

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

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## **1.0      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 waste form. 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 (Reference 1).

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 (Reference 12).

The engineering scope in Phase IV (Decision Phase) focused on the technical uncertainties for the remaining primary and backup alternatives in a greater level of detail to support the recommendation of the most technically suited alternative. HLW Process Engineering completed material balances and revised the Process Flow Diagrams. Additional data obtained through continuing research, calculations, and experiments on the selected alternatives were used to address some uncertainties and assumptions

remaining from Phase III. 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 pre-conceptual facility layouts developed as a part of Phase IV.

In February of 2000 the DOE requested that the work on the solvent extraction flowsheet should be continued. (Reference 2) R&D was initiated. The original solvent extraction flowsheet has been modified as a result of continued research.

Also, DOE directed that the precipitate hydrolysis process from the DWPF Salt Cell be moved into the Small Tank Tetraphenylborate Precipitation alternative. (Reference 3) This work has been completed.

In addition, the alpha sorption flowsheet has been re-configured as the result of ongoing R&D efforts and a new trade study. (Reference 68)

This document provides the technical bases, assumptions and results of these continuing engineering efforts.

## 1.1 Background

The High-Level Waste System is a set of seven different interconnected processes (Figure 1.1-1) operated by the High Level Waste and Solid Waste Divisions. These processes function as one large treatment plant that receives, stores, and treats high-level wastes at SRS and converts these wastes into forms suitable for final disposal. The three major permitted disposal forms are borosilicate glass, planned for disposal at a Federal Repository; saltstone grout, disposed in vaults on the SRS site; and treated water effluent, released to the environment. Final disposition of mercury metal, which is recovered and purified as part of vitrification, has not been fully defined.

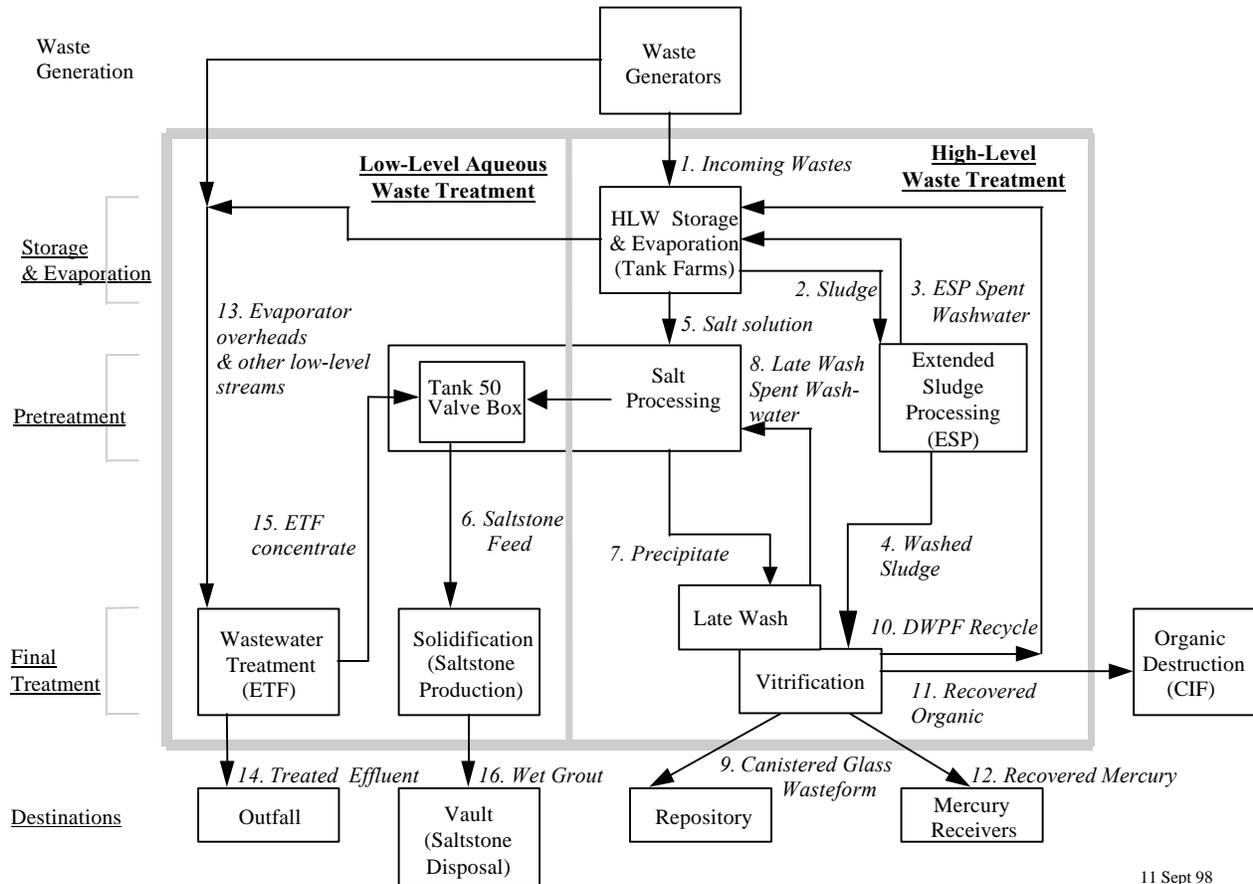
As originally designed, these processes include:

- 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 Facility)
- 7) Organic Destruction (Consolidated Incineration Facility)

F and H Tank Farms, Extended Sludge Processing, Defense Waste Processing Facility, Effluent Treatment Facility, Saltstone Facility 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).

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. This resulted in a WSRC recommendation to the Department of Energy in January 1998 to conduct a systems evaluation of salt disposition options and to recommend the preferred alternative. The salt will remain in storage until an alternative salt pre-treatment process is identified and implemented. Alternative processes were evaluated throughout 1998 and 1999.



11 Sept 98

**Figure 1.1-1 HLW System Major Interfaces**

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 (Reference 4). 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 for all HLW facilities. Additionally, the selected alternative must interface safely and efficiently with the remainder of processing facilities

outside of HLW. Timely selection of an alternative is key to support tank farm space and water inventory management 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.

## **1.2 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) borosilicate glass to be sent to a Federal repository, 2) 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 removal of the waste 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, 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”.

## **1.3 High Level Waste System Overview**

Figure 1.1-1 schematically illustrates the normal flow of wastes through the HLW System. The various processes within the system and external processes are shown in

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rectangles. The numbered streams identified in *italics* are the interface streams between the various processes. The discussion below represents the HLW system configuration as of January 1998.

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 liquid from the evaporators is sent to the Effluent Treatment Facility (ETF) (Stream 13).

The insoluble sludge that settles to the bottom of waste receipt tanks in HLW Storage and Evaporation are slurried 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).

Salt cake is dissolved using hydraulic slurring techniques similar to those used for sludge slurring. As currently designed, the salt solutions from this operation and other salt solutions from HLW Storage and Evaporation were intended for feed to Salt Processing (ITP) (Stream 5). In ITP, the salt solution is processed to remove radionuclides, which are concentrated into an organic precipitate. The decontaminated filtrate is then sent to Tank 50. The process produces concentrated organic precipitate containing most of the radionuclides. This precipitate is washed with water to remove soluble salts. However, some soluble corrosion inhibitors which interfere with DWPF processing must be left in the precipitate slurry after washing, because the slurry is stored in carbon steel tanks, which are susceptible to corrosive attack by uninhibited precipitate slurries.

The precipitate is transferred to the Late Wash Facility for further washing in stainless steel tanks to reduce the level of soluble corrosion inhibitors to acceptable levels for the DWPF process (Stream 7). The wash water from this process is returned to ITP to be reused in the ITP process (Stream 8).

The washed precipitate from Late Wash is then sent to the DWPF Vitrification building (221-S). In the Vitrification Building, the precipitate is catalytically decomposed and separated into two streams: a mildly contaminated organic stream and an aqueous stream containing virtually all of the radionuclides. The mildly contaminated organic stream is stored at DWPF and eventually transferred to the Consolidated Incineration Facility (CIF) (Stream 11). The aqueous stream is combined with the washed sludge from ESP, which has undergone further processing within the DWPF, and the resulting mixture vitrified.

The washed sludge from ESP (Stream 4) is chemically adjusted in the DWPF to prepare the sludge for feed to the glass melter. As part of this process, mercury is stripped from the sludge slurry, purified and sent to mercury receivers (Stream 12). The aqueous product from organic decomposition is added to the chemically adjusted sludge. The mixture is then combined with glass frit and sent to the glass melter. The glass melter drives off the water and melts the wastes into a borosilicate glass matrix, which is poured into a canister. The canisters of glass waste form are 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 recycled to HLW Storage and Evaporation for processing (Stream 10).

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. 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 from the water are concentrated and sent to Tank 50 (Stream 15).

In Tank 50 the concentrate from the ETF is combined with the decontaminated filtrate from the ITP and sent to Saltstone (Stream 6). In the Saltstone Facility the liquid waste is combined with cement formers and pumped as a wet grout to a landfill vault (Stream 16). In the vault, the cement formers hydrate and cure, forming a solid saltstone monolith. The Saltstone Facility vaults will eventually be closed as a landfill.

**NOTE:** After processing the available decontaminated waste inventory in Tank 50, the Saltstone Facility was placed in lay-up in 1999. It may operate intermittently to support continuing operation of ETF until the proposed Salt Waste Processing Facility is constructed and is operational.

## **2.0 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 (Reference 5), 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<sup>TM</sup> flowsheet environment were used to execute the models and generate the performance results and material balances for the alternatives.

### **2.1 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 a “Road Mapping” approach, a logical and consistent plan of action was applied to the scope of work activities for each alternative and a work scope matrix reflecting integrated commitments was developed for managing outstanding items, work activities, deliverables, and plans. The completed version of the work scope matrix is shown in Reference 5.

The scope of work matrix identifies the reference/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 the DOE assigned the Research and Development activities including implementation of scope, schedule and/or budget changes to the Tank Focus Area (TFA). (Reference 6) In addition the day-to-day management and integration of R&D activities would be 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 7.

## **2.2 Engineering Approach**

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.

### **2.2.1 Process Flow Diagram Development**

The revised PFDs are based on the PFDs presented during Phase III of the salt disposition efforts. The PFDs have been updated to incorporate results from recent research conducted as a part of the Decision Phase. The material balances shown on the PFDs are based on average tank farm salt solution. This basis was chosen so that a typical material balance was available for starting conceptual design of the selected alternative. 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.

### **2.2.2 Facility Layout Development**

The Facility Layouts for Phase III were 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.

#### 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 (All Options) to ensure a daily processing rate of 25,000 gallons per day. These tanks are sized to decouple the continuous flow 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 farm. Sizing of other process tanks was based on the type of process, a nominal 17.5 gpm salt solution feed flow rate 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.

### 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.

### Office Building

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

### Site Selection

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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 (Reference 8). See plot plan in Appendix G.

Facility Site Selection is a formal documented process (Reference 9), 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 it is likely that neither Precipitate slurry or CST loaded resin slurry could be pumped much farther than that distance using existing technology without including additional pumping. 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 (Reference 10).

#### *Feed Material from the HLW Tank Farm to the SWPF*

Fresh 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, it will be transferred to the new Salt Disposition Facility.

The salt solution (i.e., the HLW feed to the facility) will then be pumped to the new SWPF via an existing HLW transfer line which 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 LW. A section of new transfer line will be needed to connect this existing transfer line to the new Facility. This tie-in will be near the LPPP and the new transfer line will run about 550 feet to the SWPF.

#### *DSS from the SWPF and ETF to Z-Area*

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The Decontaminated Salt Solution (DSS) from the SWPF will be transferred to the Saltstone Facility in Z-Area via a new line which runs about 300 feet to a new valve box connected to the existing line from Tank 50 to the Salt Solution Hold Tank (SSHT) in Z-Area. This tie-in will be between the SSHT and the Low Point Drain Tank (LPDT). The LPDT provides a place to drain the line to Z-Area, and it will retain this function. A stream (ETF Evaporator Bottoms) from the SRS Effluent Treatment Facility (ETF) is currently routed to Z-Area and this route will be preserved.

Eventually, the ETF Bottoms will be transferred to a new 50,000-gallon (or larger) ETF Bottoms Tank (Reference 11). The new ETF Bottoms Tank will hold approximately 4-5 months of ETF Evaporator Bottoms based on current production rates. The ETF Bottoms can either be campaigned 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 it could be integrated into the SWPF project.

#### Streams to the DWPF

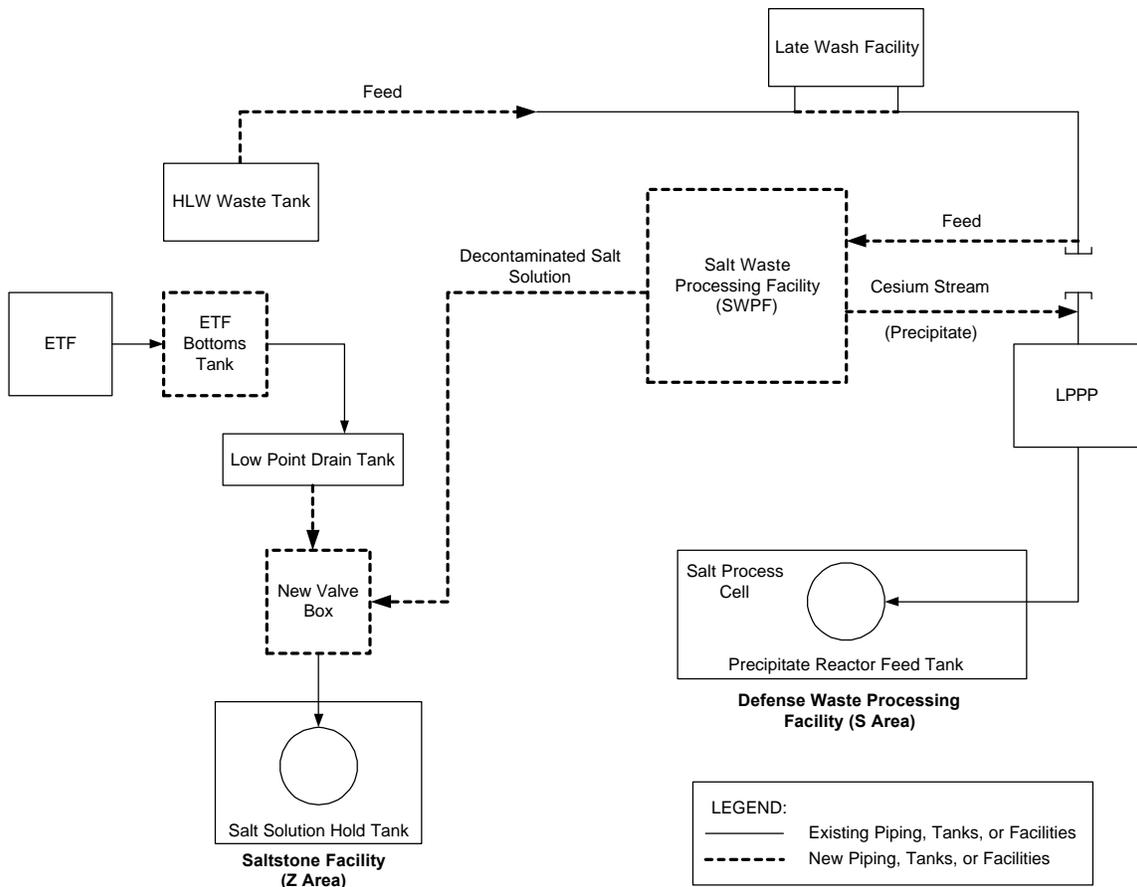
The SWPF product streams containing the radioactive contaminants removed from salt solution differs for each of the three alternatives.

If CST Non-Elutable Ion Exchange (CST-IX) or Caustic Side Solvent Extraction (CSSE) is selected, two streams containing contaminants removed from salt solution must be transferred to the DWPF, so two separate transfer routes must be provided. For these two alternatives, the salt solution is first treated using Monosodium Titanate (MST) to remove uranium, plutonium, and strontium from the salt solution. The salt solution is then filtered to remove the sludge solids and the MST solids. After washing to remove soluble salts, these solids will be pumped to a new Pump Pit via a new HLW transfer line.

For the CST-IX alternative, a slurry of cesium-loaded resin is also generated for transfer to the DWPF, while the CSSE alternative generates an acidic cesium nitrate solution. Spent organic solvent from CSSE operation would be periodically transferred to the CIF and burned.

The MST treatment is performed concurrently with the precipitation step in the Small Tank Tetraphenylborate Precipitation (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) that is transferred to the Consolidated Incinerator Facility and burned. A single Precipitate Hydrolysis Aqueous (PHA) product slurry containing all the radioactive contaminants removed from salt solution is transferred to the DWPF. This acidic stream contains soluble cesium and potassium formate salts generated from the acid hydrolysis of CsTPB and KTPB, the insoluble sludge solids removed from the salt solution and the MST added during the precipitation step that removes soluble strontium and alpha contamination.

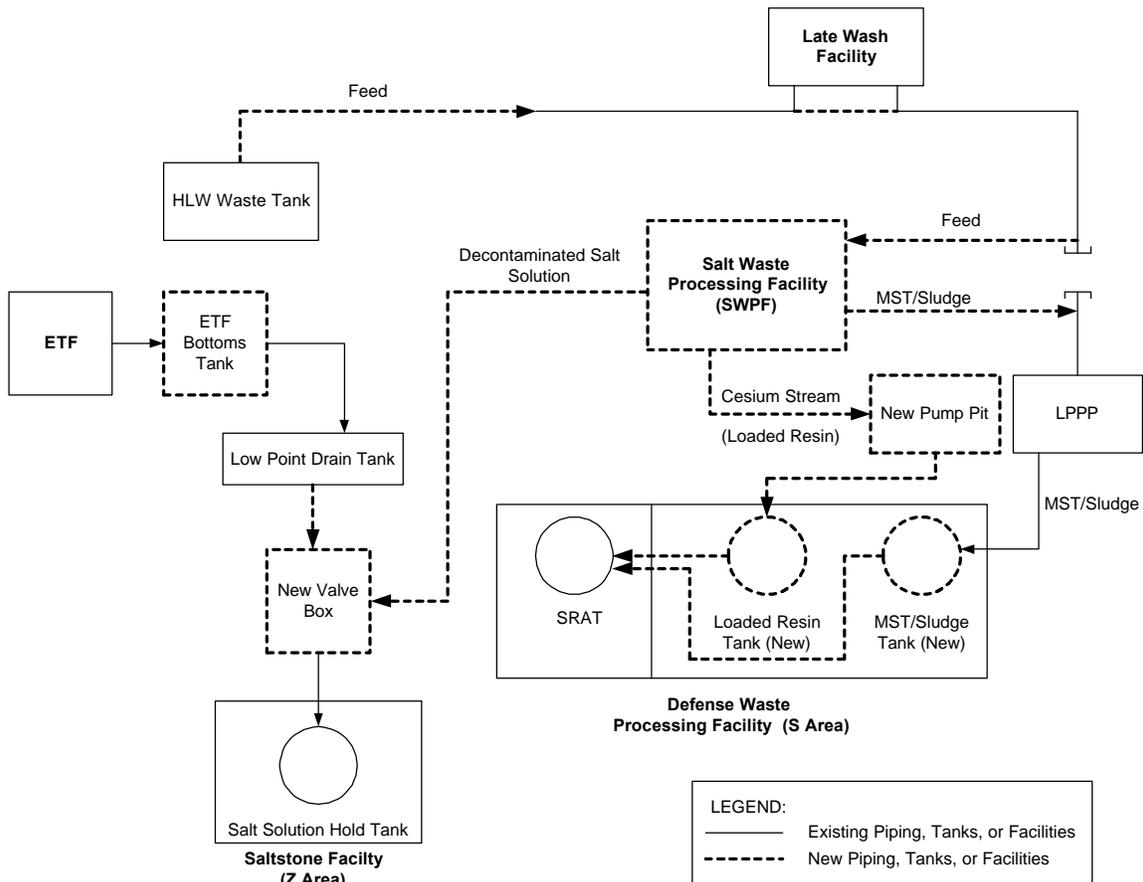
The cesium-containing product stream (PHA) from STTP is routed from the SWPF through a new HLW transfer line (about 550 feet long) to the LPPP Precipitate Tank (LPPPPT). From there, the PHA is transferred 1200 feet through an existing line to the existing Precipitate Reactor Feed Tank (PRFT) located in the SPC of the DWPF. This is the arrangement shown in Figure 2.2-1.



**Figure 2.2-1 Small Tank TPB Alternative Transfer Lines**

The route from the SWPF to the DWPF shown in Figure 2.2-1 can also be used for one of the two product streams generated by the CST-IX or CSSX alternatives, requiring a new transfer line that is about 550 feet long to connect the SWPF to the LPPPPT. However, as noted above, a separate transfer route from the SWPF to the DWPF is needed for these two alternatives to handle the two streams that will be transferred to the DWPF. This additional transfer route 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 tank located in the Salt Process Cell (SPC) of the DWPF. Although either product stream can be routed

through the new pump pit, the arrangement shown in Figure 2.2-2 shows the cesium product stream from either of these alternatives is routed through the new line and new pump pit while the MST/Sludge stream is routed through the LPPPPT.



**Figure 2.2-2 CST Ion Exchange Alternative Transfer Lines**

If the CSSX alternative is chosen, Fresh Waste will be pumped to Tank 50. The salt solution will either be sampled and ‘qualified’ prior to being pumped to Tank 50 or will be sampled while in Tank 50 prior to transfer to the new Solvent Extraction Facility.

The salt solution will then be pumped to the new Solvent Extraction Facility via the existing interarea transfer line, which will be modified. The new Solvent Extraction Facility will be located near the current Late Wash Facility. A section of new interarea transfer line will be needed to connect the current interarea transfer line to the new Facility. This tie-in will be near the Late Wash Facility.

The salt solution in the new Solvent Extraction Facility will be treated using Monosodium Titanate (MST) to remove uranium, plutonium, and strontium from the salt

solution. The salt solution is filtered to remove the sludge solids and the MST solids. These solids will be pumped to a new Pump Pit sludge tank via a new interarea transfer line. This new Pump Pit will be in the vicinity of the current Low Point Pump Pit (LPPP) in the Defense Waste Processing Facility (DWPF).

A new interarea transfer line will be required between the new Pump Pit and the DWPF Salt Processing Cell (SPC). The MST solids and the sludge solids will be pumped via this new interarea transfer line to a new tank located in the SPC. The MST solids and sludge solids will then be pumped to the Sludge Receipt and Adjustment Tank (SRAT).

The Cesium Strip Solution will be transferred from the new Solvent Extraction Facility to the Low Point Pump Pit Precipitate Tank (LPPPPT) via a new interarea transfer line. This new interarea transfer line can tie into the 'abandoned' precipitate line from the Late Wash Facility.

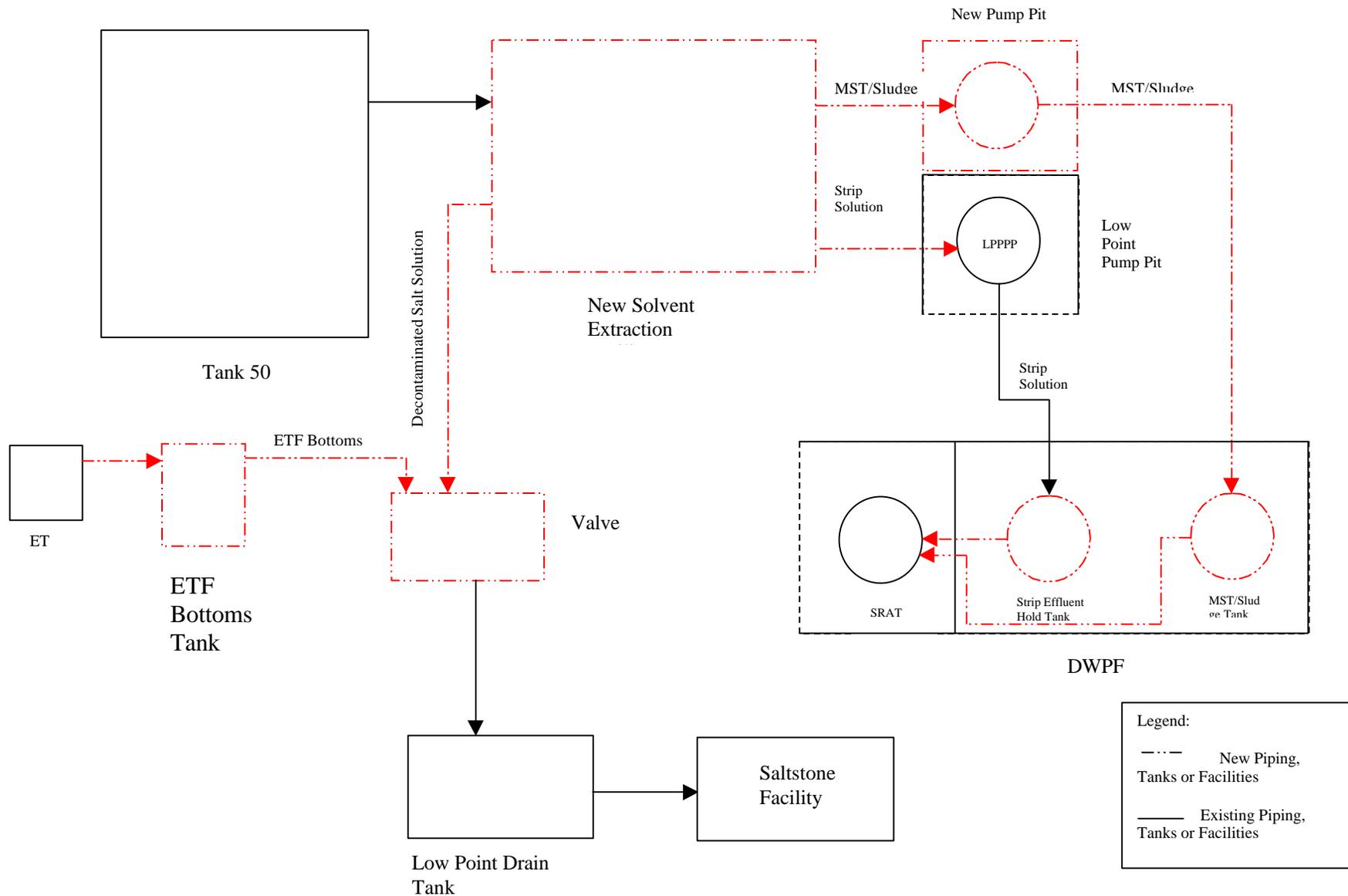
The Cesium Strip Solution will then be transferred from the LPPPPT to a new Strip Effluent Hold Tank located in the SPC. This transfer will occur via the existing interarea transfer line.

