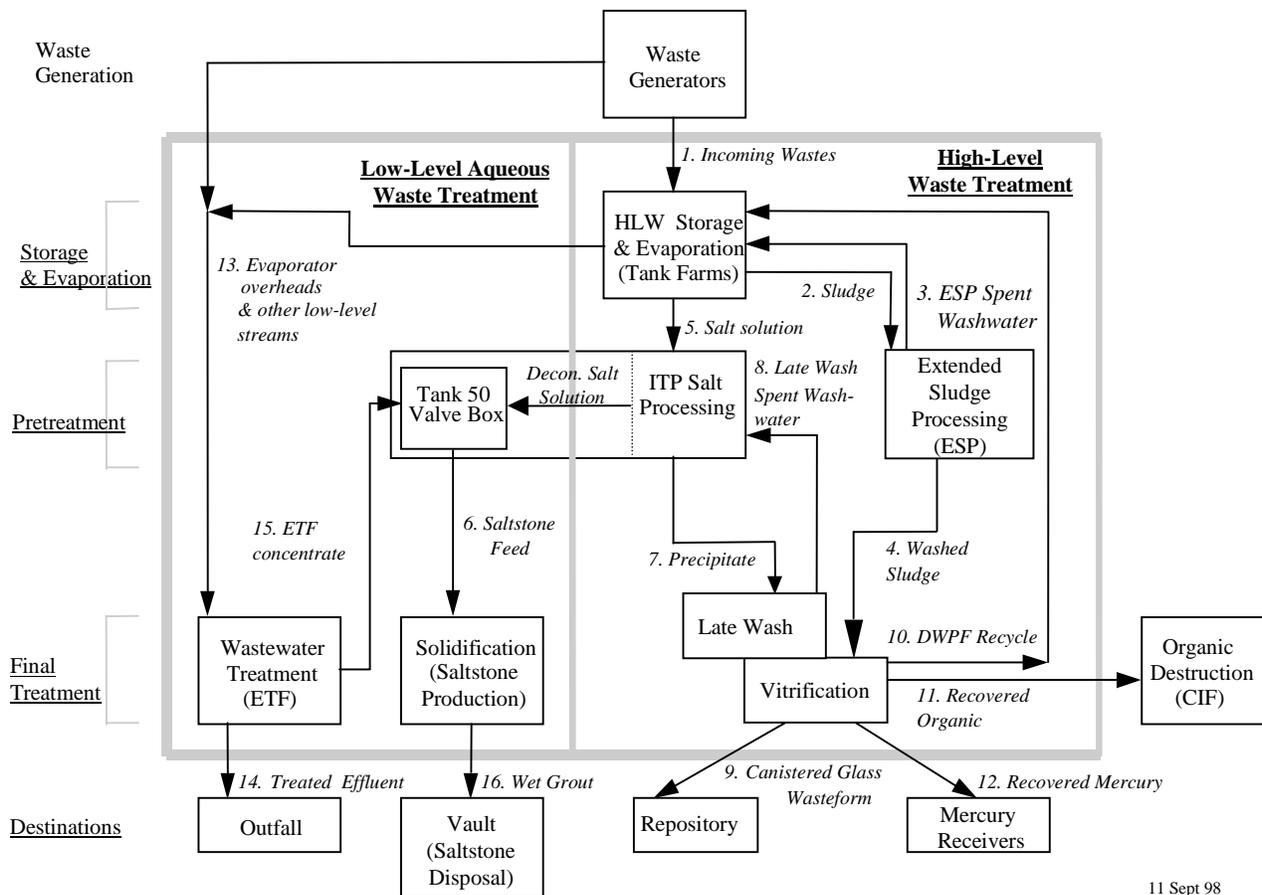


Figure 3.1-1 Major Interfaces in the Original HLW System (1995)

In August 1996, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1. The DNFSB recommended that operating and testing in the ITP Facility not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In response to Recommendation 96-1, the chemical, physical, and mechanical properties

for the large-tank ITP process were studied to understand and explain benzene generation, retention, and release. This research was done from August 1996 through March 1998.

These studies indicated that production goals and safety requirements for processing of HLW could not be met in the ITP Facility, as configured. Based on these results, WSRC recommended to the Department of Energy in January 1998 to conduct a systems evaluation of salt disposition options and to select a preferred alternative to the large-tank ITP process. The salt will remain in storage until a process is identified and implemented for the proposed Salt Waste Processing Facility.

In March 1998, a team was selected to perform a structured Systems Engineering analysis of options for salt disposition. Guidance for the Team is documented in their charter (Ref. 11). Evaluation of salt disposition is broad based in technical scope and is not limited to any single process. Precipitation methods, ion exchange processes, other chemical or mechanical separation techniques, direct vitrification options, or combinations of these options were considered.

Although the process selected will be specifically for HLW salt disposition, the Team must address the system impact on all HLW facilities. The selected alternative also must interface safely and efficiently with any processing facilities outside of the HLW System. Timely selection of an alternative is key to support tank farm space recovery, water inventory management within the HLW System and the Federal Facility Agreement (FFA) for tank closure. The FFA for SRS addresses the DOE committed schedule for removing the wastes from the tanks.

3.2 High Level Waste System Mission

The mission of the HLW System is to receive and store SRS high-level wastes in a safe and environmentally sound manner and to convert these wastes into forms suitable for final disposal. The planned forms are: 1) HLW borosilicate glass to be sent to a Federal repository, 2) LLW saltstone to be disposed of on site, and 3) treated wastewater to be released to the environment. The storage tanks and facilities used to process the high-level waste also must be left in a state such that they can be closed and decommissioned in a cost-effective manner and in accordance with applicable regulations and regulatory agreements.

The FFA requires the waste to be removed from the high-level waste tanks to resolve several safety and regulatory concerns. Some tanks have leaked observable quantities of waste from primary to secondary containment. Other tanks have known penetrations above the liquid level, although no waste has been observed to leak through these penetrations. The "old style" tanks do not meet EPA secondary containment standards for storage of hazardous waste (effective January 12, 1987).

All high-level wastes in storage at SRS are Land Disposal Restricted (LDR) wastes, which are prohibited from permanent storage or direct disposal. Since the planned processing of these wastes will require considerable time and therefore continued storage of the waste, the DOE has entered into a compliance agreement with the EPA and the South Carolina Department of Health and Environmental Control (SCDHEC). This compliance agreement is implemented through the Site Treatment Plan (STP) which requires processing of all the high-level waste at SRS according to a schedule negotiated among the parties.

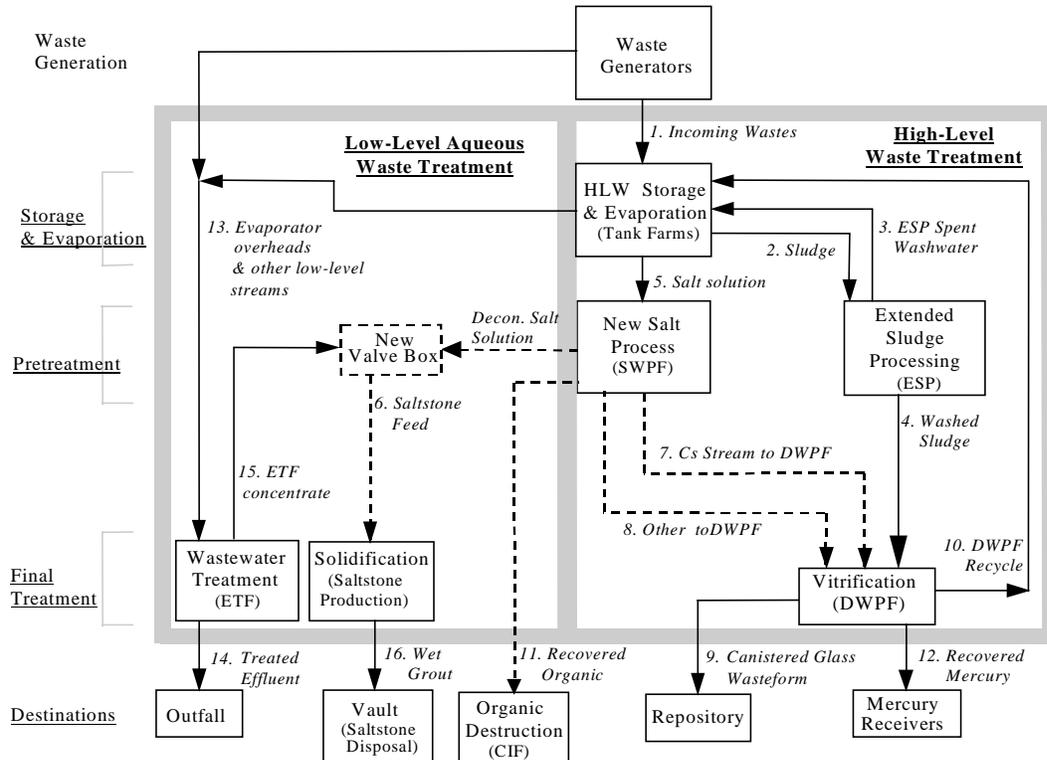
The problem confronting the HLW overall mission is that the currently configured In-Tank Precipitation process cannot simultaneously meet the HLW flowsheet production goals and the

safety requirements. The WSRC recommended that alternative concepts and technologies be evaluated. The HLW Salt Disposition Systems Engineering Team was formed and chartered to perform this task. The Mission Need defined for the Team is:

“The SRS HLW salt needs to be immobilized for final disposition in support of environmental protection, safety, and current and planned missions”.

4.0 OVERVIEW OF PROPOSED HIGH LEVEL WASTE SYSTEM

The discussion below describes the proposed HLW System configuration and interface streams with an alternative process replacing the ITP/Late Wash process shown in Figure 3.1-1. Figure 4.0-1 schematically illustrates the normal flow of wastes through this modified HLW System that incorporates a new Salt Waste Processing Facility (SWPF). The various processes within the proposed system and external processes are shown in rectangles. The numbered streams identified in *Italics* are the interface streams between the various processes. The proposed HLW system differs only in the process to be used for decontaminating salt solution. Interface streams that may change as a result of a new SWPF process are noted by dashed lines in Figure 4.0-1. Note that the Late Wash Facility has been eliminated from the proposed HLW system. Two streams will interface between the new SWPF and the DWPF, while the former interface between the DWPF and the CIF has been moved to the SWPF. An overview of the process requirements and goals, along with the three salt pretreatment (SWPF) process alternatives, are described separately in section 4.4.



January 01

Figure 4.0-1 Major Interfaces in the Proposed HLW System (2010)

4.1 Waste Receipt, Concentration and Storage

Incoming high-level wastes are received into HLW Storage and Evaporation (F and H Tank Farms) (Stream 1). The function of HLW Storage and Evaporation is to safely receive, store, and concentrate these wastes until downstream processes are available for further processing. The decontaminated aqueous liquid (overheads) from the evaporators is sent to the Effluent Treatment Facility (ETF) and combined with other aqueous LLW for treatment in the ETF (Stream 13).

4.2 Sludge Pretreatment

The insoluble sludge that settles to the bottom of waste receipt tanks in HLW Storage and Evaporation are suspended using hydraulic slurring techniques and sent to Extended Sludge Processing (ESP) (Stream 2). In ESP, sludges high in aluminum are processed to remove some of the insoluble aluminum compounds. All sludges, including those that have been processed to remove aluminum, are washed with water to reduce their soluble salt content. The spent wash water from this process is returned to the HLW Storage and Evaporation (Stream 3). Washed sludge is sent to Vitrification (DWPF) for feed pretreatment and vitrification (Stream 4).

4.3 HLW Salt Removal and Blending

Salt cake is dissolved using hydraulic slurring techniques similar to those used for sludge slurring. The salt solutions from this operation and other salt solutions from HLW Storage and Evaporation will feed the proposed SWPF (Figure 4.0-1, Stream 5). Blending of waste from different tanks must be controlled during salt waste removal to assure soluble alpha concentration in the feed stream is within the capabilities of the SWPF process for alpha removal. Key alpha emitters controlling the degree of blending are ^{238}Pu and ^{237}Np .

In the waste removal study conducted during Phase III (Ref. 2), the highest Hg concentration projected for the annual blends was approximately 50 mg/L, which is well within the EPA LDR restriction of 260 mg/L that requires separate treatment to remove and recover mercury. Accordingly, Hg removal by ion exchange has been removed from the CSTIX and CSSX alternatives, based on the assumption that blending during waste removal will be controlled to yield salt solution feed to the SWPF (Stream 5) containing mercury at a concentration less than 250 mg/L. Mercury concentration in salt solution feed must be monitored and controlled for the CSTIX and CSSX alternatives to assure the mercury concentration is within the mercury limit (250 mg/L) specified in the Waste Acceptance Criteria for saltstone production in the Saltstone Production Facility (SPF). (Ref. 12)

Mercury is not an issue with the STTP alternative, since this process precipitates soluble mercury as diphenyl mercury and reduces the soluble concentration well below the concentration of 250 mg/L that would prevent processing of decontaminated salt solution (DSS) into saltstone for disposal.

4.4 Salt Waste Processing Facility (SWPF)

The proposed Salt Waste Processing Facility (SWPF) will replace the Large Tank ITP and Late Wash processing facilities in the existing HLW system (compare Figure 3.1-1 and Figure 4.0-1). Functionally, the SWPF will process HLW salt solution to remove entrained sludge and reduce the concentration of key soluble radionuclides (i.e., Cs, Sr and alpha contamination). This

treatment will enable on-site processing and disposal of decontaminated salt solution (DSS) (Stream 6) in the form of saltstone, a solid Low-Level Waste (LLW).

Note that spent wash water was formerly designated as interface Stream 8 between the Late Wash Facility and ITP, as shown on Figure 3.1-1. Spent wash water will be internally recycled within the proposed SWPF, and has been eliminated as an interface stream for the proposed HLW System shown in Figure 4.0-1. Stream 8 is now designated as an interface stream between the SWPF and the DWPF.

Stream 11, the interface stream between DWPF and CIF in the previous system configuration shown in Figure 3.1-1, has been moved to interface between the SWPF and the CIF for the two alternatives that would generate an organic waste stream in the proposed SWPF (STTP and CSSX).

Radioactive and/or chemical contaminants removed from the HLW salt solution in the SWPF will be diverted to the DWPF (in either Stream 7 or Stream 8) for further treatment and eventual disposal as components of HLW glass. Organic wastes (Stream 11) will be sent to the CIF for destruction. The bulk of the soluble salts now stored in the HLW tanks will flow through the SWPF unchanged and then will be transferred to the SPF for treatment and disposal as LLW saltstone.

The actual compositions of the interface streams between the SWPF and any of the downstream facilities will depend on which of the three proposed process alternatives is chosen. Process requirements and goals for the SWPF that will assure interface streams are acceptable for transfer to other facilities are described in section 4.4.1, below. The three proposed SWPF alternative processes are discussed briefly below (Sections 4.4.2 through 4.4.4) and also in greater detail in Section 6.0.

4.4.1 SWPF Process Requirements and Goals

Key process requirements for the proposed SWPF are:

- Safely process HLW soluble waste in a manner that complies with all applicable regulatory requirements;
- Support the schedule for emptying and closing all Type I, II and IV waste tanks as described in the FFA; and
- Assure all liquid and solid waste generated in the SWPF can be processed successfully and packaged in downstream facilities to yield acceptable waste forms suitable for final disposal.

A primary goal for the SWPF process is to minimize the impact on the Authorization Basis, Operating Permits and demonstrated processes of all downstream treatment and disposal facilities, particularly the Saltstone Production Facility (SPF) and the Saltstone Disposal Facility (SDF), since a major effluent stream from the SWPF is decontaminated salt solution (DSS) that will be transferred to the SPF.

Decontaminated salt solution (DSS) will be generated within the SWPF for subsequent treatment and disposal as saltstone. The DSS (Stream 6) will be transferred to the Saltstone Production Facility (SPF) for treatment and subsequent disposal in vaults located in the Saltstone Disposal Facility (SDF). The SDF is a near surface, non-hazardous industrial waste landfill located at the SRS. Limits and process goal concentrations for key contaminants are summarized below. Limits

specified in the Waste Acceptance Criteria (WAC) for the SPF account for the mass of dry materials added to yield solid saltstone within the required limits for disposal as solid LLW.

4.4.1.1 ¹³⁷Cesium

Radioactive cesium (¹³⁷Cs) is the principal gamma-emitting contaminant in HLW salt solution. As a basis for comparison of alternatives, the preliminary concentration ratio in feed to the SWPF is 0.2 Ci of ¹³⁷Cs per mole of sodium. At an assumed nominal concentration of 6.44 M sodium in feed from the HLW Tank Farm, this ratio corresponds to a maximum ¹³⁷Cs concentration of 1.3 Ci/L (5 Ci/gal). In the SWPF, ¹³⁷Cs concentration must be reduced to enable subsequent processing and disposal as saltstone, a LLW solid waste form.

In the current SPF AB, the ¹³⁷Cs concentration limit specified for DSS to be transferred to the SPF is 100 nCi/g. The current SPF WAC limits ¹³⁷Cs to 45 nCi/g (about 0.00006 Ci/L or 0.00047 Ci/gal, based on a projected solution density of about 1.25 Kg/L). The WAC limit is a factor of about 20 below a DSS concentration that would yield saltstone within the NRC Class A limit for ¹³⁷Cs. This lower concentration ¹³⁷Cs limit is specified to provide radiation protection for facility workers because the existing SPF and SDF are designed for contact maintenance. Because other gamma emitters may also be present in the DSS, the Cs-removal process goal for the three proposed SWPF alternatives is to yield decontaminated salt solution containing ¹³⁷Cs at a concentration less than 40 nCi/g (< 0.000050 Ci/L or < 0.00019 Ci/gal) to assure adequate radiation protection for facility workers (see Table 5.3.4).

4.4.1.2 ⁹⁰Strontium

In the current SPF AB and the SPF WAC, the ⁹⁰Sr concentration limit specified for DSS to be transferred to the SPF is 40 nCi/g (about 0.000050 Ci/L or 0.00019 Ci/gal, based on a projected solution density of about 1.25 Kg/L). The AB (and WAC) limit is set slightly below the concentration that would yield saltstone within the NRC Class A waste disposal limit for ⁹⁰Sr. The Sr-removal process goal for the three proposed SWPF alternatives is to yield DSS containing < 40 nCi/g to assure that the overall average concentration for all waste placed within the SDF is within the NRC Class A limit for ⁹⁰Sr (see Table 5.3.4).

4.4.1.3 Total Alpha

In the current SPF AB, the AB limit is set at 50 nCi/g, the maximum limit that assures the SPF is classified as no greater than a Category 3 nuclear facility, as defined in DOE guidance for compliance with DOE Orders related to operational safety. (Ref. 13) This total alpha limit also assures saltstone will not be classified as TRU waste, which would require packaging and transfer offsite.

In the current SPF WAC, the total alpha concentration limit specified for DSS to be transferred to the SPF is < 18 nCi/g (about 0.000023 Ci/L or 0.000085 Ci/gal, based on a projected solution density of about 1.25 Kg/L). The WAC limit is set at the alpha concentration that would yield saltstone within the NRC Class A waste disposal limit of 10 nCi/g for alpha contamination after accounting for the mass of dry materials added to produce saltstone grout. The Alpha-removal process goal for the three proposed SWPF alternatives is to yield DSS containing < 18 nCi/g to assure that the overall average concentration for all waste placed within the SDF is within the NRC Class A limit for Alpha contamination (see Table 5.3.4).

4.4.1.4 ^{237}Np

In the current SPF WAC, the ^{237}Np concentration limit specified for DSS to be transferred to the SPF is 0.03 nCi/g (about 38 nCi/L or 140 nCi/gal, based on a projected solution density of about 1.25 Kg/L). The WAC limit is set at the ^{237}Np concentration limit that would yield a maximum ^{237}Np groundwater concentration within drinking water standards at the compliance monitoring well near the landfill. This limit is based on the projected long-term performance assessment for the SDF (Ref. 14) and conservatively assumes neptunium leaches from saltstone in the landfill similarly to nitrate. The ^{237}Np -removal process goal for the three proposed SWPF alternatives is to yield DSS containing < 0.03 nCi/g to assure that the overall average concentration for all waste placed within the SDF is within the limit that will assure groundwater specifications for alpha contamination are met (see Table 5.3.4).

4.4.1.5 Mercury and Chromium

Of the hazardous metals identified as being present in HLW soluble waste, only chromium and mercury are present in significant concentrations. Mercury is also subject to a special Land Disposal Restriction (LDR) of 260 mg/L. If mercury exceeds the LDR limit in a liquid waste, the waste must be processed to remove and recover the mercury before the waste can be transferred for further processing and disposal.

Solid waste containing non-radioactive hazardous metal contaminants must pass the Toxicity Characteristic Leaching Procedure protocol (TCLP), as defined by the Environmental Protection Agency, before it can be disposed in a near-surface solid waste landfill. Saltstone produced in the SPF must be periodically tested using the TCLP protocol, and results must be reported to SCDHEC to demonstrate non-hazardous classification of saltstone produced for disposal.

Limits for several hazardous metals have been established for DSS, based on TCLP testing of saltstone. Based on TCLP testing of saltstone, DSS containing up to ~3000 mg/L of chromium and up to ~1000 mg/L of mercury yields non-hazardous saltstone, as defined by the EPA regulations. In the current SPF AB and the SPF WAC, the chromium concentration limit specified for DSS is 1100 mg/L. The mercury concentration limit specified for DSS is 250 mg/L to assure a LDR is not imposed on the SPF or SDF operations (see Table 5.3.5).

4.4.1.6 Organics

In the current SPF WAC, limits are specified for organics to assure the vapor composition within the Salt Solution Hold Tank in the SPF remains below the Composite Lower Flammability Limit (See Table 5.3-5). Limits are specified for benzene (< 3 mg/L), phenol (< 1000 mg/L), butanol + isopropanol (3000 mg/L), methanol (< 300 mg/L), other volatile organics (< 20 mg/L). Limits have also been established for tetraphenylborate (< 16,000 mg/L), which could decompose to yield benzene, and tributylphosphate (< 400 mg/L), which could decompose to yield butanol.

Methanol and isopropanol are components of the MST slurry used in all of the proposed SWPF alternatives. Tributylphosphate and butanol are known components of the HLW from its use in Canyon processes at the SRS and could also be present for all of the proposed alternatives.

Benzene, phenol and tetraphenylborate would be present in decontaminated salt solution if the STTP alternative is selected.

Iso-ParTM L, classified as “other volatile organics”, would be present in decontaminated salt solution if the CSSX alternative is selected.

4.4.1.7 Soluble Salts

Non-radioactive salt contaminants in DSS are required to be monitored and reported by the operating permits issued by SCDHEC, but no specific concentration limit is imposed by either the SPF process requirements or operating permits. However, full-scale production of saltstone grout using salt solution at a molarity less than 3.5 M sodium or greater than 6.0 M sodium has not been demonstrated.

4.4.1.8 SPF Temperature Limits

To assure acceptable physical properties and resistance to leaching, saltstone must be cured at a temperature less than 90 °C. To assure that this temperature is not exceeded during the curing of the large saltstone monolith placed in a SDF vault, a temperature limit of < 45 °C is imposed on any salt solution transferred to the SPF for treatment and disposal as saltstone. When SWPF operations begin, each day's disposal operation will also rotate among 4 to 6 separate disposal cells within an SDF disposal vault to assure saltstone grout does not exceed 90 °C during curing.

4.4.2 Small Tank Tetraphenylborate Precipitation (STTP) Alternative

In the proposed continuous STTP process, HLW salt solution is treated in Stirred Tank Reactors with a solution of sodium tetraphenylborate to precipitate cesium, potassium and mercury. A slurry of monosodium titanate is added at the same time to sorb soluble strontium and alpha contaminants. The resulting organic precipitate slurry is then concentrated by filtration. Filtration also removes any entrained sludge solids present in the salt solution received in the SWPF. The decontaminated salt solution (filtrate) is sent to interim storage within the SWPF. After confirming that the DSS is within the limits of the Waste Acceptance Criteria specified for saltstone production (Ref. 12) (see Tables 5.3-4 and 5.3-5 for the WAC limits), it is sent to the SPF (Stream 6).

The concentrated precipitate slurry is washed with water to remove soluble salts, specifically nitrite, which may react with TPB during hydrolysis to generate undesirable nitroaromatic compounds. Spent wash water is internally recycled within the SWPF. The washed precipitate slurry is then catalytically decomposed and separated into four streams:

- a Precipitate Hydrolysis Aqueous (PHA) slurry stream containing the radionuclides and residual insoluble solids (sludge/MST solids) removed from the salt solution during initial treatment and subsequent filtration,
- aqueous condensate that is recycled and used to dilute HLW salt solution feed,
- a mercury metal stream that is accumulated in the SWPF, and
- a mildly contaminated organic stream (principally benzene).

The PHA is stored in the SWPF until it can be transferred to the DWPF for further processing (Stream 7). The mercury metal generated in the SWPF acid hydrolysis vessels is retained until sufficient mercury has accumulated to enable removal, packaging and transfer to the DWPF mercury cell for further processing (Stream 8). The mildly contaminated organic stream is stored at the SWPF until it can be transferred to the Consolidated Incineration Facility (CIF) and burned (Stream 11).

4.4.3 Crystalline Silicotitanate Ion Exchange (CSTIX) Alternative

In the proposed CSTIX process, HLW salt solution (Stream 5) is first treated with a slurry of monosodium titanate to sorb soluble strontium and alpha contaminants in a batch operation within the SWPF. After sorption is complete, the resulting slurry is concentrated by filtration. This filtration also removes any entrained sludge solids present in the salt solution received in the SWPF. Insoluble solids must be removed to minimize the potential for plugging downstream ion-exchange columns. The concentrated MST/sludge slurry from Alpha Sorption filtration is washed with water to remove soluble salts; spent wash water is internally recycled within the SWPF to the Alpha Sorption Tank. The washed MST/sludge slurry is stored in the SWPF until it can be transferred to the DWPF as a separate stream for further processing (Stream 8).

The clarified salt solution (filtrate) from alpha sorption is continuously processed through ion exchange columns loaded with CST resin to remove Cs. Decontaminated salt solution (DSS) from ion exchange is sent to interim storage within the SWPF. After confirming that the DSS is within the limits of the SPF WAC (see Tables 5.3-4 and 5.3-5), it is sent to the Saltstone Production Facility (Stream 6) for further treatment and disposal. As noted in Section 4.3, soluble mercury in the feed to the SWPF passes through the CSTIX process and remains in the decontaminated salt solution sent to the SPF.

Four columns are provided (3 active; 1 in standby mode) to minimize interruption of the continuous ion exchange operation when resin in the lead column is loaded with Cs. After the CST resin in the lead column is loaded with Cs, it is taken off-line and the standby column placed into service. The Cs-loaded resin in the off-line column is first washed with caustic, then with water and finally slurried with water to remove the resin from the column. The resulting spent resin slurry is stored in the SWPF until it can be transferred to the DWPF (Stream 7). The empty IX column is then reloaded with fresh CST resin that has been conditioned with caustic to assure it is in the sodium form.

Spent wash water and spent caustic solution from spent resin washing and fresh resin conditioning are internally recycled in the SWPF by combining them with untreated salt solution in the Alpha Sorption Tank.

Except for trace levels of methanol and isopropanol that are components of the MST slurry used in Alpha Sorption, organic liquids are neither used nor generated in the CSTIX process. The organic storage tank and transfer line to CIF are not needed for CSTIX (i.e., Interface Stream 11 shown on Figure 4.0-1 would not exist for the CSTIX process alternative).

4.4.4 Caustic Side Solvent Extraction (CSSX) Alternative

In the proposed CSSX process, the salt solution (Stream 5) is first treated with a slurry of monosodium titanate to sorb soluble strontium and alpha contaminants in a batch operation within the SWPF. After sorption is complete, the resulting slurry is concentrated by filtration. This filtration also removes any entrained sludge solids present in the salt solution received in the SWPF. Insoluble solids must be removed to minimize the potential for process upsets in subsequent solvent extraction operations due to the presence of three phases (liquid organic, liquid aqueous, insoluble solids).

The concentrated MST/sludge slurry from Alpha Sorption filtration is washed with water to remove soluble salts. Spent wash water is internally recycled within the SWPF to the Alpha

Sorption Tank. The washed MST/sludge slurry is stored in the SWPF until it can be transferred to the DWPF as a separate stream for further processing (Stream 8).

The clarified salt solution (filtrate) from alpha sorption is sent through a solvent extraction process that uses a calixarene complexing agent dissolved in an organic alkane solvent to yield an organic phase containing cesium and an aqueous salt solution essentially free of Cs, Sr and alpha contaminants.

The Cs-loaded organic phase from the extraction cycle is contacted with dilute nitric acid (0.05 M) to remove residual salts (Na, Al, K) that may have been retained. Spent aqueous scrub solution from this operation is combined with the aqueous salt solution from Cs extraction to yield decontaminated salt solution.

The resulting decontaminated salt solution from the combined aqueous streams from extraction and scrubbing operations is stored in the SWPF until it is confirmed to be within the limits of the SPF WAC (see Tables 5.3-4 and 5.3-5). It is then sent to the Saltstone Production Facility (Stream 6) for further treatment and disposal as saltstone. As noted in Section 4.3, soluble mercury salts in the feed to the SWPF passes through the CSSX process and remains in the decontaminated salt solution sent to the SPF.

The washed organic phase from the washing cycle is then contacted with very dilute nitric acid solution (0.001 M) in a stripping extraction cycle to yield an aqueous solution of weakly acidic cesium nitrate and stripped organic solvent. The cesium nitrate solution from the stripping extraction cycle is stored within the SWPF until it can be transferred to the DWPF for further processing (Stream 7). The stripped organic solvent containing calixarene is adjusted as needed and then recycled to the solvent extraction banks.

Liquid organic waste streams from calixarene recovery, solvent cleaning, solvent adjustment or solvent replacement are combined and stored within the SWPF until the combined liquid organic stream can be transferred to the CIF for destruction (Stream 11).

4.5 Vitrification (DWPF)

The aqueous cesium-containing product stream from the SWPF (Stream 7 = PHA slurry from STTP, CST resin slurry from CSTIX or acidic cesium nitrate solution from CSSX) is combined with the washed sludge from ESP (Stream 4) in the DWPF SRAT. The MST/sludge slurry from alpha removal in the SWPF (Stream 8 for the CSTIX or the CSSX alternatives) is also added to the SRAT.

The resulting blend of ESP sludge and SWPF input streams is chemically adjusted in the SRAT to prepare the sludge for feed to the glass melter. As part of this process, mercury is stripped from the sludge slurry, collected, purified and sent to mercury receivers (Stream 12). Mercury collected in the SWPF in the STTP alternative (Stream 8 for the STTP alternative) will also be transferred periodically to the DWPF and combined with mercury stripped from sludge.

The adjusted sludge mixture is then transferred to the DWPF SME and combined with glass frit. The resulting slurry is then sent to the glass melter. The glass melter drives off the water and melts the solids into a borosilicate glass matrix, which is poured into a canister. The canisters of glass waste are sealed, sent to site interim storage, and will eventually be shipped to a Federal repository for disposal (Stream 9).

The water vapor driven from the melter is condensed and combined with other aqueous streams generated throughout the DWPF Vitrification Building. This aqueous waste is treated with caustic and sodium nitrite before it is recycled to HLW Storage and Evaporation for storage and processing (Stream 10).

4.6 Effluent Treatment Facility

Overheads from the HLW Storage and Evaporation evaporators are combined with overheads from evaporators in the F and H Area Separations processes and other low-level streams from various waste generators. This mixture of low-level wastes is sent to the ETF (Stream 13). In the ETF, these low-level wastes are decontaminated by a series of cleaning processes, including clarification, reverse osmosis and evaporation.

The decontaminated water effluent is sent to the H Area outfall and eventually flows to local creeks and the Savannah River (Stream 14).

The contaminants removed in the ETF are concentrated in an aqueous solution, treated with caustic and stored until the solution can be sent to the SPF for conversion into saltstone (Stream 15). After confirming that the solution is within the limits of the WAC specified for saltstone production (See Tables 5.3-4 and 5.3-5), it is sent to Saltstone Production Facility. This concentrate from the ETF can be combined with the decontaminated salt solution from the SWPF or processed separately. ETF concentrate thus represents a portion of Stream 6 after the SWPF is operational. Aqueous overheads from ETF evaporation are internally recycled through reverse osmosis before releasing them to the environment.

4.7 Saltstone Production and Disposal Facilities

In the Saltstone Production Facility (SPF), the liquid wastes from the SWPF and/or the ETF are combined with cement formers and pumped as a wet grout to a vault in the Saltstone Disposal Facility (SDF) (Stream 16). In the vault, the cement formers hydrate and cure, forming a solid saltstone monolith. The Saltstone Disposal Facility vaults will eventually be closed as an industrial waste landfill, in accord with applicable SCDHEC regulations. WAC limits for the SPF are discussed above, in the context of SWPF requirements and process goals. The SPF process is also discussed in detail in Section 5.3.1.3. If the WAC limits are met, then the long-term performance criteria for the SDF will also be met.

NOTE: When the ITP process was found to be incompatible with safety and production goals using the present plant configuration, the need to keep the SPF and SDF in operational readiness to periodically process salt solution generated by ETF could not be economically justified. After processing the available decontaminated waste inventory in Tank 50, the SPF and SDF were placed in lay-up in 1999. These two facilities may operate intermittently to support continuing operation of ETF until the proposed Salt Waste Processing Facility (SWPF) is constructed and is operational.

4.8 Consolidated Incinerator Facility

In the Consolidated Incinerator Facility (CIF), liquid organic waste from the SWPF is combined with fuel oil and fed to the incinerator as fuel. Non-volatile contaminants are collected as ash and combined with water and cement formers in a container. The resulting grout is allowed to set, and then the solidified waste is stored until it can be transferred to an appropriate disposal site, as dictated by the radioactive contaminants in the solid waste form [SRS burial ground for LLW;

Waste Isolation Pilot Plant (WIPP) for TRU]. The CIF limits the total gamma activity in organic waste to < 0.5 nCi/ml (< 1000 dpm/ml).

NOTE: Benzene waste from processing precipitate slurry in the DWPF is not being generated at this time. Since the benzene was a significant waste stream to be sent to the CIF, continuing operation of CIF has been evaluated recently. In September of 2000, CIF was placed in layup. The SCDHEC has requested the DOE to decide by 2002 on whether the CIF will ever resume operations. However, the DOE projects this decision will likely not be made before 2004, after various commercial treatment alternatives have been evaluated (Ref. 15). Should the DOE decide not to resume CIF operations, other disposal methods would be needed for organic waste generated for either the proposed STTP alternative (Section 4.4.2) or the proposed CSSX alternative (Section 4.4.4) described above.

5.0 ENGINEERING APPROACH

The flowsheets for Phase III were initially developed from the basis established by the Phase II modeling efforts. The Phase III model results were used to produce equipment lists, equipment sizes, and building layout requirements. These equipment lists, sizing and building layout information were used to estimate the construction, startup, and operations costs for each shortlist alternative.

The mass balances for determining expected flowsheet performance have incorporated additional data from research efforts during the Decision Phase to confirm or disposition uncertainties and eliminate assumptions defined in Phase III, as that data became available. The physical components of the Decision Phase models, such as tanks and ion exchange columns, are defined to a greater level of detail. Actual dimensions based on existing equipment characteristics and thermodynamic values were considered in the development of the models.

The additional experimental data, as defined in the Decision Phase scope of work (Ref. 16), was developed at the Savannah River Technology Center (SRTC) and Oak Ridge National Laboratory (ORNL).

The models, developed in the Decision Phase, describe the alternative processes mathematically by way of algebraic and differential equations used to represent system components and performance. The models were developed from consistent bases, assumptions, and constraints with as many common unit operations as possible. Engineering calculations and the SPEEDUP™ flowsheet environment were used to execute the models and generate the performance results and material balances for the alternatives.

5.1 Work Scope Planning, Management, Application, and Control

For the Decision phase of the Salt Disposition effort, a scope of work matrix was developed and distributed by the Salt Waste Processing Program. The matrix was used to identify specific work activities for HLW Process Engineering, Research and Development, and Safety Management support organizations. This matrix laid the foundation for evaluating the various areas of engineering, research and development, and safety management as they apply to the confirmation or disposition of technical uncertainties from the previous phases.

Through the use of “Road Mapping”, a logical and consistent plan of action was applied to the work scope for each alternative. A work scope matrix reflecting integrated commitments was developed to manage outstanding items, work activities, deliverables, and plans. The completed version of the work scope matrix is shown in Reference 16.

The work scope matrix identifies the references; commitment items; considerations used by the Team during the evaluation; and a recommended path forward that identifies resources, timing, scope, deliverables, and the responsible organization.

In May 2000, the DOE assigned the Research and Development activities including implementation of scope, schedule and budget changes to the Tank Focus Area (TFA) (Ref. 3). In addition the day-to-day management and integration of R&D activities is now managed by the TFA. The TFA developed a R&D plan that incorporated the previous roadmaps and additional scope identified by the TFA team. This plan is contained in Reference 17.

5.2 Engineering Development of Process Alternatives

During Phase III process flow diagrams (PFDs) and facility layout specifications were developed based on the existing knowledge of the chemistry for the various processes. During the Decision Phase and Demonstration Phase additional research has been completed to reduce the uncertainties in various areas of the flowsheets for the three remaining alternatives. The results of this experimental work have been evaluated to determine their impact on the PFDs and Facility Layouts. The PFDs and Layouts were updated to incorporate the necessary modifications resulting from the new process knowledge gleaned from the R&D program.

5.2.1 Process Flow Diagram (PFD) Development

The PFDs have been updated to incorporate results from recent research and trade studies conducted as a part of the Decision Phase. The material balances shown on the PFDs are based on average tank farm salt solution. The PFDs for all three alternatives have been updated to reflect an SWPF startup date of March 2010. The PFDs are shown in Appendix A for CST Non-Elutable Ion Exchange, Appendix C for Small Tank Tetraphenylborate Precipitation with Precipitate Hydrolysis, and Appendix E for Caustic Side Solvent Extraction.

The appended PFDs reflect the stage of development as of the date of issue of the latest revision to this document. They are provided for information and completeness. However, the revisions shown in this document should be considered as “information only” for general comparison of the proposed alternatives at the time of this revision. The PFDs are maintained separately and subject to change as additional information becomes available from continuing studies. Before beginning a detailed review of the PFDs in the Appendices, they should be verified to be the latest versions.

5.2.2 Facility Layout Development

The Facility Layouts are based on the unit operations required to complete the necessary decontamination of the salt feed. These layouts have been updated to incorporate the necessary changes made to the PFDs as a result of the Decision Phase research program. The revised Facility Layouts are shown in Appendix B for CST Non-Elutable Ion Exchange, Appendix D for Small Tank Tetraphenylborate Precipitation with Precipitate Hydrolysis, and Appendix F for Caustic Side Solvent Extraction. These layouts reflect the stage of development as of the date of issue of this document. They are provided for information and completeness. However, the revisions shown in this document should be considered as “information only” for general comparison of the proposed alternatives at the time of this revision. The Facility Layouts are maintained separately and subject to change as additional information becomes available from continuing studies. Before beginning a detailed review of the layouts in the Appendices, they should be verified to be the latest versions.

5.2.2.1 Process Building

The process building is constructed of reinforced concrete and contains heavily shielded processing cells and maintenance areas partially below grade. The building is patterned after the SRS DWPF process building. Adjacent operating areas are at grade.

The shielded process cells are lined with stainless steel, and contain storage and processing tanks along with related components, including agitators, transfer and sample pumps, and sumps with

leak detection and leakage collection capability. The process cells are protected by concrete cell covers. In-cell tanks and components are designed for remote maintenance, replacement, and later decommissioning. Interconnections between process tanks are accomplished through the use of jumpers that can be installed and replaced remotely. An overhead bridge crane is provided to remove cell covers for access, to facilitate jumper changes and to install, remove or replace equipment for maintenance. Process cell widths are set by the diameter of the largest vessel within the cells.

Shielded maintenance areas are provided for remote equipment laydown, remote equipment decontamination, and bridge crane maintenance. The building configuration is designed to permit crane access to all shielded process, maintenance and sampling areas.

The building footprint for Caustic Side Solvent Extraction and CST Non-Elutable Ion Exchange is driven by the need for large alpha sorption tanks and decontaminated salt solution tanks (DSS tanks are required for all three alternatives) to ensure a daily processing rate of 25,000 gallons per day. The Alpha Sorption batch tanks are sized to decouple the continuous flow filtration and cesium removal processes from the tank farm batch flows and ensure the capability to process the expected annual transfer capacity of 6,000,000 gallons from the Tank Farms. Sizing of other process tanks was based on the type of process, a nominal 17.5 gpm salt solution feed flow rate into the SWPF and the capacity necessary to support the daily process flow.

The operating area extends around the perimeter of the process cells and contains chemical feed pumps and tanks, process support laboratories for testing samples, electrical equipment, mechanical equipment, HVAC areas, a shielded filter-backpulse chamber area, a truck unloading area, a maintenance area and decontamination areas.

5.2.2.2 Service Building

A standard commercial office building design is assumed for the service building in each option. This building contains the control rooms (Process, Crane, and Supervising), maintenance shops (Mechanical, Manipulator Repair, Electrical and Instrumentation), direct supervision offices, and change rooms.

5.2.2.3 Office Building

A standard commercial office building for support personnel (approximately 100 people) is assumed for each option.

5.2.2.4 Site Selection

A proposed site has been selected for the Salt Waste Processing Facility (SWPF). It is within the existing S-Area, ~600 feet ENE of 511-S Low Point Pump Pit Building and approximately 800 feet SE of the 221-S Vitrification Building (Ref. 18). See the plot plan in Appendix G.

Facility Site Selection is a formally documented process (Ref. 19), which seeks to optimize siting of facilities with respect to facility-specific engineering requirements, sensitive environmental resources and applicable regulatory requirements.

Siting of the SWPF was constrained to be within 2000 feet of either the Low Point Pump Pit or the Vitrification Building, since Precipitate slurry, MST/sludge slurry or CST loaded resin slurry could not be pumped much farther than that distance using existing technology unless an additional pump station is installed. This limitation and other factors that could preclude or delay

construction, limit the location of the facility to a large area between S and H Areas and includes parts of each. Thirteen sites large enough for the facility were identified. Four leading candidates were selected from these.

The four candidate sites were scored using weighted criteria for ecological, human health, geoscience and engineering impacts. The two highest scoring sites were selected for further geotechnical characterization, but one of them was found to interfere with a proposed expansion to an existing facility and may intrude partially into a known waste site.

The remaining site's geotechnical characterization indicates that it has suitable topography, is free of surface hydrology or floodplain issues and has no significant groundwater contamination. There are no known geophysical faults effecting this location. There are minor soft zones along one boundary, but there is no need to build heavy structures with deep foundations in that small part of the site (Ref. 20).

5.2.2.5 Feed Material from the HLW Tank Farm to the SWPF

Soluble HLW waste will be pumped to a HLW tank for blending and staging. The salt solution will be sampled and qualified either prior to being pumped to the staging tank or while in the staging tank. After the salt solution is qualified for transfer, it will be transferred to the new Salt Waste Processing Facility (SWPF).

The HLW salt solution (i.e., the HLW feed) will be pumped to the new SWPF via an existing HLW transfer line which now goes from the In-Tank Precipitation (ITP) facilities via the Late Wash Facility (LW) toward the Low Point Pump Pit (LPPP). This line will require new tie-ins at ITP and between the LW facility and the LPPP to provide feed to the SWPF. A section of new transfer line will be needed to connect this existing transfer line to the new SWPF. The tie-in for this new line will be near the LPPP. The new transfer line will run about 550 feet to the SWPF.

5.2.2.6 DSS from the SWPF and ETF Evaporator Bottoms to the SPF

For all three alternatives, the Decontaminated Salt Solution (DSS) from the SWPF will be transferred to the SPF via a new transfer line which runs about 300 feet to a new valve box. This new valve box will be connected to the existing line from Tank 50 to the Salt Solution Hold Tank (SSHT) located in the SPF. This tie-in will be between the SSHT and the Low Point Drain Tank (LPDT). The LPDT provides a place to drain the line leading to the SPF, and it will retain this function. The new valve box and transfer line from the SPF to the LPDT are common to the transfer line layouts for each alternative (Fig. 5.2-1, 5.2-2, 5.2-3).

The ETF Evaporator Bottoms from the SRS Effluent Treatment Facility (ETF) are currently routed to the SPF via Tank 50. This route will be retained for the immediate future. Eventually, the ETF evaporator bottoms will be transferred to a new 50,000-gallon (or larger) ETF Bottoms Tank (Ref. 21). The new ETF Bottoms Tank will hold approximately 4-5 months of ETF evaporator bottoms based on current production rates. The ETF evaporator bottoms can either be campaigned through the SPF while a new salt solution batch is being sampled and qualified or combined with feed from the SWPF. The location for the new ETF Bottoms Tank has not been selected, and its construction is integrated into the SWPF project.

5.2.2.7 SWPF Product Streams to the DWPF and CIF

The SWPF product streams containing the radioactive contaminants removed from salt solution differs for each of the three alternatives.

STTP Alternative

The MST treatment is performed concurrently with the precipitation step in the STTP alternative. The single product slurry from precipitation is washed to reduce the sodium content, and then sent forward to the acid hydrolysis operation that is also located in the SWPF. Hydrolysis of the TPB salts generates a decontaminated organic stream (principally benzene) and a Precipitate Hydrolysis Aqueous (PHA) product stream containing the radioactive contaminants removed from the salt solution in the SWPF.

Diphenylmercury also precipitates during the STTP precipitation step, removing mercury from the salt solution. During the hydrolysis operation, diphenyl mercury is reduced to mercury metal, which accumulates in the hydrolysis reactor or the decanter associated with the reactor. The accumulated mercury would be periodically removed from the STTP process vessels, packaged for transport and sent to the DWPF by truck for processing with mercury recovered from DWPF processing. Because of the small volume of mercury generated, a separate transfer line is not needed. Mercury is not shown as an SWPF outlet stream on Figure 5.2-1.

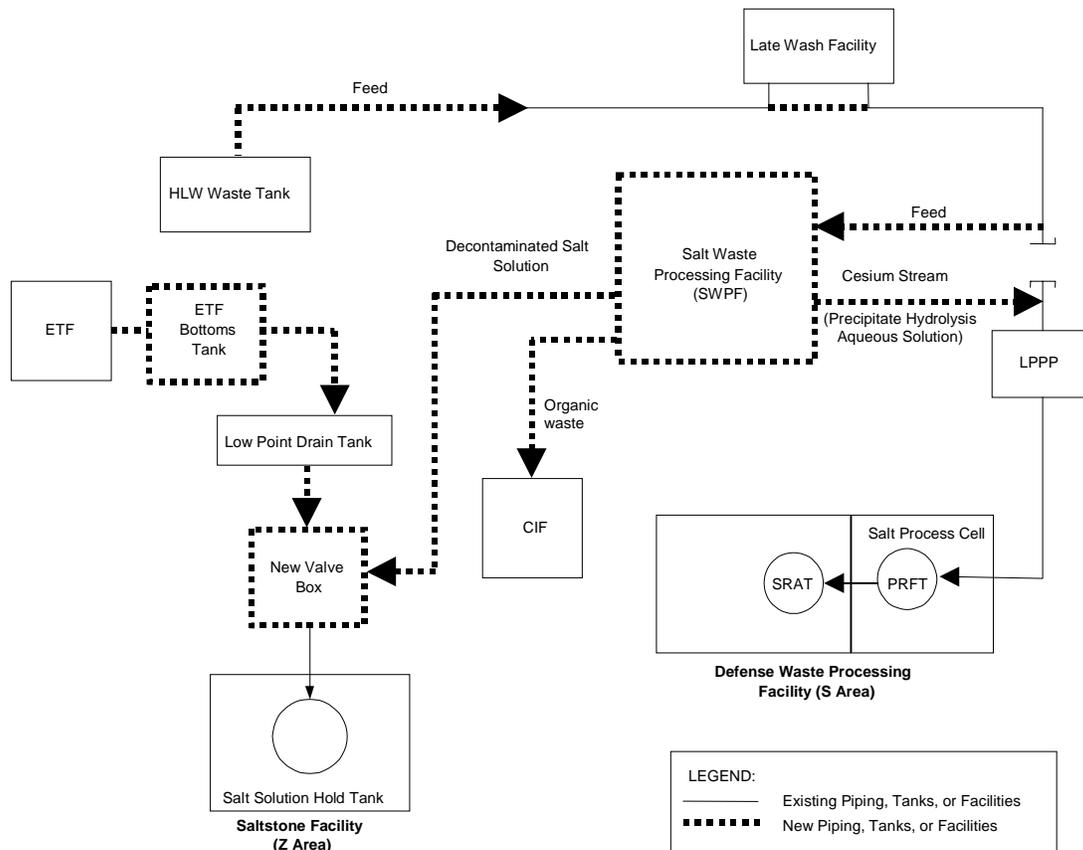


Figure 5.2-1 STTP Alternative - Interarea Transfer Lines

The organic stream would be transferred to the Consolidated Incinerator Facility via a new transfer line from the SWPF to the CIF, as shown in Figure 5.2-1. Alternatively, the organic could be accumulated and trucked periodically to the CIF or an off-site facility for final disposition.

The PHA stream would be transferred to the existing Salt Process Cell (SPC) in the DWPF. The acidic PHA stream contains soluble cesium and potassium formate salts generated from the acid hydrolysis of CsTPB and KTPB, sodium formate, formic acid, boric acid, the insoluble sludge solids removed from the salt solution (at least some of the sludge solids would dissolve in the acidic PHA solution) and the MST added during the precipitation step that removes soluble strontium and alpha contamination.

The PHA from STTP would be routed from the SWPF through a new HLW transfer line (about 550 feet long) running from the SWPF to the LPPP Precipitate Tank (LPPPPT). From there, the PHA would be transferred 1200 feet through an existing line to the existing Precipitate Reactor Feed Tank (PRFT) located in the Salt Processing Cell of the DWPF for subsequent feeding to the SRAT. This is the arrangement shown in Figure 5.2-1.

CSTIX Alternative

If CST Non-Elutable Ion Exchange (CSTIX) is selected, two streams containing radioactive contaminants removed from salt solution must be transferred to the DWPF. For this alternative, the salt solution will be treated separately using Monosodium Titanate (MST) to remove uranium, plutonium, neptunium and strontium from the salt solution. The salt solution then will be filtered to remove any entrained sludge solids and the MST solids. After washing to remove soluble salts, these solids will be pumped to the DWPF via a new HLW transfer line. Based on the proposed Alpha Sorption process (see Section 6.2), a batch transfer of this MST/sludge slurry to the DWPF would be made at a frequency of 1 to 3 transfers each month.

A slurry of cesium-loaded CST resin will also be generated for transfer to the DWPF. The resin slurry would be routed through a separate new transfer line via a new pump pit. Based on the resin loading/unloading cycle described in Section 6.3, 6 to 8 batches of resin slurry will be generated in the SWPF each year and must be transferred to the DWPF.

The route from the SWPF to the DWPF shown in Figure 5.2-1 for the STTP alternative can be used for one of the two product streams generated by CSTIX, and would thus require the same new transfer route described above that includes a new transfer line about 550 feet long to connect the SWPF to the LPPPPT. Although either product stream can be routed through this line, the arrangement shown in Figure 5.2-2 shows the MST/Sludge stream is routed through the LPPPPT and then on to a new MST/Sludge Receipt Tank located in the existing Salt Process Cell (SPC) of the DWPF. The MST and sludge solids slurry will then be pumped from this tank to the Sludge Receipt and Adjustment Tank (SRAT) in the Chemical Processing Cell (CPC) of the DWPF.

The additional transfer route to handle the resin slurry would consist of a new pump pit and connecting transfer lines. This new pump pit can be adjacent to the existing LPPP, so a new transfer line that is about 550 feet long is also needed to connect the SWPF to the new pump pit. About 1200 feet of new transfer line would then connect the new pump pit to a new CST Receipt Tank also located in the SPC of the DWPF. Additional equipment may also be required in the SWPF or the SPC to reduce the size of the resin before combining it with the MST/sludge slurry and sludge slurry from ESP in the SRAT. This equipment is not indicated in Figure 5.2-2. Resin slurry is shown to go directly to the SRAT.

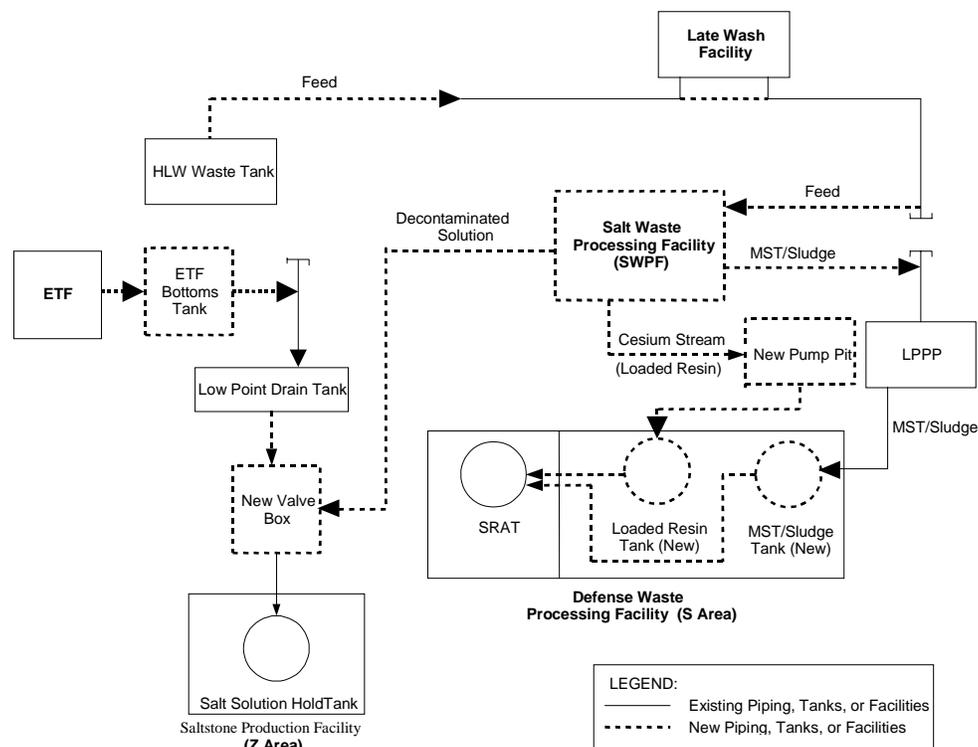


Figure 5.2-2 CST Ion Exchange Alternative - Interarea Transfer Lines

CSSX Alternative

If Caustic Side Solvent Extraction (CSSX) is selected, two streams containing radioactive contaminants removed from salt solution must be transferred to the DWPF. For this alternative, the salt solution will be treated separately using Monosodium Titanate (MST) to remove uranium, plutonium, neptunium and strontium from the salt solution. The salt solution then will be filtered to remove any entrained sludge solids and the MST solids. After washing to remove soluble salts, these solids will be pumped to the DWPF via a new HLW transfer line. Based on the proposed Alpha Sorption process (see Section 6.2), a batch transfer of this MST/sludge slurry to the DWPF would be made at a frequency of 1 to 3 transfers each month.

An acidic solution of cesium nitrate will also be generated for transfer to the DWPF. Presently this solution would also be routed through a separate new transfer line via a new pump pit. Based on the solvent extraction cycle described in Section 6.4, a batch transfer of this solution to the DWPF would be made at a frequency of 4 to 5 transfers each month.

The route from the SWPF to the DWPF shown in Figure 5.2-1 for the STTP alternative and in Figure 5.2-2 for the CSTIX alternative can be used for one of the two product streams generated by CSSX. This alternative would thus require the same new transfer route described above that includes a new transfer line about 550 feet long to connect the SWPF to the LPPPPT. Although either product stream can be routed through this line, the arrangement shown in Figure 5.2-3 shows the MST/Sludge stream is routed through the LPPPPT and then on to a new MST/Sludge Receipt Tank located in the existing Salt Process Cell (SPC) of the DWPF. The slurry would then be pumped directly from this tank to the Sludge Receipt and Adjustment Tank (SRAT) in the Chemical Processing Cell (CPC) of the DWPF.

The additional transfer route to handle the acidic cesium nitrate solution would consist of a new pump pit and connecting transfer lines. This new pump pit can be adjacent to the existing LPPP, so a new transfer line that is about 550 feet long is also needed to connect the SWPF to the new pump pit. About 1200 feet of new transfer line would then connect the new pump pit to a new Cesium Receipt Tank also located in the SPC of the DWPF. This solution would also be pumped directly to the SRAT.

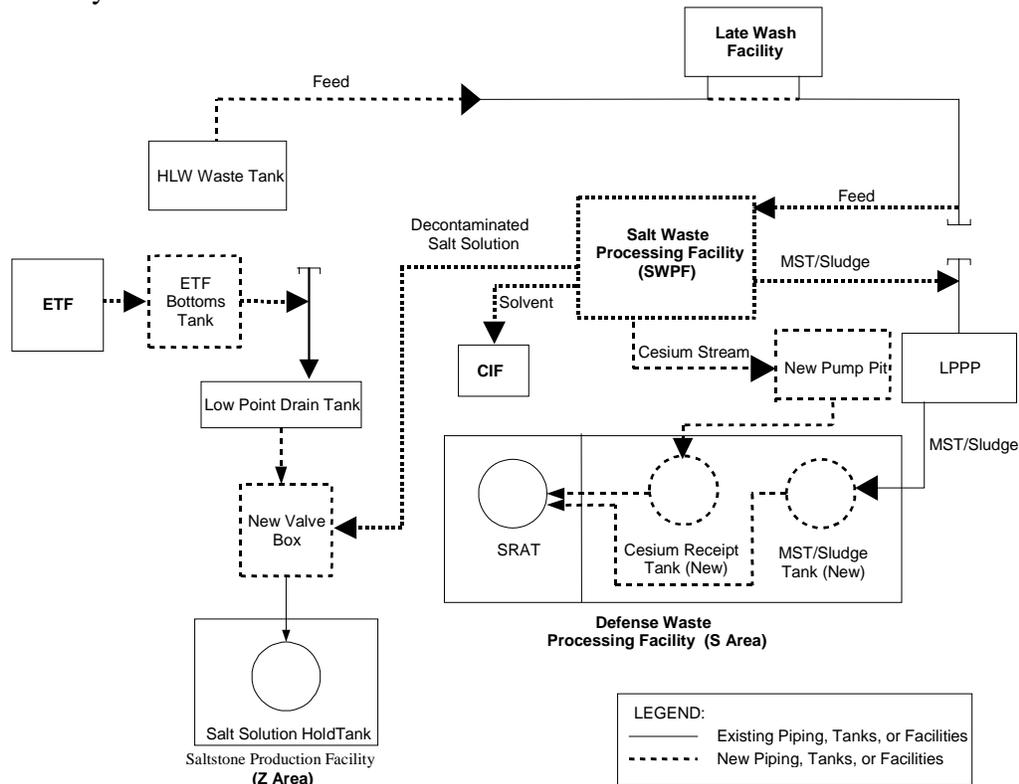


Figure 5.2-3 Caustic Side Solvent Extraction Alternative - Interarea Transfer Lines

5.3 Common Bases and Assumptions

5.3.1 Production Rate Constraints

The production rates and their corresponding material balances for the Decision Phase Alternatives are constrained by the various process limitations described below. Each limitation is an independent limit. Each limitation is described and the most restrictive is applied to the CSTIX, CSSX and STTP alternatives.

5.3.1.1 Salt Removal Limitations

The salt solution removal rate (at an average of 6.44 M Na⁺) is projected to average 6,000,000 gallons annually, based on logistical constraints imposed by the infrastructure of the Tank Farms (Ref. 22).

For these options which couple with the DWPF, a projected maximum of 6,000,000 gallons of salt solution are made available every year from the Tank Farm. However, the DWPF forecasts that the melter must be replaced every 2 years, which requires a six-month outage. To achieve the long-term average salt solution rate of 6,000,000 gallons annually, The DWPF and SWPF must operate at the equivalent rate of 7,500,000 gallons annually to account for the six-month melter outage that occurs every 2.5 years. The SWPF alternative processes have included 60 days of product storage capacity in their respective Process Flow Diagrams (PFDs). This storage allows any of the options to operate 2.17 years out of every 2.5 years, reducing the required capacity to 6,900,000 gallons of 6.44M salt solution on an annualized basis.

Therefore, the instantaneous HLW salt solution feed rate for each SWPF alternative is 13.1 gpm at 100 % attainment, corresponding to 17.5 gpm at 75 % attainment. These are the maximum processing rates applied to each alternative.

5.3.1.2 Defense Waste Processing Facility (DWPF)

Each of the proposed SWPF process alternatives send cesium, in some form, to the DWPF for further processing and vitrification. The processing capacity for an alternative can be limited by chemical cell processing or the melt rate in the DWPF, depending on the overall composition of the product stream(s) sent to the DWPF.

5.3.1.2.1 Chemical Processing Cell

Over the initial two years of radioactive operations, total batch cycle time of 125 hr has been needed to prepare a SME batch in the Chemical Processing Cell (CPC). The CPC cycle time consists of the following steps:

SRAT: Sludge transfer to the SRAT	14 hrs
Sample and Analyze	32 hrs
Heat SRAT and Add Acids	6 hrs
Reflux to remove Hg	17 hrs
Feed solution containing Cs	20 hrs
Cool, Sample and Analyze	<u>36 hrs</u>
SRAT Total	125 hrs

SME:	Transfer SRAT product to SME	2 hrs
	Heat and Concentrate Material (CDC frit)	40 hrs
	Add process frit and Concentrate	30 hrs
	Formic Acid Addition	4 hrs
	Analyze SME product	<u>48 hrs</u>
	SME Total	125 hrs

The CPC processes have been changed to partially offset this increased cycle time, which is significantly longer than the design basis cycle time of 86 hr for the CPC. These changes have increased the average canister production to 6.25 cans for each SME batch. Assuming 125-hr batch cycle time and 75% attainment for the CPC processes, a total of 52 to 53 SME batches can be produced annually.

5.3.1.2.2 Canister Production Rate

The DWPF canister production rate is limited by the sustainable melt rate. Although slurry-fed melters "similar" to the DWPF at different scales have shown a melt flux of 8 pounds per ft²-hr (228 pph, the DWPF original design basis), DWPF has not sustained this rate. The apparent sustainable melt rate, based on FY98 data, is about 195 pph. Based on 4000 pounds net glass in each canister, this rate is equivalent to 425 canisters per year at 100% attainment or 320 canisters at 75% attainment. Including an allowance for lengthy outages to replace a failed melter (2-year design life basis; 6 months to replace), the long term average canister rate is 320 (2/2.5) = 256 canisters per year.

A maximum annual production capacity of 320 canisters per year is assumed to estimate the operating life cycle cost for the three proposed SWPF flowsheets.

5.3.1.2.3 HLW Glass Properties

The Technical Bases for estimating glass properties in the process models are identical for all three alternatives and are described below.

The glass' resistance to leaching determines its quality. This is measured by the Product Consistency Test for glass waste forms (Method ASTM C 1285-94). It can be estimated from the composition of the SME product. The elemental weight percentages of SME product constituents are converted to an oxide basis ("glass basis"). The number of moles of each oxide per 100 grams of glass is calculated and multiplied by its molar free energy of hydration (Table 5.3-1, below). The sum of these molar free energies of hydration is used to estimate boron leach rate by:

$$[\text{Boron}], \text{ g/l} = 10^{(-0.1812 * (\Sigma(\text{molar free energy}) * (\text{moles per 100 g})) - 1.9014)}$$

The benchmark glass ("Environmental Assessment" Glass) has a boron leach rate of 16 g/l. However, model and analytical measurement uncertainties associated with this calculation require a statistical offset to assure that glass will meet these limits. For the purpose of the simple model, a boron leach rate < 2.25 g/l will be used.

The equivalent expressions and limits for lithium and sodium leach rates are (Ref. 23, 24):

$$[\text{Lithium}], \text{ g/l} = 10^{(-0.1468 * (\Sigma(\text{molar free energy}) * (\text{moles per 100 g})) - 1.5459)}$$

Li leach rate < 1.84 g/l

[Sodium], g/l = $10^{(-0.1710 * (\Sigma(\text{molar free energy}) * (\text{moles per 100 g})) - 1.8012)}$

Na leach rate < 2.28 g/l

Table 5.3-1 Molar Free Energy of Hydration for Glass Oxides

Al ₂ O ₃	37.68
B ₂ O ₃	-10.43
CaO	-13.79
Cr ₂ O ₃	11.95
CuO	-4.955
Fe ₂ O ₃	14.56
K ₂ O	-76.41
Li ₂ O	-24.04
MgO	-6.57
MnO	-24.44
Na ₂ O	-53.09
NiO	0.37
SiO ₂	4.05
TiO ₂	16.27
U ₃ O ₈	-23.77
ZrO ₂	17.49

The temperature below which glass will form a separate crystalline phase is the *Liquidus*. A minimum *Liquidus* of 1050° C is required because the DWPF melter operates at around 1100° C and there are cooler zones about 50° C below the bulk temperature. Again model and measurement uncertainties require that the calculated *liquidus* be lower (1015° C). The equation used to calculate *Liquidus* is (Ref. 23):

$$\text{Liquidus, } ^\circ\text{C} = 2276.8723 \left[\frac{(-134[\text{Fe}_2\text{O}_3])}{(-155.6[\text{SiO}_2]) - (-359.88[\text{Al}_2\text{O}_3])} \right] + 803.8696$$

All concentrations used in the *Liquidus* equation are in moles per 100 grams of glass.

The viscosity of the glass melt must not be too low, which leads to uncontrollable pouring or too high, which leads to low pour rate. The limits are from 20 to 100 poise (at 1150° C). However, the calculated acceptable viscosity ranges from 24 to 90 poise, because of model and measurement uncertainty. Viscosity is calculated from the following equation (Ref. 24):

$$\text{Viscosity, poise} = 10^{((-1.5342 * (2 * ([\text{Fe}_2\text{O}_3] - [\text{Al}_2\text{O}_3] + [\text{Cs}_2\text{O}] + [\text{Li}_2\text{O}] + [\text{K}_2\text{O}] + [\text{Na}_2\text{O}]) + [\text{B}_2\text{O}_3]) / [\text{SiO}_2]) - 0.6103 + 4472.4453 / 1150)}$$

All concentrations used in the Viscosity equation are in moles per 100 grams of glass.

5.3.1.3 Saltstone Production and Disposal

The Saltstone Production Facility (SPF) has been permitted by the South Carolina Department of Health and Environmental Control (SCDHEC) as a totally enclosed, industrial wastewater treatment plant. The SPF operating permit currently limits the processing rate of decontaminated

salt solution in the SPF to 12 million gallons annually. The Saltstone Disposal Facility (SDF), located near the SPF, is also permitted by SCDHEC as an industrial waste landfill. Current permitted capacity of the SDF for disposal of saltstone is 174 disposal cells to be contained in large concrete vaults (14 12-cell vaults and 1 6-cell vault). Each cell has the capacity to contain the volume of saltstone generated from about 1.1 million gallons of salt solution, corresponding to a total disposal capacity for about 190 million gallons of salt solution. Current and projected future salt inventory will require disposal of 80 to 100 million gallons of salt solution, depending on the SWPF process alternative selected.

The DOE regulates solid LLW disposal using long-term performance criteria (Ref. 14) for near-surface disposal, as described in DOE Order 435.1. Although the NRC does not regulate saltstone disposal, the NRC Class A LLW limits and landfill design and closure specifications for solid radioactive waste disposal are used as a guide to set limits for the DOE Authorization Basis (AB) and the SPF Waste Acceptance Criteria (WAC) for DSS transferred to the SPF.

Saltstone is a solid waste form that is the product of chemical reactions between a salt solution and a blend of cementitious materials (slag, fly ash, and a lime source). An acceptable saltstone product can be produced over a broad range of these four components. The chemical composition of the dry materials used in the production of saltstone are shown in Table 5.3-2 (Ref. 25).

Table 5.3-2 Composition of Saltstone Cementitious Materials

Component	Cement Type II Santee (Wt%)	Slag Grade 120 NEWCEM ^a (Wt%)	Fly Ash Class F Low CaO (Wt%)
SiO ₂	21.10	34.70	52.17
Al ₂ O ₃	4.66	10.70	27.60
TiO ₂	0.23	0.51	1.98
Fe ₂ O ₃	4.23	0.41	4.36
MgO	1.21	11.90	0.61
CaO	64.55	39.37	0.96
MnO	0.016	0.539	0.014
BaO	0.02	0.05	0.10
Na ₂ O	0.11	0.25	0.26
K ₂ O	0.34	0.55	1.53
P ₂ O ₅	0.31	<0.05	0.12
SO ₃	2.25		0.33
SrO			0.04
LOI (900° C)	1.35	-1.34 ^b	9.92
Totals	100.40	100.36	100.00

^a Also referred to as Atlantic

^b The loss-on-ignition (LOI) values for slag is negative indicating sulfur is present either as free sulfur or metal sulfides (i.e., FeS) rather than as SO₃ (i.e., samples gained weight on heating).

The demonstrated range of acceptability for each component of saltstone with respect to physical properties and resistance to contaminant leaching is shown in Table 5.3-3 (Ref. 26).

Table 5.3-3 Demonstrated Range of Saltstone Acceptability

Saltstone Component	Nominal Blend (Wt %)	Range (Wt %)
Lime Source ^a	3	0 to 10
Fly Ash	25	10 to 40
Slag	25	10 to 40
Salt Solution	47	40 to 55

^a Either Portland Class II cement or Ca(OH)₂.

Saltstone grout is formulated to minimize bleed water from the grout during curing. An acceptable saltstone product, from the standpoint of physical properties and leaching, has been demonstrated with salt solution ranging from about 20 wt % to 32 wt % salt, corresponding to a specific gravity ranging from 1.18 to 1.32 with a sodium molarity ranging from about 3.5 M to 6 M. Bleed water during curing is minimized by controlling the water-to-premix mass ratio in the range of 0.52 to 0.60 (presently set at 0.57, based on a blended solution of ETF evaporator bottoms and the startup product from ITP). The density of cured saltstone ranges between 1.70 and 1.80 kg/L (Ref.14, 27). As presently formulated, saltstone is comprised of about 47 wt % salt solution, 25 wt % of Grade 120 slag (ASTM C989-82), 25 wt % of Class F fly ash (ASTM C618-85) and 3 wt % of type II cement (ASTM C150-85A). Calcium hydroxide can be used as a lime source instead of cement in the dry blend. The dry materials are blended to form a premix of dry solids, which is then combined with salt solution to produce a grout.

The salt solution concentration limits for radioactive contaminants in the current SPF Authorization Basis (AB) and the SPF WAC are shown in Table 5.3-4. Decontaminated salt solution within these limits would yield saltstone that is well within the NRC Class A LLW disposal limits for radioactive contaminants in solid waste. Salt solution limits that would yield NRC Class A solid waste are also shown in Table 5.3-4 for comparison to the AB and WAC limits. Similar limits for chemical contaminants are shown in Table 5.3-5. Projected concentrations for sodium salts in decontaminated salt solution from the abandoned Large Tank ITP process (and ETF bottoms), as reflected in the SPF permit application, are also shown in these two tables for comparison to the various limits shown. The permit requires these concentrations to be monitored and reported if they differ significantly from the concentrations in the permit, but the actual concentrations are not regulated by SCDHEC. Contaminants in DSS generated in the SWPF are projected to be well within the limits specified in the SPF WAC.

Table 5.3-4 SPF WAC for Radionuclide Contaminants

Radioactive Contaminant	NRC Class A Limit (nCi/g)	SPF AB Limit (nCi/g)	SPF WAC Limit (nCi/g)	SWPF Projected Conc. (nCi/g)	Basis for WAC Limits
Total Alpha	18	50	20	< 18	NRC Class A
Total with T _{1/2} < 5 yr	750,000	N/S	N/S	< 30	N/S
Total beta/gamma	~1.5E06	8600	7500	N/S	AB source term
Radiation Control Guide	N/S	< 3	< 1	< 0.9	Rad. Protection
GAMMA EMITTERS USED TO CALCULATE RCG					
⁶⁰ Co	750,000	7	6.8	< 0.5	Rad. Protection
¹⁰⁶ Ru/Rh	(a)	600	128	< 20	Rad. Protection
¹²⁵ Sb	(a)	150	76	< 5	Rad. Protection
¹²⁶ Sn	(b)	250	14	< 1	Rad. Protection
¹³⁷ Cs/Ba	1070	100	45	< 45	Rad. Protection
¹⁵⁴ Eu	(a)	16	16	< 0.5	Rad. Protection
Calculated RCG (d)	>3 E+05	10.8	< 1	< 0.9	USQE if > 1
OTHER RADIOACTIVE CONTAMINANTS					
³ H (HTO)	42,000	1800	1800	< 100	SDF Rad. Prot.
¹⁴ C	856	800	800	< 0.01	NRC Class A
⁵⁹ Ni (c)	23,529	23,000	23,000	< 0.001	NRC Class A
⁶³ Ni	3,743	3,700	3700	< 0.01	NRC Class A
⁷⁹ Se	(b)	12	12	< 1	Groundwater
⁹⁰ Sr/Y	43	120	40	< 40	NRC Class A
⁹⁴ Nb (c)	N/S	20	20	< 0.001	NRC Class A
⁹⁹ Tc	321	1000	320	< 50	NRC Class A
¹²⁹ I	1	20	2	< 0.3	Groundwater
²⁴¹ Pu	636	600	200	< 0.1	SDF Haz. Anal.
²³⁷ Np	(b)	N/S	0.03	< 0.03	Groundwater

- (a) Included in total for short-lived isotopes in NRC limits listed in 10CFR61.55; NRC Class A limit for short-lived isotopes (T_{1/2} < 5 years) is about 750,000 nCi/g, for salt solution.
- (b) No NRC limit specified for this isotope; included in total(s) for waste class and type of radioactive emission.
- (c) NRC Limits for Ni-59 and Nb-94 are based on activated metal; limits may not be applicable to salt solution or saltstone, but were included in limits recommended by SRTC (DPST-88-372, Rev.1 dated 5/19/88).
- (d) Radionuclides that emit high-energy gamma radiation must be monitored to assure radiation exposure to Z-Area personnel will not exceed RCO guidelines. Based on process knowledge and waste tank histories, the 6 isotopes shown in the equation below are the principal gamma-emitting species in salt solution from Salt Processing and ETF operations (concentrations expressed in nCi/g); these are used to calculate the Radiation Control Guide (RCG):

$$RCG = 0.145 \times [^{60}\text{Co}] + 0.0078 \times [^{106}\text{Ru}] + 0.013 \times [^{125}\text{Sb}] + 0.0705 \times [^{126}\text{Sn}] + 0.022 \times [^{137}\text{Cs}] + 0.061 \times [^{154}\text{Eu}]$$

The RCG must be < 1 to be within WAC limits based on present shielding design of SPF and SDF facilities. A USQE and installation of additional shielding in locations identified in OPS-DTZ-96-00006 is required to process waste in the SPF if the calculated RCG is ≥ 1 . Calculated RCG values (in nCi/g) for the AB and the SWPF long-term average assume all isotopes in the RCG equation are at the values shown in the table. Present saltstone properties and SDF disposal, vault and closure design meet NRC requirements for Class C waste disposal. Present SPF WAC limits for radioactive contaminants will yield saltstone well within NRC Class A limits.

N/S = limit not specified

Table 5.3-5 SPF WAC for Chemical Contaminants

Chemical Contaminant	SPF AB Limit	SPF WAC Limit	SWPF Projected Max. Conc. (a)	Basis for AB / WAC Limits
HAZARDOUS METAL IONS (units are mg/L)				
Arsenic	230	230	< 0.0003	SPF JCO, Pass TCLP
Barium	1000	1000	< 0.3	Pass TCLP
Cadmium	110	110	< 0.1	SPF JCO, Groundwater
Chromium	1100	1100	120 (142)	Pass TCLP
Lead	2000	1000	< 5	Pass TCLP
Mercury	500	250	1 (30)	LDR (260 mg/L), pass TCLP
Selenium	350	350	< 5	Groundwater
Silver	230	230	0.0008	SPF JCO, Pass TCLP
ORGANIC CONTAMINANTS (units are mg/L)				
Benzene	5	3	< 0.5 (0)	LFL in SSHT
Butanol + Isopropanol	3230	3000	< 200	(b), (c)
Methanol	397	300	< 10	(b), (c)
Tetraphenylborate (TPB)	N/A	16,000	< 960 (0)	Tank 50-to-SPF AB Limit
Phenol	1000	1000	50 (0)	(d)
Tributylphosphate (TBP)	500	400	< 100	Permit Modification (e)
Sodium EDTA	500	500	< 50	Permit Modification (e)
Other volatile organics	N/A	20	< 5	Permit Modification (e)
SOLUBLE SALT CONTAMINANTS (units are moles/L)				
Nitrate	N/A	4.5	2.1 (2.5)	N/A
Nitrite	N/A	1.0	0.60 (0.71)	N/A
Aluminate	N/A	0.6	0.40 (0.48)	N/A
Fluoride	N/A	1.0	< 0.02	N/A
Hydroxide	N/A	4.0	1.2 (1.43)	N/A
Carbonate	N/A	0.5	0.10 (0.12)	N/A
Sulfate	N/A	0.4	0.10 (0.12)	N/A
Chloride	N/A	0.3	< 0.05	N/A
Oxalate	N/A	0.2	< 0.05	N/A
Phosphate	N/A	0.2	< 0.01	N/A
Total Sodium	N/A	3.5 - 6.0 (f)	4.7 (5.6)	Range tested

- (a) Based on STTP alternative projected from blend of ITP and ETF. Values in parentheses reflect the projected nominal concentrations in feeds from CSTIX or CSSX alternatives; obtained by using a total sodium ratio factor (5.6/4.7) to the STTP alternative. Total sodium values reflect principal species only. Species designated as less than values are not included.
- (b) Isopropanol and methanol are components of sodium titanate slurry. Butanol is generated from hydrolysis of tributylphosphate (TBP) that was used as an antifoam in the Benzene Stripper Column in ITP.
- (c) Limit for methanol is based on the flammability equation developed for transfers from the ITP Filtrate Hold Tank to Tank 50 (WSRC-OX-89-15-001). Butanol+Isopropanol limit combines the limit for isopropanol (2827 mg/L) and the maximum concentration of butanol that could be generated from the limit for TBP (500 mg/L).
- (d) Present phenol limit is based on the limit in EPA's proposed rule covering TCLP leachate. When promulgated in 1991, phenol was dropped from the EPA rule controlling limits on TCLP leachate from waste.
- (e) Permits were modified, after saltstone product tests, to enable the use of cleaning agents in ETF containing EDTA, Tributylphosphate as an antifoam agent in the Benzene Stripper Column in ITP and the disposal of laboratory wastes (low volumes) containing small quantities of organic chemicals used in analytical procedures. Low concentrations of organic chemicals in the laboratory waste are exempted from regulatory control.
- (f) Acceptable saltstone properties and processability in the SPF have been demonstrated for this range in sodium molarity.

N/A = not applicable

5.3.2 Salt Processing Rates Summary

Based on the limitations in Section 5.3.1, the material balances for the remaining three salt processing options were completed at the various flow rates shown in Table 5.3-6.

Table 5.3-6 Material Balances For Salt Disposition Alternatives

Process Alternative	Salt Workoff, gpm @ 6.44 M [Na ⁺] / 75 % Attainment	One Year's Operating Production, gallons	Long Term Average (gal/yr)	[Na ⁺] into (out of) Facility, M	DSS Flow in Facility, gpm ¹	Throughput Limitation
STTP	17.5	6,900,000	6,000,000	6.44 (4.7)	24.0	Waste Removal Rate
CSTIX	17.5	6,900,000	6,000,000	6.44 (5.6)	21.0	Waste Removal Rate
CSSX	17.5	6,900,000	6,000,000	6.44 (5.0)	23.3	Waste Removal Rate

5.3.3 Salt Waste Composition

The salt composition used for the Pre-conceptual Phase is the 20-year average salt and sludge compositions (see Table 5.3-9) that were used in the Phase II flowsheets.² This provides a consistent basis for comparing the alternatives. A blending strategy was developed for system planning (Ref. 28) and was used to project composition and volumes of the feed to the SWPF. These blends are shown in Appendix H.

The data show in Table 5.3-7 below were used as an initial basis for process development. Blending will, of course, smooth out concentration spikes.

Table 5.3-7 Tank Farm Concentrations @ 6.44 M Na⁺

Component	Concentration		Activity		SPF WAC (nCi/g)	Required DFs for Average Waste	Required DFs for Bounding Waste
	Average (mg/L)	Bounding (mg/L)	Average (nCi/g)	Bounding (nCi/g)			
Pu/Am	0.21	1.1 ¹	220	1070 ¹	18 (total α)	12	55
U	63	1100 ²	0.026	0.66 ²	18 (total α)	N/A	N/A
²³⁷ Np	0.017	1.9 ³	0.01	1.1 ³	0.03	N/A	36
⁹⁰ Sr	0.0017	0.010 ⁴	191	1130 ⁴	40	4.8	28

¹ Based on predicted 5X TRU spike from blended feed studies

² Based on U in Tank 40: 4.3 Ci in 1.44 M gallons (at 6.44 M Na⁺)

³ Based on Np-237 in Tank 34: 1.8 Ci in 1.49 M gallons (at 6.44 M Na⁺)

⁴ Based on Sr-90 in Tank 19: 1280 Ci in 0.256 M gallons (at 6.44 M Na⁺)

¹ Salt fed to CSTIX and CSSX are diluted with sodium hydroxide solution to prevent precipitation of gibbsite.

² Note that the SpeedUp™ composition values shown in Table 5.3-9 for HgO have been changed to show the correct values. However, the values that were actually used in Phase IV material balances were 3.0826E-01 lb/hr and 3.3547E-03 wt% instead of 2.3562E-01 lb/hr and 2.5642E-03 wt% as shown.

5.3.4 Blending for MST Alpha and Strontium Sorption Requirements

After obtaining data on MST sorption kinetics, preliminary tank sizing was evaluated for batch MST sorption used in CSTIX and CSSX alternatives and for continuous MST sorption used in the STTP alternative. A detailed batching plan was developed for Revision 12 of the HLW System Plan (Ref. 28). The concentrations of soluble alpha emitters and strontium resulting for these are summarized in Table 5.3.8.

Table 5.3-8 Tank Farm Concentrations @ 4.7 M Na⁺

	Average Feed, nCi/g	Maximum Feed, nCi/g	Saltstone Limit		Minimum	Average	Maximum	
	(Diluted to [Na+] = 4.7) ³	(Diluted to [Na+] = 4.7)	nCi/g	Limit Driver	DF Required	DF Required	DF Required	Expected DF
Cs137	1.95E+05	8.06E+05	4.50E+01	Shielding	1.05E+3	4.33E+03	1.79E+04	4.00E+04
Np237	1.25E-02	4.29E-02	3.00E-02	Ground Water	None	4.18E-01	1.43E+00	3.10E+00
Sr90	1.46E+01	1.68E+02	4.00E+01	NRC Class A	None	3.66E-01	4.21E+00	3.30E+02
Total Alpha	1.71E+02	7.10E+02	1.80E+01	NRC Class A	1.11E+0	9.48E+00	3.94E+01	1.40E+01

Table 5.3-8 also shows the maximum blended feed concentrations, Saltstone Waste Acceptance Criteria, and the Decontamination Factors (DF) needed for the bounding concentrations to meet the SPF WAC. Conclusions drawn from Table 5.3-8 and Appendix H are:

- The Required Decontamination Factors for Sr and Alpha removal for any alternative are calculated based on achieving the maximum allowed concentration in decontaminated salt solution specified in the current WAC for the SPF (18 nCi/g total alpha; 0.03 nCi/g ²³⁷Np; 40 nCi/g ⁹⁰Sr).
- Total alpha concentration is exceeded for the maximum blend concentrations. Only 5 of the batches require DF greater than that demonstrated (~14). There are several processing variables which could be manipulated to get a higher DF, including using higher MST concentration or more contact time.
- Tanks 33 and 34, which contain essentially all of the Np, were blended well enough to avoid exceeding the Saltstone feed limit.
- DF requirements are somewhat higher for CST and CSSX. The feeds for these flowsheets are diluted to 5.6 M sodium, rather than the 4.7 M for STTP. The adjustment for DF is only about 15% up, on a mass basis.

³ This table is based on dilution to STTP flowsheet conditions. However, the discussion with respect to blending applies to all three flowsheets. They all have similar design requirements for DF.

5.3.4.1 Tank Farm

The H/F Tank Farms are assumed to provide up to an average of 6,000,000 gal/yr (Ref. 22) of 6.44 M sodium feed for the alternatives. The feed composition will vary over time, depending on the sequence of removal from different tanks. The SpaceMan model was used to generate the feed sequence.

5.3.4.2 Salt Feed Blending

Space Man was used to develop a series of proposed feed batches. These batches are shown in Appendix H..

5.3.4.3 Tank Farm Strategy

The Tank Farm Strategy is the manner envisioned to empty the tanks in the tank farms. This analysis is performed using the SpaceMan model, which has been extensively used to develop and annually revise the HLW System Plan (Ref. 22). SpaceMan tracks essentially all species of interest, through detailed tank by tank material balances. One week steps are used to follow receipts, transfers and evaporation. Radionuclide decay is also tracked. SpaceMan calculated a batching sequence and this was used in the Life Cycle Analysis (see section 7.0) for all three alternatives (See Tables 5.3-9 and Appendix H).

5.3.4.4 Flowsheet Salt Blending

The initial tank composition and tank inventory is based on information contained in the HLW Waste Characterization System (WCS), the chemical composition database for the tank farms. This database contains many more compounds than the feed vectors used in the process models, so a reduced data set was created that reflects the desired compounds to be tracked. The reduced data set maintains an overall mass balance, but partitions ions between different compounds as required by the feed vector.

Table 5.3-9 Average Composition of Blended Salt / Supernate Feed

CPES Composition:

Insolubles	MW	lb/hr
Ag ₂ O	231.74	6.910E-03
Al ₂ O ₃	101.96	8.507E-01
BaSO ₄	233.39	1.573E-02
Ca ₃ (PO ₄) ₂	310.18	7.865E-03
CaC ₂ O ₄	88.022	4.137E-02
CaCO ₃	100.08	1.510E-01
Ca ¹⁴ CO ₃	100.1	1.175E-08
CaF ₂	59.08	6.766E-03
CaO	56.08	
CaSO ₄	136.14	3.598E-02
CoO	74.9332	3.991E-04
Cr ₂ O ₃	151.99	1.389E-02
Cs ₂ O	281.81	2.948E-04
CuO	79.54	5.630E-03
Fe ₂ O ₃	159.7	1.313E+00
Group B	122.971	6.710E-02
HgO	216.59	7.300E-02
K ₂ O	94.2	
La ₂ O ₃	325.8	2.761E-02
MgO	40.3	1.187E-02
MnO ₂	86.94	2.842E-01
Na ₂ O	61.98	8.066E-05
NiO	74.7	1.578E-01
PbCO ₃	267.19	4.007E-03
PbSO ₄	303.26	1.148E-02
PdO	122.4	6.871E-03
alpha (PuO ₂)	270.9	2.566E-03
RhO ₂	134.91	
RuO ₂	133.07	1.654E-02
SiO ₂	60.09	1.360E-01
SrCO ₃	147.62	9.739E-03
TcO ₂	130.91	4.527E-03
ThO ₂	264.04	5.743E-02
TiO ₂	79.9	6.624E-05
U ₃ O ₈	842.09	4.400E-01
Y ₂ (CO ₃) ₃	351.81	1.204E-06
ZnO	81.38	1.000E-02
ZrO ₂	123.22	2.423E-02
hydrate H ₂ O	18	9.911E-01
Zeolite		1.212E-02
total insolubles = 4.798E+00		

SPEEDUP Composition:

solubles	MW	lb/hr
NaNO ₂ (l)	69	2.841E+02
NaNO ₃ (l)	85	1.446E+03
NaOH (l)	40.07	6.960E+02
Na ₂ CO ₃ (l)	106	1.299E+02
Na ₂ SO ₄ (l)	142.04	1.621E+02
NaAl(OH) ₄ (l)	118	2.841E+02
NaCl (l)	58.443	1.203E+01
NaF (l)	41.99	1.050E+01
Na ₂ C ₂ O ₄ (l)	134	2.031E+01
Ba(OH) ₂ (l)	171.33	1.258E-04
Ca(OH) ₂ (l)	74.08	3.621E-03
CsOH (l)	149.9	1.790E-01
Group A (l)	98.3738	4.230E-02
KNO ₃ (l)	101.102	2.364E+00
KOH (l)	56.105	5.530E+00
NH ₄ OH (l)	35.04	
NH ₄ NO ₃ (l)	80	2.394E-01
Na[HgO(OH)] (l)	256.58	2.787E-01
Na ₂ B ₄ O ₇ (l)	201.22	1.234E-01
Na ₂ ¹⁴ CO ₃ (l)	106	
Na ₂ CrO ₄ (l)	161.976	3.758E+00
Na ₂ MoO ₄ (l)	205.92	2.867E-01
Na ₂ RhO ₄ (l)	212.89	6.631E-03
Na ₂ RuO ₄ (l)	211.05	1.662E-01
Na ₂ SiO ₃ (l)	122.07	3.411E+00
Na ₃ PO ₄ (l)	163.944	1.004E+01
Na[Ag(OH) ₂] (l)	198.858	5.113E-03
NaI (l)	149.89	1.187E-02
NaTcO ₄ (l)	186	2.657E-02
Na ₂ [PuO ₂ (OH) ₄] (l)	389.98	2.364E-03
Pb(NO ₃) ₂ (l)	331.21	2.494E-02
Sr(OH) ₂ (l)	121.6	1.642E-02
Tritium (l)	3	8.976E-13
UO ₂ (OH) ₂ (l)	304.03	5.465E-01
Y(OH) ₃ (l)	139.906	5.780E-06
C ₆ H ₅ OH salt (l)	94	9.889E-01
C ₆ H ₅ NH ₂ (l)	93.13	6.576E-03
H ₂ O (l)	18	6.111E+03
total solubles = 9.184E+03		
total slurry = 9.189E+03		
vol. flow (GPM) = 1.448E+01		
density (lb/ft³) = 7.914E+01		

species	MW	lb/hr	wt%
H ₂ O (l)	18	6.1977E+03	6.7447E+01
misc. salts (l)		6.0806E+01	6.6172E-01
NaNO ₂ (l)	85	1.446E+03	1.5736E+01
NaNO ₃ (l)	69	2.841E+02	3.0917E+00
NaOH (l)	40.07	6.9596E+02	7.5738E+00
KNO ₃ (l)	101.102	2.3640E+00	2.5726E-02
CsNO ₃ (l)			
NH ₄ NO ₃ (l)	80	2.394E-01	2.6053E-03
NH ₄ OH (l)	35.04		
NaAlO ₂ (l)	82	1.9743E+02	2.1485E+00
HgO (l)	216.59	2.3526E-01	2.5642E-03
misc. sludge (s)		4.3123E-01	4.6929E-03
Na ₂ U ₂ O ₇ (l)	634.06	5.6989E-01	6.2019E-03
Fe(OH) ₃ (s)	106.85	1.7570E+00	1.9120E-02
Al(OH) ₃ (s)	78.006	1.3017E+00	1.4166E-02
Sr(OH) ₂ (l)	121.6	1.608E-05	1.7599E-07
Alpha (PuO ₂) (l)	270.9	1.6420E-03	1.7870E-05
C ₆ H ₆ (l)	78		
C ₆ H ₅ OH (l)	94	9.8890E-01	1.0762E-02
CsOH (l)	149.9	1.790E-01	1.9480E-03
KOH (l)	56.105	5.530E+00	6.0181E-02
CsTPB			
NaTPB			
NaTPB			
KTPB			
NH ₄ TPB			
NaTi ₂ O ₅ H			
NaTiSr(OH) ₂			
NaTiNa ₂ U ₂ O ₇			
(C ₆ H ₅) ₃ B (l)			
(C ₆ H ₅) ₂ BOH (l)			
(C ₆ H ₅)B(OH) ₂ (l)			
B(OH) ₃ (l)			
Na ₂ CO ₃ (l)	106	1.2990E+02	1.4136E+00
Na ₂ SO ₄ (l)	142.04	1.6210E+02	1.7641E+00
total solubles = 9.1840E+03			
total slurry = 9.1890E+03			1.0000E+02

Species	MW	lb/hr	wt%
K ₂ O (s)	94.2		
Li ₂ O (s)			
MgO (s)	40.3	1.1870E-02	1.2918E-04
MnO (s)	70.94	2.3190E-01	2.5236E-03
TiO ₂ (s)	79.9	6.6240E-05	7.2086E-07
U ₃ O ₈ (s)	842.09	4.4000E-01	4.7883E-03
ZrO ₂ (s)	123.22	2.4230E-02	2.6368E-04
Ca ₃ (PO ₄) ₂ (s)	310.18	7.8650E-03	8.5591E-05
P ₂ O ₅ (s)			
Cr ₂ O ₃ (s)	151.99	1.3890E-02	1.5116E-04
Cs ₂ O (s)	281.81	2.9480E-04	3.2082E-06
CuO (s)	79.54	5.6300E-03	6.1269E-05
Na ₂ O (s)	61.98	8.0660E-05	8.7779E-07
NiO (s)	74.7	1.5780E-01	1.7173E-03
SiO ₂ (s)	60.09	1.3600E-01	1.4800E-03
HgO (s)	216.59	2.3526E-01	2.5642E-03
Alpha (PuO ₂) (s)	270.9	2.5660E-03	
CaCO ₃ (s)	100.08	1.5100E-01	1.6433E-03

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5.3.5 Process Chemistry in the HLW System

Chemical reactions and related process conditions common to all three SWPF alternatives are summarized below. All reactions shown in this section are assumed to go to 100% completion unless incomplete reaction is indicated by a value in the “% Rxn” column.

5.3.5.1 Tank Farm Chemistry

Technical Bases – The composition of the existing waste inventory accounts for radiolytic decomposition of sodium nitrate to sodium nitrite and the reactive sorption of carbon dioxide from the air to form sodium carbonate. The only other radiolytic reaction product is gaseous hydrogen and oxygen, which evolves from the waste and is vented to the atmosphere.

Free hydroxide, nitrate and nitrite concentrations are monitored in stored waste and adjusted, when necessary, by adding caustic or sodium nitrite to maintain the concentrations in a range that minimizes the corrosion rate of the carbon steel waste tanks.

Future additions of HLW to the Tank Farms from continuing operations in other facilities are based on waste forecasts.

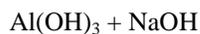
Modeling Bases – For the ProdMod Model, which is used to prepare the HLW System Plan, salts and sludges projected to be in future waste additions are assumed to be added to the existing waste inventory to provide a total projected waste inventory that must be processed. Future waste additions are assumed to be similar in composition to current waste inventory.

5.3.5.2 Extended Sludge Processing (ESP) Chemistry

Technical Bases – The primary function of ESP is to blend and wash insoluble HLW sludge solids to prepare sludge slurry for feeding to the DWPF. However, some sludges stored in the Tank Farm contain higher concentrations of aluminum hydroxide than can be processed in the DWPF. A portion of the aluminum hydroxide in these “high-Al” sludges can be converted to sodium aluminate by treatment with hot caustic solution in ESP. The resulting sludge slurry is then blended with other sludges and washed to yield an acceptable sludge feed for the DWPF. Soluble salts removed during ESP processing, including any sodium aluminate formed during aluminum dissolving, are returned to HLW storage, combined with other soluble waste, concentrated by evaporation and stored until the soluble waste can be blended and diluted appropriately for processing through the SWPF.

Tanks containing high-aluminum sludge that could be treated to reduce the insoluble aluminum content, have been identified based on analysis of sludge samples and tank waste receipt histories.

Reactants



Products



% Rxn

75

Modeling Bases – For the ProdMod Model, used to prepare the HLW System Plan, specific sludge batches are prepared by removing and blending sludges from two or more tanks. Aluminum dissolution, when required, is assumed to remove up to 75% of the aluminum contained in the sludge.

5.3.5.3 SWPF Chemistry

Reaction chemistry and conditions specific to each proposed SWPF process are included as part of the detailed description of each alternative (see Section 6.0). In general, SWPF treatment for each alternative must remove entrained sludge and soluble Cs, Sr and Pu to reduce the soluble radioactive contamination to a level that is within the WAC limits for the SPF. Streams containing the contaminants removed from salt solution are sent to the DWPF, where they will be incorporated into HLW glass. Decontaminated salt solution will be transferred to the SPF for treatment and subsequent disposal as solid saltstone.

5.3.5.4 DWPF Chemistry

The DWPF currently processes HLW sludge waste into HLW glass. Much of the chemistry, especially the melter feed preparation and sludge reactions, do not differ for the coupled processes that would incorporate waste streams from the SWPF. Chemistry common to the three alternatives is summarized below.

5.3.5.4.1 Technical Bases for SRAT/SME Acid Adjustment

Acid adjustment in the Sludge Receipt and Adjustment Tank (SRAT) and Sludge Mixer Evaporator (SME) is required for current “sludge-only” operation and will also be required after the SWPF is operational (“coupled” DWPF process). Acid adjustment alters the rheological properties of the sludge/frit blend to enable concentration up to 50 wt% total solids in the feed to the melter. Acid adjustment is partially completed by adding nitric acid to yield an acidic pH. Next, formic acid is added to reduce mercury(II) compounds to mercury(0). Mercury is then steam-stripped from the slurry to minimize the quantity of mercury sent to the melter.

Only those reactions that involve a species in the salt solution and more reactive sludge components are shown below, since the total moles of acid added is insufficient to undergo significant reaction with the bulk of the sludge solids. Reactions of sludge components will not differ significantly for current “sludge-only” operation or “coupled” operation with the additional DWPF input streams from the three proposed salt processing alternatives.

<u>Reactants</u>	<u>Products</u>	<u>% Rxn</u>
NaOH + HNO ₃	NaNO ₃ + H ₂ O	
KOH + HNO ₃	KNO ₃ + H ₂ O	
CsOH + HNO ₃	CsNO ₃ + H ₂ O	
NH ₄ OH + HNO ₃	NH ₄ NO ₃ + H ₂ O	
Mg(OH) ₂ + 2 HNO ₃	Mg(NO ₃) ₂ + 2 H ₂ O	
Ca(OH) ₂ + 2 HNO ₃	Ca(NO ₃) ₂ + 2 H ₂ O	

<u>Reactants</u>	<u>Products</u>	<u>% Rxn</u>
Ba(OH) ₂ + 2 HNO ₃	Ba(NO ₃) ₂ + 2 H ₂ O	
CoO + 2 HNO ₃	Co(NO ₃) ₂ + H ₂ O	(70%)
NaAlO ₂ + 4 HNO ₃	Al(NO ₃) ₃ + NaNO ₃ + 2 H ₂ O	
2 NaNO ₂ + 2 HNO ₃	2 NaNO ₃ + H ₂ O + NO + NO ₂	
Na ₂ U ₂ O ₇ + 6 HNO ₃	2 UO ₂ (NO ₃) ₂ + 2 NaNO ₃ + 3 H ₂ O	
Na ₂ CO ₃ + 2 HNO ₃	2 NaNO ₃ + H ₂ O + CO ₂	
CaCO ₃ + 2 HNO ₃	Ca(NO ₃) ₂ + H ₂ O + CO ₂	
SrCO ₃ + 2 HNO ₃	Sr(NO ₃) ₂ + H ₂ O + CO ₂	
MnO ₂ + 3 HCOOH	Mn(COOH) ₂ + 2 H ₂ O + CO ₂	(70%)
HgO + HCOOH	Hg + H ₂ O + CO ₂	(99%)
2 Ag ₂ O + 2 HCOOH	2 Ag + H ₂ O + CO ₂	(99%)
PdO + HCOOH	Pd + H ₂ O + CO ₂	(99%)
RhO ₂ + 2 HCOOH	Rh + 2H ₂ O + 2CO ₂	(99%)

The method for calculating acid addition and the balance between formate ion and nitrate ion are based on laboratory work (Ref. 29), DWPF cold runs and DWPF operating experience.

1. The acid required to neutralize or to stoichiometrically react with materials in the feeds to the SRAT is first calculated. One mole of acid is needed for each mole of HgO, NaOH, and KOH. Two moles of acid are needed for CoO, Ca(OH)₂, Ba(OH)₂, Mg(OH)₂ and carbonate (CO₃)⁻². Three moles of acid are needed for each mole of uranium (assumed present as U₂O₇⁻²). Four moles are needed for each mole of NaAl(OH)₄. One-quarter mole is needed for each mole of nitrite (NO₂⁻) and 0.4 moles are needed for each mole of MnO₂.
2. The **total** amount of acid needed is obtained by multiplying the “stoichiometric” amount from step 1 by 1.25 (1.37 was used for the second sludge batch).
3. In the SRAT cycle, 40% of the formic acid added is assumed to be lost to overheads. A ferrous (Fe⁺²) to total iron ratio of 0.2 is targeted. This is calculated by $Fe^{+2}/Fe(\text{total}) = 0.217 + 2.53 * [\text{total nitrate}] - 0.739 * [\text{total formate}]$ normalized to 45 wt% solids in the SME. To calculate the SRAT addition, 100 gallons of 90% formic acid is assumed to be added to the SME to provide part of the stoichiometric formic acid needed to satisfy the reactions above.

SRAT/SME Modeling Bases – Acid addition to the SRAT and SME use fixed volumes representative of plant operating practice. For each SRAT batch, these volumes of each acid are added:

- 200 gallons of 50 wt% nitric acid
- 150 gallons of 90 wt% formic acid

If nitric acid enters the SRAT through the SWPF feed stream(s) to the DWPF (as is the case in the CSSX alternative) the volume of 50 wt% nitric acid is reduced by the equivalent moles of nitric acid in the SWPF stream(s). Likewise, if formic acid enters the SRAT through the SWPF feed stream (as is the case in the STTP alternative) the volume of 90% formic acid is reduced by the equivalent moles of formic acid in the SWPF stream.

Some formic acid will be removed in the SRAT cycle during the concentration and mercury-stripping operation. The amount of acid lost is calculated by an ideal solution estimate of the vapor composition and may actually differ from the nominal 40% loss assumed.

To each SME batch, the equivalent of 100 gallons of 90 wt % formic acid are added as a component of the frit slurry. Acid-base interaction with the frit during frit slurry preparation converts the bulk of the formic acid entering the SME to alkali formate (sodium and lithium salts).

The “F – N” redox value is calculated for the SME using the following equation:

$$F - N = 0.227 * (\text{liquid density}) * (0.646 * [\text{Formate}] - 1.403 * [\text{Nitrate}])$$

Mercury is removed from the combined waste by steam-stripping during the SRAT and SME evaporation cycles, condensed with water and collected as a side stream. Mercury is tracked as HgO throughout the DWPF process model instead of as mercury metal to simplify DWPF calculations.

5.3.5.4.2 Technical Bases for Melter Chemistry

For purposes of describing the melter chemistry, formate salts added with the frit are assumed to be sodium formate. To simplify melter stoichiometry, all soluble transition metal nitrate salts are assumed to interact with sodium formate in the melter feed slurry to yield formate salts and sodium nitrate. In the melter, all nitrite salts and 50 % of the alkali nitrate salts react with sodium formate to form nitric oxide (NO). The balance of the nitrate salts react to form nitrogen (N₂). Subsequently, the NO reacts with oxygen in the melter vent system air to form nitrogen dioxide (NO₂). These reactions are summarized below.

In addition to reactions with nitrate and nitrite salts, any remaining formate salts either react with oxidizing species in the melter feed or thermally decompose to generate carbon monoxide, carbon dioxide, hydrogen, water and oxides of metal ion species. Oxalate salts and other compounds that are thermally unstable at melter temperature also decompose (e.g., CaC₂O₄, residual HgO). Residual insoluble hydroxides (*i.e.*, hydrated metal oxides) in oxidation states stable at melter temperature that remain after chemical adjustments to the melter feed simply lose water of hydration and are converted to anhydrous oxides.

In the present “sludge-only” mode, monosodium titanate (MST) and chemical species used to remove Cs from salt solution are not part of the HLW feed to the DWPF. However, all three proposed alternatives for the SWPF use MST to sorb soluble alpha contaminants and strontium from HLW salt solution. Thus at least one input stream containing MST is sent to the DWPF for all three alternatives. Reaction stoichiometry in

the melter for MST species is included below. Reaction stoichiometry in the melter for other materials unique to each alternative is shown here and in Section 6.

<u>Reactants</u>	<u>Products</u>	<u>%Rxn</u>
4 NaNO ₃ + 8 NaCOOH	6 Na ₂ O + 2 NO + N ₂ + 8 CO ₂ + 4 H ₂ O	
4 KNO ₃ + 8 NaCOOH	3 K ₂ O + 3 Na ₂ O + 2 NO + N ₂ + 8 CO ₂ + 4 H ₂ O	
4 CsNO ₃ + 8 NaCOOH	3 Cs ₂ O + 3 Na ₂ O + 2 NO + N ₂ + 8 CO ₂ + 4 H ₂ O	
4 NaNO ₂ + 2 NaCOOH	3 Na ₂ O + 4 NO + 2 CO ₂ + H ₂ O	
4 Al(NO ₃) ₃ + 24 NaCOOH	2 Al ₂ O ₃ + 12 Na ₂ O + 6 NO + 3 N ₂ + 24 CO ₂ + 12 H ₂ O	
2 NO (v) + O ₂ (v)	2 NO ₂ (v)	
2 Na ₂ SO ₄ + 2 NaCOOH	3 Na ₂ O + 2 SO ₂ + 2 CO ₂ + H ₂ O	
2 Fe ₂ O ₃ + 2 NaCOOH	4 FeO + Na ₂ O + 2 CO ₂ + H ₂ O	(20%)
2 NaCOOH	Na ₂ O + CO + CO ₂ + H ₂	
2 KCOOH	K ₂ O + CO + CO ₂ + H ₂	
4 NH ₄ COOH + 3 O ₂	2 N ₂ + 8 H ₂ O + 2 CO + 2 CO ₂ + 2 H ₂	
Mn(COOH) ₂	MnO + CO + CO ₂ + H ₂	
Ni(COOH) ₂	NiO + CO + CO ₂ + H ₂	
Ca(COOH) ₂	CaO + CO + CO ₂ + H ₂	
UO ₂ (COOH) ₂ + O ₂	U ₃ O ₈ + CO + CO ₂ + H ₂	
Cu(COOH) ₂	CuO + CO + CO ₂ + H ₂	
Co(COOH) ₂	CoO + CO + CO ₂ + H ₂	
Zn(COOH) ₂	ZnO + CO + CO ₂ + H ₂	
Mg(COOH) ₂	MgO + CO + CO ₂ + H ₂	
Sr(COOH) ₂	SrO + CO + CO ₂ + H ₂	
2 CsCOOH	Cs ₂ O + CO + CO ₂ + H ₂	
Na ₂ C ₂ O ₄	Na ₂ O + CO ₂ + CO	
CaC ₂ O ₄	CaO + CO ₂ + CO	
CaF ₂ + Na ₂ O	CaO + 2 NaF	
2 HgO	2 Hg(v) + O ₂	
Hg	Hg(v)	
Cs ₂ O	Cs ₂ O(v)	(10%)
2 MnO ₂	MnO + O ₂	
Pd(NO ₃) ₂	Pd + 2 NO + 2 O ₂	
2 MOH	M ₂ O + H ₂ O	(M = Na, K, Cs)
M(OH) ₂	MO + H ₂ O	(M = Mg, Ca, Sr, Ni, Co, Cu)
2 M(OH) ₃	M ₂ O ₃ + 3 H ₂ O	(M = Al, Fe, Lanthanides)

Additional components from SWPF:

MST Sorption (all alternatives)



<u>Reactants</u>	<u>Products</u>	<u>%Rxn</u>
2 UO ₂ (NaTi ₂ O ₅) ₂	2 UO ₂ + 8 TiO ₂ + 2 Na ₂ O + O ₂	
2 NpO ₂ (NaTi ₂ O ₅) ₂	2 NpO ₂ + 8 TiO ₂ + 2 Na ₂ O + O ₂	
Sr(NaTi ₂ O ₅) ₂	SrO + 4 TiO ₂ + Na ₂ O	
2 H(NaTi ₂ O ₅)	H ₂ O + 4 TiO ₂ + Na ₂ O	
<u>STTP Alternative</u>		
2 B(OH) ₃	B ₂ O ₃ + 3 H ₂ O	
2 (C ₆ H ₅)B(OH) ₂ + O ₂	2 C ₆ H ₅ OH + B ₂ O ₃ + H ₂ O	
2 C ₆ H ₆ + 2 O ₂	2 C ₆ H ₅ OH	
2 C ₁₂ H ₁₀ + O ₂ + 2 H ₂ O	4 C ₆ H ₅ OH	
4 C ₆ H ₅ OH + 19 O ₂	12 CO + 12 CO ₂ + 6 H ₂ + 6 H ₂ O	(85%)
<u>CSTIX Alternative</u>		
Oxides of Si, Na, Ti, other metals + water	See Table 6.3-10 for CST oxide composition	

Modeling Bases – The simplified set of reactions shown below are used to convert metal salts and other compounds into metal oxides and volatile gases during vitrification in the melter for the three proposed SWPF alternatives.

<u>Reactants</u>	<u>Products</u>
2 B(OH) ₃	B ₂ O ₃ + 3 H ₂ O
2 C ₆ H ₆ + 15 O ₂	12 CO ₂ + 6 H ₂ O
2 CsCOOH + O ₂	Cs ₂ O + 2 CO ₂ + H ₂ O
2 KCOOH + O ₂	K ₂ O + 2 CO ₂ + H ₂ O
2 NaCOOH + O ₂	Na ₂ O + 2 CO ₂ + H ₂ O
2 NH ₄ COOH + O ₂	2 NH ₃ + 2 CO ₂ + 2H ₂ O
2 Cu(NO ₃) ₂	2 CuO + 4 NO ₂ + O ₂
4 HNO ₃	4 NO ₂ + 2 H ₂ O + O ₂
2 HCOOH + O ₂	2 CO ₂ + 2 H ₂ O
2 NaOH	Na ₂ O + H ₂ O
4 NaNO ₃	2 Na ₂ O + 4 NO ₂ + O ₂
4 NaNO ₂ + O ₂	2 Na ₂ O + 4 NO ₂
2 NaTi ₂ O ₅ H	Na ₂ O + 4 TiO ₂ + H ₂ O

5.3.5.4.3 Technical Bases for the RCT Chemistry

Aqueous waste streams from the SRAT, SME and the Offgas Condensate Tank (OGCT) are combined in the Recycle Collection Tank (RCT) in the DWPF. Water evaporated from the SRAT and the SME is recycled through the SMECT to the RCT. All water fed to the melter goes to the melter off-gas stream. Steam Atomized Scrubbers and the Film Cooler also add 1000 pph water to the melter off-gas stream. Water in the melter off-gas

is condensed and collected in the OGCT and transferred to the RCT. Decontamination waste adds another 340 pph of water to the RCT.

Prior to returning this waste to the H Tank Farm, an excess of NaOH and NaNO₂ is added to the waste in the RCT to meet the WAC for waste receipts into the Tank Farm. The quantities of caustic and nitrite added are based on the DWPF Waste Compliance Plan and operating experience to yield a solution containing at least 0.5 M free hydroxide and 0.045 M nitrite. These inhibitor concentrations assure acceptably low corrosion rates of the carbon steel waste tanks. Chemical reactions during neutralization of the RCT solution are shown below.

<u>Reactants</u>	<u>Products</u>
HCOOH + NaOH	NaCOOH + H ₂ O
HCl + NaOH	NaCl + H ₂ O
HF + NaOH	NaF + H ₂ O
Pu(COOH) ₄ + 4 NaOH	PuO ₂ + 4 NaCOOH + 2 H ₂ O
UO ₂ (COOH) ₂ + 2 NaOH	UO ₂ (OH) ₂ + 2 NaCOOH
HgCl ₂ + 2 NaOH	HgO + 2 NaCl
Hg ₂ Cl ₂ + 2 NaOH	Hg + HgO + 2 NaCl + H ₂ O
Hg ₂ I ₂ + 2 NaOH	Hg + HgO + 2 NaI + H ₂ O
KCOOH + NaNO ₃	KNO ₃ + NaCOOH
NH ₄ COOH + NaNO ₃	NH ₄ NO ₃ + NaCOOH
CsCOOH + NaNO ₃	CsNO ₃ + NaCOOH
CsCl + NaNO ₃	CsNO ₃ + NaCl
Cs ₂ O + 2 NaNO ₃ + H ₂ O	CsNO ₃ + NaOH

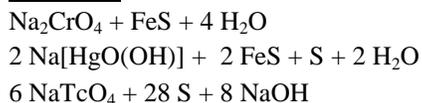
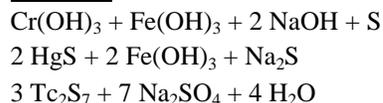
Modeling Bases - Water evaporated in the SRAT, SME and melter goes directly to the RCT in the simplified Speedup model. Caustic and inhibitor are added to the RCT to produce a recycle solution that is 0.5 M NaOH and 0.045 M NaNO₂.

5.3.5.5 Saltstone Production Chemistry

As noted in Section 5.3.1.3, the ratio of premixed dry materials to the mass of water in salt solution is controlled during the production of saltstone. An acceptable saltstone product has been demonstrated with salt solution ranging from about 20 wt % to 32 wt % salt, corresponding to a specific gravity ranging from 1.18 to 1.32 and a sodium molarity ranging from about 3.5 M to 6 M. Bleed water during curing is minimized by controlling the water-to-premix mass ratio in the range of 0.52 to 0.60 (presently set at 0.57, based on a blended solution of ETF evaporator bottoms and the startup product from ITP). The density of cured saltstone ranges between 1.70 and 1.80 kg/L. (Ref. 14, 27)

The principal chemical reaction in the production of saltstone is hydration of the dry materials that are added to produce a solid waste form. In addition to hydration reactions between the water in salt solution and the dry materials, elemental sulfur and iron(II) sulfide in the slag component react with trace soluble contaminants in the salt solution. These reactions convert these species into insoluble hydroxides or sulfides within the saltstone matrix, thus reducing their solubility and their propensity to leach from the solid

waste form after disposal. Of particular interest, are the reactions between chromate, soluble mercury and pertechnetate. (Ref. 14)

Reactants**Products**

The reactions of chromate and mercury assure that saltstone will pass the TCLP and thus be classified as non-hazardous waste, in accord with EPA requirements. Conversion of soluble sodium pertechnetate to an insoluble sulfide assures this long-lived radioactive contaminant will also be converted to a less soluble chemical form, thus reducing the long-term radiological impact of this contaminant in saltstone. (Ref. 14)

Modeling bases -To model saltstone production for the three alternatives, the mass flow ratio of water in decontaminated salt solution to dry premix is set at 0.57 to calculate the overall mass flow of saltstone grout generated. The volumetric rate of saltstone production is then calculated based on an assumed specific gravity of 1.70 for solid saltstone (measured sp. g. for saltstone ranges from 1.70 to 1.80).

5.3.6 Basis for Other Waste Generated in the SWPF

Other solid waste (excludes saltstone) and liquid byproduct waste generated from the three alternatives are summarized in Table 5.3-10 below. The DWPF portion of the SRS Forecast for FY2000 (Ref. 30) and other information from DWPF operations serve as the bases for these projected wastes.

Table 5.3-10 Waste Generated in SWPF

Waste Classification	Description / Comments	Waste Quantity
Low-Level Solid Waste (LLW)	Job-control waste, sample vials, other contaminated solids packaged in B-25 boxes	125 m ³ / yr
Transuranic Waste (TRU)	Alpha concentration and SWPF inventory is projected to be too low to generate any solid waste that would be classified as TRU.	None
Hazardous Waste (HW)	Oils, grease, solvents sorbed on solid, hazardous metals or chemicals, other materials classified as HW that must be packaged and stored by SWD until final treatment and disposal can be completed.	1 m ³ / yr
Mixed Waste (MW)	Hazardous waste potentially contaminated with low concentrations of radioactive species that must be packaged and stored by SWD until final treatment and disposal can be completed.	35 m ³ / yr
Process Equipment classified as LLW	Failed equipment to be decontaminated and transferred to SWD for disposal as LLW.	2 Jumpers / yr 1 motor / yr 1 agitator / 5 yr
Process Equipment from STTP process classified as MW	Failed filter unit due to leak, break or plug. Packaged and stored as MW by SWD until final treatment and disposal can be completed.	1 unit / 5 yr

Waste Classification	Description / Comments	Waste Quantity
Filtration Equipment from Alpha / Sr Sorption from CSSX or CSTIX classified as LLW	Failed filter unit due to leak, break or plug.	1 unit / 5 yr
Benzene from SPC (assumes acid hydrolysis process is included in SWPF)	Transferred to CIF for incineration or processed by off-site waste vendor. Credited as fuel for the incinerator.	188 m ³ / yr (49.6 kgal / yr)
Spent Solvent from CSSX	Transferred to CIF for incineration.	3.8 m ³ / yr (1 kgal / yr)
Process Equipment from CSTIX process classified as LLW	Failed ion exchange column due to leak or plug. Size reduction unit (grinder) used to reduce size of CST resin. Failed equipment must be decontaminated, packaged and transferred to SWD for disposal as LLW.	1 IX column / 5 yr 1 grinder / 5 yr
Spent Mercury Ion Exchange Resin	Mercury removal has been eliminated from the CSTIX and CSSX alternatives. If subsequent process evolution and/or regulatory restrictions require mercury removal, then 1 column volume would be consumed every two years. Spent resin requires washing, dewatering and packaging for disposal as LLW.	None

The forecasted mix of solid waste for the DWPF in FY2000 is as follows (Ref. 30):

- *Low Level Waste*: 121.1 cubic meters/yr
- *Hazardous Waste*: 0.95 cubic meters/yr
- *Mixed Waste*: 33.8 cubic meters/yr
- *Failed Equipment*: The DWPF solid waste forecast does not include any failed equipment (jumpers, motors, agitators, melters, etc.), but DWPF has 6 jumpers and three motors that must also be decontaminated, packaged and sent to E Area for disposal as LLW that have required replacement in the past 3 years. The DWPF forecast and experience with equipment failures is used as the basis for the quantities of failed process equipment that will be transferred to Solid Waste as LLW for final treatment and disposal (or treatment and shipment to another disposal site).

Benzene from Acid Hydrolysis: If the STTP alternative is chosen, then benzene will be generated as a byproduct stream. Benzene will be recovered and stored in the SWPF until it can be disposed by an off-site waste vendor or incinerated on site. The annual volume of benzene generated is based on 17.5 gpm at 100% attainment, corresponding to 9,200,000 gallons of 6.44 M salt solution annually. This processing rate consumes 1 million liters of 0.55 M NaTPB solution per year. The benzene produced is 49,600 gallons per year.

- *Spent solvent from solvent extraction:* If the CSSX alternative is chosen, then spent solvent will be generated as a consequence of radiolytic degradation of the components in the solvent blend. Some diluent (Iso-Par LTM) is consumed as part of normal operations to clean up the solvent. Although the solvent system appears to be relatively stable to radiolysis, limited experience necessitates a conservative approach in projecting annual consumption. Accordingly, a complete change out of the solvent system on an annual basis is assumed for the CSSX alternative to provide a bounding value for organic waste generated from this alternative.

5.3.7 Supplemental Environmental Impact Statement (SEIS)

The Draft SEIS for the salt disposition facility includes the alternatives as described in this document. The evaluation in the SEIS compares the committed life cycle emissions and resulting dose to the surrounding population from each alternative process. Emissions are estimated based on preliminary design information for construction, operation, and process accidents. Chemistry and radionuclide inventories are based on the characterization of process streams as presented in this document and some supplementary data (Ref. 31). Accidental releases are based on historical information on similar processes and facilities (Ref. 32). The resulting population doses from these emission estimates are calculated by modeling the environmental dispersion of the emission (Ref. 33).

For purposes of comparison, a “no action” alternative is included in the SEIS evaluation in order to indicate what environmental impact might occur if none of the alternatives are completed. The SEIS indicates that the “no action” alternative is less desirable than any of the process alternatives. Under the no action alternative, SRS will be unable to meet the commitments of the Federal Facilities Compliance Agreement. Each of the process alternatives produces only minor environmental changes (Ref. 33).

6.0 DECISION PHASE SWPF ALTERNATIVES

6.1 Small Tank TPB Precipitation (STTP)

6.1.1 Process Description

In the STTP process, soluble ions of cesium, potassium and ammonium are precipitated as insoluble TPB salts. Soluble mercury salts react with TPB to form insoluble diphenylmercury. Strontium, uranium, neptunium, and plutonium are sorbed on solid monosodium titanate. The resulting slurry, which now contains most of the radionuclides as insoluble solids, is filtered to concentrate the solids. After washing the solids to reduce the concentration of soluble sodium salts in the slurry, the precipitate is combined with formic acid and cupric nitrate to decompose all phenylborates. The benzene generated by phenylborate decomposition is stored until it can be burned in the CIF. The radioactive precipitate hydrolysis aqueous (PHA) slurry is transferred and stored until it can be incorporated into glass in the DWPF. Decontaminated salt solution, or filtrate, containing primarily sodium salts of hydroxide, nitrate, and nitrite, is transferred to the SPF located in Z Area for processing and subsequent disposal in the SDF vaults as saltstone.

6.1.1.1 Precipitation

Salt solution is pumped from the F/H Tank Farms and is decontaminated in a series of two continuously stirred tank reactors (CSTR) shown in Figure 6.1-1 (Ref. 34). In the first CSTR, salt solution is mixed with process water, recycled wash water, a solution of sodium tetraphenylborate ($\text{NaTPB} = \text{NaB}(\text{C}_6\text{H}_5)_4$), and monosodium titanate slurry ($\text{MST} = \text{NaTi}_2\text{O}_5\text{H}$).

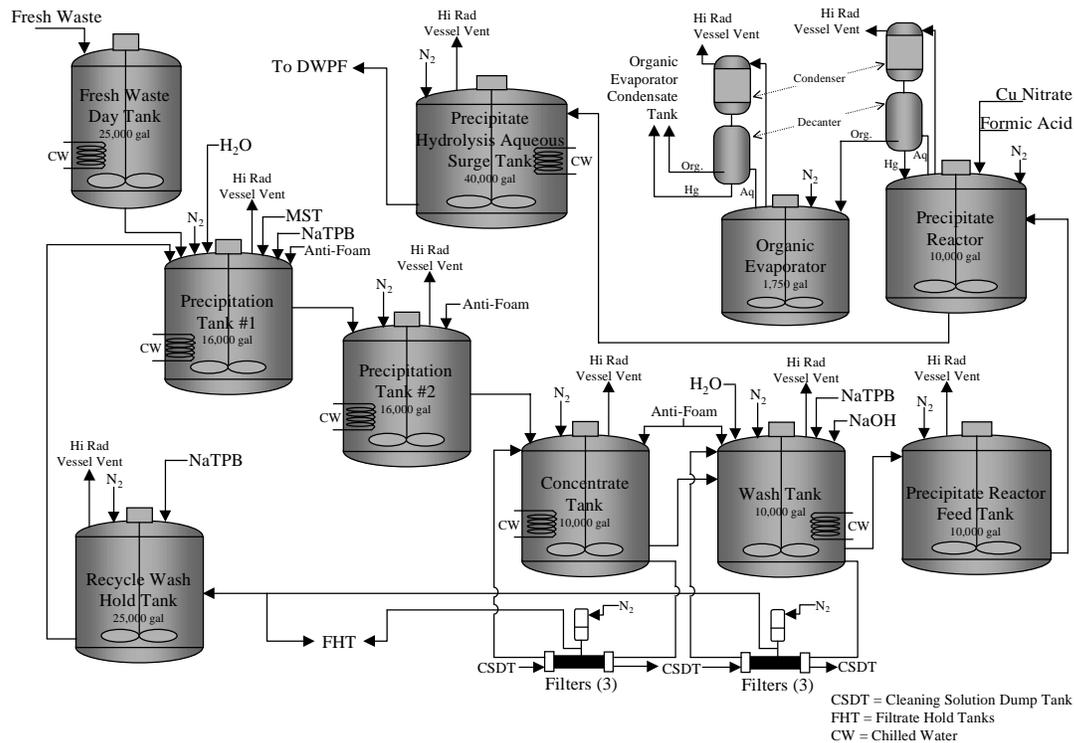


Figure 6.1-1 STTP Simplified Flow Diagram

Process water or recycled wash water is added to reduce the total sodium content to 4.7 molar to optimize the precipitation reaction. The recycled wash water also contains some of the excess NaTPB. The most abundant radionuclide present in salt solution is ^{137}Cs . Sodium tetraphenylborate is added to precipitate the cesium as a tetraphenylborate salt. The non-radioactive potassium, cesium, ammonium and mercury are also precipitated in this process. The potassium ion concentration is nominally 100 times that of the total cesium concentration, although this ratio can vary widely. An excess of NaTPB is added to suppress the solubility of cesium. Monosodium titanate is added to adsorb the soluble strontium, plutonium, and uranium ions if these radionuclides are present in quantities exceeding the limit for transfer to the SPF.

6.1.1.2 Concentration

The slurry exiting CSTR #2 contains about 1 wt% of insoluble sludge, MST and precipitated tetraphenylborate solids after precipitation. The slurry is transferred from the second CSTR to the Concentrate Tank where it is concentrated continuously by cross-flow filtration to approximately 10 wt% TPB solids. Filtrate is transferred to the Decontaminated Salt Solution Storage Tank prior to being transferred to the SPF. When 4000 to 5000 gallons of 10 wt% TPB precipitate slurry is accumulated in the Concentration Tank, it is transferred to the Wash Tank.

6.1.1.3 Precipitate Washing

The slurry is washed to remove soluble sodium salts and recover the excess NaTPB by adding process water and removing spent wash water by cross-flow filtration. The spent wash water can be transferred to either the Recycle Wash Hold Tank for use in subsequent batches as dilution water or to the Decontaminated Salt Solution Storage Tank prior to transfer to the SPF. The washing endpoint is set at 0.01 M NO_2^- . (Ref. 4) All of the vessels used to prepare washed precipitate slurry for subsequent processing are stainless steel to eliminate corrosion concerns.

6.1.1.4 Precipitate Hydrolysis

The washed precipitate is then transferred to the Precipitate Reactor Feed Tank (PRFT). Slurry is then fed from the PRFT to the Precipitate Reactor (PR) at a controlled rate where it is reacted with formic acid containing cupric nitrate as a catalyst. The hydrolysis reactions decompose most of the phenylborates into benzene. The benzene is distilled from the PR, condensed and decanted from aqueous condensate. Small amounts of aniline, diphenylamine, phenol and other organic species form from various side reactions that also distill from the PR and are condensed with the benzene. Aqueous condensate from hydrolysis is returned to the PR. The Precipitate Hydrolysis Aqueous (PHA) phase remaining in the PR at the end of hydrolysis, which contains the radioactive contaminants, is stored in the PHA Surge Tank until it can be transferred to the DWPF to be solidified as a component of HLW borosilicate glass. The benzene and other organics are transferred to the Organic Waste Storage Tank (OWT) and stored until they can be burned in the CIF. (Ref. 4, 5)

6.1.1.5 Assumptions for Modeling Filter Washing

For the filter washing model, 2 wash cycles are assumed for each filter per year. There are a total of 6 filters in the system. Three are associated with the Concentration loop and three as part of the Washing loop. A filter washing cycle consists of:

- 4000 gal. Inhibited water rinse
- 2000 gal. Oxalic acid wash
- 4000 gal. Inhibited water rinse
- 1000 gal. Caustic (2%) wash

6.1.1.6 Benzene Generation

After precipitation, NaTPB, KTPB and CsTPB undergo radiolytic degradation (See Section 6.1.3.4) and, under certain conditions, catalytic degradation (See Section 6.1.3.5). MTPB decomposes to aromatic organics (benzene, biphenyl, and triphenyl and trace amounts of substituted derivatives) and salts of sodium and boron. The exact mechanism for the catalytic degradation is not completely understood. The catalytic decomposition of TPB results in the formation of triphenylborane, diphenylborinic acid, phenylboric acid, and benzene. The degradation intermediates also decompose catalytically to form benzene. Testing has demonstrated that catalysis with copper ions and sludge solids (Pd(0) as reduced from soluble Pd has been identified as a primary catalyst in the sludge solids) can significantly increase the rate of decomposition of tetraphenylborate slurries.

The kinetics for these decomposition mechanisms is described in Sections 6.1.3.4 and 6.1.3.5.

The benzene generation is set at 10 mg/L-hr when soluble NaTPB is present and 1 mg/L-hr when only KTPB and CsTPB are present. These are set at these maximum values to match the current test results by SRTC for decomposition at 25°C (Ref. 35). The STTP TPB Precipitation operating conditions are summarized in Table 6.1-1.

Table 6.1-1 Summary of STTP Operating Parameters

Parameter	Operating Specification
Excess TPB	60 mole%
Na ⁺ Concentration after precipitation	4.7 M
¹³⁷ Cs Concentration after precipitation	< 45 nCi/g
Alpha Concentration after MST sorption	<18 nCi/g
Maximum Temperature	25 °C
Filtrate Flow rate during Concentration	24 gpm
Filtrate Flow Rate during Washing	5 gpm
Washing Endpoint	0.01 M NO ₂ ⁻
Cu ⁺ concentration during hydrolysis	950 ppm
Formic acid after hydrolysis	0.25 M
Final organic concentration (phenylboric acid)	< 53 ppm
Final diphenylmercury	< 260 ppm

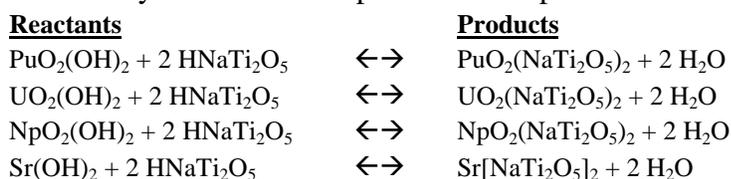
6.1.2 Research and Development

The scope of the research and development for the STTP process has focused on five areas: alpha removal kinetics, precipitation kinetics, filtration of the tetraphenylborate slurry, decomposition kinetics and impact of coupled operation within the DWPF.

The precipitation kinetic research was conducted to demonstrate the ability to operate the precipitation process in a continuous mode and to verify that the CSTRs were sized properly for the necessary Cs decontamination. The filtration research was conducted to insure that historical filter performance data was applicable to the proposed continuous operation and to insure that the filters in the STTP process were sized properly. The decomposition kinetic research was conducted to determine the effect of tetraphenylborate decomposition on the precipitation process efficiency. The DWPF work focused on two areas: (1) the impact on hydrolysis of processing precipitate that may have aged for up to four months since washing, and (2) glass variability studies with increased PHA and MST concentrations.

6.1.2.1 Strontium and Alpha Removal Kinetics

Reaction stoichiometry assumed for Alpha and Sr sorption on MST is shown below:



The alpha removal kinetic studies confirmed that the CSTR size specified during Phase III would produce the necessary alpha decontamination. Experimental work (Ref. 8, 9, 10) to examine the kinetics of Strontium (Sr), Plutonium (Pu), Uranium (U) and Neptunium (Np) removal by adsorption onto Monosodium Titanate successfully reduced Sr and the Transuranics (TRU) to concentrations that are within WAC limits for the SPF when 4.5 M Na⁺ salt solutions are treated with 0.4 g/L MST. The WAC limits for transfer to the SPF for ¹³⁷Cs, ⁹⁰Sr, total alpha and ²³⁷Np are shown in Table 5.3-4, while the decontamination requirements for these species are described in Table 5.3-8.

Data for Sr, Pu, and U removal at 4.5 M Na⁺ with 0.2 and/or 0.4 g/L MST (Ref. 8) are shown in Figures 6.1-2 through 6.1-6. U has such a low specific activity that U removal is not required. The blending scheme developed for Revision 12 of the HLW System Plan reduces the maximum expected Np237 concentration to 0.043 nCi/g of Saltstone feed. The limit is 0.03 nCi/g and the expected DF is 3. Therefore, blending appears to be adequate to allow Saltstone feed to meet its Np-237 requirement.

Strontium Removal

Figures 6.1-2 and 6.1-3 show that Sr removal is very rapid and requires less than 30 minutes to obtain the required DFs in a batch mode. Rapid Sr removal was confirmed in the 20-L CSTR tests at ORNL (Ref. 36). In Figures 6.1-2 and 6.1-3, for a starting Sr concentration of 90 µg/L, a concentration of 18 µg/L is required for a DF of 5 (DF for average waste) and 3.5 µg/L is required for a DF of 26 (DF for bounding waste).

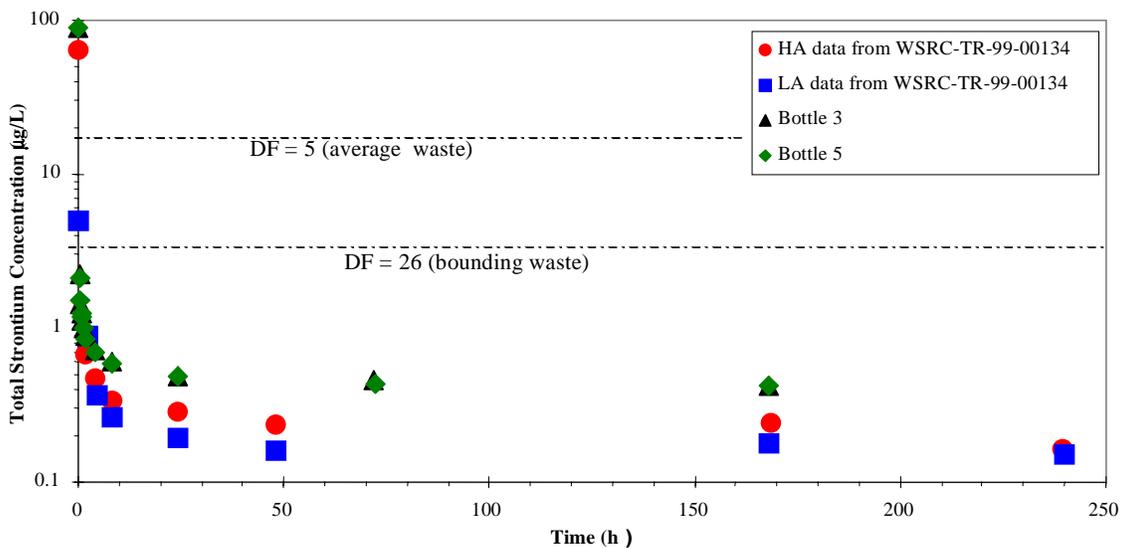


Figure 6.1-2 Comparison of Strontium Concentration Tests at 4.5 M Na and 0.2 g/L MST

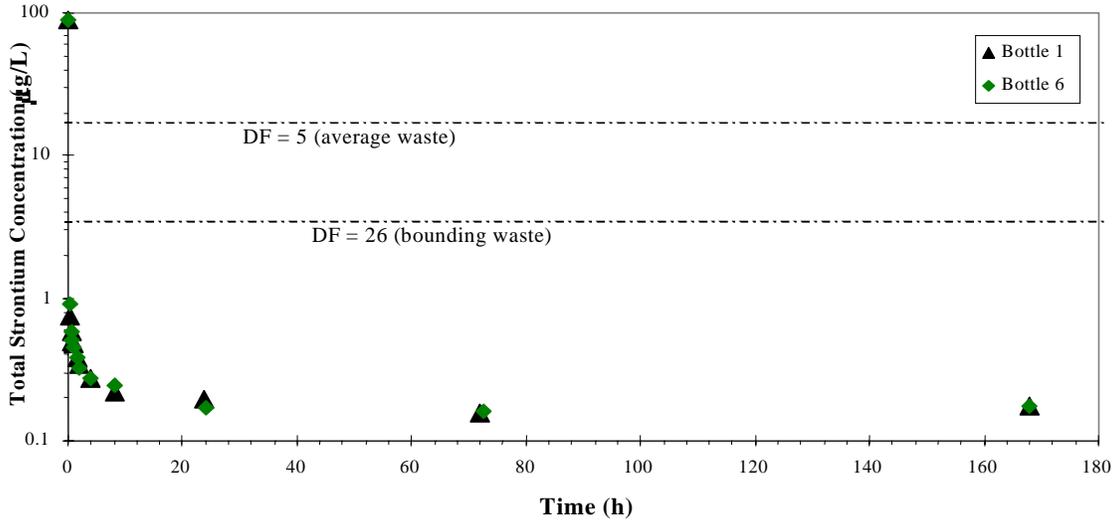


Figure 6.1-3 Comparison of Strontium Concentration Tests at 4.5 M Na and 0.4 g/L MST

Plutonium and Uranium Removal

Pu removal is significantly slower than Sr removal. Starting at a concentration of 64 µg/L, a concentration of 5.3 µg/L is required for a DF of 12 (DF for average waste), while 1.15 µg/L is required for a DF of 55 (DF for bounding waste). As shown in Figure 6.1-4, about 4 hours is required in a batch test to achieve a DF of 12 but it takes about 90 hours to reach a DF of 55. The residence time in the CSTRs totals about 20 hours, so Pu would be expected to reach at least a DF of 12. However, blending will likely be necessary to smooth out Pu peaks in the salt solution feed to any of the processes.

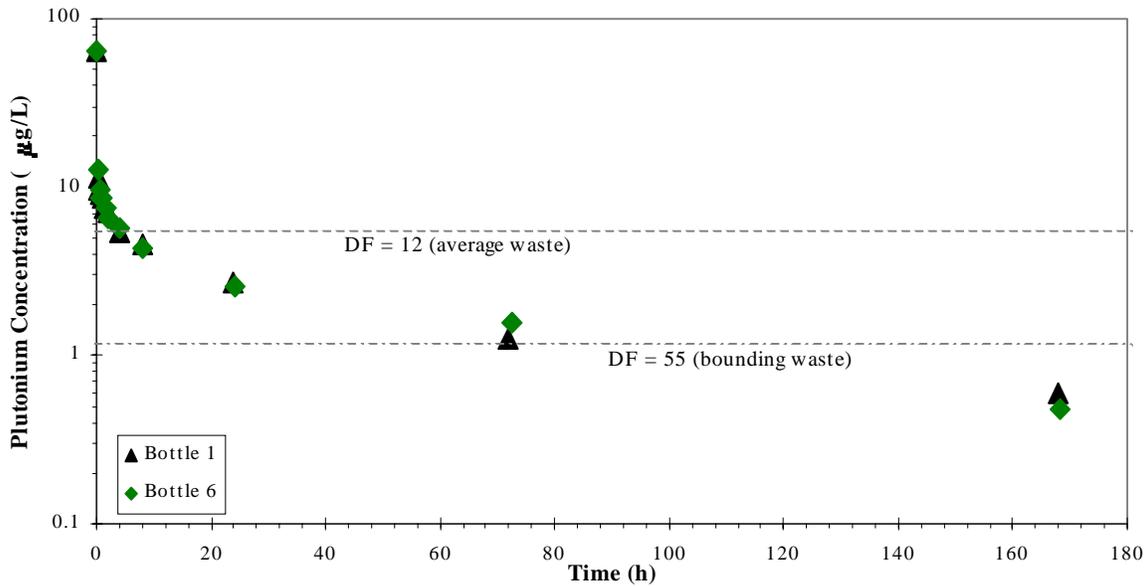


Figure 6.1-4 Comparison of Plutonium Concentration Tests in 4.5 M Na and 0.4 g/L MST

Additional testing using real waste (Ref. 37) shows Pu bounding waste conditions are readily met. The real salt waste solution contained plutonium at 63900 dpm/mL for ^{238}Pu and 1860 dpm/mL for $^{239/240}\text{Pu}$ (after accounting for the dilution the salt feed undergoes in the reaction). An analysis of the Plutonium-238 data (Figure 6.1-5) shows that the plutonium concentration dropped rapidly, reaching an average concentration of $1.33\text{E-}05$ mg/L. This in turn gives an average DF of 126. The plutonium-239/240 data is more difficult to analyze due to the inability to deconvolute the two isotopes; but following the same rationale, achieved an average DF of 83.3.

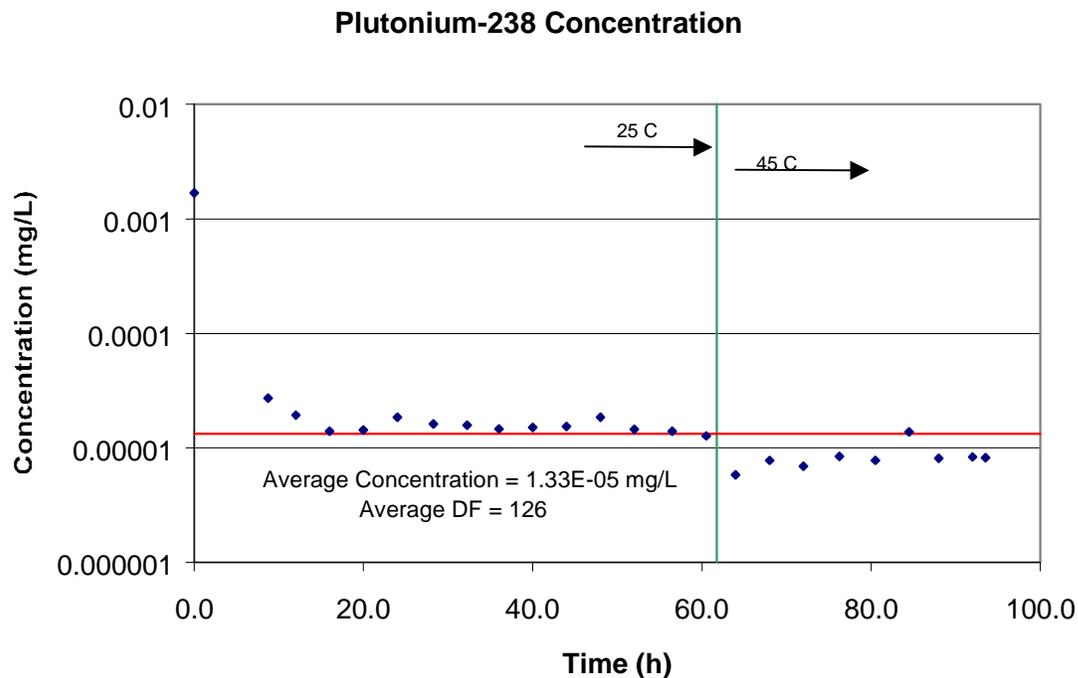


Figure 6.1-5 Real Waste Testing, Pu Concentration over Time

In Figure 6.1-6, the uranium kinetics are very similar to the Pu kinetics. The “knee” for both curves occurs at approximately the same time (about 4 to 6 hours). The measured equilibrium DF for uranium with 0.4 g/L MST was 1.5. Uranium was included in the simulant feed in the ORNL 20-L CSTR tests. In these tests, a DF of ~ 2 was obtained in the two-CSTR system with a total residence time of 16 hours (two-thirds of design). (Ref. 36)

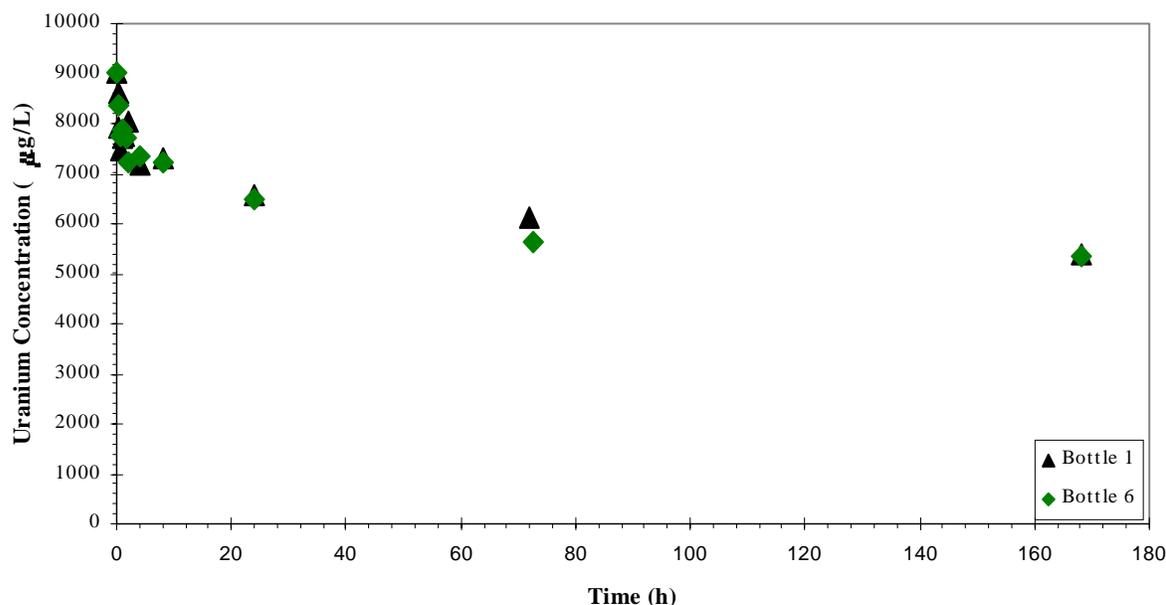


Figure 6.1-6 Comparison of Uranium Concentration Tests at 4.5 M Na and 0.4 g/L MST

6.1.2.2 Precipitation Kinetics

The rates of cesium and potassium precipitation using tetraphenylborate (TPB) from moderately concentrated (3.5 to 7.0 M Na⁺) mixed salt solutions have been studied (Ref. 38). The solutions tested are made up to simulate concentration ranges of sodium, potassium and cesium expected in real waste solutions. The ability to estimate fundamental rate constants is confounded because both potassium and cesium are competing for TPB ion and the solubility of NaTPB is limited at the relatively high sodium concentrations in these solutions. In these tests, the re-dissolution rate of NaTPB clearly influenced the rates of potassium and cesium precipitation. The discussion that follows relates to sodium concentration of 4 to 5 M, which is the range of interest.

Initial experiments at SRTC were done in a single 500-mL CSTR with an 8-hour mean residence time. These tests were run at 4.7 M [Na], with a 60 % molar excess of NaTPB (i.e. 1.6 times the sum of the cesium and potassium molarity). The reaction started with cesium and potassium pre-reacted so the concentration of these increased with time. Ratios of cesium concentration in the feed to the steady state cesium concentration in the product (Decontamination Factor or “DF”) were in the range of 10 to 20, which was unexpectedly low by a factor of about 10 based on estimates from the batch data (Ref. 39). NaTPB was fed at 0.55 M, near its solubility limit in water.

Oak Ridge National Laboratory (ORNL) conducted larger scale (20-L CSTR) tests. These tests were a more complete demonstration of the process. The bench scale system included two reactors in series and tanks with crossflow filters for concentrating and washing the solids. The first test was operated open loop; that is, the concentrated solids were not washed and recycle wash water was provided by a simulant. NaTPB was added

at 1.60 moles per mole of potassium plus cesium (“60 % molar excess”). A stoichiometric quantity of NaTPB was fed as a 0.55 M solution while the excess was provided by NaTPB in the simulated recycle stream. The mean residence time was 8 hours. The DF for this test was > 40,000 in the concentrate tank filtrate (decontaminated salt solution) (Ref. 36, 40).

SRTC offered an explanation of the difference between the SRTC and ORNL results, based on the initial precipitation of NaTPB as it is fed. In the case of the SRTC tests, all of the NaTPB was added at 0.55 M. Using an “expanding drop” model, which follows the diffusion of the NaTPB into the bulk volume of the reactor, they estimated that only 7 % of the NaTPB remained in solution (denoted as 7% utility of the NaTPB). The combination of high Na molarity and potassium concentration (from the salt solution) and the high NaTPB concentration (from the NaTPB feed) causes the NaTPB to precipitate. Further, they determined in separate experiments that the re-dissolution rate of solid NaTPB is relatively slow, so that it did not re-dissolve to precipitate potassium and cesium in the time it remained in the reactor (Ref. 41). However, the utility of the NaTPB added at a lower concentration by combining with the recycle water before adding it to the reactor is much greater in the tests at ORNL – estimated to be 70%. These phenomena were modeled semi-quantitatively, as discussed in Section 6.1.3.2. The results of this modeling provides sufficient understanding of the reaction rates to size reactors for a full scale Salt Disposition Facility.

ORNL ran a second closed-loop test in which the concentrated precipitate was washed and the wash water recycled. The feed also contained the enhanced catalyst system (ECC) with 5X the Pd (Ref. 36). This test lasted approximately 10 days and produced four batches of concentrated precipitate. The DF for the decontaminated salt solution varied from 30,000 to 60,000 (See Figure 6.1-7). Generally, the process operated smoothly except that only 11% to 29% of the excess TPB was recovered during washing, depending on the rate of wash water addition. The cause of the low NaTPB recovery in the wash step is not known, but is likely due to inadequate mixing during washing. In fact, it was observed that the surface in the wash tank was not moving during washing, indicative of poor mixing.

A mixed crystalline form that is not readily dissolved – even at low Na concentrations – may have also formed. NaTPB was added to the wash water to preserve the target excess TPB in the CSTRs. Sr removal was rapid and the U DF was as expected. HPLC analyses of the decontaminated salt solution and the recycle wash water indicated no TPB decomposition caused by the ECC with 5X Pd.