The Raffinate from the new Solvent Extraction Facility will be transferred to a new valve box which will allow the Saltstone Facility to receive material from ETF or the new Solvent Extraction Facility.

The ETF Bottoms will be transferred to a new 50,000-gallon ETF Bottoms Tank via a new interarea transfer line. The new interarea transfer line is needed because the current line will be used to transfer high activity salt solution to the new Solvent Extraction Facility. The new ETF Bottoms Tank will hold approximately 4-5 months of ETF Evaporator Bottoms based on current production rates. The ETF Bottoms can then be campaigned when a new salt solution batch is being sampled.

The new valve box will then be used to transfer either the Raffinate or the ETF Bottoms to the Saltstone Facility via the current interarea transfer line at the Low Point Drain Tank. See Figure 2.2-3.

**Figure 2.2-3 Caustic Side Solvent Extraction Interarea Transfer Lines**



## **2.3 Common Bases and Assumptions**

### **2.3.1 Production Rate Constraints**

The production rates and their corresponding material balances for the Decision Phase Alternatives were 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 CST and Small Tank options.

#### **2.3.1.1 Salt Removal Limitations**

The salt solution removal rate (at an average of 6.44 M Na<sup>+</sup>) is projected to average 6,000,000 gallons annually, based on logistical constraints imposed by the infrastructure of the Tank Farms (Reference 15).

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 the PFDs. This storage allows either 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 salt solution processing rate for each SWDF alternative is 13.1 gpm @ 100% attainment, corresponding to 17.5 gpm @75% attainment. These are the maximum processing rates applied to either option.

#### **2.3.1.2 DWPF**

The salt disposition options send cesium, in some form, to the DWPF for vitrification. The processing capacity for a salt disposition option can be limited by the melt rate or chemical cell processing in the DWPF.

##### **2.3.1.2.1 DWPF Melt Rate**

DWPF 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 foot<sup>2</sup>-hour (228 pph, DWPF basis), DWPF has not sustained this rate. The apparent sustainable melt rate (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, the long term average canister rate is  $320 (2/2.5) = 256$  canisters per year.

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

#### 2.3.1.2.2 Chemical Processing Cell

Over the initial two years of radioactive operations, the processes in the Chemical Processing Cell (CPC) process were changed to partially offset the longer than design basis cycle time (86 hours). This has increased the average canister production to 6.25 cans for each SME batch. Assuming the CPC process does not limit the overall DWPF production rate, then 50 cycles per year are required ( $320/6.25$ ), corresponding to 131 hrs per batch ( $8760*0.75/50$ ) or 5.5 days. The CPC cycle time consists of the following steps:

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
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

Therefore, the CPC in DWPF does not limit production for any of the three salt processing options.

### 2.3.1.3 Salt Processing Rates Summary

Based on the limitations in Section 2.3.1, the material balances for the remaining three salt processing options were completed at the various flow rates shown in Table 2.3-2.

**Table 2.3-2 Material Balances For Salt Disposition Alternatives**

Option	Salt Workoff, gpm @ 6.44 M [Na+] / 75 % Attainment <sup>1</sup>	One Year's Operating Production, gallons	Long Term Average (gal/yr)	[Na+], M within Facility	Flow Rate, within Facility gpm	Throughput Limitation
Small Tank ITP	17.5	6,900,000	6,000,000	6.44 (4.7)	17.5	Waste Removal Rate
CST Ion Exchange	17.5	6,900,000	6,000,000	6.44 (5.6)	20.1	Waste Removal Rate
CSSX	17.5	6,900,000	6,000,000	6.44 (5.6)	20.1	Waste Removal Rate

### 2.3.2 Salt Waste Composition

The Decision Phase salt composition is the 20-year average salt and sludge compositions (see Table 2.3-5) that were used in the Phase II flowsheets.<sup>2</sup> This will provide a consistent basis for comparing the alternatives. A blending strategy to provide salt solution to each of the alternatives was developed for Phase III (see Table 2.3-6 and Table 2.3-7) and the basis is provided below for comparison to the average. The values for Pu/Am, U, Np, and Sr were developed during Phase III. The methodology from Phase III is reproduced below.

#### Tank Farm Blending: MST Sorption Requirements for Alpha and Strontium

After obtaining data on MST sorption kinetics, preliminary evaluation of tank sizing for batch MST sorption (CST Non-Elutable Ion Exchange and Caustic Side Solvent Extraction) and for continuous MST sorption (Small Tank TPB Precipitation) was performed.

<sup>1</sup> The flowrate is not 19.0 gpm based on a storage period of only two months.

<sup>2</sup> The reader should note that the SpeedUp™ composition values shown in Table 2.3-5 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.

To gain a perspective on the alpha and strontium sorption requirements, the average concentrations for the Tank Farms were evaluated. Using 72.5E6 gallons at 6.44 M Na+, Sp. g. = 1.28 at 6.0 M Na+, and using the quantities in Table 2.3-3 (obtained from Appendix D of Reference 12), the average values in Table 2.3-4 were computed.

**Table 2.3-3 Tank Farm Quantities**

<i>Component</i>	<i>Total Ci</i>	<i>Total grams</i>
Pu/Am	7.69E4	5.79E4
U	9.07	1.74E7
Np	3.22	4.57E3
Sr	6.75E4	4.77E2

Table 2.3-4 also shows worst case (bounding) values as noted, the Saltstone Waste Acceptance Criteria, and the required  $K_d$  for the bounding values assuming 0.2 g/L of MST.

**Table 2.3-4 Tank Farm Concentrations @ 6.0 M Na<sup>+</sup>**

<b>Component</b>	<b>Concentration</b>		<b>Activity</b>		<b>Saltstone WAC (nCi/g)</b>	<b>Required <math>K_d</math> w/ 0.2 g/L MST</b>	<b>Required DFs for Average Waste</b>	<b>Required DFs for Bounding Waste</b>
	<b>Average (mg/L)</b>	<b>Bounding (mg/L)</b>	<b>Average (nCi/g)</b>	<b>Bounding (nCi/g)</b>				
Pu/Am	0.20	1.0 <sup>1</sup>	205	1000 <sup>1</sup>	18 (total $\alpha$ )	2.73E5	12	55
U	59.1	1030 <sup>2</sup>	0.024	0.62 <sup>2</sup>	18 (total $\alpha$ )	Not req'd	N/A	N/A
Np	0.016	1.8 <sup>3</sup>	0.009	1.0 <sup>3</sup>	0.03	3.67E4	N/A	33
Sr	0.0016	0.0095 <sup>4</sup>	178	1050 <sup>4</sup>	40	1.26E5	4.5	26

<sup>1</sup> Based on predicted 5X TRU spike from blended feed studies

<sup>2</sup> Based on U in Tank 40: 4.3 Ci in 1.44 M gallons (at 6.0 M Na<sup>+</sup>)

<sup>3</sup> Based on Np-237 in Tank 34: 1.8 Ci in 1.49 M gallons (at 6.0 M Na<sup>+</sup>)

<sup>4</sup> Based on Sr-90 in Tank 19: 1280 Ci in 0.256 M gallons (at 6.0 M Na<sup>+</sup>)

**Note:** Tank 11, which contains approximately 30,000 nCi/g, provides a much higher “bounding” value for Sr than Tank 19. The required  $K_d$  would be  $3.75 \times 10^6$  for 0.2 g/L MST. This required  $K_d$  is not achievable based on the data in Reference 13. The contents of this tank need to be blended over several salt batches.

Tank 11 provides a much higher “bounding” value for Sr than Tank 19. It is Tank 11 which contains approximately 30,000 nCi/g. The required  $K_d$  would be  $3.75 \times 10^6$  for 0.2 g/L MST. This required  $K_d$  is not achievable based on the data in Reference 14. The contents of this tank need to be blended over several salt batches.

Conclusions drawn from Table 2.3-4 include the following:

- While the concentration of U can be high, its contribution to total  $\alpha$  is negligible.
- Based on data in Reference 14, the required  $K_d$  for the bounding Np is apparently so high that removal by MST is not likely to be successful. Tanks 33 and 34, which contain essentially all of the Np in the Tank Farm, need to be blended over several salt batches.
- The predicted peak concentrations of TRU contribute the greatest burden to meeting the total  $\alpha$  removal requirements. (Approximately 65% of the TRU is predicted to be processed in just two out of 12.5 years for the CST blends; these spikes are reflected in the bounding Pu/Am concentration.)

#### 2.3.2.1.1 Tank Farm

The H/F Tank Farms are assumed to provide up to 6,000,000 gal/yr (Reference 15) of 6.44 molar sodium feed for the alternatives on an average basis. The feed composition will vary over time based on the sequence of the feed tanks. The ProdMod model was used to generate the feed sequence. ProdMod is the model used to determine tank transfers in the development of the High Level Waste System Plans. Various scenarios were run for each of the alternatives based upon when their assumed start-up would occur. The feed stream composition to an alternative was then determined based on a yearly combination of the feed tanks produced by ProdMod.

#### 2.3.2.1.2 Salt Feed Blending

An expected range of compositions was developed to provide a basis for sensitivity analysis over the projected life of the alternative processes. A tank farm feed strategy for each alternative was developed to provide the average composition to be fed each year that the process was projected to operate. These different compositions of the feed stream were then compared to selected feed compositions, which represented the extremes that could be fed to an alternative. This approach ensured the potential variations in chemical and radioactive components that could impact a process alternative were bounded. The development of the salt feed strategy and the assessment of the feed variation for each alternative is briefly discussed below.

#### 2.3.2.1.3 Tank Farm Strategy

The Tank Farm Strategy is the manner in which it is envisioned to empty the tanks in the tank farms. This analysis is performed by the ProdMod model, which has been extensively used for the development and annual revision of the HLW System Plans

(Reference 15). ProdMod contains sufficient detail so that a few important parameters can be tracked to determine the efficacy of a plan. ProdMod was run for the assumed life of an alternative, which is the time for all the salt in the tank farms to be processed. ProdMod uses one-year time steps and bases the waste composition for the salt solution feed on the yearly average of the tanks' content. ProdMod performs all the transfers expected within the HLW system along with evaporating waste.

Four ProdMod runs were made for Phase III, one for each alternative. These separate runs were made because of different projected start-up times and processing rates for each alternative. The different start-up times yielded slightly different strategies for the tank farms, and these differences are reflected in the early feed compositions. Once these strategies were developed, they were fed to a blending routine (TFARM) which generated the annual salt waste compositions.

#### 2.3.2.1.4 Flowsheet Salt Blending

Once the feed schedule to the alternatives was determined, it was necessary to develop the feed composition vectors. The feed vector consists of 51 compounds, but all were not calculated because those present in very small concentrations have no effect on the models. The concentrations of each compound were calculated based on the schedule provided by ProdMod. The schedule supplied both a transfer schedule and the amount transferred for all tanks in the tank farms. For each year of an alternative there is a unique feed stream composition. These feed streams compositions were then assessed to determine the periods of interest, and then these were run with the flowsheet model.

The initial tank composition and tank inventory was based upon the information contained in HLCATS, the chemical composition database of the tank farms. This database contains many more compounds than called for in the feed vector, so a reduced data set was created that reflected the desired compounds. The reduced data set maintained an overall mass balance, but partitioned ions between different compounds as required by the feed vector.



**Table 2.3-6 Small Tank Feed Compositions**

Component	Average	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8	Year 9	Year 10	Year 11	Year 12	Year 13	Year 14	Year 15
H <sub>2</sub> O, wt%	67.4	68.0	66.4	65.9	66.6	66.8	66.7	66.5	67.0	67.3	66.4	71.3	73.1	72.3	71.5	67.8
NaNO <sub>3</sub> , wt%	15.8	13.1	16.9	18.0	18.6	17.0	16.4	17.8	17.0	16.8	18.4	15.5	14.7	11.8	14.6	15.7
NaOH, wt%	7.56	8.99	6.60	6.07	5.64	6.81	6.84	6.44	6.39	6.79	6.46	6.20	5.53	7.11	5.82	6.52
NaNO <sub>2</sub> , wt%	3.09	4.72	3.68	3.05	2.39	3.09	3.66	2.62	3.32	2.94	2.23	1.63	1.22	3.83	2.51	3.82
NaAlO <sub>2</sub> , wt%	2.15	1.81	2.24	2.30	2.09	2.32	2.53	2.00	2.22	1.87	1.79	1.44	1.74	1.96	1.89	2.27
Na <sub>2</sub> SO <sub>4</sub> , wt%	1.76	0.83	1.74	2.04	2.32	1.88	1.75	1.94	1.86	2.08	2.32	2.00	1.89	1.31	1.67	1.80
Na <sub>2</sub> CO <sub>3</sub> , wt%	1.41	1.86	1.59	1.70	1.47	1.24	1.25	1.80	1.33	1.31	1.63	1.19	1.06	0.95	1.25	1.23
Other salts, wt%	0.67	0.56	0.74	0.85	0.80	0.70	0.75	0.67	0.70	0.70	0.67	0.57	0.54	0.64	0.63	0.76
KOH, wt%	0.074	0.086	0.063	0.061	0.069	0.076	0.067	0.074	0.079	0.083	0.094	0.095	0.093	0.067	0.062	0.049
NH <sub>4</sub> NO <sub>3</sub> , wt%	2.6E-03	3.2E-03	4.4E-03	4.2E-03	1.2E-03	2.6E-03	4.9E-03	2.2E-03	3.3E-03	3.3E-03	0	0	0	5.4E-03	2.7E-03	5.9E-03
CsOH, wt%	1.9E-03	2.6E-03	1.7E-03	1.4E-03	1.1E-03	1.4E-03	1.1E-03	1.5E-03	2.1E-03	1.5E-03	1.0E-03	8.8E-04	5.6E-04	3.6E-03	2.5E-03	2.3E-03
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> , wt% <sup>1</sup>	6.2E-03	0.011	6.3E-03	3.3E-03	5.0E-03	0.017	5.9E-03	0.043	0.038	0.011	0.032	0.016	0	1.7E-03	0	1.7E-03
Sr(OH) <sub>2</sub> , wt% <sup>2</sup>	1.8E-07	trace														
sludge, wt%	0.048	0.030	0.062	0.070	0.067	0.058	0.065	0.056	0.060	0.062	0.060	0.053	0.051	0.047	0.055	0.065
HgO, wt%	2.6E-03	2.7E-03	2.1E-03	1.7E-03	1.9E-03	2.7E-03	2.3E-03	2.6E-03	2.6E-03	2.5E-03	2.0E-03	1.9E-03	7.9E-04	2.8E-03	2.8E-03	2.4E-03
<b>Total, wt%</b>	<b>100.0</b>															
Density, lbs/gal	10.58	10.41	10.77	10.83	10.80	10.81	10.79	10.73	10.72	10.69	10.70	10.34	10.19	10.34	10.37	10.73
Density, Kg/L	1.267	1.247	1.291	1.298	1.294	1.295	1.293	1.285	1.285	1.281	1.283	1.239	1.222	1.240	1.242	1.286
Volume, Kgal/yr	4868	2593	5676	5521	5873	5709	5289	4548	4936	4738	4946	4625	4047	4684	4903	4930
Volume, m <sup>3</sup> /yr	18427	9816	21486	20901	22232	21610	20020	17216	18684	17934	18721	17507	15320	17733	18560	18662
[Na+], M	6.29	6.43	6.44	6.44	6.21	6.38	6.40	6.35	6.25	6.24	6.35	5.32	4.85	5.35	5.27	6.16
[K+], M	0.017	0.019	0.014	0.014	0.016	0.018	0.016	0.017	0.018	0.019	0.022	0.021	0.020	0.015	0.014	0.011
[Hg], mg/L	30	32	25	21	23	32	27	31	31	29	24	22	9	32	32	28
[ <sup>137</sup> Cs], Ci/gal	1.7	2.4	1.6	1.4	1.2	1.3	1.0	1.6	2.0	1.4	1.1	0.8	0.6	3.2	2.3	2.3
[ <sup>137</sup> Cs], Ci/L	0.44	0.63	0.42	0.37	0.32	0.34	0.26	0.42	0.53	0.37	0.29	0.21	0.16	0.85	0.61	0.61
Alpha, Ci/gal	3.2E-04	5.8E-04	3.3E-04	1.7E-04	2.7E-04	9.0E-04	3.1E-04	2.2E-03	2.0E-03	5.9E-04	1.7E-03	8.0E-04	0.0E+00	8.6E-05	0.0E+00	8.8E-05
Alpha, Ci/L	8.5E-05	1.5E-04	8.8E-05	4.6E-05	7.0E-05	2.4E-04	8.2E-05	5.9E-04	5.3E-04	1.6E-04	4.4E-04	2.1E-04	0.0E+00	2.3E-05	0.0E+00	2.3E-05
<sup>137</sup> Cs:K, Ci/mole	26.0	28.9	25.6	22.3	15.7	17.4	14.9	19.3	25.2	16.9	10.1	8.9	5.7	50.7	38.7	45.0

<sup>1</sup> The model grouped all Alpha into a single component for the purpose of tracking. See table 2.3-3 for breakdown of various alpha emitters.

<sup>2</sup> Strontium concentrations are extremely low and are not tracked in the model. See Table 2.3.4

**Table 2.3-7 CST Ion Exchange and CSSX Feed Compositions**

Component	Average	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7	Year 8	Year 9	Year 10	Year 11	Year 12	Year 13
H <sub>2</sub> O, wt%	67.4	65.6	67.0	65.8	66.1	68.1	67.2	65.6	67.7	65.8	68.6	70.0	69.5	77.8
NaNO <sub>3</sub> , wt%	15.8	19.4	15.2	19.1	19.1	13.4	16.6	19.8	14.1	19.8	17.1	14.0	14.5	9.77
NaOH, wt%	7.56	5.78	7.42	5.34	5.07	8.80	7.58	5.44	8.51	6.12	5.79	6.69	6.32	5.46
NaNO <sub>2</sub> , wt%	3.09	2.39	4.33	2.62	2.69	4.21	2.70	1.97	4.29	1.36	2.07	3.82	3.87	2.53
NaAlO <sub>2</sub> , wt%	2.15	1.92	2.26	2.24	2.22	2.51	2.14	2.02	1.90	1.99	1.75	2.09	2.19	1.54
Na <sub>2</sub> SO <sub>4</sub> , wt%	1.76	2.24	1.46	2.39	2.43	1.07	1.58	2.47	1.45	2.61	2.24	1.48	1.54	1.18
Na <sub>2</sub> CO <sub>3</sub> , wt%	1.41	1.84	1.42	1.48	1.41	1.15	1.54	1.80	1.23	1.51	1.66	0.98	1.23	1.23
Other salts, wt%	0.67	0.68	0.81	0.87	0.85	0.60	0.56	0.71	0.69	0.69	0.61	0.77	0.74	0.41
KOH, wt%	0.074	0.063	0.066	0.048	0.053	0.115	0.102	0.071	0.097	0.094	0.085	0.059	0.048	0.054
NH <sub>4</sub> NO <sub>3</sub> , wt%	2.6E-03	1.5E-04	6.1E-03	3.7E-03	3.4E-03	4.2E-03	4.9E-04	5.0E-04	4.4E-03	5.3E-02	3.6E-04	6.5E-03	6.3E-03	1.5E-03
CsOH, wt%	1.9E-03	1.3E-03	1.4E-03	9.6E-04	9.2E-04	2.1E-03	2.1E-03	1.6E-03	1.3E-03	8.7E-04	2.7E-03	2.3E-03	2.2E-03	3.7E-03
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> , wt%	6.2E-03	0.013	3.4E-03	1.8E-02	1.3E-04	7.6E-03	6.9E-02	1.3E-04	0.042	6.5E-06	2.4E-03	8.1E-03	1.1E-03	3.4E-03
Sr(OH) <sub>2</sub> , wt%	1.8E-07	trace												
sludge, wt%	0.048	0.062	0.060	0.078	0.079	0.040	0.040	0.066	0.054	0.070	0.053	0.063	0.061	0.025
HgO, wt%	2.6E-03	2.1E-03	2.0E-03	1.6E-03	1.6E-03	3.4E-03	4.0E-03	1.4E-03	3.5E-03	1.2E-03	1.9E-03	2.2E-03	2.3E-03	2.8E-03
<b>Total, wt%</b>	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Density, lbs/gal	10.58	10.80	10.71	10.91	10.84	10.63	10.67	10.86	10.58	10.85	10.54	10.51	10.54	9.86
Density, Kg/L	1.267	1.294	1.283	1.308	1.299	1.274	1.279	1.301	1.268	1.301	1.263	1.259	1.263	1.181
Volume, Kgal/yr	5531	4691	6443	6298	6056	6140	5464	5871	6506	6799	4968	5110	4708	2850
Volume, m <sup>3</sup> /yr	20937	17757	24391	23840	22924	23242	20685	22223	24626	25736	18807	19343	17820	10787
[Na+], M	6.29	6.43	6.44	6.35	6.21	6.43	6.40	6.39	6.43	6.43	5.81	5.69	5.76	4.09
[K+], M	0.017	0.015	0.015	0.011	0.012	0.026	0.023	0.017	0.022	0.022	0.019	0.013	0.011	0.011
[Hg], mg/L	30	26	24	19	19	40	48	16	41	14	23	26	27	30
[ <sup>137</sup> Cs], Ci/gal	1.7	1.2	1.3	0.9	0.8	1.9	2.0	1.5	1.2	0.7	2.5	2.1	2.0	3.2
[ <sup>137</sup> Cs], Ci/L	0.44	0.32	0.34	0.24	0.21	0.50	0.53	0.40	0.32	0.18	0.66	0.55	0.53	0.85
Alpha, Ci/gal	3.2E-04	6.8E-04	1.8E-04	9.6E-04	7.0E-06	3.9E-04	3.6E-03	7.0E-06	2.2E-03	3.5E-07	1.3E-04	4.1E-04	5.8E-05	1.7E-04
Alpha, Ci/L	8.5E-05	1.8E-04	4.7E-05	2.5E-04	1.8E-06	1.0E-04	9.6E-04	1.8E-06	5.8E-04	9.2E-08	3.3E-05	1.1E-04	1.5E-05	4.4E-05

**2.3.3 Basis for Other Waste Generated in the SWPF**

Solid waste and liquid byproduct waste generated from the two alternatives are summarized in Table 2.3-8 below. The DWPF Waste Forecast for FY2000 and other information from DWPF operations serve as the bases for these projected wastes (Reference 16).

**Table 2.3-8 Generated Waste 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 <sup>3</sup> /yr
Trans-Uranic 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 <sup>3</sup> /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 <sup>3</sup> /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 STTPB 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
Benzene (if acid hydrolysis process is included in SWPF)	Transferred to CIF for incineration. Credited as fuel for the incinerator.	208 m <sup>3</sup> /yr (54.9 kgal/yr)

Waste Classification	Description / Comments	Waste Quantity
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 CST Non-Elutable Ion Exchange Alternative. If subsequent process evolution and/or regulatory restrictions require mercury removal, then 1 column volume would be consumed every two years. Resin requires washing, dewatering and packaging for disposal as LLW.	None

The DWPF (S Area) forecasts the following mix of solid waste that must be handled for FY2000: (Reference 16)

- *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 solid wastes that will be transferred to Solid Waste for final treatment and disposal (or treatment and shipment to another disposal site). (Reference 16)
- *Benzene from Acid Hydrolysis*: If the STTPB alternative is chosen, then benzene will be generated as a byproduct stream. Benzene is recovered and stored in SWPF until it can be transferred to the Consolidated Incinerator Facility. The total 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. Using this volume and the largest potassium concentration expected over 10 years (year 10  $[K^+] = 0.022 \text{ M}$ ) as the basis (see Table 2.3-5), the bounding annual flow rate for potassium is:

$$(9.2 \times 10^3 \text{ kgal/yr})(3.7854 \text{ kL/kgal})(0.022 \text{ kg-mole/kL}) = 766 \text{ kg-mole } K^+/\text{yr}$$

The kg-moles of benzene, and the corresponding volume, are calculated from the moles of  $\text{TPB}^-$  sent forward to acid hydrolysis per mole of  $\text{K}^+$ . The moles of  $\text{TPB}^-$  added (1.60 kg-moles/kg-mole  $\text{K}^+$ ) must be corrected for the moles of  $\text{TPB}^-$  recycled with washes (0.2 kg-moles/kg-mole  $\text{K}^+$ ) and the portion of  $\text{TPB}^-$  (0.08 kg-moles/kg-mole  $\text{K}^+$ ) sent to Saltstone with decontaminated salt solution to obtain the moles sent to the acid hydrolysis process.

$$(766 \text{ kg-mol K}^+/\text{yr})[(1.6-0.26-0.05) \text{ kg-mol TPB}^-/\text{kg-mol K}^+] = 988 \text{ kg-mol TPB}^-/\text{yr}$$

To bound the mass and volume of benzene, 4 kg-moles are assumed for each kg-mole of  $\text{TPB}^-$  sent to acid hydrolysis. No adjustments are made for any degradation or vapor losses that may occur during processing or storage:

$$(988 \text{ kg-mol TPB}^-/\text{yr})(4 \text{ mol benzene/mol TPB}^-) = 3952 \text{ kg-mol benzene/yr}$$

Based on a molecular wt of 78.11 kg/kg-mol and a liquid density of 0.879 kg/L (879 kg/kL), the mass and volume of benzene produced is calculated as follows:

$$(3952 \text{ kg-mol benzene/yr})(78.11 \text{ kg/kg-mol}) = 3.09 \times 10^5 \text{ kg benzene/yr}$$

And:

$$(3.09 \times 10^5 \text{ kg benzene/yr}) / (879 \text{ kg/kL})(1 \text{ m}^3/\text{kL}) = 351 \text{ m}^3/\text{yr} (92.7 \text{ kgal/yr})$$

This calculated volume of benzene bounds the volume generated for each year that the STTPB process operates. For the range of annual volume and potassium molarity shown in Table 2.3-6 for the projected 15-year operating period, the annual volume of benzene produced ranges from 223  $\text{m}^3/\text{yr}$  (59 kgal/yr) in year 3 to 351  $\text{m}^3/\text{yr}$  (92.7 kgal/yr) in year 10. By the tenth year of operation, sufficient tank space should be available to enable additional blending, if needed, to avoid higher  $\text{K}^+$  concentration in feed solution that would lead to benzene production that exceeds the recommended bounding value.