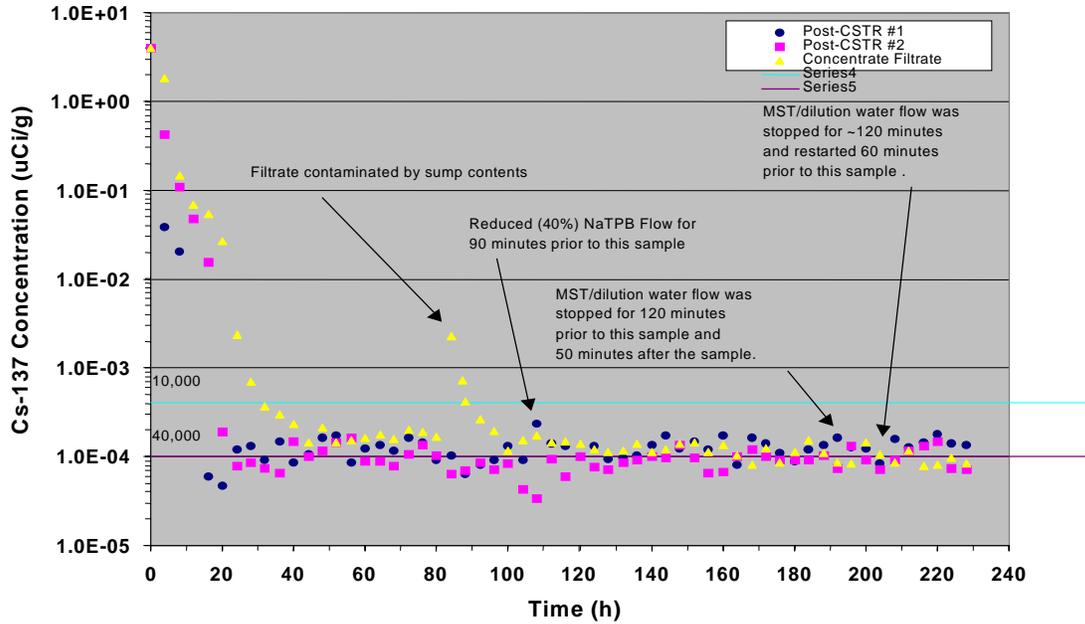


Figure 6.1-7 ORNL Integrated Demonstration Test 2

ORNL conducted a third test to examine the effectiveness of an improved antifoam (IIT B52) in minimizing foam formation and to determine if its presence had a deleterious effect on the removal of Cs, Sr and U from simulated waste (Ref 42). To more aggressively test the antifoam, the slurry in each vessel was mixed at 1200 to 1250 rpm while maintaining the temperature at 25°C. The antifoam was pumped continuously into each of the process vessels with syringe pumps. There was no evidence of foam formation during the test. Cesium, strontium, and uranium removal performance in this test indicated that the antifoam did not interfere with the precipitation reaction. Cesium DFs for the product filtrate ranged between 21,000-59,000, exceeding 40,000 consistently by the end of the test (See figure 6.1-8). Strontium DFs ranged from 30-100, while the uranium DF reached 5 by the end of the test.

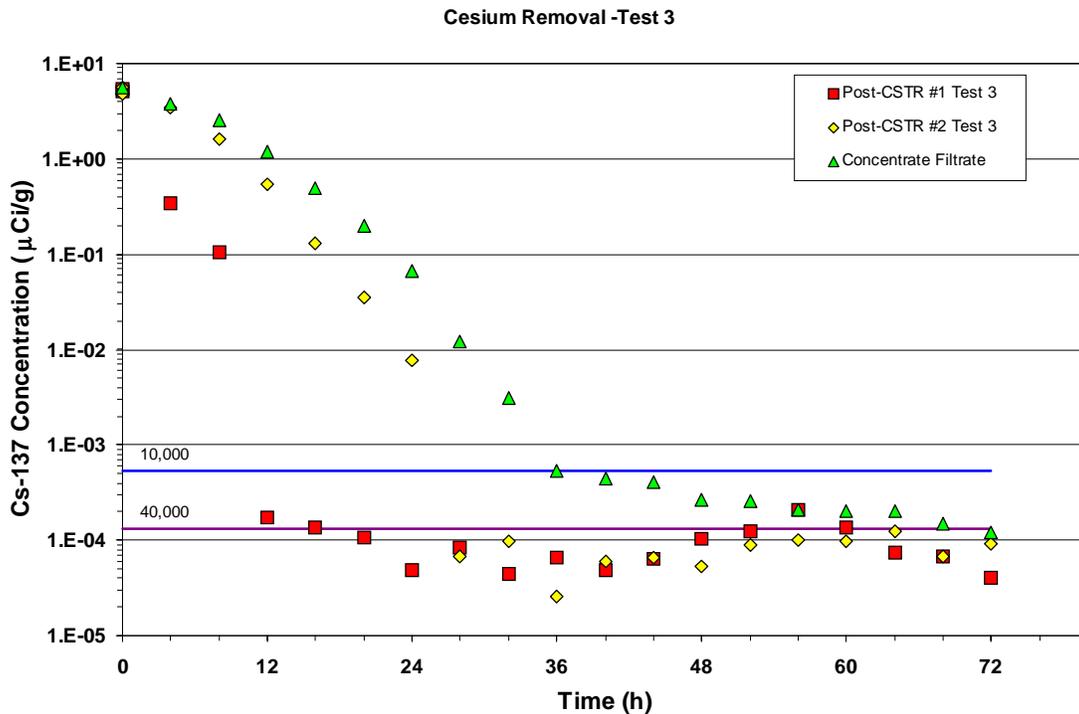


Figure 6.1-8 Cesium Results from ORNL Test 3

In October of 2000, ORNL conducted a fourth test to verify that the small tank tetraphenylborate process could obtain DF while the TPB was actively decomposing (Ref 43). Antifoam was added to minimize foam formation. A recommended catalyst system (RCS) developed by SRTC was added during the test. The RCS consisted of Pd(0) on alumina powder, mercury (II) salt, penylboronic acid (IPB) and benzene. Results show that the decomposition reaction was successfully initiated and maintained throughout the test. The rate of decomposition varied with temperature with increasing rates at elevated temperatures. Despite the high rate of decomposition, the cesium DF for the product filtrate ranged from 47,000-646,000 during the test (See Figure 6.1-9).

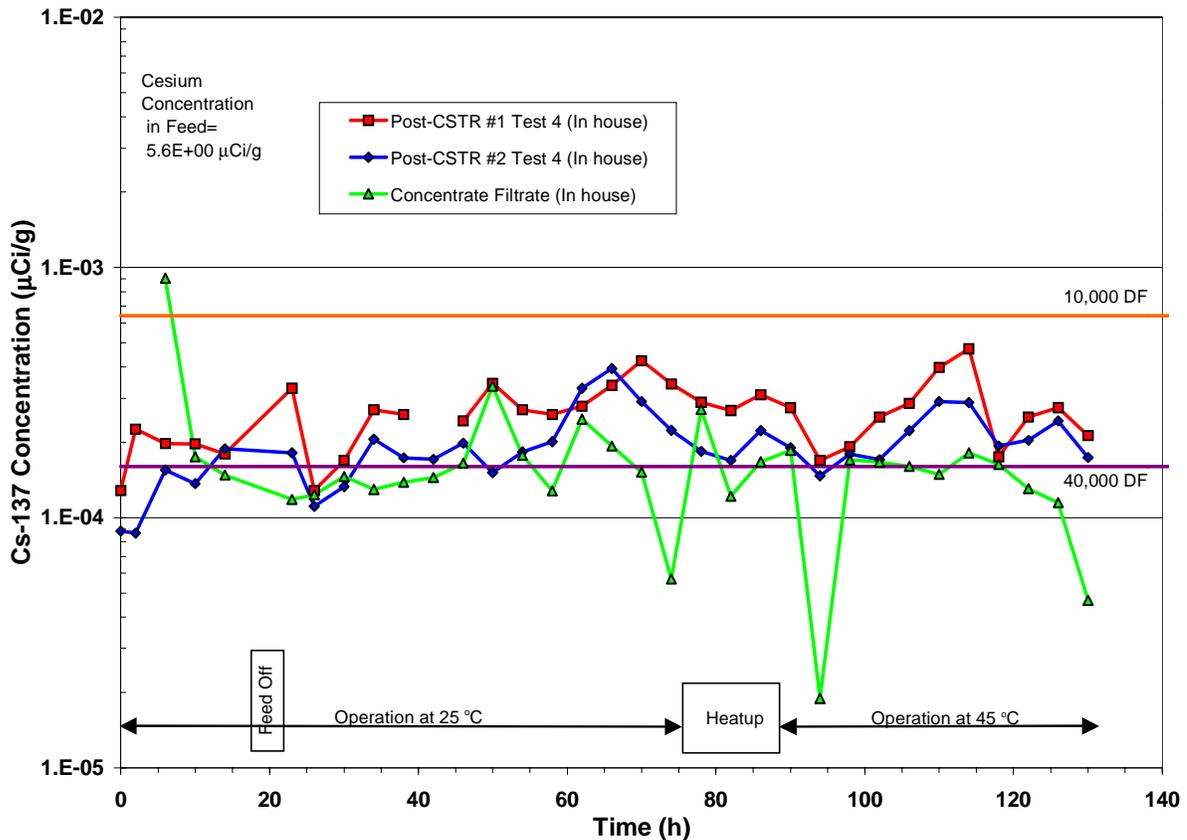


Figure 6.1-9 Cesium Results from ORNL Test 4

ORNL conducted a fifth test with the objective of demonstrating the acceptable performance of the 20-L CSTR system in a fully integrated, closed-loop operation (with TPB recovery and recycle) with TPB actively decomposing under steady state conditions. (Ref. 44) The RCS was used to cause TPB degradation, with the exception of benzene addition. By not adding benzene to the process vessels, any benzene detected in the off-gas of these vessels would provide a real-time indication of TPB decomposition. There were few operational problems through most of the campaign, however, the test had to be terminated 2.5 days prematurely due to the failure of the fluid seals on the slurry pump. No loss of cesium DF in the concentrate filtrate occurred during the test. Cesium decontamination was maintained at >40,000 DF in the filtrate product (see Figure 6.1-10). The operating data indicated that acceptable performance of the 20-L CSTR system could be maintained in closed-loop operation with TPB actively decomposing. However, the data trends for the TPB decomposition products detected in the process vessels did not support the achievement of steady state conditions in all cases.

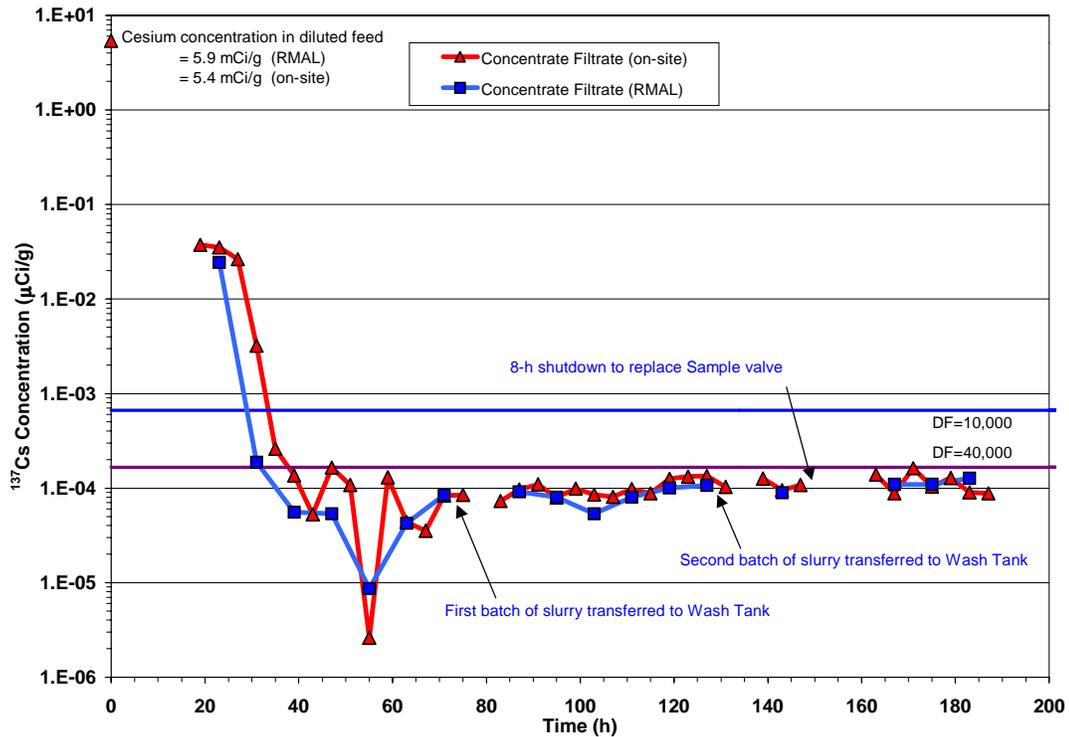


Figure 6.1-10 Cesium Results from ORNL Test 5

In addition to the ORNL tests, SRTC ran a real waste test using two-CSTRs with 60% excess TPB – again with 8-hour residence times (Ref. 45). In this test, all NaTPB (stoichiometric plus excess) was combined with the dilution water. Operation proceeded smoothly with the exception of foaming problems and water/TPB feed interruptions. The system recovered quickly from these interruptions and the observed DF returned to 1×10^6 or greater. Near the end of this test, CSTR #1 and CSTR #2 agitator speeds were reduced from 400 to 100 rpm due to foam buildup in the reactors. With reduced mixing, DF decreased to approximately 100 and was never re-established (See Figure 6.1-11).

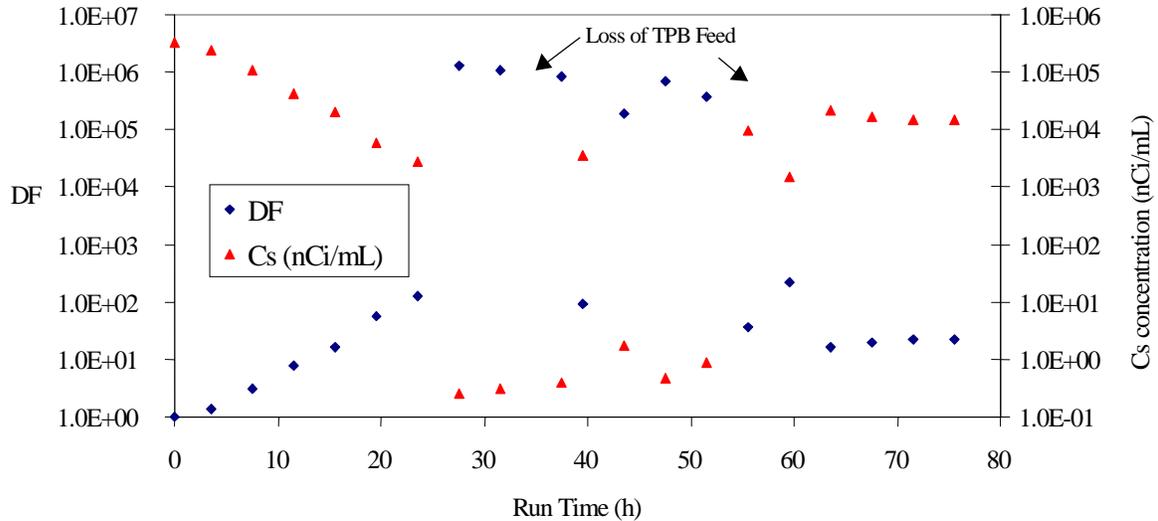


Figure 6.1-11 Cesium Results from Real Waste CSTR Testing

SRTC performed additional real waste testing using 1 L CSTRs in order to demonstrate the continuous precipitation of cesium, strontium and various actinides at 25 and 45 °C (Ref. 37). Antifoam was also used in these experiments. Operation proceeded smoothly with the exception of overflow line between the CSTRs plugging approximately 10 hours after increasing the temperature to 45 °C. The backup pump was used to control the liquid level and ran flawlessly for the remainder of the test. There was very little evidence of foaming throughout the test. Cesium decontamination ranged from 884,000-2,600,000 at 25 °C and steady state conditions, and 72,000-3,020,000 at 45 °C (See Figure 6.1-12). One data point did not meet DF and saltstone requirements (after reaching steady-state). A duplicate analysis of this sample (from the same bottle) showed approximately the same results, so analytical error has been ruled out. A potassium analysis of the same sample also showed an anomalous spike. Considering the nature of the data points surrounding it in time, it is likely that this sample suffered from contamination from its time in the high activity cells, and not a failure of the process. Due to the consistent and high DF values achieved, the requirement for cesium removal was demonstrated successfully. Similarly, strontium and plutonium also show successful decontamination after steady state. The slurry showed evidence of a small amount of catalytic decomposition of the tetraphenylborate during the testing at 45 °C.

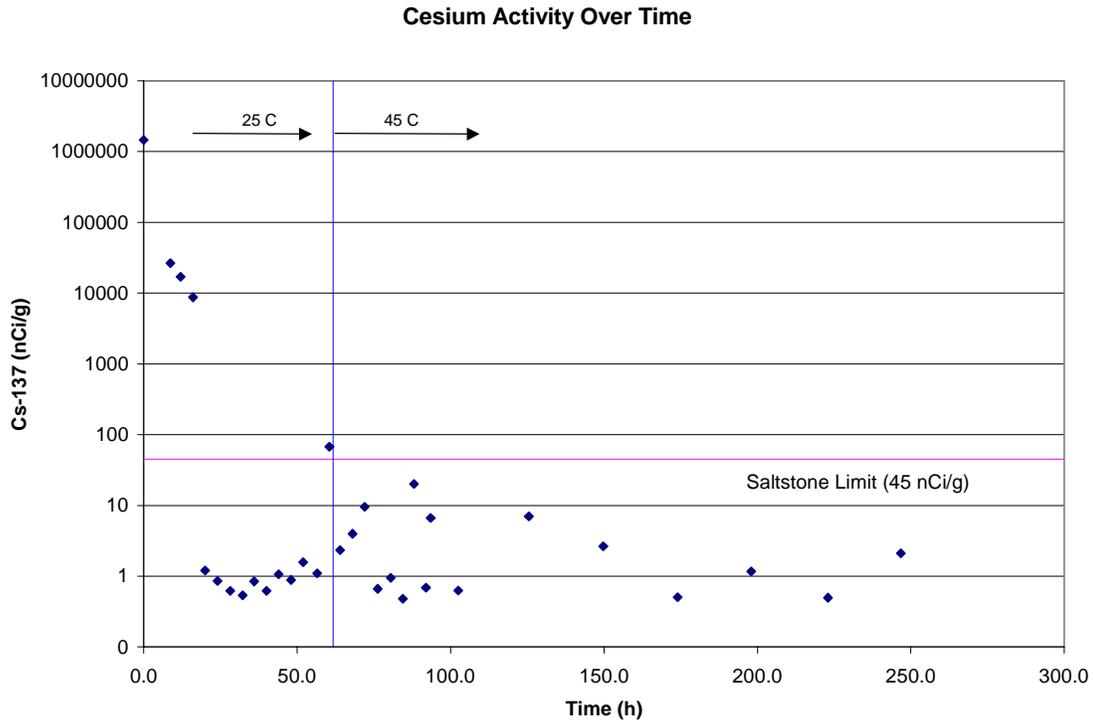


Figure 6.1-12 Cesium Results from SRTC Real Waste Test

6.1.2.3 Decomposition Kinetics

Several tests have incorporated the effects of tetraphenylborate decomposition in the overall test objectives. ORNL tests 4 and 5 studied the effects of cesium decontamination under active decomposition. SRTC CSTR real waste testing also looked for evidence of tetraphenylborate decomposition. Additionally a batch study on real waste was conducted at SRTC specifically for studying the potential catalytic properties of additional high level waste.

The objective of the fourth ORNL test was to verify that the STTP process could achieve and maintain the necessary cesium decontamination while TPB was actively decomposing (Ref 43). A recommended catalyst system (RCS) developed by SRTC was added during the test. The RCS consisted of Pd(0) on alumina powder, mercury (II) salt, phenylboronic acid (1PB) and benzene. Results show that the decomposition reaction was successfully initiated and maintained throughout the test. At 25°C, the decomposition/benzene generation rate was about 1.5 mg benzene/(L•h) in CSTR 1 and 3 mg/(L•h) in the SCT while at 45°C, the rate in CSTR 1 was greater than 5 mg/(L•h) and 3.0 mg/(L•h) in the SCT. The target for benzene generation was 2.5 mg/(L•h) based on the single decomposition reaction of TPB to triphenylborane (3PB). If all of the TPB molecule were decomposed, the rate would be four times higher, or 10 mg/(L•h). At the

end of the test, about 4.2% of the total TPB in the first CSTR vessel was being decomposed. Despite the high rate of decomposition, the cesium concentrations for the product filtrate exceeded the DF of 40,000 throughout the test.

The fifth ORNL test demonstrated the acceptable performance of the 20-L CSTR system in a fully integrated, closed-loop operation (with TPB recovery and recycle) with TPB actively decomposing under steady state conditions (Ref. 44). The RCS was used to cause TPB degradation, with the exception of benzene addition. By not adding benzene to the process vessels, any benzene detected in the off-gas of these vessels would provide a real-time indication of TPB decomposition. The operating data indicated that acceptable performance of the 20-L CSTR system could be maintained in closed-loop operation with TPB actively decomposing. However, the data trends for the TPB decomposition products detected in the process vessels did not support the achievement of steady state conditions in all cases. During production of the first batch of concentrated slurry and the first half of the second batch, the TPB decomposition monitored by the formation of 3PB and the production of benzene in the off gas of system vessels indicated slight TPB decomposition in CSTR 1. The low decomposition rate was expected because it took about 36 h to reach a steady-state concentration of the RCS in CSTR 1. While in the later stage of processing the second batch of concentrated slurry and during the processing of the third batch, the TPB decomposition in both CSTRs increased and stabilized at a combined benzene rate of about 2.4-2.5 mg/(L•h) (equivalent to ~10 mg/(L•h) benzene for complete TPB decomposition) as measured by both 3PB production and benzene in the off gas of both vessels. The increase in decomposition activity in CSTRs for this test could have been related to the changes in recycle wash water composition, the change in antifoam batch source, and/or a prolonged activation period for the catalyst system. The fluctuation in the data and the time relationship of these changes complicated the ability to narrow the cause to any one factor. Decomposition reactions in the concentration tank were less stable. During the later stage of processing for the second slurry batch, the 3PB concentration increased rapidly, providing a benzene rate of more than 6 mg/(L•h) just before the batch was finished. When concentration of the third batch was started, the benzene rate was about 2.5-3 mg/(L•h), and it continued to fluctuate at that rate until processing of the third batch was complete. The overall average benzene rate during the last 60 h of the test was about 5 mg benzene/(L•h) (computed for the TPB to 3PB reaction only), with the majority produced in the SCT and CSTR 1. It is likely that the increased decomposition activity in the SCT was due to the increase in the Pd catalyst content, which would have overwhelmed any possible effects from changes in recycle wash water or antifoam.

During the CSTR test with real waste, TBP decomposition was observed. The decomposition product data indicates that throughout the experiment there were little, if any, detectable amounts of 3, 2, 1PB, or phenol. This, in turn, shows that TPB decomposition was extremely slow. The slurry showed evidence of small amount of

catalytic decomposition of the tetraphenylborate during the testing at 45 °C, giving a calculated benzene generation rate of 2.4 mg/(L•h).

SRTC also performed batch testing of six different tank wastes for catalytic NaTPB decomposition (Ref. 46). Tests with wastes from six tanks were performed at both ambient (22-26 °C) and 45 °C. Five tests exhibited rapid cesium decontamination. Three tests produced more moderate rates of cesium decontamination. The remaining four tests showed very slow rates of decomposition. The most probable cause of the low decontamination rates is inadequate mixing. Only six tests (representing four different tanks) showed detectable concentrations of soluble NaTPB. Both the low and high temperature tests with Tank 35H waste produced detectable concentrations of triphenylborane, a NaTPB decomposition product. No other test or waste showed evidence of NaTPB decomposition. The calculated maximum theoretical rate of benzene generation from the 45 °C test with Tank 35H waste was less than 0.2 mg/(L•h). The lower temperature test yielded a substantially smaller rate. The low benzene generation rate is more than two orders of magnitude less than obtained in testing in 1997 with a high level tank waste composite with added sludge. The increased concentration of soluble mercury appears to be a significant difference between the Tank 35H sample and the other five tank waste samples.

6.1.2.4 Filtration Results

Recent studies have been completed by SRTC to evaluate cross-flow filter performance of washed and unwashed 10 wt% TPB precipitate slurries containing sludge and MST. These studies show that filtrate flux rates responded as expected to changes in axial velocity and transmembrane pressure (Ref. 47).

Flux rates from these studies averaged from 0.081 gpm/ft² (See Figure 6.1-13) for an axial velocity of 6 fps and 15 psi transmembrane pressure. For design purposes, a flux of 0.04 gpm/ft² is assumed for similar operating parameters. The resulting filter size is provided in Table 6.1-3.

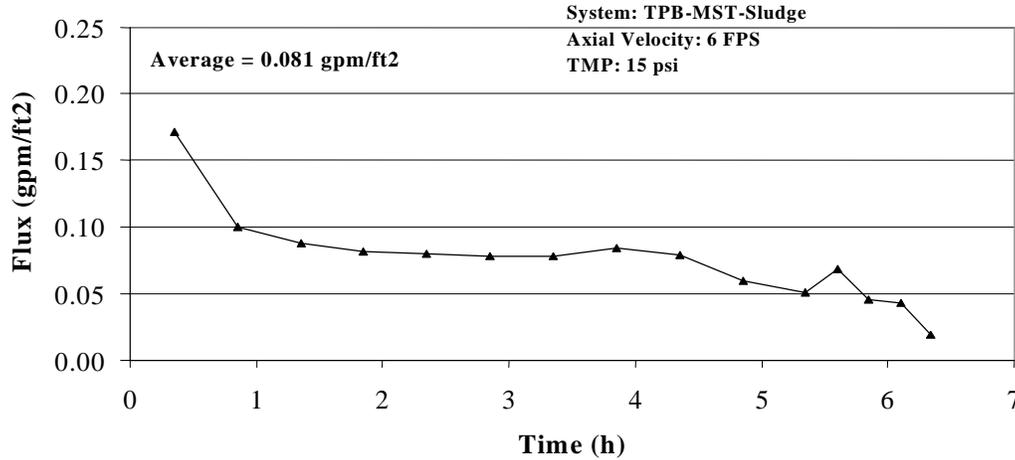


Figure 6.1-13 Sample Filter Flux Profile during Concentration

Table 6.1-2 STTP Filter Sizing Results

Filter	Filter Area (FT ²)	Filter Tubes (10 ft long)	Filter Feed Rate (gpm)	Filtrate Flow Rate (gpm)
Concentrate	600	366	2070	24
Wash	125	76	430	5

6.1.2.5 Precipitate Washing

Precipitate washing performs three functions:

- reduces nitrite concentration to ≤ 0.01 M for proper Precipitate Hydrolysis operation,
- reduces the $[Na^+]$ to a level acceptable for glass production, and
- recovers a portion of the excess NaTPB and recycles it to CSTR #1.

As unreacted (excess) NaTPB flows from CSTR #2 to the Concentrate Tank (CT) and to the Wash Tank (WT), it will split among three different paths as follows:

- soluble NaTPB in the slurry flowing to the CT will be lost with the DSS; insoluble NaTPB will flow from the CT to the WT,
- NaTPB dissolved during the wash cycle will be recovered and recycled to CSTR #1 providing a portion of the TPB⁻ for precipitation, and
- NaTPB that is not dissolved during washing will be lost to Precipitate Hydrolysis where it competes with KTPB and CsTPB for reactor capacity.

The loss of NaTPB to the DSS is unavoidable. In a process running with a feed of 1.6X the stoichiometric quantity (60 % excess), 62.5 % (1/1.6) of the TPB is precipitated as sparingly soluble salts (K^+ , Cs^+ , NH_4^+ as TPB salts; Hg^{+2} as $[(C_6H_5)_2Hg]$). About 5 % (0.08/1.6) is lost to the DSS as soluble NaTPB. The remaining 32.5 %, which precipitates

as NaTPB in the resulting 4.7 M Na⁺ solution, is potentially recoverable in the wash step. Based on prior tests (Ref. 47), about 80 % of the solid NaTPB fed to the Wash Tank (26 % of the total added) was expected to be recovered by dissolution in the wash water. The remaining insoluble NaTPB (6.5 % of the total added) would be lost to the Precipitate Hydrolysis process.

The second CSTR test at ORNL operated closed loop. That is, concentrated precipitate was washed and the spent wash water was recycled to the first CSTR. The progress and efficiency of washing was monitored by measuring the nitrite concentration as a function of time, the amount of wash water required to reach 0.01 M nitrite, and the total NaTPB recovered in the spent wash water. Washing is considered to be complete when the nitrite in the spent wash water is ≤ 0.01 M (≤ 46 mg/L). Table 6.1-3 shows NaTPB recovery for the four wash rates tested during ORNL CSTR Test 2 and Figure 6.1-14 shows the nitrite concentration versus time. (Ref. 36)

Table 6.1-3 ORNL 20-L CSTR Wash Results

Wash Step	Wash Water Rate (mL/min)	Wash Time (hours)	TPB Recovery (%) ¹
1	10.5	28	11.4
2	14.7	31	13.9
3	8.3	43	21.1
4	5.5	44	28.6

¹ Expected recovery was 80 %

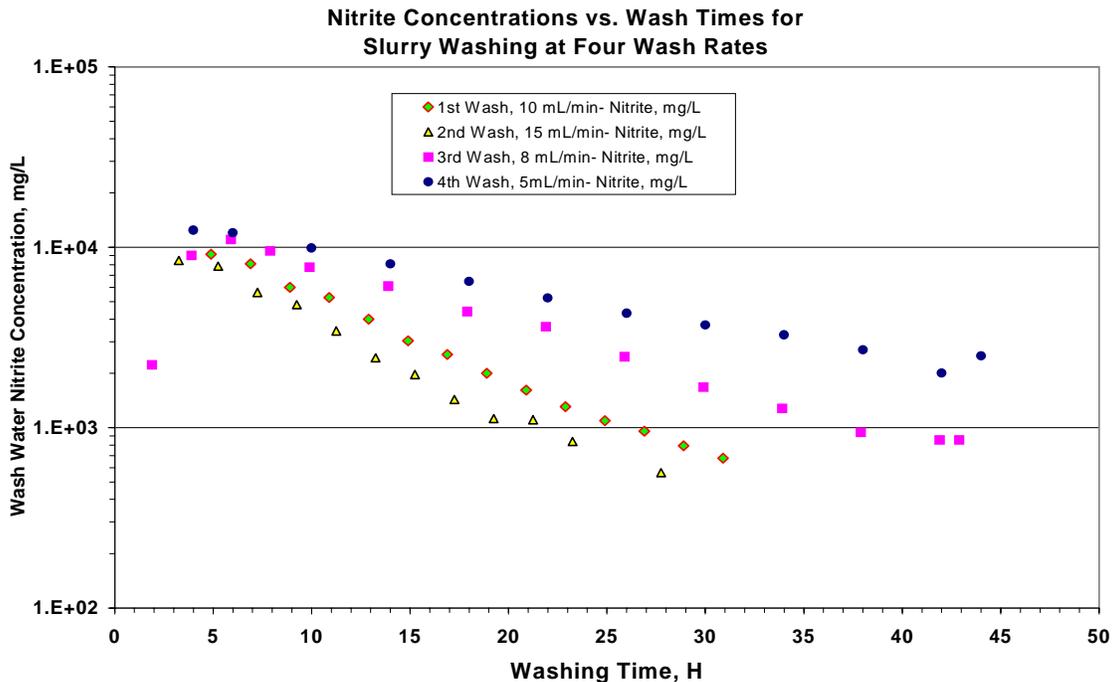


Figure 6.1-14 Nitrite Concentration versus Time for ORNL Washing

The wash step in the STTP process is a constant volume wash. That is, wash water is fed at a fixed rate and spent wash water is withdrawn at a rate to maintain a fixed volume in the wash tank. The governing equation is:

$$C = C_0 e^{-\frac{t}{\tau}}$$

where τ is the residence time or $\frac{\text{volume to be washed}}{\text{wash rate}}$.

The theoretical wash water requirement is thus calculated as follows:

$$\text{volume to be washed} * \ln \frac{[\text{NO}_2^-]_i}{[\text{NO}_2^-]_f}$$

These relationships indicate the log of the nitrite concentration versus time should be a straight line – as is evident in Figure 6.1-14. As previously mentioned, the wash endpoint was determined by monitoring the nitrite concentration in the spent wash water. In two of the washes, the required wash water was 30 – 35 % greater than theoretical. That is, the slopes of the curves in Figure 6.1-14 should have been steeper than they are – thus indicating that washing was less than 100 % efficient.

There are three possible contributors to the washing inefficiency:

- inaccurate tank level measurement,
- a heel from the previous wash, and
- poor mixing.

The tank level was measured by ΔP using bubbler tubes at different tank heights. Since the specific gravity of the salt solution starts at about 1.21 and ends at almost 1.00, the actual level in the tank rises by about 20 % even though the indicated level based on ΔP is constant. Even though the ORNL wash tank drains from the bottom, there is a “heel” of water left from the previous wash in the cross-flow filter and the tubing which dilutes the slurry and increases the actual wash volume. As previously discussed, there was probably insufficient mixing.

The wash was not only less than 100 % efficient with respect to nitrite washing, but the NaTPB recovery was much poorer than expected. Two possible explanations are poor mixing (especially in terms of moving the solids and contacting them with dilute salt solution) and a new crystal form that impedes NaTPB dissolution.

Washing studies were also performed in the third ORNL test (Ref. 42). The progress and efficiency of washing was monitored by measuring the nitrite concentration as a function of time, the amount of wash water required to reach 0.01 M nitrite, and the total NaTPB recovered in the spent wash water. Washing is considered to be complete when the nitrite in the spent wash water is ≤ 0.01 M. Results are shown in Table 6.1-4 and Figure 6.1-15 and indicate that TBP recovery and nitrite washing were less than expected.

Table 6.1-4 ORNL 20-L CSTR Wash Results, Test 3

Wash Cycle	Time (h)	Wash Rate (mL/min)	Recyle Wash Water Collected (L)	TPB Recovered (mol)	TPB ^a (mol/L)	Excess TPB (%)
1 ^b	16	10	12.3	0.0578	0.0047	8.7
2	31	10	18.6	0.0723	0.0039	7.3
3	28	15	25	0.1154	0.0046	8.6
4	43	8	20.6	0.1480	0.0072	13.4
5	44	5	13.2	0.1381	0.0105	19.5

^aTesting goal was to obtain enough TBP in recycle wash water to provide a 60% excess (~0.0322 mol/L)

^bRecycle wash water was obtained from washing Test 1a concentrated slurry solids

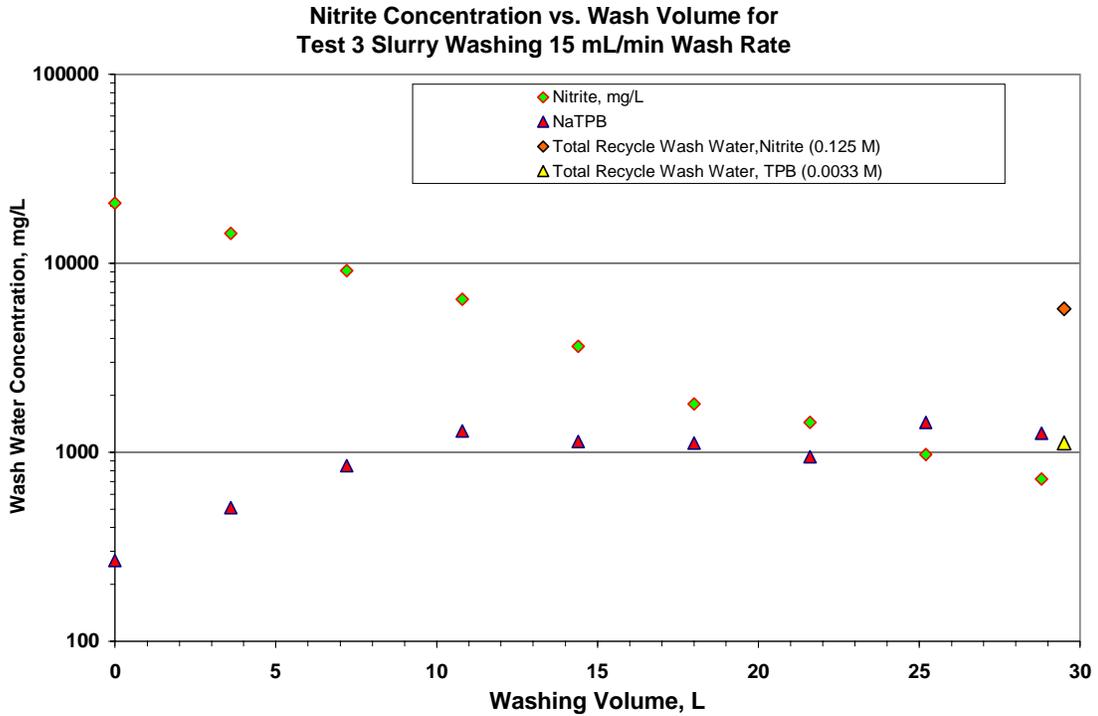


Figure 6.1-15 Nitrite Concentration versus Time for ORNL Washing, Test 3

Similarly, the efforts to remove the excess TPB by washing the produced slurries in the fourth ORNL test were not very successful (Ref. 43). The washing efforts only removed about a 10—15% of the excess TPB that was calculated to be in the sodium form. The problems with dissolving the NaTPB appear to be related to the use of IITB52 as the antifoam agent for the process. The IITB52 prevented foam formation in all phases of the testing but appears to inhibit the dissolution of soluble NaTPB from the concentrated slurry.

The fifth ORNL test also shows inefficient TBP recovery (Ref. 44). Water washing of both batches of slurry concentrate in this test were extremely ineffective (about 11% of the available TPB was recovered from the first batch and ~3% from the second). TPB recoveries achieved from earlier tests indicate results that are comparable or superior to the Test 5 washing results.

The most successful effort of all of these tests recovered only 29% of the available TPB (See Table 6.1-5). The results of the tests strongly suggest that the presence of IITB52 antifoam inhibits TPB dissolution and recovery and inhibits the removal of nitrite during the slurry washing process. The best recovery of total TPB occurred in a test where antifoam was used, but the washing was performed at a higher mixing speed than the other tests and the results cannot be directly compared to tests without antifoam. The other tests, where washing conditions were similar (but not identical), the amount of TPB recovered was greater for tests where IITB52 was not used.

Table 6.1-5 ORNL 20-L CSTR Wash Results

Test	Wash cycle	Time (h)	Wash rate (mL/min)	Available TPB ^a (mol)	RWW ^b (L)	TPB recovered (mol)	TPB ^c (mol/L)	Percent recovered ^d
1a	1 ^e	16	10	0.48	12.3	0.058	0.0047	12
2	1	31	10	0.86	18.6	0.072	0.0039	9
2	2	28	15	0.63	25	0.115	0.0046	18
2	3	43	8	0.76	20.6	0.148	0.0072	19
2	4	44	5	0.69	13.2	0.138	0.0105	20
3	1 ^f	32	15	0.33	28.8	0.095	0.0033	29
4	1 ^g	30	20	1.09	35.4	0.117	0.0033	11
4	2 ^g	29	20	1.11	34.6	0.111	0.0032	10
5	1	24	20	0.48	28.8	0.055	0.0019	11
5	2	24	20	0.64	28.8	0.021	0.0007	3

^aMoles of excess TPB as NaTPB in batch available to be dissolved by water washing.

^bRWW = recycle wash water.

^cTesting goal was to obtain enough TBP in recycle wash water to provide a 60% excess (~0.033 mol/L).

^d(mol TPB recovered)/(mol available TPB in batch).

^eRecycle wash water used in Test 2.

^fRecycle wash water used in Test 4.

^gRecycle wash water used in Test 5.

TPB recovery can likely be improved. Clearly, agitation and mixing can be improved. Besides redesign of the agitator, addition of antifoam has been shown to reduce yield stress and consistency thus improving mixing and pumping. (Ref. 47) Note also that recovery improves when the washing rate is slower, which provides more time for dissolution. It takes about three days to accumulate a batch of concentrated precipitate for washing and wash times could be extended to about that duration. Another strategy would be to stop the addition of wash water part way through the cycle (when the $[\text{Na}^+]$ is low and the NaTPB solubility is high) and then resume washing after dissolving more of the NaTPB.

Based on test and modeling results, the design CSTR residence times remain at 10 hours. However, since these tests yielded low TPB recovery during washing, modeling and the material balance assumes only 10% of insoluble NaTPB sent forward to the wash tank is recovered in the wash step. The impacts of this assumption are as follows: (1) additional NaTPB is consumed (a cost penalty) and (2) a larger quantity of washed TPB solids per unit of salt solution processed is generated (which will impact DWPF throughput). Continuing washing studies, including the use of antifoams, are planned to establish if NaTPB recovery can be improved.

6.1.2.6 Hydrolysis

Washed precipitate is transferred to the Precipitate Reactor Feed tank. The salt cell is designed to process two batches of washed precipitate at a time, so the precipitate is

accumulated for approximately 96 hours. First, it was determined that the Cu concentration could be approximately doubled (to 1800 ppm in the PHA or 1 wt% in the glass) without impacting the glass durability (Ref. 48). However, at this concentration and with somewhat reducing conditions, metallic copper is present. Then, hydrolysis was performed on unirradiated and irradiated TPB precipitate slurries with 1800 ppm Cu (Ref. 49). Both achieved more than satisfactory Phenylboric Acid (PBA) removal (a primary criterion for complete reaction). The PHA is then transferred to the PHA Surge Tank where it is held until transfer to DWPF. Benzene and water is collected by a condenser/decanter from the reactor and then evaporated in the Organic Evaporator. Again the benzene and water vapor is collected by a condenser/decanter. The decanter sends water to the Precipitate Reactor Overheads Tank, and the remaining solution, which is mostly benzene with some water, to the Organic Evaporator Condensate Tank to await transfer to the Organic Waste Storage Tank.

One observation from hydrolysis tests raises a potential concern. During exposure to radiation, the nitrite concentration increases due to radiolysis of nitrate and the slurry turned a tan color (typical for irradiated TPB precipitate). High nitrite is known to cause formation of higher boiling, black/brown compounds. When the irradiated feeds were hydrolyzed, a dark organic phase was recovered and black deposits were observed on the agitator. Because of the formation of these products, fouling of cooling coils, tank surfaces and condensers could be of concern for equipment in the Chemical Processing Cell, especially the Mercury Water Wash Tank.

Antifoam IIT B-52 has been adopted for use in the Small Tank Tetraphenylborate Process. A key element into the antifoam evaluation is its effect on the hydrolysis kinetics of phenylboric acid (PBA) (Ref. 50). PHA must be below 53 ppm in PBA to insure that a flammable mixture cannot be formed during SRAT processing. Precipitate hydrolysis tests were performed with and without antifoam at target copper concentrations of 475 and 950 ppm, respectively. Results show that the addition of 2000 ppm of IIT B-52 antifoam to the precipitate slurry has no detrimental effects upon the PBA hydrolysis kinetics. Decomposition of the IIT B-52 in the precipitate hydrolysis process was rapid, with no detectable quantity of the antifoam agent in any of the product streams. Operation of the precipitate hydrolysis process with IIT B-52 antifoam and a target copper concentration of 950 ppm will allow product and cycle times to be met.

6.1.2.7 Coupled DWPF Operation

This research focused on glass variability studies. The STTP process will require higher PHA loading and MST loading (TiO_2) than previously tested. Glasses were made with 7, 10, and 13 wt% PHA oxides and 1.25 and 2.5 wt% oxides of MST (equivalent to 0.2 and 0.4 g/L MST usage and equivalent to 1 and 2 wt% TiO_2 in the glass (Ref. 51). Durabilities were very good and were predictable, although the glasses did not meet the homogeneity constraint (may form a separate phase). Viscosities were acceptable although lower than predicted. The *liquidus* results were also low. Glass re-qualification is not required.

6.1.2.8 Computational Fluid Dynamic Modeling

A computational fluid dynamics model was developed to assess the mixing performance of several of the vessels of the STTP process. The models are of the Oak Ridge 20 L Demonstration Unit. These vessels are scaled to represent the behavior of the full size vessels, so it was decided to model these vessels. An advantage of modeling these vessels is that due to their relatively small size, a computational mesh of reasonable size could be constructed and still represents all the mixing phenomena expected. The modeling showed that adequate mixing was expected in the CSTRs but not in the wash tank.

The CSTR and wash tank in the Oak Ridge test loop were designed to be geometrically similar. The physical aspects of the tanks were obtained from References 52 and 53. The model was constructed using the code MixSim™ and the CFD portion was run using Fluent™. The model contained the tube coil and baffles along with the appropriate impeller. Because of the symmetry of the tank, a 90° sector was sufficient for modeling. The computational grid consisted of 36,652 cells. Sensitivity was run with approximately double the number of computational cells, but no differences in the results were observed. Because of the relatively small size of the test vessel this number of computational cells gave a good representation of the fluid flow phenomena present. Time dependant and steady state cases were run, as will be discussed below.

The first case modeled was that of the CSTR. This case involved Newtonian flow with a free surface. Of interest was if the impeller would begin to entrain air. The calculation was begun with a quiescent tank and run until a quasi-steady state was reached. A true steady state was not reached due to the behavior of the free surface. The calculation showed that air would be ingested if the impeller speed were high enough, but in the runs planned for the experiment, no air ingestion was anticipated. This would also imply that in the scaled up vessel air ingestion would not be expected at normal operating conditions.

The second case, the wash tank, proved to be much more interesting. The washing will occur at 10 wt% solids, and a TPB slurry at this concentration shows decided non-Newtonian properties, approximated by a Bingham plastic model. To represent this the Herschel-Buckley model was used. The model is given by:

$$\tau = \tau_0 + \mu S$$

Where: τ_0 = yield stress
 S = stress rate
 $\tau < \tau_0$ then material is rigid
 $\tau \geq \tau_0$ then material obeys a power law

Which is implemented in the code as

$$\tau = \tau_0 + (kS^{n-1})S$$

Where: $n = 1$ for a Bingham plastic
 k = slope after yield (linear for Bingham plastic)

The slope for this case was derived from Reference 54. The 10-wt% slurry has very high critical shear and yielding viscosity, 260 dynes/cm² and 46 cp respectively. With these values one would not expect much fluid motion, and that was indeed the case. Figure 6.1-16 shows the velocity contours for the case with a 10 wt% slurry. One can see that except in the area immediately about the impeller the velocities are quite low.

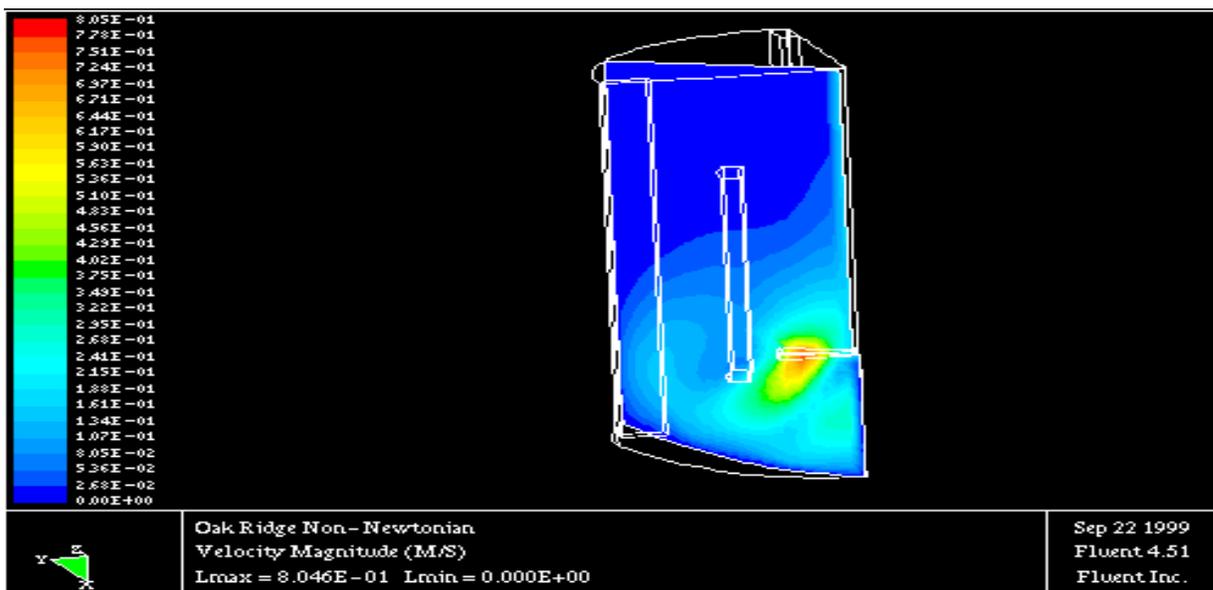


Figure 6.1-16 Velocity Contours for the 10 Wt% Slurry Case

The calculation shows a small recirculation zone within the tube coil off the tip of the impeller, but little fluid motion in the rest of the tank. This calculation implies that washing will not be as effective as expected, if the geometry of the tank remains as it is envisioned. Possibilities for improvement include removing the baffles, which had no effect on mixing due to the essentially no-flow condition at the wall, and using an anchor or ribbon impeller design. Either of these designs would by necessity move more slowly, but would provide better, and faster, mixing by engaging more of the slurry. With the present design, the theoretical limit of the wash will not be approached.

6.1.3 Bases for Flowsheet Models

The SPEEDUP™ representation of the Small Tank TPB Precipitation (STTP) alternative is a comprehensive dynamic model of the overall process. This model is composed of variants of pre-existing models originally developed for the High Level Waste Integrated Flowsheet Model (HLWIFM). Thus precipitation kinetics, filtration, solubility, evaporation, decomposition, absorption, and dissolution are treated in full dynamic detail as part of the mass balance for 34 distinct chemical species. The basic building block of the models is the original HLWIFM Tank 48 model, with modifications to suit the new STTP design. The main extension to the original Tank 48 model is the addition of the dynamic equations to calculate benzene generation due to soluble NaTPB decomposition in the presence of copper or palladium catalyst. A brief summary of the models follows:

Accum_Tank: An artificial construct used to interface the continuous precipitation and concentration unit operations with the batch-wise, precipitate-washing step. Based on Tank 48 model with filtration logic removed. Accumulates concentrated product until the predefined batch volume is available, then passes batches forward to be washed.

Collect_Tank: Used to integrate the grout volume leaving Saltstone_Complex.

Conc_Tank: Represents the concentration operation that follows the precipitation steps. Based on Tank 48 model running in a continuous operation mode. Holds up slurry from precipitation operation until solids weight percent criterion is met through filtration; then starts transferring concentrated product continuously to Accum_Tank.

Filtrate_Tank: Combines filtrate from Conc_Tank and spent wash water from Spent_Wash_Tank and passes result onwards to Saltstone_Complex.

Precip_Tank: Represents the precipitation operation. Accumulates slurry from either the Salt_Feed_Tank or the downstream Precip_Tank for the duration of the defined hold-up interval, then passes precipitated slurry on to either the next Precip_Tank or the Conc_Tank. Current representation has two Precip_Tank modules in series, with NaTPB and MST additions into the first tank only. Based on Tank 48 model running in a continuous operation mode with filtration logic removed.

Recycler: Controls dilution water source, either provided by Spent_Wash_Tank or by a fixed source.

Saltstone_Complex: Represents the Saltstone grout production processes in the SPF, based on the same model in HLWIFM.

Salt_Feed_Tank: Used to provide the salt solution feed that drives the entire process. Combines the input composition with sufficient dilution water to meet the Na molarity specification.

Spent_Wash_Tank: Used to accumulate spent wash from Wash_Tank and send it on either for use as dilution in Salt_Feed_Tank or for mixing into Filtrate_Tank.

Wash_Tank: Represents the precipitate-washing batch process. Fed by Accum_Tank with the batch steps under control of the External Data Interface. Washed precipitate is sent onward to the DPWF process, which is outside the current model. Based on Tank 48 model.

6.1.3.1 Alpha and Strontium Removal Model Bases

Experimental work (Ref. 8, 9, 10) for alpha sorption kinetics shows that the sorption rate for Uranium and Plutonium at 0.4 g/L MST are sufficiently rapid to use previously determined equilibrium constants, K_d as the basis for the STTP process. The equilibrium constants, used in modeling alpha removal kinetics in the Phase III BAR work, have been used for Phase IV modeling of the Plutonium, and Uranium MST sorption kinetics. In addition, the equilibrium constant of ^{90}Sr has been modeled using Equation 1 below, which is normalized to 90 $\mu\text{g/L}$.

$$K_e = \frac{(1 + d \cdot t + e \cdot t^2)}{\left(1 + \frac{b}{a} \cdot t + \frac{c}{a} \cdot t^2\right)} - 1 \quad (1)$$

Where K_e is unitless

t = time is in hours

a , b , c , d , and e are equilibrium factors from Table 6.1-5.

Table 6.1-6 Sr Equilibrium Factors

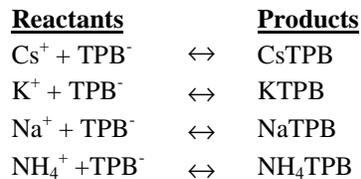
Constants	Value
a	90
b	340
c	58.6
d	725
e	363

6.1.3.2 Cs Decontamination by Tetrphenylborate Precipitation

6.1.3.2.1 Solubilities

The salt solution is decontaminated by the addition of sodium tetrphenylborate (NaTPB). The tetrphenylborate (TPB) ion in solution then reacts with potassium, cesium and ammonium ions to form solids with limited solubility. The presence of high salt concentrations reduces the solubility for these species as well as the parent NaTPB.

The reaction stoichiometry for the tetrphenylborate reactions with Cs^+ , K^+ , Na^+ and NH_4^+ , which are controlled by their respective equilibrium solubility product constants (K_{sp}), are shown below:



The solubility product constant, K_{sp} , of a 1:1 ionic compound, MX, is defined as:

$$K_{sp} = (a_{M^+}) (a_{X^-})$$

where 'a' is the chemical activity of the ionic species, M^+ and X^- respectively, in the solution. The activity of the ionic species is related to their molar concentrations, C , by multiplying the molarity by their respective activity coefficient, γ , in solution:

$$a_{M^+} = \gamma_{M^+} \cdot C_{M^+}$$

$$a_{X^-} = \gamma_{X^-} \cdot C_{X^-}$$

The activity coefficients (Ref. 55) were determined using commercially available software as:

$$\gamma_{Cs} = 0.0258 I_m^2 - 0.160 I_m + 0.783$$

$$\gamma_k = 0.0284 I_m^2 - 0.219 I_m + 0.777$$

$$\gamma_{Na} = 0.0088 I_m^2 - 0.0701 I_m + 0.701$$

$$\gamma_{TPB} = 1.91 I_m^3 - 4.54 I_m^2 + 5.48 I_m + 0.712$$

where γ is the activity coefficient and I_m is the ionic strength based on the molality of all ionic species in the solution. The ionic strength of any solution is defined by the following equation (Ref. 55):

$$I_m = 0.5 \cdot \sum m_i \cdot z_i^2$$

Where z_i is the charge of ion i and m_i is the molal concentration of ion i (moles/1000 g of solvent).

Cesium or potassium concentrations in solution can then be determined from their respective solubility equilibrium (K_{sp}) equations:

$$K_{sp(Cs)} = (\gamma_{Cs} \cdot [Cs^+]) (\gamma_{TPB} \cdot [TPB^-])$$

$$K_{sp(K)} = (\gamma_K \cdot [K^+]) (\gamma_{TPB} \cdot [TPB^-])$$

Because the sodium ion concentration is so high (~ 4.7 M), the sodium contribution from dissolved NaTPB at equilibrium is negligible, and the $[TPB^-]$ in solution can be determined by simply rearranging the $K_{sp(Na)}$:

$$[TPB^-] = \frac{K_{sp(Na)}}{[Na^+] \gamma_{Na} \cdot \gamma_{TPB}}$$

After Reference 55 was issued, the solubility of TPB in high salt concentrations containing potassium was questioned. Subsequent laboratory tests (Ref. 56) indicated that the mass action thermodynamic approach described above predicts higher TPB solubility than observed experimentally. The degree of overprediction is a function of salt concentration and the initial TPB/K ratio. Some solubility data is also provided in Reference 56 for 4.0 to 4.7 molar salt solution over a range of TPB/K ratios. The TPB solubility was about 200 mg/L when 60 % stoichiometric molar excess was used in a 4.7 molar salt solution. This solubility was used for modeling precipitation for the STTP process.

6.1.3.2.2 Precipitation Kinetics Model

During the decision phase, data from Continuous Stirred Tank Reactors (CSTRs) at bench scale became available. These data, in combination with earlier batch test and

NaTPB re-dissolution (shown to be quite slow) allow semi-quantitative modeling of the precipitation reaction set, described below. These ordinary differential equations were solved using standard techniques and were used to gain some insight into how the reactions proceed.

Notation for Precipitation Kinetics Model

N, sodium ion concentration, M

K, potassium ion concentration, M

C, cesium ion concentration, M

T, tetraphenylborate ion concentration, M

NT_s, solid NaTPB concentration, moles per liter

KT_s, solid KTPB concentration, moles per liter

[NOTE: Solid CsTPB is not tracked because the effect on the material balance is negligible because it dissolves very slowly.]

f, subscript for the feed condition

*, any concentration at equilibrium

M_{NT}, mass transfer coefficient for dissolution of NaTPB [dimensionless – the value is a function of the nature and quantity of the solids].

M_{KT}, mass transfer coefficient for dissolution of KTPB [dimensionless].

X, the fraction of TPB which precipitates instantly as NaTPB on feeding (the observed crash), dimensionless

k_N, NaTPB precipitation rate constant, l/mol-hr

k_K, KTPB precipitation rate constant, l/mol-hr

k_C, CsTPB precipitation rate constant, l/mol-hr

K_N, NaTPB solubility product, mols²/l²

K_K, KTPB solubility product, mols²/l²

K_C, CsTPB solubility product, mols²/l²

$\frac{F}{V}$, Flow rate per volume, inverse of the residence time, hr⁻¹

6.1.3.2.3 Model Equations

For potassium, the change in concentration in a CSTR with respect to time is represented by the following equation.

$$\frac{dK}{dt} = -k_K(K \cdot T - M_{KT} \cdot K_K) + \frac{F}{V} (K_f - K)$$

In this equation, the first term on the right side represents the rate of change in potassium ion concentration due to the combination of an increase from dissolution and a decrease from precipitation. The second term represents the change due to flow through the CSTR and accounts for the difference in the potassium concentrations for the feed into and the slurry leaving the reactor.

For cesium, the change in concentration with respect to time is represented by the following equation.

$$\frac{dC}{dt} = -k_C(C \cdot T - K_C) + \frac{F}{V}(C_f - C)$$

This equation is identical in form to the equation for potassium, except the mass transfer coefficient (M_{CT}) for Cesium is assumed to be 1, and thus does not appear in the equation.

For TPB⁻ ion, the change in concentration with respect to time is represented by the following equation.

$$\frac{dT}{dt} = -k_N(N \cdot T - M_{NT} \cdot K_N) - k_K(K \cdot T - M_{KT} \cdot K_K) - k_C(C \cdot T - K_C) + \frac{F}{V}((1 - X)T_f - T)$$

In this equation, the first three terms on the right side represent the rate of change of TPB ion concentration due to the combination of an increase from dissolution and a decrease from precipitation for NaTPB, KTPB and CsTPB, respectively. The fourth term represents the change due to flow through the CSTR and accounts for the difference in the TPB concentrations for feed into and slurry leaving the reactor.

For solid NaTPB, the change in concentration with respect to time is represented by the following equation.

$$\frac{dNT_s}{dt} = k_N(N \cdot T - M_{NT} \cdot K_N) + \frac{F}{V}(X \cdot T_f - NT_s)$$

For solid KTPB, the change in concentration with respect to time is represented by the following equation.

$$\frac{dKT_s}{dt} = k_K(K \cdot T - M_{KT} \cdot K_K) + \frac{F}{V}(K_f - KT_s)$$

These two equations are identical in form to the equation for potassium, with the first term on the right side accounting for changes due to precipitation and dissolution of either NaTPB or KTPB. As in the other equations above, the second term accounts for the change in concentration due to flow through the reactor and the difference in concentrations of the entering and leaving streams.

These equations described above actually apply to the first (fed) reactor. The modifications to the equations for the second reactor, which is in series with the first, require accounting for the solids being fed from the first reactor. In addition, the T_f , K_f and C_f terms also vary over time.

The mass transfer coefficients are assumed to drive concentrations to equilibrium. For NaTPB, the mass transfer coefficient for dissolution of NaTPB is:

$$M_{NT} = NT_s / (T_f - K_f - C_f - T^*)$$

The denominator in the above equation approximates the amount of solid NaTPB made when all species have equilibrated. Small amounts of potassium and cesium still in solution are ignored in this equation. This forces the mass transfer coefficient for NaTPB to 1, when all species are equilibrated.

For KTPB, the mass transfer coefficient for dissolution of KTPB is:

$$M_{KT} = K T_s / K_f$$

this forces the potassium concentration to equilibrium when precipitation is complete.

6.1.3.2.4 Initial Conditions

For batch calculations, K and Cs ions were set at the feed concentration. TPB ion was set to the amount left after the initial rapid precipitation. Solid NaTPB was set to the amounts precipitated by the initial rapid precipitation. NaTPB was assumed to be added rapidly at 0.55 M. Peterson has estimated that 93% would precipitate under these conditions and that fraction of initial precipitation was used. Sodium concentration can be changed, but all the fundamental constants change, too, because of their ionic strength functionality. A concentration of 4.7 M was used for sodium throughout. Table 6.1-7 summarizes the conditions and rate constants used.

Table 6.1-7 Concentrations and Conditions for Batch Precipitation

	[TPB ⁻]	[K ⁺]	[Cs ⁺]
Initial Concentration, M	0.00E+00	1.23E-02	1.20E-04
NaTPB Added, M	0.019872		
% NaTPB Initially Precipitated	93%		
Final Concentration, M	5.93E-04	7.64E-07	9.98E-10
Decontamination Factor (Dimensionless)		1.61E+04	1.20E+05
	NaTPB	KTPB	CsTPB
Solubility Product, mols ² / l ²	2.95E-03	4.53E-10	5.92E-13
Precipitation Rate Constant, l/mol-hr	2.66E-01	5.00E+04	2.00E+05

Figure 6.1-17 shows the progression of the batch reaction.

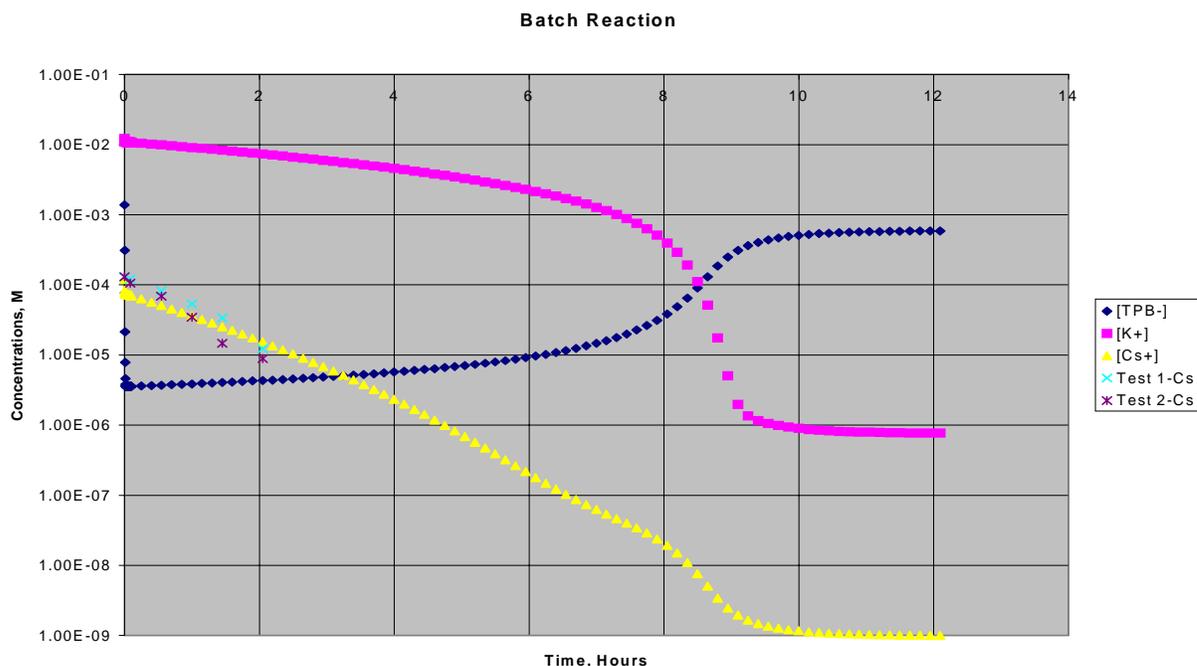


Figure 6.1-17 Progression of Batch TPB Reaction

Initially, the TPB left in solution precipitates as CsTPB and KTPB. Then the NaTPB solids, which precipitated when the NaTPB solution was added, re-dissolve and precipitate KTPB and CsTPB. After the potassium is precipitated quantitatively, the cesium can precipitate to the low level desired. After about 10 hours, the solution is in equilibrium with the three solid TPB salts. This behavior was observed qualitatively in several batch experiments. However, in the batch experiments, the potassium and the cesium concentrations drop initially more rapidly than calculated here. Cesium data from the batch experiment closest to the conditions simulated is also plotted. Note that the slope of the calculated cesium decrease and the experimental decrease are about the same. This slope is determined (largely) by the re-dissolution rate of NaTPB solids. These experimental data were used to estimate that rate. The experimentally observed initial drop in cesium was normalized out of the data set.

For CSTR calculations, the two reactors are assumed to be filled with salt solution at the feed concentrations. No NaTPB is initially present. This is probably not how the actual reactors would be operated during startup, but the conditions are comparable to those used at ORNL. NaTPB is assumed to be added at 0.55 M for fresh NaTPB solution and at 0.033 M NaTPB for the recycle (wash) solution. In the nominal flowsheet, 1.6 moles of TPB⁻ are added for every mole of potassium, cesium and ammonium ion. This ratio provides “160% of stoichiometry”. For this calculation, the fresh NaTPB solution is added to provide 100 mole % of the $K^+ + Cs^+ + NH_4^+$ and the recycle stream provides 60% of the total TPB added (i.e. – the excess over stoichiometric requirements). Concentrations and conditions for CSTR precipitation are summarized in Table 6.1-8.

The equilibria and rate constants used are the same as those used in the batch calculations. Sodium concentration was again assumed to be 4.7 M.

Table 6.1-8 Concentrations and Conditions for CSTR Precipitation

Process Variable	[TPB-]	[K+]	[Cs+]
Initial Concentration, M	0.00E+00	1.23E-02	1.20E-04
Feed Concentration, M	1.99E-02	1.23E-02	1.20E-04
Mean Residence Time, hr	8		
% NaTPB Initially Precipitated	70%		
Steady State Concentration, Reactor 1	6.81E-05	4.42E-04	1.10E-06
Steady State Concentration, Reactor 2	5.09E-04	3.04E-06	2.51E-09
Decontamination Factor, Reactor 1		28	109
Decontamination Factor, Reactor 2		145	439
Decontamination Factor, Overall		4041	47811
	NaTPB	KTPB	CsTPB
Solubility Product, $\text{mols}^2 / \text{l}^2$	2.95E-03	4.53E-10	5.92E-13
Precipitation Rate Constant, $1 / \text{mol-hr}$	2.66E-01	5.00E+04	2.00E+05

Figure 6.1-18 shows the concentration response in the first reactor. The cesium and potassium concentrations drop smoothly as the TPB concentration increases.

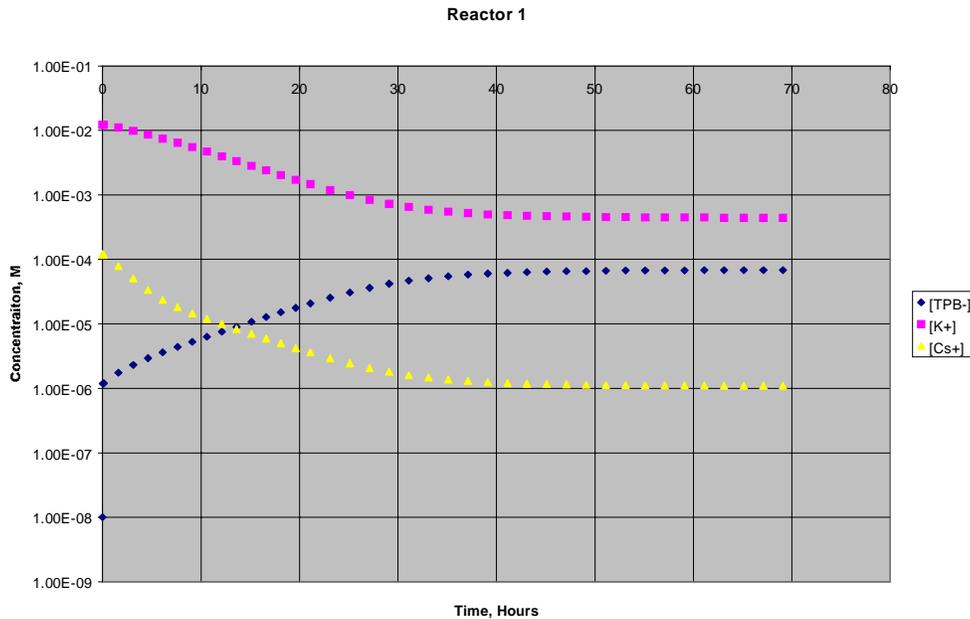


Figure 6.1-18 Concentration Response in First Reactor

As can be seen in Figure 6.1-19, potassium and cesium concentration drop slowly in the second reactor until the TPB concentration exceeds the potassium concentration. Then both cesium and potassium precipitate rapidly. After both reactors are at steady state, the concentrations are time invariant, and the amount of potassium and cesium precipitated is equal to the amount fed to each reactor.

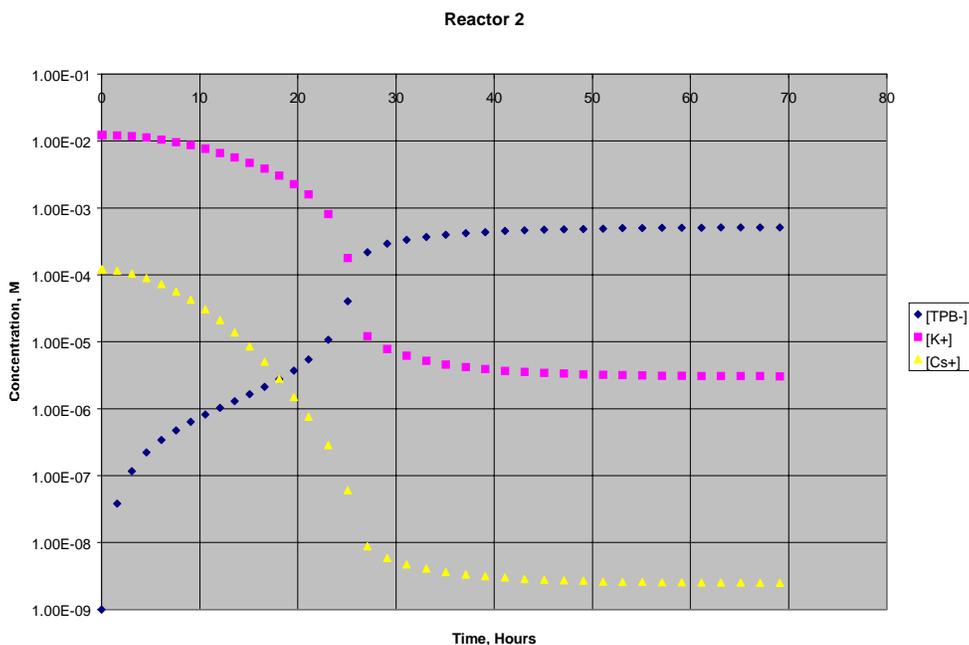


Figure 6.1-19 Concentration Response in Second Reactor

[NOTE: A functioning plant would not operate in the manner described above. At startup or resumption of operations, the first reactor would likely be inventoried with TPB solution and MST slurry before salt solution is fed to the first reactor. Thus reactions would occur before the continuous feeding from the first reactor into the second reactor begins. Furthermore, the NaTPB re-dissolution rate used here is somewhat low in order that the two reactors would be different (for the purpose of illustration). In tests, both reactors have achieved DF and their time dependent concentrations are nearly identical, except for the lag time needed for the second reactor to reach steady state.]

As discussed above (Ref. 57), NaTPB precipitates and the solids redissolve to precipitate the less soluble CsTPB and KTPB. The method of adding the NaTPB precipitating agent determines how much of the NaTPB is precipitated rapidly and how much is initially in the reactor as a solid. The portion of the NaTPB that does not precipitate rapidly will precipitate K^+ and Cs^+ . Potassium must be precipitated quantitatively before $[Cs^+]$ can be reduced to the desired level. This is why $[Cs^+]$ drops slowly for some period in batch test and then drops rapidly to the desired levels.

Table 6.1-9 compares model results with experimental results from the single CSTR tests at SRTC. The test investigated the impact of mixing, the NaTPB addition method, the residence time and the sodium concentration.

Table 6.1-9 Single CSTR Laboratory Data vs. Model

Test ID	Tracer	Mean Res. Time Hours	NaTPB/K TPB Molar ratio	Description	NaTPB Addition Method	Observed Cs DF at Steady State	Modeled Cs DF at Steady State	Modeled [TPB ⁻] > [K ⁺] at Steady State?	Test and Model in Qualitative Agreement?
4.1-1	YES	8	1.6	Initial Conditions: Pre-reacted heel, mixed flow agitator	All added at 0.55 M	13	17	NO	YES
4.1-2	YES	8	1.6	Same as 4.1-1, except high flow agitator	All added at 0.55 M	21	17	NO	YES
4.1-3	YES	8	1.6	Same as 4.1-1, except high shear agitator	All added at 0.55 M	27	17	NO	YES
4.1-4	NO	8	1.6	Initial Condition: Un-reacted Salt Heel, Non-Rad Cs Only	All added at 0.55 M	21	17	NO	YES
4.2-1	YES	8	2.0	Same as 4.1-4 except Cs tracer added and	All added at 0.55 M	9	13	NO	YES
4.3-1	NO	1	1.6	Same as 4.1-4	All added at 0.55 M	6	2	NO	YES
4.3-2	NO	1	1.3	Same as 4.3-1 except [K] & [Cs] 4.5 X Nominal	All added at 0.55 M	44	3	NO	YES
4.4-1	NO	24	1.6	Same as 4.1-4	All added at 0.55 M	>80 (below Detection)	1450	YES	YES
4.4-2	YES	4	1.6	Same as 4.1-4 except salt solution diluted to [Na] = 3.5 M	All added at 0.55 M	> 27000	61 ("sample DF" = 13000)	YES	YES
9.1	YES	8	1.6	Same as 4.1-4	100% Stoichiometric added at 0.55M, 60% at 0.03 M in dilution water	65	320	YES (Essentially Equal)	YES
9.2	YES	8	1.3	Same as 4.1-4	100% Stoichiometric added at 0.55M, 30% at 0.03 M in dilution water	43	15	NO	NO (Model Under-predicts actual performance)
9.3	YES	8	1.6	Same as 4.1-4	130% Stoichiometric added at 0.55M, 30% at 0.03 M in dilution water	8	32	NO	YES

The model predicts the behavior of the system reasonably well. The key to reactor performance is whether the [TPB⁻] in solution is greater than the [K⁺]. When this condition exists, modeling predicts and experiment confirms that the cesium will precipitate quantitatively. This is equivalent to a high decontamination factor. The model matched the qualitative results in eleven of 12 experiments. In test 9.2, cesium and potassium (K⁺ DF not tabulated) were precipitated to a greater extent than modeled. Tetraphenylborate concentration was apparently higher than potassium, but this was not predicted. The model predicts that test 9.3 will not achieve DF for potassium and it does not. Logically, the conditions of test 9.3 should have given a higher DF than test 9.2, because a greater excess of TPB was added. Therefore, the anomalous behavior is the relative good results of test 9.2.

The model was also used to predict the performance of the 15-L tests performed at ORNL. Figures 6.1-20 and 6.1-21 show the cesium concentration measured and

predicted. Two CSTRs in series (15 L each) were tested. These plots show data from two similar tests. The principal difference is that catalyst, which promotes degradation of the TPB, was added in the second test and the second test was a full simulation of the flowsheet, including washing the precipitate during the test and recycling wash water.

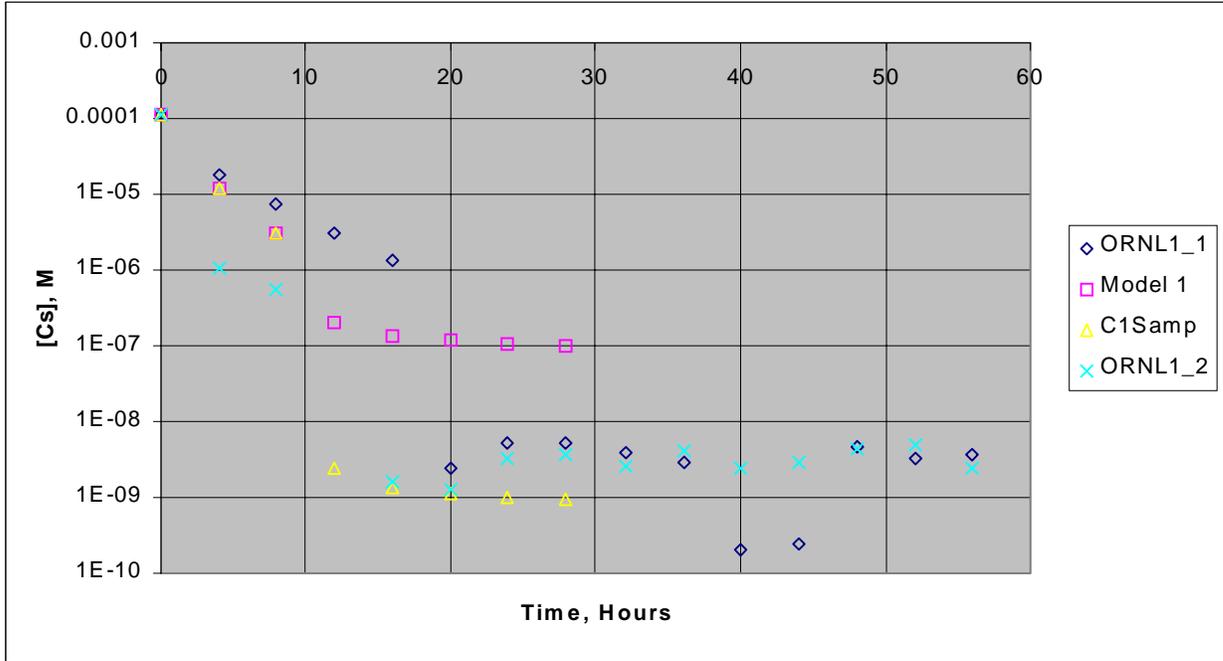


Figure 6.1-20 ORNL CSTR #1 vs. Model

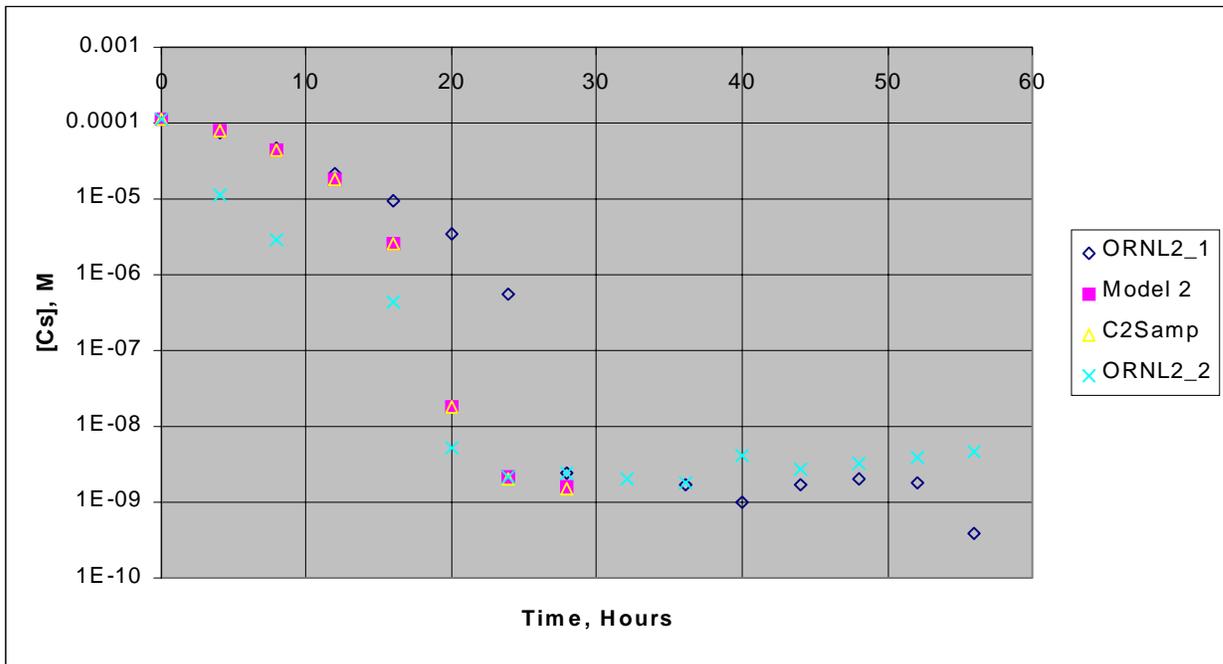


Figure 6.1-21 ORNL CSTR #2 vs. Model

The conditions were set up to be identical, except for potential degradation of TPB, so the model results for both tests should be the same. The model and the actual concentrations fit quite well for the second reactor. This is because the second reactor gets to a nearly equilibrated state between TPB in solution and the three solid salts, Na, K and CsTPB.

ORNL 20 L CSTR Tests 3, 4 and 5 confirmed that the CSTRs provided cesium DF as expected (Ref. 42, 43, 44). Real waste testing also confirmed that reaction rates were adequate to achieve the expected cesium removal (Ref. 37).

The model predicted cesium concentrations vs. time higher than the samples showed. However, the model accounts for the fact that the reactor is a flowing system, with un-precipitated material being fed, which keeps the reactor from reaching equilibrium. The sampling process allows equilibration, which is rapid if the TPB concentration is greater than the potassium concentration (i.e. – most of the potassium has been precipitated). When the post-precipitation of the sample is accounted for, the model and sample results correspond more closely. This correction also explains the observed rapid drop in cesium vs. time observed. As soon as the TPB concentration in solution exceeds the potassium in solution, the samples should equilibrate to a low level of cesium.

6.1.3.3 Radiolysis of Water and Salt Solutions

The radiolysis of water forms hydrogen. The formation of hydrogen by radiolysis is expressed in terms of a G value. The G value is expressed as the number of molecules of hydrogen formed per 100 eV of radiation energy. The G value for hydrogen in water is generally accepted as 0.46 molecules of hydrogen formed per 100 eV of radiation energy. The G value for hydrogen in salt solutions can be calculated using the following equations (Ref. 58):

$$G = 0.4597 - 0.3803 * ([NO_3^-] + 0.5 * [NO_2^-])^{1/3}$$

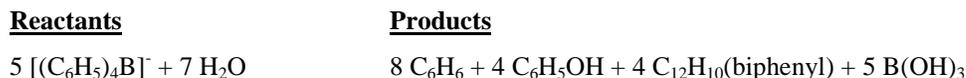
$$\text{when: } ([NO_3^-] + 0.5 * [NO_2^-])^{1/3} \leq 1$$

$$\text{And } G = 0.1199 - 0.0504 * ([NO_3^-] + 0.5 * [NO_2^-])^{1/3}$$

$$\text{when: } 1 < ([NO_3^-] + 0.5 * [NO_2^-])^{1/3} \leq 2.$$

6.1.3.4 Radiolysis of Tetraphenylborate

Tetraphenylborate also decomposes radiolytically. The radiolytic decomposition stoichiometry can be modeled using the following reaction:



The measured product split for the radiolytic decomposition of TPB is 50 % benzene, 25 % phenol, and 25% biphenyl (Ref. 59). The above equation approximates the experimental results.

The G value for the formation of benzene from the radiolytic decomposition of TPB is 0.71 ± 35% molecules of benzene formed per 100 eV radiation dose to 10 weight percent slurry. A bounding value of 0.96 has been used in prior authorization bases for the ITP facility. This bounding value is applied for all precipitation cases.

The amount of benzene generation varies with the specific activity of the slurries. Given the energy from Cs decay as 4.84 watts/kCi, and the conversion factor of 1 eV/sec is 1.6E-19 watts, the baseline benzene generation rate from radiolysis is:

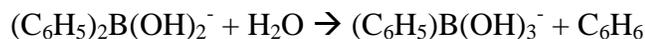
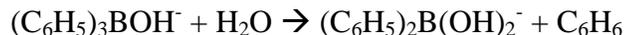
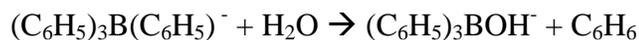
$$= \frac{0.96 \text{ molecules}}{100 \text{ eV}} * \frac{4.84 \text{ watts}}{1000 \text{ Ci}} * \frac{1 \text{ eV/sec}}{1.6\text{E} - 19 \text{ watts}} * \frac{25 \text{ Ci}}{\text{gal}} * \frac{1 \text{ gal}}{\text{L}} * \frac{78,120 \text{ mg}}{6.02\text{E}23 \text{ molecules}} * \frac{3600 \text{ sec}}{\text{hr}}$$

$$= 0.9 \text{ mg/L-hr}$$

6.1.3.5 Chemical Decomposition of TPB

6.1.3.5.1 Benzene Generation and TPB Decomposition

Laboratory studies indicate that tetraphenylborate decomposes in a series of reactions given below:



Each mole of TPB or intermediate produces one mole of benzene. Other reaction paths also exist depending upon the presence or absence of oxygen and resulting in the production of phenol instead of benzene. This study assumes 100% production of benzene. The classic kinetic model expected takes the following form:

$$\frac{d[\text{TPB}]}{dt} = -k_1[\text{TPB}] - \text{Radiolysis}$$

$$\frac{d[\text{3PB}]}{dt} = k_1[\text{TPB}] - k_2[\text{3PB}]$$

$$\frac{d[\text{2PB}]}{dt} = k_2[\text{3PB}] - k_3[\text{2PB}]$$

$$\frac{d[\text{1PB}]}{dt} = k_3[\text{2PB}] - k_4[\text{1PB}]$$

where:

[TPB], [3PB], [2PB], [1PB] are the molar concentrations of $(\text{C}_6\text{H}_5)_4\text{B}^-$, $(\text{C}_6\text{H}_5)_3\text{B}$, $(\text{C}_6\text{H}_5)_2\text{B}(\text{OH})_2^-$ and $(\text{C}_6\text{H}_5)\text{B}(\text{OH})_3^-$ respectively.

Radiolysis is the loss of TPB associated with the radiolytic destruction of KTPB solids. The sequential rate constants for each of the decomposition reactions are k_1 , k_2 , k_3 , and k_4 . Based on laboratory studies, these rate constants have been determined to be a function of catalyst type, ionic strength, temperature and potentially other factors.

6.1.3.5.2 Decomposition when KTPB is Present

The TPB decomposition rate equation was set to zero order (constant decomposition rate) for this study. The rate constant (k_1) is then defined as the desired rate divided by four expressed as mMoles/L-hr. For example, the base case assumes an overall benzene generation rate of 10 mg/L-hr and TPB decomposition is responsible for ¼ of the total benzene production, corresponding to 2.5 mg/L-hr. Converting this quantity to mMoles yields 0.0320 mMoles/L-hr.

Since the decomposition of TPB is set, the formation of 3PB is also set by k_1 (0.0320 mMoles/L-hr, in the base case). A material balance around 3PB results in the following equation for the rate of change in the concentration of 3PB:

$$\frac{d[3PB]}{dt} = k_1 - k_{2Pd} * [3PB] - k_{2Cu} * [3PB]$$

The two additional rate constants (k_{2Pd} and k_{2Cu}) are based on laboratory studies and are provided by the following equations (Ref. 60):

$$k_{2Pd} = 1224 * [Na]^{4.59} * [Pd]^{0.905} * e^{-5985.42/T}$$

$$k_{2Cu} = 3.1 \times 10^7 * [Cu]^{0.36} * [OH]^{-0.72} * e^{-7867.23/T}$$

where T = temperature, ° K.

A material balance around 2PB results in the following expression for the rate of change of 2PB:

$$\frac{d[2PB]}{dt} = k_{2Pd} * [3PB] + k_{2Cu} * [3PB] - k_3 * [2PB]$$

The additional rate constant (k_3) is also based on laboratory studies and is provided by the following equation (Ref. 61):

$$k_3 = 6.17 \times 10^8 * [OH]^{0.28} * [Cu]^{0.3} * e^{-7923.7/T}$$

A material balance around 1PB results in the following expression for the rate of change of 1PB:

$$\frac{d[1PB]}{dt} = k_3 * [2PB] - k_4 * [1PB]$$

where the rate constants are based on laboratory studies and provided by the following equation (Ref. 61):

$$k_4 = 5.09 \times 10^{10} * [OH]^{0.26} * [Cu]^{0.8} * e^{-9087.6/T}$$

6.1.3.5.3 Decomposition in Filtrate

The decomposition rates for TPB and 3PB are much slower in filtrates that do not contain KTPB and sludge solids. For filtrate, the catalytic decomposition rate is set to the copper-only catalyzed rates. This is justified since the copper catalyst is soluble and will pass through the filter to promote decomposition. For filtrate, the decomposition rate for TPB based on a material balance around TPB becomes:

$$\frac{d[4TPB]}{dt} = -k_1[4TPB][Cu] - \text{Radiolysis}$$

Where the rate constants are based on laboratory studies and provided by the following (Ref. 61):

$$\ln(k_1) = 35.4 - 1.10 \times 10^4/T$$

where T = temperature, ° K

The rate constants for the remaining species are the same as the copper catalyzed reactions noted above:

$$k_2 = k_{2Cu}$$

$$k_{2Cu} = 3.1 \times 10^7 * [Cu]^{0.36} * [OH]^{-0.72} * e^{-7867.23/T}$$

$$k_3 = 6.17 \times 10^8 * [OH]^{0.28} * [Cu]^{0.3} * e^{-7923.7/T}$$

$$k_4 = 5.09 \times 10^{10} * [OH]^{0.26} * [Cu]^{0.8} * e^{-9087.6/T}$$

6.1.3.5.4 Decomposition in SDF Disposal Vaults

In addition to the potential to release benzene from the DSS received in the SPF for the STTP alternative, benzene may be released from the SDF disposal vaults because of degradation of TPB residuals. Reference 62 included an estimated benzene release and permitted release levels. New data suggest that the emission rates may be different from those initially reported. Reference 63 indicates maximum benzene generation can be calculated by:

$$\begin{aligned} \text{Total Benzene} = & ([TPB] \times 0.001 \text{ g benzene/g TPB} + \\ & [3PB] \times 0.394 \text{ g benzene/g 3PB} + \\ & [2PB] \times 0.091 \text{ g benzene/g 2PB} + \\ & [1PB] \times 0.006 \text{ g benzene/g 1PB}) \times \\ & 3.785 \text{ L/gal} \times 2.2 \text{ lb/1000 g} \times \# \text{ gal DSS/yr} \end{aligned}$$

where 3PB indicates triphenylborane, 2PB indicates diphenylborinic acid, 1PB indicates phenylboric acid and the brackets, [], indicate the g/L of the species in DSS. Table 6.1-10 shows the expected average concentrations for each of these species in the DSS. Table 6.1-10 also shows the maximum possible annual DSS production (100% attainment in the SWPF). Using the equation above, the annual benzene evolution from the SDF vaults can be calculated.

Table 6.1-10 Estimated Annual Benzene Emissions from SDF Vaults for STTP

Conditions and Sources	Base Case (17.5 gpm feed rate)
Salt Solution to SDF vaults (gal/min)	24
Salt Solution to SDF vaults (gal/year)	1.26E+07
1PB (g/L of DSS)	0.0023
2PB (g/L of DSS)	0.014
3PB (g/L of DSS)	0.35
TPB (g/L of DSS)	0.20
Benzene lb/year	1.45E+04

If steady production rates are maintained, approximately equal quantities of grout will be produced each day. Thus, the age distribution of grout at any time will be essentially constant and the peak rates would normally be very close to the average annual rate. However, peak rates of benzene evolution will depend on maximum capacity at the SPF.

If processing actually occurs in variable short periods of processing, the age distribution is no longer constant. To estimate a theoretical maximum peak evolution rate from the vaults, the entire annual DSS production is processed at the design basis capacity of the SPF. In addition, elevated temperatures will cause evolution at a faster rate (Ref. 64). At 85°C, the evolution rate increases nearly 40%.

To calculate a potential maximum benzene evolution rate, the annual DSS production is assumed to be processed through the SPF at the design basis maximum of 100 gpm in three 6 hour processing shifts per day. Maximum per day processing is 108,000 gallons. The theoretical maximum evolution rate is 9.6 lb. of benzene per hour at the vaults.

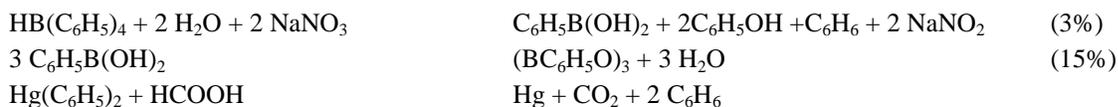
6.1.3.6 Benzene Depletion in the STTP Facility

In the proposed STTP facility, all of the tanks are well agitated. Under these conditions, the release rate of benzene is equal to the generation rate. A small nitrogen purge maintaining the tanks at positive pressure will remove generated benzene to the Process Vessel Vent System. Current operating conditions in the Small Tank Facility, however, are thought to be sufficient to significantly reduce the amount of benzene produced and released. The process is maintained at 25° F to prevent catalyst activation, and the processing rate is fast enough to minimize radiolytic decomposition of TPB. Once in the DWPF salt cell, any benzene produced is passed through a chilled vent condenser to remove any benzene before it is vented.

6.1.3.7 Precipitate Hydrolysis Technical Bases

The bases for the SPC operating cycle times and parameters were developed experimentally and are documented (Ref. 4, 5). The “Large Heel” process is used. Approximately 1500 gallons are left in the PR as the heel for the next batch. This saves raw materials because less copper and formic acid must be added. SPC cycle time is saved because less water is used, which requires less concentration time, and DWPF cycle time is saved because the product has a higher weight percent of solids. The chemical additions and cycle times are based on hydrolyzing sodium tetraphenylborate completely (removing all four phenyl groups to produce four benzene molecules) and to reduce the level of organic (principally phenylboric acid) to < 53 ppm in the aqueous product (PHA). Further, the mercury level is to be reduced to < 260 ppm as diphenylmercury. Experimentation shows that phenylboric acid is destroyed in less than 3 hours and diphenylmercury is destroyed in less than 5 hours (Ref. 5). Therefore, both the phenylboric acid and diphenylmercury limits are easily achieved during the PR cycle time.

<u>Reactants</u>	<u>Products</u>	<u>% Reaction</u>
CsB(C ₆ H ₅) ₄ + HCOOH	CsCOOH + HB(C ₆ H ₅) ₄	
KB(C ₆ H ₅) ₄ + HCOOH	KCOOH + HB(C ₆ H ₅) ₄	
NaB(C ₆ H ₅) ₄ + HCOOH	NaCOOH + HB(C ₆ H ₅) ₄	
NH ₄ B(C ₆ H ₅) ₄ + HCOOH	NH ₄ COOH + HB(C ₆ H ₅) ₄	
HB(C ₆ H ₅) ₄ + 2 H ₂ O	C ₆ H ₅ B(OH) ₂ + 3 C ₆ H ₆	(4%)
HB(C ₆ H ₅) ₄ + H ₂ O + NaNO ₃	C ₆ H ₅ B(OH) ₂ + (C ₆ H ₅) ₂ + C ₆ H ₆ + NaNO ₂	(9%)
HB(C ₆ H ₅) ₄ + 3 H ₂ O	B(OH) ₃ + 4 C ₆ H ₆	(84%)



The bases for the SWPF precipitate hydrolysis parameters are:

- ~1500 gallons of previous batch is left in PR as a heel.
- Target acid concentration is 0.25 M in PHA (after neutralizing base equivalents of carbonate, hydroxide, TPB- and nitrite)
- Copper(II) catalyst target concentration is 950 ppm in PHA
- PR Temperature during feeding - 90°C
- Post Feed Reaction Period Hold at 90°C - 5 hours
- Aqueous Boil Period (Strip) ≥ 5 hours
- Total Aqueous Boiled Volume - > 10,000 gallons

Modeling Bases - The simplified reaction scheme shown below was used to model the hydrolysis reactions in the salt cell. Benzene is the only organic species tracked in the model.

Reactants

$\text{CsB}(\text{C}_6\text{H}_5)_4 + \text{HCOOH}$
 $\text{KB}(\text{C}_6\text{H}_5)_4 + \text{HCOOH}$
 $\text{NaB}(\text{C}_6\text{H}_5)_4 + \text{HCOOH}$
 $\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4 + \text{HCOOH}$
 $\text{HB}(\text{C}_6\text{H}_5)_4 + 3 \text{H}_2\text{O}$

Products

$\text{CsCOOH} + \text{HB}(\text{C}_6\text{H}_5)_4$
 $\text{KCOOH} + \text{HB}(\text{C}_6\text{H}_5)_4$
 $\text{NaCOOH} + \text{HB}(\text{C}_6\text{H}_5)_4$
 $\text{NH}_4\text{COOH} + \text{HB}(\text{C}_6\text{H}_5)_4$
 $\text{B}(\text{OH})_3 + 4 \text{C}_6\text{H}_6$

Fixed volumes of formic acid and copper catalyst are added to each PR batch:

- 345 gallons of 90 wt% formic acid and
- 244 gallons of 15 wt% copper nitrate to reach the target of 950 ppm of Cu in the PHA at the end of a batch cycle.

Two batches of washed precipitate are transferred to make up one PR batch. The large product (PHA) storage volume allows the Precipitate Hydrolysis process to be decoupled from the DWPF feed preparation. The OE is not modeled since benzene separation is essentially complete in the PR boiling. Temperature is not tracked, since energy balances are not performed.

6.1.4 Results Applied to CSTR Sizing for MST and TPB Strike

Strontium, alpha and Cesium contaminants are removed from contaminated salt solution by reaction with monosodium titanate (MST) and tetraphenylborate (TPB). These reactions are to be carried out in continuous stirred tank reactors (CSTRs). Based on the kinetics of the reactions, the CSTRs must be sized to provide the residence time necessary to achieve the desired percent conversion or decontamination factor. This section of the document provides a summary of the batch kinetic data provided by SRTC during Phase III and the required tank sizes determined for this batch data. Tanks in series are considered to minimize the total tank volume. Based on continued tests, the previously recommended 16,000-gallon size for each reactor remains valid.

6.1.4.1 Sizing Methodology

The sizing of a continuous stirred tank reactor begins with a material balance for species A in the reactor (Ref. 65). This material balance results in an expression relating the required residence time (τ) to the initial reactant's concentration (C_{A0}), the percent conversion (X_A) which is a representation of DF ($DF=C_{A0}/C_A$), and the rate of destruction of A ($-r_A$). The tank volume (V) is determined by multiplying the residence time by the volumetric flow rate through the tank (v_0).

$$\tau = \frac{V}{v_0} = \frac{C_{A0} X_A}{-r_A} \quad \text{with } X_A = 1 - \frac{C_A}{C_{A0}}$$

Based on the above equation, if $C_{A0}/(-r_A)$ is plotted against X_A , the area containing the curve represents the residence time. If multiple tanks in series are chosen for the process design, the X_A range can be divided into various segments with each segment representing the required residence time of each individual tank (τ_i).

$$\tau_i = \frac{V_i}{v_0} = \frac{C_{A0} (X_{A(i)} - X_{A(i-1)})}{-r_{A(i)}}$$

This method of CSTR sizing is independent of reaction rate order. The only information required is a measure of reaction rate as a function of percent conversion. This information is provided through batch experimentation.

6.1.4.2 MST Kinetics

MST kinetics have been reported as a function of temperature (25°C), sodium concentration (4.5-7.5M), MST concentration (0.2-2.0 g/L), plutonium concentration (0.1-1.0 mg/L), and degree of mixing (Ref. 66). In this report, the percent conversion of TRU elements is traced in time. Recent testing has focused on flowsheet conditions: 4.5-7.5N Na solutions and 0.2-0.4 g/L MST additions.(Ref. 8, 9, 10, 69) Based on tank farm inventory and expected TRU concentrations (see section 5.3.4), plutonium is bounded by 500 $\mu\text{g/L}$ and requires a $DF=40$. Therefore, the sizing of the MST continuous stirred tank reactors is based on the high plutonium, 25 °C, 4.5M Na, 0.4 g/L MST experimental data. (Ref. 9)

Table 6.1-12 contains the plutonium versus time information necessary for CSTR sizing. The method described in section 6.1.4.1 above is used. These data are from References 9, and 10. Figure 6.1-22 is a plot of the MST kinetic data used to graphically estimate the residence time needed to sorb plutonium. This figure displays both the batch reactor data used in the sizing and the tank volume calculation using the removal rate information. Pu decontamination at 4.5M Na is very quick and results in negligible tank volumes. The Pu decontamination rate is high through the desired target concentration of 12.5 $\mu\text{g/L}$. The lower plot in Figure 6.1-22 demonstrates the calculation of each tank volume required to proceed from 0% conversion to the target 80% conversion. The area of the rectangles determines the mean residence time of each tank. For 73% conversion of the initial Pu concentration (63.5 $\mu\text{g/L}$), only 0.72 hours of mean residence time are required. For conversion from 73% to 84%, only 0.8 hours of mean residence time are required.

For a throughput of 17.5 GPM, these tanks would be 760 and 840 gallons respectively. With such small mean residence times required, the TRU decontamination can occur in the same tanks as the Cesium decontamination due to a designed eight hours of mean residence time for two CSTR's.

One issue that arises with original batch kinetics data is the possibility that an initial Pu concentration of 63.5 $\mu\text{g/L}$ is not representative of the bounding alpha concentrations in the Tank Farm. Based on Tank Farm Blending, the bounding Pu concentration is 500 $\mu\text{g/L}$. The impact of this eightfold increase in initial concentration can not be strictly accounted for without additional batch kinetic data. The approach taken in this analysis is to extrapolate the initial Pu decontamination rate to the higher initial concentration and determine the impact on the required tank residence times. If one were to start with 500 $\mu\text{g/L}$ Pu and utilize the same initial removal rate of 169.9 ($\mu\text{g/L/hr}$), only $(500\mu\text{g/L} - 63.5 \mu\text{g/L})/169.9 = 2.6\text{hr}$ of additional batch reaction time would have been required to reach 63.5 $\mu\text{g/L}$. This 2.6 hours of residence time combined with the 1.5 hours, from Figure 6.1-22 associated with decreasing the Pu from 63.5 to 12.5 $\mu\text{g/L}$ indicates that 2 CSTR's - with 8 hours of residence time each are sufficient to decontaminate the worst alpha batch to the Small Tank TPB alternative.

Table 6.1-11 Plutonium Concentration vs. Time Data for CSTR Sizing

Elapsed Time (h)	Total Pu ($\mu\text{g/L}$)	Percent Conversion	R_{Pu} ($\mu\text{g/L/hr}$)	$\text{Pu}_0/r_{\text{Pu}}$ (hours)
0	63.5	0	169.9	0.4
0.28	12.1	71.6	90.5	1.0
0.52	9.59	84.4	18.5	6.0
0.76	8.95	86.2	2.8	24.2
1.01	8.65	86.4	1.3	49.4
1.52	7.56	88.2	2.1	30.8
2.03	6.88	89.6	1.1	61.4
4.03	5.54	91.1	0.4	168.2
8.04	4.47	93.1	0.2	315.9
23.98	2.64	96.0	0.07	1071.3
72.23	1.41	97.5	0.02	4057.4
168.05	0.544	99.2	0.01	5641.8

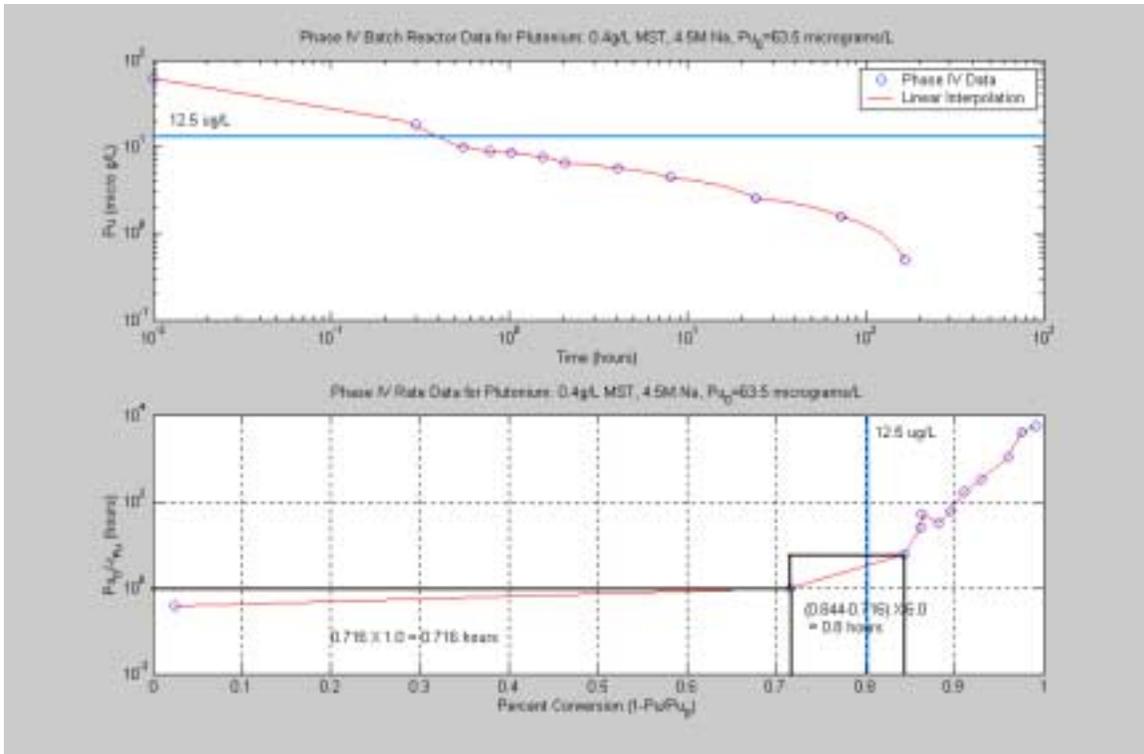


Figure 6.1-22 CSTR Sizing Data

6.1.4.3 TPB Kinetics

The precipitation of cesium by tetraphenylborate (TPB) has been characterized as a function of sodium concentration (4-6M), percent excess TPB (33-100%), and degree of stirring (Ref. 38). The fastest reaction rates occur with low sodium concentration, high excess TPB, and pronounced stirring (300 rpm versus 70 rpm). At a fixed sodium concentration (5M), the removal rate of cesium benefits from both increased TPB excess and agitation. Figure 6.1-23 (top graph) reveals how favorable the rates kinetics are for excess TPB (100%)/good mixing (300 rpm) and how unfavorable the rate kinetics are for low excess TPB (33%)/poor mixing (70 rpm). The individual benefit of % excess TPB versus increased agitation rate is undetermined based on the plateaus in the cesium versus time graph. The experiments appear to suffer from insufficient mixing in general, and inadequate mixing negates the benefit of excess TPB by limiting the amount of TPB making it into solution. Only the high excess TPB/high agitation experiment appears to proceed smoothly with no unusual or unexpected periods with little or no reaction. In order to provide an adequate CSTR design, the HLW Salt Disposition Process Engineering Team chose to size the CSTRs based on each experimental data set in Figure 6.1-23 and to follow these scenarios with a discussion of how the CSTR size is completely determined by the degree of mixing.

As in the MST sizing analysis, the rate of cesium removal must be known as a function of percent conversion. A linear interpolation routine was used to smooth the experimental data. The lower graph in Figure 6.1-23 displays the required residence time as a function of percent conversion. As a rule, the required residence time increases with increased DF or percent conversion. Determining the size and number of CSTRs is performed by placing rectangles in the Figure 6.1-23 (lower graph) that include the data points and the desired percent conversion. Three CSTRs in series were used in the following analysis. Table 6.1-12 provides the tank sizes required to achieve the DF as a function of the kinetic batch data.

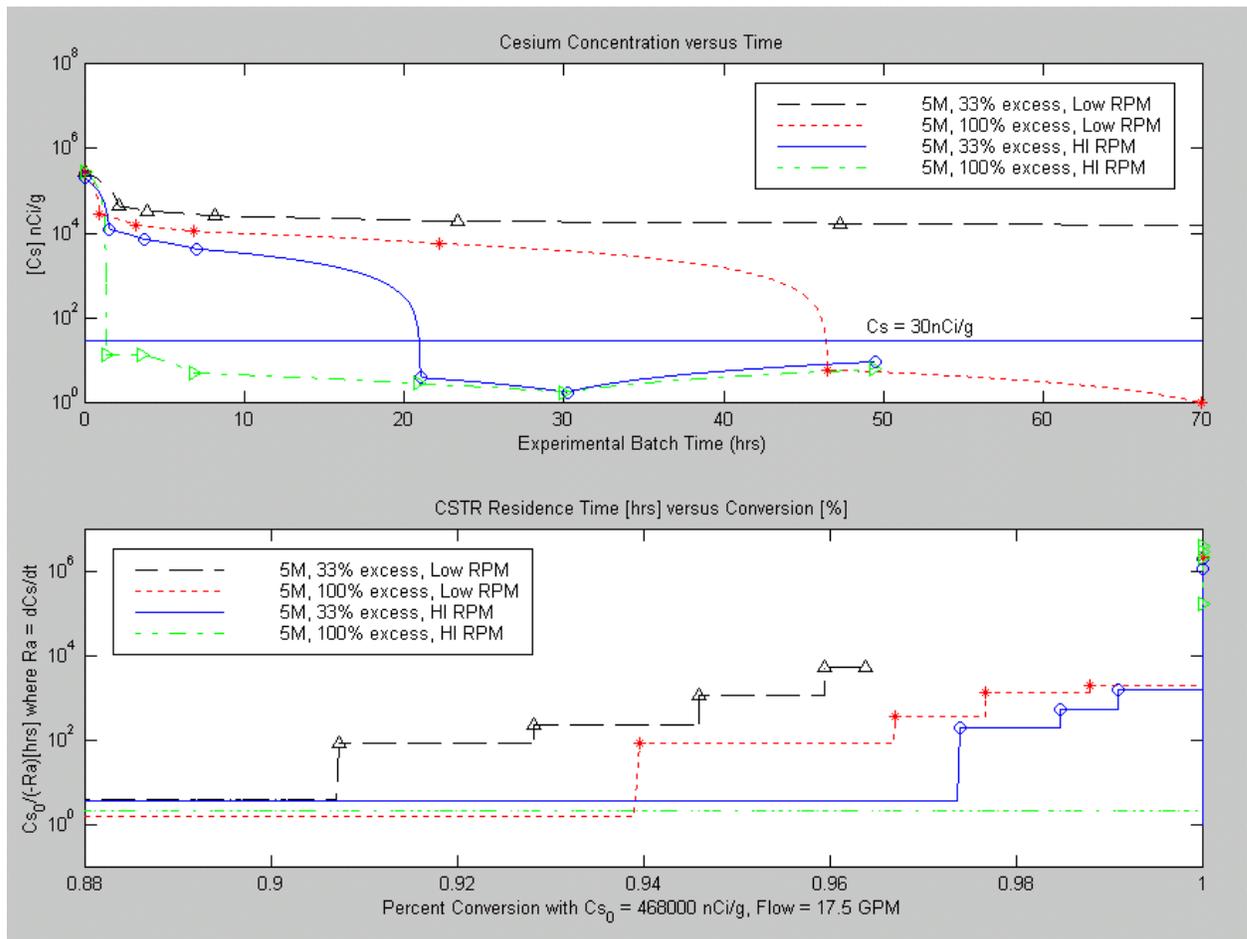


Figure 6.1-23 Rate of Cesium Precipitation by TPB

The rate of cesium precipitation by TPB is shown on Figure 6.1-23 for four 5M-sodium batch runs with varying degrees of percent excess TPB and agitation. The upper graph reveals the apparent inability to react the excess TPB due to lack of adequate mixing. Several runs contain a time frame where the reaction rate slows down and then speeds up. Only the high excess TPB/high agitation run reveals the lack of “plateau”. The lower graph indicates that various residence times required for various ranges in percent conversion. These residence times are converted into tank volumes in Table 6.1-12.

CSTR sizes depend on the ability to dissolve TPB into solution. As shown in Table 6.1-12, at low percent excess TPB and low agitation rates, the CSTRs must be very large to provide the residence time for the percent conversion. At high percent excess TPB and high agitation rates, the CSTRs are very small. This large discrepancy in CSTR sizes suggests the need for full understanding of how to dissolve TPB into solution. The salt work-off rate is 17.5 GPM. If one assumes that either temperature and/or proper agitation will solve the dissolution issue, two 16,000-gallon tanks would easily suffice.

Table 6.1-12 STTP CSTR Volumes

Tank #	5M, 33% excess TPB, 70 rpm	5M, 100% excess TPB, 70 rpm	5M, 33% excess TPB, 300 rpm	5M, 100% excess TPB, 300 rpm
1	3900 gallons	1600 gallons	3900 gallons	2000 gallons
2	59000 gallons	17900 gallons	9000 gallons	100 gallons
3	294600 gallons	50400 gallons	16200 gallons	100 gallons

6.1.5 Equipment

6.1.5.1 Building Layout

Building layout based on shielding and functional area sizes of the STTP alternative compared to equivalent DWPF facility layouts are provided below in Table 6.1-13. Major process equipment consists of chemical storage and feed tanks, continuously stirred reactors (CSTR), transfer pumps, agitators, 2 sets of crossflow filters, wash and concentration tanks, reactor, evaporator, 2 condenser/decanter, filter cleaning tanks and product hold tanks.

Table 6.1-13 STTP Building Layout Compared to the DWPF

	DWPF	STTP Alternative	STTP % of DWPF
AREA (SQ.FT):			
SHIELDED	16,278	12,030	74%
UNLOADING WELL	2,175	2,100	96%
LOW SHIELD		2,100	
OPERATING CORRIDOR	59,029	36,960	63%
CRANE OPERATING	18,457	19,020	103%
TOTAL AREA	95,939	72,210	75%
VOLUME(CU.FT):			
SHIELDED	640,344	541,350	84%
UNLOADING WELL	86,348	100,800	117%
LOW SHIELD		100,800	
OPERATING CORRIDOR	1,081,583	1,118,040	103%
CRANE OPERATING	700,261	1,008,060	144%
TOTAL VOLUME	2,508,536	2,869,050	114%

6.1.5.2 Tanks and Other Equipment

Table 6.1-14 Tanks for the STTP Alternative

Tank	Tank Size	Sizing Assumption
Fresh Waste Day Tank	25,000 gallons	Sized to hold about 24 hours of 6.44 M Na ⁺ feed for the ST TPB process.
Precipitation Tank	2 tanks each 16,000 gallons	Sized for about a 20 hour hold up (10 hours each) to allow the monosodium titanate (MST) contact time with the salt solution prior to concentration
MST Storage Tank	400 gallons	Sized for approximately four days of storage
Process Water Tank	80,000 gallons	Provides storage capacity for approximately one week for supplying dilution water to the Precipitation Tank and wash water for the Wash Water Tank.
NaTPB Storage Tank	20,000 gallons	Sized for approximately four weeks of storage
Concentrate Tank	10,000 gallons	As precipitate is concentrated, the required storage capacity in the Concentrate Tank decreases as compared to the Precipitation Tank. Concentrated precipitate will be produced at a rate of approximately 1900 gallons/day. Storage capacity for two batches is assumed. The concentrated precipitate will be transferred when approximately 4000 gallons have been collected, which will take about 48 hours.
Filtrate Hold Tanks	2 tanks each 100,000 gallons	Approximately 35,000 gallons of filtrate per day will be produced. 100,000 gallons is equivalent to approximately 3 days of production. (Note: the SPF can process approximately 60,000 gallons of salt solution per day assuming two-shift operation.) The Filtrate Hold Tanks also allow hold-up of material for analyses to ensure that the SPF Waste Acceptance Criteria are met (assumes analysis for Benzene, TPB, Hg, Sr, Pu, U, and others as necessary.) Two tanks are specified to allow sampling and analyses of one tank while the second tank is being filled.
Wash Tank	10,000 gallons	As the precipitate is concentrated, the required storage capacity in the Wash Tank decreases, compared to the Precipitation Tank. Precipitate will be produced at a rate of approximately 1900 gallons/day. 4000 gallons of concentrated precipitate can be washed in 48 hours at a wash rate of about 5 gpm. Increasing the wash rate decreases the wash time, but the concentrate tank requires ~50 hours to collect 4000 gallons of concentrated precipitate.
Recycle Wash Hold Tank	25,000 gallons	This tank is added to reduce the amount of process water used as dilution water in the Precipitation Tank. The tank is sized to hold 75% of the wash water from a single batch.
Precipitate Reactor Feed Tank	10,000 gallons	This tank holds washed, concentrated precipitate until it can be hydrolyzed in the Precipitate Reactor. It is sized to hold precipitate produced from 70 hours of continuous operation.
Precipitate Reactor	15,000 gallons	This tank is used to hydrolyze the washed precipitate to form precipitate hydrolysis aqueous (PHA) and benzene. It is sized to accommodate the large heel process.

Tank	Tank Size	Sizing Assumption
Precipitate Reactor Condenser/Decanter	100 gallons	This unit condenses the benzene and water vapor from the Precipitate Reactor and decants the liquid benzene for continuous transfer to the Organic Evaporator and aqueous condensate from concentration of the PHA after hydrolysis is complete to the Precipitate Reactor Overheads Tank.
Precipitate Hydrolysis Aqueous Surge Tank	60,000 gallons	The Precipitate Hydrolysis Aqueous Surge Tank was added to hold the PHA (bottoms) from the Precipitate Reactor until it can be transferred to the DWPF for vitrification. The vessel has been sized to accommodate 2 months storage of PHA (bottoms) with 66% of the water evaporated. The amount of water evaporated can decrease depending the on the sludge batch and will be addressed after downselect..
Precipitate Reactor Overheads Tank	7,500 gallons	This tank collects the aqueous stream from the Precipitate Reactor concentration for reuse as precipitate wash water in the Wash Tank.
Organic Evaporator	2,100 gallons	The Organic Evaporator is used to collect, wash and evaporate the benzene produced in the Precipitate Reactor.
Organic Evaporator Condenser/Decanter	100 gallons	This unit condenses the vapor from the Organic Evaporator and decants the purified benzene for continuous transfer to the Organic Evaporator Condensate Tank.
Organic Evaporator Condensate Tank	1,500 gallons	The condensed benzene from the Organic Evaporator Decanter is collected and held in this tank until analysis is completed. Once testing verifies that specifications have been met, the contents are transferred to the Organic Waste Storage Tank.
Organic Waste Storage Tank	40,000 gallons	This tank stores liquid benzene from the salt cell until it is burned in CIF.
Cleaning Solution Dump Tanks	2 Tanks each 1000 gallons	The Cleaning Solution Dump Tanks will receive chemicals sequentially for cleaning of the concentrate tank filters and wash tank filters.

6.1.5.3 Jumpers

Table 6.1-15 Summary of Jumper Usage for STTB Alternative

Jumper Application	Number of Jumpers
Process Jumpers	130
Process Jumpers with MOVs	28
3-way Process Jumpers	3
3-way Process Jumpers w/2 MOVs	1
Electrical Jumpers	53
Instrumentation Jumpers	48
TOTAL	263

6.2 Strontium / Alpha Sorption by Monosodium Titanate (MST) Addition

6.2.1 Process Overview

Both the Caustic Side Solvent Extraction (CSSX) and Crystalline Silicotitanate Non-Elutable Ion Exchange (CSTIX) processes contain an Alpha Sorption batch operation using MST addition to remove sufficient Strontium (Sr), Plutonium (Pu), Neptunium (Np), and Uranium (U) to be within the SPF Waste Acceptance Criteria. After 24 hours of contact with MST in the Alpha Sorption Tank (AST), the resulting slurry is transferred to the Filter Feed Tank (FFT) and continuous cross-flow filtration is used to remove and concentrate MST and entrained sludge to ~5 wt % solids in the FFT. The concentrated MST/sludge slurry is then washed to remove sodium salts before transfer to DWPF for incorporation into glass. Clarified salt solution, the filtrate from the process, is transferred to the Salt Solution Feed Tank for the CSSX alternative or the Recycle Blend Tank (RBT) for CSTIX alternative.

6.2.2 Trade Study Results

Two trade studies have been completed related to Alpha Sorption. The first study investigated the possibility of using existing facilities for Alpha Sorption, eliminating this operation from the proposed SWPF. (Ref. 67) The second study evaluated alternative equipment configurations to reduce the size and improve the utility of Alpha Sorption filters and pumps. (Ref. 7)

6.2.2.1 Use of Existing Facilities for MST Treatment and Filtration

In the Phase III pre-conceptual design (Ref. 2), equipment for Alpha Sorption and subsequent feed clarification is located in the proposed SWPF for the CSTIX and CSSX alternatives. Using an existing facility to do these operations could reduce the size and the cost of the proposed SWPF, if either of these alternatives are adopted. In particular, a study was completed to determine if using parts of the existing In-Tank Precipitation Facility or Late Wash Facility for treatment and filtration could be technically and economically justified. This was studied as part of Phase IV (Ref. 67).

Ideas for implementation were developed by a brainstorming team and evaluated by a panel of knowledgeable SRTC and HLW engineers and scientists. The evaluators determined the minimum functional requirements of a feed clarification facility and evaluated the proposals against this. Technical risk and maturity, potentially large cost and uncertainties leading to extended or expensive R&D were considered. None of the ideas met the feed clarification functional requirements within the limits of known technology. Further, the value of the scope reduction to the new facility was estimated to be “only” \$60 million. This is a relatively small savings compared to the increased risk of not meeting key functional requirements, such as production rate, which has life cycle costs of about \$350M per annum. Any of the ideas to implement feed clarification outside the facility that were workable at all, had associated development and

implementation cost, which would likely be comparable to the money “saved” from scope reduction of the baseline CSTIX or CSSX facility.

6.2.2.2 Alternative Configuration for Alpha Sorption in the SWPF

Because of the large size and less than optimum utility for Alpha Sorption equipment installed in the SWPF in Revision 0 of the BAR, a study of alternative configurations was completed. Based on results of this study (Ref. 7), the Alpha Sorption equipment configuration was changed (see Table 6.2-1). A filter feed tank has been added to increase the process utility of the filter units, enabling the size of the filter units and the pumps used to feed the filter units to be substantially reduced. A second, smaller filter unit has also been added for use in the MST / Sludge washing operation, eliminating the need to interrupt salt solution feed filtration to wash and filter the concentrated MST / Sludge solids slurry generated during salt solution feed clarification. (Ref. 7)

In addition, the filtration rate for the Alpha Sorption cycle has decreased to 21 gpm as a result of this process alternatives study for the Alpha Removal Process (Ref. 7). The process was modified to separate the filtration feed function from the AST by addition of a Filter Feed Tank (FFT). A smaller crossflow filter unit for MST/sludge solids washing has also been added (Table 6.2-1).

Table 6.2-1 Summary of Alpha Removal Equipment Changes

Alpha Removal Equipment	Previous Configuration	Current Configuration
Alpha Sorption Tank (AST)	125,000 gallons (working volume)	88,000 gallons (working volume)
Filter Feed Tank (FFT)	<i>Not included</i>	111,000 gallons (working volume)
CSTIX Recycle Blend Tank (RBT) <u>or</u> CSSX Salt Solution Feed Tank (SSFT)	125,000 gallons (working volume)	30,000 gallons (working volume)
Clarified Salt Solution Crossflow Filter Area	3,000 ft ²	1,000 ft ²
MST / Sludge solids Wash Cycle Filter Area	<i>Not included</i>	150 ft ²
Filter Feed Pump Capacity requirement @ axial velocity of 6 ft/sec	5,600 gpm	3,630 gpm
Filter Feed Pump Capacity requirement @ axial velocity of 9 ft/sec	8,500 gpm	5,450 gpm

This new configuration allows continuous filtration of clarified salt solution while a fresh batch of Salt Solution is treated and analyzed for Sr and alpha decontamination in the AST. By employing a continuous filtration step, the required filter area decreases to ~1,000 ft² and the filter feed pump capacity requirements decreases to 3,630-5,450 gpm (axial velocity ranging from 6 to 9 ft/sec).

6.2.3 R&D Results for Alpha Sorption

R&D activities for Alpha Sorption have focused on the use of Monosodium Titanate to remove Strontium (Sr), Plutonium (Pu), Neptunium (Np), and Uranium (U) from 5.6 M Na salt solution.

6.2.3.1 MST Concentration and Kinetics

The adsorption of Sr, Pu, U and Np on MST has been extensively studied and reported (Ref. 8-10). These studies were performed at MST concentrations of 0.2, 0.4, 1.1 and 2.0 g/L MST and at sodium concentrations of 4.5 and 7.5 M. Sr removal is very fast at both Na concentrations (See Figure 6.2-1), but both the extent and rate of Pu removal is limited at 7.5 M (See Figure 6.2-2). Test results show that both the extent and rate of Pu removal improves as the Na concentration is reduced and as the MST concentration is increased (See Figure 6.2-3). The average salt solution is predicted to be 6.44 M Na. The sodium concentration chosen for CSTIX and CSSX processes is 5.6 M. To ensure removal of Pu at average concentration and activity (See Section 5.3.4), the salt solution is diluted before MST addition and the maximum MST concentration (0.4 g/L) shown to be acceptable for DWPF glasses is added (Ref. 68).

A study (Ref. 69) of MST kinetics at 5.6 M Na shows rapid Sr removal at a MST concentration of 0.4 g/L (See Figure 6.2-4). In addition, it shows that a 24-hour reaction period will reduce the soluble Pu concentration to less than 20 $\mu\text{g/L}$ ($\text{DF} \geq 10$) at this sodium concentration (See Figure 6.2-5). Since the soluble alpha activity in average waste is dominated by Pu, these conditions ensure that the SPF alpha limit can be met after 24 hours contact time for the overall average of blended salt solution fed to the CSSX or CSTIX processes. However, the range of soluble Pu concentrations in the Tank Farm (both total concentration and isotopic distribution) is poorly characterized. Additional work is needed to assure that sufficient Pu can be removed at more bounding conditions.

There is built-in conservatism regarding the contact time between the MST and the salt solution. The proposed batch cycle has a 24-hour reaction period during which the goal is to attain sufficient adsorption to meet the SPF WAC requirement. In the proposed batch process, the salt solution actually will have considerably longer contact time with MST. The 24-hour reaction period is followed by an additional 20-hour hold period in the AST for sampling and analysis. After analysis is complete, the transfer of the AST contents to the Filter Feed Tank (FFT) then takes 11 hours, assuming a transfer rate of 130 gpm. Finally, it takes about 70 hours to filter and send the filtrate to the Recycle Blend Tank for CSTIX or the Salt Solution Feed Tank for CSSX. Thus the salt solution from a single AST batch averages an additional 50 to 60 hours of contact time with MST. In addition, five to eight batches of clarified salt solution must be processed to accumulate enough MST and sludge solids for a washing batch. This means that by the seventh batch, the MST to salt solution ratio in the FFT will be 7X higher than the nominal 0.4 g/L. If the MST is not saturated from previous batches (which is likely), there will be additional adsorption capacity over and above that from the freshly added MST.

6.2.3.2 Dilution in Alpha Sorption Tank (AST)

ORNL recommended that salt solution feed be diluted with NaOH (1.5 to 2 M) to maintain the hydroxide activity and to prevent aluminum precipitation. This dilution will be performed in the AST. The Alpha Sorption portion of the CSTIX and CSSX flowsheets has been modified to include dilution in the AST with dilute NaOH. The addition of dilute NaOH increases the CSTIX column feed rate or the CSSX extraction feed rate by approximately 1 gpm over dilution with water only. At 6.9 M gallons per year of salt solution workoff, about 800 Kgal of 2 M NaOH is required – equivalent to about 84 Kgal of 50 % NaOH. The dilution caustic will produce an incremental flow of approximately 400,000 gallons of additional DSS per year and about 640,000 gallons of additional saltstone per year. Performing dilution in the AST increases the required working volume of the AST by approximately 20 %.

6.2.3.3 Rerouting of Water from Column Loading and Unloading

For the CSTIX process, HLW Process Engineering recommends that water from column loading and excess water from column unloading should be sent to the Wash Water Hold Tank (WWHT) and combined with spent washes from filter cleaning, instead of directly to the Recycle Blend Tank (RBT) that will contain clarified salt solution. By sending this water to the WWHT (which eventually recycles to the AST), any CST fines from loading and unloading a resin column are removed by filtration, thus preventing column plugging. This does not change the overall material balance since water from column loading and unloading was previously included as part of the clarified salt solution feed to the columns. For the revised material balance, the water is apportioned to each batch of treated salt solution as part of the dilution water added to the AST. However, the water will actually be produced in large batches at intervals of 3 to 5 months in the CSTIX alternative. This large volume of potentially contaminated water may require special handling at the AST and a change in the saltstone formulation to handle more dilute solutions when it is processed.

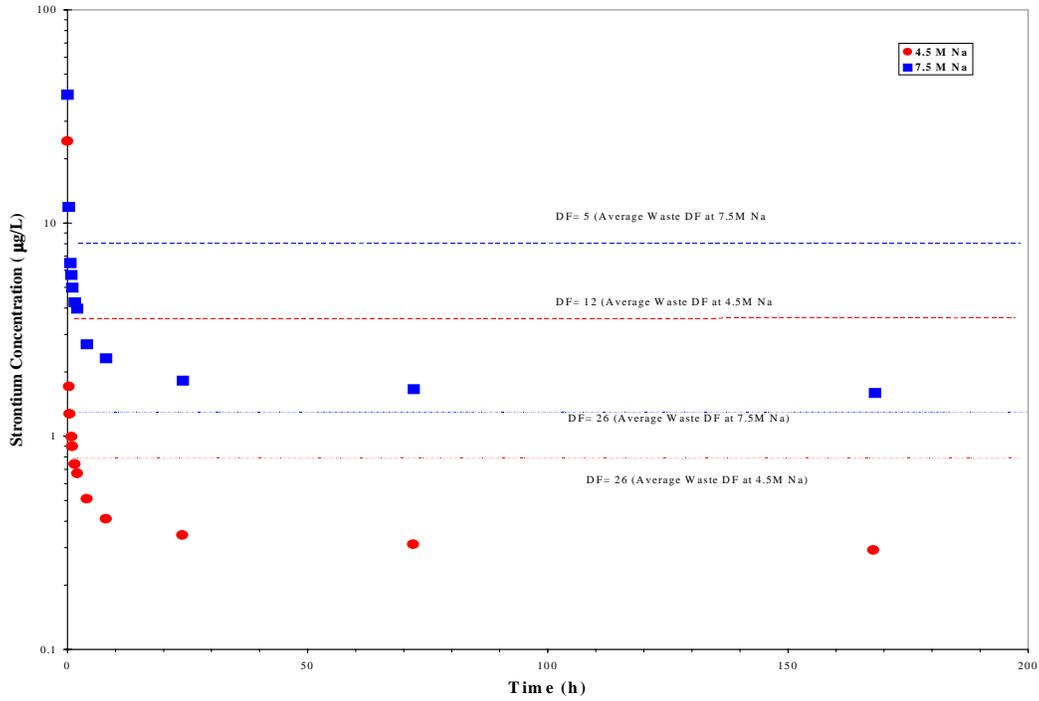


Figure 6.2-1 Sr Removal Kinetics at 0.2 g/L MST Addition

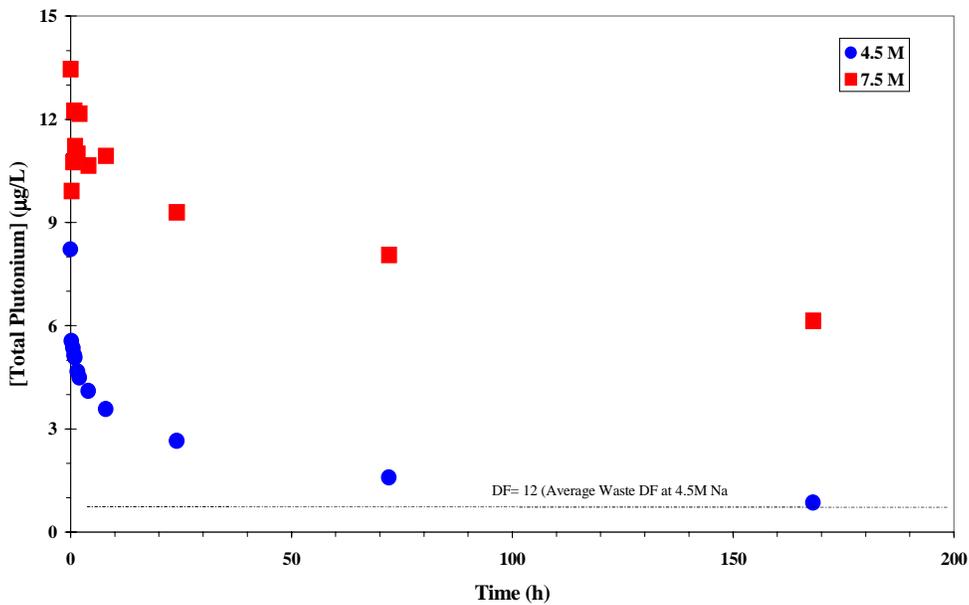


Figure 6.2-2 Pu Removal Kinetics at 0.2g/L MST Addition

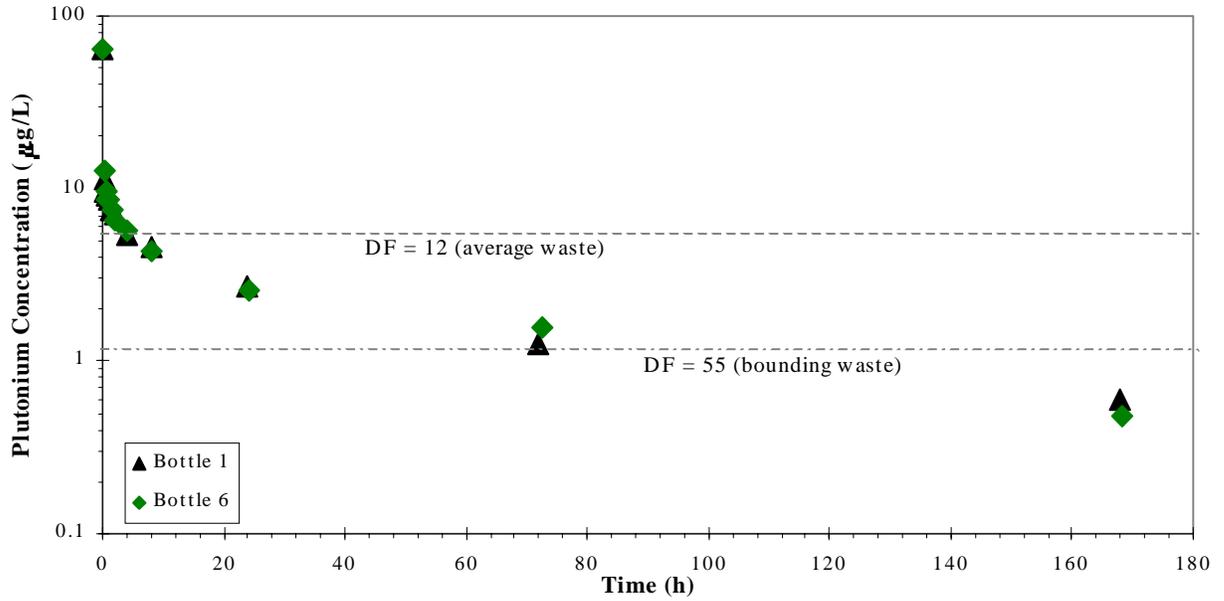


Figure 6.2-3 Comparison of Plutonium Concentration Tests in 4.5 M Na and 0.4 g/L MST

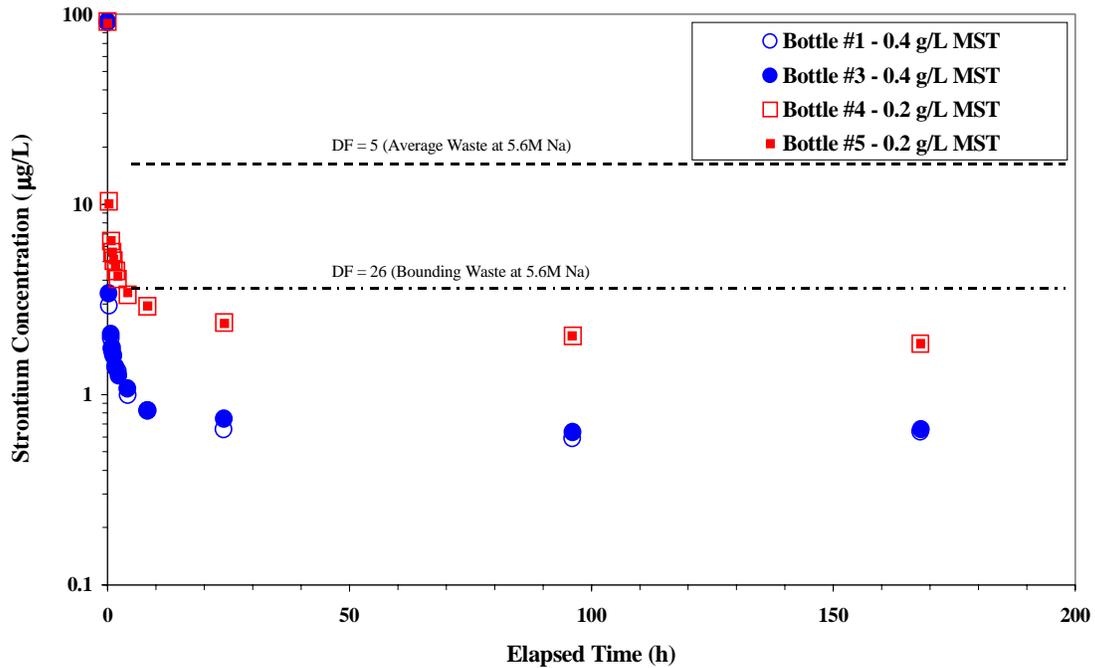


Figure 6.2-4 Comparison of Sr Removal Kinetics 5.6 M Na at 0.2 and 0.4 g/L MST

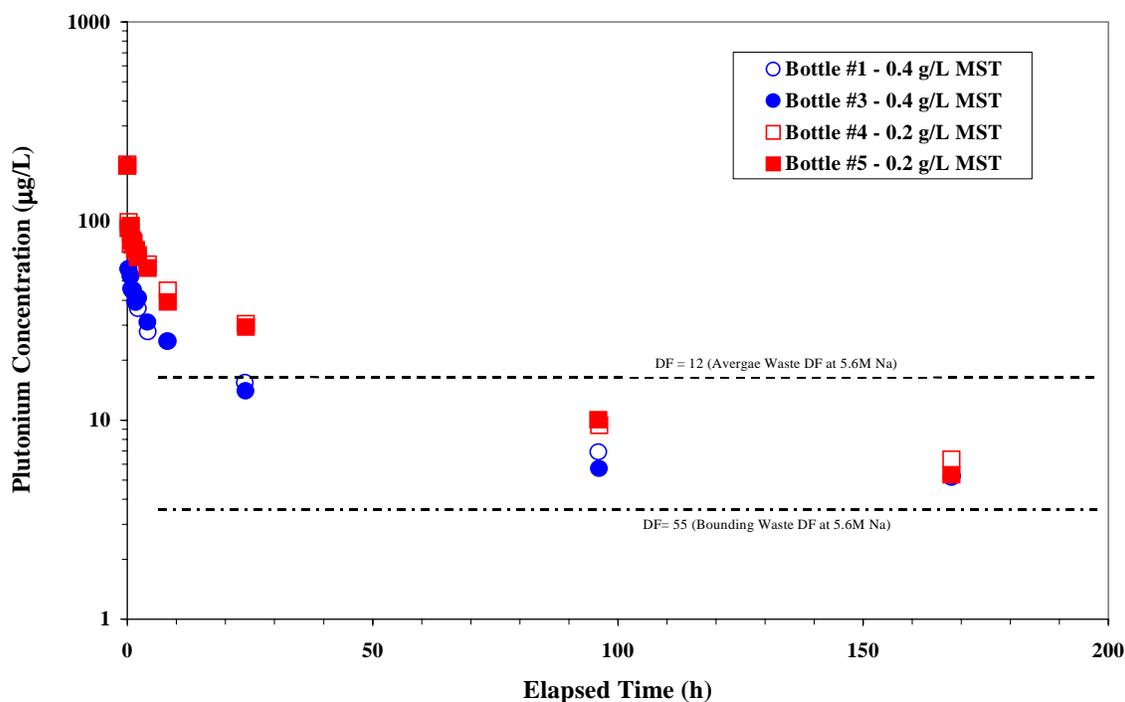


Figure 6.2-5 Comparison of Pu Removal Kinetics in 5.6 M Na at 0.2 and 0.4 g/L MST

6.2.3.4 MST / Sludge Filtration

Tests on filtration of MST/sludge simulant mixtures alone (Ref. 70) and with additives and flocculants to improve filtration rates (Ref. 71, 72) were performed during Phase IV. Various MST/sludge simulant mixtures (1:2, ~1:1, 2:1) were filtered up to ~5 wt % in the SRTC Parallel Rheology Experimental Filter (PREF). The filter fluxes were, on average, about 0.02 gpm/ft² and did not vary significantly with composition (See Figure 6.2-6). Bentonite and polyethylene oxide, the most promising additives tested, increased filtration rates by 25 – 35 %. Hydroxamated amines by Cytec and Alclar® 600, the most promising flocculants tested, increased filtration rates 25 - 30%. Real waste filtration test data (Ref. 73) from testing using the SRTC Cells Unit Filter (CUF) with actual sludge samples combined with MST and supernate from HLW Tanks 37H and 44F show reasonable agreement between filtration with real waste and filtration testing with simulant (See Figure 6.2-7). The filtration testing with real waste confirms that simulant testing provided a conservative design basis for filtration equipment sizing.

The Alpha Sorption cycle time is based on a filtrate rate of 21 gpm. At an average of 0.02 gpm/ft² filter flux, the required filter area is ~1000 ft². Based on preliminary tube sizing, a filter unit containing 609 tubes that are 0.75 inches OD (outside diameter) and 10 feet long would yield the required filter area. These tubes would be contained within a 28-

inch diameter tube bundle. The filter feed rate would be 3,630 gpm to yield an axial velocity of 6 ft/sec or 5,450 gpm for an axial velocity of 9 ft/sec.

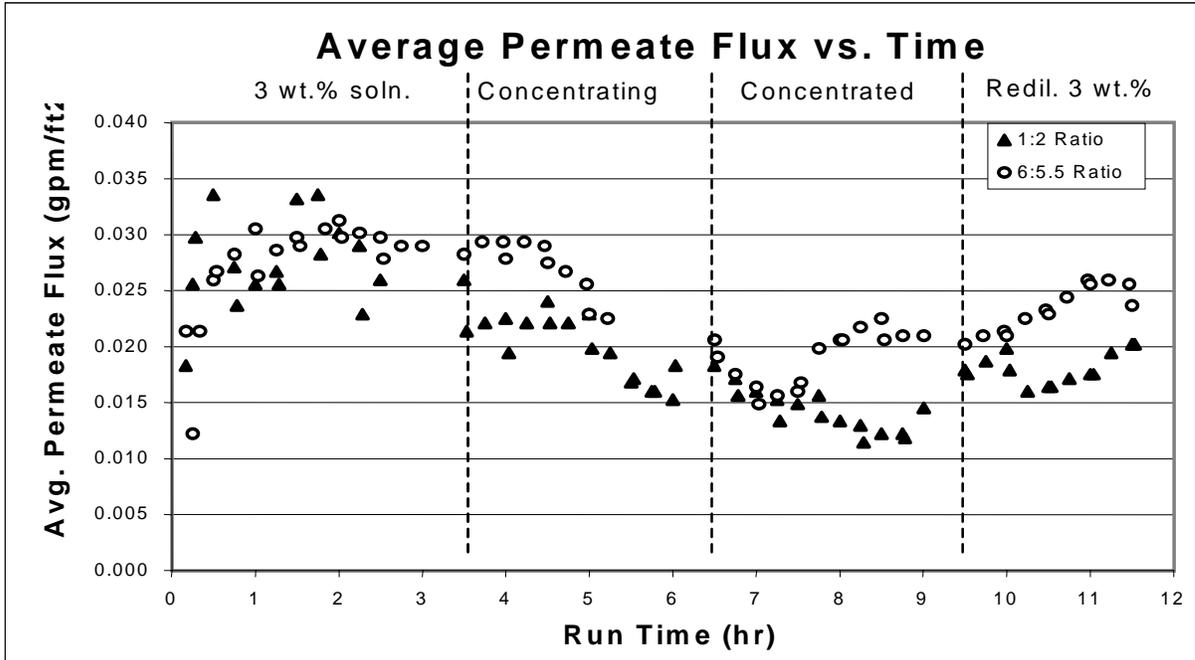


Figure 6.2-6 MST/Sludge Filtration Rates

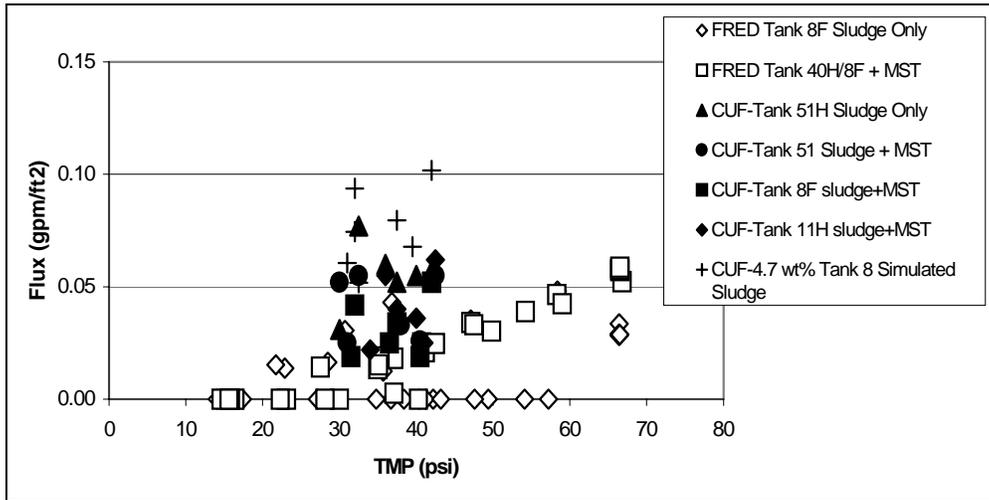


Figure 6.2-7 CUF Real Waste MST/Sludge Filtration Date at 6 wt% solids

6.2.3.5 MST / Sludge Resuspension

Tests were performed at Oak Ridge National Laboratory (ORNL) to study the rheology and resuspension characteristics of MST/sludge slurries at both lab and pilot scale. Tests showed that settled slurry is relatively easy to resuspend at pilot scale after settling for 14 days – although it is possible that not all the MST was resuspended (Ref. 74). After 60 days settling time, the slurry could not be completely resuspended even at an impeller tip-speed of 300 m/min. Storage of MST/sludge mixtures at 80 °C for as little as 3 days had a dramatic effect on yield stress and consistency. After 60 days at 80 °C, the yield stress increased by a factor of 300 and the consistency by a factor of 30. These measurements indicate MST/sludge must be cooled to assure resuspension, in the event agitation is lost for an extended period. The AST, the SSRT and the downstream tanks (i.e., intermediate pump pit tanks and MST /Sludge processing tanks located in the DWPF) will require both cooling coils and high powered/high tip-speed agitators to ensure resuspension of settled solids.

A CFD model was developed to simulate the resuspension of sludge and MST tests run at ORNL (Ref. 74). This model contained 13552 computational cells. The tank geometry allowed the problem to be run using 120° symmetry. This test was of interest to modeling because it contained a piece of flow information to which calculated results could be compared. A velocity meter was positioned in the tank near the intersection of the side and bottom walls. In steady state, which was the only mode in which the calculation was run, there was quite good agreement between the calculated velocity from the model and that measured during the test.⁴ This gives some confidence that the calculation adequately represents the physical phenomena in the tank. It would also imply that the velocities in the tank are, on the whole, rather low and that resuspension with this arrangement in a large tank would be impractical. Previous analyses of the large waste tanks in the High Level Waste system have shown that even with 150 hp slurry pumps the velocities in tanks are too low to suspend an MST sludge. This again points to the impracticality of using an existing waste tank as the actinide removal facility.