### **3.0 DECISION PHASE ALTERNATIVES**

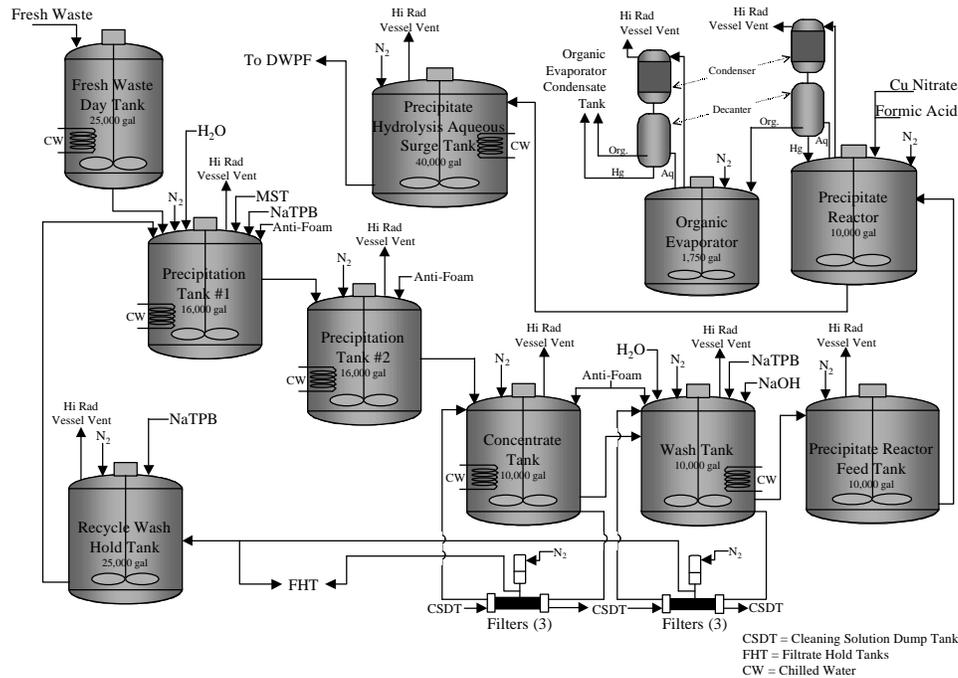
#### **3.1 Small Tank TPB Precipitation**

##### **3.1.1 Alternative Description**

In the Small Tank Tetraphenylborate (STTPB) precipitation process, soluble ions of cesium, potassium and ammonium are precipitated as insoluble TPB salts. Soluble mercury ions react with TPB to form insoluble diphenylmercury. Strontium, uranium, 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 the phenylborate decomposition is stored until it can be burned in the CIF. The radioactive precipitate hydrolysis aqueous (PHA) is transferred and stored until it can be incorporated into glass in the DWPF. The decontaminated salt solution, or filtrate, containing primarily sodium salts of hydroxide, nitrate, and nitrite, is transferred to Z Area for processing and disposal as Saltstone.

##### **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 3.1-1 (Reference 17). In the first CSTR, salt solution is mixed with process water, recycled wash water, a solution of sodium tetraphenylborate (NaTPB or  $\text{NaB}(\text{C}_6\text{H}_5)_4$ ), and monosodium titanate slurry (MST or  $\text{NaTi}_2\text{O}_5\text{H}$ ). 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  $^{137}\text{Cs}$ . Sodium tetraphenylborate is added to precipitate the cesium as a tetraphenylborate salt. The non-radioactive potassium, cesium, ammonium and mercury ions 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 in Saltstone.



**Figure 3.1-1 Small Tank TPB Simplified Flow Diagram**

**Concentration**

The slurry exiting CSTR Tank #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 Saltstone. When 4000 to 5000 gallons of 10 wt% TPB precipitate slurry is accumulated in the Concentration Tank, it is transferred to the Wash Tank.

**Precipitate Washing**

The slurry is then 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 Saltstone. The washing endpoint is set at 0.01 M  $\text{NO}_2^-$ . All of the vessels used in this part of the process are stainless steel to eliminate corrosion concerns.

### **Precipitate Hydrolysis**

The washed precipitate is then reacted with formic acid and cupric nitrate. The reaction decomposes most of the phenylborates into benzene, which is condensed and decanted, and leaves PHA. Small amounts of aniline, diphenylamine, and other organic species are the result of various side reactions in the Precipitate Reactor and leave with the benzene. The PHA, which contains the radioactive ions, is transferred to DWPF to be solidified as borosilicate glass. The benzene is concentrated and stored until it can be burned in the CIF.

### **Assumptions for Modeling Filter Washing**

For this 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 cycle consists of:

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

### **Benzene Generation**

After precipitation, NaTPB, KTPB and CsTPB undergo radiolytic degradation (See Section 3.1.3.4) and, under certain conditions, catalytic degradation (See Section 3.1.3.5). 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 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 3.1.3.4 and 3.1.3.5.

The benzene generation will be set at 10 mg/L-hr when soluble NaTPB is present and 1 mg/L-hr when only KTPB and CsTPB are present. These have been set at these maximum values to match the current test results by SRTC for decomposition at 25°C (Reference 18).

The Small Tank TPB Precipitation operating conditions are outlined in Table 3.1-1.

**Table 3.1-1 Small Tank Tetraphenylborate Operating Parameters**

Parameter	Operating Specification
Excess TPB	60 mole%
Na <sup>+</sup> Concentration after precipitation	4.7 M
<sup>137</sup> Cs Concentration after precipitation	< 35 nCi/g
Alpha Concentration after Titanate addition	<18 nCi/g (Ref. 1)
Maximum Temperature	25 °C
Maximum filtrate rate	Determined by the model to allow future filter sizing
Wash Rate	Determined by the model to allow future filter sizing
Washing Endpoint	0.01 M NO <sub>2</sub> <sup>-</sup>
Cu <sup>+</sup> concentration during hydrolysis	900 ppm
Formic acid after hydrolysis	0.25 M
Final organic concentration (phenylboric acid)	< 53 ppm
Final diphenylmercury	< 260 ppm

### 3.1.2 Research and Development

The scope of the research and development for the small tank process focused on four areas: alpha removal kinetics, precipitation kinetics, filtration of the tetraphenylborate slurry, and impact of coupled operation with DWPF. The alpha removal kinetic studies were focused on insuring that the CSTR size specified during Phase III would produce the necessary alpha decontamination. 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 new continuous operation and to insure that the filters in the small tank process were sized properly. 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.

#### 3.1.2.1 Alpha Removal Kinetics

Experimental work (References 19, 20, 21) 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 Z-Area limits when 4.5 M Na<sup>+</sup> salt solutions are treated with 0.4 g/L MST. Table 3.1-2 shows the decontamination requirements for these species (it is the same as Table 2.3-4).

**Table 3.1-2 Sr and Alpha Removal Requirements**

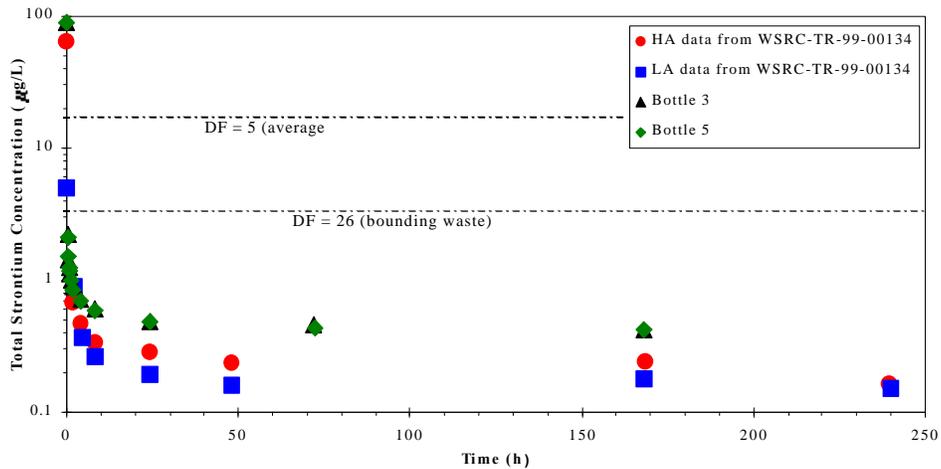
Component	Concentration		Activity		Saltstone WAC (nCi/g)	Required DF Avg / Bound
	Average (mg/L)	Bounding (mg/L)	Average (nCi/g)	Bounding (nCi/g)		
Pu/Am	0.20	1.0 <sup>1</sup>	205	1000 <sup>1</sup>	18 (total α)	12 / 55
U	59.1	1030 <sup>2</sup>	0.024	0.62 <sup>2</sup>	18 (total α)	1 / 1
Np	0.016	1.8 <sup>3</sup>	0.009	1.0 <sup>3</sup>	0.03	1 / 33
Sr	0.0016	0.0095 <sup>4</sup>	178	1050 <sup>4</sup>	40	5 / 26

<sup>1</sup> Based on predicted 5X TRU spike from blended feed studies  
<sup>2</sup> Based on U in Tank 40: 4.3 Ci in 1.44 M gallons (at 6.0 M Na<sup>+</sup>)  
<sup>3</sup> Based on Np-237 in Tank 34: 1.8 Ci in 1.49 M gallons (at 6.0 M Na<sup>+</sup>)  
<sup>4</sup> Based on Sr-90 in Tank 19: 1280 Ci in 0.256 M gallons (at 6.0 M Na<sup>+</sup>)

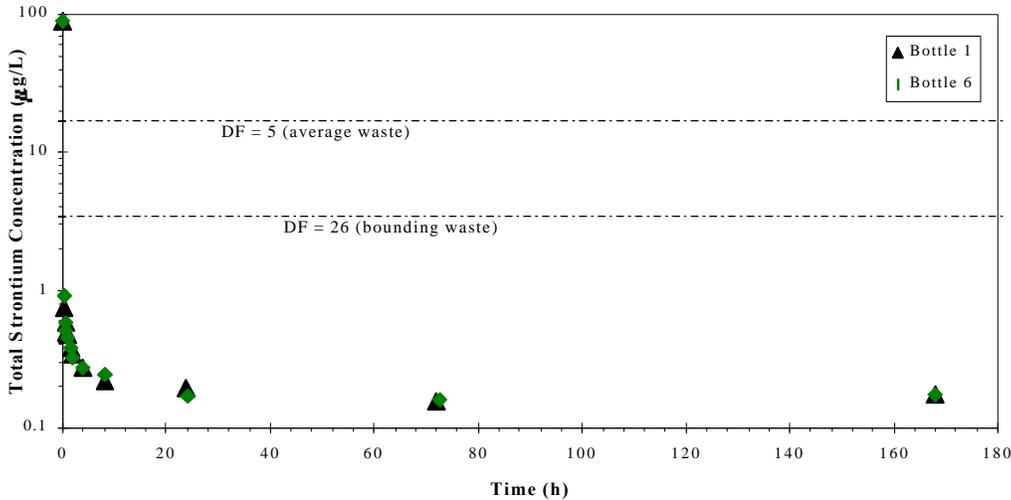
Data for Sr, Pu, and U removal at 4.5 M Na<sup>+</sup> with 0.2 and/or 0.4 g/L MST (Reference 20) are shown in Figures 3.1-2 through 3.1-5. As seen in the above table, U has such a low specific activity that U removal is not required. Data were also collected on removal of Np. Np DFs are insufficient to remove the peak Np concentrations (Tanks 33 and 34); blending will be required to meet the Saltstone specification for Np.

Strontium removal

Figures 3.1-2 and 3.1-3 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 (Reference 32). In Figures 3.1-2 and 3.1-2, 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 3.1-2 Comparison of Strontium Concentration Tests at 4.5 M Na and 0.2 g/L MST**

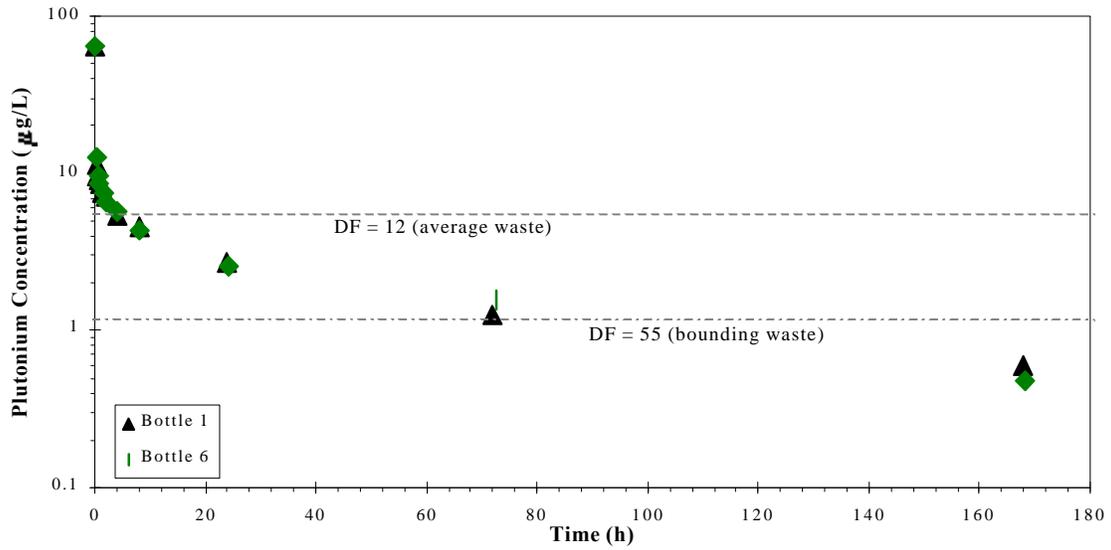


**Figure 3.1-3 Comparison of Strontium Concentration Tests at 4.5 M Na and 0.4 g/L MST**

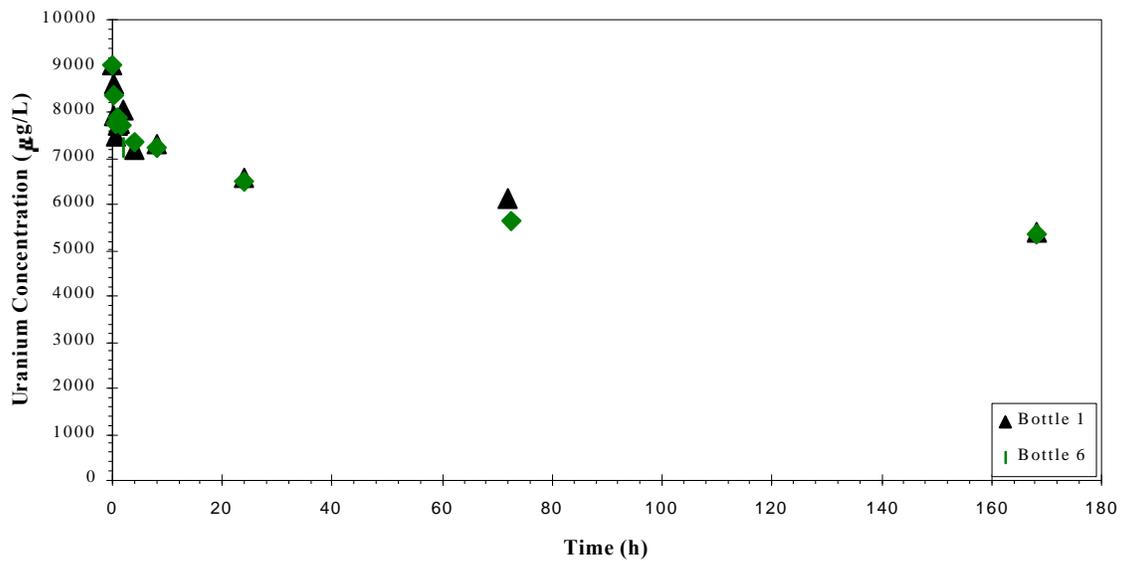
### Plutonium removal

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) and 1.15 µg/L is required for a DF of 55 (DF for bounding waste). As shown in Figure 3.1-4, 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 either process.

Note in Figure 3.1-5, 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 those tests, a DF of ~ 2 was obtained in the two-CSTR system with a total residence time of 16 hours (two-thirds of design) (Reference 32). Therefore, it is reasonable to expect a Pu DF of > 12 in the Small Tank TPB Precipitation process.



**Figure 3.1-4 Comparison of Plutonium Concentration Tests in 4.5 M Na and 0.4 g/L MST**



**Figure 3.1-5 Comparison of Uranium Concentration Tests at 4.5 M Na and 0.4 g/L MST**

### 3.1.2.2 Precipitation Kinetics

The rates of cesium and potassium precipitation using tetraphenylborate (TPB) from moderately concentrated (3.5 to 7.0 M Na<sup>+</sup>) mixed salt solutions have been studied for some time (Reference 22). The solutions tested are made up to simulate ranges of sodium, potassium and cesium expected in real waste solutions. The estimation of 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 tests, the re-dissolution rate of NaTPB clearly influences the rates of potassium and cesium precipitation. The discussion that follows relates to sodium concentration of about 4.5 M, which is the range of interest.

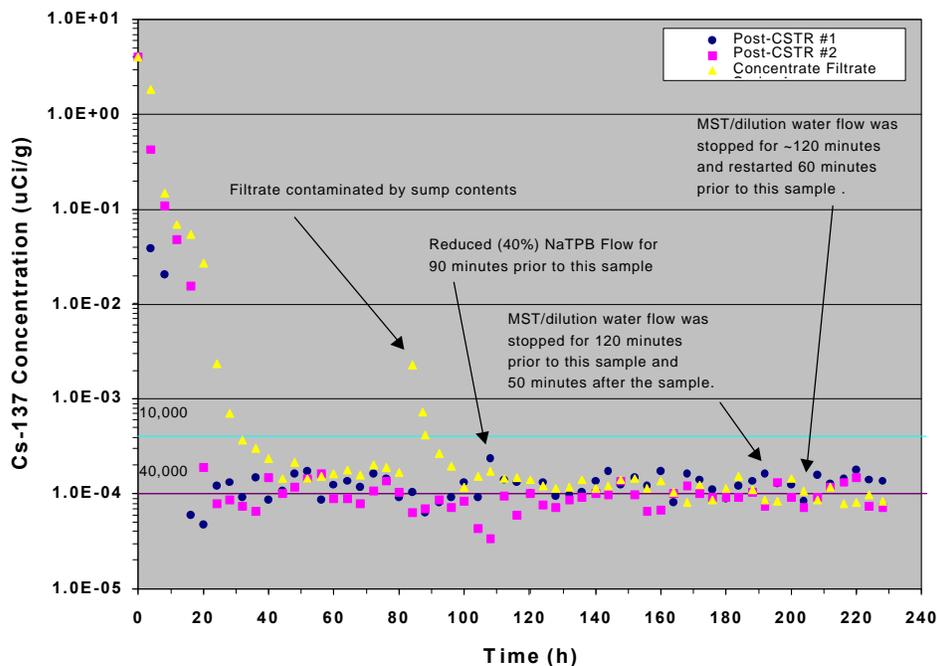
Initial experiments at SRTC were done in a single 500-mL CSTR with an 8-hour mean residence time. These tests were run at 4.7 M [Na], and 60 % molar excess of NaTPB (i.e. 1.6 times the sum of the cesium and potassium molarity). The reaction started with cesium and potassium pre-reacted so the concentration 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 (Reference 23). NaTPB was fed at 0.55 M, near its solubility limit in water.

Oak Ridge National Laboratory (ORNL) conducted larger scale (15-L) 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. TPB was added at 1.60 moles per mole of potassium plus cesium (“60 % molar excess”). A stoichiometric quantity of TPB was fed as a 0.55 M solution while the excess was provided by TPB 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) (Reference 24 and 25).

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 the TPB 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 TPB 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 TPB 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 and precipitate potassium and cesium in the time it remained in the reactor (Reference 26). However, the utility of the TPB added with the recycle water at ORNL is much greater – estimated to be 70%. These phenomena were modeled semi-quantitatively, as discussed in Section 3.1.3.2. The

results of this modeling provides sufficient understanding of the reaction rates to size reactors for a full scale Salt Disposition Facility.

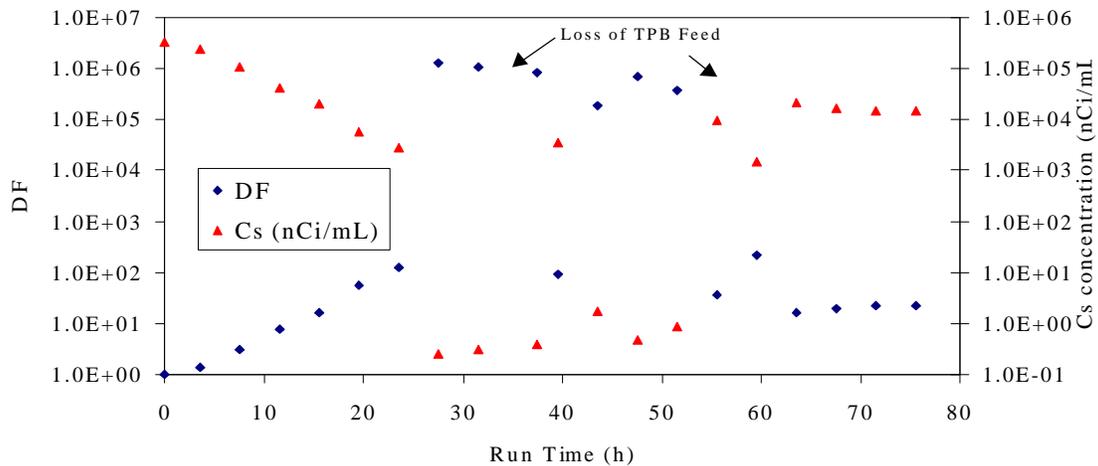
ORNL ran a second closed-loop test in which the concentrated precipitate was washed and the wash water recycled. The feed also contained the enhanced catalyst system (ECC) with 5X the Pd (Reference 25). This test lasted approximately 10 days and produced four batches of concentrated precipitate. The DF for the decontaminated salt solution varied from 30,000 to 60,000 (See Figure 3.1-6). Generally, the process operated smoothly except that only about 10% to 20% of the excess TPB was recovered during washing. The cause of the low NaTPB recovery in the wash step is not known. Possible causes are inadequate mixing or a crystalline form that is not readily dissolved – even at low Na concentrations. 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 3.1-6 ORNL Integrated Demo Test 2**

SRTC subsequently ran a real waste test using two-CSTRs with 60% excess TPB – again with 8-hour residence times (Reference 27). In that 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 and the observed DF returned to  $1 \times 10^6$  or greater. Towards 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 3.1-7).



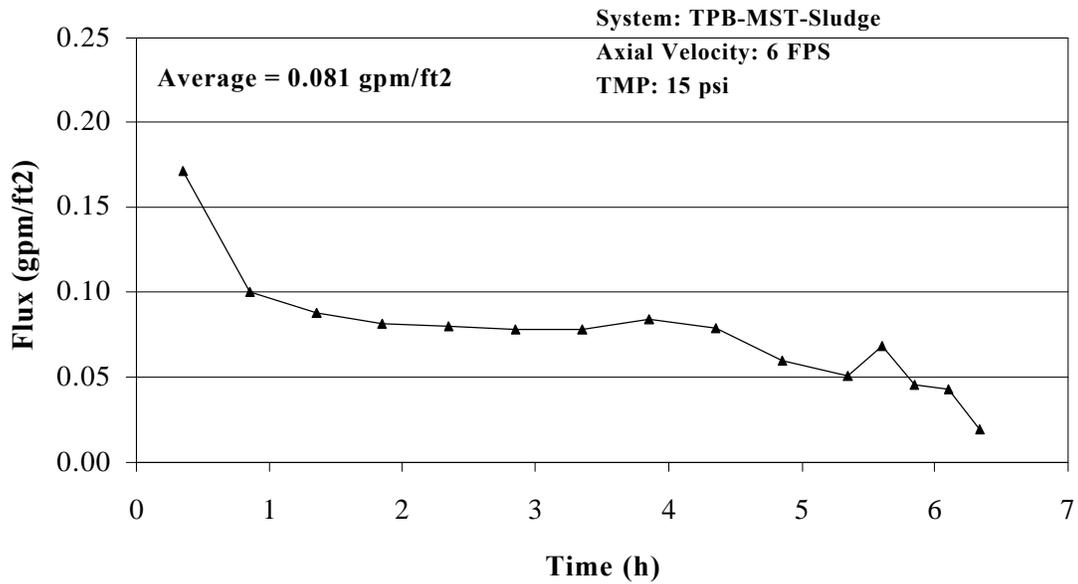
**Figure 3.1-7 Cesium Results from Cells CSTR Testing**

Based on test and modeling results, the design CSTR residence times remain at 10 hours. However, since the cause of the low TPB recovery during washing is not known, modeling and the material balance will assume only 30% recovery of NaTPB 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).