Figure 6.2-8 shows the velocity contours, in meters/second, for the resuspension test. These contours show the expected zero velocity in the center of the tank under the impeller and the decrease in the velocity along the bottom of the tank as the fluid reaches the outer wall.

⁴ The test measured velocity was 0.48 m/s which is well within the range of the contour in that portion of the tank.

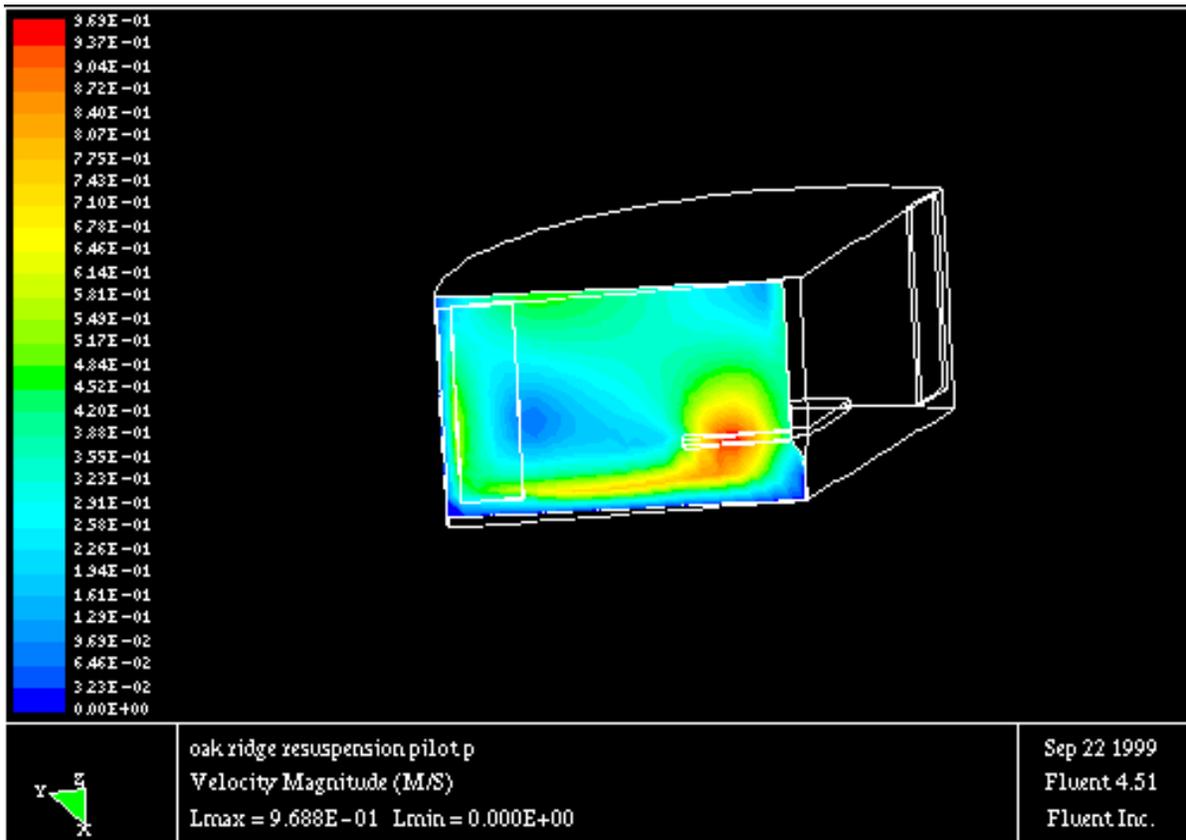


Figure 6.2-8 Velocity Contours for the Resuspension Test

6.2.4 Bases for Alpha and Sr Sorption in CSTIX and CSSX Material Balances

6.2.4.1 Alpha and Strontium Decontamination by MST Addition

The CSTIX and CSSX alternatives require a separate batch operation for MST treatment and feed clarification to prepare salt solution for subsequent treatment to remove cesium. A slurry of monosodium titanate (MST) is first added to diluted salt solution. MST sorbs soluble alpha contamination and strontium. After agitating for 24 hours, the resulting mixture is filtered, separating the MST solids and entrained sludge from the clarified salt solution (filtrate). These operations are designated as Alpha Sorption for CSTIX and CSSX..

6.2.4.2 Detailed Process Description

For the CSTIX or the CSSX Processes, a salt solution feed batch of ~73,500 gallons at 6.44 M Na⁺ will be transferred to the 88,000 gallon (working volume) Alpha Sorption Tank (AST) for dilution to ~5.6 M [Na⁺]. (See Figure 6.2-9) In the modified equipment configuration now adopted for Alpha Sorption, salt solution is received into the AST, where it is diluted and batch treated with a slurry of MST to sorb Pu, Np, U and Sr onto the MST. After 24 hours of sorption time, the dilute MST/sludge slurry in the AST is transferred to the 111,000-gallon Filter Feed Tank (FFT).

MST/sludge slurry will be fed continuously from the FFT to a cross-flow filter unit to remove both MST and sludge solids. The filtrate stream (clarified salt solution) will be sent to the CSTIX Recycle Blend Tank or the CSSX Salt Solution Feed Tank (different name for the two alternatives). When the 10,000 gallon heel in the FFT is concentrated to about 5 wt % solids (five to eight salt solution feed batches), it will then be transferred to the Sludge Solids Receipt Tank (SSRT) for washing to reduce the sodium concentration in the solution associated with the MST/sludge solids to less than 0.5 M. A separate, smaller crossflow filter to be used in the MST/sludge washing cycle to avoid interrupting the production of clarified salt solution. The washed solids are then stored within the SWPF until they can be transferred to the DWPF for further processing. Cleaning solutions will be run through the crossflow filter unit after two or three 73,500-gallon batches of salt solution have been processed through as CSSX or CSTIX feed to minimize fouling and plugging of the sintered metal filter media.

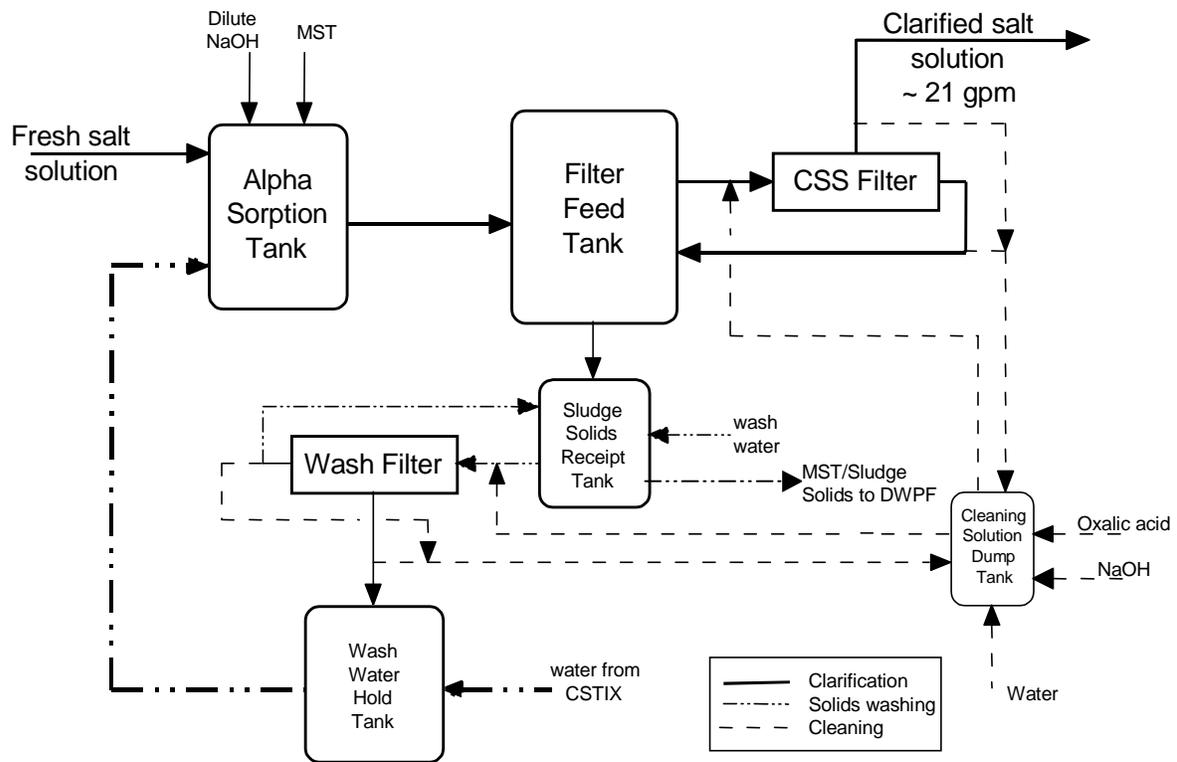


Figure 6.2-9 Alpha Decontamination by MST Addition

6.2.4.3 Technical Bases

6.2.4.3.1 MST addition and Sr/Pu adsorption

Phase III, IV and V R&D results on MST adsorption kinetics (Ref. 8, 9,10, 69) have shown that a MST concentration of 0.4 g/L will be needed to ensure adequate adsorption of Pu, Np and ⁹⁰Sr to achieve the desired decontamination of 5.6 M Na⁺ salt solution. Experimentally, both strontium (Sr) and plutonium (Pu) sorb faster at the higher MST concentration of 0.4 g/L. Based on the sorption rates for Pu found in Phase V MST sorption kinetics testing (Ref. 69), a minimum reaction time of 24 hours is needed to achieve a decontamination factor (DF) of 12 for an initial Pu concentration of 0.2 mg/L. In contrast Sr sorbs rapidly onto MST, reaching the required DF in less than 2 hours.

6.2.4.3.2 Details of Alpha Sorption Process

For the CSTIX and CSSX processes, MST sorption and filtration is required prior to ion exchange or solvent extraction processing. A batch of salt solution will be diluted with water from the Wash Water Hold Tank (and/or fresh process water), then treated with MST for alpha and Sr removal in the Alpha Sorption Tank (AST). The resulting slurry will then be transferred to the Filter Feed Tank and filtered using the CSS Filter. Filtrate goes to the Recycle Blend Tank (RBT) in the CSTIX process or to the Salt Solution Feed Tank (SSFT) in the CSSX process. In addition to the MST solids, any sludge solids entrained in the salt solution will also be removed during filtration in order to meet the SPF WAC. Sludge solids must also be removed to prevent plugging of the lead CSTIX ion exchange column or avoid introducing insoluble solids into the CSSX extraction banks that could interfere with effective separation of the organic and aqueous phases .

Accumulated sludge and MST solids from the heel of the Filter Feed Tank (FFT) must be washed prior to transfer to the DWPF to reduce the soluble salt content associated with the solids. The concentrated MST/sludge slurry will be transferred to the Sludge Solids Receipt Tank (SSRT) where the solids are washed with water and filtered using the Wash Filter to maintain the solids content at 5 wt% during washing. Spent wash water is held in the Wash Water Hold Tank (WWHT) until it can be recycled as part of the dilution water added to the AST for a subsequent batch of salt solution feed.

For the CSTIX alternative only, water used to load and unload resin from the columns will also be sent to the WWHT and then on to the AST to ensure removal of any CST fines. For material balance purposes, water from column loading and unloading is gradually recycled to the WWHT, but the large volumes of water generated when a column is loaded or unloaded may occasionally require diluting the salt solution below 5.6 M in AST operations for a brief period. Based on projected column cycles, these volumes could be generated in a relatively short time every 2 to 3 months. Transfers to the WWHT from column loading (47,100 gal), column unloading (25,950 gal) and solids washing (~25,000 gallons) must be staged appropriately, since the proposed design capacity of the WWHT is presently 25,000 gallons.

MST Treatment

For the CSTIX and CSSX alternatives, blending during waste removal may be necessary to reduce mercury (Hg) concentration to less than 250 mg/L. Up to 73,500 gallons of salt solution containing suspended sludge solids is transferred at an average rate of 130 gpm to the AST. The salt solution is diluted with wash water and NaOH to 5.6 M Na⁺. Subsequently, about 300 gallons of MST slurry is then added to the AST. The resulting slurry is mixed for 24 hours to assure adequate sorption time for the ⁹⁰Sr and alpha contaminants. The slurry is then sampled, filtered and analyzed to confirm adequate decontamination to be within WAC limits for the SPF ([total alpha] < 18 nCi/g and [⁹⁰Sr] < 40 nCi/g). After analysis is completed, the slurry is transferred to the Filter Feed Tank (FFT) for crossflow filtration.

Filtering

Using one of two cross-flow filter units, the slurry in the FFT is continuously filtered at a filtrate production rate of 21 gpm to yield about 88,000 gallons of clarified salt solution for further processing. A heel of about 10,000 gallons of more concentrated slurry of residual insoluble solids remains in the FFT at the end of filtration. The insoluble solids (Table 6.2-2) from five to eight consecutive batches are allowed to accumulate in the FFT before further processing.

Table 6.2-2 Components in Insoluble Solids

Insoluble Species
Fe(OH) ₃
Al(OH) ₃
NaTi ₂ O ₅ H
NaTiSr(OH) ₂
NaTiNa ₂ U ₂ O ₇
Al ₂ O ₃
B ₂ O ₃
Cr ₂ O ₃
CuO
Fe ₂ O ₃
HgO
K ₂ O
NiO
SiO ₂
TiO ₂
U ₃ O ₈
ZrO ₂

For the CSTIX process, clarified salt solution is transferred directly to the Recycle Blend Tank to provide feed for the next process operation, ^{137}Cs removal by CST ion exchange. For the CSSX process, clarified salt solution is transferred directly to the Salt Solution Feed Tank to provide feed for the next process operation, ^{137}Cs removal by solvent extraction.

Residual Solids Washing

After the MST and sludge solids from five to eight salt solution batches (~ 5 wt % insoluble solids) have accumulated in the heel of the FFT, filtration is halted and the 10,000 gallon heel is transferred to the Sludge Solids Receipt Tank (SSRT). Process water is added to the SSRT at a rate of 4.5 gpm to wash the solids, while simultaneously filtering to yield clarified wash water at the same rate. Washing continues until the sodium concentration is reduced to <0.5 M in the solution. At the end of washing a batch, approximately 25,000 gallons of wash water will have accumulated in the Wash Water Hold Tank. The spent wash water will be used in diluting the next five to eight incoming 73,500-gallon batches of salt solution feed.

Filter Unit Cleaning

To maintain optimum filtration rates, the cross-flow filter units must be cleaned periodically. A filter cleaning operation is assumed to be required after processing 200,000 gallons of salt solution, corresponding to a cleaning operation after two or three 73,500-gallon batches of salt solution feed have been processed through the AST. For a filter cleaning cycle, these steps and volumes of solution or water are assumed:

- 1) 1,000 gallons of about 1 M NaOH are prepared by adding 945 gallons of process water and 55 gallons of 50 wt % sodium hydroxide (sp. g. = 1.525) from the Caustic Storage Tank to the Cleaning Solution Dump Tank (CSDT).
- 2) The 1 M NaOH solution is circulated through the filter unit while periodically back-pulsing the filter unit to dislodge any accumulated solids.
- 3) The NaOH solution in the filter unit and CSDT is transferred to the AST.
- 4) To reduce the residual NaOH concentration remaining in the filter unit and CSDT, 1,000 gallons of inhibited water is added to the CSDT and circulated through the filter unit while periodically back-pulsing the filter unit.
- 5) The water rinse is transferred from the CSDT and filter unit to the AST.
- 6) 1,000 gallons of about 4 wt % oxalic acid (sp. g. = 1.014) are prepared in the CSDT.
- 7) The oxalic acid is circulated from the CSDT through the filter unit and returned to the CSDT while periodically backpulsing the filter unit.
- 8) At the end of the acid cleaning cycle, the oxalic acid is transferred from the filter unit and the CSDT to the AST, where it reacts with excess NaOH to yield sodium oxalate.
- 9) 1,000 gallons of about 1 M NaOH is prepared by adding 945 gallons of process water and 55 gallons of 50 wt % NaOH from the Caustic Storage Tank to the CSDT.
- 10) The NaOH solution is circulated from the CSDT through the filter unit to condition the filter. Circulation of the solution is stopped and the filter unit is left filled with

the caustic solution until placed in service for processing either salt solution from the AST (for the AST filter unit) or wash water from the SSRT (for the SSRT Washing filter unit).

Bases for Cycle Times, Vessel Sizing and Process Flow Rates

For the MST treatment and filtration steps of the CSTIX or CSSX alternatives, the following bases for major process evolutions affecting cycle time, vessel sizing and process flow rates are given:

- Fill AST with 73,500 gallons of salt solution @ 130 gpm	10 hours
- Addition of NaOH, Wash Water and MST to the AST	5 hours
- Reaction time for MST with alpha contaminants and Sr	24 hours
- Hold time for sampling & analysis of treated salt solution in AST	20 hours
- Transfer AST to Filter Feed Tank @ 130 gpm	11 hours
- <u>Filter 88,000 gallons treated salt solution @ 21 gpm</u>	<u>(70 hours)*</u>
- Total Cycle Time	70 hours

* The filtration cycle time in parentheses does not add to the total cycle time because a separate Filter Feed Tank is used while a new batch of salt solution is transferred and treated in the AST in parallel with the filtration cycle.

6.2.4.3.3 Application of Continuous Stirred Reactors to Alpha Removal

The removal of Strontium and Actinides from contaminated salt solution is to be performed by reaction with monosodium titanate (MST). Sr/Alpha removal by MST is common to all salt disposition options, but only the STTP option is to utilize continuous stirred tank reactors (CSTR's) due to the reactors already being used for Cesium decontamination. Based on the kinetics of the reactions, the CSTR's must be sized to provide the residence or hold up time necessary to achieve the desired percent conversion. Utilizing batch Pu removal kinetics for 5.6 M Na solution with 0.4 g/L MST addition, sizes of CSTR's were calculated for the Alpha Removal process for CST and CSSX.

Sizing Methodology for CSTR's in STTP was discussed in Sections 6.1.4.1 and 6.1.4.2. This approach was taken with the 5.6M Na batch kinetic data to size two CSTR's for the CSSX and CST Alpha Removal process. Table 6.2-3 provides the raw batch data and decontamination rates at 5.6 M Na and 0.4 g/L MST utilized for CSTR sizing.

Figure 6.2-10 plots both the Phase V simulant testing batch kinetic data (Ref. 69) and the decontamination rate information for Pu required to size the two tanks. The lower plot in the figure demonstrates the calculation of each tank volume required to proceed from 0% conversion to the target 93.5% conversion for an initial Pu concentration of 191 µg/L. The area of the rectangles determines the mean residence time of each tank. For 80% conversion of the initial Pu concentration (191.4 µg/L), 32.6 hours of mean residence time are required. For conversion from 80% to 93.5%, 70.2 hours of mean residence time are required. For a throughput of 17.5 GPM, these tanks would be 35,000 and 74,000 gallons respectively. This preliminary sizing with a residence time of 103 hours indicates that two very large reactors are needed to perform Alpha Sorption with two CSTRs in series.

Table 6.2-3 Plutonium Concentration versus Time for Phase V Simulant data

Elapsed Time (hr)	Total Pu ($\mu\text{g/L}$)	Percent Conversion	R_{Pu} ($\mu\text{g/L/hr}$)	$\text{Pu}_0/r_{\text{Pu}}$ (hours)
0	191.4	0	518	0.4
0.3	62.2	67.5	274.3	0.7
0.7	51.7	73.0	18.2	10.9
0.9	45.8	76.1	18.1	10.6
1.2	42.0	78.0	9.0	22.4
1.7	38.9	79.7	6.7	28.6
2.3	35.0	81.7	4.8	40.8
4.1	31.0	83.8	1.8	106
8.2	24.9	87.0	1.1	179
24.1	14.1	92.6	0.4	557
96.2	5.7	97.0	0.1	3818
167.8	5.2	97.3	0.01	30000

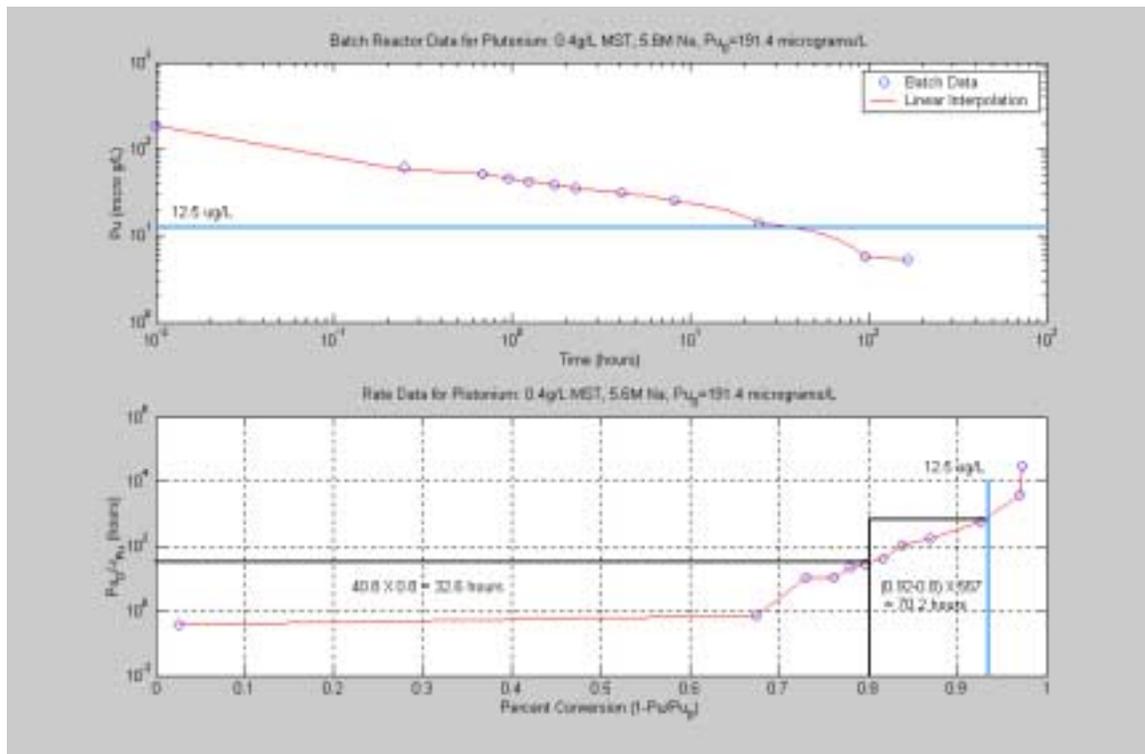


Figure 6.2-10 CSTR Sizing Data for 5.6 M Na with 0.4 g/L MST

6.2.5 Description of the Alpha Sorption SpeedUp™ Model

A relatively detailed and complete dynamic SpeedUp™ model of the alpha sorption process to pretreat salt solution has been developed. By using fractional cleaning cycles and washing cycles the Alpha Sorption steady-state process flow diagram material balance is preserved for the current Alpha Sorption configuration. A schematic diagram of the model is shown in Figure 6.2-10. The model considers the four main tanks in the process: the Alpha Sorption Tank (AST), the CSTIX Recycle Blend Tank (RBT), the Sludge Slurry Receipt Tank (SSRT) and the Wash Water Hold Tank (WWHT). The time delay associated with the Filter Feed Tank (FFT) and analytical time is conservatively ignored, since the AST is sampled after 24-hr sorption. The total cycle time for the alpha sorption process is 70 hours. The operation of each tank as implemented in the model is described below.

6.2.5.1 Alpha Sorption Tank (AST) / Filter Feed Tank (FFT)

Salt solution is added to the AST in 73.5 kgal batches. In addition, 11.5 kgal of 2.0 M NaOH, 373 gal of 12.8 wt % MST and 2.8 kgal of water are added to the tank with each salt batch. The water addition is from ion-exchange operations loading and unloading the CST into the columns. If at least 5 kgal of spent wash water are in the WWHT, a 5-kgal batch of spent wash water is also added to the AST. Adsorption of alpha emitting species by MST is assumed to proceed to equilibrium. Decontamination factors (DF) for uranium, strontium and plutonium are calculated from their respective equilibrium relationships and K_d factors using

$$DF = \frac{C_0}{C_f} \quad \text{and} \quad K_d = (DF - 1) \frac{V}{m}$$

where C_0 is the initial concentration of the adsorbed species, C_f is the final concentration at equilibrium, m is the mass of MST (in grams) added to the solution and V is the solution volume in mL (For 0.4 g MST/L solution, $V/m = 2500$ mL/g). A time delay of 24 hours is built into the AST/ FFT cycle to allow time for the adsorption equilibrium to be achieved. Table 6.2-4 shows the DF and K_d values used in the material balance.

Table 6.2-4 DF and K_d Values Used in Material Balances

Element	DF	K_d
Sr	100	2.48E5
Pu	50	1.23E5
U	1.5	1.25E3

Each batch of material in the AST is treated by transferring to the FFT and then passing it through a filter. No credit is taken in the model for the average residence time in the FFT. Filtration is assumed to be 100% efficient in removing solids. Filtrate flow to the RBT (or the SSFT) is 21 gpm and the slurry is returned to the FFT. Filtration proceeds until the level in the FFT drops to ~10 kgal of concentrated slurry.

6.2.5.2 Recycle Blend Tank (RBT)

Clarified salt solution from the FFT filtration is collected in the RBT (or the SSFT). After the first batch is added, the tank is continuously emptied to represent treatment of the salt solution by the CST ion-exchange or CSSX solvent extraction. Simulations show that clarified salt solution must be processed continuously at a rate of about 21 gpm to work off the RBT (or the SSFT) inventory.

6.2.5.3 Sludge Slurry Receipt Tank (SSRT)

When the 10-kgal heel in the FFT exceeds 5 wt % solids, the heel is transferred into the SSRT. Simulations indicated that this occurs after about every 6-7 AST batches. When a batch is transferred into the SSRT, water is added at 50 gpm to wash the slurry to 0.5 M sodium. During the wash cycle, the tank contents are passed through a filter to remove solids and the spent wash water collected in the WWHT. Concentrate (high solids) from the filter is recycled to the SSRT. When the SSRT solution is reduced to 0.5 M NaOH, the washing is stopped and the tank contents emptied to simulate feeding the DWPF process. It is assumed that the tank can be emptied immediately following a wash cycle.

6.2.5.4 Wash Water Hold Tank (WWHT)

Spent wash water from the SSRT filtration is collected in the WWHT. The simulations show that just over 20 kgal of spent wash water is collected from each SSRT batch. When available, the spent wash water is recycled to the AST in 5 kgal batches. This means that, since it takes about five salt batches in the AST to produce a batch in the WWHT, four out of the five AST batches will also have spent wash water added to the tank.

concentration and activity (1.33 Ci/g). Bounding soluble Pu concentrations and isotopic distributions must be characterized and tested to ensure Alpha Removal by MST will achieve decontamination of Pu for all Tank Farm salt solution feeds. Also, continued development of rapid analytical techniques is required to meet design cycle times.

Low filtration flux rates for MST / sludge slurries previously required a large cross-flow filter (~3,000 ft²) and a filter circulation rate in the range of 5,500 to 8,500 gpm. Based on results of a trade study of alternative process configurations for Alpha Removal (Ref. 7), a Filter Feed Tank and a smaller filter unit for solids washing have been added to the Alpha Removal process to allow continuous filtration of MST/Sludge solids. The separation of the filtration step results in a lower filtrate flow of ~21 gpm and a smaller crossflow filter area of ~1,000 ft². Filter circulation rates decrease into the range of 3,600 to 5,400 gpm as a result of the smaller crossflow filter sizes.

6.3 CST Non-Elutable Ion Exchange (CSTIX)

The proposed CSTIX process would use crystalline silicotitanate (CST) resin to remove Cs from clarified salt solution generated from the Alpha Sorption operation described in Section 6.2. Since the Cs cannot be eluted from the CST without destroying the ion exchange properties of the resin, the loaded resin would be transferred to the DWPF to be combined with sludge and frit to produce borosilicate glass. The decontaminated salt solution would go to the Saltstone Production Facility.

The overall process would thus include these steps:

- MST addition to remove Sr, Pu, Np and U to be within the SPF WAC TRU limits.
- Filtration to remove sludge and MST solids from the salt solution to prevent plugging of the ion exchange (IX) columns. After washing to remove soluble salts, these solids would flow to the DWPF.
- Clarified salt solution flows through a series of CST beds (columns) to remove the Cs.
- Cs-loaded CST is slurried from the bed and transferred to the DWPF.
- Decontaminated salt solution would be transferred to the SPF for treatment and disposal.

6.3.1 CSTIX Process Overview

The salt solution contains insoluble sludge and soluble species that must be removed to meet the SPF WAC requirements. In addition, the sludge must be removed to prevent plugging the IX column bed.

The first step for this process is to add MST (an insoluble solid) that sorbs the soluble Sr, Pu, Np and U to reduce their soluble concentrations to be within the SPF WAC limits. Both the MST and sludge are then removed by cross-flow filtration, concentrated to about 5 wt % solids and washed to remove sodium salts to avoid sending excessive alkali salts to the DWPF. The washed solids from Alpha Sorption are then transferred to the DWPF for incorporation in the glass. (See Section 6.2 for a detailed description of Alpha Sorption.)

The clarified salt solution flows to the Recycle Blend Tank (RBT) in the cesium removal portion of the CSTIX process (Figure 6.3-1). The train consists of three columns in series where the Cs is exchanged onto the CST resin. The effluent from the last bed is passed through a fines filter to prevent Cs-loaded fines from contaminating the salt solution. The filtered salt solution flows to the Product Hold Tanks (not shown in Figure 6.3-1) where the activity is measured to ensure it meets the SPF WAC limit for ^{137}Cs . From there, it flows to the Decontaminated Salt Solution tanks and then to the SSHT in the SPF.

A fourth column is provided to allow continued operation while Cs-loaded resin is removed and fresh resin is placed in the column. When the first column in the train is close to saturation (expected to be > 98%), that column is removed from service, the second column becomes the lead column, the third column becomes the middle column,

and the fresh, standby column becomes the third, or guard, column. The Cs-loaded resin from the first column is then sluiced with water into the Loaded Resin Tank where it is combined with the fines from the fines filter. Excess sluicing water is removed to produce a 10 wt% CST resin slurry in water. The excess water is sent to the Alpha Sorption Tank where it is mixed with fresh salt solution and 2-3 M NaOH to avoid aluminum precipitation in the recycle blend tank and CST columns. The CST/water slurry is transferred to the DWPF.

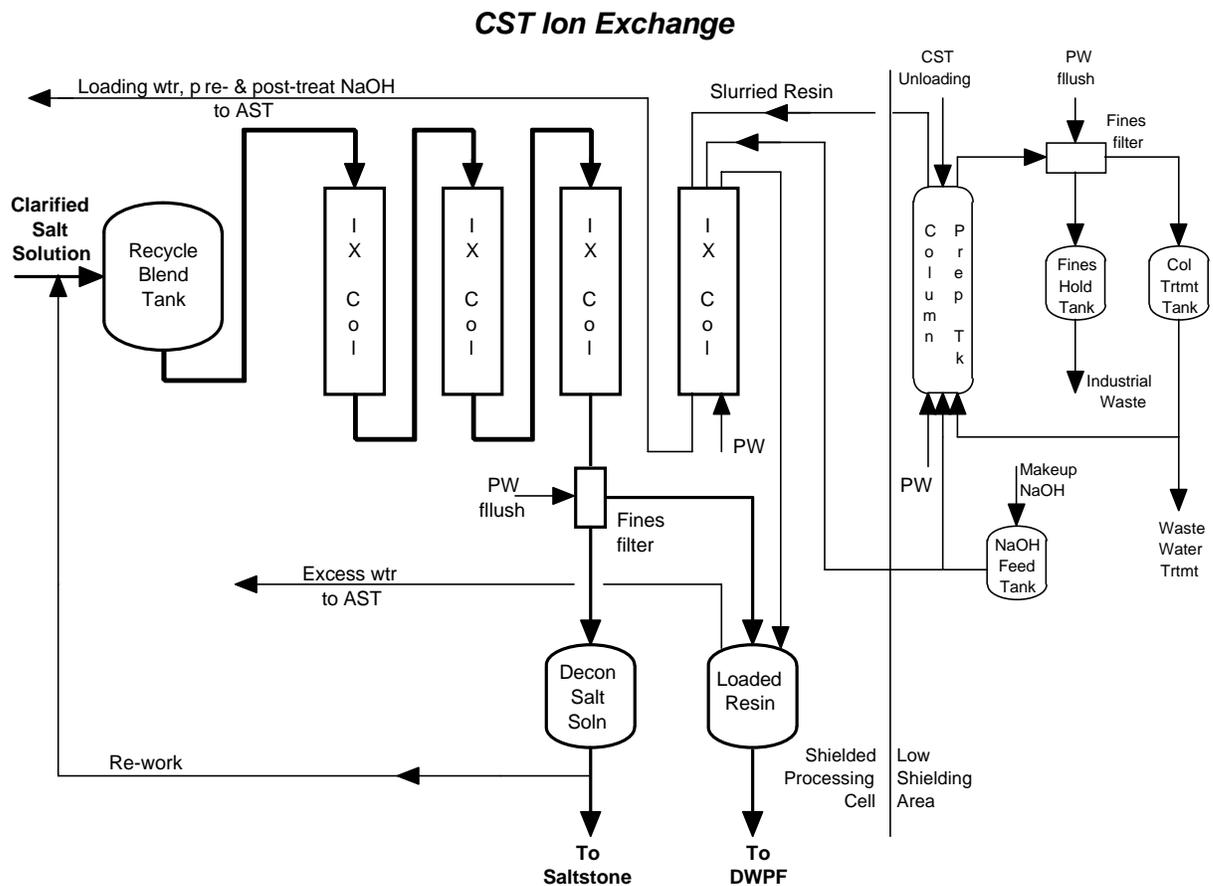


Figure 6.3-1 CSTIX Simplified Flow Diagram

Before being loaded into a column, the CST must undergo two treatments. First, the CST is loaded into the Column Preparation Tank, similar in diameter to an IX column bed, but about twice as tall to allow space to fluidize the resin. The CST is then backflushed with water to float off the fines. These fines are removed by a filter for disposal as Industrial Waste. The second treatment involves a 24-hour caustic soak. The “as-received” CST is primarily in the sodium form, but at lower than process pH. The pH is raised by circulating a NaOH solution through the bed for 24 hours. Any “as-received” CST in the

hydrogen form is converted to the sodium form with this treatment. The material is then ready to load into an empty standby column by sluicing with water. As with excess water from unloading, the water used to load the column is sent to the Alpha Sorption Tank.

Prior to placing the freshly loaded standby column in service, the water must be displaced by a 3 M NaOH solution. If this is not done, aluminum may precipitate from the initial salt solution feed as the pH is reduced by mixing with the residual water. (Water must be maintained in the bed to exclude air which might cause channeling in the bed.) A similar NaOH flush is required after the bed is removed from service and before the CST is sluiced from the bed with water.

6.3.2 R&D Results

The scope of CST research and development efforts focused on five main areas: CST performance under various conditions, thermal stability, physical properties of CST and salt solutions, the quantities of and effects of gas generation on column hydraulics, and CST impacts on DWPF. CST performance was evaluated in static (K_d) and/or dynamic (flowing column) conditions for impacts of pretreatment steps, organics, velocity, pressure, lot-to-lot variability, temperature, radiation, treatment of real waste and tall column operation (16 ft tall). DWPF impacts included studies on H_2 formation and foaming in feed preparation, homogeneity and sampling in feed preparation, and glass variability (durability, *liquidus*, and viscosity).

6.3.2.1 Granular Engineered CST

The Texas A&M University CST equilibrium model (Ref. 75) has been shown to correctly predict the K_d for CST powder with various SRS wastes. (Ref. 76) In Phase III, prior work indicated that the granular, engineered form may not have a K_d equivalent to the powder, presumably due to the binder used to form the granular material from the powder. Data analyzed from testing of CST in similar waste solutions indicated the granular form was about 60 to 70 % as effective (on a weight basis) as the powder (Ref. 80). For this reason, a “dilution factor” of 0.70 was used in the Phase III CSTIX modeling and in estimates of CST usage (e.g., g CST used per g Cs removed). Subsequent work indicates the K_d of the granular form is approximately the same as predicted by the Zheng, Anthony, and Martin (ZAM) CST equilibrium model. (Ref. 76)

Capacity experiments performed on re-engineered IE-911 indicate that a dilution effect exists between the CST powder and the engineered form as shown in Table 6.3-1. However, in the compositions of interest for the CSTIX process the ZAM model predicts the performance of the engineered form within reasonable error. In addition, real waste tests from a variety of waste compositions show that the ZAM model predicts the CST performance within $\pm 33\%$. (Ref. 77)

Table 6.3-1 Cesium Capacity Measurements for Sorbents

(Conditions: UOP simulant, 35 °C, initial Cs = 100 mg/L). (Ref. 78)

	K_d mL/g	Capacity mg/g
Baseline IE-911 (9090-76)	669±15	10.36±.14
	694±56	10.71±.19
Laboratory IE-911 (30950-49)	569±11	9.52±.16
Pre-production IE-911 (9098-9)	683±16	9.91±.10
IE-910	950±30	9.91±.11
ZAM prediction	652	

Since the flowsheet material balance is based on the predictions of the ZAM model, the Phase IV K_d 's used for column modeling and estimates of CST usage are "undiluted". With this change, CST usage is decreased by 30% and the column cycle time is increased by 43% (time/0.7). Interestingly, changing the ion exchange capacity (Q_T in the Langmuir isotherm) does not affect the column sizing because the length of the mass transfer zone (MTZ) does not change (Ref. 79). Only the total Cs loading on granular CST is affected.

6.3.2.2 VERSE Validation

During Phase III, two ion exchange column models originating from universities were used to model and size IX columns based on various SRS waste compositions (Ref. 80). R. G. Anthony *et al.* from Texas A&M University used their Texas A&M column carousel model while N. H. Wang *et al.* used their VERSE modeling package. (See Section 6.3.3.2 for a more detailed discussion of Phase III modeling work.) The Salt Disposition Modeling Team (SDMT) at SRTC obtained a license for VERSE and has been using it to predict column breakthrough curves for CST column experiments conducted during Phase IV (See Figures 6.3-2 and 6.3-3). In general, predicted results compare favorably with measured results (Ref. 81, 82), except in tests which had known interferences (e.g., lot 96-4). Efforts to improve the fit between the model and the actual results involve changing two parameters: the particle radius (R_p) (See Figure 6.3-4) and the pore diffusion (D_p) (See Figure 6.3-5). The R_p measured for CST has been 210 to 230 microns while the value used in the previous column sizing work was 188. Using the corrected particle size, the value of D_p giving the best fit is approximately double that used in column sizing. Since the MTZ length is directly proportional to the square of R_p and inversely proportional to D_p , the changes are approximately offsetting. Thus, the column sizing performed by Purdue and Texas A&M during Phase III still applies during Phase IV.

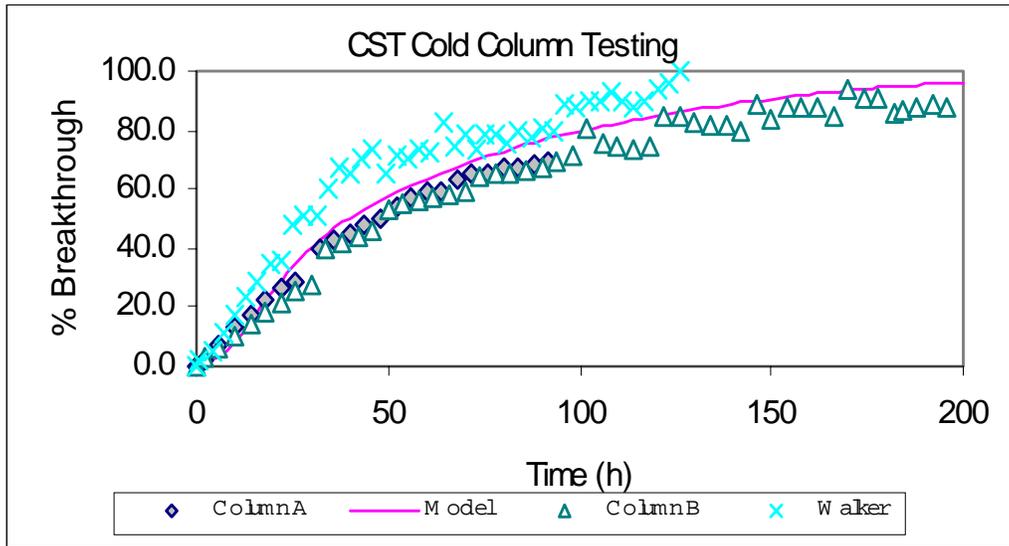


Figure 6.3-2 Non-Radioactive CST Column Testing

Cs-137 Breakthrough During Tk 44F IX Column Test

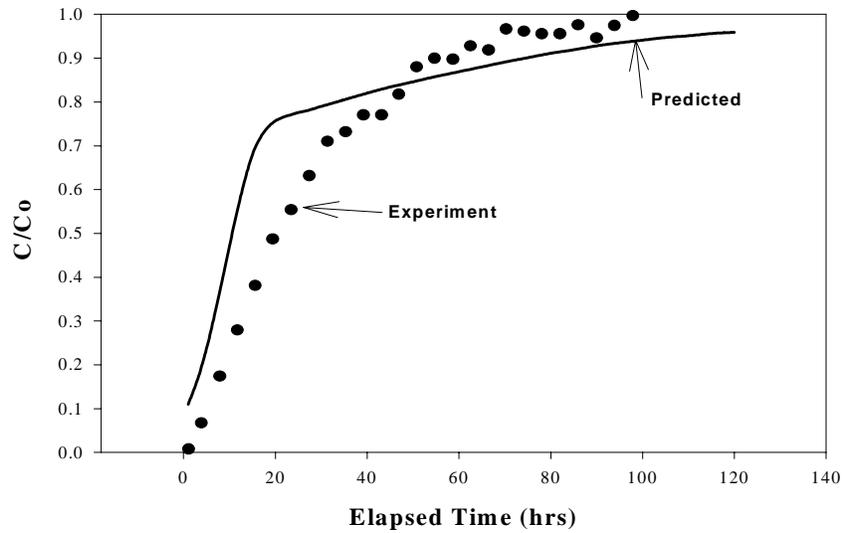


Figure 6.3-3 Radioactive CST Column Testing

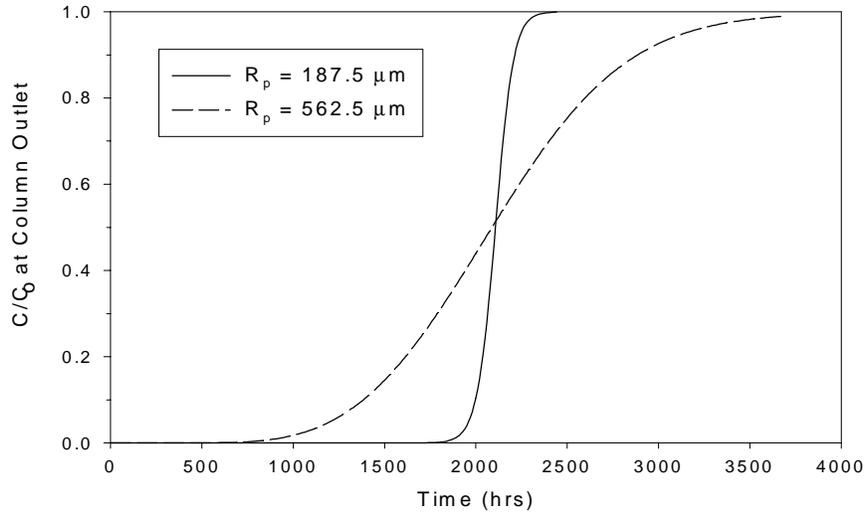


Figure 6.3-4 Effect of Particle Diameter on Mass Transfer Zone Length

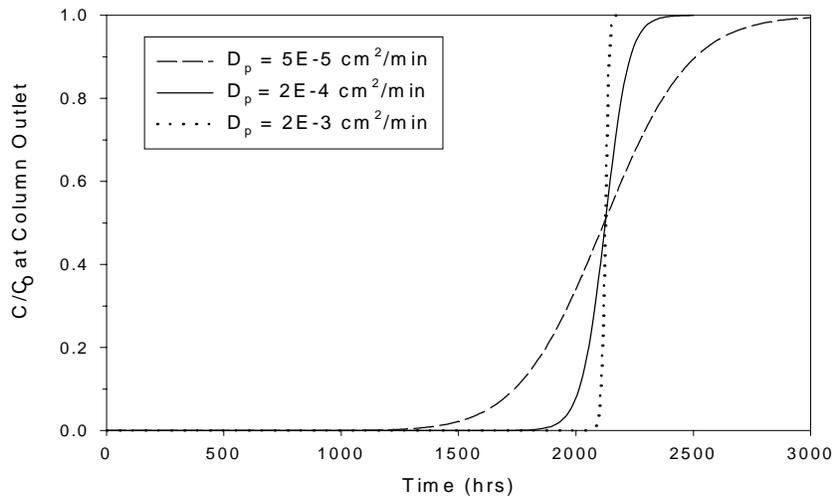


Figure 6.3-5 Effect of Pore Diffusivity on Mass Transfer Zone

6.3.2.3 CST Calcine Factor

The Immobilization Technology Section has shown that when as-received CST is dried for 4 hours at $\geq 400\text{ }^{\circ}\text{C}$, the CST loses approximately 15 % of its weight. (Ref. 68) The CST vendor indicates this is primarily loss of waters of hydration. For flowsheet

purposes, the weight of CST produced by CSTIX (based on Cs loading in mg Cs/g CST) predicted by VERSE will then be multiplied by 0.85 before being “fed” to the DWPF model. Because of these changes in the bases for CST composition, the concentration of CST in the glass is about 40 % lower than previously estimated.

6.3.2.4 CST Stability

Experiments were performed at ORNL to study the stability of Cs-loaded CST resin (Ref. 83). The adsorption and retention of Cs were studied at elevated temperatures (up to 120 °C). Researchers found the capacity to remove Cs is strongly influenced by temperature. They also found that Cs loaded at room temperature was rapidly released at temperatures ranging from 50 to 120 °C (in one day) (See Figure 6.3-6). In addition, they found evidence of leaching and precipitation of Si, Ti, and other components of the CST. Perhaps most significant, they found that Cs released at 50 to 120 °C was not re-sorbed when the solutions were cooled to room temperature – even in the experiment run at 50 °C. The implication is that after 60 days in SRS waste solutions at 50 °C, the CST had lost its ability to sorb and retain Cs. Based on the proposed equipment and column sizes for the CSTIX alternative, the CST resin would be exposed to salt solution for about 12 months at 25 to 30 °C under normal operating conditions. These findings at elevated temperatures would be significant for final design and operations, but are primarily related to upset scenarios and thus do not impact the material balances or required equipment in the current Bases and Assumptions.

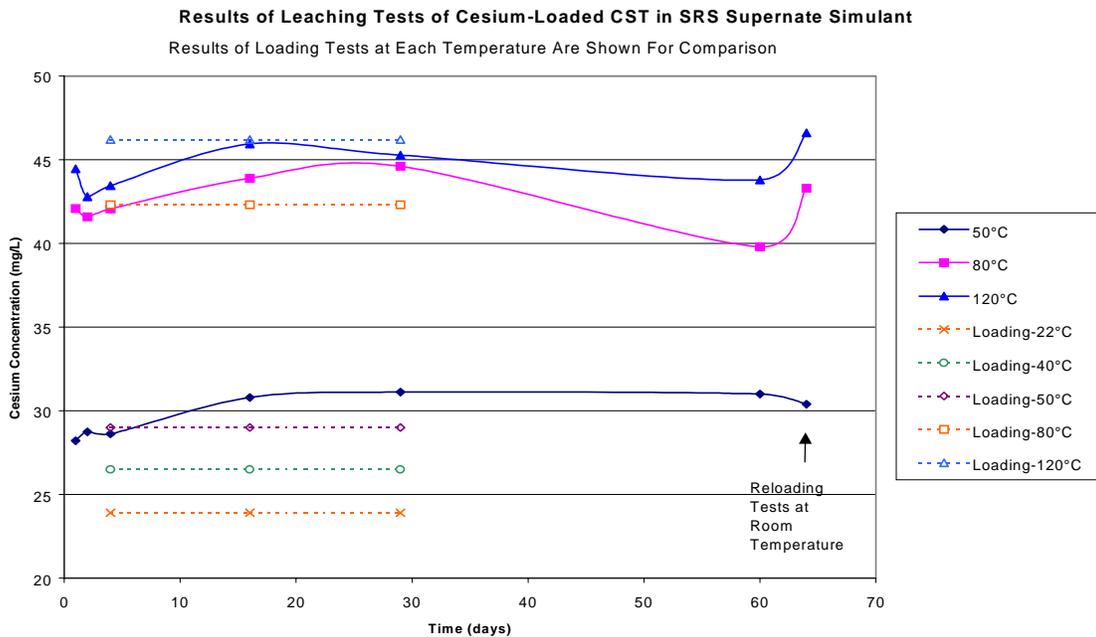


Figure 6.3-6 Cesium Leaching from CST Loaded at 22 °C

ORNL researchers completed additional long-term batch exposure tests that show consistent performance at exposure to operating temperatures, but degraded performance after exposure to elevated temperatures. (Ref. 84) Figure 6.3-7 shows the change in powder and granular CST performance over time at normal operating temperature and at the highest temperature tested. Researchers found cancrinite precipitating on the CST during the test. The additional weight of the cancrinite decreases the measured performance of the CST. In fact, the entire change in performance is attributable to the precipitated cancrinite except for the CST powder stored at 80°C. PNNL investigation of CST stability fundamentally supports the observations in the long-term exposure tests. (Ref. 85)

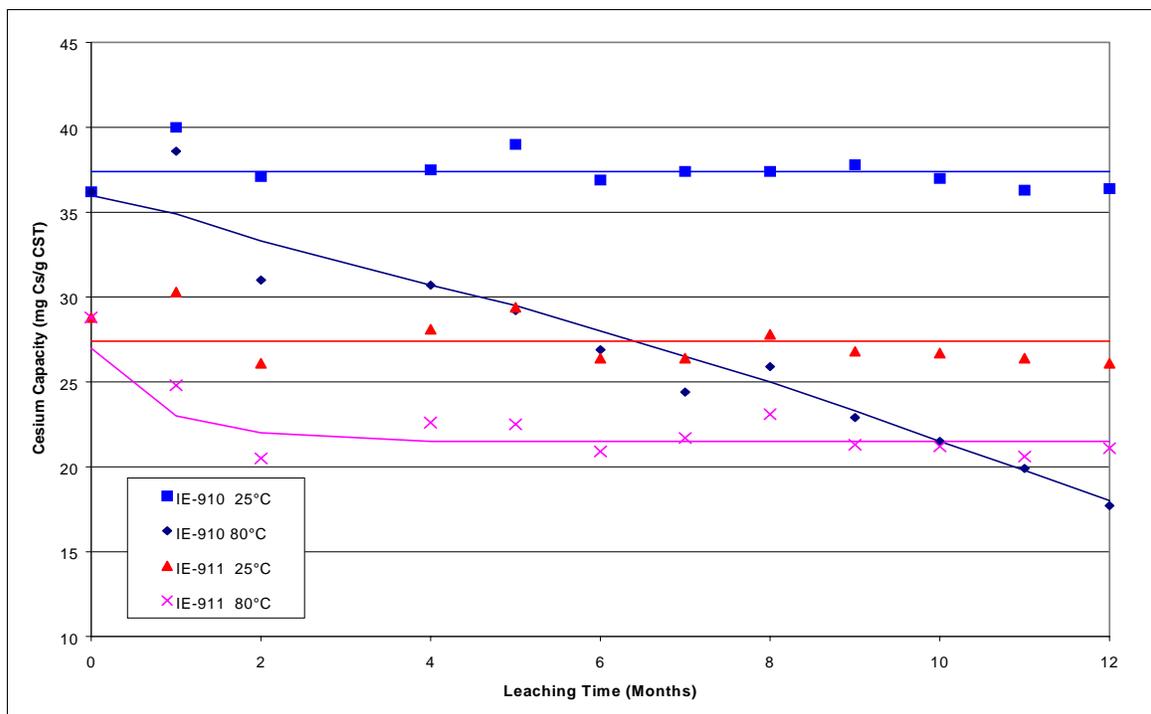


Figure 6.3-7 Results of Cesium Loading Tests for CST Samples from Batch Leaching Tests, Using 98-5 Granular CST and IE-910 Powder Stored in Average Simulant at 23 and 80°C.

Long-term column leaching tests indicate similar behavior as the batch tests for the bulk of the column as shown in Figure 6.3-8. Most of the performance change can be attributed to the increased particle weight caused by cancrinite except at the top of the column as shown in Figure 6.3-9. The difference in the last four months of exposure may be caused by another mechanism. Since this test was performed with the original engineered form of CST, this effect may be eliminated by the re-engineered material that significantly reduced leaching of material of manufacture. Long-term leaching and batch tests of the new material are in progress. Initial results indicate less change in performance.

Any reduction in the CST loading could cause a higher rate of CST consumption in the CSTIX flowsheet. Since the effect only occurs at the top of the column and affects a small fraction of the total CST, only a very small reduction in total column loading will be realized. Assuming the effect occurs in the top 1' of the column and the reduction is approximately 1/3 of original capacity, the effective reduction to a fully loaded column is less than 2%. Since the effect is smaller than the variability of loading measurements, the material balance is unaffected.

Additional tests were performed at SRTC (Ref. 86). CST in simulated salt solutions were held for 400 to 500 hours at 25 and 35 °C without radiation and at 35 °C with ~100 Mrads exposure. Leaching of components present in excess was noted. Tests suggest negligible leaching of elements from the microstructure at test conditions.

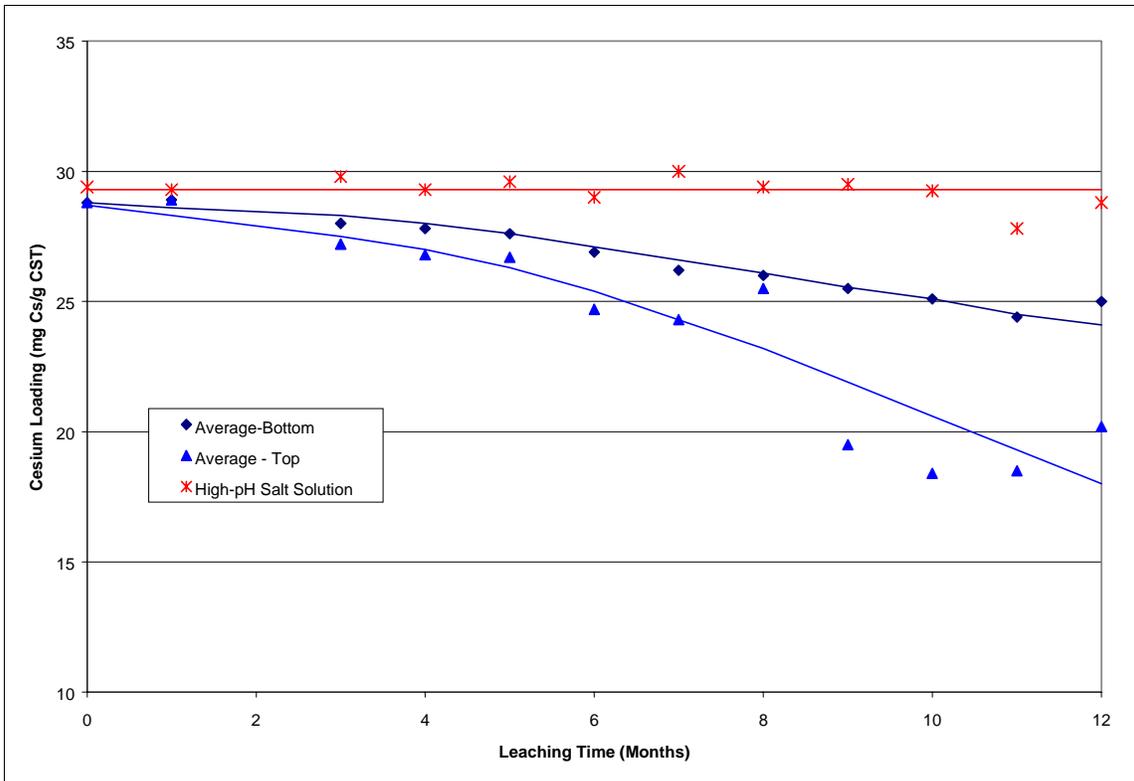


Figure 6.3-8 Cesium Distribution Coefficients for 98-5 CST Samples from the Column Leaching Tests.

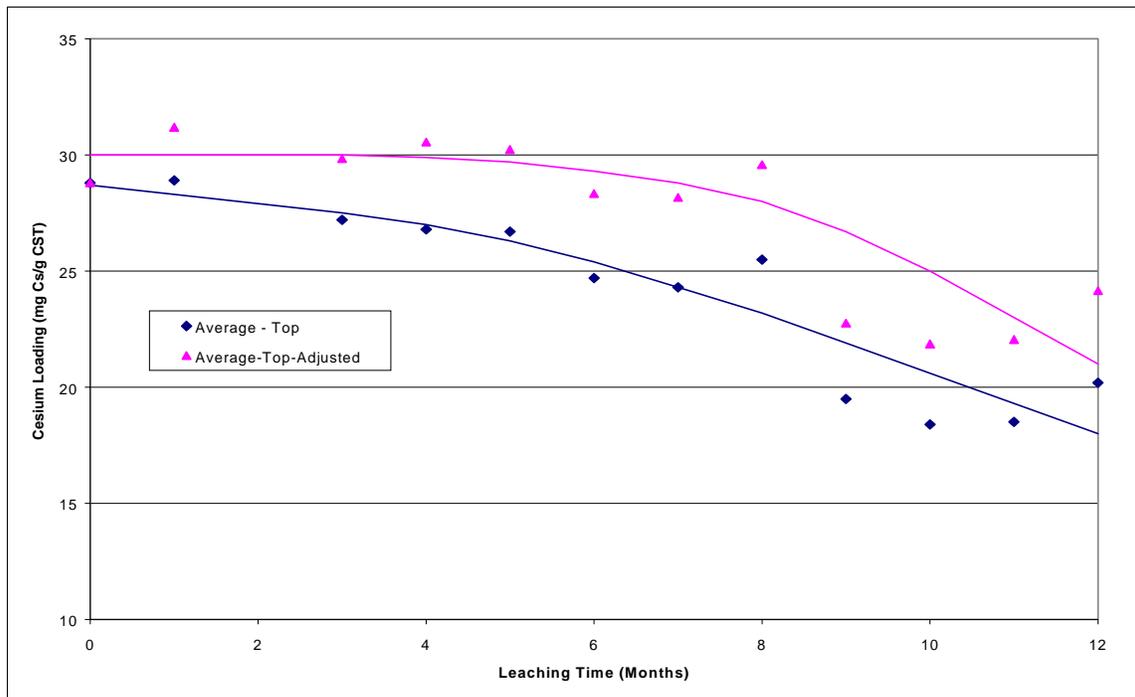


Figure 6.3-9 Comparison of Measured and Adjusted Cesium Capacities for 98-5 CST Samples from the Top of the Average Simulant Column.

(Note: The adjusted capacities are calculated by eliminating the weight of cancrinite in each sample)

6.3.2.5 CST and Salt Solution Thermal and Physical Properties

Researchers at ORNL determined thermal and physical properties (e.g., heat capacity, thermal conductivity, viscosity) for CST and various SRS simulated waste salt solutions (Ref. 87, 88). These data were obtained to support heat balance and other engineering calculations.

SRTC modeled the transient conditions resulting from a loss of flow condition in a fully loaded column. The time to reach solution boiling point was determined for two conditions. The first condition represents the expected condition if pumping stops or fails and assumes the void space in the column bed is filled with stagnant process liquid. The second condition would result if the column is somehow drained of all liquid and the void space in the column bed is filled with stagnant air. The time to reach boiling is important because of the potential to over pressurize a column from generated steam. In addition, the CST structure will degrade irreversibly and will no longer sorb cesium. Modeling predicts that boiling temperatures will be reached in the CST-salt solution and the CST-air columns in about 33 hours and 11 hours, respectively. Modeling shows that the time to reach this condition is not materially affected by increased cooling at the column wall but would affect the column wall temperature. Modeling also showed that cooling at the

column wall is only effectively control temperature of CST within 7 to 9 inches of the wall. (Ref. 89) Therefore, cooling in such large diameter columns can not be maintained with cooling jackets. Cooling can be maintained with liquid flow through the column and a backup liquid circulation system replaced the cooling jackets in the process flow diagrams.

Normal flow conditions were modeled to determine temperature profile in a fully loaded column. This modeling will determine the maximum inlet temperature and maximum temperature experienced by the CST while under normal conditions. The results will indicate the appropriate loading temperature to model for the CSTIX material balance. The maximum temperature in the column near the wall is about 34°C. The bulk temperature at the exit is about 30°C. The column bulk average temperature is about 28°C. This analysis shows that the CST performance standard at 35°C is adequate to define column performance. Previous material balances used CST performance at 25°C. The ZAM model predicts cesium loading is 15% lower for CST at 35°C versus 25°C, thus, the predicted loading rates used in the material balance are reduced by 15%. This results in a slightly higher CST consumption rate, shorter cycle time, and higher average CST loading in glass. Mass transfer zone is unaffected, thus, column size is unaffected.

6.3.2.6 Effect of Organics, Pressure, and Pretreatment on K_d and Column Performance

Researchers at SRTC performed tests to assess the effects of trace organics found in salt solutions (e.g., tri-n-butylphosphate), pretreatment, and pressure on CST K_d measurements and dynamic column performance (Ref. 81, 90). Humid air pretreatment does not impact K_d or column performance. Other pretreatment steps can affect K_d in that achievement of equilibrium (in K_d tests) is slowed but they did not have a significant effect on column performance. Pressure has no effect on K_d . Organics affected the K_d test by significantly slowing the time to equilibrium (equilibrium was not attained by the final measurement) but organics had only a small negative impact on column performance – perhaps within experimental error.

6.3.2.6.1 Effect of Temperature and Radiation

Limited work was done to test the effects of radiation and temperature on K_d (Ref. 91). The K_d under irradiation was about 1/3 lower than the control but it is not clear whether radiation had an effect due to analytical uncertainty.

CST performance was postulated to degrade in a radiation field because radiolytically induced gas generation interferes with the diffusion into the CST. To determine if there is such an effect, an additional test was conducted to identify any change in CST performance under a radiation field. Two identical short columns of CST were loaded with cesium by passing average simulated waste through the columns. One column was exposed to an intense radiation field, ~12 Mrad/hr, for 120 hours. The other column was not exposed to a radiation field, but maintained at identical hydraulic conditions for the same length of time. The breakthrough curves were compared between the two columns and to predicted performance. All three breakthrough curves were identical within

experimental error; thus, the production of radiolytic gases within a full-scale column is not expected to reduce exchange capacity of CST (Ref. 92).

K_{ds} for IE-910 (the powder) and IE-911 (the granular form) were measured at 22, 35 and 45 °C and compared to the K_{ds} predicted by the ZAM CST equilibrium model. The IE-910 performed at about 15% lower than predicted at all temperatures and decreased about 35% from 22 to 45 °C. Interestingly, the IE-911 was better than predicted at 22 °C by about 15% but worse than predicted at 45 °C by about 20%. Overall, the IE-911 K_d decreased by about 56% from 22 to 45 °C. Some material is postulated to be present in the IE-911 that adsorbs Cs at lower temperatures but does not at higher temperatures.

Additional tests described in Section 6.3.2.4 CST Stability include evaluation of CST performance at various temperatures.

6.3.2.6.2 Impact of Superficial Velocity on Column Performance

In Phase III tests, a loss of performance (early breakthrough) was noted in a column test performed at the current design superficial velocity of 4.1 cm/min when compared to performance at lower velocities (Ref. 76). Tests during Phase IV determined that (a) the effect of superficial velocity reasonably follows that predicted by the VERSE model, and (b) the cause of the Phase III result at 4.1 cm/min was caused by lot-to-lot variability – specifically the lot known as 96-4 (Ref. 81). While the as-received K_d lot 96-4 was consistent with other lots, the K_d measured after pretreatment was lower. The observed variability appears to be associated with a deficiency in capacity in the sodium form. Further, this result, and others, led to an intense exchange of information with the CST manufacturer – UOP LLC, Des Plaines, IL.

6.3.2.6.3 Information Obtained from UOP LLC

Contacts with the CST manufacturer resulted in the exchange of significant amounts of both technical and production information. The highlights are:

- a forthright and open exchange of proprietary technical and production information.
- UOP recommends diluting with NaOH and routing contaminated water from resin loading and unloading operations to the AST to avoid aluminum precipitation in clarified salt solution feed.
- UOP considers production of IE-911 is still in development.
- The anion form of the binder has not been selected (chloride or nitrate), but a single form (chloride) was used for testing at SRTC and ORNL.
- An initial concern with the presence of excess chloride has subsequently been dispositioned as no concern⁵ (Ref. 93).
- Successful production of IE-911 has only been accomplished in development-scale facilities.
- The two production runs in commercial-scale facilities have required rework.

⁵ Wilmarth and Diprete showed that essentially all the excess chloride can be removed with 50 column bed volumes (CBV) of water. Current pretreatment includes 20 CBV of water to remove fines plus 15 CBV during the NaOH soak. This is judged to be sufficient to remove the excess chloride.

- Excess materials (SiO_2 and Nb_2O_5) are added during the manufacturing process to ensure product performance. This material is not “bound” to the crystalline structure and can be leached during resin use.

The technical exchange resulted in UOP developing a re-engineered granular CST that practically eliminates the niobium leaching and reduces the silicon leach rate. UOP changed the manufacturing process to minimize the chemical instability of the resin that manifests as niobium and silicon leaching. No property or performance changes were detected in the re-engineered material that could affect the CSTIX design. The manufacturing process now being evaluated involves exposing the acid form of the IE-911 to a 3 molar sodium hydroxide solution at 50° C in the ratio of one part solid to forty parts fluid for at least six hours. The material is then washed free of most base (e.g., to a pH 9-10) prior to being shipped. The pretreatment process consumes less NaOH because the CST is predominately in the sodium form as received from the manufacture. The rate of consumption has also fallen from near 4 meq/g to less than 0.25 meq/g or about 94%. (Ref. 78)

6.3.2.6.4 “Tall Column” Operation

Tests were performed at ORNL in a 3-inch-diameter, full-length column (16 ft). The primary objectives were to study column hydraulics but the column was also used to study the impact of gas generation (see Impact of Radiolytic Gas Generation below). Researchers report that column hydraulics (pressure drop) were as expected (Ref. 94). Loading, fines removal, bed fluffing, and unloading proceeded smoothly. Particle attrition during operation is to be measured and will be reported at a later date.

The ORNL full-length column rig was modified to add a second, 5' column to represent the top of the second column in a three-column train. A gas separation device was installed on the effluent of the first column before feeding the second column. Additional tests were conducted to determine (1) the effectiveness of gas separation and (2) the impact to the downstream columns.

The gas disengaging equipment (GDE) designed for this evaluation supported four fundamental separation methods: (1) passive settling, (2) gas sparging to strip entrained gas or gas bubbles, (3) subatmospheric pressure separation, and (4) injection of ultrasonic waves to induce coalescence of bubbles with attendant settling. The GDE is equipped with a transfer pump that can be used to operate the GDE under low pressures or at system pressure. The results of the testing indicate that the gas disengaging equipment can effectively remove gas to a level that prevents bulk accumulation in the bed of downstream columns when the GDE is operated at atmospheric (or lower) pressures. Operation at system pressure removed gas bubbles from the liquid stream but gas accumulation was evident in the head of the second column. The second column was at a lower pressure than the GDE because the stream was throttled between the GDE and column. This resulted in dissolved gas evolving in the second column. The pressure in the full scale column will not be lower, but at or above (due to change in elevation) the pressure of the GDE outlet, thus, dissolved gas will not evolve.⁹⁵

Sluicing of CST from the column after the test proved more difficult than previous work with the column. The CST dissolved in the hydrogen peroxide used to simulate the generation of radiolytic gas and subsequently precipitated the dissolved materials in the bed. The precipitated material acted to bridge particles together, but not block flow through the bed. The bridged particles acted as a monolith, preventing easy sluicing. The bed in the primary column was eventually removed with mechanical agitation. The bed in the second column was removed readily after back flushing with simulant and nitrogen. Since the CSTIX process will not include hydrogen peroxide in the feed to the columns, no change is made to the flowsheets.

Gas disengagement equipment was added to the effluent stream of each column. The gas separation device is assumed to be a small tank with an air swept vapor space. The whole system is currently assumed to be part of the connecting jumper between columns. The test results will be used to define the size and design of the system.

6.3.2.6.5 Impact of Radiolytic Gas Generation

The accumulation of large quantities of Cs in the lead column (up to 5 MCi) raises a concern about radiolytic gas generation and its impact on column performance and operation. Initial estimates indicate a fully loaded column would generate sufficient oxygen to produce bubbles in the lead column under flowing conditions; bubbles would form in minutes under non-flowing conditions (Ref. 96). SRTC researchers irradiated a stagnant CST bed and noted bubble formation within eight hours. Bed expansion and bubble migration were also observed (Ref. 97). In the same reference, G values for generation of H₂, O₂, and N₂O from high nitrate and high hydroxide salt solutions in the presence of CST are reported. The G values are approximately as expected except

- the G value for H₂ from the high hydroxide solution is about twice the expected value, and
- an explosive H₂/O₂ mixture could possibly form if the H₂ and O₂ are trapped in an unpurged space (e.g., inside a column). If CSTIX is selected, this scenario will require further analysis.

A small column test in a radiation field was completed to explore the impact of forming gas bubbles in a flowing column, described in Section 6.3.2.6.1 Effect of Temperature and Radiation, above. The “tall column” test at ORNL was used to investigate the impact of gas generation in a flowing column. Gas was generated *in-situ* at a rate (in cc/L) comparable to and well in excess of that expected from a fully loaded IX column. In Reference 94, researchers at ORNL report that under flowing conditions, all bubbles formed flowed downward through the bed and exited out the bottom of the column without disrupting the bed. This information indicates that radiolytic gas generation should not cause problems under flowing conditions although the solution will need to be degassed between columns. However, the consequences and impact of continuing gas generation at no-flow or low-flow conditions is still unknown.

6.3.2.6.6 CST Column and Performance Tests Using Real Waste

At SRTC, a CST column was tested using real SRS waste salt solution (See Figure 6.3-3). The 1.5-cm diameter column was constructed from three sections: 10 cm, 75 cm, and

75 cm. It was designed to be the length of the MTZ for the waste being processed. The change in Cs concentration at the end of the 10-cm column as a function of time approximated the predicted breakthrough curve except that initial breakthrough occurred later than predicted and 90 % breakthrough occurred earlier than predicted. (Ref. 82) This result is consistent with better pore diffusion (D_p) than is being used in the VERSE model. At the end of the tests, the Cs concentration at the exits of the second and third column sections were also lower than predicted but indicated that the length of the MTZ was as predicted.

In prior tests, CST resin was pre-treated *in-situ* in a column to assure the resin was in the sodium form. To perform the NaOH soak pretreatment for this test, a solution of NaOH was circulated through the bed. During this step, the CST bed plugged. Analysis indicated that a binder constituent present in excess was leached from the CST, precipitated and then collected at the top of the bed as the NaOH was circulated. As currently shown in the process flow diagram (PFD), the circulating NaOH solution is passed through a fines filter before being returned to the column. The re-engineered granular form of CST as described in Section 6.3.2.6.3 Information Obtained from UOP LLC practically eliminated the leached material that caused the plugging problems observed during this test.

The IONSIV[®] IE-911 loaded in the real waste column test was monitored for cesium desorption during ambient temperature storage and following temperature increases to 35 and 55 °C. Cesium was desorbed and resorbed in the presence of Tank 44F waste and simulated waste solutions. The test results indicate that cesium on IONSIV[®] IE-911 desorbs about 0.03% of the cesium during nine months of storage at ambient temperatures. The tests with real waste show less desorption of cesium when the temperature increases than with simulated waste. At 35 °C, 5 to 10% of the cesium desorbed and all of the cesium resorbed afterwards. At 55 °C, 8 to 17% of the cesium desorbed. After heating to 55 °C, irreversibly desorbed cesium was less than or equal to 2.1% of the total cesium. The real waste tests are likely more representative of process temperature upsets involving loaded sorbent, whereas previous tests are more representative of upsets with unloaded or partially loaded sorbent.⁹⁸

SRTC completed additional real waste loading and loading kinetics tests with six radioactive waste samples from five high-level waste tanks in the Savannah River Site tank farm. These tests indicate that the ZAM model adequately predicts loading of cesium from a variety of Savannah River Site wastes. Measured values were mostly within 33% of the predicted values and were both higher and lower than predicted. Wastes from both F and H Areas and with high and low K/Cs ratios showed good agreement with predictions. Kinetics of sorption were nearly identical in all tests with SRS radioactive waste and simulated SRS waste, suggesting current modeling parameters are adequate for predicting radioactive waste performance.⁹⁹

6.3.2.7 Effect of CSTIX on DWPF Operations

6.3.2.7.1 Foaming and H₂ Generation in DWPF Feed Preparation

SRTC performed tests at bench scale and at pilot scale (1/240th scale in the Glass Feed Prep System – GFPS) to assess the impact of Cs- and noble-metal-loaded CST on H₂ and foam formation in the DWPF (Ref. 100, 101). Tests were performed with sludge-only, as-received CST, and size-reduced CST. Hydrogen generation rates were very low and comparable to or lower than rates observed from sludge-only operation. Rates were slightly higher in the case of size-reduced CST in the GFPS SME cycle (at the onset of boiling). No difference in foaming was noted at bench scale. In the GFPS, the size-reduced CST test produced more foaming than as-received CST and sludge-only tests. The worst foaming was noted at the start of SRAT cycle before any CST was added. There was negligible foaming in all SME cycles.