**3.1.2.3 Filtration Results**

Recent studies have been completed by SRTC to evaluate crossflow 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. (Reference 28)

Flux rates from these studies averaged from  $0.081 \text{ gpm/ft}^2$  (See Figure 3.1-8) for an axial velocity of 6 fps and 15 psi transmembrane pressure. For design purposes, a flux of  $0.04 \text{ gpm/ft}^2$  is assumed for similar operating parameters. The resulting filter size is provided in Table 3.1-3.



**Figure 3.1-8 Sample Filter Flux Profile during Concentration**

**Table 3.1-3 Small Tank Filter Sizing Results**

<b>Filter</b>	<b>Filter Area (FT2)</b>	<b>Filter Tubes (10 ft long)</b>	<b>Filter Flow Rate (gpm)</b>	<b>Filtrate Flow Rate (gpm)</b>
Concentrate	500	250	1000	20
Wash	250	125	500	10

### 3.1.2.4 Coupled DWPF Operation

This research focused on glass variability studies.

#### Glass Variability

The Small Tank TPB Precipitation process will require higher PHA loading and MST loading ( $\text{TiO}_2$ ) 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%  $\text{TiO}_2$  in the glass (Reference 29). 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

### 3.1.2.5 Precipitate Washing

Precipitate washing performs three functions:

- washes soluble nitrite down to  $\leq 0.01$  M for proper Precipitate Hydrolysis operation,
- at the same time, washes the  $\text{Na}^+$  to a level acceptable for glass production, and
- recovers a portion of the excess NaTPB and recycles it to CSTR #1.

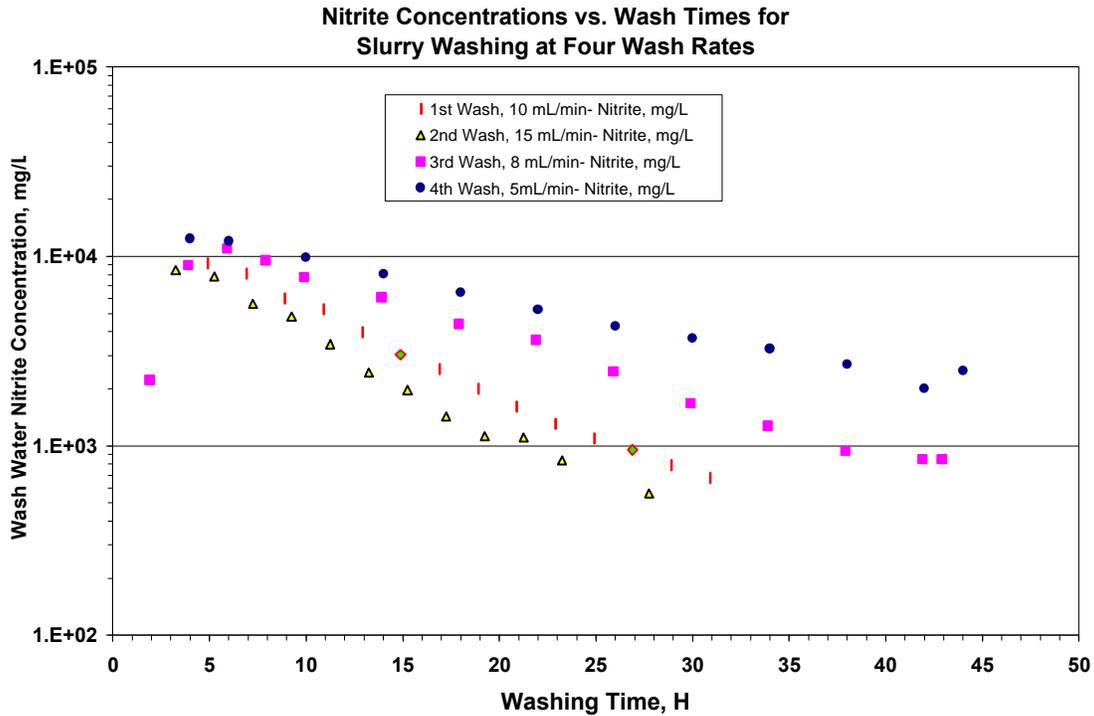
As unreacted, excess NaTPB flows from CSTR #2 to the Concentrate Tank (CT) and to the Wash Tank (WT), it will split to three different paths as follows:

- 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  $\text{TPB}^-$  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 KTPB, CsTPB, etc, about 5 % (0.08/1.6) is lost to the DSS, and the remaining 32.5 % is potentially recoverable in the wash step. Based on prior tests (Reference 28), it was expected that about 80 % of the NaTPB fed to the WT (26 % of the total) would be recovered by dissolution in the wash water. The rest (6.5 % of the total) would be lost to the Precipitate Hydrolysis process. In other words, it was expected that washing would be 80 % efficient based on the NaTPB fed to the wash step.

The second CSTR test at ORNL operated closed loop. That is, concentrated precipitate was washed and the spent wash water recycled to the first CSTR. The progress and efficiency of washing is 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. In fact, washing is completed when the nitrite in the spent wash water is  $\leq 0.01$  M. Figure 3.1-9 shows the nitrite concentration versus time

and Table 3.1-4 shows NaTPB recovery for the four washes performed during ORNL CSTR Test 2 (Reference 32).



**Figure 3.1-9 Nitrite Concentration versus Time for ORNL Washing**

The wash step for Small Tank TPB Precipitation 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  $\tau$  is the residence time or  $\frac{\text{volume to be washed}}{\text{wash rate}}$ .

It then can be shown the theoretical wash water requirement is

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

These relationships indicate the log of the nitrite concentration versus time should be a straight line – as is evident in Figure 3.1-9. 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 3.1-9 should have been steeper than they are – thus indicating that washing was less than 100 % efficient.

There are three possible contributors to the inefficiency: the level measurement, a heel from the previous wash, and poor mixing. First, the tank level was measured by  $\Delta P$ . 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 is constant. Second, even though the ORNL wash tank drains from the bottom, there is a “heel” of water left from the previous wash which dilutes the precipitate and increases the actual wash volume. This water is in the cross-flow filter and the tubing. Third, as previously discussed, there was probably insufficient mixing. In fact, it was observed that the surface in the wash tank was not moving.

**Table 3.1-4 ORNL 20 L CSTR Wash Results**

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

\* Expected recovery was 80 %

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.

It is highly likely that TPB recovery can 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 (Reference 28). Note also that recovery improves when the washing rate is slower providing 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 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.

Regardless, the NaTPB recovery is assumed to be poor for the Phase IV material balances. For the purposes of the Phase IV material balance, the wash step is assumed to be only 40 % efficient. That is, of the 32.5 % of NaTPB added that comes to the Wash Tank, only 40 % of that is recovered and recycled; the rest goes to Precipitate Hydrolysis. In other words, of the 1.60X stoichiometric NaTPB that is added, 1.00 goes to precipitating  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$  and  $\text{Hg}^{+2}$ , 0.08 is soluble in the DSS, 0.32 goes with the MTPB to Precipitate Hydrolysis and only 0.20 is recovered and recycled.

### 3.1.2.6 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 (Reference 30). However, at this concentration and somewhat reducing conditions, metallic copper is present. Then, hydrolysis was performed on unirradiated and irradiated TPB precipitate slurries with 1800 ppm Cu (Reference 31). Both achieved more than satisfactory Phenylboric Acid (PBA) removal (a primary criterion for complete reaction). More tests will be required to optimize excess formic acid, catalyst concentration, reaction times and other process parameters. 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.

### 3.1.2.7 Computational Fluid Dynamic Modeling

A computational fluid dynamics model was developed to assess the mixing performance of several of the vessels of the Small Tank Tetraphenylborate 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 32 and 33. 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 36652 cells. Sensitivity was run with approximately double the number of computational cells, but no differences in the results were seen. 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 ingest 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

$\tau_0$  = 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

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

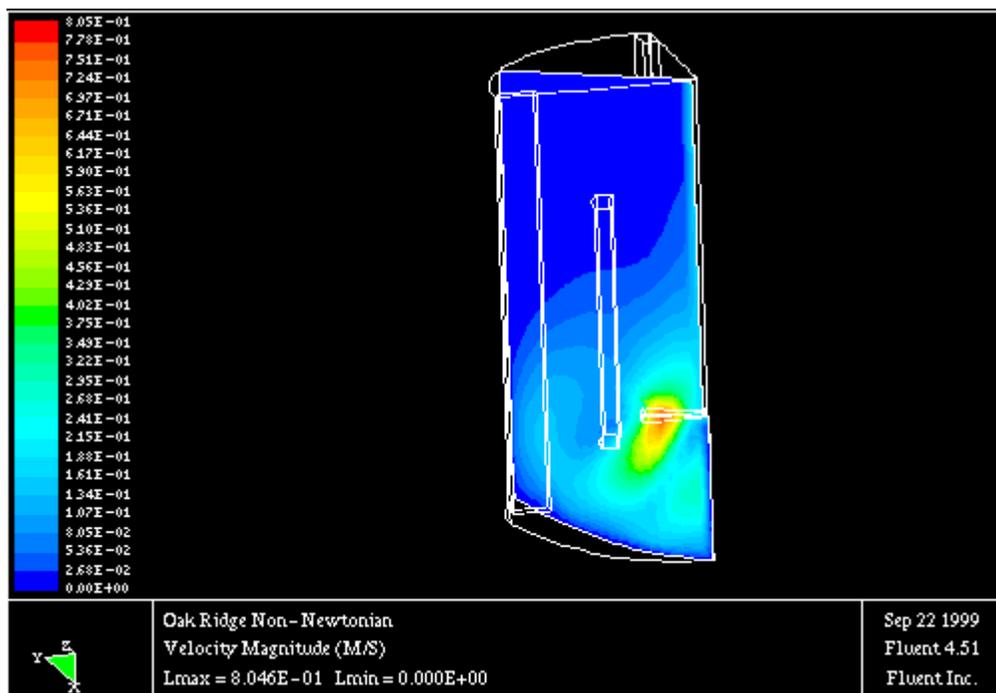
Where

$n = 1$  for a Bingham plastic

$k$  = slope after yield (linear for Bingham plastic)

The slope for this case was derived from Reference 34. The 10-wt% slurry has very high critical shear and yielding viscosity, 260 dynes/cm<sup>2</sup> and 46 cp respectively. With these values one would not expect much fluid motion, and that was indeed the case. The calculation showed 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 type impeller. One of these types of impeller would by necessity move more slowly, but by being able to engage more of the slurry would provide better, and faster, mixing. With the design as it now is, the theoretical limit of the wash will not be approached.

Figure 3.1-10 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 3.1-10 Velocity Contours for the 10 Wt% Slurry Case**

### 3.1.3 Bases for Flowsheet Models

The SPEEDUP™ representation of the Small Tank TPB Precipitation 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 small tank 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 with 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 and grout processes, 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.

### 3.1.3.1 Alpha Removal Bases

Experimental work (References 19, 20, and 21) 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,  $K_d$ , (see Table 3.1-13) as the basis for the Small Tank TPB 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  $^{90}\text{Sr}$  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 3.1-5

**Table 3.1-5 Sr Equilibrium Factors**

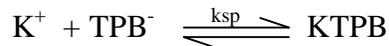
Constants	Value
<i>a</i>	90
<i>b</i>	340
<i>c</i>	58.6
<i>d</i>	725
<i>e</i>	363

### 3.1.3.2 Cs Decontamination by Tetraphenylborate Precipitation

#### Solubilities

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

The reaction stoichiometry for the tetraphenylborate reactions with Cs, K, Na, and NH<sub>4</sub> are shown below:



The activity coefficients (Reference 36) were determined using commercially available software as:

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

$$\gamma_{\text{K}} = 0.0284 I_m^2 - 0.219 I_m + 0.777$$

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

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

Where  $\gamma$  is the activity coefficient and  $I_m$  is the molar scale ionic strength of the solution:

$$I_m = 0.5\{(Z_a^2 \times M_a) + (Z_b^2 \times M_b) + (Z_c^2 \times M_c) + \dots\}$$

Where  $Z$  is the ionic charge of the ions and  $m$  is the molar concentration (moles /1000 g solvent).

Cesium or potassium concentrations in solution can then be determined by rearranging:

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

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

Because the sodium ion concentration is so high and almost constant, the TPB in solution can be determined by rearranging:

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

The activity of an ionic species is solved by:

$$K_{sp} = (a_{m+})(a_{x-})$$

Where 'a' is the activity of the ionic species and

$$a_m = \gamma_m [M]$$

After Reference 36 was issued the solubility of TPB in high salt concentrations containing potassium was questioned. Subsequent laboratory tests (Reference 37) 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. Limited solubility data is provided in this reference 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 Kinetics

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<sub>s</sub>, solid NaTPB concentration, moles per liter  
KT<sub>s</sub>, solid KTPB concentration, moles per liter  
Solid cesium is not tracked because it does not affect the material balance much and dissolves very slowly.

f, subscript for the feed condition  
\*, any concentration at equilibrium

M<sub>NT</sub>, mass transfer coefficient for dissolution of NaTPB, dimensionless – the value is a function of the nature and quantity of the solids.

M<sub>KT</sub>, mass transfer coefficient for dissolution of KTPB, dimensionless

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

k<sub>N</sub>, NaTPB precipitation rate constant, l/mol-hr  
k<sub>K</sub>, KTPB precipitation rate constant, l/mol-hr  
k<sub>C</sub>, CsTPB precipitation rate constant, l/mol-hr  
K<sub>N</sub>, NaTPB solubility product, mols<sup>2</sup>/l<sup>2</sup>  
K<sub>K</sub>, KTPB solubility product, mols<sup>2</sup>/l<sup>2</sup>  
K<sub>C</sub>, CsTPB solubility product, mols<sup>2</sup>/l<sup>2</sup>

$\frac{F}{V}$ , Flow rate per volume, inverse of the residence time, hr<sup>-1</sup>

### 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 of 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 represents 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 the 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 were taken to drive concentrations to equilibrium.

$M_{NT} = NT_s / (T_f - K_f - C_f - T^*)$  The denominator is approximately the amount of solid made when all species have equilibrated. It ignores the small amounts of potassium and cesium still in solution. This forces the mass transfer coefficient to 1, when all species are equilibrated.

$M_{KT} = KT_s / K_f$ , this forces the potassium concentration to equilibrium when all precipitation is complete.

### 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 3.1-6 summarizes the conditions and rate constants used.

**Table 3.1-6 Concentrations and Conditions for Batch Precipitation**

	[TPB]	[K <sup>+</sup> ]	[Cs <sup>+</sup> ]
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
	<b>NaTPB</b>	<b>KTPB</b>	<b>CsTPB</b>
Solubility Product, mols <sup>2</sup> / l <sup>2</sup>	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 3.1-11 shows the progression of the batch reaction. Initially, the TPB left in solution precipitates as CsTPB and KTPB. Then the NaTPB solids, which were precipitated when the NaTPB solution was added, re-dissolve and precipitate KTPB and CsTPB. When the potassium is precipitated quantitatively, the cesium can precipitate to the low level desired. After about 10 hours, the solution is 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 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 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 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, but the calculation 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 provides 60% (i.e. – the excess over stoichiometric requirements).

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

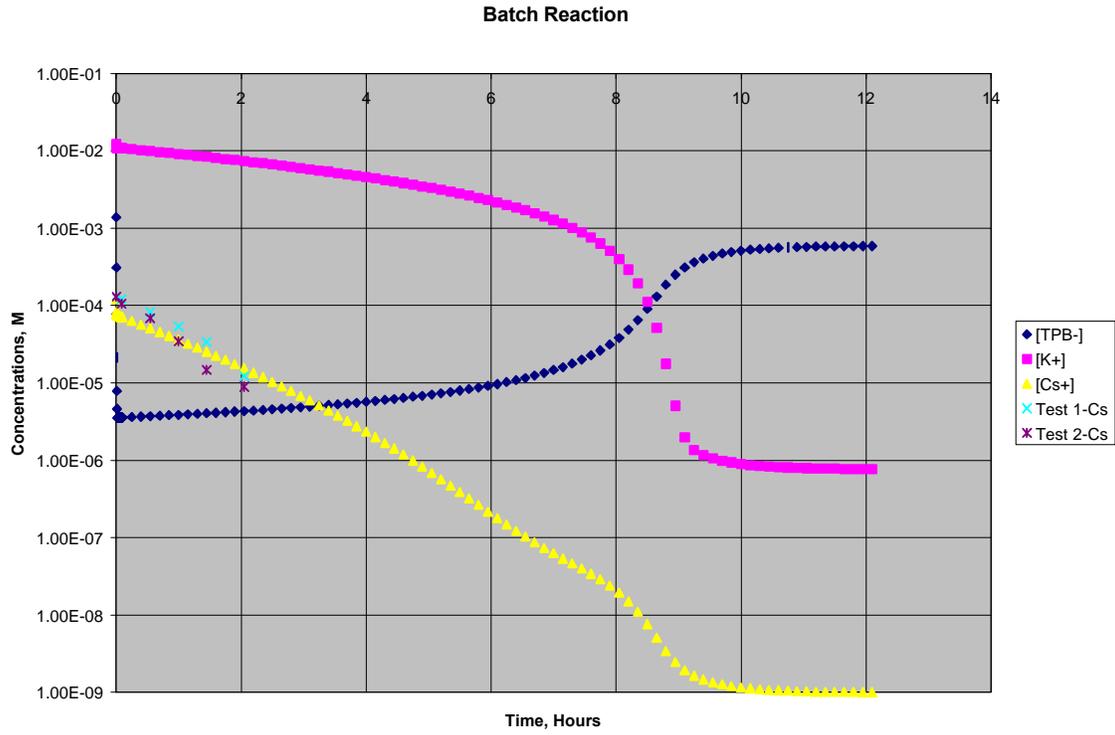
**Table 3.1-7 Concentrations and Conditions for CSTR Precipitation**

	[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%		
	[TPB-]	[K+]	[Cs+]
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, mols <sup>2</sup> / l <sup>2</sup>	2.95E-03	4.53E-10	5.92E-13
Precipitation Rate Constant, l/mol-hr	2.66E-01	5.00E+04	2.00E+05

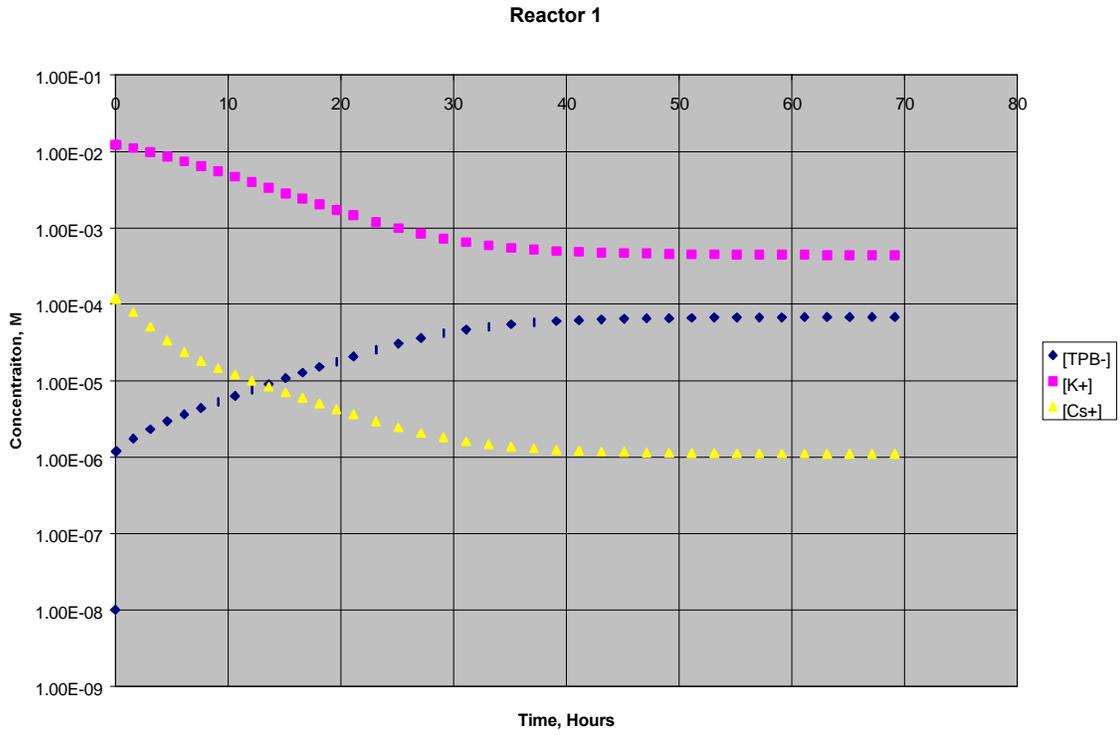
Figure 3.1-12 shows the concentration response in the first reactor. The cesium and potassium concentrations drop smoothly as the TPB concentration increases. *[Please note: a functioning plant would not operate in this manner. Both reactors would probably be inventoried with feed and TPB and the reactions would have occurred before the continuous feeding into the first reactor and out of it and the second reactor would start. Furthermore, the NaTPB re-dissolution rate used here is probably somewhat low]*

*in order that the two reactors would be different (for the purpose of illustration). In testing, both reactors have achieved DF and their time dependent concentrations are nearly identical, except for lag time it takes the second reactor to get to steady state.]*

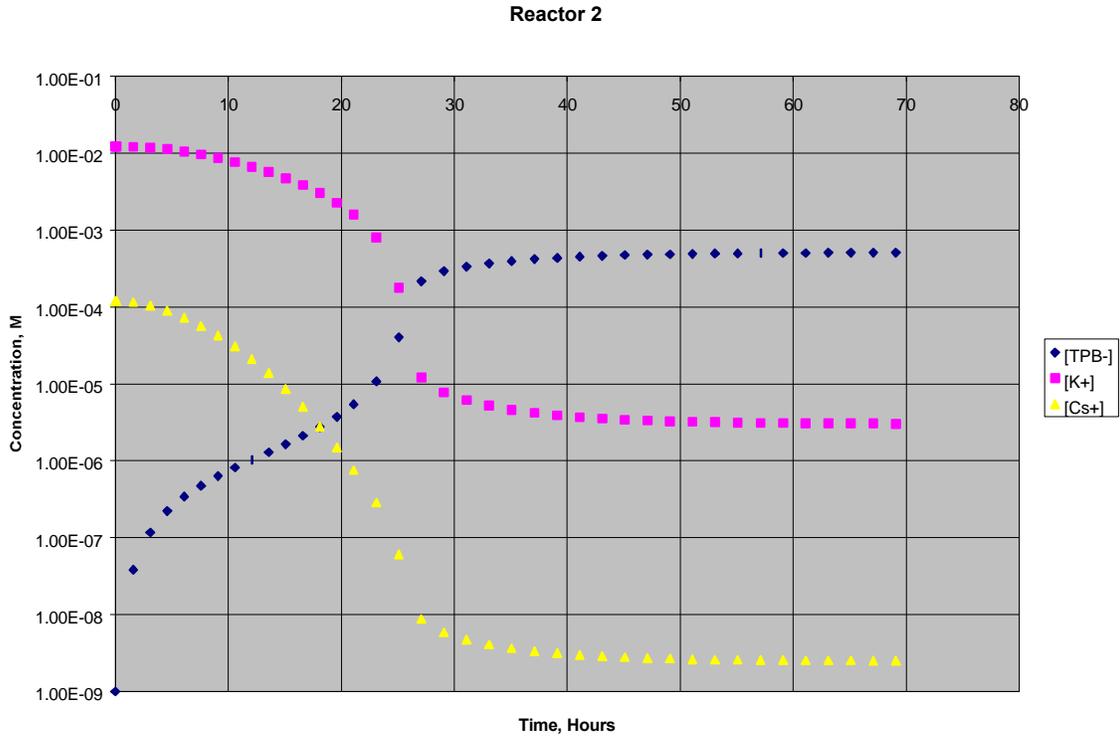
As can be seen in Figure 3.1-13 potassium and cesium concentration drop slowly in the second reactor until the TPB concentration exceeds the potassium. Then both cesium and potassium precipitate rapidly. After both reactors are at steady state, the concentrations are time invariant, with the amount of potassium and cesium precipitating equaling the amount fed to each reactor.



**Figure 3.1-11 Progression of Batch TPB Reaction**



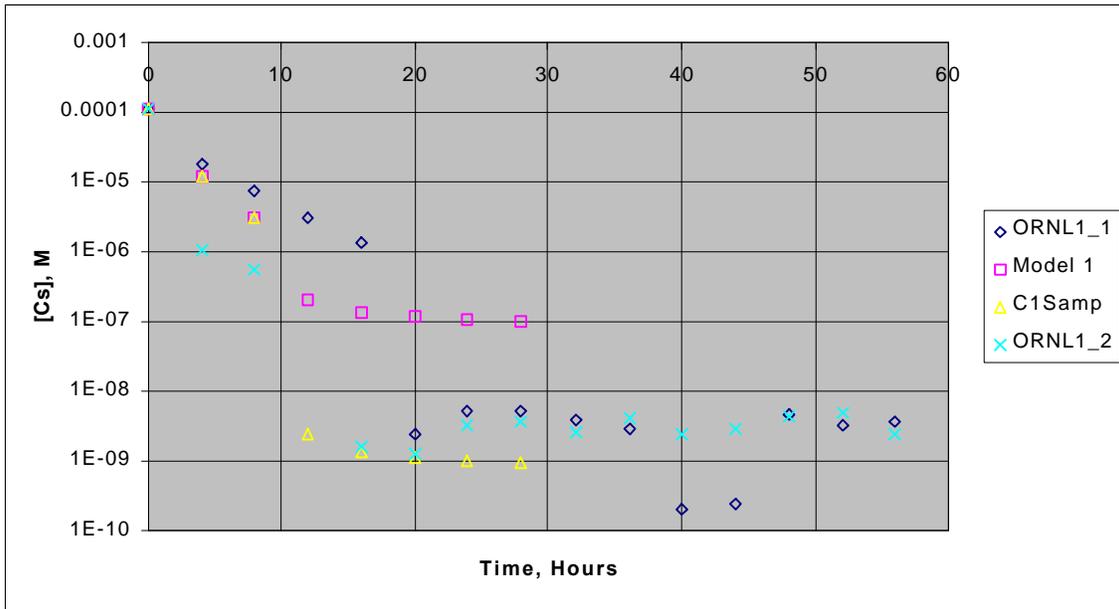
**Figure 3.1-12 Concentration Response in First Reactor**



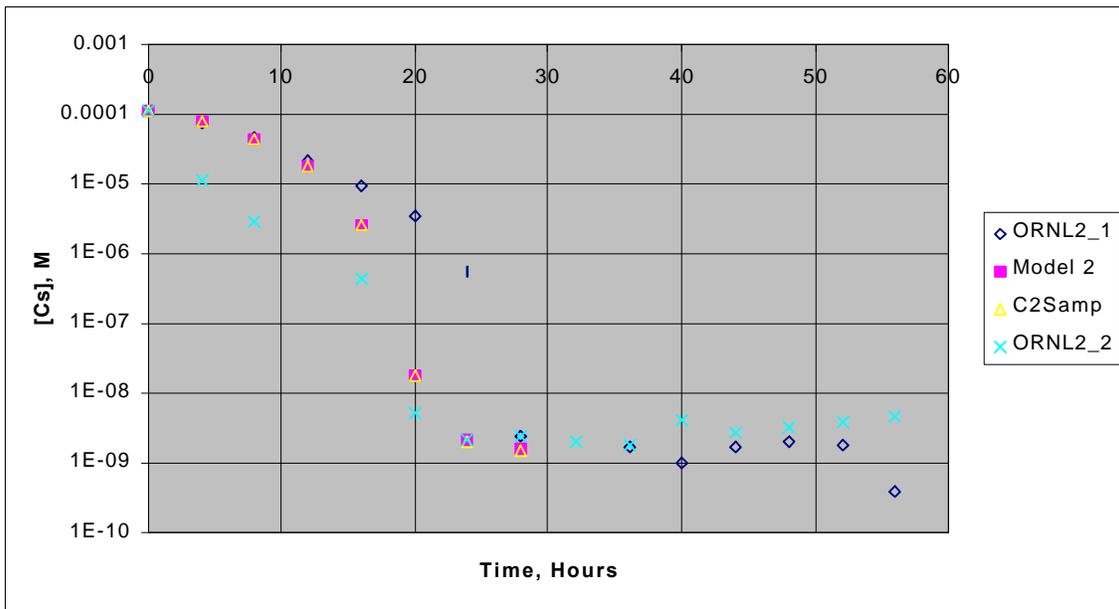
**Figure 3.1-13 Concentration Response in Second Reactor**

**Table 3.1-8 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



**Figure 3.1-14 ORNL CSTR #1 vs. Model**



**Figure 3.1-15 ORNL CSTR #2 vs. Model**

As discussed above (Reference 38), NaTPB precipitates and the solids re-dissolve 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 quickly.

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 desired levels.

Table 3.1-8 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. The model predicted 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 of eleven of twelve experiments. In test 9.2, cesium and potassium (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 there is a greater excess of TPB 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 3.1-12 and 3.1-13 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.

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.

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 unprecipitated 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.

### 3.1.3.3 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 (Reference 39):

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

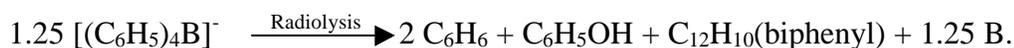
$$\text{When: } ([NO_3^-] + 0.5 * [NO_2^-])^{1/3} \leq 1$$

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

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

### 3.1.3.4 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 (Reference 40). The above equation approximates the experimental results.

The G value for the formation of benzene from the radiolytic decomposition of TPB is  $0.71 \pm 35\%$  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:

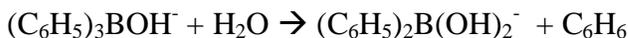
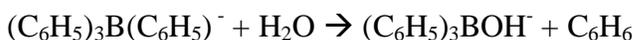
$$= \frac{0.96 \text{ molecules}}{100 \text{ eV}} * \frac{4.84 \text{ watts}}{1000 \text{ Ci}} * \frac{1 \text{ eV/sec}}{1.6\text{E}-19 \text{ watts}} * \frac{25 \text{ Ci}}{\text{gal}} * \frac{1 \text{ gal}}{\text{L}} * \frac{78,120 \text{ mg}}{6.02\text{E}23 \text{ molecules}} * \frac{3600 \text{ sec}}{\text{hr}}$$

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

### 3.1.3.5 Benzene Generation from Chemical Decomposition of Tetraphenylborate

#### 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  $(C_6H_5)_3B(C_6H_5)^-$ ,  $(C_6H_5)_3B$ ,  $(C_6H_5)_2B(OH)_2^-$  and  $(C_6H_5)B(OH)_3^-$  respectively.

Radiolysis is the loss of TPB associated with the radiolytic destruction of KTPB solids

$k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are the sequential rate constants for each of the decomposition reactions.

These rate constants have been determined to be a function of catalyst type, ionic strength, temperature and potentially other factors.

#### 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 10mg/L-hr of this tetraphenylborate decomposition is responsible for 1/4 of the total benzene production and converting to mMoles yields 0.0224 mMoles/L-hr.

Since the decomposition of TPB has been set, the formation of 3PB is also set at  $k_1$  (0.0224 mMoles/L-hr, in the base case). A material balance around 3PB results in the following equation for the rate of change of 3PB:

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

Where the rate constants are based on laboratory studies and provided by the following (Reference 41):

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

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

T = temperature, ° K

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

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

Where the rate constants are based on laboratory studies and provided by the following (Reference 42):

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

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

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

where the rate constants are based on laboratory studies and provided by the following (Reference 42):

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

### 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

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

Where the rate constants are based on laboratory studies and provided by the following (Reference 42):

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

T = temperature, ° K

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

$$k_2 = k_{2\text{Cu}}$$

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

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

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

### Decomposition in Z-Area Saltstone

In addition to the potential to release benzene from the DSS received in the Saltstone Production Facility, saltstone vaults will release benzene because of degradation of TPB residuals. Reference 43 included an estimated benzene release and permitted release levels. New data suggests that the emission rates may be different from those initially reported. Reference 44 indicates maximum benzene generation can be calculated by:

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

Where 3PB indicates triphenylborane, 2PB indicates diphenylborinic acid, 1PB indicates phenylboric acid and the brackets, [ ], indicate concentration of the species in g/L of DSS. Table 3.1-9 shows the expected average concentrations for each process flow rate. Table 3.1-9 also shows expected annual DSS production and resulting benzene evolution per year from the Z-Area vaults.

**Table 3.1-9 Estimated Annual Benzene Emissions from Saltstone Vaults**

<b>Conditions and Sources</b>	<b>Base Case (17.5 gpm feed rate)</b>
Salt Solution to Saltstone (gal/min)	26
Salt Solution to Saltstone (gal/year)	1.37E+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	1.57E+04

Normally, peak rates from the vaults should not vary much from the average annual rate. If steady production rates are maintained, at any time during the processing year, approximately equal quantities of grout will be produced each day. Thus, age distribution of grout at any time will be essentially equal. However, peak rates of benzene evolution will depend on maximum capacity at the Z-Area facility. If processing actually occurs in variable short periods of processing, the age distribution is no longer static. To estimate a theoretical maximum, assume the entire annual DSS processing is completed within the design basis capacity. In addition, elevated temperatures will cause evolution at a faster rate (Reference 45). At 85°C, the evolution rate increases nearly 40%. To calculate a potential maximum evolution rate, the annual DSS production is assumed to be processed through Z-Area facilities at the design basis maximum of 100 gpm in three 6 hour processing shifts per day. Maximum per day processing is 108,000 gallons. This theoretical maximum rate is 9.6 lb. of benzene per hour at the vaults.

### 3.1.3.6 Benzene Depletion in the Small Tank Facility

In the small tank 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 that decomposition of TPB from radiolysis is minimal. Once in the salt cell, the benzene produced is subject to a vent condenser to remove any benzene before it is vented.

### 3.1.3.7 Filtration of Tetraphenylborate Slurries

The ITP process and the LWF use Mott<sup>tm</sup> cross-flow filters with a 0.2-micron pore size to filter the slurries prepared in the referenced processes. The ITP facility contains two filters, and the LWF contains one. The performance of these filters has been previously modeled with the filter flux represented by the following equation (Reference 46):

$$F = 5325 * N * \{ 10 * Y2 - Y1 + [Y1 - Y2] * W \}$$

Where :

F = Filtrate flow rate, L/hr

N = Number of filters in operation

Y1 = Filtration rate for 10 Wt % slurry, 0.03317

Y2 = Filtration rate for 1 Wt % slurry, 0.3317

W = Current percent solids

The filtrate flow rate is dependent on the pressure drop across the filter. The equations are based on data from laboratory filter testing and actual in-plant testing at ITP prior to ITP startup (Reference 47). The filter is assumed to be 100% efficient for retention of insoluble species contained in the slurry. This would include any TPB solids, sludge, and MST. The efficiency of the filter is maintained by a backpulse system. The amount of water added to the system by the backpulse system is negligible and does not require modeling at this time.

### 3.1.3.8 Saltstone Product Bases

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 3.1-10 (Reference 48). The demonstrated range of acceptability for each component with respect to physical properties and resistance to contaminant leaching is shown in Table 3.1-11 (Reference 49). 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 substitute for the cement to function as a lime source 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.

Saltstone grout is formulated to minimize bleed water from the grout during curing. An acceptable saltstone product, from the standpoint of physical properties, has been demonstrated with salt solution ranging from about 20 wt % to 32 wt % salt, corresponding to a specific gravity ranging from about 1.18 to 1.32 with a sodium molarity of ranging from about 4 M to 6 M. Bleed water is controlled by controlling the water-to-premix mass ratio in the range of 0.52 to 0.60 (presently set at 0.57). The density of cured saltstone ranges between 1.70 and 1.80 kg/L (References 50 and 51).

**Table 3.1-10 Composition of Saltstone Cementitious Materials**

Component	Cement Type II Santee (Wt%)	Slag Grade 120 NEWCEM <sup>a</sup> (Wt%)	Fly Ash Class F Low CaO (Wt%)
SiO <sub>2</sub>	21.10	34.70	52.17
Al <sub>2</sub> O <sub>3</sub>	4.66	10.70	27.60
TiO <sub>2</sub>	0.23	0.51	1.98
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.11	0.25	0.26
K <sub>2</sub> O	0.34	0.55	1.53
P <sub>2</sub> O <sub>5</sub>	0.31	<0.05	0.12
SO <sub>3</sub>	2.25		0.33
SrO			0.04
LOI (900° C)	1.35	1.34 <sup>b</sup>	9.92
Totals	100.40	100.36	100.00

<sup>a</sup> Also referred to as Atlantic

<sup>b</sup> The loss-on-ignition (LOI) values for slag is negative indicating the existence of sulfur as free sulfur or metal sulfides (i.e., FeS) rather than SO<sub>3</sub> (i.e., samples gained weight on heating).

**Table 3.1-11 Demonstrated Range of Acceptability**

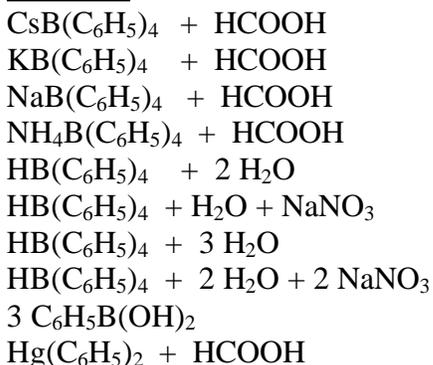
Saltstone Component	Nominal Blend (Wt %)	Range (Wt %)
Lime Source <sup>a</sup>	3	0 to 10
Fly Ash	25	10 to 40
Slag	25	10 to 40
Salt Solution	47	40 to 55

<sup>a</sup> Either Portland Class II cement or Ca(OH)<sub>2</sub>.

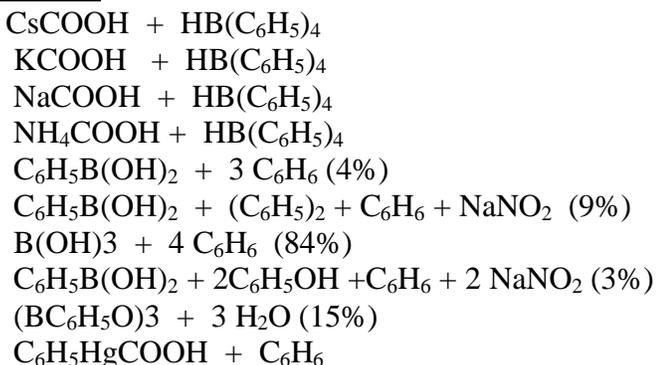
### 3.1.3.9 Precipitate Hydrolysis Bases

The bases for the SPC operating cycle times and parameters were developed experimentally and are documented (Reference 54). 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 (Reference 54). Therefore, both the phenylboric acid and diphenylmercury limits are easily achieved during the PR cycle time.

#### Reactants



#### Products



The bases for the SWPF parameters are:

~1500 gallons of previous batch is left in PR as a heel.

Target acid (after neutralizing base equivalents of carbonate, hydroxide, TPB- and nitrite) - 0.25 M in PHA

Copper(II) catalyst target – 900 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.

<u>Reactants</u>	<u>Products</u>
$\text{CsB}(\text{C}_6\text{H}_5)_4 + \text{HCOOH} + 3\text{H}_2\text{O}$	$\text{CsCOOH} + \text{B}(\text{OH})_3 + 4\text{C}_6\text{H}_6$
$\text{KB}(\text{C}_6\text{H}_5)_4 + \text{HCOOH} + 3\text{H}_2\text{O}$	$\text{KCOOH} + \text{B}(\text{OH})_3 + 4\text{C}_6\text{H}_6$
$\text{NaB}(\text{C}_6\text{H}_5)_4 + \text{HCOOH} + 3\text{H}_2\text{O}$	$\text{NaCOOH} + \text{B}(\text{OH})_3 + 4\text{C}_6\text{H}_6$
$\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4 + \text{HCOOH} + 3\text{H}_2\text{O}$	$\text{NH}_4\text{COOH} + \text{B}(\text{OH})_3 + 4\text{C}_6\text{H}_6$

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

- 292 gallons of 90 wt% formic acid and
- 186 gallons of 15 wt% copper nitrate.

The 146 gallons of copper nitrate is added to reach the target of 900 ppm of Cu in the final precipitate.

One salt cell batch was run for every chemical cell batch processed. The OE was not modeled since benzene separation was essentially complete in the PR boiling. Temperature is not tracked, since energy balances are not performed.

### 3.1.3.10 DWPF Chemical Cell Bases

#### 3.1.3.10.1 Bases for HNO<sub>3</sub> / HCOOH Addition and F-N Basis

Technical Bases - Acid adjustment in the SRAT is partially completed by adding nitric acid to yield an acid pH. The aqueous product from the acid hydrolysis, which contains an excess of HCOOH, is then fed to the SRAT. Some formic acid must be fed for any of the alternatives, since the HCOOH is added to reduce mercury(II) compounds to mercury(0). The mercury is then steam-stripped from the sludge slurry to minimize the quantity sent to the melter. Only those reactions that involve a species in the salt solution are included, since reactions of sludge components are not generally affected by the various alternatives.

<u>Reactants</u>	<u>Products</u>
NaOH + HNO <sub>3</sub>	NaNO <sub>3</sub> + H <sub>2</sub> O
NH <sub>4</sub> OH + HNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub> + H <sub>2</sub> O
NaAlO <sub>2</sub> + 4 HNO <sub>3</sub>	Al(NO <sub>3</sub> ) <sub>3</sub> + NaNO <sub>3</sub> + 2 H <sub>2</sub> O
CsOH + HNO <sub>3</sub>	CsNO <sub>3</sub> + H <sub>2</sub> O
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> + 6 HNO <sub>3</sub>	2 UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> + 2 NaNO <sub>3</sub> + 3 H <sub>2</sub> O
SrCO <sub>3</sub> + 2 HNO <sub>3</sub>	Sr(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O + CO <sub>2</sub>
CoO + 2 HNO <sub>3</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O (70%)
HgO + HCOOH	Hg + H <sub>2</sub> O + CO <sub>2</sub> (99%)
2Ag <sub>2</sub> O + 2 HCOOH	2 Ag + H <sub>2</sub> O + CO <sub>2</sub> (99%)
PdO + HCOOH	Pd + H <sub>2</sub> O + CO <sub>2</sub> (99%)
RhO <sub>2</sub> + 2 HCOOH	Rh + 2H <sub>2</sub> O + 2CO <sub>2</sub> (99%)

The method for calculating acid addition and the balance between formate ion and nitrate ion are based on laboratory work (Reference 55) and DWPF cold runs and operating experience.

- 1 Calculate the total acid required to neutralize or to react with materials in the feed. One mole acid is needed for each mole of HgO, NaOH, and KOH. Two moles of acid are needed for Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, Mg(OH)<sub>2</sub> and carbonate (CO<sub>3</sub>)<sup>-2</sup>. One-quarter mole is needed for each mole of nitrite (NO<sub>2</sub><sup>-</sup>) and 0.4 moles are needed for each mole of MnO<sub>2</sub>.
- 2 Multiply this “stoichiometric” amount by 1.25. This is the **total** amount of acid to be added.
- 3 Assume that 40% of the formic acid is lost in the SRAT cycle. Based on this, calculate how much formic acid is required such that the [formate]-[nitrate] (“F minus N”) will be 0.4 M in the SME – normalized to 45 wt% solids in the SME. Assume that 100 gallons 90% formic acid will be added to the SME to provide part of the formate needed.

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

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

If some nitric acid enters the SRAT through the salt feed stream (as was the case in some of the alternative salt processing schemes) the 200-gallon volume is reduced by the amount in the input stream.

To each SME batch, 100 gallons of 90 wt % formic acid are added. The F-N redox value is calculated for the SME using the equation:

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

Some formic acid will be removed in the SRAT cycle during the evaporation. The amount of acid lost is calculated by an ideal solution estimate of the vapor composition and may not be the nominal 40%.

Mercury is removed from the solution in the SRAT and collected as a side stream. The mercury is tracked as HgO throughout the process.

### **Bases for NaOH and NaNO<sub>2</sub> to RCT**

#### Technical Bases

##### Reactants

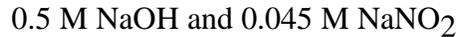
HCOOH + 4 NaOH  
Pu(COOH)<sub>4</sub> + 4 NaOH  
UO<sub>2</sub>(COOH)<sub>2</sub> + 2 NaOH  
HCl + NaOH  
HF + NaOH  
HgCl<sub>2</sub> + 2 NaOH  
Hg<sub>2</sub>Cl<sub>2</sub> + 2 NaOH  
Hg<sub>2</sub>I<sub>2</sub> + 2 NaOH  
KCOOH + NaNO<sub>3</sub>  
NH<sub>4</sub>COOH + NaNO<sub>3</sub>  
CsCOOH + NaNO<sub>3</sub>  
CsCl + NaNO<sub>3</sub>  
Cs<sub>2</sub>O + 2 NaNO<sub>3</sub> + H<sub>2</sub>O

##### Products

NaCOOH + H<sub>2</sub>O  
PuO<sub>2</sub> + 4 NaCOOH + 2 H<sub>2</sub>O  
UO<sub>2</sub>(OH)<sub>2</sub> + 2 NaCOOH  
NaCl + H<sub>2</sub>O  
NaF + H<sub>2</sub>O  
HgO + 2 NaCl  
Hg + HgO + 2 NaCl + H<sub>2</sub>O  
Hg + HgO + 2 NaI + H<sub>2</sub>O  
KNO<sub>3</sub> + NaCOOH  
NH<sub>4</sub>NO<sub>3</sub> + NaCOOH  
CsNO<sub>3</sub> + NaCOOH  
CsNO<sub>3</sub> + NaCl  
CsNO<sub>3</sub> + NaOH

The quantities of caustic and nitrite added to the RCT are based on the Waste Compliance Plan and operating experience. This is to assure that the inhibitors required to prevent corrosion of the carbon steel waste tanks are present.

Modeling Bases - Caustic and inhibitor are added to the RCT to produce a recycle solution that is



Water evaporated in the SRAT, SME and melter goes directly to the RCT in the simplified Speedup model.

**Bases for Water Additions and Recycle:**

Modeling Bases - Water evaporated from SRAT and SME is recycled through SMECT to RCT.

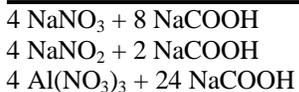
All water fed to the melter goes to the Offgas Condensate Tank and then to the RCT

Steam Atomized Scrubbers and Film Cooler add 1000 pph water to off-gas stream. This water is condensed and recycled. Decontamination waste adds another 340 pph of water to the RCT.

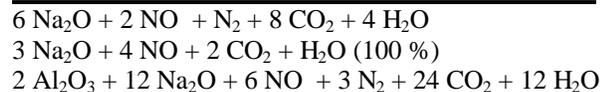
**Bases for NO<sub>x</sub> Produced in the Melter**

Technical Bases - In the melter, 50 % of the nitrate salts and all of the nitrite salts react with sodium formate to form nitric oxide (NO). The balance of the nitrate salts react to form nitrogen (N<sub>2</sub>). Subsequently, the NO reacts with oxygen in the air to form nitrogen dioxide (NO<sub>2</sub>).

**Reactants**



**Products**



Modeling Bases - The reactions shown below as the Modeling Bases for Vitrification, closely approximate the NO<sub>2</sub> emission. Since complete oxidation is assumed, carbon monoxide and hydrogen in the melter off-gas are not accounted for.

## Bases for Vitrification in the Melter

### Technical Bases

In addition to reactions with nitrate and nitrite salts, formate salts either react with other 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.,  $\text{CaC}_2\text{O}_4$ ,  $\text{HgO}$ ).

<u>Reactants</u>	<u>Products</u>
4 $\text{Al}(\text{NO}_3)_3 + 18 \text{NaCOOH}$	2 $\text{Al}_2\text{O}_3 + 9 \text{Na}_2\text{O} + 12 \text{NO} + 18 \text{CO}_2 + 9 \text{H}_2\text{O}$
2 $\text{Na}_2\text{SO}_4 + 2 \text{NaCOOH}$	3 $\text{Na}_2\text{O} + 2 \text{SO}_2 + 2 \text{CO}_2 + \text{H}_2\text{O}$
4 $\text{Fe}_2\text{O}_3 + 2 \text{NaCOOH}$	4 $\text{FeO} + \text{Na}_2\text{O} + 2 \text{CO}_2 + 7 \text{H}_2\text{O}$
2 $\text{NaCOOH}$	$\text{Na}_2\text{O} + \text{CO} + \text{CO}_2 + \text{H}_2$
2 $\text{KCOOH}$	$\text{K}_2\text{O} + \text{CO} + \text{CO}_2 + \text{H}_2$
4 $\text{NH}_4\text{COOH} + 3 \text{O}_2$	2 $\text{N}_2 + 8 \text{H}_2\text{O} + 2 \text{CO} + 2 \text{CO}_2 + 2 \text{H}_2$
$\text{Mn}(\text{COOH})_2$	$\text{MnO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Ni}(\text{COOH})_2$	$\text{NiO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Ca}(\text{COOH})_2$	$\text{CaO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{UO}_2(\text{COOH})_2 + \text{O}_2$	$\text{U}_3\text{O}_8 + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Cu}(\text{COOH})_2$	$\text{CuO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Co}(\text{COOH})_2$	$\text{CoO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Zn}(\text{COOH})_2$	$\text{ZnO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Mg}(\text{COOH})_2$	$\text{MgO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Sr}(\text{COOH})_2$	$\text{SrO} + \text{CO} + \text{CO}_2 + \text{H}_2$
2 $\text{CsCOOH}$	$\text{Cs}_2\text{O} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Na}_2\text{C}_2\text{O}_4$	$\text{Na}_2\text{O} + \text{CO}_2 + \text{CO}$
$\text{CaC}_2\text{O}_4$	$\text{CaO} + \text{CO}_2 + \text{CO}$
$\text{CaF}_2 + \text{Na}_2\text{O}$	$\text{CaO} + 2 \text{NaF}$
$\text{Sr}(\text{OH})_2$	$\text{SrO} + \text{H}_2\text{O}$
$\text{HgO}$	$\text{Hg}(\text{v}) + \text{O}_2$
$\text{Hg}$	$\text{Hg}(\text{v})$
$\text{Cs}_2\text{O}$	$\text{Cs}_2\text{O}(\text{v})$ (10%)
2 $\text{MnO}_2$	$\text{MnO} + \text{O}_2$
$\text{Pd}(\text{NO}_3)_2$	$\text{Pd} + 2 \text{NO} + 2 \text{O}_2$
2 $\text{PuO}_2(\text{NaTi}_2\text{O}_5)_2$	2 $\text{PuO}_2 + 8 \text{TiO}_2 + 2 \text{Na}_2\text{O} + \text{O}_2$
$\text{Sr}(\text{NaTi}_2\text{O}_5)_2$	$\text{SrO} + 4 \text{TiO}_2 + \text{Na}_2\text{O}$
2 $\text{H}(\text{NaTi}_2\text{O}_5)$	$\text{H}_2\text{O} + 4 \text{TiO}_2 + \text{Na}_2\text{O}$

Modeling Bases - The following simplified oxidation reactions were used to convert metal salts and other compounds into oxides in the glass melter:

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

### 3.1.3.11 DWPF Glass Property Bases

The Technical and Modeling Bases for estimating glass properties are identical 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 3.1-12, below). The sum of these molar free energies of hydration is used to estimate 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 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 leach rate < 2.25 g/l will be used.