6.3.2.7.2 DWPF Feed Homogeneity

One of the principal requirements in the DWPF glass quality program is feed homogeneity, which requires accurate sampling of the solids slurries in the Feed Preparation system. Tests were completed to determine if CST can be maintained in a homogeneous mixture and if the CST can be representatively sampled. Testing includes determination of hydrodynamic properties, performance of DWPF Hydragard[®] sampler with CST, and requirements for suspension in a mixing tank. As-received CST was shown to settle in water much faster than frit. However, when size-reduced to a particle size range comparable to frit, the CST behaved hydrodynamically the same as frit (Ref. 102). In a tank built to scale to DWPF mixing and equipped with a full-scale Hydragard[®] sampler, researchers have shown (Ref. 103, 104):

- a 10 wt % slurry of as-received CST could be easily resuspended,
- a 10 wt % slurry of as-received CST in water could not be homogeneously suspended at DWPF conditions or at 20 % higher agitator speed,
- agitation and pumping (1300 turnovers) broke up the CST in a bi-modal distribution – some in very small pieces (≤ 10 micron) and the rest essentially unbroken,
- a slurry of as-received CST with sludge and frit plugged the Hydragard[®] sampler, and
- a slurry of size-reduced CST with sludge and frit samples representatively. Size reduced CST behaves the same as sludge for sampling purposes.
- Sampling results demonstrate no dependency on sampling time.

The sampling tests demonstrated substantial difficulties with mixing high weight percent sludge/frit/CST slurries. (Ref. 105) Additional rheological testing revealed that the yield stress of the slurry increased with increasing percent solids more in sludge/frit/CST slurries than in sludge/frit slurries though the behavior of slurry consistency is less definitive. The yield stresses of sludge/frit/CST melter feeds equaled the yield stresses of sludge/frit melter feeds that contained higher weight percent total solids. The difference in weight percent total solids between the sludge/frit/CST and sludge/frit melter feeds was anywhere from 0 – 4 wt.% total solids, depending on the selected yield stress. This

means that the presence of CST in the DWPF melter feed would potentially lead to reduction in melt rate due to the additional water in the sludge/frit/CST melter feeds. (Ref. 106)

Size-reduced CST was observed to form a rigid cake after settling for five days. The cake was very difficult to break and resuspend. Mixing tests with size reduced CST demonstrated that homogeneous slurry can be achieved. Settled size reduced CST was readily resuspended. (Ref. 107)

If CSTIX is selected, equipment will have to be provided to reduce the size of the CST beads. Testing included demonstrating commercial size reduction equipment with CST. Two vendor tests demonstrated that single pass size reduction to less than 177 microns is possible. (Ref. 108) Also, modifications will be required to maintain/resuspend the size-reduced CST and to representatively sample the CST/sludge/frit slurries.

6.3.2.7.3 DWPF Glass Quality

Glasses containing 3, 6, and 9 wt % CST (after drying at 400 °C) and 1.25 and 2.5 wt % MST (equivalent to 0.2 and 0.4 g/L MST, respectively) were produced and analyzed by SRTC researchers (Ref. 109). Analyses included composition (as-measured and bias-corrected), durability (PCT), *liquidus*, and viscosity. (Durability is a waste acceptance requirement; *liquidus* and viscosity are melter operability requirements.) Results from these tests show:

- durabilities are all very good but not predictable with current models,
- *liquidus* temperatures are acceptable but lower than predicted,
- viscosities for Purex glasses are good but lower than predicted,
- viscosities for HM glasses are high (~160 poise) and exceed the DWPF limit of 100 poise, and
- all glasses failed the homogeneity constraint (a phase separation tool) but none were found to be phase separated by SEM analysis (which is not a very rigorous method for finding phase separation).

SRTC completed additional testing to demonstrate the affect of cooling rate on glass quality with CST. The test compared rapidly quenched glass with centerline cooled glass. The results revealed tat there was no practical difference between the durability for glass subjected to the two cooling profiles. The results also show that no deleterious amorphous phase separation or crystalline phase occurred under either cooling profile.¹¹⁰

If CST is selected, all correlations will have to be revised. The proposed CST frit must be reformulated to produce an acceptable glass viscosity with HM sludge.

6.3.3 Technical Bases for CSTIX Material Balances

6.3.3.1 CST Ion Exchange Model

6.3.3.1.1 Overview of CSTIX Modeling

The CSTIX ion exchange modeling for the Salt Disposition effort has progressed through nine steps:

- 1) Characterization of SRS waste composition
- 2) Development of equilibrium isotherms⁶ for SRS wastes and other similar wastes (e.g., Hanford DSSF, Melton Valley)
- 3) Development of an initial model by Salt Disposition Process Engineering Team
- 4) Location of existing ion exchange models and expertise
- 5) Tuning of models using isotherms and published breakthrough curves for similar wastes
- 6) Development of preliminary column design for Phase III
- 7) Use of VERSE to predict and analyze the results of Phase IV CST column tests using SRS simulants and real waste
- 8) Further tuning of VERSE based on test results
- 9) Re-evaluation of column design based updated VERSE model parameters

All nine steps have been completed. Based on steps 8 and 9, the preliminary column design from step 6 is still valid.

6.3.3.1.2 Resin Loading Properties

The adsorption of Cs^+ ion onto crystalline silicotitanate exchanges a Na^+ ion for the cesium ion. Since this is truly an ion exchange process, the environment (the salt solution) has a profound effect on the equilibrium between the liquid and solid phases. SRS salt solutions are very concentrated – typically 5 to 7 M Na^+ – and ions such as OH^- , NO_3^- , and NO_2^- , exert influence primarily through ionic strength (chemical activity). Also, while CST is highly specific for cesium, there are other ions that are also exchanged onto the CST and, therefore, compete with cesium. Most notably, these are potassium, strontium, and rubidium. All these factors affect the capacity of CST to adsorb cesium; thus potentially impacting both column size and CST usage. The composition of SRS waste can vary considerably (see Section 6.3.3.3.3), so the impact the various waste compositions have on the capacity of the CST must be evaluated. The Texas A&M CST equilibrium model (Ref. 75) was used to assess these impacts; these model results have subsequently been confirmed by tests at SRTC (Ref. 76).

Na^+ – Most of the soluble salts in SRS wastes are sodium salts. Sodium is the primary indicator of total ionic strength. In general, the distribution coefficient (K_d) decreases as

⁶ Isotherms provide the equilibrium concentration ratio of Cs in solution to Cs exchanged onto the CST. The isotherms are one of the primary parameter inputs to any ion exchange model. Using the waste composition, the waste-specific isotherm for CST is calculated using the Texas A&M CST equilibrium model (Reference 75).

the ionic strength increases. Also, the solution viscosity decreases (lower column pressure drop) and the diffusivity increases (shorter MTZ) with dilution. On the other hand, dilution requires higher process throughput (i.e., larger equipment) and produces more saltstone, since the volume of DSS increases with dilution. A sodium molarity of 5.6 was selected to provide a balance among these considerations.

K^+ – Potassium competes weakly with cesium for adsorption onto the CST. In some of the DOE wastes (e.g., Hanford), the $[K^+]$ can be as high as 0.5 M. As a result, the Cs K_d s in these wastes is relatively low. Initially, there was a concern that the $[K^+]$ in some SRS wastes might be as high as 0.1 to 0.15 M. However, estimates indicate the $[K^+]$ in the blended SRS wastes will only range from 0.009 to 0.022 M; thus the impact of potassium on CST capacity will be small. A Cs isotherm that includes the effect of potassium is used to account for this minor impact.

Sr^{+2} and Rb^+ – There is essentially no rubidium in SRS waste. Also, because of the very high pH ($[OH^-] > 1.5$ M) and the presence of carbonate and fluoride in the waste, most of the strontium is precipitated. What little strontium remaining in solution is then removed by MST, effectively eliminating any impact on Cs loading on CST.

OH^- and NO_3^- – In addition to their contribution to ionic strength, these anions also affect the equilibrium between the liquid and the solid. Isotherm development at the waste composition extremes (high hydroxide and high nitrate) show that high hydroxide waste has a higher K_d while the K_d for high nitrate is approximately the same as for average waste.

Temperature – Temperature also affects the Cs K_d . For example, an increase from 25 °C to 35 °C, decreases the K_d , and thus CST capacity, for average SRS waste by about 20%.

Granular CST dilution factor – As discussed in Section 6.3.2.1, tests show the granular form of CST has the same K_d as predicted by the ZAM CST equilibrium model. Therefore, the K_d 's and isotherms predicted by the ZAM CST equilibrium model are used for column modeling.

Other – Testing at SRTC and TAMU evaluated the effect of carbonate ion, oxalate ion, peroxide, and three alkaline earth metal ions, calcium, barium, and magnesium. Testing shows no negative effect on cesium loading of granular CST at expected concentrations in column feed though loading increased with increasing carbonate concentration. (Ref. 111, 112, 113) These results and the effect on cesium loading will be incorporated into the ZAM model.

6.3.3.1.3 Feed Compositions and Isotherms for Phase III and IV Modeling

For Phase III, numerous waste compositions and isotherms were developed for the model development phase – step 5 (Ref. 2). These included compositions and isotherms for Hanford's DSSF and 241-AW-101, Oak Ridge's MVST-27 and -29, and SRS average, high hydroxide, high nitrate and bounding K^+ for each SRS waste. After the waste removal studies, it was found that the isotherms for SRS without bounding K^+ adequately represented the extremes for K_d and equilibrium.

To provide a direct comparison of material balances for Non-elutable Ion Exchange and Small Tank TPB Precipitation, the average SRS waste composition at 6.44 M Na⁺ as defined Table 5.3-9 is being used in Phase IV. In addition, per UOP's recommendation NaOH is being used to dilute the salt solution to 5.6 M Na⁺. Table 6.3-2 compares the various SRS waste compositions. Figures 6.3-10 and 6.3-11 show the isotherms for these wastes. Note that there is essentially no difference in the isotherms for previous average, new average diluted with water, and new average diluted with NaOH (Figure 6.3-10).

Table 6.3-2 SRS Waste Simulant Composition for CSTIX Modeling

Component	Average (M)	High OH ⁻ (M)	High NO ₃ ⁻ (M)	New Avg. SRS waste diluted w/ water (M)	New Avg. SRS waste diluted w/ NaOH (M)
Na ⁺	5.6	5.6	5.6	5.6	5.6
Cs ⁺	0.00014	0.00037	0.00014	0.000143	0.000137
K ⁺	0.015	0.030	0.0041	0.0146	0.0140
OH ⁻	1.91	3.05	1.17	2.086	2.233
NO ₃ ⁻	2.14	1.10	2.84	2.039	1.955
NO ₂ ⁻	0.52	0.74	0.37	0.494	0.473
AlO ₂ ⁻	0.31	0.27	0.32	0.289	0.277
CO ₃ ²⁻	0.16	0.17	0.16	0.147	0.141
SO ₄ ²⁻	0.15	0.030	0.22	0.137	0.131
Cl ⁻	0.025	0.010	0.040	0.025	0.024
F ⁻	0.032	0.010	0.050	0.030	0.029
PO ₄ ³⁻	0.010	0.008	0.010	0.007	0.007
C ₂ O ₄ ²⁻	0.008	0.008	0.008	0.018	0.017
SiO ₃ ²⁻	0.004	0.004	0.004	0.003	0.003
MoO ₄ ²⁻	0.0002	0.0002	0.0002	0.0002	0.0002

Isotherms for SRS avg waste

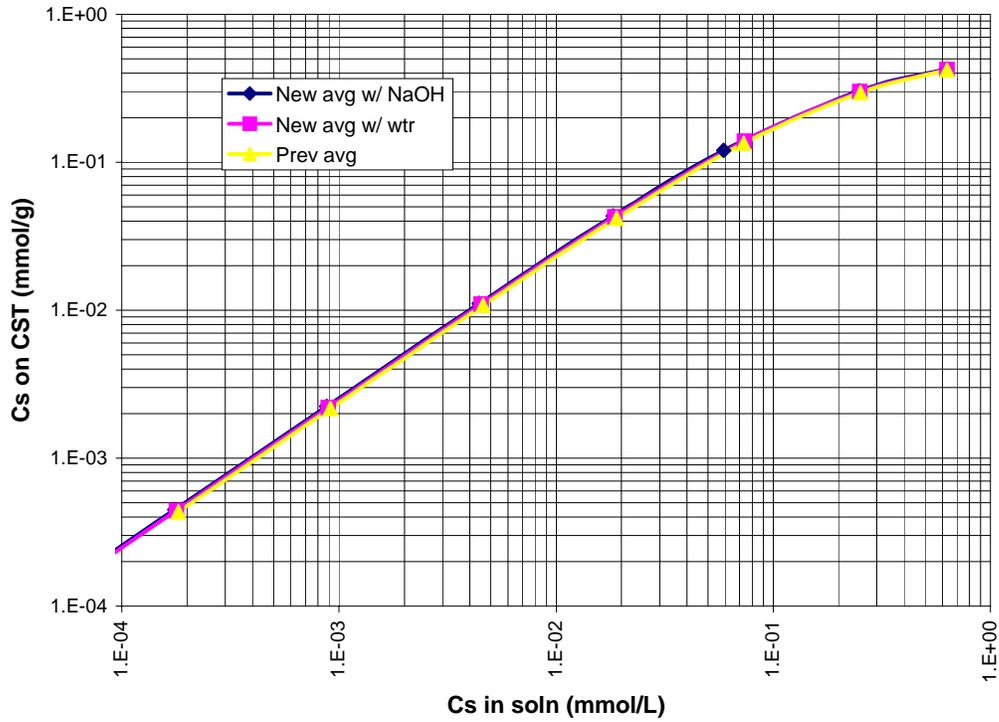


Figure 6.3-10 SRS Average Waste Isotherms at 25°C

SRS Waste Isotherms

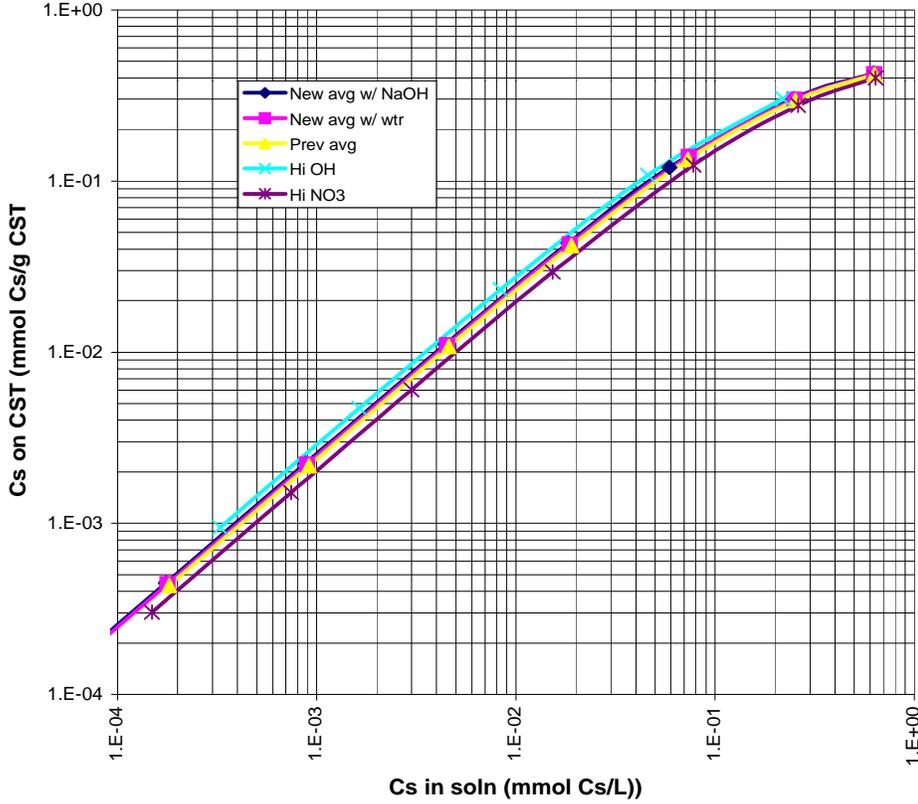


Figure 6.3-11 SRS Waste Isotherms at 25°C

Tables 6.3-3 through 6.3-7 contain the data for the isotherms as calculated from the waste compositions with the ZAM CST equilibrium model.

Table 6.3-3 SRS Average Waste Isotherm at 25°C

$C_{(avg)}$ (mmol Cs/L)	$Q_{(avg)}$ (mmol Cs/g CST)
6.31E-01	4.19E-01
7.30E-02	1.34E-01
1.90E-02	4.20E-02
4.61E-03	1.08E-02
9.14E-04	2.17E-03
1.82E-04	4.35E-04
3.65E-05	8.71E-05
9.12E-06	2.18E-05
1.82E-06	4.35E-06

Table 6.3-4 SRS High Hydroxide Isotherm at 25°C

$C_{(OH)}$ (mmol Cs/L)	$Q_{(OH)}$ (mmol Cs/g CST)
7.70E-01	4.60E-01
2.19E-01	3.03E-01
4.60E-02	1.08E-01
8.38E-03	2.32E-02
1.64E-03	4.71E-03
3.27E-04	9.45E-04
8.18E-05	2.36E-04
1.64E-05	4.73E-05
4.09E-06	1.18E-05

Table 6.3-5 SRS High Nitrate Isotherm at 25°C

$C_{(NO_3)}$ (mmol Cs/L)	$Q_{(NO_3)}$ (mmol Cs/g CST)
6.39E-01	4.01E-01
7.78E-02	1.24E-01
1.53E-02	2.95E-02
2.99E-03	6.02E-03
7.44E-04	1.51E-03
1.49E-04	3.03E-04
2.97E-05	6.05E-05
4.96E-06	1.01E-05

Table 6.3-6 SRS New Average Waste Diluted w/Water Isotherm at 25°C

$C_{(H_2O_{new})}$ (mmol Cs/L)	$Q_{(H_2O_{new})}$ (mmol Cs/g CST)
6.29E-01	4.23E-01
2.50E-01	3.00E-01
7.35E-02	1.39E-01
1.86E-02	4.28E-02
4.51E-03	1.10E-02
8.94E-04	2.21E-03
1.78E-04	4.43E-04
3.57E-05	8.86E-05
8.92E-06	2.22E-05
1.78E-06	4.43E-06

Table 6.3-7 SRS New Average Waste Diluted w/NaOH Isotherm at 25°C

$C_{(\text{NaOHnew})}$ (mmol Cs/L)	$Q_{(\text{NaOHnew})}$ (mmol Cs/g CST)
6.27E-01	4.26E-01
2.48E-01	3.03E-01
5.90E-02	1.20E-01
1.83E-02	4.34E-02
4.43E-03	1.11E-02
8.78E-04	2.24E-03
1.75E-04	4.49E-04
3.51E-05	8.99E-05
8.76E-06	2.25E-05
1.75E-06	4.49E-06

6.3.3.2 Summary of Models Used

Four ion-exchange models were used to provide information for the Phase III decision. The ion-exchange models offered varying degrees of complexity from the very simple to the state-of-the-art. The goal of the HLW Salt Disposition Process Engineering was to provide an ion-exchange column design that would be validated by the more complex models. Purdue University and Texas A&M University provided the more comprehensive models for ion-exchange column design. The purpose of this section is to briefly outline the models used in providing the ion-exchange flowsheets to the Salt Disposition Team during Phase III.

Table 6.3-8 summarizes the four models used by HLW Process Engineering, the Salt Disposition Modeling Team (SDMT), Purdue University (PU), and Texas A&M University (A&M). The HLW Process Engineering model is the simplest ion-exchange model. The column is modeled as a long tube and the non-linear isotherm is assumed to be linear over the entire cesium concentration range for mathematical simplification. This model tends to predict a conservative mass transfer zone and a non-conservative cycle time and CST loading due to assuming the isotherm is linear. The SDMT model is a modified version of the HLW Process Engineering model that accounts for the non-linear isotherm and carousel arrangement of the columns. The non-linear isotherm in this model should eliminate the lack of conservatism in cycle time. The SDMT also provides a new piece of information not available to the HLW Process Engineering: the cycle time of the second column after partial loading. The cycle time is important, because all columns after the very first will be partially loaded with cesium upon rotation to the lead position. This cycle time is certainly smaller than that predicted by the unloaded column. The Purdue and Texas A&M models are the most comprehensive due to the various mass transfer mechanisms employed. The Purdue and Texas A&M models also offer the ability to track more than cesium through the column: multi-phase isotherms.

The purpose in using four ion exchange models was to provide varying degrees of complexity to an identical problem. Each model provided a measure of checks and balances to the other models. Table 6.3-8 provides the primary purpose of each model.

Table 6.3-8 Summary of Models Used in Preliminary Ion-Exchange Column Design

Contributor	Ion-Exchange Column Model Description	Purpose
HLW Process Engineering simulated this model using MATLAB™.	<ol style="list-style-type: none"> 1. “Lumped Resistance” mechanism, 2. Linear Isotherm 3. Single Long Column 4. Constant feed composition 5. Zero cesium loaded initially 6. Mass transfer coefficient calculated from bench-scale non-SRS wastes. 	<ul style="list-style-type: none"> • Check on preliminary sizing • Compare/validate other models: Purdue Texas A&M
Salt Disposition Modeling Team simulated this model using SpeedUp™. (SDMT)	<ol style="list-style-type: none"> 1. “Lumped Resistance” mechanism, 2. Non-Linear Isotherm 3. 3 Column Carousel 4. Variable feed composition 5. Calculates cycle time for partially loaded column. 6. Mass transfer coefficient calculated from bench-scale non-SRS wastes. 	<ul style="list-style-type: none"> • Provide material balances • Compare/validate other models: Purdue Texas A&M
Purdue University has developed the numerical techniques required to solve this system of equations. (PU)	<ol style="list-style-type: none"> 1. Various mass transfer mechanisms, 2. Non-Linear Isotherm 3. 3 Column Carousel 4. Variable feed composition 5. Mass transfer coefficient calculated from pilot-scale non-SRS wastes. 	<ul style="list-style-type: none"> • Perform column sizing evaluation • Cross check WSRC models: HLW Process Engineering and SDMT
Texas A&M University has developed the numerical techniques required to solve this system of equations. (A&M)	<ol style="list-style-type: none"> 1. Various mass transfer mechanisms, 2. Non-Linear Isotherm 3. Single Long Column 4. Variable feed composition 5. Mass transfer coefficient calculated from pilot-scale non-SRS wastes. 	<ul style="list-style-type: none"> • Perform column sizing evaluation • Cross check WSRC models: HLW Process Engineering and SDMT

6.3.3.2.1 Results of Texas A&M and Purdue Phase III Modeling

R. G. Anthony at Texas A&M and N.-H. Wang at Purdue were requested to model several different cases for six SRS wastes: The most applicable cases were a 4 ft diameter column with feed rates of 15 gpm and 25 gpm. The six wastes were SRS average, high hydroxide, high nitrate, and all three wastes with bounding K^+ (0.15 M). Their results are presented in Table 6.3-9.

The ion exchange column arrangement for Phase III consisted of a single train with 3 columns. Each column is 5 feet in diameter and 16 feet long. Based on a Purdue report (Ref. 79), the mass transfer zone length is directly proportional to the superficial velocity and inversely proportional to the square of column diameter. Therefore, the results in Table 6.3-9 are scaled to Phase III column dimensions and work-off rates. The scaled values are shown bolded. After scaling the column lengths to account for differences in work-off rate and column diameter, all designs indicate that 16 feet is sufficient to contain the cesium wave front for both nominal SRS waste and the variations to SRS waste.

Table 6.3-9 Summary of Modeling Results Including Scaling to 5 ft Diameter & 20 gpm

Feed Type	Flow Rate (GPM)	Column Diameter (ft)	Column Length (ft) Texas A&M (Ref. 114)	Column Length (ft) Purdue (Ref. 115)
High OH	15	4	7.41	7.3
	25	4	12.3	12.2
Average	15	4	16.3	15.6
	25	4	27.2	25.7
High NO ₃ ⁻	15	4	18.6	18.3
	25	4	31.0	30.5
High OH	20	5	6.3	6.2
Average	20	5	13.9	13.3
High NO₃⁻	20	5	15.9	15.6

6.3.3.2.2 CST Loadings and Cycle Times

The modeling work (both for Phase III and Phase IV) has shown that at 90 % breakthrough, the CST in the lead column is > 95 % loaded; that is, the concentration on the CST is approximately that which is in equilibrium with the Cs concentration in the feed stream. Though Cs concentration on the CST is a strong function of the Cs concentration and the salt composition, loading can be closely estimated based on cesium concentration alone because the column feed maintains a constant sodium concentration. In other words, the ionic strength of the feed does not vary greatly over the life cycle of the facility. The correlation of loading with cesium concentration is demonstrated in Figure 6.3-12. The various feed streams plotted include projected yearly average compositions from the waste removal study performed during Phase III (Ref. 2). The correlation also includes the compositions of the three simulated waste solutions, average, high hydroxide, and high nitrate, used during testing.

Table 6.3-10 shows, among other things, batch-by-batch estimates of consumed CST, Cs loading on CST, CST quantities to the DWPF, CST concentration in the glass, and total TiO₂ in the glass (from CST and MST). The assumptions used to develop these estimates are:

- perfect loading e.g. no wasted CST,
- 0.4 g/L MST at 5.6 M Na⁺,
- no binder dilution factor,
- 98% loading on the CST at 35°C, and
- 0.85 calcine factor for CST in the melter.

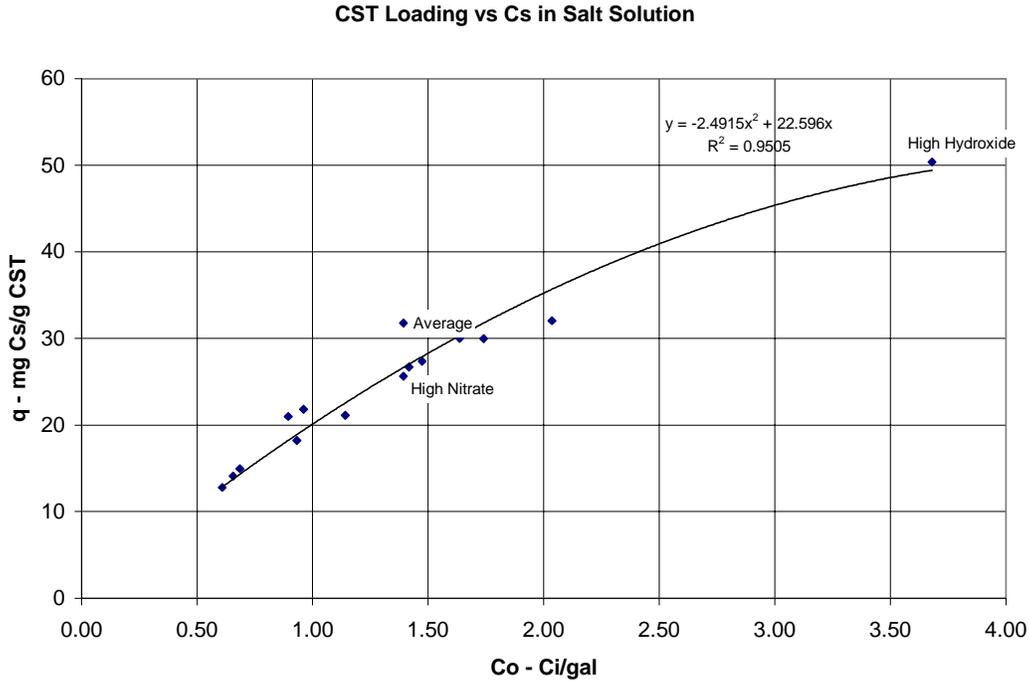


Figure 6.3-12 CST Loading versus Cesium Concentration in Column Feed

Table 6.3-10 Batch by Batch CST Loading and Consumption

Batch	SPT001	SPT002	SPT003	SPT004	SPT005	SPT006	SPT007	SPT008	SPT009	SPT010
CSTIX										
Salt soln supply vol - k gals	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
Salt soln supply [Na+] - M	6.44	6.61	6.06	6.55	6.22	6.16	6.31	5.81	6.63	6.23
Dilution Caustic Concentration	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Salt soln vol @ 5.60 M Na+ - k gals	1541	1601	1411	1579	1467	1445	1498	1324	1607	1469
Density of 5.6 M salt soln - lbs/gal	11.22	11.24	10.97	11.21	11.09	11.21	11.10	11.04	11.35	10.79
Wtr in 5.6 M Na+ salt soln - lbs/gal	7.59	7.71	7.70	7.51	7.65	7.59	7.64	8.41	7.45	7.55
@ 5.60 M Na+:										
K+ - M	0.0221	0.0233	0.0227	0.0210	0.0219	0.0220	0.0253	0.0254	0.0241	0.0266
Cs+ - M	1.64E-04	1.39E-04	4.54E-04	2.44E-04	2.72E-04	1.04E-04	1.35E-04	2.63E-04	1.89E-04	2.41E-04
Cs+ - Ci/gal	1.67	1.41	4.61	2.47	2.76	1.05	1.37	2.67	1.92	2.45
Cs in salt soln - mg/L	22.1	18.8	61.2	32.8	36.6	14.0	18.2	35.5	25.5	32.5
Cs/CST equilibrium:										
Cf - mg/L	22.1	18.8	61.2	32.8	36.6	14.0	18.2	35.5	25.5	32.5
Q - mg/g	26.1	22.9	43.5	34.5	36.8	17.9	22.4	36.2	29.1	34.3
VALUES FOR BATCH										
CST IX (5.60 M Na+ feed)										
Cs ldg on CST - mg Cs/g CST	26.1	22.9	43.5	34.5	36.8	17.9	22.4	36.2	29.1	34.3
Total Cs in batch - mg	1.05E+08	8.87E+07	2.89E+08	1.55E+08	1.73E+08	6.61E+07	8.62E+07	1.68E+08	1.20E+08	1.54E+08
Loaded CST produced from batch - kg	4003	3872	6649	4494	4695	3697	3852	4635	4145	4477
Loaded CST produced from batch - k lbs	8.83	8.54	14.66	9.91	10.35	8.15	8.49	10.22	9.14	9.87
Fraction of loaded column	0.41	0.40	0.68	0.46	0.48	0.38	0.39	0.47	0.42	0.46
DWPF										
Canister production per batch	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9
CST slurry activity - Ci/gal (10 wt %)	216	190	361	286	305	148	186	300	241	285
CST in glass - wt % (calined)	4.00%	3.87%	6.65%	4.49%	4.89%	3.70%	3.85%	4.63%	4.14%	4.47%
MST usage - k lbs	5.14	5.34	4.71	5.27	4.89	4.82	5.00	4.42	5.36	4.90
[TiO2] in glass - wt %	3.50%	3.54%	4.17%	3.71%	3.62%	3.26%	3.39%	3.40%	3.64%	3.55%
Fraction TiO2 from CST	0.373	0.356	0.519	0.394	0.423	0.369	0.370	0.445	0.371	0.411
Watts per canister	265	234	672	403	417	157	212	366	318	371
Saltstone										
Decon salt soln - M gal	1.58	1.64	1.48	1.62	1.51	1.48	1.54	1.37	1.65	1.51
Na+ in decon salt soln - M	5.47	5.48	5.37	5.46	5.44	5.47	5.47	5.43	5.47	5.45
Premix usage - M lbs	21.10	22.22	20.00	21.45	20.35	19.79	20.62	20.20	21.59	20.12
Grout produced - M gal	2.73	2.86	2.54	2.79	2.61	2.56	2.65	2.48	2.83	2.56

Table 6.3-10 Batch by Batch CST Loading and Consumption (continued)

Batch	SPT018	SPT019	SPT020	SPT021	SPT022	SPT023	SPT024	SPT025	SPT026	SPT027
CSTIX										
Salt soln supply vol - k gals	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
Salt soln supply [Na+] - M	6.56	6.42	6.30	6.69	6.46	6.31	6.35	6.40	6.40	6.33
Dilution Caustic Concentration	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Salt soln vol @ 5.60 M Na+ - k gals	1583	1536	1492	1627	1549	1497	1511	1527	1526	1504
Density of 5.6 M salt soln - lbs/gal	11.03	10.93	11.13	11.32	11.46	11.44	11.38	11.11	11.11	11.11
Wtr in 5.6 M Na+ salt soln - lbs/gal	7.51	7.52	7.42	7.37	7.94	7.66	7.78	7.66	7.65	7.68
@ 5.60 M Na+:										
K+ - M	0.0197	0.0206	0.0070	0.0181	0.0180	0.0140	0.0177	0.0161	0.0160	0.0154
Cs+ - M	1.93E-04	2.08E-04	2.85E-05	9.26E-05	8.03E-05	3.72E-05	8.24E-05	8.93E-05	8.82E-05	8.71E-05
Cs+ - Ci/gal	1.96	2.12	0.29	0.94	0.82	0.38	0.84	0.91	0.89	0.88
Cs in salt soln - mg/L	26.0	28.1	3.8	12.5	10.8	5.0	11.1	12.0	11.9	11.7
Cs/CST equilibrium:										
Cf - mg/L	26.0	28.1	3.8	12.5	10.8	5.0	11.1	12.0	11.9	11.7
Q - mg/g	29.5	31.2	5.4	16.2	14.2	7.0	14.6	15.7	15.5	15.3
VALUES FOR BATCH										
CST IX (5.60 M Na+ feed)										
Cs ldg on CST - mg Cs/g CST	29.5	31.2	5.4	16.2	14.2	7.0	14.6	15.7	15.5	15.3
Total Cs in batch - mg	1.23E+08	1.33E+08	1.81E+07	5.90E+07	5.12E+07	2.37E+07	5.25E+07	5.69E+07	5.62E+07	5.55E+07
Loaded CST produced from batch - kg	4168	4263	3376	3646	3591	3410	3600	3631	3626	3621
Loaded CST produced from batch - k lbs	9.19	9.40	7.44	8.04	7.92	7.52	7.94	8.01	7.99	7.98
Fraction of loaded column	0.43	0.44	0.35	0.37	0.37	0.35	0.37	0.37	0.37	0.37
DWPF										
Canister production per batch	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9
CST slurry activity - Ci/gal (10 wt %)	244	258	45	134	118	58	121	130	128	127
CST in glass - wt % (calined)	4.17%	4.26%	3.37%	3.64%	3.59%	3.41%	3.60%	3.63%	3.62%	3.62%
MST usage - k lbs	5.28	5.12	4.98	5.43	5.17	5.00	5.04	5.10	5.09	5.02
[TiO2] in glass - wt %	3.61%	3.58%	3.22%	3.50%	3.37%	3.24%	3.32%	3.36%	3.35%	3.32%
Fraction TiO2 from CST	0.376	0.388	0.341	0.339	0.347	0.343	0.353	0.352	0.352	0.355
Watts per canister	320	335	45	158	130	58	130	143	141	137
Saltstone										
Decon salt soln - M gal	1.62	1.58	1.53	1.66	1.58	1.53	1.55	1.56	1.56	1.54
Na+ in decon salt soln - M	5.47	5.46	5.40	5.49	5.49	5.49	5.48	5.48	5.48	5.48
Premix usage - M lbs	21.46	20.86	19.91	21.56	22.09	20.61	21.15	21.04	21.01	20.78
Grout produced - M gal	2.77	2.68	2.60	2.84	2.83	2.68	2.73	2.70	2.70	2.66
Batch										
	SPT035	SPT036	SPT037	SPT038	SPT039	SPT040	SPT041	SPT042	SPT043	SPT044
CSTIX										
Salt soln supply vol - k gals	1203	1250	1250	1248	1214	1236	1248	1248	1247	1238
Salt soln supply [Na+] - M	6.09	6.51	6.65	6.62	6.39	6.12	6.27	5.99	6.48	6.44
Dilution Caustic Concentration	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Salt soln vol @ 5.60 M Na+ - k gals	1367	1568	1614	1602	1480	1414	1482	1384	1551	1527
Density of 5.6 M salt soln - lbs/gal	11.05	11.30	11.27	11.32	11.35	11.24	11.35	11.00	11.23	11.34
Wtr in 5.6 M Na+ salt soln - lbs/gal	7.77	7.53	7.73	7.90	7.79	7.81	7.69	7.89	8.18	7.81
@ 5.60 M Na+:										
K+ - M	0.0157	0.0137	0.0163	0.0123	0.0180	0.0166	0.0162	0.0180	0.0179	0.0189
Cs+ - M	9.38E-05	6.18E-05	1.07E-04	8.34E-05	7.39E-05	6.97E-05	5.29E-05	1.04E-04	1.31E-04	7.42E-05
Cs+ - Ci/gal	0.95	0.63	1.08	0.85	0.75	0.71	0.54	1.05	1.33	0.75
Cs in salt soln - mg/L	12.6	8.3	14.4	11.2	10.0	9.4	7.1	14.0	17.6	10.0
Cs/CST equilibrium:										
Cf - mg/L	12.6	8.3	14.4	11.2	10.0	9.4	7.1	14.0	17.6	10.0
Q - mg/g	16.4	11.2	18.3	14.7	13.2	12.5	9.7	17.9	21.7	13.3
VALUES FOR BATCH										
CST IX (5.60 M Na+ feed)										
Cs ldg on CST - mg Cs/g CST	16.4	11.2	18.3	14.7	13.2	12.5	9.7	17.9	21.7	13.3
Total Cs in batch - mg	5.75E+07	3.94E+07	6.80E+07	5.30E+07	4.57E+07	4.39E+07	3.36E+07	6.61E+07	8.30E+07	4.68E+07
Loaded CST produced from batch - kg	3514	3511	3712	3599	3461	3505	3468	3692	3819	3529
Loaded CST produced from batch - k lbs	7.75	7.74	8.18	7.93	7.63	7.73	7.65	8.14	8.42	7.78
Fraction of loaded column	0.36	0.36	0.38	0.37	0.35	0.36	0.35	0.38	0.39	0.36
DWPF										
Canister production per batch	45.1	46.9	46.9	46.8	45.5	46.4	46.8	46.8	46.8	46.4
CST slurry activity - Ci/gal (10 wt %)	136	93	152	122	110	104	80	148	180	110
CST in glass - wt % (calined)	3.65%	3.51%	3.71%	3.60%	3.56%	3.54%	3.47%	3.70%	3.83%	3.56%
MST usage - k lbs	4.56	5.23	5.39	5.35	4.94	4.72	4.94	4.62	5.18	5.09
[TiO2] in glass - wt %	3.21%	3.38%	3.51%	3.46%	3.33%	3.19%	3.24%	3.18%	3.46%	3.36%
Fraction TiO2 from CST	0.370	0.339	0.345	0.339	0.349	0.362	0.349	0.379	0.360	0.346
Watts per canister	140	101	181	140	118	104	82	151	213	120
Saltstone										
Decon salt soln - M gal	1.40	1.60	1.65	1.64	1.51	1.45	1.52	1.42	1.59	1.56
Na+ in decon salt soln - M	5.47	5.49	5.49	5.49	5.48	5.48	5.48	5.47	5.48	5.49
Premix usage - M lbs	19.14	21.22	22.42	22.73	20.73	19.89	20.49	19.68	22.80	21.43
Grout produced - M gal	2.44	2.77	2.89	2.90	2.67	2.55	2.65	2.48	2.86	2.75

Table 6.3-10 Batch by Batch CST Loading and Consumption (continued)

Batch	SPT052	SPT053	SPT054	SPT055	SPT056	SPT057	SPT058	SPT059	SPT060	SPT061
CSTIX										
Salt soln supply vol - k gals	1249	1250	1250	1250	1250	1250	1250	1250	1250	1250
Salt soln supply [Na+] - M	6.62	6.61	6.69	6.78	6.73	6.63	6.57	6.61	6.62	6.65
Dilution Caustic Concentration	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Salt soln vol @ 5.60 M Na+ - k gals	1604	1601	1629	1660	1641	1606	1588	1601	1603	1616
Density of 5.6 M salt soln - lbs/gal	11.27	11.26	11.24	11.25	11.25	11.27	11.29	11.31	11.26	11.09
Wtr in 5.6 M Na+ salt soln - lbs/lbs	7.35	7.28	7.55	7.54	7.55	7.59	7.61	7.61	7.51	7.28
@ 5.60 M Na+:										
K+ - M	0.0168	0.0135	0.0170	0.0190	0.0178	0.0177	0.0175	0.0176	0.0167	0.0182
Cs+ - M	6.52E-05	5.28E-05	8.26E-05	9.19E-05	8.55E-05	9.52E-05	9.51E-05	9.50E-05	9.01E-05	9.85E-05
Cs+ - Ci/gal	0.66	0.54	0.84	0.93	0.87	0.97	0.96	0.96	0.91	1.00
Cs in salt soln - mg/L	8.8	7.1	11.1	12.4	11.5	12.8	12.8	12.8	12.1	13.3
Cs/CST equilibrium:										
Cf - mg/L	8.8	7.1	11.1	12.4	11.5	12.8	12.8	12.8	12.1	13.3
Q - mg/g	11.8	9.7	14.6	16.1	15.1	16.6	16.6	16.5	15.8	17.1
VALUES FOR BATCH										
CST IX (5.60 M Na+ feed)										
Cs ldg on CST - mg Cs/g CST	11.8	9.7	14.6	16.1	15.1	16.6	16.6	16.5	15.8	17.1
Total Cs in batch - mg	4.15E+07	3.36E+07	5.26E+07	5.85E+07	5.45E+07	6.07E+07	6.06E+07	6.05E+07	5.74E+07	6.27E+07
Loaded CST produced from batch - kg	3523	3473	3601	3643	3614	3658	3657	3657	3635	3673
Loaded CST produced from batch - k lbs	7.77	7.66	7.94	8.03	7.97	8.06	8.06	8.06	8.01	8.10
Fraction of loaded column	0.36	0.36	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.38
DWPF										
Canister production per batch	46.8	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9	46.9
CST slurry activity - Ci/gal (10 wt %)	98	80	121	133	125	137	137	137	131	142
CST in glass - wt % (calculated)	3.52%	3.47%	3.60%	3.64%	3.61%	3.66%	3.66%	3.65%	3.63%	3.67%
MST usage - k lbs	5.35	5.34	5.43	5.54	5.48	5.36	5.30	5.34	5.35	5.39
[TiO2] in glass - wt %	3.43%	3.41%	3.49%	3.55%	3.51%	3.48%	3.45%	3.47%	3.47%	3.50%
Fraction TiO2 from CST	0.335	0.332	0.336	0.334	0.335	0.343	0.345	0.343	0.342	0.342
Watts per canister	110	89	141	160	147	160	158	159	151	167
Saltstone										
Decon salt soln - M gal	1.64	1.64	1.66	1.70	1.68	1.64	1.62	1.64	1.64	1.65
Na+ in decon salt soln - M	5.49	5.49	5.49	5.49	5.49	5.49	5.49	5.49	5.49	5.49
Premix usage - M lbs	21.18	20.94	22.10	22.49	22.25	21.90	21.74	21.90	21.64	21.17
Grout produced - M gal	2.79	2.77	2.87	2.92	2.89	2.84	2.82	2.84	2.82	2.78

These calculations, including CST capacity and K_d 's, are specific for the batch salt compositions. Cs loading on CST averages 18.9 mg Cs/g CST ranges from 5.4 to almost 43.5 mg Cs/g CST. The number of column cycles averages 2.0 per year – or at a frequency of about once every 6 months when 75% utility is included. The concentration of CST in glass averages 3.8 wt.% and ranges from 3.4 to 6.7 wt %. Since this estimate is based on a batch by batch analysis, 2 to 3 batches are required to completely load a column, and column behavior changes with each batch, determining actual cycle times and total column loadings requires a dynamic simulation. The existing models were not run for this revision. Previous estimates based on year by year average compositions show Cs contained in the lead column ranges from 2.5 to 5.8 M Ci.

6.3.3.2.3 Use of VERSE in Phase IV Modeling

As previously discussed (see Section 6.3.2, VERSE validation), the Salt Disposition Modeling Team (SDMT) has been using the VERSE modeling package to predict and compare to Phase IV experimental results. Based on these results, two parameters in VERSE (D_p and R_p) can be adjusted to provide an improved fit with the Real Waste breakthrough curve. In Phase III, the SpeedUp™ flowsheet/material balance calculations for the CSTIX alternative were performed with a modified version of the HLE Process Engineering model (see Section 6.3.3.3.4). For the Phase IV SpeedUp™ modeling, a computational method similar to the VERSE and Texas A&M models is being used to perform the CSTIX calculations (see SpeedUp™ Model Description in Section 6.3.3.2.4).

6.3.3.2.4 Description of SpeedUp™ Model for CSTIX and DWPF

The SpeedUp™ models were not updated for the changes made in this revision. The previous results were adjusted by engineering analysis for flowsheet changes.

SpeedUp™ Model Functionality

- 1) The feed composition is the average salt composition SpeedUp™ vector as shown in Table 5.3-9. The feed composition will be diluted to ~5.6 M Na⁺ and the TRU and sludge components removed by Alpha Sorption (see Section 6.2.3.3). Including the water and NaOH added to the feed by CSTIX operations (see (2) below), the feed rate to the IX columns is 21 gal/min.
- 2) Certain batch operations will be performed each time a column is emptied and inventoried. The water is recycled to Alpha Sorption to prevent CST fines from plugging the lead column while NaOH is added at the RBT. For material balance purposes, the water is added in equal-sized batches at the AST while the NaOH is added continuously at the RBT based on the column cycle time. The bases for the additions are:
 - water to inventory column = 20 col vols = 47,100 gallons/cycle
 - 2 M NaOH pre-treatment = 5 col vols = 11,750 gallons/cycle
 - 2 M NaOH post-treatment = 5 col vols = 11,750 gallons/cycle
 - excess water to slurry resin from col = 25,950 gallons/cycle⁷

The ion exchange reaction of Cs onto the CST is modeled using a method applicable to the transient operation of a packed column similar to Purdue's VERSE modeling package and the Texas A&M column carousel model. In addition to the feed composition and feed rate, the model requires a feed-specific, liquid-solid equilibrium isotherm.

- 3) The feed-specific isotherm for CST is provided per Section 6.3.3.3.3. The isotherm is for the average SRS waste and includes dilution with caustic to prevent aluminum precipitation.
- 4) The IX train is three columns in series with each containing a bed that is 5-ft in diameter and 16-ft long (314.16 ft³). (There is a fourth column that is filled with fresh resin that is ready for use when the first column is loaded with Cs.) The granular CST has a dry bulk density of 1.0 g/ml so a column contains 19,600 lbs of CST. A cycle begins when feed is started to a column that has been rotated from the second position to the first.
- 5) A cycle ends when either the Cs concentration in the liquid at the exit of the first column reaches 90% of the inlet cesium concentration or the Cs concentration at the exit of the second column reaches 1.3 micrograms Cs/L (corresponding to 20 nCi/g for average waste). At that time, the first column is taken off-line and unloaded, the second becomes the first, the third becomes second, and the fresh spare becomes the third. When the column is unloaded, 20 column volumes of water are used. A 10 wt % CST slurry in water goes to DWPF (21,150 gallons). The rest of the water is diverted as described in (2).

⁷ Based on 20 col vols less the water needed to produce a 10 wt % CST slurry.

- 6) Two reactions that occur in the IX bed are ignored because they are inconsequential to the material balance. The Cs^+ is exchanged for a Na^+ , which then goes with the decontaminated salt solution. A small amount of K^+ also exchanges with Na^+ and goes with the CST resin to the DWPF. This is estimated to be less than 0.02 lbs/hr.

There are, of course, two product streams: Decontaminated Salt Solution and CST slurry.

- 7) The decontaminated salt solution is simply the column feed stream less the Cs removed by the column.
- 8) The CST slurry contains one column volume of CST (19,600 lbs) along with the Cs removed during the cycle and sufficient water to produce a 10-wt % slurry (21,150 gallons). This is fed to DWPF at a rate of 196,000 lbs divided by the cycle time as determined in (5) above.

The DWPF model requires additional inputs, as described below.

- 9) In addition to the CST slurry stream, there are three other inputs required to the DWPF:
- MST/sludge stream from alpha removal matching the salt work-off rate,
 - the washed, average sludge feed rate, and
 - the reformulated frit tailored to handle the CST resin stream.

The washed, average sludge rate and frit rate/composition is based on a DWPF recipe developed by HLW-PE. HLW-PE will also supply the CST composition. By virtue of the composition information provided for the CST and frit, the PCCS algorithms in the DWPF model should provide reasonable information. However, built-in constraints or adjustments based on the PCCS calculations, such as items associated with high TiO_2 in the glass, do not apply.

- 10) The following SpeedUp™ outputs are required including stream compositions:
- 5.6 M CSTIX feed stream
 - water and NaOH added to the feed
 - decontaminated salt solution
 - CST slurry stream
 - CST cycle time
 - loading of Cs on CST (mg Cs/g CST) in the CST slurry
 - DWPF feed streams (CST slurry, MST/sludge, washed sludge, frit)
 - glass product stream
 - TiO_2 in the glass including contribution from MST
 - results of PCCS calculations

SpeedUp™ Model Description

A SpeedUp™ model for CST Ion Exchange (IX) column has been developed for this phase, to describe the process of loading cesium onto the granular CST fixed bed in an IX column. The computational method applicable to the transient operation of a packed column is similar to that used in Purdue University's VERSE code or Texas A&M's IX

Column model. The governing transport equations include convection, axial dispersion, film mass transfer, and pore diffusion. The numerical approach to solve these equations is based on the orthogonal collocation technique. The model allows the use of a non-linear Langmuir isotherm.

As shown in Figure 6.3-13, the entire SpeedUp™ CSTIX model consists of six units: **Feeder**, **IX1**, **IX2**, **IX3**, **Decon_Product**, and **CST_Info**. **IX1**, **IX2** and **IX3** are physical units representing the three CST IX columns. **Feeder**, **CST_Info** and **Decon_Product** are non-physical units used for information extraction. **Decon_Product** provides information for the decontaminated salt solution to be sent to the SPF for conversion to saltstone. **CST_Info** provides information about the CST slurry to be sent to DWPF. The slurry results from treatment of the loaded CST resin in the lead column rotated from service at the end of a cycle. In addition to the slurry information, cycle time and total cesium loading are also given. The model appropriately simulates the column changeover operation in each cycle.

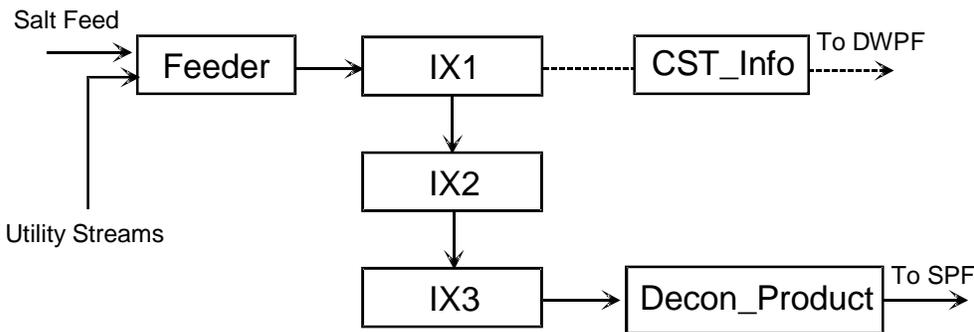


Figure 6.3-13 Schematic of SpeedUp™ Flow Diagram of CSTIX Process

<u>Unit</u>	<u>Description</u>
Feeder	Combines the salt solution and utility streams to a single feed stream to the first CSTIX column, and converts the 51-component feed stream into a 2-component stream.
IX1	Models the CSTIX first (lead) column. IX1 is a macro consisting of STAGE and MONITOR submodels. STAGE computes the material balance in a section of column of length dz. MONITOR provides data at the column outlet (i.e. DFs, Cs mass concentration, and Cs amount adsorbed on CST bed)
IX2	Models the CSTIX second column. Functions are similar to IX1.
IX3	Models the CSTIX third (guard) column. Functions are similar to IX1 and IX2.
Decon_Product	Converts the 2-component product stream at the outlet of the third CSTIX column (IX3) back to a 51-component decontaminated salt solution stream.
CST_Info	Provides information about the 10 wt% CST slurry to be sent to DWPF. The slurry results from treatment of the loaded CST resin in the lead column rotated from service at the end of a cycle. In addition to the slurry information, cycle time and total Cs loading are also given.

6.3.3.2.5 Results of CSTIX Ion Exchange Model

This model produces two streams: the decontaminated salt solution that flows to the Saltstone production model and the Cs-loaded CST that is one of the input streams to the DWPF model. The decontaminated salt solution flow is 20.9 gpm (12890 lbs/hr). The model predicts this stream will have $< 0.1E-9$ g-mole/L of Cs. This is equivalent to < 1 nCi/g. (This very low concentration is due to the guard column.) The CST will also sorb any of the Sr that is not sorbed by the MST. The model also predicts a column cycle time of ~ 2930 hours. This produces 6.7 lbs/hr CST (uncalcined basis) in a 10 wt % CST slurry. The slurry flow is 0.13 gpm (69 lbs/hr) containing 0.192 lbs/hr Cs. The slurry activity is ~ 220 Ci/gal.

6.3.3.3 CSTIX Impact on DWPF Vitrification

6.3.3.3.1 Technical Bases

The Technical Bases for the operation of the DWPF and flowsheet modeling bases are the same as those used in Phase III. Since the general operations of the DWPF in the Chemical Process Cell and the melter are common to any alternative, the details for DWPF processing are described in Section 5.3.5.4. Key impacts of CSTIX alternative on DWPF processes and products are discussed below.

6.3.3.3.2 CSTIX Feed Streams to the DWPF

The feed streams modeled in the flowsheet are based on average sludge. The CST usage rate is reduced to that produced with average salt, assuming no CST granular dilution factor for the engineered form. The CST rate matches that used in the CST Ion Exchange portion of the model. A correction was made to the basis for CST to account for the water of hydration. This reduces the quantity of each oxide sent to DWPF by 15%. An additional correction was made for a change in maximum operating temperature from 25°C to 35°C. This change results in a 15% decrease in cesium loading on CST and, thus, a 15% increase in CST sent to DWPF. The oxide basis for the washed CST feed stream used in the model has the composition shown in Table 6.3-11 below.

Table 6.3-11 Washed CST Composition Modeled

Oxide	Weight %
Al ₂ O ₃	0.3
Nb ₂ O ₅	17.0
B ₂ O ₃	0.2
CaO	0.6
CuO	0.3
Fe ₂ O ₃	0.1
H ₂ O	15.0
K ₂ O	1.1
MgO	0.2
Na ₂ O	9.9
PbO	0.2
SiO ₂	15.3
TiO ₂	27.7
ZnO	0.1
ZrO ₂	12.2

Glass formers are introduced into the DWPF as ground up glass or frit. The high silica and titania content of CST will require a change in the frit used in the DWPF. The composition of frit used for modeling purposes is shown in Table 6.3-12.

Table 6.3-12 CST Frit Composition Modeled - Weight %

Oxide	CST Frit
B ₂ O ₃	10
Li ₂ O	9
Na ₂ O	6
SiO ₂	75
MgO	0

The composition of the sludge (in both the washed sludge and the washed sludge/MST streams) is the same as used in Phase III. The rate of sludge processing was the same as Phase III and the sludge/MST flow was an output of the Alpha Sorption portion of the model.

6.3.3.3.3 R&D Impacts on DWPF Operation

Several of the R&D results, discussed in Section 6.3.2, have impact on the operability of the DWPF vitrification based on the CSTIX alternative.

Sampling - As-received CST resin plugged the slurry samplers of the DWPF design. Size reduction of the CST is required because representative samples (and their reliable analysis) are required for both process control and acceptance of the DWPF waste form,

glass contained in sealed canisters. HLW glass is not sampled frequently, and the acceptability of the glass waste form does not rely on glass sampling. Instead, waste form acceptability depends on a tested, qualified system of sampling of the feed to the DWPF melter to demonstrate compliance with Waste Acceptance Product Specifications. This system was reviewed in great depth and at a high level by the DOE and it is unlikely that it will be modified. A statistically rigorous test shows that size reduce CST does not affect the currently installed sampling system in DWPF, thus, no modification is necessary (Ref. 116). However, size reduction or grinding equipment must be included in the flowsheet at some point between the column unloading and the Sludge Receipt and Adjustment Tank in DWPF. Size reduction equipment is added to the process flowsheets in the SWPF, but final location will depend on the design of the grinding system.

Glass Durability – DWPF Waste Acceptance requires that properties of the glass be predictable from samples of the feed to the melter. Though the glasses made during Phase IV were durable, the existing property model overestimated their durability. This model was reviewed and accepted by a DOE Technical Review Group; acceptance of this approach and property model was a condition to operate the DWPF. A new durability model for CST glasses would have to be developed, reviewed and approved. This was a lengthy process prior to DWPF startup and would not necessarily be quick and straightforward for these glasses.

Glass Melt Viscosity – Some of the glasses made during Phase IV testing had melt viscosities of about 160 poise at normal melter temperature of 1150°C. The design basis and limit of large scale testing for the DWPF melter is 100 poise. This high viscosity would lead to lower melt and glass pouring rates and more frequent plugging of the melter pour spout. This would reduce the production capability of the DWPF. Reformulation of the frit to reduce the viscosity is a possible resolution. This would likely require re-qualification for Waste Acceptance.

CST/Frit/Sludge Slurry Rheology – CST/frit/sludge and frit/sludge slurries behave rheologically a bingham plastic. The yield stress of CST/frit/sludge slurries is higher than sludge/frit slurries though consistency remains similar. The increase in yield stress can affect the ability to achieve homogeneous flow at high percent solids slurries fed to the melter. At yield stresses of sludge/frit/CST melter feeds equal to the yield stresses of sludge/frit melter feeds, the difference in weight percent total solids is anywhere from 0 – 4 wt.% total solids, depending on the selected yield stress. Potentially, the reduced solids feed could lower the melter production rate.

6.3.3.3.4 CST-DWPF Model (SpeedUp™)

The DWPF model used for the CST options was the same as that in Phase III. It is the same as the sludge-only model except changes made specifically for CST listed below:

- CST composition, as shown in Table 6.3-11.
- The modeling outputs of Alpha Sorption and CST IX provided inputs to the DWPF model. This included two source vectors: a CST slurry containing sorbed cesium

from ion exchange and an MST/sludge slurry containing alpha constituents removed from the source salt stream.

- A modified frit composition was used for the glass calculation, as shown in Table 6.3-12.
- The high TiO_2 content introduced from both the CST and the MST input vectors exceeds the current limit in the PCCS calculation. This limit must be redefined for CSTIX.
- Results from the DWPF model are given as yearly average values. These values are determined by discarding the first 600 hours of the calculation and averaging over the remaining 2400 hours of a transient calculation. This avoids startup effects in the yearly averages.

6.3.3.3.5 CST-DWPF Model Results

The DWPF model combines the CST slurry, the washed MST/sludge slurry, and the washed sludge slurry with frit to produce glass. At 100 % attainment, 191 lbs/hr glass is produced containing 3.45 % CST (calcined basis), 2.2 % MST, and ~ 30 % sludge oxides. The total TiO_2 from CST and MST is 2.7 %. The MST concentration is within the range tested in the CST glass variability study (Ref. 109). The sludge and MST concentrations are at the limit of the glass variability study; the sludge is at the upper limit of testing and the CST is at the lower limit (tests were from 22 to 30 wt % sludge oxides and 3 to 9 wt % CST). A very similar glass in the variability study (ID No. cst16: 3 % CST, 2.5 % MST, 30 % sludge) had these properties: ΔG_p of -10.84 ; viscosity was not measured (predicted was ~ 45 poise but all Purex/CST glasses were 10 – 20 poise lower than predicted); and *liquidus* of < 950 °C. As reported in Reference 109, the glasses tend to be less durable and have lower viscosity and *liquidus* than currently predicted by the glass correlations. While this glass is very durable, it was the least durable of all the glasses produced in the study.

6.3.3.4 Saltstone Production and Disposal

The Flowsheet Model for saltstone production and disposal is identical for both CSTIX and CSSX alternatives. The flowsheet model bases is described in Section 5.3.5.5. Results from modeling, based on average waste, yields 20.9 gpm of decontaminated salt solution, corresponding to a maximum weekly production rate of 210,672 gallons. The SPF is capable of processing up to 360,000 gallons weekly based on a 5-day, two-shift operating schedule.

6.3.3.5 Material Balance Results

The results of the material balances are summarized in Table 6.3-13. The Phase IV material balances are quite similar to Phase III material balances with the exception of results associated with the granular dilution factor. For example, the cycle times, the CST usage rate (in lbs/hr), and the CST concentration in the glass differ.

Table 6.3-13 Summary of CSTIX Material Balance Results

Process Variable	Average Waste
Fresh waste feed, gal/min	17.5
[Na ⁺] in fresh waste, M	6.44
Sludge in feed, lbs/hr	5.8
MST added (dry basis), lbs/hr	4.2
Washed MST/sludge, lbs/hr total	186
Fraction sludge in MST/sludge solids	0.52
IX column feed, gal/min	20.7
[Na ⁺] in SPF feed, M	5.61
Decon salt soln to SPF, gal/min	20.9
Saltstone Grout production, gal/min	34.7
Cs concentration, Ci/gal @ 5.6 M	1.37
Granular CST dilution factor	1.0
Cs loading on CST, mg Cs/g CST ³	24.2
Column cycle time, hours	2495
CST rate to DWPF, lbs/hr	7.70
Activity of CST slurry, Ci/gal	187
Glass production rate, lbs/hr	191.4
CST (calcined) in glass, wt %	3.42
Total TiO ₂ in glass, wt %	2.86
Fraction of TiO ₂ from CST	0.39
Sludge oxides, wt %	30.2
Glass Properties	Ref. 109
Durability, ln NL(B) g/L	-10.84
Viscosity, poise	25 – 35
Liquidus, °C	< 950

¹Assuming 10 wt % slurry of CST in water

Using a granular dilution factor of 1.0, relative to ZAM model predictions, has three noteworthy impacts. First, the column cycle times are longer because the CST has a higher capacity. For the average salt solution, the cycle time is about 2500 hours or four months. Second, the quantity of Cs in a loaded column increases. For the average salt solution, the Cs in the lead column will be about 5 million Ci. Third, the 10 wt % CST slurry is “hotter”. The slurry would contain about 220 Ci/gal.

6.3.3.6 Conclusions

A great deal of information on the Alpha Decontamination/CST Ion Exchange/DWPF coupled alternative was developed during Phase IV.

6.3.3.6.1 CST Ion Exchange

Experimentation and modeling confirmed the Phase III column design (three 5 ft diameter by 16 ft long columns in series). Using a granular “dilution factor” of 1.0 (no dilution) rather than 0.7 (30 % dilution) resulted in decreasing the CST flow to DWPF by 30 %. The CST concentration in the glass dropped correspondingly. On the other hand, the increase in K_d increases the Cs accumulated in a column. This will further add to the

engineering challenges associated with gas and H₂ generation in a cesium-loaded CST column and storage tanks, temperature control and heat removal, and accident scenarios and recovery.

Experimentation with CST revealed many parameters had little or no impact on the CSTIX process. The presence of organics in the feed, pressure, velocity, and pretreatment had little effect on column performance. Column models correlated well with measured performance in these cases. Extra-particle gas generation did not have significant effects on column hydraulics and the full-length column loaded and unloaded easily. Gas generation by radiolysis was generally as expected. Testing showed that most of the long term reduction in cesium capacity results from precipitation of sodium aluminosilicate on to the CST particles. Leaching from CST was largely resolved with re-engineering by the manufacturer.

However, concerns and issues were raised in the area of sodium aluminosilicate and other aluminum compound precipitation from supersaturated waste solutions, rapid desorption of Cs at moderate temperature (50 °C), and strong temperature dependence of K_d in IE-911 (the engineered resin form of CST).

6.3.3.6.2 CST Impact on the DWPF Process and Product

Further experiments were completed to address potential issues related to DWPF melter feed preparation, melter processes and waste glass properties. Results indicate hydrogen generation is not a concern for the CSTIX alternative; CST resin addition to the SRAT/SME operations only slightly increases foaming during melter feed preparation in the Chemical Processing Cell. The CST glasses were very durable although properties were not predictable. Viscosity and *liquidus* values were within required ranges with the exception of glass made with HM sludge which produced a viscosity of ~ 160 poise (versus the DWPF limit of 100 poise). As-received CST plugged the Hydragard[®] sampler, but size-reduced CST was sampled representatively by the Hydragard[®] sampler. Size reduced CST was demonstrated to suspend homogeneously in a water slurry of CST.

Other highlights include:

- The first (lead) column in the carousel will load cesium at efficiencies greater than 95% of that predicted by the isotherm and entry cesium concentrations.
- The ion exchange process will meet the required decontamination and send about 7.7 lbs/hr of CST to DWPF with the average waste. .
- The performance of the ion exchange process depends primarily on deviations in SRS waste from the nominal composition.
- *Ci/gal in CST slurry to DWPF* – The concentration of Cs-137 in the 10 wt% CST slurry sent to DWPF ranges from 100 to 250 Ci/gal with the average waste at 187 Ci/gal.
- *Cycle time* – The times show how cycle times can vary depending on waste composition – from 4 to 5.5 months at 100 % attainment. Cycle times are longer when utility is accounted for.

- *Total Cs-137 Ci/batch* – The total Cs-137 accumulated in a column during a column batch cycle ranges from 2.5 M to almost 6 M Ci with the average waste at 5 M Ci.
- *CST usage rate* – At 75 % utility, the CST usage rate (including 5 % fines loss) ranges from 39 to 54 klbs per year with the average waste using 53 klbs in a year.
- *CST loading in glass* – Loading in glass is shown to be from 3.4 to 6.6 wt % with the average waste at 3.4 wt %.
- *TiO₂ in the glass* – The total TiO₂ in the glass ranges from 3.2 to almost 4.6 wt % with the average waste at 3.4 wt %. CST contributes ~ 40 % to the total.
- *Sludge oxides and glass properties* – The sludge oxide concentration is ~ 30 wt % and the CST concentration is 3.4 %. These are at the limit of current glass variability testing. Tests show the durability is acceptable. The viscosity is borderline low at 25 to 35 poise. The *liquidus* is < 950 °C.

6.3.4 Equipment

6.3.4.1 Building layout

Building layout based on shielding and function area sizes of the Non-Elutable Ion Exchange alternative compared to equivalent DWPF facility layouts are provided below in Table 6.3-14. Major process equipment consists of chemical storage and feed tanks, a large alpha sorption tank, filter feed tank, transfer pumps, agitators, 2 sets of crossflow filters, wash and concentration tanks, filter cleaning tanks, cesium removal ion exchange columns, resin hold tanks, and product hold tanks.

Table 6.3-14 CSTIX Building Layout Compared to the DWPF

	DWPF	CST	CST % of DWPF
AREA (SQ.FT)			
Shielded	16,278	9,795	60%
Unloading Well	2,175	2,100	97%
Low Shielded		2,100	
Operating Corridor	59,029	32,400	55%
Crane Operating	18,457	16,800	91%
Total Area	95,939	63,195	66%
VOLUME(CU.FT)			
Shielded	640,344	440,775	69%
Unloading Well	86,348	94,500	109%
Low Shielded		94,500	
Operating Corridor	1,081,583	980,100	91%
Crane Operating	700,261	890,400	127%
Total Volume	2,508,536	2,500,275	~100%

6.3.4.2 Tanks

Table 6.3-15 Tanks for Non-Elutable Ion Exchange Alternative

Tank	Tank Size	Sizing Assumption
Loaded Resin Hold Tanks	2 tanks each 15,000 gallons	Sized for one batch storage of loaded resin to de-couple the CST Facility from DWPF.
Caustic Feed Tank (2.0 M caustic)	15,000 gallons	Sized to support pre-treatment of CST resin for resin change out and caustic dilution water in the Alpha Sorption Tank.
Caustic Storage Tank (50% caustic)	5000 gallons	Sized to receive a typical tanker truck delivery.
DSS Hold Tanks	2 tanks each 100,000 gallons	Sized to allow five days of hold-up of the material to verify mercury removal, if applicable, meets the SPF Waste Acceptance Criteria. The tanks also allow hold-up of material during the time that the SPF and SDF are de-staffed and somewhat de-couple the SPF from the CSTIX Facility. Two tanks will allow filling of one tank while waiting for sample results of the second. NOTE: These tanks allow for five days of product storage from the CSTIX Facility. This five days of product is less than two days of operation of the SPF, assuming two-shift operation.
Process Water Tank	20,000 gallons	Sized to support the make-up of CST resin columns, cooling water system, and chemical addition tanks.
MST Storage Tank	400 gallons	Sized for one batch of MST slurry addition.
Alpha Sorption Tank	88,000 gallons	Sized to hold one batch of salt solution.
Filter Feed Tank	111,000 gallons	Sized to hold one batch from the alpha sorption tank plus 15% for slight decoupling between the alpha sorption tank and the filter feed tank, with allowance for up to 10,000 gallons solids accumulation..
Recycle Blend Tank	30,000 gallons	Sized to hold one day of feed to CST columns.
Sludge Solids Receipt Tank	10,000 gallons	Sized to receive multiple filter cleaning cycles as well as sludge solids prior to pumping to DWPF.
Oxalic Acid Feed Tank	200 gallons	Sized to hold the solution to clean one cross-flow filter.
Filter Cleaning Caustic Tank	500 gallons	Sized to hold the solution to clean one cross-flow filter.
Cleaning Solution Dump Tank	1000 gallons	Sized to circulate material to clean the cross-flow filters.
Wash Water Hold Tank	25,000 gallons	Sized to hold the entire wash water volume from a single MST/sludge solids wash cycle.
Product Holdup Tanks 1 and 2	2 tanks each 5000 gallons	Two tanks allow one tank to fill while the second tank is checked for ¹³⁷ Cs and pumped forward. The tank size allows for approximately three hours of storage.
Fines Hold Tank	1000 gallons	Sized to hold fines from removed during resin preparation
In-Cell Caustic Hold Tank	15,000 gallons	Sized to hold the spent solution from one caustic treatment for one column. After a column is charged with fresh CST, the residual water from resin transport is displaced with 5 column volumes of 2 M NaOH solution.
Column Treatment Tank	5000 gallons	Sized to support resin preparation before column loading.
Column Preparation Tank	3000 gallons	Sized to hold one column volume of resin during resin preparation.

Tank	Tank Size	Sizing Assumption
Ion Exchange Columns	4 columns each 5' diameter with 16' bed length	

6.3.4.3 Jumpers

Table 6.3-16 Summary of Jumper Usage for CSTIX Alternative

Jumper Application	Number of Jumpers
Process Jumpers	151
Process Jumpers with MOVs	13
3-way Process Jumpers	4
3-way Process Jumpers w/2 MOVs	1
Electrical Jumpers	46
Instrumentation Jumpers	47
TOTAL	262

6.4 Caustic Side Solvent Extraction (CSSX)

The proposed CSSX process uses a counterflow solvent extraction process to remove Cs from clarified salt solution generated from a Sr and Alpha Sorption operation. The overall process includes these steps:

- MST is added to salt solution from the tank farms to sorb soluble Sr, Pu, Np and U.
- Slurry from MST treatment is filtered to avoid sending solids forward to solvent extraction. The solids are washed to remove soluble salts, and then sent to the DWPF.
- Clarified salt solution is processed through solvent extraction to remove the Cs.
- A dilute aqueous solution of cesium nitrate from solvent extraction is sent to the DWPF.
- Decontaminated salt solution from solvent extraction is transferred to the SPF.
- Spent organic solvent is transferred to the CIF.

6.4.1 CSSX Process Overview

Initially, strontium and actinides are removed from the waste by sorption onto solid monosodium titanate, as described in Section 6.2. This slurry is filtered to remove and concentrate the MST and sludge solids. These solids are washed and transferred to the DWPF to incorporate them into HLW glass. Clarified salt solution from filtration is then treated to remove Cs using solvent extraction. Figure 6.4-1 schematically shows the overall process for the CSSX alternative.

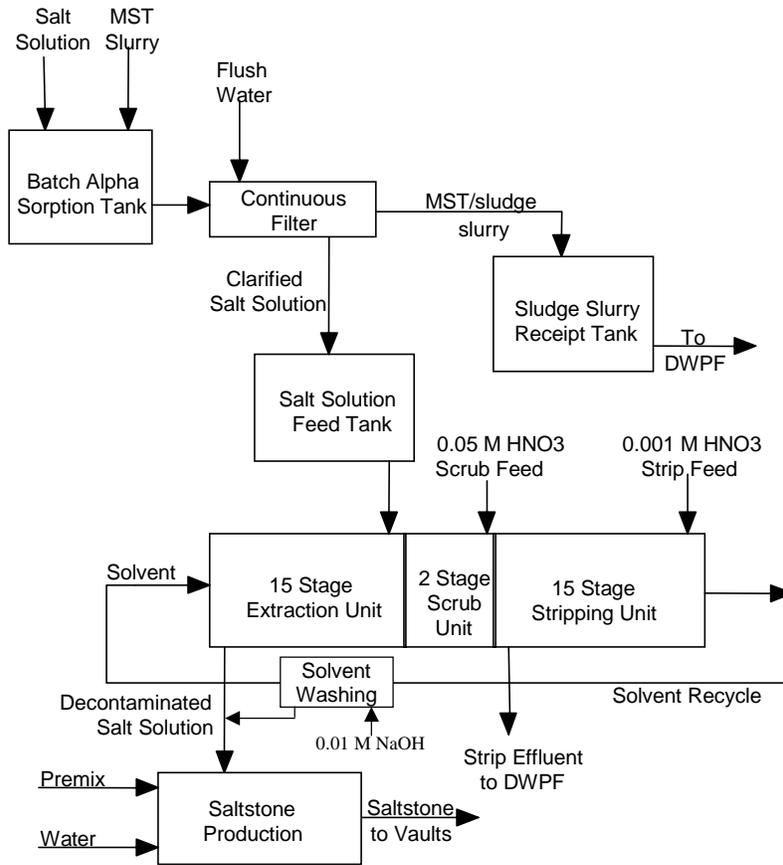


Figure 6.4-1 Schematic Representation of CSSX Process

6.4.2 Solvent Extraction Process

The basic principle of solvent extraction is to use a sparingly soluble diluent material that carries an extractant that will complex with the cesium ions in the caustic solution. The decontaminated aqueous stream (raffinate) is then sent to the SPF where it is processed into saltstone for disposal. The cesium contained in the organic phase (solvent) can then be stripped into an aqueous phase ready for transfer to DWPF. The solvent is recycled after being washed to remove impurities. The Caustic Side Solvent Extraction (CSSX) process uses a novel organic solvent blend made up of four components:

- calix[4]arene-bis-(*tert*-octylbenzo-crown-6) known as BOBCalixC6 at 0.01 M,
- 1-(4-*tert*-octylphenoxy)-3-(1,1,2,2-tetrafluoroethoxy)-2-propanol known as modifier Cs-7SB at 0.5 M,
- trioctylamine known as TOA at 0.001 M, and
- Iso-par™ L, used as a diluent.

This solvent blend is contacted with the alkaline waste stream in a series of countercurrent centrifugal contactors (the extraction stages) to extract cesium from the clarified salt solution. The resulting decontaminated aqueous raffinate is collected,

monitored to confirm acceptable decontamination and then transferred to the SPF for further processing and disposal as saltstone. Following cesium extraction, the solvent is scrubbed with dilute acid to remove other soluble salts from the solvent stream (the scrub stages). The scrubbed solvent then passes into the strip stages where it is contacted with a very dilute (0.001 M) acid stream to transfer the cesium to the aqueous phase. The aqueous strip effluent is transferred to the DWPF, where it is blended with sludge slurry from the tank farms, the MST/sludge slurry from feed clarification in the SWPF and glass frit to prepare melter feed. The blended solids are then vitrified in HLW glass, poured into canisters and stored at the SRS until the canisters can be transferred to the HLW Repository.

In the extraction stages, cesium and nitrate are extracted into the solvent phase. The cesium is stabilized in the solvent phase by the calixarene molecule while the modifier molecules stabilize the nitrate ion. Due to the size of the opening in the calixarene molecules, cesium is removed in dramatic preference to other cations, in particular sodium and potassium. Cesium selectivity is more than two orders of magnitude higher than for potassium and more than four orders of magnitude higher than for sodium. This high selectivity is required to achieve the desired separation of the cesium ions from the bulk sodium ions.

In the proposed CSSX extraction process, the cesium concentration in the organic phase is 3 times that in the aqueous feed solution. For a typical high level waste feed solution containing 0.17 millimolar (mM) cesium, the concentration in the organic stream leaving the extraction stages is approximately 0.44 mM.

$$0.17 \text{ mM}_{\text{Cs}} * (5.6 \text{ M}_{\text{Na}}/6.44 \text{ M}_{\text{Na}}) * 3 \approx 0.44 \text{ mM}_{\text{Cs}}$$

Note that this is significantly below the 10-mM concentration of calixarene in the solvent. Thus, a large excess of available calixarene sites are available for extraction. However, due to the high concentrations of sodium and potassium in the feed stream, a measurable quantity of both sodium and potassium are extracted, and thus take up a portion of the sites.

To provide an essentially pure cesium nitrate raffinate stream, the potassium and sodium are scrubbed from the organic phase using two scrubbing stages between the extraction and strip stages. These stages also scrub trace levels of any ionic aluminum, iron or mercury carryover. The acid solution used in the scrub stages also neutralizes any hydroxide carryover into the scrub stages. The removal of these metals and neutralization of the hydroxide is essential to prevent precipitation and to allow stable operation of the stripping stages. Since the strip stages employ a weakly acidic solution, introduction of caustic into the strip stages would likely result in significant pH shifts which could adversely affect process operability. The basic solvent extraction portion of the CSSX flow sheet is shown in Figure 6.4-8. As noted above, a separate stream containing MST and sludge solids from strontium and alpha sorption would also be generated and transferred to the DWPF. The alpha sorption portion of the overall CSSX process is not shown in the figure.

Over long periods of time in a radiation field, either the modifier or the calixarene may degrade. The modifier is most likely to degrade and form a phenolic compound that is very soluble in the organic phase. Gradual degradation of the solvent will result in some loss of performance. The proposed flowsheet contains two additional unit operations intended to maintain solvent performance.

In the two proposed unit operations, the solvent is first washed with acid and then with caustic. These two wash stages are intended to remove any acidic or caustic impurities that may develop in the solvent system over time. In particular, the caustic wash removes many of the modifier degradation products. To maintain the solvent extraction system performance, the proposed flowsheet assumes the solvent will be replaced annually.

After extraction, the aqueous phase will contain either soluble or entrained organics. The proposed process contains two additional contactor stages designed to remove soluble organics and in particular to remove solvent from the exiting aqueous raffinate stream. A small amount of Iso-par L[®] is introduced into these two stages to extract any of the solvent from the aqueous phase. The aqueous phase from this stage is then sent to a settling tank where any remaining entrained organics (mostly the Iso-par L[®] that was added) floats to the surface and is then decanted. The aqueous raffinate is transferred from the settling tank to one of two hold tanks to allow decay of any short half-life gamma emitters in the raffinate stream. These two tanks are sized to allow a hold time for sufficient decay to facilitate determination whether the target decontamination has been met. After verifying the ¹³⁷Cs concentration is within WAC limits for the SPF, the decontaminated salt solution can be transferred to the SPF for treatment and disposal as saltstone. The aqueous scrub solutions from the organic clean up process are combined with the decontaminated salt solution and included in the transfer to the SPF.

A similar solvent recovery process has been designed for the strip aqueous effluent containing the ¹³⁷Cs. The proposed process contains two additional contactor stages designed to remove soluble organics from the exiting strip effluent. Again, a small amount of Iso-par L[®] is introduced into the stages and used to extract any of the solvent from the aqueous phase. The aqueous phase leaves the clean-up stages and is transferred to a settling tank where the Iso-par L[®] floats to the surface and is decanted.

Since Iso-par L[®] was added in the two solvent recovery processes, this additional diluent must be removed in order for the solvent components to remain at the proper concentrations. A kerosene still allows the excess Iso-par L[®] to be removed while preserving the heavier, more expensive solvent components. The removed material is sent to CIF. The cleaned and adjusted solvent stream is sent back to the solvent hold tank for use in the process.

The feed stream to the process comes from a 111,000-gallon filter feed tank to a 30,000-gallon salt solution feed tank. The use of a relatively large salt solution feed tank provides approximately 1 day of feed storage and some decoupling of the solvent extraction process from the up stream sorption process. The aqueous strip effluent is transferred from the settling tank to a large storage tank (60 days capacity). The use of a large storage tank provides for some decoupling of the solvent extraction process and the

DWPF. The solvent extraction process can only operate as long as DWPF is operating or storage volume remains in the storage tanks between the solvent extraction process and DWPF. Note, however, that DWPF can operate completely decoupled from the solvent extraction process (i.e., DWPF can run with or without feed from the solvent extraction process), since the feed stream to DWPF from solvent extraction contains only nitric acid and CsNO_3 at low concentrations.

Cold chemical feed tanks have generally been designed to provide one day's worth of feed to the process. These feed tanks are fed from larger feed makeup tanks that will provide a buffer in operations to allow for limited (less than a week) outages of process water and other input chemicals.

Strip effluent storage is provided to accommodate the batch cycle times for the SRAT in the DWPF and to allow for disengagement of any organic carry-over from the extraction process. Strip effluent will be provided at a rate of ≤ 1.5 gpm, thereby eliminating the need for an evaporator. The strip effluent transferred to DWPF is assumed to contain the diluent at the saturation limit (20 mg/L). The strip effluent is evaporated in the DWPF SRAT where the nitric acid in the strip effluent is used to partially offset the nominal nitric acid requirement. The effluent would contain < 0.01 M Na and < 0.001 M of other metals.

6.4.3 R&D Results

An extensive experimental program was completed in support of phase III and phase IV evaluation of CSSX. The results of these investigations have been evaluated to determine the potential impacts on the proposed CSSX process. The following is a summary of those impacts. Results that impact the CSSX process have been incorporated in the solvent extraction process described in Section 6.4.2.

6.4.3.1 High Level Waste Performance

SRTC personnel tested the extraction, scrubbing and stripping performance of the solvent system with a sample of SRS High Level Waste (Ref. 117). This test used two extraction, one scrub and three strip contacts. Personnel determined distribution coefficients for each of these contacts. The measured distribution coefficients for extraction exceeds 11, compared to the design basis value of 8. In addition, the measured stripping distribution coefficients were less than 0.1, again an improvement over the design basis value of 0.2. The additional margin between the measured values and those employed in the design basis indicate that the present design basis is conservative.

6.4.3.1.1 Real Waste Test

Flowsheet tests with actual SRS tank waste have been performed at SRTC. The testing was performed with a 33-stage, 2-cm contactor consisting of 15 extraction stages, 2 scrub stages, 15 strip stages, and one solvent wash stage. Testing proceeded in three stages: a non-radioactive simulant run, a spiked simulant run, and a real waste run using a composite waste of Tanks 37 and 44.

As in several previous tests using 2-cm contactors, hydraulic performance was sensitive to disruption. Slightly misaligned interstage lines caused flow restrictions during cold runs that had to be corrected for the system to operate. Once hydraulic performance was verified, the apparatus was transferred to the SRTC Shielded Cells for hot operations. During testing with real waste, an inconsistency was noticed between the flow meters and the balances measuring mass flows of the feeds. The balances showed a lower flow than the flow meters indicated which resulted in low concentration factors (CF) in the strip. Flows were adjusted in an effort to meet the CF requirement of 15 as discussed below. The increase in waste feed rate surpassed the capacity of the small contactors. The apparatus was shutdown, and a maximum feed rate was estimated. When the contactors were restarted, the feed rate was gradually increased to the value decided. The contactors then flooded again requiring another shutdown, flow adjustment and restart. Once again, the new feed rate caused the contactors to flood. This upset also resulted in contamination of the solvent reservoir. The waste feed flow was reset to its original value while the strip feed setpoint was decreased 0.4 mL/min to 2.45 mL/min. The system was then restarted. The final 10.5 hours of operation were run without incident. Recovery was achieved from all three upsets. The hydraulic difficulties of the contactors likely arises from a combination of 1) misaligned interstage lines inaccessible in the shielded cells and 2) differences in densities/viscosities between the simulants and the actual waste. Neither of these issues is expected to cause problems when larger (full-scale) contactors are used. (Ref.118)

Two simulated wastes were spiked for use in the simulant runs: SRS average waste simulant and a Tank 37/44 composite simulant. The purpose of using two simulants was to verify the ANL flowsheet proof-of-concept test with the average simulant, and provide verification of simulant testing by comparing a simulant test with the real waste test using the Tank 37/44 simulant. Each simulant was fed for 6 hours of operation. The real waste test was 47 hours in duration. The Tank 37/44 waste composite had previously undergone a MST strike to meet the Sr and alpha requirements of the Saltstone facility. (Ref. 93)

6.4.3.1.2 Decontamination Performance

Because of the short operation time for each simulant, it is difficult to tell from the data whether steady state was reached or not. Figures 6.4-2, 6.4-3 and 6.4-4 show the analytical results of the simulant tests compared to the real waste test. An average of the decontamination factors from 1.5 to 6 hours (average simulant) yields a value of 43,000; while an average from 7 to 12 hours (Tank 37/44 simulant) yields a value of 63,000. Both simulant tests exceeded the target DF of 40,000. (Ref. 118)

The real waste required a DF of >13,000 with a target of 40,000. Despite the process upsets mentioned above the composite DF was 40,000 for the entire 47 hours of operation. Prior to the first upset, the composite DF was 804,000, and 511,000 prior to the second upset. After the final upset (when the solvent was contaminated), the DF started out below the required value, but they steadily increased throughout the remainder of the test in excess of the 40,000 target. The low DF values indicate that the system was restarted too quickly after the solvent was contaminated. Despite restarting too quickly,

the system still recovered and met the process DF goals. Even in light of the process upsets and low DFs after the final upset, the solvent DF remained above the target DF of 40,000. A plot of the waste raffinate DF results for the real waste test and the simulant runs is shown in Figure 6.4-2, and the solvent DF results are shown in Figure 6.4-3. (Ref. 118)

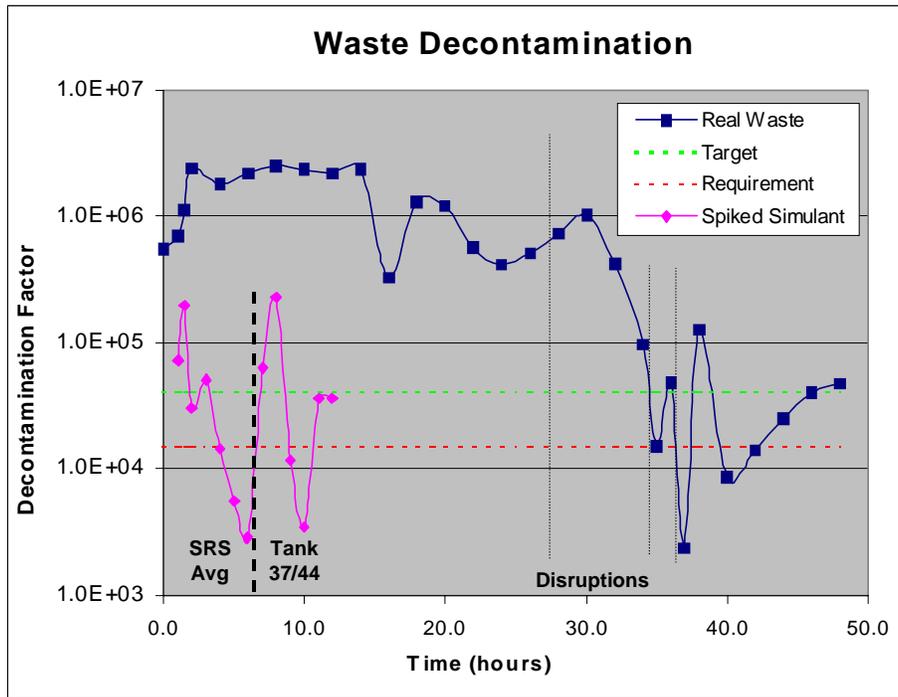


Figure 6.4-2 Waste Decontamination Trend

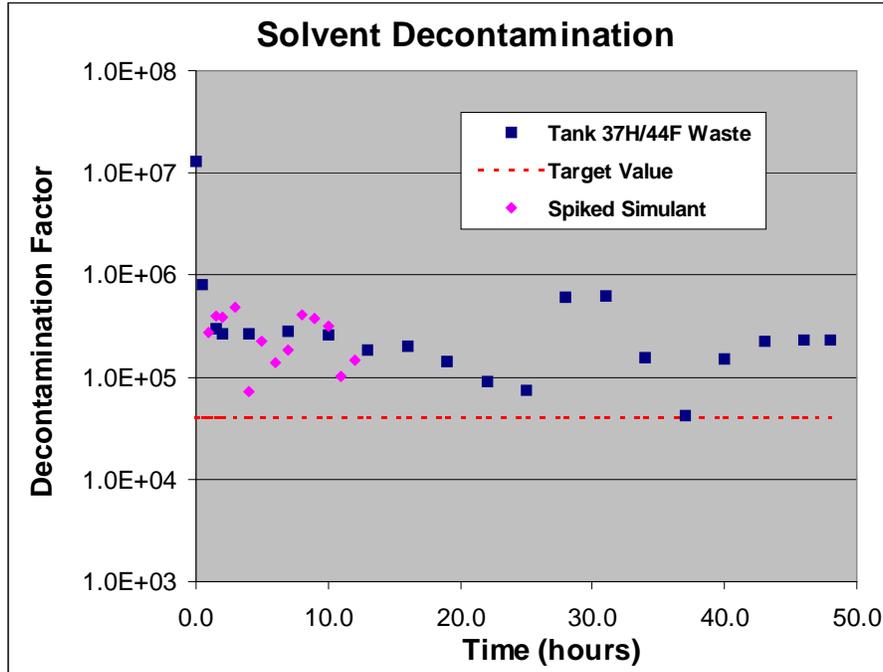


Figure 6.4-3 Solvent Decontamination Trend

6.4.3.1.3 Cesium Concentration

A target CF of 15 was established to meet the requirements of the production facility. The average concentration factors for each simulant test were 14.8 and 13.8 respectively. The average simulant CF continually increased as the test progressed indicating that steady state had not yet been reached, while the CF values for the Tank 37/44 simulant were consistent. (Ref. 118)

The average CF for the real waste test was 12.8 prior to increasing the feed rate. As mentioned previously, the first upset occurred after increasing the waste feed rate in an attempt to increase the CF to the target of 15. During the period of non-steady state operation (after increasing the feed rate) the CF varied between 13.7 and 15.5. Once the waste feed rate was returned to its original value and the strip feed was lowered, the CF averaged 14.4 for the final 10.5 hours of operation. Figure 6.4-4 shows the concentration data for both spiked simulant runs as well as the real waste test. (Ref. 118)

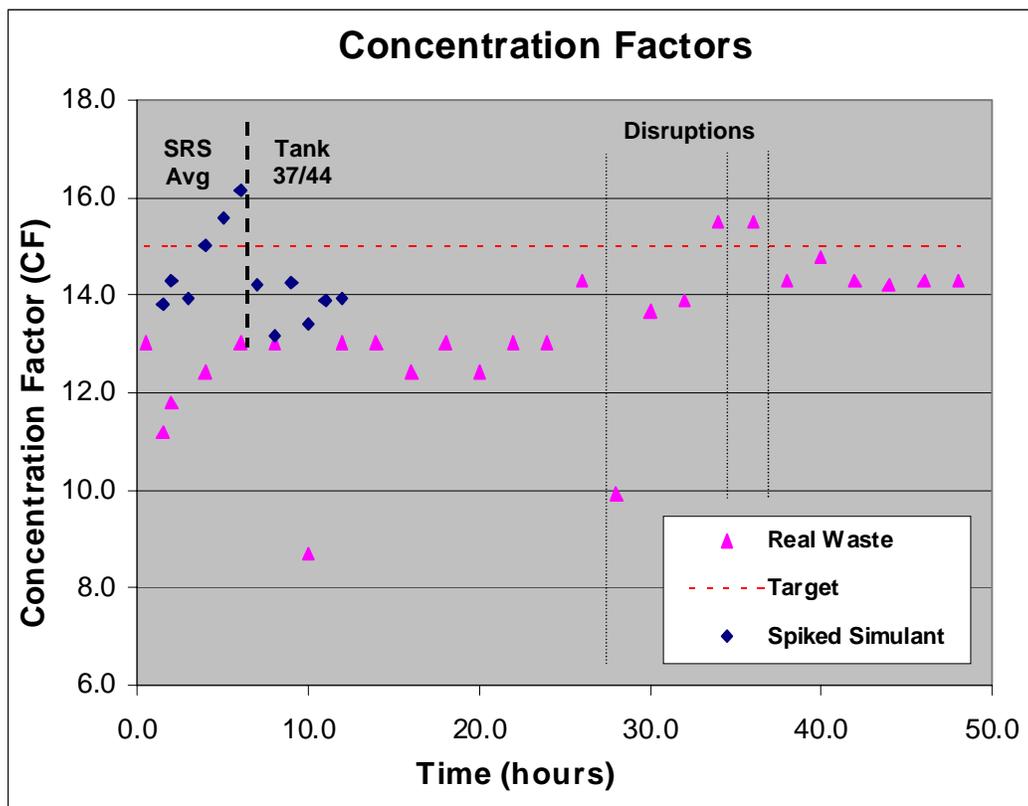


Figure 6.4-4 Cesium Concentration Trend.

6.4.3.2 Temperature Control

The cesium equilibrium between solvent and aqueous phase is strongly dependent upon the temperature of the system. During typical extraction conditions for expected plant operations, the equilibrium distribution coefficients will decrease 6 to 10 % for every 1 °C increase above 25°C. Selection of the organic flow rate is highly dependent upon these distribution coefficients. Therefore, to facilitate smooth operation of the proposed solvent extraction facility, limited temperature control is required. Based on the proposed organic flow rate, this requirement is manifested as operational temperature limits of 33 ± 3 °C for the strip stages (to obtain $D_{CS} \geq 0.2$) and 23 ± 3 °C in the extraction stages (to obtain $D_{CS} \leq 8.0$).

Similarly, the addition of 1×10^{-3} M trioctylamine (TOA) to the solvent decreases the stripping distribution coefficient by 10 fold. (Ref. 119)

6.4.3.3 Solvent Recovery

Calixarene and the modifier are sparingly soluble in aqueous solutions. (Ref. 119) The partition coefficients for modifier are on the order of 50,000 while those for calixarene are greater than 1 million. Based on these values, less than 15 % of the low cost modifier and less than 1 % of the calixarene would be lost from the system in a year. Thus, simply decanting the raffinate and the effluent should prove sufficient for solvent recovery and

limit the organic carryover to downstream processes. Decanting is included in the Process Flow Diagrams. More recent testing confirms these partitioning values to the extent possible. The partition coefficient for modifier was estimated to be the same as above with a lower bound of 8000. The extractant P is greater than 12,500 which was the detection limit of the analytical equipment, so the value is probably higher. The TOA was estimated to have a $P > 30,000$ with a lower bound at 6000. (Ref. 121)

For the CSSX Real Waste Test, a process goal of <1% second phase entrainment was established. During steady state operation, entrainment was maintained well below 1%. Monitoring the decanters during testing proved to be valuable in diagnosing hydraulic problems.

6.4.3.4 Solvent Stability and Cleanup

Chemical stability testing under caustic conditions at 53°C (the extraction stages) indicated that the old modifier, Cs-3 decomposed at a rate of 2% per day. (Ref. 119) The primary products of decomposition were p-(t-octyl)phenol and fluorinated alcohols. Under these conditions, no detectable decomposition of the calixarene was observed. (Ref. 119) The new modifier, now adopted for use (Cs-7SB) has exhibited a significant decrease in decomposition over the previous modifier. (Ref. 120) Long term exposure to scrub solution (0.05 M HNO₃) at 60°C appears to cause TOA in the solvent to degrade to dioctylamine (DOA), but there is no notable decay of the other solvent components. Also, when the solvent is in contact with SRS full simulated waste at 60°C over long periods, some minor in-growth of low molecular weight cationic species is detected indicating slight degradation is taking place. In short, the current solvent matrix is thermally stable at temperatures well exceeding normal operating parameters. (Ref. 121)

Based on an average concentration of 3.5×10^{-5} M ¹³⁷Cs in the organic phases, the solvent is expected to receive about 0.0917 Mrad of dose (Ref. 122). Before changing to the current solvent matrix, a solvent sample was analyzed following exposure to 25 Mrad of dose. No noticeable degradation of calixarene was detectable and less than 5 % degradation of the modifier Cs-3 was observed. (Ref. 123) Additional tests with the current modifier, Cs-7SB, indicate the new modifier is much more stable than the previous Cs-3 modifier. (Ref. 124) The primary decomposition product from Cs-7SB is 4-sec-butylphenol (4-SBP). Partitioning coefficients indicate that none of the aqueous process solutions (salt waste, scrub, or strip) are suitable for removing 4-sec-butylphenol when it is present at concentrations large enough to affect stripping. Partitioning coefficients are shown in Table 6.4-1. At concentrations of 10 mM and larger, stripping performance begins to degrade; however, the net estimated annual production is estimated to be only 0.3 mM/yr. Considering the slow production rate and the amount removed by the waste raffinate, the estimated steady state concentration is only expected to be 0.002 mM. Based on this information, solvent washing is not required to control the concentration of 4-sec-butylphenol. The optimum wash solution was found to be 0.3 M NaOH, which removes about 56% of the phenol per cycle, but since washing is not necessary for phenol, a wash concentration of 0.01 M NaOH was chosen because the lower NaOH concentrations are more effective at removing organic acids. (Ref. 122)

Table 6.4-1 4-Sec-Butylphenol Partitioning Coefficients.

Aqueous Stream	P_{SBP}	Error
Waste Raffinate	50	Estimated value
Scrub	338	± 33
Strip	298	± 27

These preliminary results on the effect of radiation on degradation suggested that less than 10% of the calixarene is likely to require replacement each year. This low rate of calixarene replacement would reduce the estimated annual cost of solvent (presently based on 100 % replacement each year of operation). More recent results evaluating solvent performance have not shown any obvious solvent degradation with internal irradiation doses equivalent to 13.5 years of plant operation. Organic-aqueous separation times remained about the same, and no third phase formation was observed. Organic analysis of the solvent matrix revealed some degradation occurring. There was no significant decrease in extractant or modifier concentrations, but TOA concentration decreased by up to a half over the 13.5 year equivalent dose as seen in Figure 6.4-5. 4-*sec*-butylphenol was also detected despite the modifier concentration remaining essentially constant. The phenol concentration increased with dose as seen in Figure 6.4-6, which is consistent with radiolytic decomposition of the modifier. (Ref. 122)

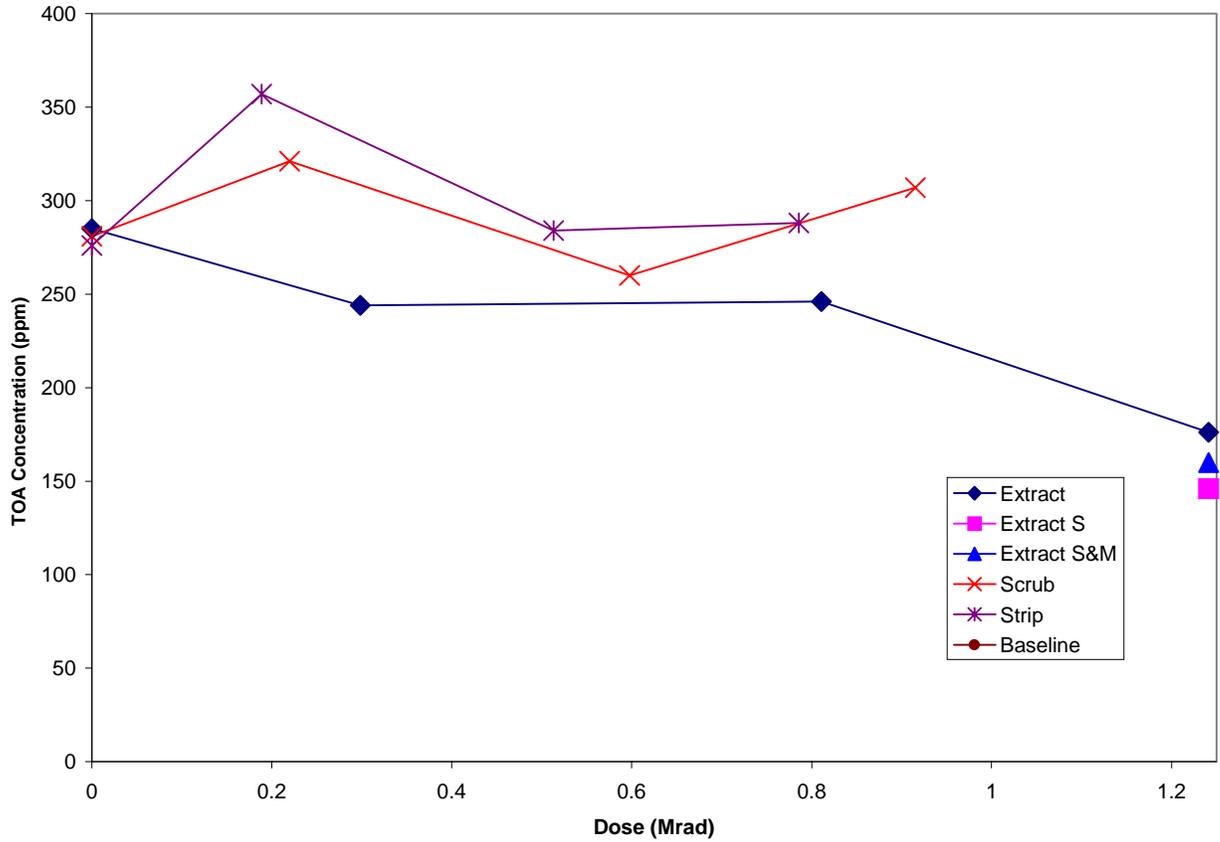


Figure 6.4-5 Solvent Tri-octylamine (TOA) Concentration with Self-Irradiation

Note: “Extract” denotes batch extraction in contact with full simulant; “Extract S” denotes salts only simulant; and “Extract S&M” is salts and metals only simulant.

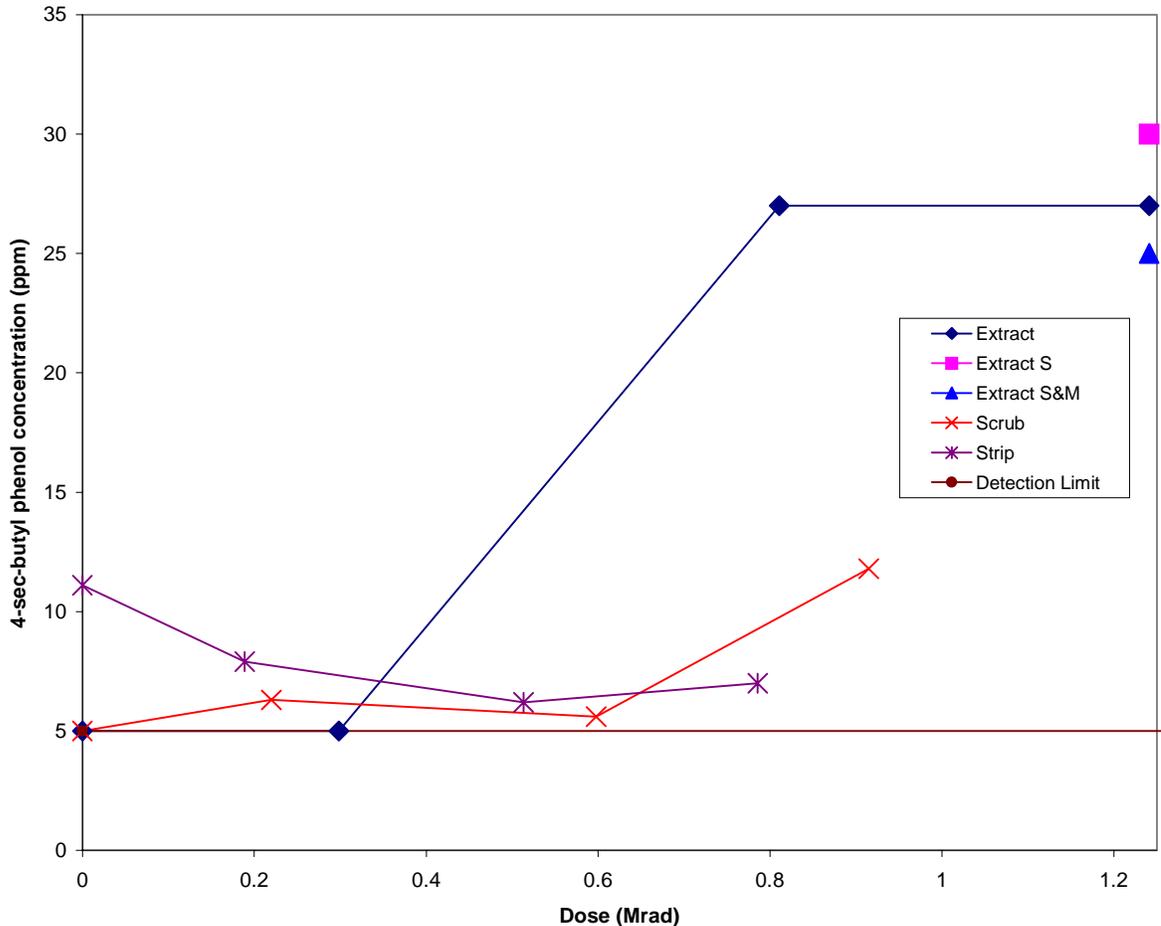


Figure 6.4-6 Solvent 4-Sec-Butyl Phenol Concentration with Self-Irradiation

Note: "Extract" denotes batch extraction in contact with full simulant; "Extract S" denotes salts only simulant; and "Extract S&M" is salts and metals only simulant.

No decrease in extraction or scrubbing performance was noted, but stripping performance declined with increased self-irradiation dose. This is attributed to the decrease of TOA in the solvent, which is demonstrated in Figure 6.4-7. The decrease in stripping ability might be attributed to the increase in 4-sec-butylphenol; however, the concentrations detected in the test were below those that began to cause stripping problems in previous tests. Analysis of all of the self-irradiation data indicate that even without washing or TOA replenishment, the solvent will maintain its performance for up to 3 years. In addition, the solvent performance was restored with a mild caustic wash and replacement of the TOA for the entire 13.5-year equivalent duration of the test. (Ref. 122) Testing at

ORNL shows that a 0.01 M caustic wash efficiently controls the concentration of degradation products in the solvent system. (Ref. 119, 121, 124,125)

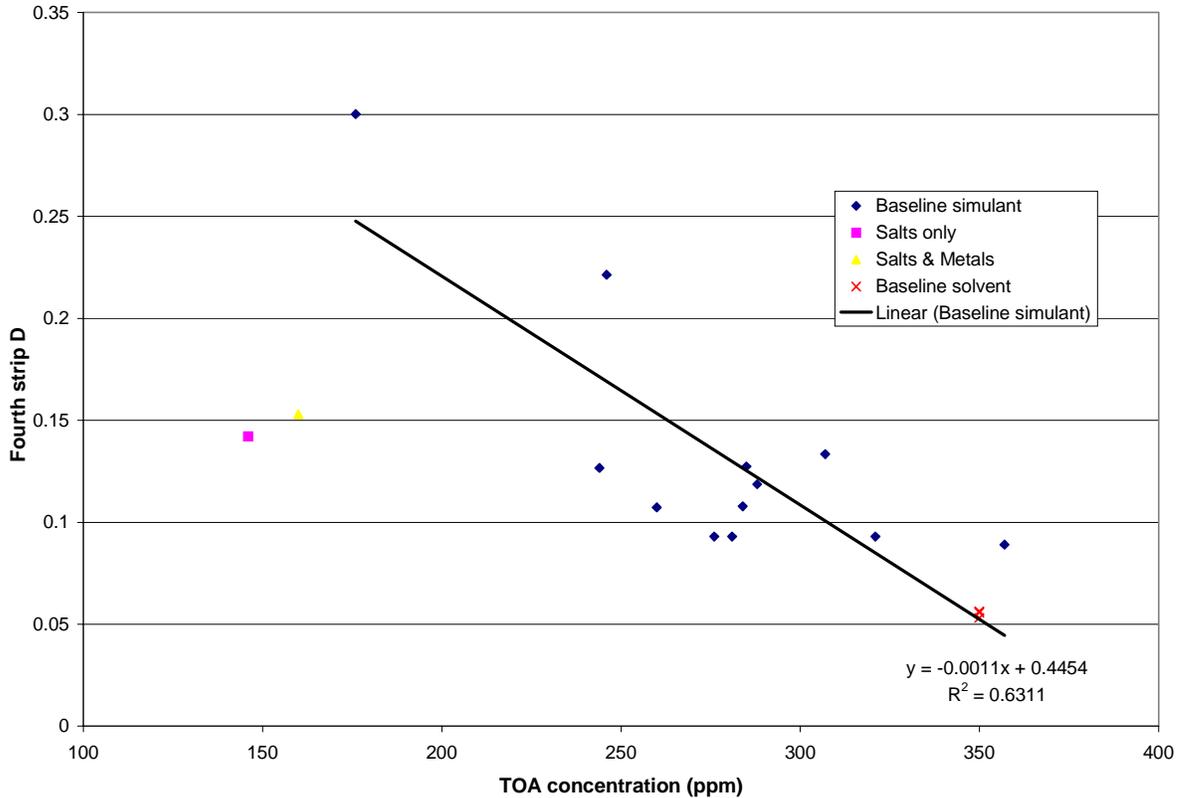


Figure 6.4-7 ESS 4th Strip Cs Distribution Coefficient (D) vs Solvent TOA Concentration

Third phase formation is of concern in the CSSX process. Insoluble phases encountered in solvent extraction are typically pure solid compounds or heavy liquid organic phases rich in extractants and extracted solutes. The heavy liquid phases are typically referred to as third phases. Liquid-liquid contacting equipment is normally not designed to accommodate formation of solid precipitates or third-phases. Although minor amounts of such phases might be tolerable, continued buildup eventually causes poor hydraulic performance or deterioration of extraction, stripping, or selectivity. Testing has been done to determine the conditions in which third phase formation can occur. In short, third phase formation does not appear to be affected by chemical or radiolytic decomposition. When contacted with simulants having high potassium concentrations at

low temperatures, an additional phase is formed. When the potassium concentration in the waste feed is ≥ 50 mM, a third phase forms at 19°C and below. This temperature is very close to the desired operating temperature of the extraction section at $23 \pm 3^{\circ}\text{C}$. The blending basis for revision 12 of the HLW System Plan, however, shows that potassium concentrations for the 67 proposed blends are well below 50 mM, except for the final 3 blends. Batches 65-67 have potassium concentrations of 51, 59, 63 mM respectively. The final blend, batch 67, has a relatively high sodium molarity, which will require additional dilution in the AST, further reducing the potassium concentration. After dilution in the AST, batch 66 may be the only batch that encroaches on the 50 mM potassium limit. At the time of the blend revisions, the R&D for third phase formation had not yet been completed, so maintaining the concentrations below 50 mM was not a criterion. Since the “problem” blends are at the end of the blending strategy, there will be plenty of empty tanks available for additional blending. If CSSX is the chosen technology for the SWPF, Revision 13 of the HLW System Plan will include a revised blending strategy to maintain the potassium concentration below 50 mM. (Ref. 121, 126)

6.4.4 Technical Bases

6.4.4.1 Sr and Alpha Sorption

The technical bases for Sr and Alpha Sorption are discussed in Section 6.2.

6.4.4.2 Solvent Extraction

The basis for the development of caustic side solvent extraction is laboratory testing from Oak Ridge National Laboratory. (Ref. 127, 128, 129, 130) The lab testing measured the single contact distribution ratio for cesium using the proposed solvent. These tests used a typical SRS High Level Waste salt solution composition that was 7 M in sodium salts. The solvent consisted of:

- 0.01 M BoBCalixC6 extractant
- 0.2 M Cs-3 modifier
- Isopar L diluent (balance)

Equal parts solvent and salt solution were contacted and then separated and the concentration of cesium in each stream were determined. These measurements were then used to determine the distribution coefficient:

$$D = C_{S_{org}}/C_{S_{aq}}$$

The solvent extraction process consists of three processing segments, aqueous extraction, solvent scrubbing and solvent stripping segments. Each segment is comprised of multiple stages of aqueous-organic contacting and separation. Therefore, in addition to contacting the salt solution, the scrub solution and the strip solution were also contacted with the solvent and distribution ratios were measured. Measured results were:

Table 6.4-2 Distribution Coefficients

	Extraction	Scrub	Strip
D(Cs)	8 (25°C)	0.6 (25°C)	0.16 (30°C)

Using these data, a proposed flowsheet for the extraction of cesium from typical salt solution waste (1.7×10^{-4} molar cesium) was developed using the Excel macro SASSE developed by Ralph Leonard at Argonne National Laboratory. This flowsheet assumed a feed of 20.1 gpm at a concentration of 5.6 M sodium. In addition, the flowsheet targets a raffinate cesium concentration of less than 40 nCi/g. The spreadsheet output for the rates for the various streams are:

Table 6.4-3 Flowsheet Streams

Salt Feed (gpm)	Scrub Feed (gpm)	Strip Feed (gpm)	Aqueous Raffinate (gpm)	Strip Effluent (gpm)	Solvent (gpm)
20.1	1.32	1.33	21.42	1.33	6.6

The Cs-containing effluent would contain <0.01 M Na, <0.001 M of other metals. By changing the modifier to Cs7-SB and adding TOA, flowsheet performance has improved notably. The flowsheet requirements, however, were established to ensure meeting the FFA and to keep the basis for all three technologies the same. Despite changes in the baseline solvent, this model still represents the flowsheet requirements.

This flowsheet assumes 15 stages of extraction, 2 stages of scrubbing and 15 stages of stripping. This number of stages was used to achieve an approximate 15-fold increase in the Cs concentration of the effluent over the feed. Use of additional stages can further increase the concentration achieved while use of fewer stages reduces the concentration achieved.

This flowsheet was developed under the assumption of equilibrium stages (a relatively accurate assumption for centrifugal contactors as indicated by testing at ANL in Reference 131). A further assumption was of minimal other phase carry over. This assumption implies that good phase disengagement is achieved. Phase disengagement was confirmed during testing at ANL. Significant other phase carryover would likely significantly reduce the efficiency of the process.

Cesium material balances can be determined for each stage n as follows:

$$Cs \text{ In} = Cs \text{ Out}$$

$$M_{aq} * [Aq_{n+1}] + M_{org} * [Org_n] = M_{aq} * [Aq_n] + M_{org} * [Org_{n-1}]$$

Where:

- M_{aq} is the mass flow rate of the aqueous phase,
- M_{org} is the mass flowrate of the organic phase,
- $[Aq_{n+1}]$ is the Cs concentration in the aqueous phase entering this stage,
- $[Org_n]$ is the Cs concentration in the organic phase exiting this stage,
- $[Aq_n]$ is the Cs concentration in the aqueous phase exiting this stage and

[Org_{n-1}] is the Cs concentration in the organic phase entering this stage.

Since each stage is in equilibrium the distribution coefficient relationship above allows the determination of a single unknown for each stage.

The technical bases for DWPF operations are common to all alternatives. These bases are described in Section 5.3.5.4.

6.4.4.3 Saltstone Production and Disposal

The technical bases for saltstone production and disposal operations are common to all alternatives. These bases are described in Section 5.3.1.3.

6.4.5 Flowsheet Model Bases

A schematic of the overall process in Figure 6.4-1 shows the principal operations that serve as the bases for the CSSX material balance model.

6.4.5.1 Strontium and Alpha Sorption

The Flowsheet Model for Strontium and Alpha Sorption is identical for both CSTIX and CSSX alternatives. This model is described in Section 6.2. Results from modeling are identical for these two alternatives, and are also provided in Section 6.2.

6.4.5.2 Solvent Extraction

The solvent extraction process uses a continuous counter-current solvent extraction process to remove cesium from clarified salt solution. After cesium is removed, decontaminated salt solution can then be transferred to the SSHT in the SPF for subsequent treatment and disposal as saltstone.

The solvent extraction model consists of three parts:

- A 15-stage extraction unit where cesium is removed from the salt solution into the solvent. The aqueous effluent from the extraction stage is sent to the grout plant.
- A 2-stage scrub section where 0.05 M nitric acid is added the aqueous phase.
- A 15-stage stripper where 0.001 M nitric acid is used to strip the cesium from the organic phase back into the aqueous phase. The aqueous phase from the stripper is accumulated and added as an input stream to the DWPF model.

Figure 6.4-8 shows a schematic diagram of the Solvent Extraction portion and the corresponding flow rates for this segment of the CSSX alternative.

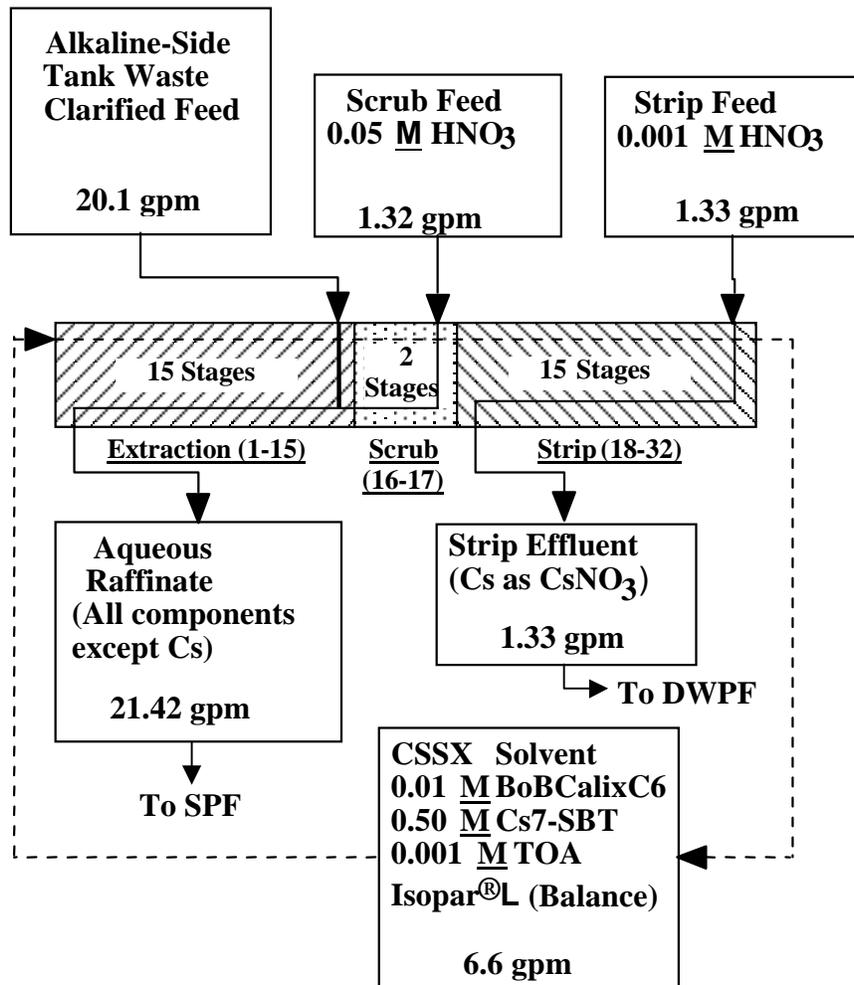


Figure 6.4-8 CSSX Flowsheet

The organic solvent used in the extraction unit is continuously recycled from the output of the stripping stages to the input of the extraction stages. A series of trial calculations show that a solvent flow rate of 6.6 gpm maximizes the amount of cesium removed from the salt solution. The scrub flow is set to 20% of the solvent flow and the strip flow is fixed at 1.33 gpm. Cesium is assumed to be the only component extracted from the salt solution.

The SPEEDUP model was modified to provide material balances for the proposed solvent extraction process. These modifications include increasing the salt flow rate, decreasing the strip flow rate and adding the caustic wash solution.

6.4.5.3 DWPF Vitrification

The flowsheet modeling bases for the DWPF are the same as those used in Phase III, and are generally identical for all three alternatives. The bases for melter feed preparation and melter chemistry are shown in Section 5.3.5.4.

The CSSX alternative has the least impact on current “sludge-only” DWPF operations and chemistry, from the standpoint of frit changes or melter feed preparation. The waste streams sent to the DWPF are generally compatible with current “sludge-only” operations in the DWPF.

6.4.5.4 Saltstone Production and Disposal

The Flowsheet Model for saltstone production and disposal is identical for both CSTIX and CSSX alternatives. The flowsheet model bases are described in Section 5.3.5.5. Results from modeling, based on average waste, yields 20.9 gpm of decontaminated salt solution at 100% attainment, corresponding to a maximum weekly production rate of 210,672 gallons. Accounting for the scrub and the solvent wash, the actual DSS production rate is 23.3 gpm corresponding to 234,864 gallons weekly. The SPF is capable of processing up to 360,000 gallons weekly based on a 5-day, two-shift operating schedule.

6.4.6 Flowsheet Model Results

The raffinate sent to the SPF from the CSSX process will contain less than 40 nCi/g of ^{137}Cs and only trace (< 20 ppm) concentrations of organics. This feed stream to the SPF is approximately 5 M sodium. The strip effluent sent to DWPF from this process contains approximately 20 Ci/gallon of Cs^{137} and contains only trace (< 20 ppm) concentrations of organics. This feed stream to DWPF consists primarily of dilute nitric acid and cesium nitrate. Integration of this stream into the DWPF process is relatively seamless.

The overall results of the CSSX flowsheet model are summarized in Table 6.4-4.

Table 6.4-4 Summary of CSSX SPEEDUP Flow Sheet Model Results

Parameter (@ 100 % attainment)	Model Result
Salt Solution Processed (kgal/yr)	9,198
Decontaminated Salt Solution (kgal/yr)	10,577
Grout Made (kgal/year)	19,815
Strip Solution to DWPF (kgal/yr)	699
Canisters (per yr)	372
Solvent Used (kgal/yr)	1

6.4.7 Equipment

6.4.7.1 Building Layout

The Building layout based on shielding and functional area sizes of the Caustic Side Solvent Extraction alternative is compared to the equivalent DWPF facility layout in Table 6.4-5. Major process equipment consists of chemical storage and feed tanks, an alpha sorption process, transfer pumps, agitators, 1 set of crossflow filters, filter cleaning tanks, resin hold tanks, mercury removal ion exchange columns, product hold tanks,

multi-stage extraction contactors, multi-stage effluent strip contactors, organic removal contactors, and solvent cleanup tanks.

Table 6.4-5 CSSX Building Layout Compared to the DWPF

	DWPF	CSSX	CSSX %DWPF
AREA (SQ. FT):			
SHIELDED	16,278	12,360	76%
UNLOADING WELL	2,175	2,100	97%
LOW SHIELD		2,100	
OPERATING CORRIDOR	59,029	37,440	63%
CRANE OPERATING	18,457	19,200	104%
TOTAL AREA	95,939	73,200	76%
VOLUME(CU. FT):			
SHIELDED	640,344	556,200	87%
UNLOADING WELL	86,348	94,500	109%
LOW SHIELD		94,500	
OPERATING CORRIDOR	1,081,583	1,132,560	105%
CRANE OPERATING	700,261	1,017,600	145%
TOTAL VOLUME	2,508,536	2,895,360	115%

6.4.7.2 Tanks

Table 6.4-6 Tanks for CSSX Alternative

Tank	Tank Size	Sizing Assumption
Scrub Feed Tank	2500 gallons	Sized to provide storage for one day of processing material.
Strip Feed Tank	4000 gallons	Sized to provide storage for one day of processing material.
Solvent Makeup Tank	1000 gallons	Sized to hold the estimated volume of the 36 centrifugal contactors, Solvent Hold Tank, and associated piping. The tank volume will allow make-up of the full solvent system if complete changeout of solvent is needed.
Solvent Hold Tank	1000 gallons	Sized to hold the estimated volume of the 36 centrifugal contactors and associated piping and provide on-line make-up for the solvent recirculation system.
Nitric Acid Feed Tank	1000 gallons	Sized to provide make-up for the strip feed and scrub feed systems.
Process Water Tank	25,000 gallons	Sized to provide make-up for the chemical addition tanks, GT-73 resin make-up, and cooling system.
DWPF Salt Feed Tank	100,000 gallons	This tank will hold a 45-day supply of salt for processing in DWPF. The Solvent Extraction Facility will be effectively de-coupled from DWPF.
Solvent Wash Solution Make-up Tank	1000 gallons	Sized to hold the wash solution for cleaning the solvent.
Caustic Solvent Wash Tank	1000 gallons	Sized to receive the wash solution from the solvent wash solution makeup tank.
Solvent Wash Tank	1000 gallons	Sized to provide surge capacity for solvent washing.
Strip Effluent Stilling Tank	500 gallons	Sized to hold-up the strip solution to allow decanting the organic from the aqueous in the strip stream.
Aqueous Raffinate Stilling Tank	500 gallons	Sized to hold up the raffinate solution to allow decanting the organic from the aqueous raffinate stream.
Ba-137 Decay Tank	2 tanks each 2500 gallons	Allows one tank to be filled while the raffinate in the second tank is monitored for Cs-137 activity prior to pumping forward. The tanks are sized for approximately three hours of storage.
Isopar Make-up Tank	2000 gallons	Sized for one week of storage for make-up to the Raffinate Organic Removal Stages and the Strip Organic Removal Stages
MST Storage Tank	400 gallons	Sized for one batch of MST addition.
Alpha Sorption Tank	88,000 gallons	Sized to hold one batch of salt solution.
Salt Solution Feed Tank	30,000 gallons	Sized to provide continuous feed to CSSX from new alpha sorption process
Sludge Solids Receipt Tank	10,000 gallons	Sized to receive multiple filter cleaning cycles and sludge solids prior to pumping to DWPF.
Wash Water Hold Tank	25,000 gallons	Sized to receive multiple sludge solids washes.
Oxalic Acid Feed Tank	200 gallons	Sized to hold the solution to clean one cross-flow filter.
Filter Cleaning Caustic Tank	500 gallons	Sized hold the solution to clean one cross-flow filter.

Tank	Tank Size	Sizing Assumption
DSS Hold Tanks	2 tanks, each 100,000 gallons	The tanks are sized to allow five days of hold-up of the material to verify mercury removal, if applicable, meets the SPF Waste Acceptance Criteria. The tanks also allow hold-up of material during the time that the SPF is de-staffed and somewhat de-couples the SPF from the Solvent Extraction Facility. Two tanks will allow filling of one tank while waiting for sample results for the second. NOTE: These tanks allow for five days of product storage from the Solvent Extraction Facility. This five days of product is less than four days of operation of the SPF.
Chemical Additive Tank	100 gallons	Sized to support the make-up of small volumes of additives such as the CsNO ₃ .
Isopar Hold Tank	5000 gallons	Sized to provide storage of the Isopar prior to use in the Solvent Make-up Tank and Kerosene Make-up Tank.
Isopar Feed Tank	500 gallons	Sized to support makeup of modifier and extractant.
Cleaning Solution Dump Tank	1000 gallons	Sized to circulate solutions used in cleaning of cross-flow filters.
Extractant Makeup Tank	50 gallons	Sized to provide the make-up necessary for the Solvent Make-up Tank and any addition to the Solvent Hold Tank during operation.
Modifier Makeup Tank	500 gallons	Sized to provide the make-up necessary for the Solvent Make-up Tank and any addition to the Solvent Hold Tank during operation.
TOA Tank	6 gallons	Sized to provide the make-up necessary for the Solvent Make-up Tank and any addition to the Solvent Hold Tank during operation.
Nitric Acid Charge Tank	1 gallon	Sized to provide the 50% Nitric Acid necessary to reach the 0.0001M HNO ₃ for the Strip Feed Tank.
Scrub Make-up Tank	15,000 gallons	Sized to make-up one week of scrub feed. This will allow chemical mixing and sampling prior to pumping to the Scrub Feed Tank.
Strip Make-up Tank	25,000 gallons	Sized to make-up one week of strip feed. This will allow chemical mixing and sampling prior to pumping to the Strip Feed Tank.
Filter Feed Tank	111,000 gallons	Sized to hold one batch from the alpha sorption tank plus 15% for slight decoupling between the alpha sorption tank and the filter feed tank, with allowance for up to 10,000 gallons solids accumulation.
Caustic Storage Tank (50% Caustic)	5000 gallons	Sized to provide caustic for dilution, washing, and filter cleaning.
Caustic Dilution Feed Tank (2.0 M Caustic)	15,000 gallons	Sized to provide dilution to salt solution feed.
Caustic Feed Tank	1000 gallons	Sized to receive the 50% caustic solution and store for use in the Re-alkaline Stages of the solvent extraction process.
Caustic Make-up Tank	1000 gallons	Sized to make-up the caustic to the molarity needed in the Re-alkaline Stages of the solvent extraction process.
Kerosene Vacuum Still	250 gallons (still) 250 gallons (condensate tank)	Used to remove excess organic diluent from the solvent system. Excess diluent will be transferred to the Consolidated Incineration Facility (with Kerosene Condensate Tank).
Kerosene Condensate Tank	1000 gallons	Sized to hold contents of kerosene still.
Re-Alkaline Stages	2 Stages	These stages are used to increase the pH in the solvent after scrubbing.
Strip Organic Removal Stages	2 Stages	These stages are used to remove organic from the aqueous strip stream.

Tank	Tank Size	Sizing Assumption
Raffinate Organic Removal Stages	2 Stages	These stages are used to remove organic from the aqueous raffinate stream.
Extraction Stages	15 Stages	These stages are used to remove Cs from clarified salt solution.
Strip Stages	15 Stages	These stages are used to strip Cs from the solvent into a mildly acidic aqueous phase for transfer to DWPF.
Acid Wash Stages	2 Stages	These stages
Simulated Salt Solution Make-up Tank	4000 gallons	Sized to prepare one batch of waste salt solution simulant for processing.
Simulated Salt Solution Feed Tank	4000 gallons	Sized to provide 3 hours of continuous feed of waste salt solution simulant to the extraction stages.

6.4.7.3 Jumpers

Table 6.4-7 Summary of Jumper Usage for CSSX Alternative

Jumper Application	Number of Jumpers
Process Jumpers	158
Process Jumpers with MOVs	15
3-way Process Jumpers	5
3-way Process Jumpers w/2 MOVs	1
Electrical Jumpers	95
Instrumentation Jumpers	37
TOTAL	311

7.0 LIFE CYCLE COMPARISONS

Couple operation was assumed to be April 1, 2010 for Revision 12 of the HLW System Plan (Ref. 28) All three flowsheets process salt at a rate, which matches the Waste Removal Programs capacity (an average of 6 million gallons per year).

The instantaneous processing rate must be greater than this to allow for downtime (25% or inverted, 75% attainment) and melter outages of 6 months every other year. Because the facilities all have 2 months product storage, the facilities can operate 26 months out of the 30 months in the DWPF melter life cycle (24 months operation, 6 months to replace the melter). Therefore, all processes now have the same basis for production.

However, each flowsheet produces a different product for DWPF to process. In addition, there are other processing differences that impact saltstone production, MST consumption and glass production. The quantity of materials consumed and saltstone produced are shown for each flowsheet on Process Flow Diagrams in the Appendices.

The interfaces between Extended Sludge Processing (ESP) or the SWPF and the DWPF will be managed using the concept of a macrobatch. A quantity of sludge and a quantity of salt solution (if applicable) feed are qualified and then isolated from the rest of the HLW system. This assures that the products of these two facilities can be blended with glass formers (“frit”) to produce glass meeting the Waste Acceptance Product Specification (“WAPs”). Sludge batch blends were used to estimate quantities and properties, shown in Table 7.0-1, below. Sixty-seven salt batches were specified for the HLW System plan and these are the basis for quantities in Table 7.0-1.

Table 7.0-1 shows the canisters produced for each sludge batch. Revision 12 of the SRS HLW System Plan (Ref. 28) assumed a production rate of 230 cans per annum for its “Superstreich Case” and this rate was used for this study.

All calculations for glass quantities and properties were done using Glassmaker, a model developed by G. A. Taylor. The same bases for acceptability as the HLW System Plan were used. The sludge only cans are shown for information and are used to calculate the canisters produced for Batch 1A through the sludge only portion of Batch 5. Blends for sludge only glass were made at the maximum waste loading consistent with good processing and a large blend window in DWPF (typically at a *liquidus* temperature of 1010 °C, though some blends could not match this parameter). CST glasses were based on a 4% CST oxide loading, which was derived from calculating the amount of CST required to process the 67 salt feed batches. Except for MST solids, the CSSX feed to DWPF adds very little glass mass.

The canister totals are only accurate to $\pm 10\%$, though comparisons among cases are valid, because the same methods and assumption were used for all cases. “PHA” and “CST” both add metal elements, which become oxides in the glass matrix. Never the less, the quantity of glass produced is very nearly the same for all three flowsheets. The quantity of glass produced is almost certainly in the proper relationship (Solvent Extraction < CST < PHA).

Table 7.0-1 Canisters Production for the Salt Processing Flowsheets

Sludge Batch	System Plan Rev. 12 Tanks (% Used)	Sludge- Only Cans (before SWPF S/U)	STTP Cans	CSSX Cans	CST Cans
1A	51	492	492	492	492
1B	42	658	658	658	658
2	8, 40	471	471	471	471
3	7(70%) 18 (70%) 19(70%)	490	490	490	490
4	7(30%) 11 18(30%) 19(30%)	409	409	409	409
5 – Sludge	15 26	267	267	267	267
5 – Coupled	15 26		219	202	208
6	5 6 12 13(30%)		598	585	603
7	13(70%) 4 33		652	662	682
8	21 22 23 34 39 47		584	552	570
9	32 43		387	364	375
10	ESP Heels 35 Other Insoluble Solids		357	659	679
10 – Sludge Only	ESP Heels 35 Other Insoluble Solids		322		
Sludge Only Cans		2787	3109	2787	2787
Cans With Salt Product			2797	3024	3117
Grand Total			5906	5811	5904

The design basis sodium concentration in the feed to Continuous Stirred Tank Reactors used in STTB is 4.7 molar. The other two flowsheets are operated using 5.6 molar. This requires dilution of the 6.44 molar stream from the HLW Tank Farm. The diluted stream (Decontaminated Salt Solution) is disposed of as Saltstone. The CSSX process adds an appreciable amount of waste in its scrubbing section and this water goes to Saltstone, so its Saltstone volume exceeds that for CST. Both CST and CSSX may require dilution with NaOH to preclude in-process precipitation of Gibbsite ($Al_2O_3 \cdot 3H_2O$). This may result in an increase of up to 10% in Saltstone volume, shown below in Table 7.0-2, for both processes.

Table 7.0-2 Saltstone Product by Flowsheet

	STTP	CST	CSSX
Saltstone Cells (100'X100'X25'), current flowsheet	110	94	102
Saltstone Cells (100'X100'X25') with maximum NaOH dilution	Not required	~103	~112

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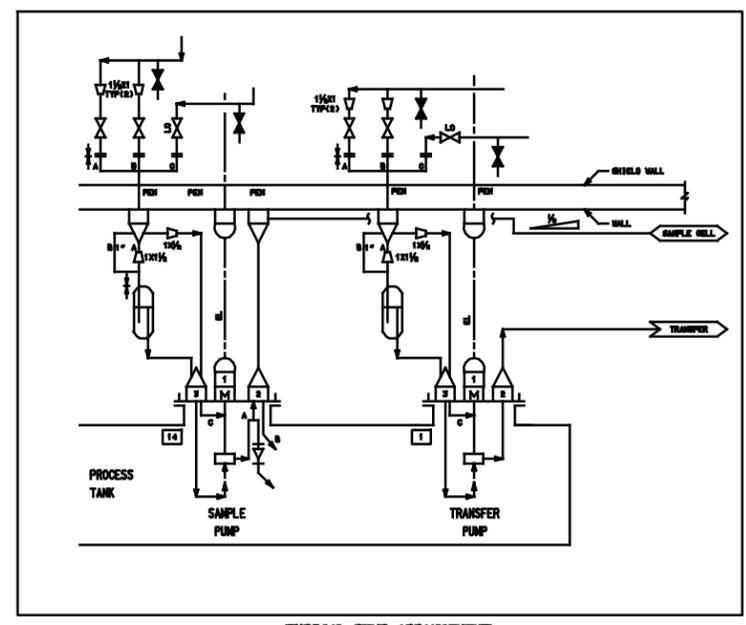
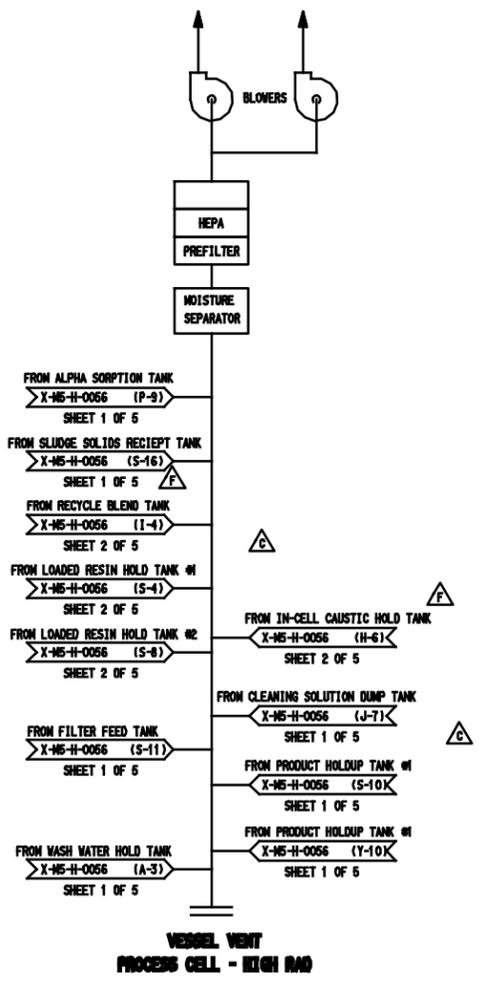
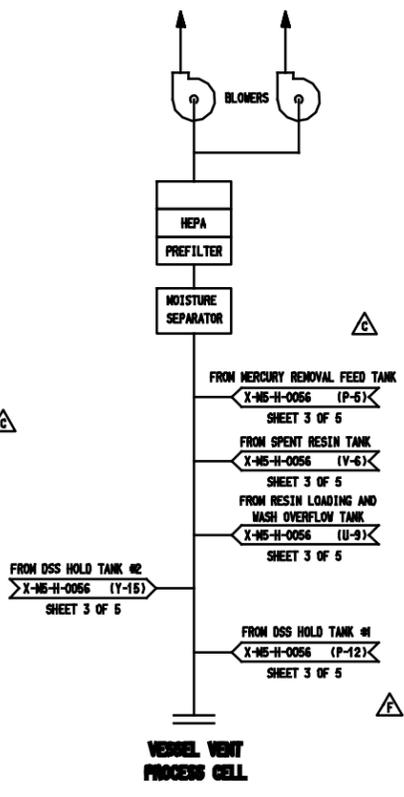
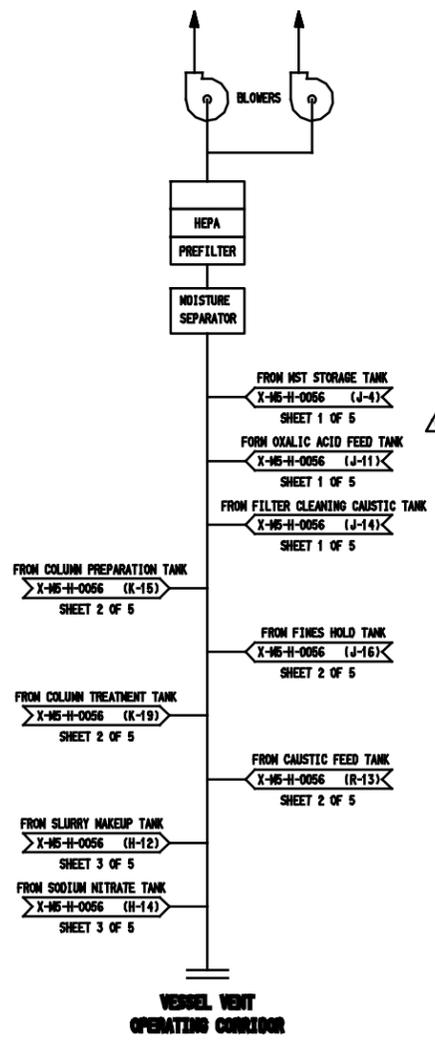
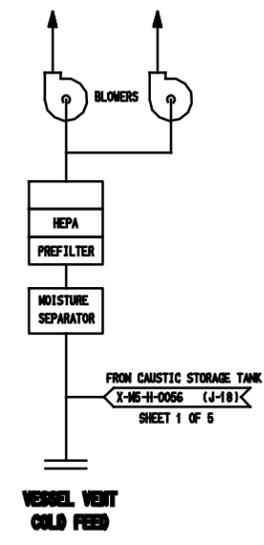
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Appendix A
WSRC-RP-99-0006, Rev. 3

CST Ion Exchange Flow Diagrams

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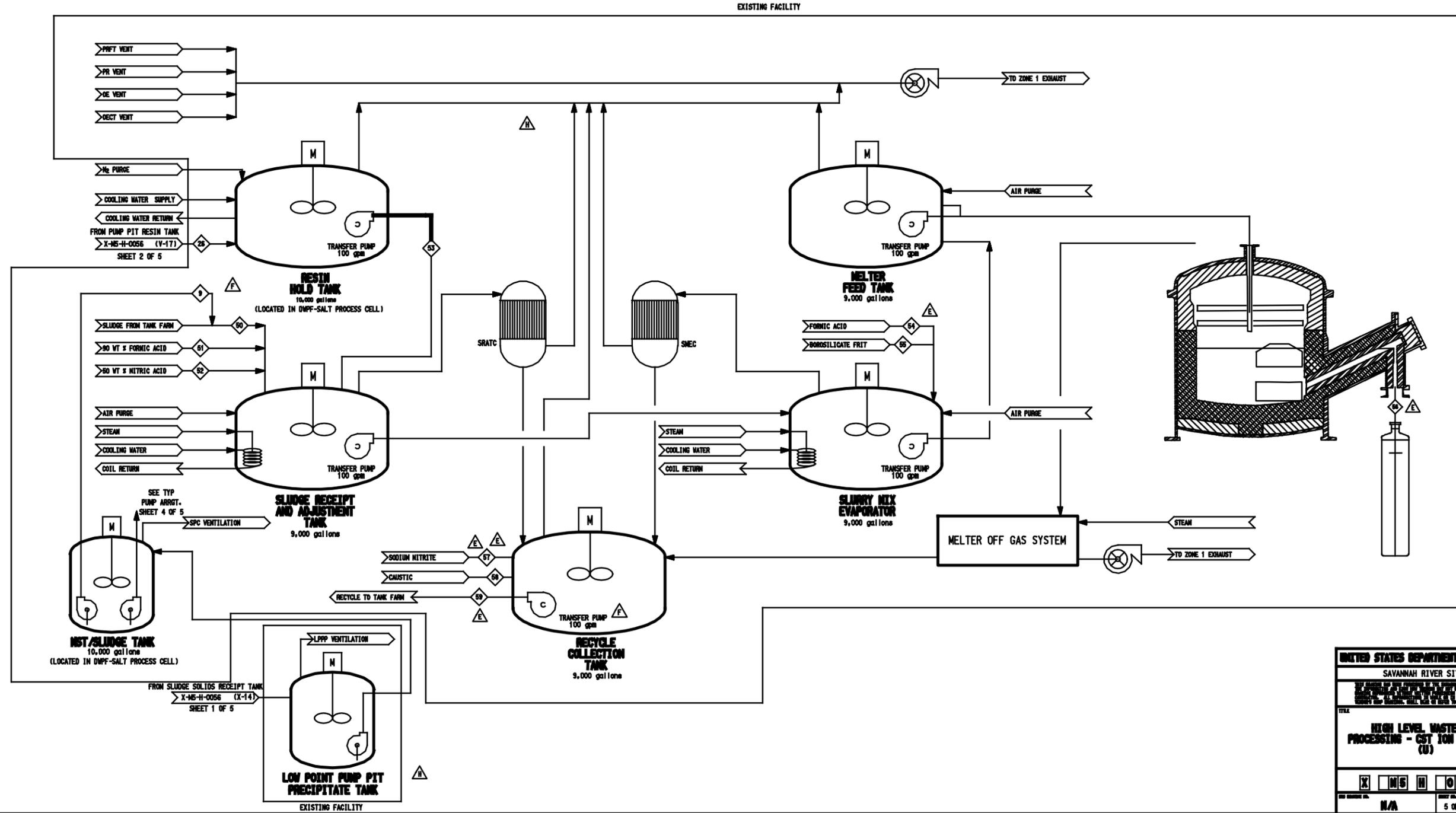
UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE

SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT
PROCESSING - CST ION EXCHANGE
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REV. NO. 4 OF 5

STREAM NUMBER	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	
STREAM NAME / COMPONENT	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	
PLUG, lbs/hr	184.7	81.9	923.3	13.8	16.8	7.9	382.2	182.8	14.7	78.8	188.1										
A RES	1.8	0.0	7.2					6.7													
B RES		0.0						12.4	12.4												
C RES		0.7																			
F RES	2.1	0.0	20.8					23.2													
H ₂ O	0.0		11.8																		
K ₂ O	0.0	0.1	0.0					0.1													
L ₂ O								11.1	11.1												
MgO	0.0	0.0	0.3					0.0	0.0												
Na ₂ O	0.0		3.2					3.2													
SiO ₂	0.1	0.1	7.4					7.4	18.8												
SO ₂	0.2	1.3	2.8					22.8	26.4												
TiO ₂	3.4	2.2	0.0					6.4													
USO ₃	0.7		6.8					7.9													
ZnO		1.4						1.4													
ZrO ₂	0.0	0.0	0.3					11.2													
OTHER COMPOUNDS	4.7	2.3	1.4					5.9													
WATER	188.9	78.9	372.1	1.4	0.3		0.0	222.4		0.0	37.9	1844.7									
FORMIC ACID				12.4				7.1				11.8									
NITRIC ACID				0.3								37.9									
NaOH	1.7											5.9									
H ₂ SO ₄												5.9									
AT 100% ATTAINMENT																					
ANNUAL FLOWRATE - lbs/hr	1817.9	709	3709.2	121.0	122.3		69.6	3094.4	1807.3	128.4	685.9	1844.1									
CYCLE TIME - HOURS			128	128	128		128	128				128									
BATCHES/YR			70	70	70		70	70				70									



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SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT PROCESSING - CST ION EXCHANGE (U)

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REV. NO. N/A

5 OF 5

REV. NO. I

Appendix B
WSRC-RP-99-0006, Rev. 3

CST Ion Exchange General Arrangement Diagrams

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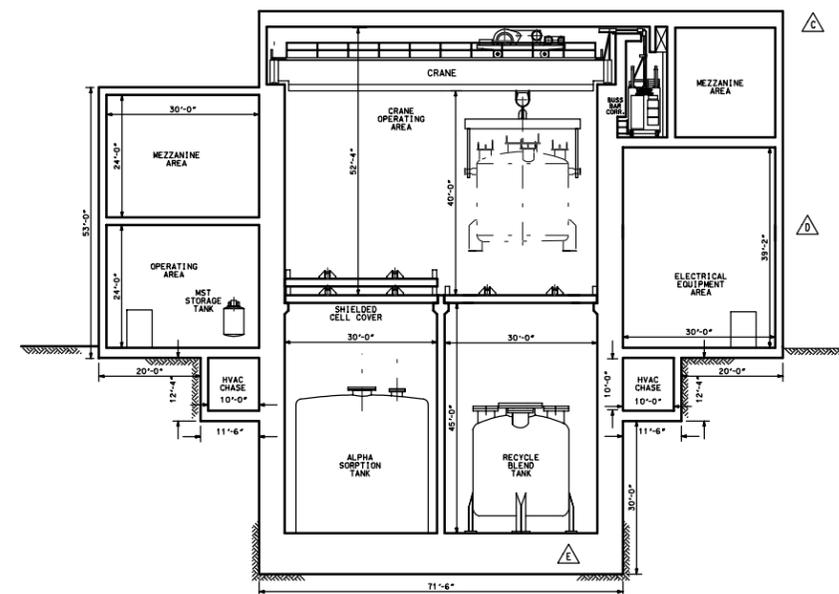
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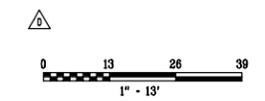
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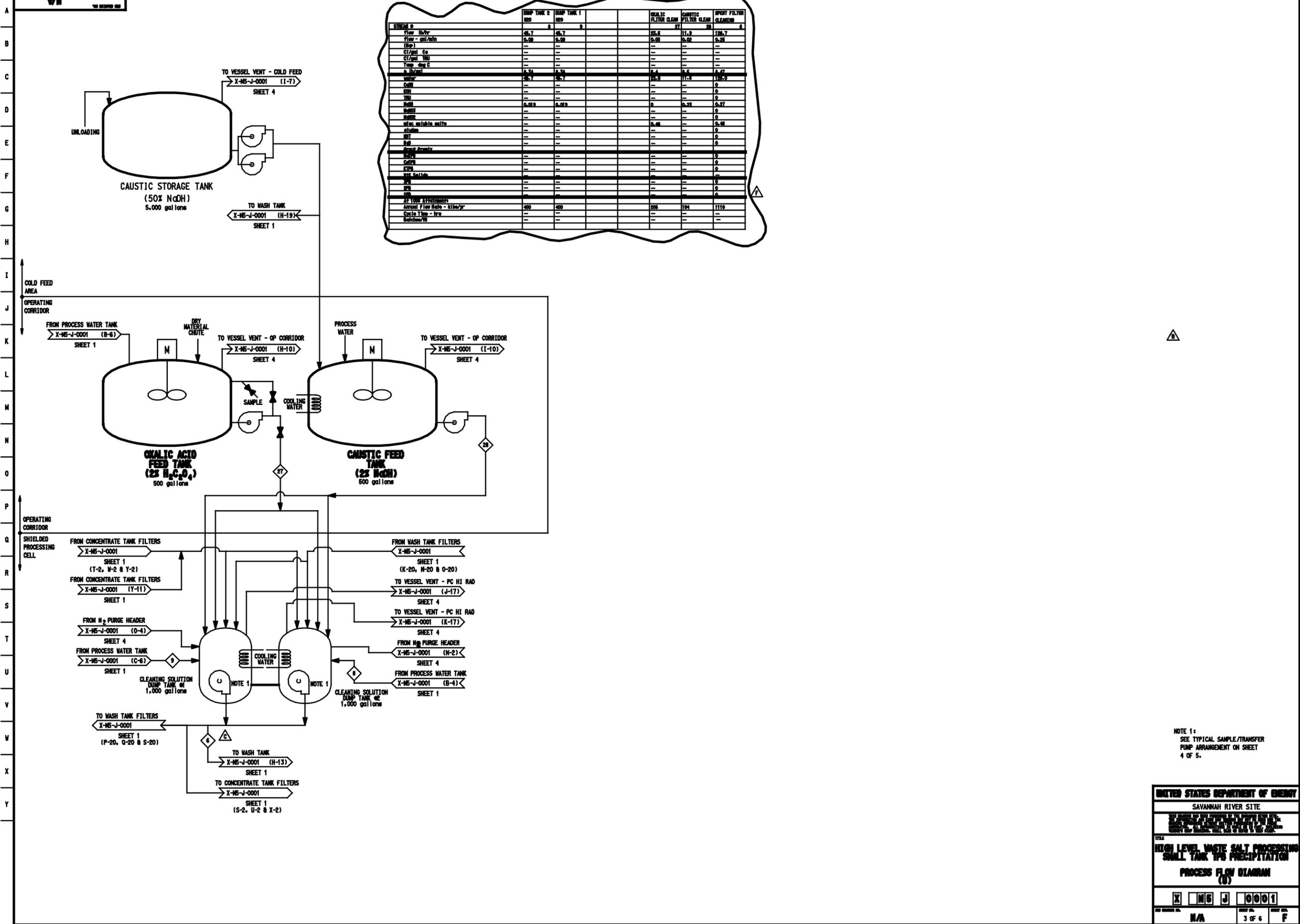
SECTION **B**
SHEET 1



UNITED STATES DEPARTMENT OF ENERGY		
SAVANNAH RIVER SITE		
THIS DRAWING HAS BEEN FURNISHED BY THE SAVANNAH RIVER SITE. THE INFORMATION AND KNOWLEDGE THEREIN MAY NOT BE USED FOR THE DRAWING REPRODUCED WITHOUT WRITTEN PERMISSION OF THE PRIME CONTRACTOR. ALL REPRODUCTIONS IN WHOLE OR IN PART, INCLUDING VENDORS SHOP DRAWINGS, SHALL BEAR OR REFER TO THIS STAMP.		
TITLE		
HIGH LEVEL WASTE SALT PROCESSING CST ION EXCHANGE GENERAL ARRANGEMENT (U)		
X	P	H
0003	0003	
SRS DRAWING NO.	SHEET NO.	SHEET REV.
N/A	3 OF 3	F

Appendix C
WSRC-RP-99-0006, Rev. 3

Small Tank TPB Flow Diagrams



STREAM #	DUMP TANK 2		DUMP TANK 1		OXALIC FILTER CLEAN	CAUSTIC FILTER CLEAN	SPENT FILTER CLEANING
	REV	REV	REV	REV			
Flow - lb/hr	46.7	46.7			25.8	11.9	126.7
Flow - gal/min	0.59	0.59			0.32	0.15	1.61
(Imp)							
Cl/Feed - Cu							
Cl/Feed - Zn							
Temp - deg C							
D - lb/min	0.31	0.31			0.4	0.5	0.47
Water	26.7	26.7			26.9	11.9	126.9
CaCl							0
NaOH							0
HCl	0.018	0.018			0	0.22	0.27
NaNO3							0
NaNO2							0
Other soluble salts					0.48		0.48
Sludge							0
HT							0
Fe							0
Gravel Density							0
NaCl							0
CaCl							0
KCl							0
Na2SO4							0
Na							0
Ca							0
HT							0
AT Total Accumulation							0
Annual Flow Rate - lb/day	400	400			200	104	1110
Cycle Time - hrs							
Batches/yr							

NOTE 1:
SEE TYPICAL SAMPLE/TRANSFER
PUMP ARRANGEMENT ON SHEET
4 OF 5.