The equivalent expressions and limits for lithium and sodium are (Reference 23):

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

leach rate < 1.84 g/l

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

leach rate < 2.28 g/l

**Table 3.1-12 Molar Free Energy of Hydration for Glass Oxides**

Al <sub>2</sub> O <sub>3</sub>	37.68
B <sub>2</sub> O <sub>3</sub>	-10.43
CaO	-13.79
Cr <sub>2</sub> O <sub>3</sub>	11.95
CuO	-4.955
Fe <sub>2</sub> O <sub>3</sub>	14.56
K <sub>2</sub> O	-76.41
Li <sub>2</sub> O	-24.04
MgO	-6.57
MnO	-24.44
Na <sub>2</sub> O	-53.09
NiO	0.37
SiO <sub>2</sub>	4.05
TiO <sub>2</sub>	16.27
U <sub>3</sub> O <sub>8</sub>	-23.77
ZrO <sub>2</sub>	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 for liquidus is (Reference 56):

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

All concentrations 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 range that is acceptable is from 24 to 90 poise, because of model and measurement uncertainty.

Viscosity is calculated from (Reference 57):

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

All concentrations are in moles per 100 grams of glass.

### 3.1.4 Results

#### 3.1.4.1 CSTR Sizing for TRU Removal and TPB Strike

The separation of TRU and Cs from contaminated salt solution is to be performed by reaction with monosodium titanate (MST) and tetraphenylborate (TPB) respectively. The 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 testing during the decision, these reactor sizes are still valid.

#### Sizing Methodology

The sizing of a continuous stirred tank reactor begins with a material balance for species A in the reactor (Reference 58). This material balance results in an expression relating the required residence time ( $\tau$ ) to the initial reactant's concentration ( $C_{A0}$ ), the percent conversion ( $X_A$ ) which is a representation of DF ( $\text{DF} = C_{A0}/C_A$ ), 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 ( $v_0$ ).

$$\mathbf{t} = \frac{V}{\mathbf{u}_0} = \frac{C_{A0}X_A}{-r_A} \text{ with } X_A = 1 - \frac{C_A}{C_{A0}}$$

The above equation shows that if one plots the  $C_{A0}/(-r_A)$  versus  $X_A$ , the area containing the curve represents the residence time. If one chooses to design multiple tanks, the  $X_A$  range can be divided into various segments with each segment representing the required residence time of an individual tank ( $\tau_i$ ).

$$\mathbf{t}_i = \frac{V_i}{\mathbf{u}_0} = \frac{C_{A0}(X_{A(i)} - X_{A(i-1)})}{-r_{A(i)}}$$

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.

### **MST Kinetics**

MST kinetics have been reported (Reference 14) 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 (Reference 14). In this report, the percent conversion of TRU elements is traced in time. Based on tank farm inventory and expected TRU concentrations (see section 2.32, Tank Farm Blending: MST Sorption Requirements for Alpha and Strontium), plutonium is bounded by 1 mg/L and requires a  $DF=56$ ,  $X_A=1-(1/DF)=0.982$ . Based on the titanium limit in glass, the MST addition is closer to 0.2 g/L. Therefore, the sizing of the MST continuous stirred tank reactors is based on the high plutonium, 25 °C, 4.5M Na, 0.2 g/L MST experimental data. Table 3.2-2 contains the  $K_d$  versus time information necessary for CSTR sizing.

The determination of reaction rate as a function of percent conversion is susceptible to experimental noise. Therefore, a smooth curve is drawn through the data points. The rate, change in concentration/change in time, is based on the smooth curve and not the experimental data. The choice of curve fitting is arbitrary as long as the curve provides an adequate representation of the entire data set. A non-linear interpolation routine was used with the MST kinetics.

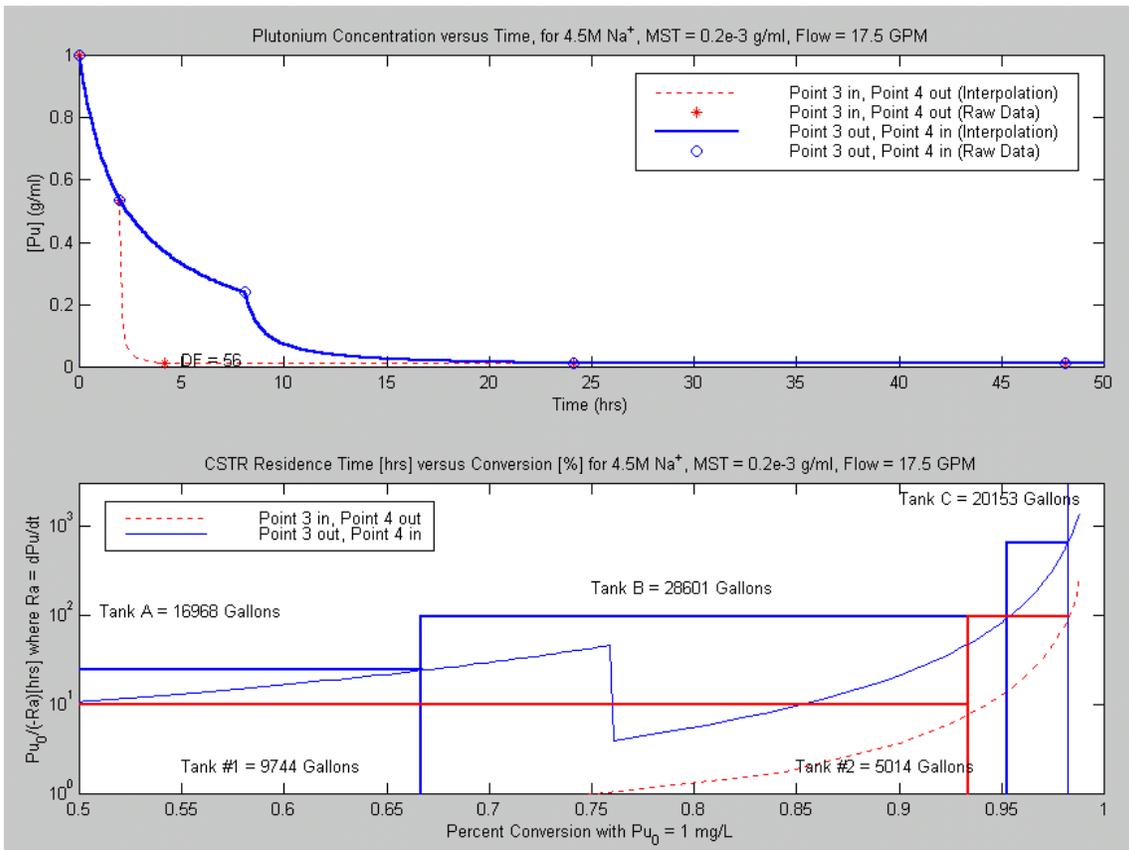
Table 3.1-13 contains the plutonium versus time information necessary for CSTR sizing. This table contains anomalies at 4 and 8 hours that have not been resolved at the time of this report. The plutonium concentration can not decrease and then increase between 4 and 8 hours. Therefore, one of these data points is incorrect. In order to provide a bounding design, two scenarios are generated based on the inclusion/exclusion of the 4 and 8-hour data points.

Figure 3.1-16 provides the plutonium concentration versus time for the two scenarios mentioned above. Including the 4-hour data point (excluding the 8-hour) yields a very rapid response. Based on the sizing methodology mentioned above, two 10,000-gallon tanks operating at 17.5 GPM would achieve the DF. These tanks are labeled Tank #1 and Tank #2 in the lower graph. Including the 8-hour data point (excluding the 4-hour point) yields a sluggish response. Performing the sizing calculation reveals that approximately three 30,000 tanks operating at 17.5 GPM would achieve the DF. These tanks are labeled Tank A, Tank B, and Tank C in the lower graph.

Based on the uncertainty in the experimental data, the number and size of tanks required to achieve a  $DF_{Pu}$  of 56 can vary between two 10,000-gallon tanks and three 30,000-gallon tanks.

**Table 3.1-13 Plutonium Concentration vs. Time Data for CSTR Sizing**

Elapsed Time (h)	Kd (mL/g)
0	
1.98	4.33E+03
4.17	4.10E+05
8.10	1.59E+04
24.10	4.10E+05
48.13	4.10E+05
168.33	4.10E+05
239.40	NA



**Figure 3.1-16 CSTR Sizing Data**

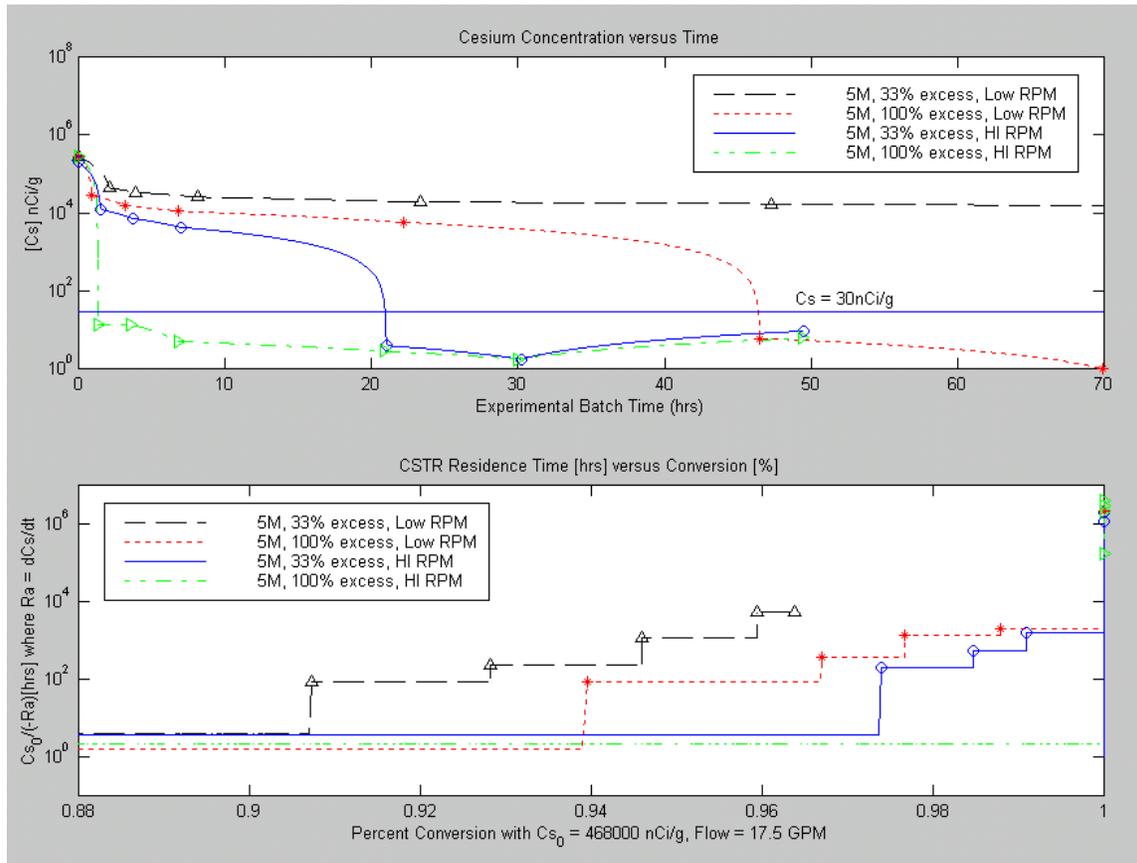
Figure 3.1-16 plots the information necessary to size the CSTR's. The top graph is a plot of plutonium concentration versus time. The solid line represents the inclusion of the 8 hour data point, exclusion of the 4 hour point. The solid line provides a sluggish response. The dotted line represents the inclusion of the 4 hour data point, exclusion of

the 8 hour point. This response is very rapid. The lower figure plots the percent conversion as a function of inverse rate. Partitioning the lower curves into tanks shows that if the rapid response is used, the desired DF could be obtained with two approximately 10,000 gallon tanks

### **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 (Reference 22). 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 3.1-17 (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 3.1-17 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 3.1-17 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 3.1-17 (lower graph) that include the data points and the desired percent conversion. Three CSTRs in series were used in the following analysis. Table 3.1-14 provides the tank sizes required to achieve the DF as a function of the kinetic batch data.



**Figure 3.1-17 Rate of Cesium Precipitation by TPB**

The rate of cesium precipitation by TPB is shown on Figure 3.1-17 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 timeframe 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 3.1-14.

CSTR sizes depend on the ability to dissolve TPB into solution. As shown in Table 3.1-14, 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 3.1-14 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

### 3.1.5 Equipment

#### 3.1.5.1 Building Layout

Building layout based on shielding and functional area sizes of the Small Tank ITP alternative compared to equivalent DWPF facility layouts are provided below in Table 3.1-15. 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 3.1-15 Small Tank ITP**

	DWPF	SMALL TANK	SMALL TANK %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	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	2,508,536	2,869,050	114%

**3.1.5.2 Tanks**

**Table 3.1-16 Tanks for Small Tank TPB Alternative**

<b>Tank</b>	<b>Tank Size</b>	<b>Sizing Assumption</b>
Fresh Waste Day Tank	25,000 gallons	Sized to hold about 24 hours of 6.44 M Na <sup>+</sup> 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 weeks 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 will decrease 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.

Tank	Tank Size	Sizing Assumption
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 storage. (Note: Saltstone Facility can process approximately 60,000 gallons of salt solution per day assuming two-shift operation.) The Filtrate Hold Tanks also allows hold-up of material for analysis to ensure that the Saltstone Waste Acceptance Criteria is met (assumes that analysis for Benzene, TPB, Hg, Sr, Pu, U, and others as necessary.) Two tanks are identified to allow the sampling 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 will decrease as 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 can decrease the wash time, but the concentrate tank requires ~50 hours to collect 4000 gallons of concentrated precipitate.
Recycle Wash Hold Tank	25,000 gallons	The Recycle Wash Hold Tank was 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 designed to hold 70 hours of precipitate.
Precipitate Reactor	10,000 gallons	This tank is designed to hydrolyze the washed precipitate to form precipitate hydrolysis aqueous and benzene.
Precipitate Reactor Condenser/Decanter	100 gallons	This unit condenses the vapor from the Precipitate Reactor and decants the liquid benzene for continuous transfer to the Organic Evaporator.

Tank	Tank Size	Sizing Assumption
Precipitate Hydrolysis Aqueous Surge Tank	40,000 gallons	The Precipitate Hydrolysis Aqueous Surge Tank was added to hold the precipitate hydrolysis aqueous from the Precipitate Reactor until transfer to the DWPF for vitrification.
Precipitate Reactor Overheads Tank	7,500 gallons	This vessel collects the aqueous stream from the Precipitate Reactor concentration for use as precipitate wash water in the Wash Tank.
Organic Evaporator	1,750 gallons	The Organic Evaporator washes and evaporates 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	1,000 gallons	This tank collects the condensed benzene from the Organic Evaporator Decanter 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 its destruction 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.

### **3.1.8 Supplemental Environmental Impact Statement (SEIS)**

SEIS for the salt disposition facility is drafted to include 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 (Reference 59). Accidental releases are based on historical information on similar processes and facilities (Reference 60). The resulting population doses from these emission estimates are calculated by modeling the environmental dispersion of the emission (Reference 61).

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 two process alternatives produces only minor environmental changes (Reference 61).

## **3.2 Strontium/Alpha Sorption by Monosodium Titanate (MST) Addition**

### **3.2.1 Process Description**

Both the Caustic Side Solvent Extraction (CSSX) and Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange processes contain an Alpha Sorption by MST addition step to remove Strontium (Sr), Plutonium (Pu), Neptunium (Np), and Uranium (U) sufficient to meet Saltstone specifications. Filtering by cross-flow filtration to remove and concentrate MST and entrained sludge to ~5 wt % solids is performed, and the MST/sludge solids are 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 CSSX or the Recycle Blend Tank (RBT) for CST processing.

### **3.2.2 R&D Results for Alpha Sorption**

Research and Development activities for Alpha Sorption were focused on the study of Monosodium Titanate removal of Strontium (Sr), Plutonium (Pu), Neptunium (Np), and Uranium (U) in 5.6 M Na salt solution.

#### **3.2.2.1 R & D Results that Impact Bases and Assumptions**

##### MST Concentration and Kinetics

The adsorption of Sr, Pu, U and Np on MST has been extensively studied and reported (References 19, 20, and 21). 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 3.2-1), but Pu removal (both extent and rate) is limited at 7.5 M (See Figure 3.2-2). The references show that Pu removal (both extent and rate) improves as the Na concentration is reduced and as MST concentration is increased (See Figure 3.2-3). The average salt solution is predicted to be 6.44 M Na. The sodium concentration chosen for CST IX and CSSX is 5.6 M. To ensure removal of Pu at average concentration and activity (0.2 mg/L and 205 nCi/g – see Section 2.3.2), we have chosen to dilute the salt solution before MST addition and to use the maximum MST concentration (0.4 g/L) shown to be acceptable in CST DWPF glasses (Reference 62).

Recent study (Reference 63) of MST kinetics at 5.6 M Na shows rapid Sr removal at a MST concentration of 0.4 g/L (See Figure 3.2-4). In addition, it shows that a 24-hour reaction period will be sufficient for removal of Pu at this sodium concentration (See Figure 3.2-5). Since nearly all of the alpha activity is due to Pu, these conditions ensure that the Saltstone alpha limit can be met for the average Pu concentration and activity in the average salt solution fed to the CSSX or CST processes. However, the Pu distribution in the Tank Farm (both concentration and isotopic distribution) is poorly characterized.

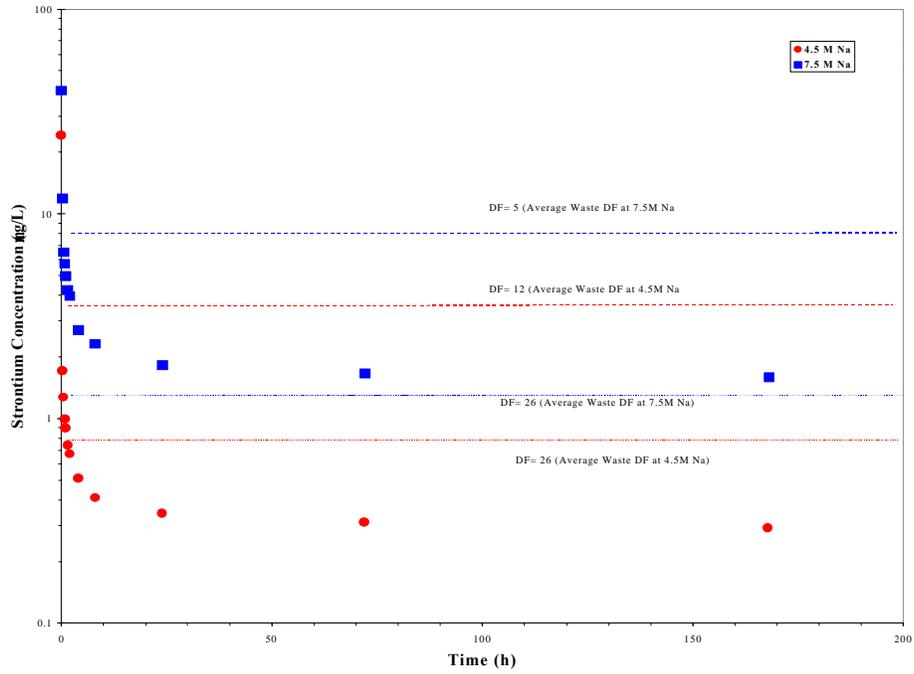
Additional work is needed to assure that Pu removal can be achieved at more bounding conditions.

There is built-in conservatism regarding the contact time between the MST and the salt solution. The batch cycle has a 24-hour reaction period during which the goal is to attain sufficient adsorption to meet the Saltstone requirement. In reality, the salt solution has considerable additional contact. The 24-hour reaction period is followed by a 20-hour sample/analyze period. The transfer of the AST contents to the filter feed tank then takes 11 hours. Finally, it takes about 70 hours to filter and send the filtrate to the Recycle Blend Tank for CST or the Salt Solution Feed Tank for CSSX. The salt solution averages an additional 60 hours of contact time. 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.

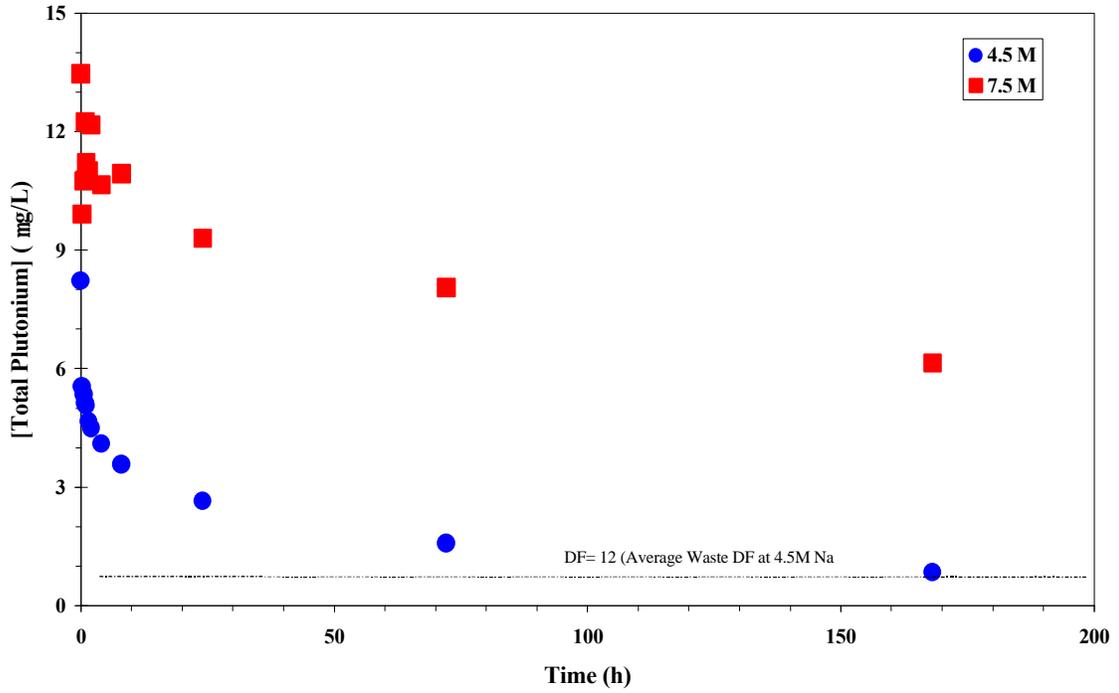
#### Dilution in Alpha Sorption Tank (AST)

The CST vendor has recommended that dilution be performed with dilute NaOH (1.5 to 2 M). This is required to maintain the hydroxide activity and to prevent aluminum precipitation. The dilution will be performed in the AST and the flowsheet has been modified to include dilution in the AST with dilute NaOH. The addition of dilute NaOH increases the CST column feed rate by approximately 1 gpm over dilution with water only. At 6.9 M gallons per year of salt solution workoff, about 800 k gallons of 2 M NaOH is required – equivalent to about 84 k gallons 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 by approximately 20 %.