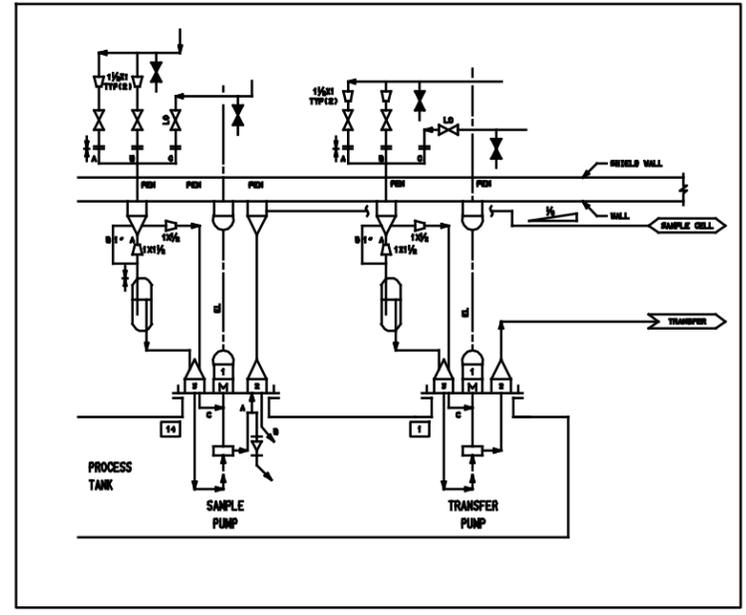
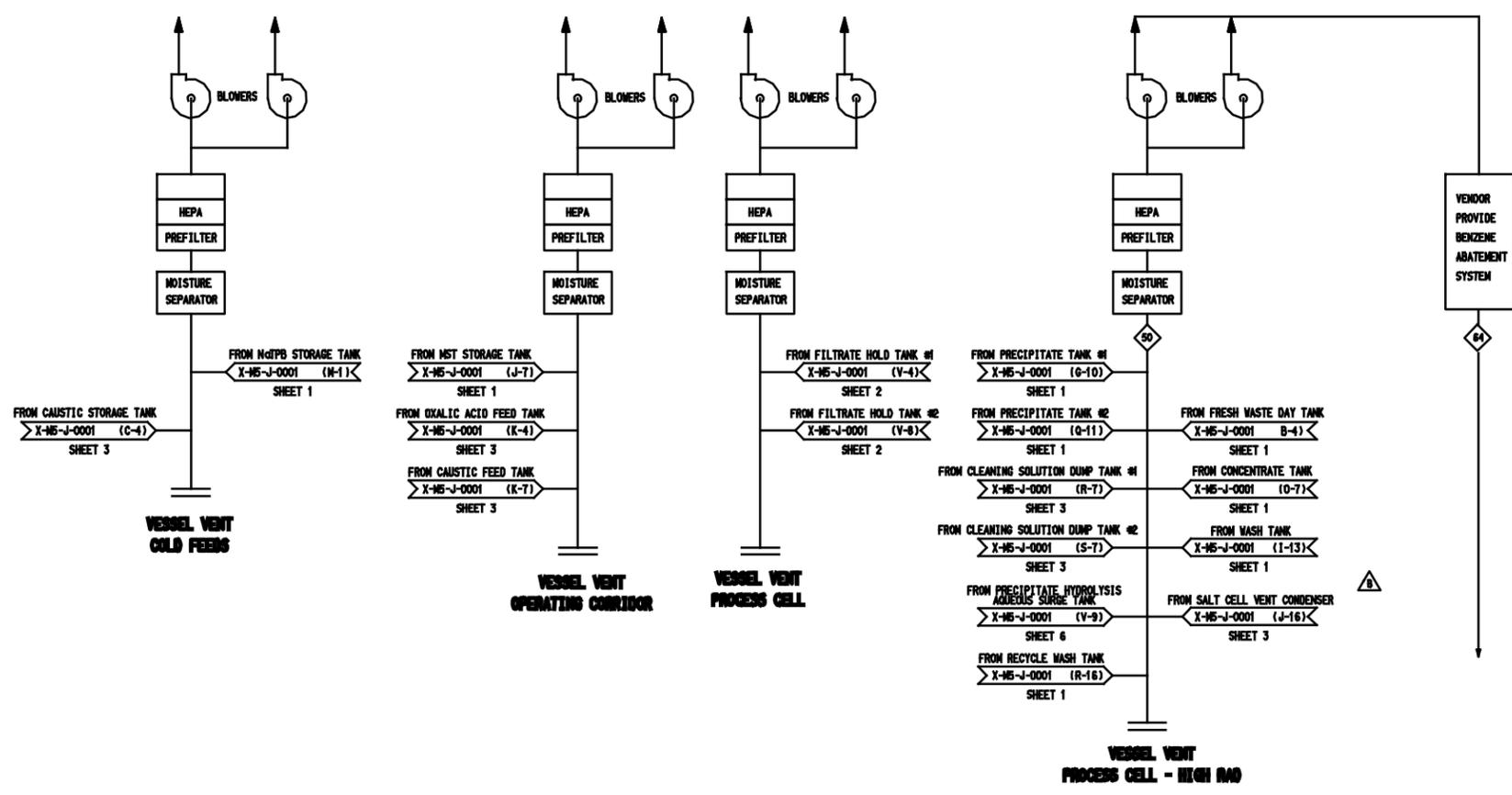
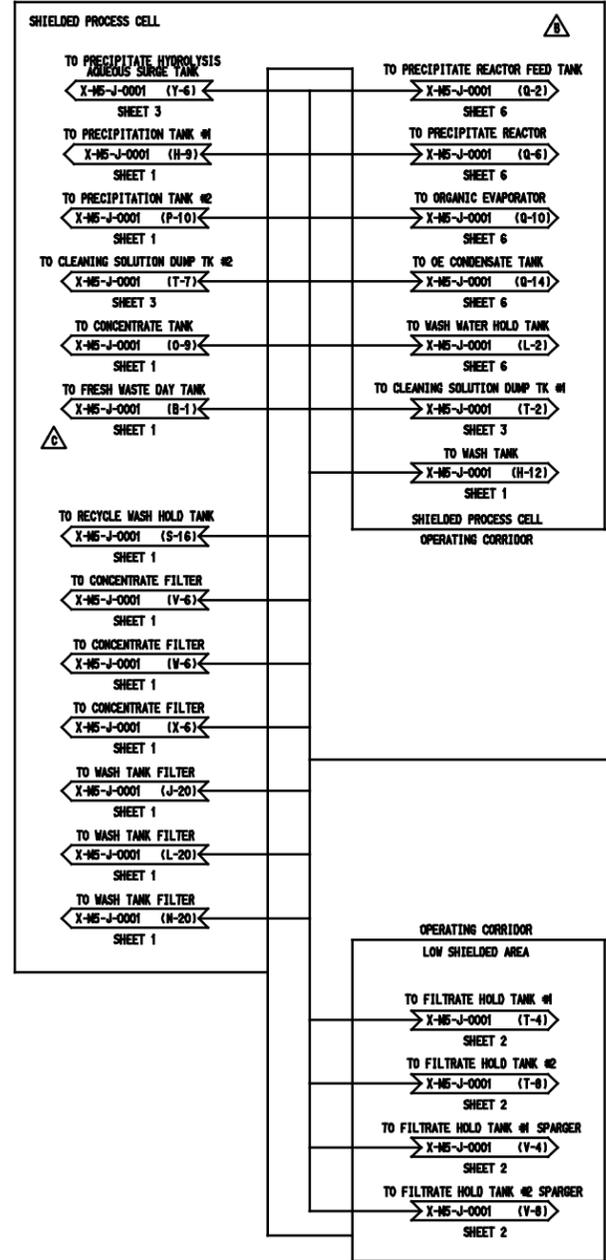
UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT PROCESSING
SMALL TANK TPO PRECIPITATION
PROCESS FLOW DIAGRAM
(8)

X MS J 0001

REV. NO. 3 OF 6

DATE: 6-9-01

STREAM NUMBER	ISO	ISA
STREAM NAME / COMPONENT	ISO	ISA
FLOW - lb/hr	4.34	0.22
FLOW - gal/min		
Sp - ml/hr		
CHST - 61/mil		
TRU - 61/mil		
TEMPERATURE - deg C		
DENSITY - lb/hr		
AT TRK ATTAINMENT		
ANNUAL FLOWRATE - khr/yr	36.0	1.90



UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE

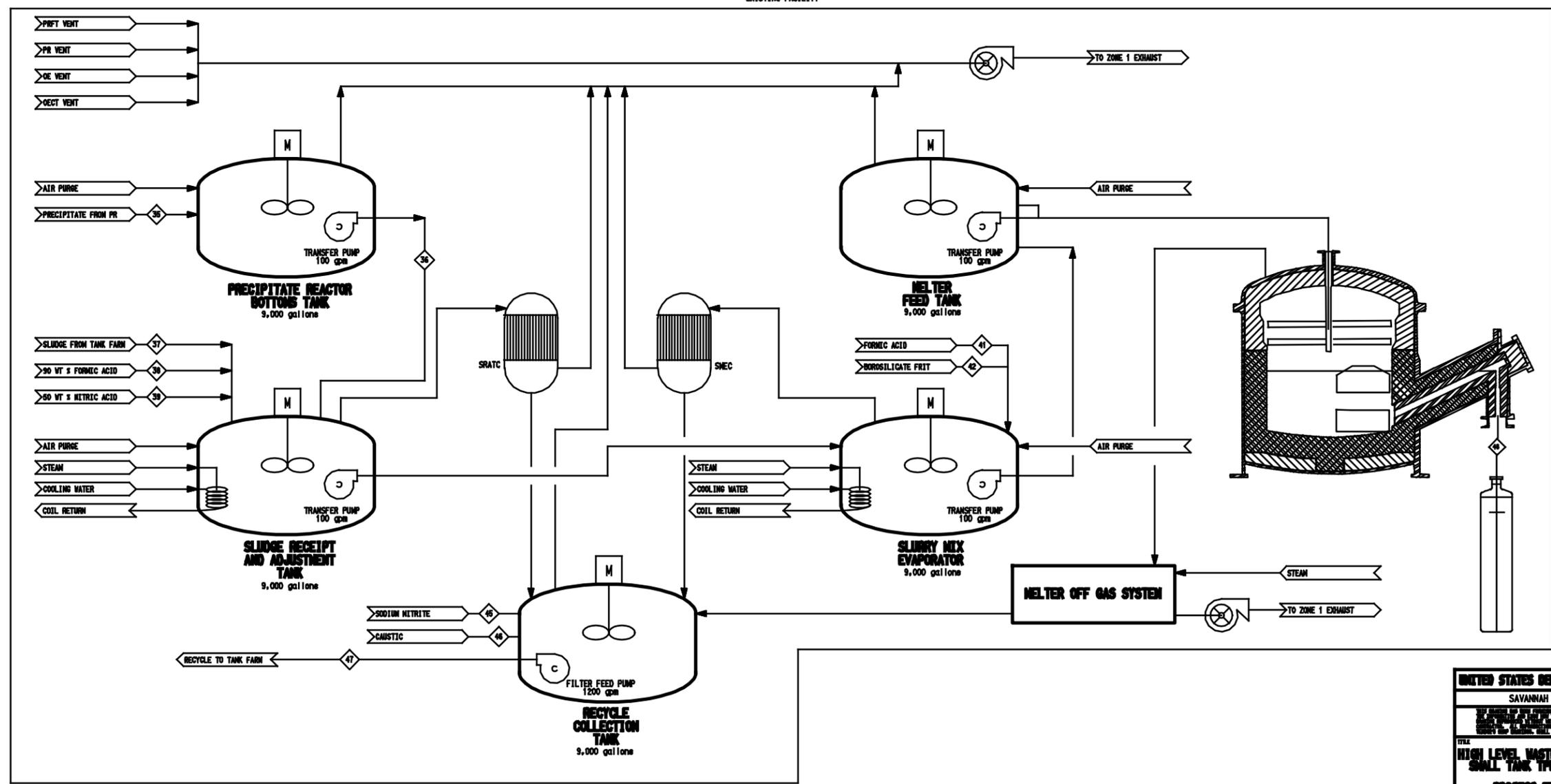
HIGH LEVEL WASTE SALT PROCESSING
SMALL TANK TFS PRECIPITATION
PROCESS FLOW DIAGRAM
(6)

X MS J 0001

REV. NO. N/A
PAGE NO. 4 OF 6
REV. DATE F

STREAM NUMBER	13	13a	13b	13c	13d	13e	14	14a	14b	14c	14d	14e	14f	14g	14h	14i	14j	14k	14l	14m	14n	14o	14p	14q	14r	14s	14t	14u	14v	14w	14x	14y	14z	
STREAM NAME / COMPONENT	LPP	PA	SLUDGE TO SRAT	FORMIC ACID TO SRAT	METRIC ACID TO SRAT	NOT USED	FORMIC ACID TO SNE	FRIT TO SNE	NOT USED	NOT USED	NOT USED	CAUSTIC TO RCT	TANK FARM RECYCLE	CLAR	NOT USED																			
FLOW - lbs/hr			372.0	18.1	18.3		388.6					388.9	3428.1	172.6																				
A 200		1.0																																
B 200		5.8	6.2																															
C 200		0.2																																
F 200		2.2	18.1																															
H 200		1.4																																
I 200		6.9	0.0																															
L 200																																		
M 200			0.3																															
N 200			2.8																															
O 200		4.7	6.4																															
P 200			2.4																															
Q 200			0.0																															
R 200			2.0																															
S 200			0.7																															
T 200			8.8																															
OTHER COMPOUNDS		18.9	8.8																															
WATER		250.1	281.8	1.8	5.8		1.0	288.7				11.8	48.4	2388																				
WASH		8.74		13.6			8.1							10.8																				
WHS		1.42			8.8																													
WHT																																		
WHS		0.48																																
AT TANK ATTACHMENT																																		
ANNUAL FLOWRATE - lbs/hr		8881	3888	139.6	188.9		88.4	3881				188.2	888.8	21244	1811																			
CYCLE TIME - HOURS		88	139	139	139		139	139						88																				
MATCHES/yr		138.7	87	87	87		87	87						438																				

EXISTING FACILITY

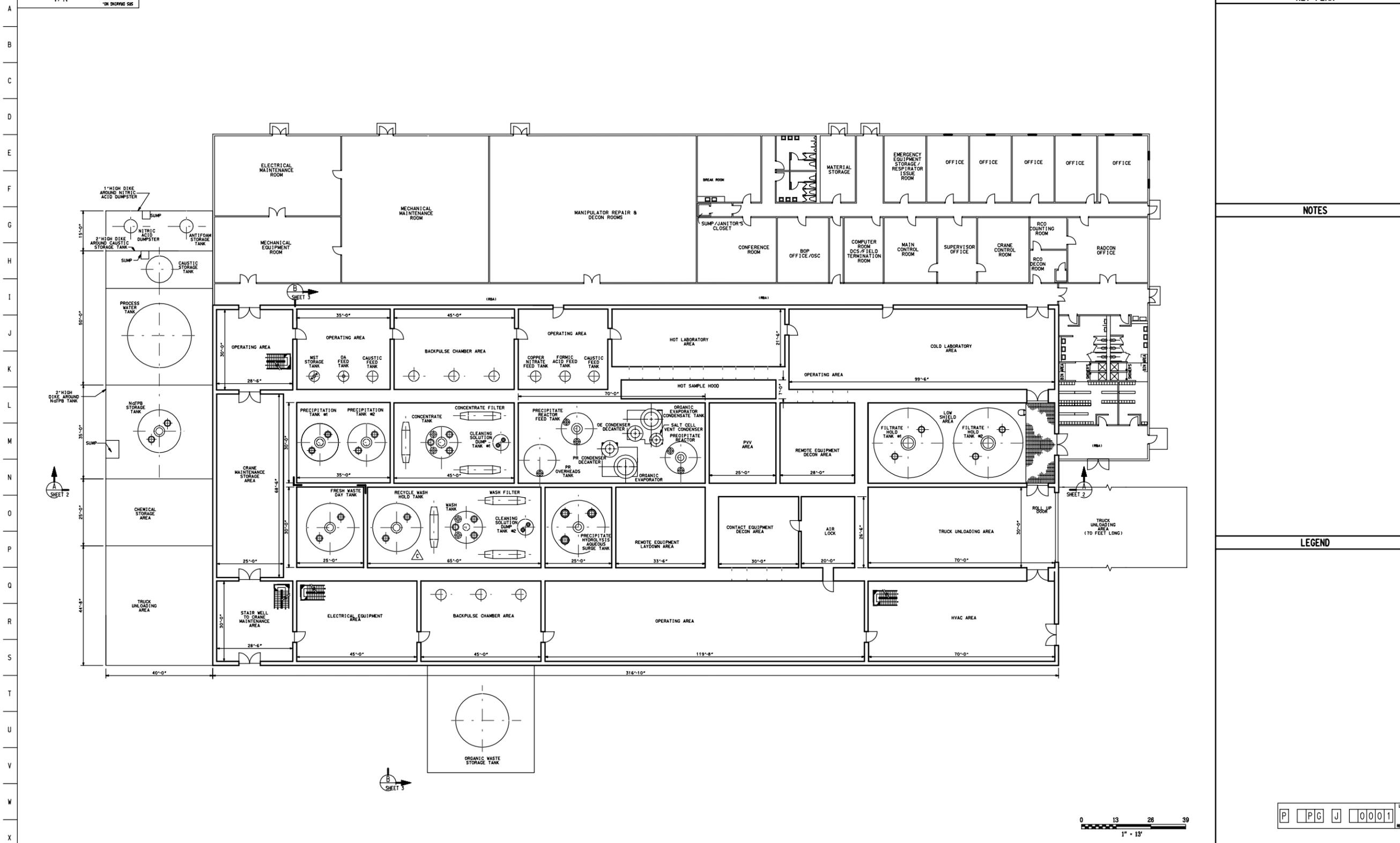


UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT PROCESSING
SMALL TANK TPO PRECIPITATION
PROCESS FLOW DIAGRAM
(6)

REV. NO. 00001
REV. DATE 5 OF 6
REV. BY F

Appendix D
WSRC-RP-99-0006, Rev. 3

Small Tank TPB General Arrangement Diagrams



KEY PLAN

NOTES

LEGEND

P	PG	J	0001	LATEST
				REVISION
				A

UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE

BLDG. NO.	SITE CLEARANCE NO.	DESIGN AREA NO.	DESIGN GROUP
TITLE			
H/W SALT PROCESSING SMALL TANK TETRAPHENYLBORATE PRECIPITATION PROCESS GENERAL ARRANGEMENT (U)			
SCALE	SRS DRAWING NO.	SHEET NO.	LATEST REVISION
AS NOTED	N/A	1 OF 3	A

PROJ.	REV. NO.	DATE	REVISION	PRP'D	LEAD ENG	CHK'D	APR'D	APR'D	APR'D	PROJ.	REV. NO.	DATE	REVISION	PRP'D	LEAD ENG	CHK'D	APR'D	APR'D	APR'D	

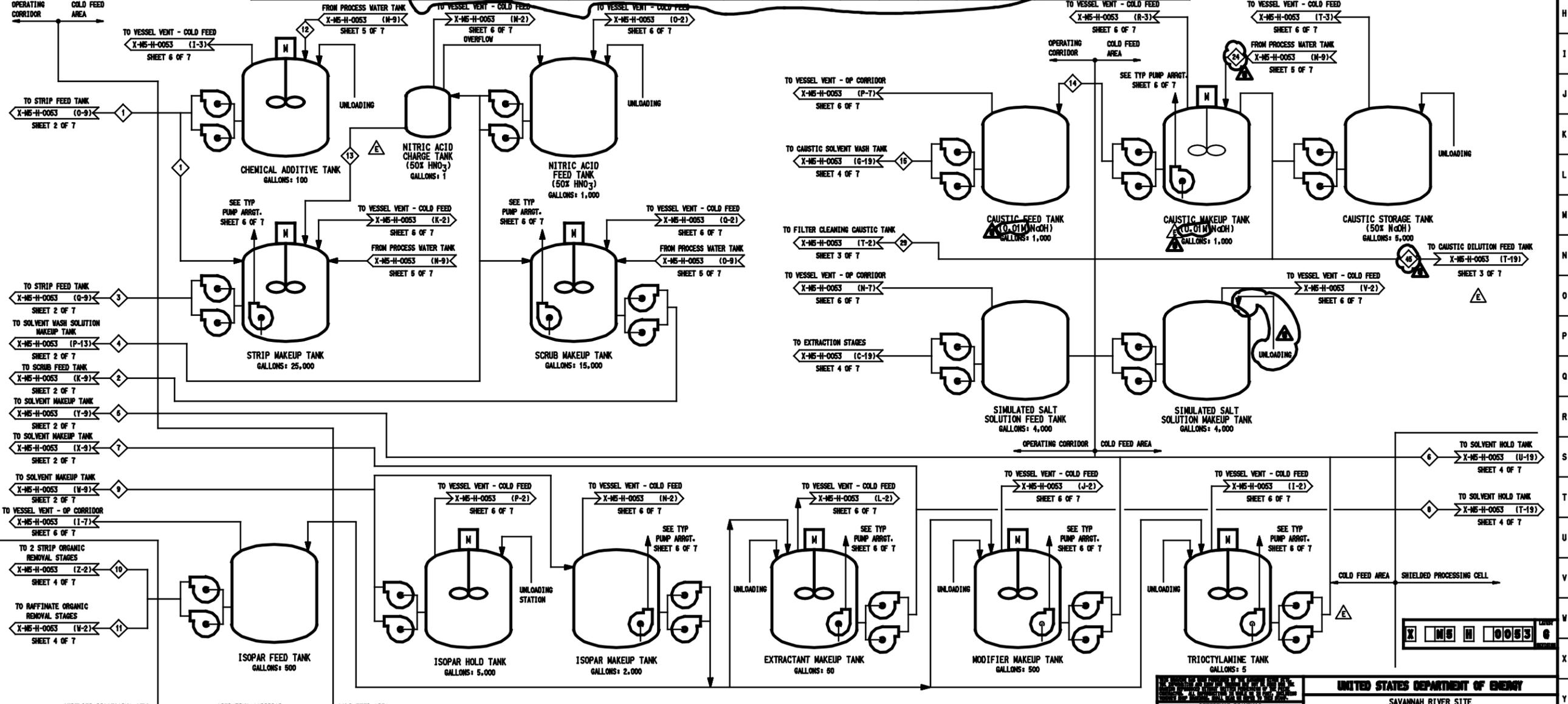
Appendix E
WSRC-RP-99-0006, Rev. 3

CSSX Flow Diagrams

NOTES

1. REVISION TRIANGLES ARE NOT SHOWN FOR CLARITY. THE CLOUDED AREAS REPRESENT CHANGES FOR THIS REVISION ONLY.
2. STREAM NO. 7 (SEVEN) CONTAINS 0.000001% OF CALIXARENE.
3. PREVIOUS REVISION WERE REMOVED FROM THE TABLE FOR CLARITY.

STREAM NUMBER	STREAM NAME / COMPONENT	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	CHEM ADD TO STRIP FEED TX	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
2	SOLVENT FEED TO STRIP FEED TX	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32
3	STRIP FEED TO STRIP FEED TX	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
4	ISOPAR TO SOLVENT WASH	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
5	ISOPAR TO ONLY HOLD TX	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	ISOPAR TO ONLY HOLD TX	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
7	EXTRACT TO ONLY HOLD TX	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
8	EXTRACT TO ONLY HOLD TX	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
9	ISOPAR TO STRIP WASH	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
10	ISOPAR TO STRIP WASH	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
11	ISOPAR TO ADDITIVE TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
12	ISOPAR TO ADDITIVE TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
13	ISOPAR TO ADDITIVE TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
14	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
15	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
16	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
17	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
18	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
19	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
20	ISOPAR TO CAUSTIC FEED TX	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004



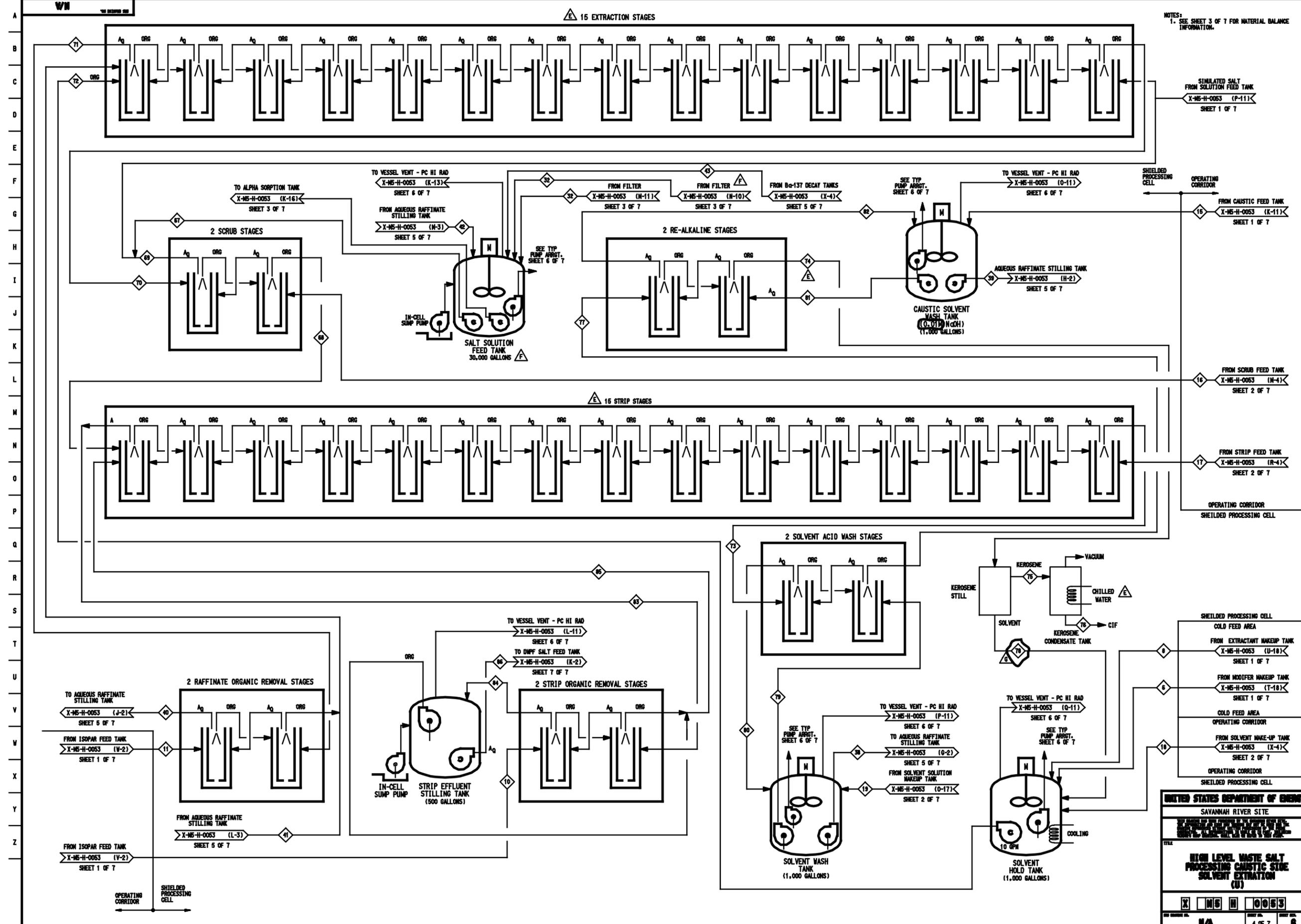
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	B	10/01/00	INCRP REGULINES AS SHOWN		B	10/01/00	INCRP REGULINES AS SHOWN		B	10/01/00	INCRP REGULINES AS SHOWN		B	10/01/00	INCRP REGULINES AS SHOWN
	C	10/04/00	REVISED MATERIAL BALANCE TABLES		C	10/04/00	REVISED MATERIAL BALANCE TABLES		C	10/04/00	REVISED MATERIAL BALANCE TABLES		C	10/04/00	REVISED MATERIAL BALANCE TABLES
	D	10/22/00	REVISED MATERIAL BALANCE TABLES		D	10/22/00	REVISED MATERIAL BALANCE TABLES		D	10/22/00	REVISED MATERIAL BALANCE TABLES		D	10/22/00	REVISED MATERIAL BALANCE TABLES
	E	02/05/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00170.		E	02/05/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00170.		E	02/05/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00170.		E	02/05/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00170.
	F	02/22/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00220.		F	02/22/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00220.		F	02/22/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00220.		F	02/22/00	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0000-00220.
	G	08/01/01	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0001-00172		G	08/01/01	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0001-00172		G	08/01/01	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0001-00172		G	08/01/01	REVISED TO INCORPORATE ECF NO. HLJ-SPT-0001-00172

UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE

PROJECT: 704-3N
DRAWING NO: N/A
DATE: 8-4-01

**HIGH LEVEL WASTE SALT PROCESSING
CAUSTIC SIDE SOLVENT EXTRACTION
(U)**

SCALE: NONE
SHEET NO: 1 OF 7
LAST CHG REV. BY: WATTS
DATE: 8-4-01



NOTES:
1. SEE SHEET 3 OF 7 FOR MATERIAL BALANCE INFORMATION.

SIMULATED SALT FROM SOLUTION FEED TANK
X-MS-H-0053 (P-11)
SHEET 1 OF 7

TO VESSEL VENT - PC III RAD
X-MS-H-0053 (K-13)
SHEET 6 OF 7

FROM FILTER
X-MS-H-0053 (N-11)
SHEET 3 OF 7

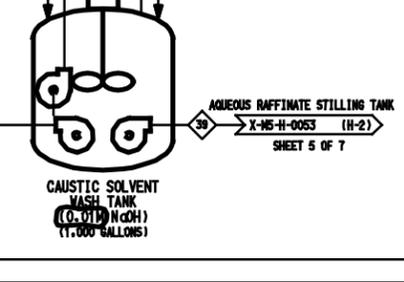
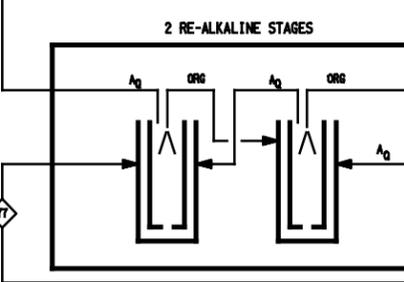
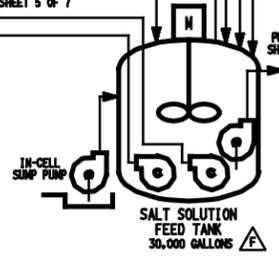
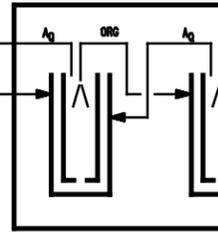
FROM FILTER
X-MS-H-0053 (N-10)
SHEET 3 OF 7

FROM Bc-137 DECAY TANKS
X-MS-H-0053 (X-4)
SHEET 5 OF 7

TO VESSEL VENT - PC III RAD
X-MS-H-0053 (O-11)
SHEET 6 OF 7

FROM CAUSTIC FEED TANK
X-MS-H-0053 (K-11)
SHEET 1 OF 7

TO ALPHA SORPTION TANK
X-MS-H-0053 (K-16)
SHEET 3 OF 7

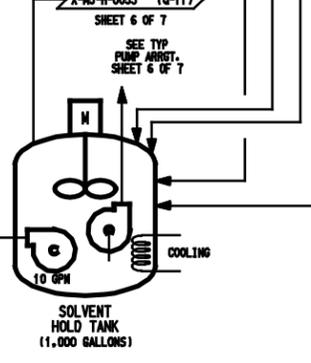
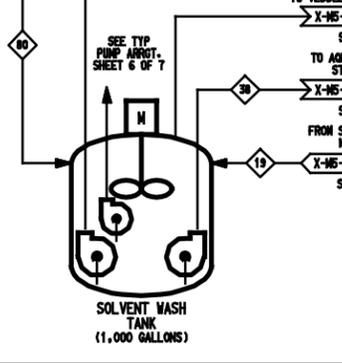
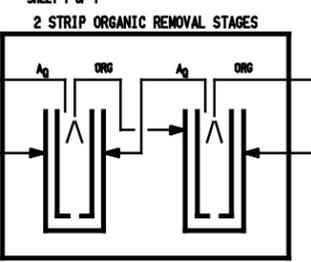
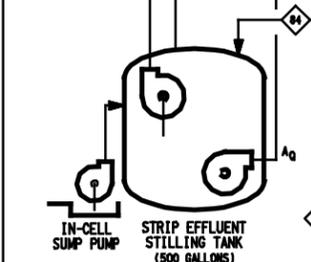
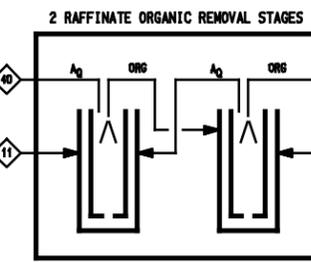
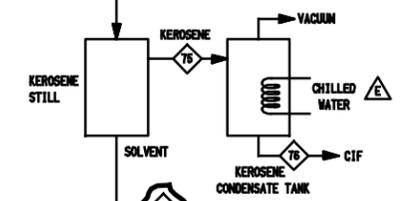
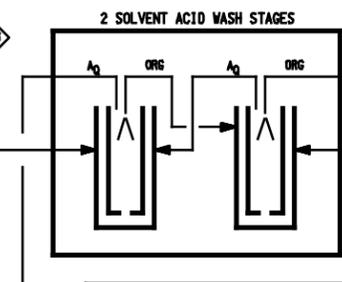


AQUEOUS RAFFINATE STILLING TANK
X-MS-H-0053 (H-2)
SHEET 5 OF 7

FROM SCRUB FEED TANK
X-MS-H-0053 (M-4)
SHEET 2 OF 7

15 STRIP STAGES

FROM STRIP FEED TANK
X-MS-H-0053 (R-4)
SHEET 2 OF 7



SHIELDED PROCESSING CELL
COLD FEED AREA

FROM EXTRACTANT MAKEUP TANK
X-MS-H-0053 (U-10)
SHEET 1 OF 7

FROM MODIFIER MAKEUP TANK
X-MS-H-0053 (T-10)
SHEET 1 OF 7

COLD FEED AREA
OPERATING CORRIDOR

FROM SOLVENT MAKEUP TANK
X-MS-H-0053 (X-4)
SHEET 2 OF 7

OPERATING CORRIDOR
SHIELDED PROCESSING CELL

UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE

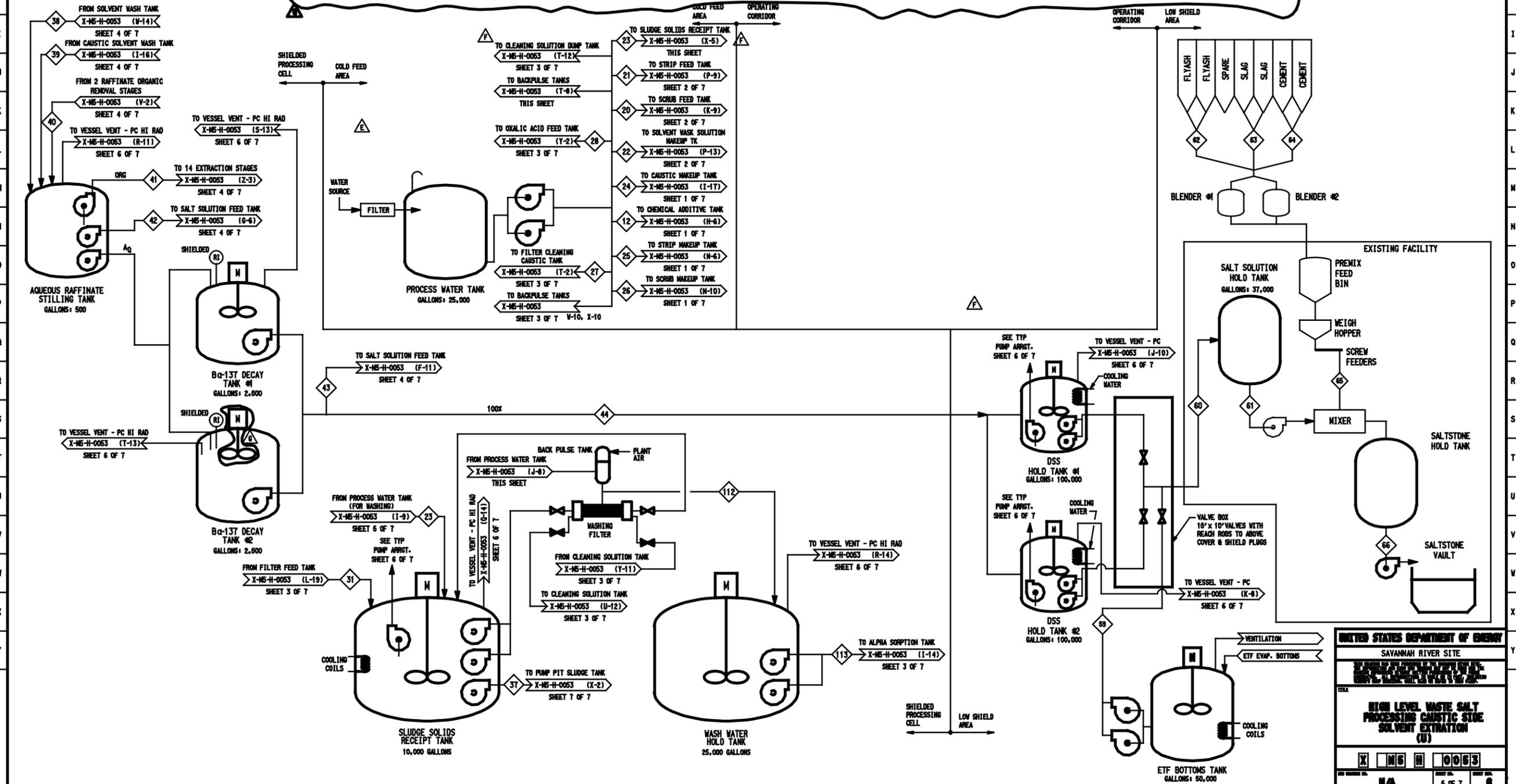
SAVANNAH RIVER ENERGY RESEARCH ESTABLISHMENT
SOLVENT EXTRACTION DIVISION

TRIAL

HIGH LEVEL WASTE SALT PROCESSING CAUSTIC STAGE SOLVENT EXTRACTION (U)

X	MS	H	0053
REV. NO.	DATE	REV. NO.	DATE
N/A		4 OF 7	6

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
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902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921
942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961
982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001



UNITED STATES DEPARTMENT OF ENERGY
SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT PROCESSING CAUSTIC SIDE SOLVENT EXTRACTION (U)
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Appendix F
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CSSX General Arrangement Diagrams

Appendix G
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HLW Salt Processing
Salt Disposition Facility
Master Plot Plan

Appendix H
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Salt Solution Feed Blends

Appendix H
Salt Feed Blends

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Appendix H

Batch		SPT001	SPT002	SPT003	SPT004	SPT005	SPT006	SPT007	SPT008	SPT009	SPT010	SPT011
Supernate	(gals)	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000
Supernate	(liters)	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794
SpG	(g/cc)	1.34587	1.34722	1.31582	1.34416	1.33018	1.34415	1.33075	1.32406	1.36077	1.29372	1.35037
Na	(moles)	30469000	31283000	28691400	30986500	29456600	29165400	29880000	27511800	31365700	29490700	29070000
Na	(M)	6.437846	6.609837	6.062254	6.547189	6.223934	6.162406	6.313395	5.813014	6.627311	6.231139	6.142249
NO3	(moles)	13013100	10831800	10489600	13280900	11837000	13726900	11513100	5090550	14701900	8850900	11559300
NO2	(moles)	1133000	1778170	975134	1059190	1031510	1452350	1840460	309615	2048990	3212690	966735
OH	(moles)	10647900	13849800	12297500	10889400	11374300	8431310	10127100	19276900	9109350	11197400	12056200
AlO2.2(H2O)-	(moles)	1767030	1737900	1513870	1726640	1584610	1663520	1569740	1172930	1699190	1427460	1339220
CO3	(moles)	799345	612250	463778	747652	625513	796856	1016010	182891	860509	1088760	674836
PO4	(moles)	23089.2	48106.5	24693.5	22886.1	21227.4	26955.2	31454.3	30821.3	20104	28903.9	28536.8
SO4	(moles)	1024420	816983	1218610	1188990	1136270	1112720	921670	759506	1169290	640741	958543
K	(moles)	104403	110181	107605	99462.5	103467	104191	119517	120151	113958	125794	104376
Hg	(moles)	798.899	934.352	786.105	743.257	839.125	429.464	1906.43	2672.71	290.507	2541.43	1248.82
Cu	(moles)	5574	7070.85	6263.31	5348.92	5641.33	3842.93	5566.5	7897.27	4723.44	7389.16	4948.58
TPB	(moles)	0	0	0	0	0	0	0	0	0	0	0
NaT	(moles)	0	0	0	0	0	0	0	0	0	0	0
Cs	(Ci)	2081750	1766660	5764210	3091470	3445050	1315500	1716880	3342380	2398740	3060860	1272290
Sr	(Ci)	103.917	79.9775	1203.37	447.138	535.825	50.957	71.9207	681.982	3.83548	1.14943	154.63
H3	(Ci)	688.64	805.242	13647.9	4842.25	5934.36	358.285	498.218	4974.57	24.6438	7.8062	496.119
Th232	(Ci)	0.00133	5.86E-05	0.001665	0.001331	0.002298	0.000971	0.001417	0.007546	0.00029	0.000367	0.003199
U232	(Ci)	0.001278	0.002983	0.00147	0.001241	0.001206	0.000508	0.000972	0.000887	0.00014	0.000591	0.000366
U233	(Ci)	0.046412	0.003717	0.058085	0.046455	0.05774	0.025807	0.037371	0.188259	0.017583	0.033282	0.080088
U234	(Ci)	0.026438	0.033891	0.03315	0.026899	0.034446	0.015264	0.02212	0.187376	0.007293	0.012654	0.080456
U235	(Ci)	0.004582	0.005527	0.008064	0.005334	0.005311	0.001877	0.002919	0.008634	0.00063	0.001354	0.002909
U236	(Ci)	0.00198	0.008082	0.006282	0.003305	0.005997	0.001773	0.002595	0.037478	0.001204	0.002123	0.015154
U238	(Ci)	0.238175	0.466614	0.605082	0.336738	0.372104	0.089282	0.137524	0.410067	0.026936	0.056769	0.084593
Np237	(Ci)	0.096288	0.247827	0.296383	0.15584	0.181215	0.052663	0.078081	0.251177	0.013749	0.02143	0.079343
Pu238	(Ci)	1403.08	2097.26	1410.92	1272.23	1268.46	475.816	677.118	3938.46	410.161	800.722	1680.67
Pu239	(Ci)	166.805	246.89	208.336	163.372	154.849	46.0292	66.0566	136.639	21.5935	39.1865	50.3452
Pu240	(Ci)	43.0612	59.9611	96.8007	56.2374	57.8306	13.0918	18.8868	57.5347	6.45631	12.169	17.2137
Pu241	(Ci)	907.254	1147.55	3631.39	1690.3	1839.91	285.604	404.219	1907.39	149.63	288.039	450.752
Pu242	(Ci)	0.017479	0.014074	0.024829	0.018316	0.016342	0.006107	0.009466	0.032503	0.005961	0.013486	0.013198
Am241	(Ci)	175.84	392.028	268.42	194.554	209.547	86.1357	166.719	316.74	39.2342	135.988	124.31
Am242	(Ci)	55.0045	66.2217	802.772	292.822	356.466	28.4223	40.2068	319.016	2.13052	0.777784	40.9841
Cm244	(Ci)	49.159	0.25799	60.5576	47.9959	34.5345	17.4324	24.6328	67.9861	0.984178	0.537134	28.2488
Cm245	(Ci)	0.005027	1.13E-05	0.006292	0.005027	0.003648	0.001856	0.002643	0.007454	0.000109	6.14E-05	0.003174

Appendix H
Salt Feed Blends

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Appendix H

Batch		SPT012	SPT013	SPT014	SPT015	SPT016	SPT017	SPT018	SPT019	SPT020	SPT021	SPT022
Supernate	(gals)	1250000	1155070	1250000	1224080	1243840	1250000	1250000	1250000	1250000	1250000	1250000
Supernate	(liters)	4732794	4373367	4732794	4634655	4709471	4732794	4732794	4732794	4732794	4732794	4732794
SpG	(g/cc)	1.35929	1.29512	1.33764	1.32496	1.34137	1.34053	1.32197	1.31039	1.33494	1.35711	1.37356
Na	(moles)	29685100	27740200	30811500	28510600	29875100	30649500	31038900	30397700	29803700	31638800	30574500
Na	(M)	6.272214	6.342985	6.510213	6.151612	6.343621	6.475984	6.558261	6.422781	6.297273	6.685015	6.460137
NO3	(moles)	13138800	8751700	10762900	8894230	10160300	10096900	9515320	8949190	14532000	16133800	12075700
NO2	(moles)	1084150	3769640	4389460	3367840	3124340	3177280	4236610	4235750	3208590	1481980	1224870
OH	(moles)	10443100	10986700	10754500	11891000	11404600	12159500	12454700	12626200	7401030	9338750	12678600
AlO2.2(H2O)-	(moles)	1380530	2008240	2204170	1958060	1781150	1835770	1955540	1922200	1442370	1516630	1369770
CO3	(moles)	777915	425583	541742	428021	599504	589939	565598	529305	557238	633078	700945
PO4	(moles)	27151.6	64506.6	76989.7	67335.6	68324.8	69222.1	66932	64193.6	58191	25225.6	17879.7
SO4	(moles)	1090160	491819	685148	670423	722693	729752	548424	504739	726634	1004300	984423
K	(moles)	98883.2	113784	101613	113288	72792.8	82020.8	93162.8	97588.7	33101	85738.3	85308.9
Hg	(moles)	915.933	680.946	565.062	870.911	808.141	877.536	564.724	554.984	408.172	597.514	1104.09
Cu	(moles)	4227.27	4607.15	3139.31	4188.27	3459.55	4009.91	5456.52	5853.42	1140.55	4571.89	4454.81
TPB	(moles)	0	0	0	0	0	0	0	0	0	0	0
NaT	(moles)	0	0	0	0	0	0	0	0	0	0	0
Cs	(Ci)	1046620	2273010	1510920	1546580	1087380	1283550	2447950	2644320	361289	1174380	1018920
Sr	(Ci)	104.847	0.011116	2.27407	56.3317	43.5752	51.495	0	0	0.822985	124.521	27.0985
H3	(Ci)	326.627	0.074012	7.15303	352.355	274.778	322.468	-1.86E-06	0	5.05251	469.706	159.853
Th232	(Ci)	0.002202	0.000374	0.000261	0.002044	0.001584	0.001884	0.000378	0.000413	7.15E-05	0.004588	0.001106
U232	(Ci)	0.000263	0.000149	8.49E-05	0.000664	0.000521	0.000619	0.000149	0.000162	2.6E-05	0.000461	0.000523
U233	(Ci)	0.055304	0.038487	0.025512	0.049259	0.033832	0.04056	0.035944	0.039206	0.004541	0.074496	0.044478
U234	(Ci)	0.055397	0.013194	0.00859	0.02756	0.039645	0.043059	0.029714	0.029627	0.017674	0.033323	0.056543
U235	(Ci)	0.00205	0.000762	0.000447	0.002673	0.002363	0.002753	0.001029	0.001083	0.000351	0.002363	0.002255
U236	(Ci)	0.010425	0.002182	0.001407	0.004695	0.00797	0.00852	0.006055	0.005957	0.003995	0.004458	0.011511
U238	(Ci)	0.059049	0.034761	0.019089	0.162379	0.128978	0.153391	0.03737	0.040758	0.006541	0.115012	0.105867
Np237	(Ci)	0.05557	0.014092	0.010026	0.081211	0.072188	0.083734	0.021341	0.021858	0.010688	0.050987	0.06058
Pu238	(Ci)	1162.04	795.738	435.921	709.392	963.931	1058.17	1207.1	1253.43	448.093	1229.71	1436.36
Pu239	(Ci)	35.3302	35.9989	19.2605	61.7826	49.7727	59.1749	39.7748	43.2441	5.95039	94.5885	85.1949
Pu240	(Ci)	11.9866	11.2123	6.03915	17.0564	14.0575	16.6435	12.6521	13.7076	2.09557	27.5585	21.5261
Pu241	(Ci)	307.049	270.78	143.983	321.626	286.203	330.668	309.108	328.58	62.9895	542.076	366.037
Pu242	(Ci)	0.009193	0.012155	0.006435	0.006922	0.006519	0.00759	0.014141	0.015256	0.00248	0.015795	0.008643
Am241	(Ci)	87.6253	60.3024	34.332	126.498	106.814	125.34	69.6586	74.6467	16.0333	130.445	91.4941
Am242	(Ci)	27.5094	0.043564	0.630881	31.2827	24.6694	29.2612	0.042387	0.045181	0.482984	42.3355	15.7348
Cm244	(Ci)	19.2684	0.139378	0.483939	13.2135	10.3162	12.1415	0.189784	0.196431	0.256332	22.7649	6.28491
Cm245	(Ci)	0.002182	1.99E-05	5.8E-05	0.001515	0.001191	0.001413	2.56E-05	2.7E-05	3.01E-05	0.002786	0.00076

Appendix H
Salt Feed Blends

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Appendix H

Batch		SPT023	SPT024	SPT025	SPT026	SPT027	SPT028	SPT029	SPT030	SPT031	SPT032	SPT033
Supernate	(gals)	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1248620	1218820	1235050	1250000
Supernate	(liters)	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4727569	4614739	4676190	4732794
SpG	(g/cc)	1.37198	1.36417	1.33221	1.33219	1.33187	1.33135	1.33844	1.34406	1.35833	1.35829	1.34046
Na	(moles)	29871200	30064900	30279100	30267600	29959200	29764400	30104400	29587400	29960200	30389400	30516700
Na	(M)	6.311536	6.352463	6.397722	6.395292	6.330129	6.28897	6.360809	6.25848	6.492284	6.498752	6.447924
NO3	(moles)	15452900	13136300	9840270	9895070	9862560	9744650	12372700	14252600	14580100	14747500	13290000
NO2	(moles)	1037400	1426640	4478770	4475720	4481590	4501800	4411800	4186670	4265950	4327620	4055250
OH	(moles)	7717440	10591300	11761700	11681200	11442000	11383900	9258880	7287260	7186860	7342610	8788620
AlO2.2(H2O)-	(moles)	1480400	1440620	1400540	1402340	1371230	1361410	1096000	836832	839133	851773	1147640
CO3	(moles)	907312	754184	917442	920791	918236	914879	825793	721710	725167	732323	759335
PO4	(moles)	12919.9	15374.7	49621.5	49541	48707.6	48938.5	29903.3	12526.8	12200.6	12491.3	28718.1
SO4	(moles)	1279290	1064640	531680	536466	532573	520443	733989	893384	918448	928393	813016
K	(moles)	66436	83830.7	76215.8	75909.6	72791	72168.5	70537.5	68490.4	67287.9	68115.4	75924.2
Hg	(moles)	242.039	446.988	1082.28	1068.29	1042.88	1046.1	905.02	739.62	728.938	710.459	732.849
Cu	(moles)	2827.98	4115.98	4324.68	4298.27	4113.59	4088.67	4151.93	4188.91	4102.92	4156.02	4299.41
TPB	(moles)	0	0	0	0	0	0	0	0	0	0	0
NaT	(moles)	0	0	0	0	0	0	0	0	0	0	0
Cs	(Ci)	472000	1045150	1132400	1118310	1105310	1094180	1248860	1374150	1362620	1373650	1288390
Sr	(Ci)	9.28856	35.0429	124.179	123.264	127.182	127.162	178.782	221.162	222.479	223.747	161.249
H3	(Ci)	54.4344	200.313	338.668	333.104	310.36	306.812	385.358	448.201	446.087	445.876	318.784
Th232	(Ci)	0.000356	0.001346	0.003453	0.00344	0.003006	0.003018	0.00319	0.003327	0.003319	0.00336	0.002532
U232	(Ci)	0.000343	0.000606	0.004343	0.004331	0.004296	0.004319	0.004317	0.004313	0.00412	0.004166	0.005159
U233	(Ci)	0.007613	0.028267	0.062438	0.06184	0.055185	0.05533	0.05324	0.05109	0.050898	0.051573	0.042522
U234	(Ci)	0.004894	0.017117	0.04235	0.041512	0.038825	0.038957	0.031542	0.024671	0.024538	0.024919	0.018976
U235	(Ci)	0.000969	0.001872	0.006189	0.006168	0.006001	0.00603	0.00597	0.005907	0.005702	0.005778	0.006581
U236	(Ci)	0.00077	0.002612	0.007199	0.007025	0.006735	0.006762	0.005136	0.003631	0.003614	0.003675	0.002738
U238	(Ci)	0.074301	0.11985	0.374787	0.374275	0.368211	0.369894	0.3744	0.378021	0.363863	0.368648	0.43428
Np237	(Ci)	0.012952	0.046851	0.289912	0.28914	0.285325	0.287372	0.285853	0.284188	0.273206	0.276843	0.330834
Pu238	(Ci)	525.295	778.853	989.278	972.927	926.566	921.967	898.127	865.752	867.165	877.02	639.324
Pu239	(Ci)	74.5185	92.8777	91.1692	90.996	86.6946	86.07	88.168	89.8044	87.4695	88.6003	91.8732
Pu240	(Ci)	17.2219	22.8505	25.2612	25.1914	23.9584	23.8321	25.2525	26.3941	25.9133	26.2396	25.2197
Pu241	(Ci)	244.483	346.49	451.545	445.062	423.041	417.546	463.737	499.454	490.386	491.237	422.517
Pu242	(Ci)	0.00415	0.006916	0.012904	0.012831	0.012235	0.012248	0.013879	0.015186	0.015156	0.015338	0.012395
Am241	(Ci)	33.7091	87.6459	742.394	741.236	732.801	738.341	745.191	750.455	721.294	730.584	873.284
Am242	(Ci)	5.41005	20.0755	32.7081	32.5086	30.5066	30.4673	37.9822	44.1945	44.3931	44.854	32.9109
Cm244	(Ci)	2.10878	7.84149	17.587	17.3814	16.5604	16.4713	21.2127	25.0555	25.0469	25.1256	18.1156
Cm245	(Ci)	0.000257	0.000966	0.002199	0.002191	0.002107	0.002112	0.002761	0.003299	0.003326	0.003363	0.00243

Appendix H
Salt Feed Blends

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Appendix H

Batch		SPT034	SPT035	SPT036	SPT037	SPT038	SPT039	SPT040	SPT041	SPT042	SPT043	SPT044
Supernate	(gals)	1250000	1202990	1250000	1250000	1247980	1214150	1236090	1248000	1248000	1246960	1237610
Supernate	(liters)	4732794	4554803	4732794	4732794	4725146	4597058	4680128	4725222	4725222	4721284	4685883
SpG	(g/cc)	1.43945	1.3247	1.3554	1.35093	1.35769	1.36044	1.3483	1.36083	1.31865	1.34647	1.35957
Na	(moles)	29975700	27747500	30831600	31470300	31292100	29372300	28639200	29645500	28310300	30588900	30181800
Na	(M)	6.333616	6.09192	6.51446	6.649412	6.622462	6.389369	6.11932	6.273885	5.991317	6.478936	6.441006
NO3	(moles)	11407900	9057260	13819400	9937960	8907680	12266900	12267700	14241400	8771720	6513750	11933300
NO2	(moles)	4410840	2901280	2084730	3462720	4014500	1693210	1582960	1348190	2561220	3318500	1799810
OH	(moles)	9583380	10884100	8975720	12969800	14189600	10420300	9920280	8424310	13335600	18153900	12095100
AlO2.2(H2O)-	(moles)	1279880	1879540	1758570	1959900	1594320	1363700	1334920	1499260	1380300	974255	1277930
CO3	(moles)	748310	487106	850940	513184	448980	687439	675642	789120	436693	329341	707962
PO4	(moles)	43293.8	65348.2	38882.8	68191.8	57001.5	17602.9	17129.1	20286.5	35218.4	16268.3	13692.6
SO4	(moles)	863020	596826	1057810	643696	560706	972731	967945	1136060	612097	444079	952205
K	(moles)	82283.1	71615	64586.8	76938.5	58080.1	82678.9	77564.7	76409.9	85011.1	84402.3	88550.4
Hg	(moles)	834.689	799.733	611.607	922.452	979.931	616.875	548.794	385.746	812.414	1399.3	803.962
Cu	(moles)	4457.42	3268	2801.55	3578.33	2601.13	3679.65	3404.18	3055.99	4306.66	4782.63	4588.65
TPB	(moles)	0	0	0	0	0	0	0	0	0	0	0
NaT	(moles)	0	0	0	0	0	0	0	0	0	0	0
Cs	(Ci)	1654140	1144520	783828	1355050	1055840	910904	873831	669479	1315630	1653140	931884
Sr	(Ci)	111.712	140.168	81.2933	136.164	28.9117	51.6847	41.512	35.7845	64.6683	52.5537	34.4585
H3	(Ci)	426.953	431.286	248.766	406.402	153.444	188.139	163.27	127.929	276.68	269.858	141.435
Th232	(Ci)	0.002432	0.004606	0.002591	0.004259	0.001223	0.00184	0.00147	0.001212	0.002437	0.002226	0.001291
U232	(Ci)	0.001131	0.000301	0.001995	0.000386	0.000379	0.000521	0.0005	0.000435	0.000691	0.000762	0.000518
U233	(Ci)	0.039991	0.080382	0.044868	0.076899	0.031415	0.032896	0.027374	0.021388	0.04742	0.047322	0.024774
U234	(Ci)	0.02709	0.033301	0.019098	0.033243	0.016374	0.016634	0.014875	0.011109	0.027032	0.028943	0.013948
U235	(Ci)	0.002885	0.001944	0.003146	0.002067	0.001283	0.001788	0.001653	0.00142	0.002389	0.002553	0.001677
U236	(Ci)	0.004981	0.004417	0.002593	0.004527	0.002465	0.002376	0.002216	0.001638	0.004077	0.004433	0.002098
U238	(Ci)	0.204412	0.078528	0.19048	0.090335	0.068981	0.112866	0.107395	0.097537	0.138447	0.146769	0.112099
Np237	(Ci)	0.102565	0.0539	0.141154	0.060532	0.0452	0.037576	0.036759	0.026046	0.070175	0.0802	0.035756
Pu238	(Ci)	1305.85	918.524	550.586	909.838	400.96	836.79	756.805	716.564	904.439	861.321	763.972
Pu239	(Ci)	124.418	50.7887	55.0688	55.7343	36.4108	96.9629	89.96	89.575	91.6856	89.5695	96.0601
Pu240	(Ci)	33.2547	17.89	16.0836	18.5914	10.0449	24.3724	22.3745	21.8902	24.2761	23.4981	23.4726
Pu241	(Ci)	531.571	359.107	270.99	348.243	146.931	332.941	297.281	283.209	336.928	313.147	291.199
Pu242	(Ci)	0.01372	0.013344	0.008856	0.012617	0.004039	0.008591	0.007437	0.006975	0.009447	0.008436	0.00723
Am241	(Ci)	202.52	122.746	361.552	128.083	72.7371	85.2616	77.8141	62.7901	127.656	134.688	75.3949
Am242	(Ci)	45.1711	44.8934	26.5754	43.6821	17.91	21.1638	18.7865	14.6647	32.9505	33.2248	17.143
Cm244	(Ci)	11.7284	22.3993	12.6612	20.7458	6.27509	9.01355	7.22654	5.8076	11.9918	11.2363	6.22176
Cm245	(Ci)	0.001605	0.003073	0.001741	0.002887	0.000865	0.001267	0.001022	0.000831	0.001717	0.001611	0.000906

Appendix H
Salt Feed Blends

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Appendix H

Batch		SPT045	SPT046	SPT047	SPT048	SPT049	SPT050	SPT051	SPT052	SPT053	SPT054	SPT055
Supernate	(gals)	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1249200	1250000	1250000	1250000
Supernate	(liters)	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4729765	4732794	4732794	4732794
SpG	(g/cc)	1.36738	1.36738	1.372	1.36842	1.37197	1.36038	1.35153	1.35128	1.35025	1.34795	1.34902
Na	(moles)	30468400	30102400	30110900	30239800	30023000	30711300	31767300	31321800	31288200	31663400	32090100
Na	(M)	6.437719	6.360386	6.362182	6.389418	6.34361	6.489042	6.712166	6.622274	6.610936	6.690213	6.780371
NO3	(moles)	15502000	15306600	15417600	14990800	15417200	15042600	14834400	14614000	15324800	11165700	10983000
NO2	(moles)	996464	985432	1055550	1214350	1056270	3565670	5537010	5518970	5732900	3952390	3961000
OH	(moles)	8378950	8289420	8764240	9383010	8756110	7564400	7045590	6906800	5740780	11480200	12101600
AlO2.2(H2O)-	(moles)	1465010	1447530	1407210	1362660	1398990	1053070	808025	787992	729548	1961370	1997920
CO3	(moles)	941804	929891	963180	935395	965927	883329	825410	811663	848334	542906	532539
PO4	(moles)	11750.2	11640.6	11817.3	11641.2	11744.2	13037	14762	14590.6	12134.7	71104.8	72097
SO4	(moles)	1285780	1269330	1277290	1236230	1277690	1149310	1051680	1033520	1098130	696594	673868
K	(moles)	83334.4	82498.6	89541.5	88241.7	89527.8	81640.8	80774.4	79476.1	63789.2	80589.3	89960.3
Hg	(moles)	428.871	424.673	430.774	424.108	427.526	414.901	432.276	426.034	344.614	700.572	752.148
Cu	(moles)	3903.41	3866.76	4266.91	4220.32	4263.55	4182.68	4421.68	4359.57	3427.25	3677.6	4236.46
TPB	(moles)	0	0	0	0	0	0	0	0	0	0	0
NaT	(moles)	0	0	0	0	0	0	0	0	0	0	0
Cs	(Ci)	463270	457666	437973	463737	425514	635079	837200	826456	669572	1047820	1165110
Sr	(Ci)	16.5115	16.4275	14.2402	14.4957	13.5948	61.1576	98.8155	98.1028	85.1369	33.1445	39.4728
H3	(Ci)	49.7302	49.1514	42.3265	42.9776	39.8779	231.679	375.49	370.513	328.168	108.878	128.065
Th232	(Ci)	0.000531	0.000531	0.000462	0.000474	0.000446	0.001398	0.002227	0.00222	0.001832	0.000988	0.001185
U232	(Ci)	0.000342	0.000338	0.00034	0.000335	0.000334	0.000442	0.000552	0.000546	0.000445	0.000248	0.000298
U233	(Ci)	0.008607	0.008607	0.007499	0.007709	0.007233	0.024312	0.03891	0.038796	0.032419	0.02632	0.03027
U234	(Ci)	0.00406	0.00406	0.003537	0.003648	0.003412	0.011939	0.019151	0.019097	0.016067	0.009025	0.010663
U235	(Ci)	0.00103	0.001022	0.001014	0.001006	0.001	0.001734	0.002374	0.002359	0.001995	0.000953	0.001141
U236	(Ci)	0.000583	0.000583	0.000508	0.000525	0.00049	0.001426	0.002262	0.002254	0.001832	0.001152	0.00137
U238	(Ci)	0.082521	0.081823	0.082627	0.081511	0.081621	0.10967	0.137434	0.136233	0.112284	0.058103	0.07005
Np237	(Ci)	0.008357	0.008357	0.007282	0.007542	0.007023	0.029791	0.048248	0.048136	0.041655	0.020865	0.024511
Pu238	(Ci)	616.073	610.057	611.205	602.338	601.157	722.33	873.223	862.929	678.914	428.978	517.265
Pu239	(Ci)	89.8042	88.9779	90.9456	89.3643	89.9989	95.7873	107.129	105.814	83.8569	50.8356	61.5264
Pu240	(Ci)	20.8858	20.7012	21.0361	20.7007	20.7993	24.3257	28.6688	28.364	22.8245	13.0947	15.8189
Pu241	(Ci)	242.19	237.733	236.75	231.134	228.973	300.609	372.552	365.466	295.009	157.927	188.671
Pu242	(Ci)	0.005467	0.005429	0.005347	0.005302	0.005262	0.007873	0.010448	0.01037	0.008384	0.004767	0.00575
Am241	(Ci)	34.1541	33.9821	32.2261	32.3516	31.5093	65.6656	96.0545	95.549	78.9777	44.7466	53.3136
Am242	(Ci)	5.79792	5.79212	5.04154	5.17831	4.85269	29.406	48.2203	48.0958	43.1746	14.2458	16.9245
Cm244	(Ci)	2.39549	2.37636	2.05455	2.09104	1.95018	10.8151	17.5632	17.3932	15.3943	5.26995	6.22762
Cm245	(Ci)	0.000356	0.000356	0.00031	0.000318	0.000299	0.001659	0.002715	0.00271	0.002416	0.000838	0.000999

Appendix H
Salt Feed Blends

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Appendix H

Batch		SPT056	SPT057	SPT058	SPT059	SPT060	SPT061	SPT062	SPT063	SPT064	SPT065	SPT066
Supernate	(gals)	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000	1250000
Supernate	(liters)	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794	4732794
SpG	(g/cc)	1.34841	1.35163	1.35382	1.35597	1.34967	1.3299	1.32569	1.32772	1.32295	1.30383	1.2698
Na	(moles)	31834100	31355300	31110800	31293400	31308900	31489100	30175200	30952800	32292100	32801000	30972100
Na	(M)	6.72628	6.625114	6.573453	6.612035	6.61531	6.653384	6.375768	6.540069	6.823052	6.930578	6.544147
NO3	(moles)	11127000	11385600	11527800	11602200	12145300	12891000	10328700	13092900	5946450	4199790	2716480
NO2	(moles)	3971950	3939130	3881270	3904620	4293610	5179930	4992400	5158570	4974230	2937570	2233400
OH	(moles)	11682300	11676600	11688900	11748600	10619000	8866030	11930800	8052030	20829100	23484300	23824600
AlO2.2(H2O)-	(moles)	1965970	1791000	1705560	1715410	1524460	1085080	577571	1049920	287552	1720210	2135040
CO3	(moles)	541232	562696	576949	580701	663291	823767	510559	840671	77822.9	187177	123488
PO4	(moles)	71018.2	74643.2	75741.1	76186.5	66003.9	42200.6	22009.7	40517.6	12140.2	64290.2	55455.8
SO4	(moles)	690728	730640	753916	758993	828588	935911	644711	964353	132969	172836	67423.1
K	(moles)	84226.2	83559.2	82977.1	83303.3	79164	86119.5	29019.7	73672	62521.2	241583	277354
Hg	(moles)	718.494	635.699	592.796	595.451	587.089	643.338	281.1	585.65	337.573	1710.37	1772.91
Cu	(moles)	3900.76	3555.94	3404.37	3414.47	3367.26	4252.66	1277.01	3546.69	3477.22	12749.8	17177.9
TPB	(moles)	0	0	0	0	0	0	0	0	0	0	0
NaT	(moles)	0	0	0	0	0	0	0	0	0	0	0
Cs	(Ci)	1084270	1207980	1205960	1205000	1142670	1249460	1046720	1053990	2131920	4038510	4385340
Sr	(Ci)	35.8188	14.4654	8.53239	8.43379	21.5066	60.7039	64.9025	55.2844	99.7296	214.552	206.901
H3	(Ci)	116.202	46.3253	27.1393	26.6609	68.5675	192.678	83.223	173.557	89.1062	617.319	889.803
Th232	(Ci)	0.001074	0.000472	0.000297	0.000295	0.000612	0.001626	0.000662	0.001468	0.000903	0.00534	0.00597
U232	(Ci)	0.000269	0.000117	7.34E-05	7.28E-05	0.000219	0.000621	0.000299	0.000588	0.000228	0.002133	0.002848
U233	(Ci)	0.027965	0.01809	0.014171	0.014186	0.017366	0.031124	0.011129	0.027087	0.021258	0.098041	0.157417
U234	(Ci)	0.009741	0.004919	0.003403	0.003395	0.006712	0.016758	0.007438	0.015459	0.00814	0.056275	0.093152
U235	(Ci)	0.001037	0.000449	0.000279	0.000278	0.000663	0.001822	0.000798	0.001679	0.000878	0.006113	0.011283
U236	(Ci)	0.001245	0.000607	0.00041	0.000409	0.001041	0.002798	0.001359	0.002652	0.001076	0.009671	0.010814
U238	(Ci)	0.063325	0.026237	0.015715	0.015608	0.043362	0.123868	0.05614	0.11547	0.054257	0.420613	0.582453
Np237	(Ci)	0.022502	0.011572	0.008111	0.008097	0.021328	0.056897	0.02853	0.054591	0.018986	0.199056	0.298244
Pu238	(Ci)	465.081	198.817	121.741	120.767	285.691	787.476	339.669	719.718	395.31	2611.62	3051.01
Pu239	(Ci)	55.3771	23.0158	13.7748	13.6769	30.4349	84.1117	33.7985	75.8412	46.8487	275.791	352.445
Pu240	(Ci)	14.2633	5.95652	3.58392	3.55944	8.01977	22.1528	9.04501	20.0478	12.0886	72.9219	94.3698
Pu241	(Ci)	168.59	69.1913	41.0049	40.3048	94.4513	260.948	108.871	232.928	133.217	830.562	1044.17
Pu242	(Ci)	0.00519	0.002196	0.001336	0.001328	0.003152	0.008738	0.003779	0.007999	0.004514	0.029134	0.039979
Am241	(Ci)	48.4396	22.8073	15.0645	15.0045	41.7885	115.108	56.348	109.592	41.4874	399.325	501.822
Am242	(Ci)	15.534	6.25787	3.70704	3.68113	9.5783	27.2042	11.8972	25.041	12.9868	90.9999	141.591
Cm244	(Ci)	5.66507	2.27307	1.33848	1.31971	2.60017	7.01438	3.35443	6.07744	5.8469	22.0397	64.814
Cm245	(Ci)	0.000916	0.000371	0.00022	0.000219	0.000436	0.001186	0.000576	0.001045	0.001013	0.003853	0.011156