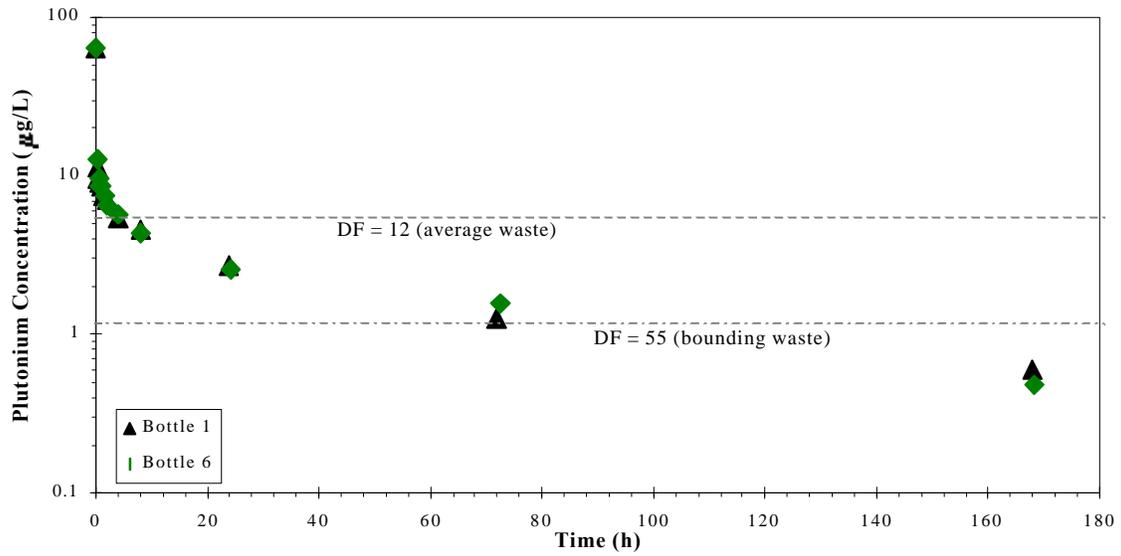
For the CST process, HLW Process Engineering has also recommended that water from column loading and excess water from column unloading should be sent to the Wash Water Hold Tank (WWHT), not to the Recycle Blend Tank. By sending this water to the AST, the CST fines from loading and unloading the column can be filtered thus preventing column plugging. This does not change the overall material balance since the water was previously included. For the new material balance, the water will be apportioned to each batch of treated salt solution as part of the dilution water added to the AST. However, in reality the water will be produced in large batches at intervals of 3 to 5 months. This may require special handling at the AST and a special Saltstone formulation.



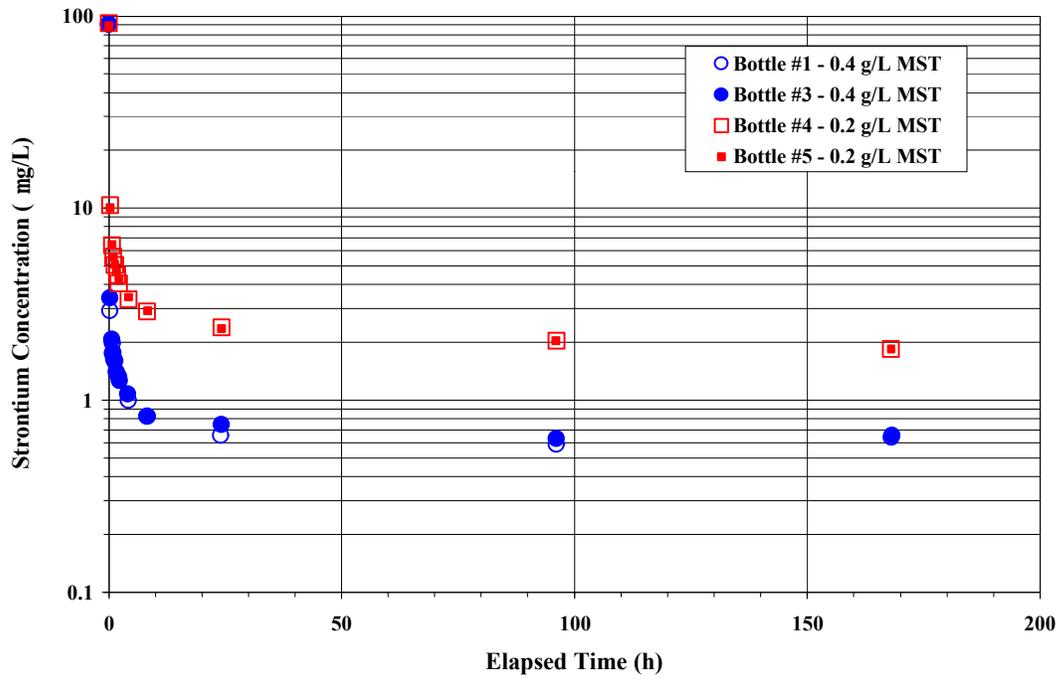
**Figure 3.2-1 Sr Removal Kinetics at 0.2 g/L MST Addition**



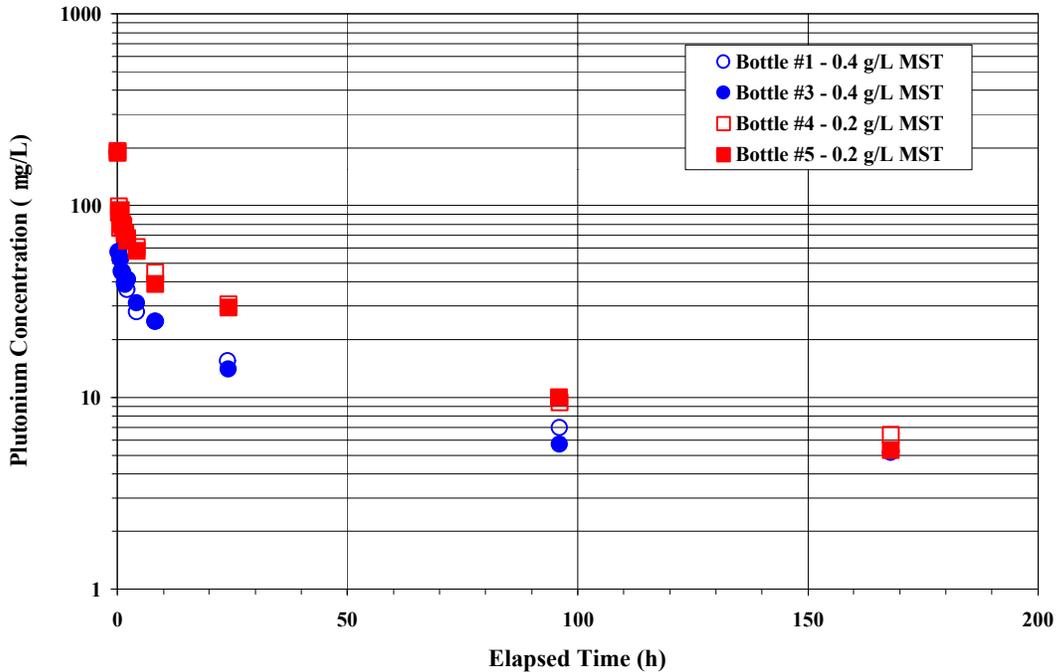
**Figure 3.2-2 Pu Removal Kinetics at 0.2g/L MST Addition**



**Figure 3.2-3 Comparison of Plutonium Concentration Tests in 4.5 M Na and 0.4 g/L MST**



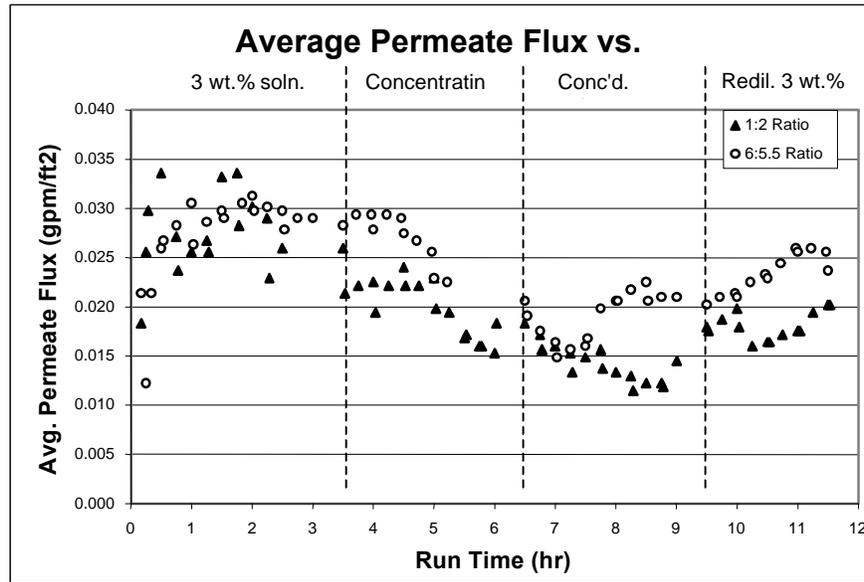
**Figure 3.2-4 Comparison of Sr Removal Kinetics 5.6 M Na at 0.2 and 0.4 g/L MST**



**Figure 3.2-5 Comparison of Pu Removal Kinetics in 5.6 M Na at 0.2 and 0.4 g/L MST**

MST/Sludge Filtration and Washing

Tests on filtration of MST/sludge mixtures alone (Reference 64) and with additives to improve filtration rates (Reference 65) were performed during Phase IV. Various MST/sludge 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/ft<sup>2</sup> and did not vary significantly with composition (See Figure 3.2-6). The most promising additives were bentonite and polyethylene oxide. They increase filtration rates by 25 –35 %. The Alpha Sorption cycle is based on a filtration rate of 21 gpm. Therefore, the required filter area is ~ 1,000 ft<sup>2</sup>. Based on preliminary sizing, a 1,000-ft<sup>2</sup> filter unit would contain 510 filter tubes that are 0.75 inch OD, 10 feet long and contained within a 28-inch diameter tube bundle. The filter feed rate would be 1,850 gpm to yield an axial velocity of 6 ft/sec or 2,850 gpm for 9 ft/sec.



**Figure 3.2-6 MST/Sludge Filtration Rates**

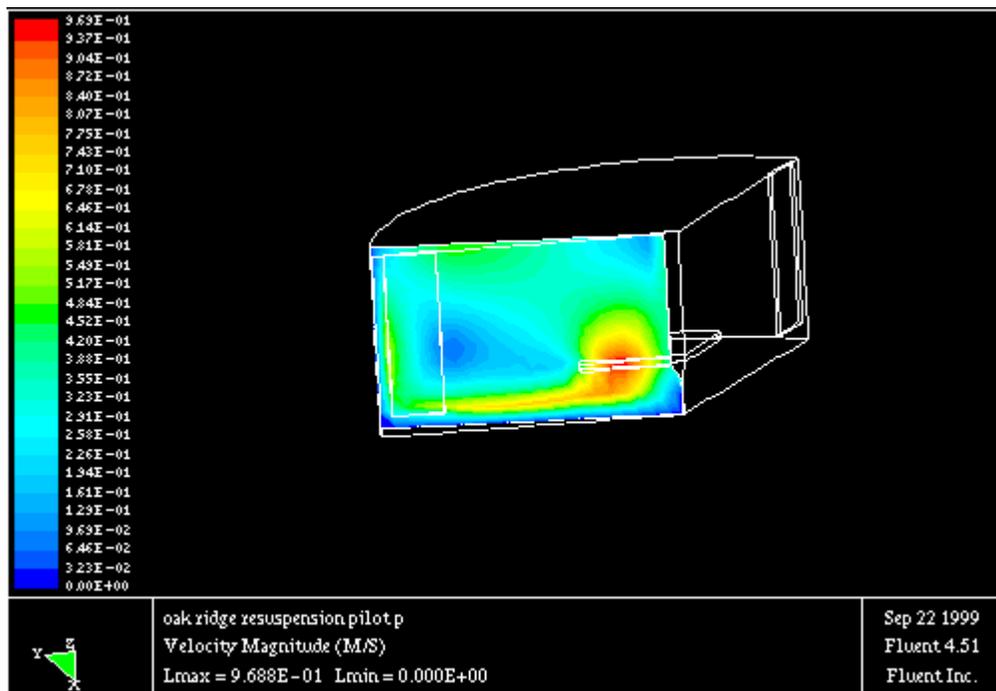
MST/sludge Resuspension

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 (Reference 66). 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 that a settled MST/sludge must be cooled to assure resuspension. The AST, the SSRT, and in the downstream tanks (i.e., pump pit tanks and DWPF CST processing tanks) 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 (Reference 67). 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.<sup>1</sup> 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 3.2-7 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.



**Figure 3.2-7 Velocity Contours for the Resuspension Test**

<sup>1</sup> The test measured velocity was 0.48 m/s which is well within the range of the contour in that portion of the tank.

### **3.2.3 Bases for Material Balances**

#### **3.2.3.1 Changes from Phase III**

The changes from the Phase III Bases and Assumptions are discussed in Section 3.2.2.1. In summary, they are:

- The feed composition to the non-elutable ion exchange and the solvent extraction processes has been changed to the average feed as shown in Section 2.3.2.
- MST concentration in the AST is 0.4 g/L based on 5.6 M salt solution; the hold period is maintained at 24 hours.
- Dilution of the salt solution is moved to the AST to provide faster MST sorption kinetics.
- Dilution is performed with ~ 2 M NaOH to maintain hydroxide activity and prevent aluminum precipitation.
- Contaminated water from the CST IX system is recycled to the Alpha Sorption process to remove CST fines from the column feed.
- The AST, SSRT, and downstream tanks require cooling coils and high powered/high tip-speed agitators to ensure resuspension of MST/sludge mixtures.
- The Alpha Sorption process configuration has been modified to include an Alpha Sorption Tank (AST), Filter Feed Tank (FFT), separate Crossflow Filter for the Wash Cycle, and the resulting configuration allows continuous filtration of clarified salt solution (CSS).

#### **3.2.3.2 Changes from Rev. 0 of the Phase IV BAR**

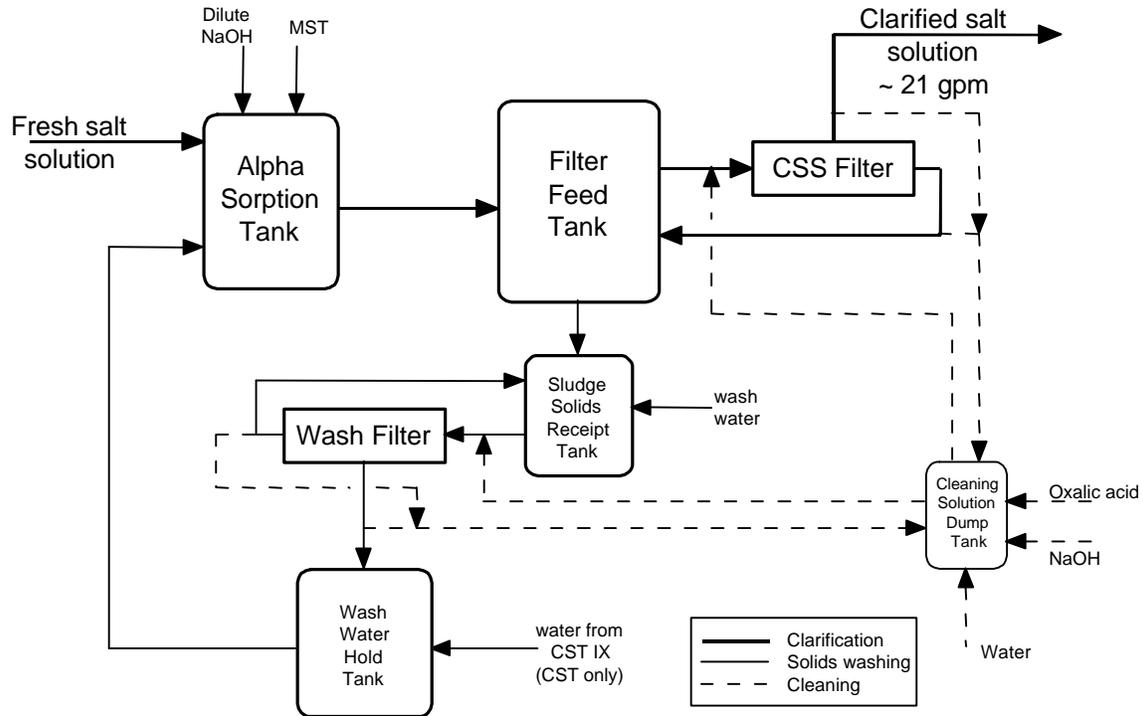
The following additional changes have been made for this revision of the Base, Assumptions and Results document:

- Revision to the Alpha Sorption Process configuration results in a continuous filtration step with a filtrate flow rate of ~21 gpm requiring approximately 1,000 ft<sup>2</sup> crossflow filter area assuming a 0.02 gpm/ft<sup>2</sup> flux rate.
- An ITP-size filter (230 ft<sup>2</sup>) is assumed for the permeate flow calculations for the separate Wash Cycle filter.
- In order to preserve the same quantities of cleaning solution and wash water as the previous flowsheet material balance, the Alpha Sorption Process revisions require utilization of fractional batches for the filter cleaning and sludge washing cycle steps. These fractional batches for the filter cleaning and sludge washing are 2.7 and 6.8, respectively. The change allows the CSS stream to remain unchanged as it feeds other material balances (CSSX or CST).
- Quantities of cleaning solution from the previous flowsheet material balance are assumed sufficient to clean both the CSS and Wash Cycle Filter due to the reduction in total filter area to 1,150-1230 ft<sup>2</sup> versus the previous CSS filter area of 3,000 ft<sup>2</sup>.
- Caustic Side Solvent Extraction is included in this revision to the Bases, Assumptions and Results document as a Salt Disposition Alternative.

### **3.2.3.3 Alpha Decontamination by MST Addition**

#### **3.2.3.3.1 Process Description**

For the CST or the CSSX Processes, a salt solution feed batch of ~73,500 gallons at 6.44 M Na<sup>+</sup> will be transferred to the 88,000 gallon (working volume) Alpha Sorption Tank (AST) for dilution to ~5.6 M Na<sup>+</sup>. (See Figure 3.2-8) Subsequent addition and mixing of the MST slurry for 24 hours will decontaminate the salt solution by sorption onto the MST of the TRU (Pu, Np and U) and Sr present. As a result of a process alternatives trade study for Alpha Sorption (Reference 68), a number of changes to the Alpha Removal Process have been made including addition of a Filter Feed tank (FFT) to separate the filtration step and make it a continuous operation. This change results in the slurry in the AST being transferred to the 111,000-gallon filter feed tank where it will be filtered to remove both MST and sludge solids. The filtrate stream (clarified salt solution) will be sent on to the CST Recycle Blend Tank or CSSX Salt Solution Feed Tank. When the 10,000 gallon heel in the AST accumulates about 5 wt % solids (five to eight batches), it will then be transferred to the Sludge Solids Receipt Tank (SSRT) for washing to <0.5 M Na<sup>+</sup>. Another change to the process will be the addition of a separate crossflow filter to be utilized in the MST/sludge washing cycle to allow the filtration of clarified salt solution to remain continuous. The washed solids are then transferred to DWPF for further processing. Cleaning solutions will be run through the crossflow filter unit after two to three 73,500-gallon batches of salt solution have been processed through as CSSX or CST feed to minimize fouling and plugging of the sintered metal filter media.



**Figure 3.2-8 Alpha Decontamination by MST Addition**

3.2.3.3.2 Bases

MST addition and Sr/Pu adsorption

Phase III, IV and V work (References 15, 16, 17 and 69) on MST adsorption kinetics have shown that a MST concentration of 0.4 g/L will be necessary to ensure adequate adsorption of transuranics (TRU) and <sup>90</sup>Sr to achieve decontamination at 5.6 M Na<sup>+</sup> salt solution. Experimental work found faster adsorption rates for both strontium (Sr) and plutonium (Pu) at the higher MST concentration of 0.4 g/L. Based on the sorption rates for Pu found in Phase V MST adsorption kinetics testing (Reference 69) a minimum reaction time of 24 hours will be necessary to achieve a decontamination factor (DF) of 12 for an initial Pu concentration of 0.2 mg/L. In contrast Sr has a relatively rapid rate of adsorption onto MST, reaching DF in less than 2 hours.

### 3.2.3.3.3 Details of Cycle

For the CST Ion Exchange (CST) and Caustic Side Solvent Extraction (CSSX) processes, a MST sorption and filtration process is required prior to ion exchange or solvent extraction processing. MST treatment of salt solution feed for alpha and Sr removal will be performed in the Alpha Sorption Tank (AST) and will be followed by filtration of the MST slurry with filtrate going to the Recycle Blend Tank for CST processing or the Salt Solution Feed Tank for CSSX processing. In addition, the sludge solids entrained in the salt solution must also be removed to meet Saltstone acceptance criteria and to prevent plugging of the lead CST ion exchange column. Washing and filtering of accumulated sludge and MST solids from the heel of the Filter Feed Tank (FFT) will be performed prior to transfer to DWPF with spent wash water being recycled to the AST as dilution water. Water used to load and unload CST from the columns will be sent to alpha Sorption to ensure removal of CST fines collected. For material balance purposes, it is assumed this water is gradually recycled to the Wash Water Hold Tank (WWHT) for dilution.

#### MST Treatment

For the CST Ion Exchange alternative, 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<sup>+</sup>. Subsequently, about 300 gallons of MST slurry is then added to the AST. The resulting slurry is mixed for 24 hours to assure adequate adsorption of <sup>90</sup>Sr and TRU contaminants. The slurry is then sampled, filtered and analyzed to confirm adequate alpha decontamination to be within Class A disposal limits ([total alpha] < 20 nCi/g and Sr < 40 nCi/g). Blending during waste removal may be necessary to reduce mercury (Hg) concentration to less than 250 mg/L. Upon completion of the analytical step, the slurry is transferred to the Filter Feed Tank (FFT) for crossflow filtration.

#### Filtering

Using one of two cross-flow filter units, the slurry is then filtered at a 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 3.2-1) from five to eight consecutive batches are allowed to accumulate in the AST before further processing.

For the CST process, clarified salt solution is transferred directly to the Recycle Blend Tank to provide feed for the next process operation, <sup>137</sup>Cs decontamination by CST Ion Exchange. For the CSSX, clarified salt solution is transferred directly to Salt Solution Feed Tank to provide feed for the next process operation, <sup>137</sup>Cs decontamination by Caustic Side Solvent Extraction.

**Table 3.2-1 Insoluble Species**

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

**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, the 10,000 gallon heel is transferred to the Sludge Solids Receipt Tank (SSRT). Adding process water at a rate of 4.5 gpm washes 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 utilized 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 to 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 process 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 2 wt % oxalic acid (sp. g. = 1.014) are prepared in the Oxalic Acid Feed Tank.
- (7) The oxalic acid is transferred to the CSDT and circulated through the filter unit while periodically backpulsing the filter unit.
- (8) The oxalic acid is transferred from the filter unit and the CSDT to the AST, where it reacts with excess NaOH to produce 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 in the CSDT is circulated 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 or wash water from the SSRT.

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### Bases for Cycle Times, Vessel Sizing and Process Flow Rates

For the MST treatment and filtration steps of the CST Ion Exchange Process, 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 step cycle time in parentheses does not add to the total cycle time because filtration occurs in a separate Filter Feed Tank while a new batch of untreated salt solution is transferred to the AST for processing in parallel with the filtration cycle.

#### 3.2.3.3.4 Description of SpeedUp™ Model

(**Note:** The description of the Alpha Sorption SpeedUp™ is unchanged from Revision 0 of this document. By utilizing fractional cleaning cycles and washing cycles the Alpha Sorption steady-state process flow diagram material balance is preserved. As the Speedup model for Alpha Sorption was a batch model, it was not necessary to rerun the model because it would produce the same results.)

#### MST Alpha Sorption SpeedUp™ Model

A relatively detailed and complete dynamic model of the alpha sorption process to pretreat salt solution has been developed. A schematic diagram of the model is shown in Figure 3.2-9. The model considers the four main tanks in the process: the Alpha Sorption Tank (AST), the CST Recycle Blend Tank (RBT), the Sludge Slurry Receipt Tank (SSRT) and the Wash Water Hold Tank (WWHT). The total cycle time for the alpha sorption process is 95 hours. The operation of each tank as implemented in the model is described in the following paragraphs.

#### Alpha Sorption Tank (AST)

Salt solution is added to the AST in 100 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 given  $K_d$  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 cycle to allow time for the adsorption equilibrium to be achieved. Table 3.2-2 shows the DFs and  $K_d$ s used in the Phase IV material balance.

**Table 3.2-2 DFs and  $K_d$ s 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 passing it through a filter. It is assumed that the filtration is 100% efficient in removing solids. Filtrate is sent to the RBT at 61 gpm and the concentrate returned to the AST. Filtration proceeds until the level in the AST drops to 10 kgal.

Recycle Blend Tank (RBT)

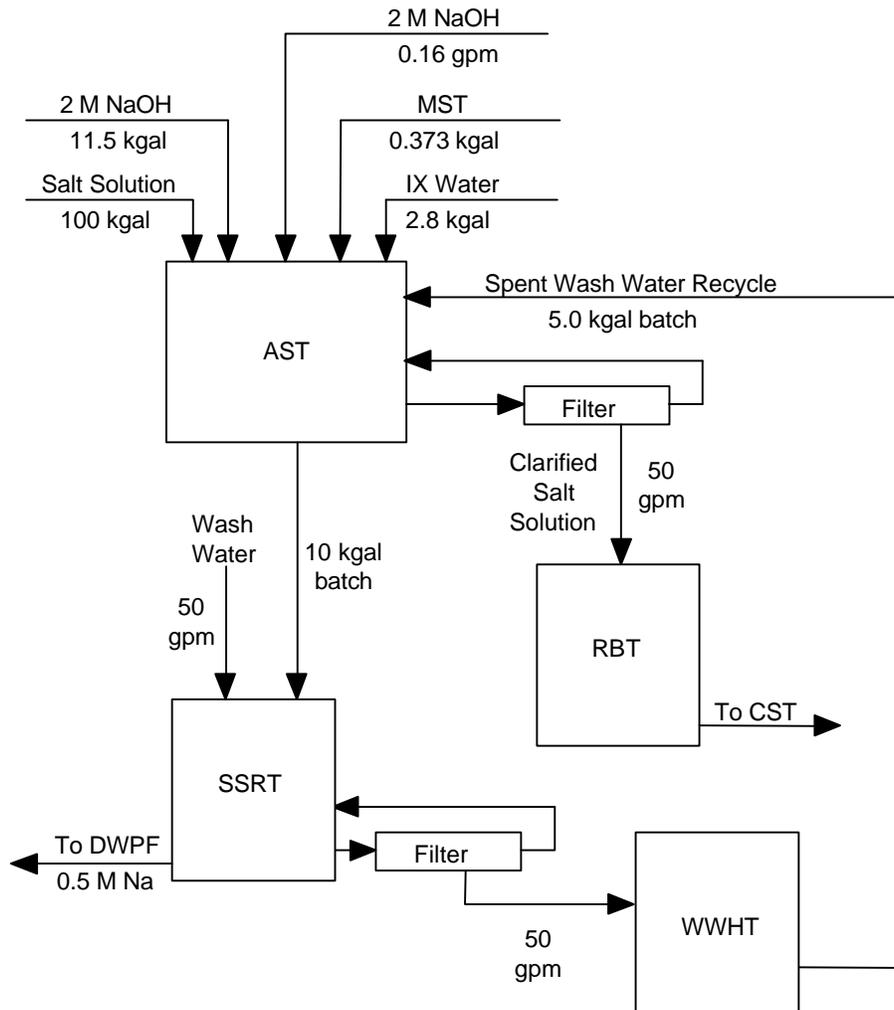
Clarified salt solution from the AST filtration is collected in the RBT. A small side stream of 2.0 M NaOH is also added to this tank at a rate of 0.16 gpm. This stream comes from caustic pre-treatment of the CST ion-exchange resin. After the first batch is added, the tank is continuously emptied to represent treatment of the salt solution by the CST ion-exchange columns. Simulations show that clarified salt solution must be processed continuously at a rate of about 21 gpm to work off the RBT inventory.

Sludge Slurry Receipt Tank (SSRT)

When the 10-kgal heel in the AST exceeds 5 wt% solids, the heel is transferred into the SSRT. Simulations indicated that this occurs after about every five 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.

Wash Water Hold Tank (WWHT)

Spent wash water from the SSRT filtration is collected in the SWWT. 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 SWWT, four out of the five AST batches will also have spent wash water added to the tank.



**Figure 3.2-9 Alpha Sorption Model**

#### 3.2.3.2.5 Alpha Decontamination Model Results

Two streams from the Alpha Decontamination Model flow to downstream models: the clarified salt solution is the feed to the CST IX model and the washed MST/sludge is one of the feeds to the DWPF model. The clarified salt solution is 20.7 gpm (12815 lbs/hr) with 5.63 M Na<sup>+</sup>. The entrained sludge has been removed and the Sr and Pu sorbed on MST to meet Saltstone requirements. The washed MST/sludge stream is 0.35 gpm (186 lbs/hr) with 0.5 M Na<sup>+</sup>. The solids concentration is ~ 5.4 wt %, corresponding to 4.2 lbs/hr MST and 5.8 lbs/hr sludge.

#### 3.2.4 Conclusions

Research studies at 5.6 M Na and 0.4 g/L MST (Reference 69) have shown that Sr adsorption occurs rapidly and Pu removal is adequate at the Tank Farm average Pu (0.2 mg/L) and activity (1.33 Ci/g). Characterization of bounding soluble Pu concentrations and isotopic distributions will be needed 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 time

Low filtration flux rates for MST/sludge slurries previously required a large cross-flow filter (~3,000 ft<sup>2</sup>) and a filter circulation rate in the range of 5500-8500 gpm. A trade study of alternative process configurations for Alpha Removal (Reference 68) resulted in a revision to the Alpha Removal process by the addition of a Filter Feed Tank 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 ft<sup>2</sup>. Filter circulation rates decrease into the range of 1800 to 2900 gpm as a result of the decrease in crossflow filter size.

### **3.3 CST Non-Elutable Ion Exchange**

The proposed process would employ crystalline silicotitanate (CST) resin to remove Cs from the salt solution. Sr, Pr, and U are removed beforehand by monosodium titanate (MST) addition. Since the Cs cannot be eluted from the CST, 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 Facility.

The process would include these steps: MST addition to remove Sr, Pu, and U to meet Saltstone 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, the solids would flow to the DWPF. The 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. The decontaminated salt solution would be transferred to the Saltstone Facility to produce a Class A waste.

#### **3.3.1 Alternative Description**

The salt solution contains insoluble sludge and soluble species that must be removed to meet Saltstone requirements. In addition, the sludge must be removed to prevent plugging the IX column bed. The first step is to add MST (an insoluble solid) that sorbs the soluble Sr, Pu, and U sufficient to meet Saltstone specifications. Both the MST and sludge are then removed by cross-flow filtration, concentrated to about 5 wt % solids and washed to remove sodium salts. (See Section 3.2 for a detailed description of Alpha Sorption.) These solids are transferred to the DWPF for incorporation in the glass but must be washed first to avoid excessive alkali to DWPF.

The clarified salt solution flows to the Recycle Blend Tank (RBT) in the CST IX portion of the process (Figure 3.3-1).



Before being loaded into a column, the CST must undergo two treatments. First, the CST is loaded into the Column Preparation Tank, similar in dimensions to an IX column bed. 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 partially in the hydrogen form and partially in the sodium form. It is converted to the sodium form by circulating a NaOH solution through the bed for 24 hours. 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 2 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.

### **3.3.2 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).

#### Granular Engineered CST

The Texas A&M University CST equilibrium model (Reference 70) has been shown to correctly predict the  $K_d$  for CST powder with various SRS wastes (Reference 71). In Phase III, some prior work indicated that the granular, engineered form might not have a  $K_d$  equivalent to the powder, presumably due to the binder, which is 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 (Reference 73). For this reason, a “dilution factor” of 0.70 was used in the Phase III CST modeling and in estimates of CST usage (e.g., g CST used per g Cs removed). However, subsequent work indicates the  $K_d$  of the granular form is approximately the same as the CST powder (Reference 71). Therefore, the Phase IV  $K_d$ 's used for column modeling and estimates of CST usage are “undiluted”; that is, they are the same as predicted by the Zheng, Anthony, and Martin (ZAM) CST equilibrium model. The primary impact is that 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 (Reference 72); only the Cs loading on the CST is affected.

### VERSE Validation

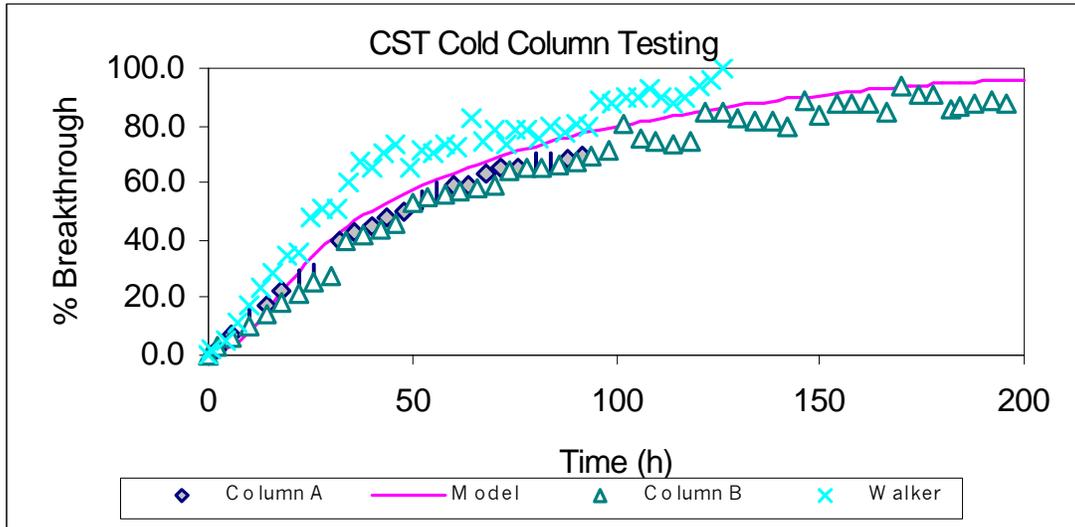
During Phase III, two ion exchange column models originating from universities were used to model and size IX columns based on various SRS waste compositions (References 72 and 73). R. G. Anthony *et al.* from Texas A&M University used their Texas A&M column carousel model while N.-H. Wang *et al.* used their VERSE modeling package. (See Section 3.3.3.3 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 3.3-2 and 3.3-3). In general, comparisons between predicted and measured have been good (References 74 and 75) – 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 3.3-4) and the pore diffusion ( $D_p$ ) (See Figure 3.3-5). 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.

### CST Calcine Factor

The Immobilization Technology Section has shown that when as-received CST is dried for 4 hours at  $\geq 400$  °C, the CST loses approximately 15 % of its weight (Reference 62). The CST vendor indicates this is primarily loss of waters of hydration. For flowsheet purposes, the weight of CST produced by IX (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. This, combined with not using a binder “dilution factor”, will decrease the concentration of CST in the glass by about 40 %.

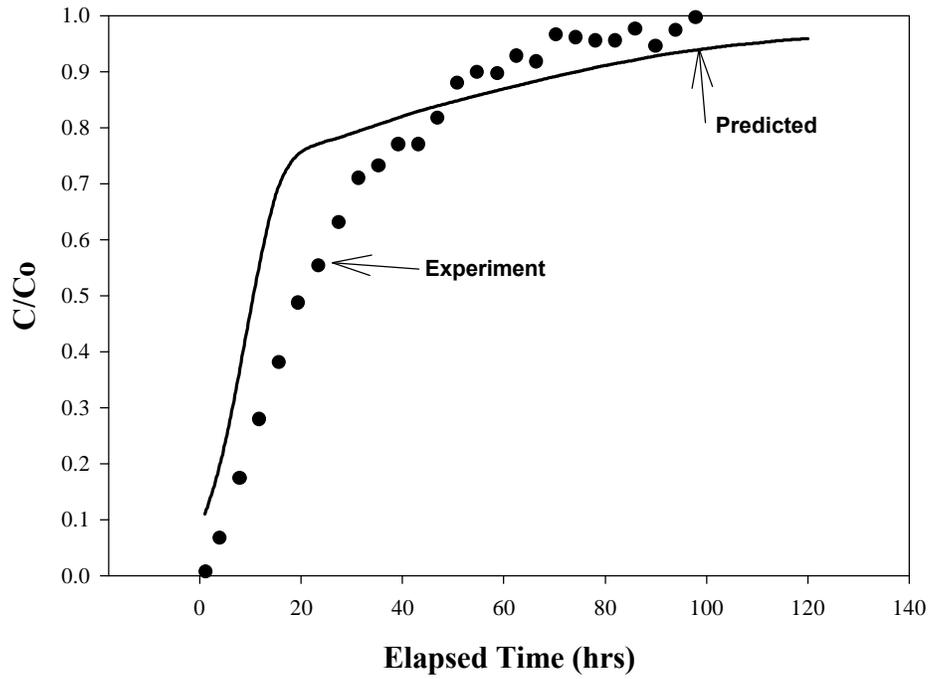
### Mercury Removal

The acceptance limit for Hg in the salt solution going to Saltstone is 250 mg/L. In the waste removal study conducting during Phase III (Reference 12), the highest annual Hg concentration was approximately 50 mg/L. Therefore, Hg removal by ion exchange has been removed from the CST IX option.

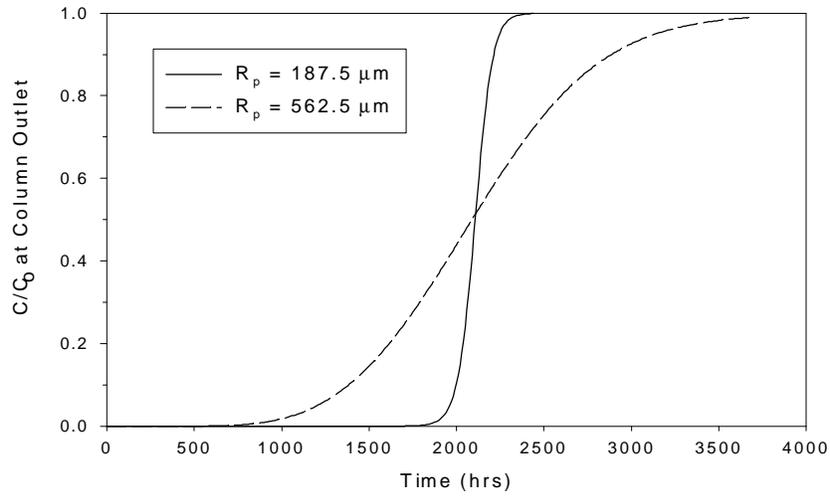


**Figure 3.3-2 Non-Radioactive CST Column Testing**

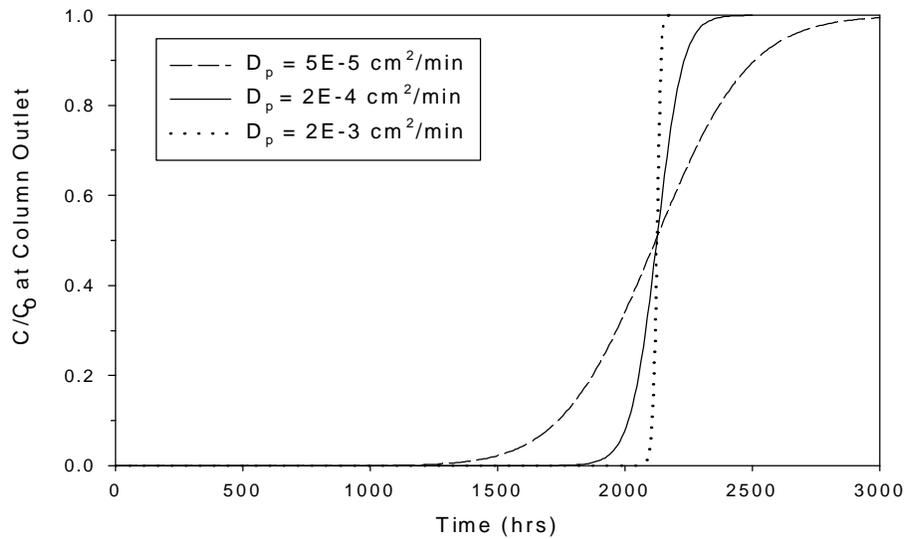
### Cs-137 Breakthrough During Tk 44F IX Column Test



**Figure 3.3-3 Radioactive CST Column Testing**



**Figure 3.3-4 Effect of Particle Diameter on Mass Transfer Zone Length**



**Figure 3.3-5 Effect of Pore Diffusivity on Mass Transfer Zone**

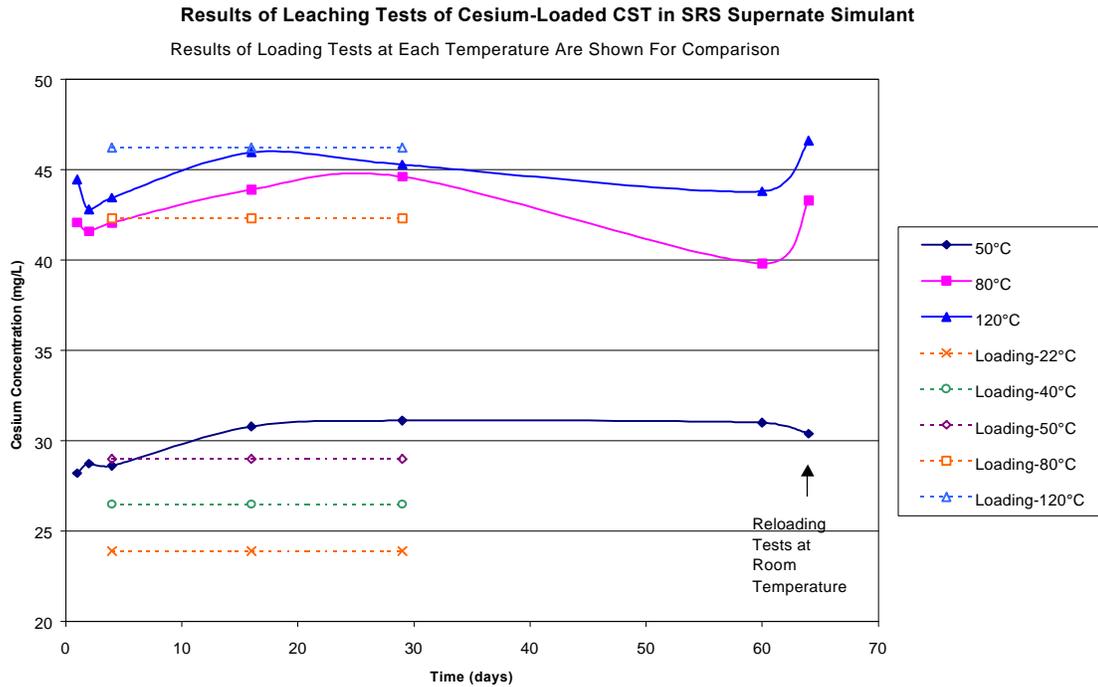
### **3.3.2.1 Summary of Other R & D Results**

The following is a summary of R & D results that do not impact the Bases and Assumptions.

#### CST Stability

Experiments were performed at ORNL to study the stability of Cs-loaded CST (Reference 76). 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 3.3-6). 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 Cs. As currently designed, under normal operating conditions the CST would be exposed to salt solution for about 12 months at 25 to 30 °C. These findings are, of course, significant but are related to upset scenarios and thus do not impact the material balances or required equipment in the current Bases and Assumptions.

Additional tests were performed at SRTC (Reference 77). 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 3.3-6 Cesium Leaching from CST Loaded at 22 °C**

CST and Salt Solution Thermal and Physical Properties

Researchers at ORNL determined thermal and physical properties (heat capacity, thermal conductivity, viscosity, etc.) for CST and various SRS simulated waste salt solutions (Reference 78). These data were obtained to perform future heat balances and other engineering calculations.

Effect of Organics, Pressure, and Pretreatment on CST  $K_d$  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 (References 74 and 79). Researchers found that 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 did not have a significant effect on column performance. It was found that 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 a small negative impact on column performance – perhaps within experimental error.

### Effect of Temperature and Radiation

SRTC researchers performed limited tests on the effects of radiation and temperature on  $K_d$  (Reference 80). 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.  $K_d$ s for IE-910 (the powder) and IE-911 (the granular form) were measured at 22, 35 and 45 °C and compared to the  $K_d$ s 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. It is postulated there is a material in the IE-911 that adsorbs Cs at lower temperatures but does not at higher temperatures.

### 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 (Reference 71). 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 lot-to-lot variability – specifically the lot known as 96-4 (Reference 74). While the as-received  $K_d$  lot 96-4 was consistent with other lots, the  $K_d$  measured after pretreatment was lower. It appears the variability is 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.

### 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 recommended diluting with NaOH and route contaminated water to the AST to avoid aluminum precipitation
- UOP considers production of IE-911 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.
- there was a concern with the presence of excess chloride which has subsequently been dispositioned as no concern<sup>3</sup> (Reference 81)
- successful production of IE-911 has only been accomplished in development-scale facilities
- the two production runs in commercial-scale facilities have required rework

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<sup>3</sup> Wilmarth 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 (S, O<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub>) 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.

#### “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 (Reference 82). 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.

#### Impact of Radiolytic Gas Generation

The accumulation of large quantities of Cs in the lead column (up to 5 M Ci) 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 (Reference 83). SRTC researchers irradiated a stagnant CST bed and noted bubble formation within eight hours. Bed expansion and bubble migration were also observed (Reference 84). In the same reference, G values for generation of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>O 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 H<sub>2</sub> from the high hydroxide solution is about twice as large as expected, and
- an explosive H<sub>2</sub>/O<sub>2</sub> mixture could possibly form if the H<sub>2</sub> and O<sub>2</sub> were trapped in an unpurged space (e.g., inside a column). If CST is selected, this scenario will require further analysis.

One test scheduled in this series was dropped because it was found to be technically infeasible given the time and facilities constraints in which the test had to be performed. This was a small column test in a radiation field that was intended to explore the impact of forming gas bubbles in a flowing column (Reference 83). However, 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 82, 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 it will be necessary to degas the solution between columns. However, the consequences and impact of continuing gas generation at no-flow or low-flow conditions is still unknown.

### Real Waste Tests in CST Column

At SRTC, researchers performed a CST column test using real SRS waste salt solution (See Figure 3.3-3). The 1.5-cm diameter column was in 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 Cs concentration at the end of the 10-cm column approximated the predicted breakthrough curve except that initial breakthrough occurred later than predicted and 90 % breakthrough occurred earlier than predicted. (Reference 75). This is consistent with better pore diffusion ( $D_p$ ) than is being used in the VERSE model. At the end of the tests, the Cs at the exits of the second and third column were also lower than predicted but indicated that the length of the MTZ was as predicted.

Prior to this test, the CST was being pre-treated *in-situ* in the column. To perform the NaOH soak pretreatment, a solution of NaOH was recirculated 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 re-circulated. As currently shown in the process flow diagram (PFD), the NaOH soak is performed by recirculating NaOH through a fines filter. This result (the leaching and bed plugging), when combined with leaching and precipitation previously discussed in the CST Stability section, will require the CST manufacturer to perform additional production steps to eliminate the excess materials.

### Foaming and H<sub>2</sub> Generation in DWPF Feed Preparation System

SRTC performed tests at bench scale and at pilot scale (1/240<sup>th</sup> scale in the Glass Feed Prep System – GFPS) to assess the impact of Cs- and noble-metal-loaded CST on H<sub>2</sub> and foam formation in the DWPF (References 85 and 86). Tests were performed with sludge-only, as-received CST, and size-reduced CST. H<sub>2</sub> generation rates were very low and comparable to sludge-only operation with Tank 42 sludge. Hydrogen rates were generally less than rates observed for 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.

### DWPF Feed Homogeneity

One of the principal requirements in the DWPF glass quality program is homogeneity and accurate sampling of the solids slurries in the Feed Preparation system. Researchers at SRTC performed tests to determine if CST can be maintained in a homogeneous mixture and if the CST can be representatively sampled. 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 (Reference 87). In

a tank built to scale to DWPF mixing and equipped with a full-scale Hydragard<sup>®</sup> sampler, researchers have shown (Reference 88):

- an as-received 10 wt % slurry of CST in water could not be homogeneously suspended at DWPF conditions or at 20 % higher agitator speed,
- the as-received CST could be easily resuspended,
- agitation and pumping (1300 turnovers) broke up the CST in a bi-modal distribution – some in very small pieces ( $\leq 10$  micron) and the rest essentially unbroken,
- the as-received CST with sludge and frit plugged the Hydragard<sup>®</sup> sampler, and
- the size-reduced CST with sludge and frit was not representatively sampled (it was approximately 12 % depleted in frit).

Researchers also found that the size-reduced CST formed a rigid cake after settling for five days. The cake was very difficult to break and resuspend. If selected, equipment will have to be provided to size reduce the CST. Also, modifications will be required to maintain/resuspend the size-reduced CST and to representatively sample the CST/sludge/frit slurries.

#### 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 (Reference 89). 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.) The results are:

- 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).

If CST is selected, all correlations will have to be revised and the CST frit may have to be reformulated to produce an acceptable glass viscosity with HM sludge.

### **3.3.3 Bases for Material Balances**

#### **3.3.3.1 Changes from Phase III**

The changes from the Phase III Bases and Assumptions are discussed in Section 3.3.2.1. In summary, they are:

- Granular (engineered) CST has the same  $K_d$  as CST powder; therefore, there is no “dilution factor” due to the presence of binder.
- A “calcine factor” of 0.85 is applied in the DWPF calculations to the as-received weight of CST (i.e., the weight of CST as delivered to the CST IX process) to account for the water of hydration that is driven off in the melter.
- Mercury removal by ion exchange is deleted since waste removal studies show it is not required.

#### **3.3.3.3 CST Ion Exchange**

##### **3.3.3.3.1 Overview of CST IX Modeling**

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

1. Characterization of SRS waste composition
2. Development of equilibrium isotherms<sup>4</sup> 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.

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<sup>4</sup> 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 70).

### 3.3.3.3.2 Resin Loading Properties

The adsorption of  $\text{Cs}^+$  ion onto crystalline silicotitanate exchanges a  $\text{Na}^+$  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  $\text{Na}^+$  – and ions such as  $\text{OH}^-$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$ , 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 3.3.3.3.3), so it is necessary to evaluate the impact the various waste compositions can have on the capacity of the CST. The Texas A&M CST equilibrium model (Reference 70) was used to assess these impacts and results have been confirmed by tests at SRTC (Reference 71).

$\text{Na}^+$  – 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 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 results in more saltstone production and higher process throughput requirements (i.e., larger equipment). A sodium molarity of 5.6 was selected to provide a balance among these considerations.

$\text{K}^+$  – Potassium competes weakly with cesium for adsorption onto the CST. In some DOE wastes (e.g., Hanford), the  $[\text{K}^+]$  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 some SRS wastes might have as high as 0.1 to 0.15 M K. However, estimates indicate the blended SRS wastes will only be 0.009 to 0.022 M K; thus the impact of potassium on CST capacity will be small. This small impact is accounted for by using a Cs isotherm that includes the effect of potassium.

$\text{Sr}^{+2}$  and  $\text{Rb}^+$  – There is essentially no rubidium in SRS waste. Also, because of the very high pH ( $[\text{OH}^-] > 1.5 \text{ M}$ ), most of the strontium is precipitated. What little strontium remaining in solution is then removed by MST.

$\text{OH}^-$  and  $\text{NO}_3^-$  – 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 lower  $K_d$  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 3.2.2.1, it has been determined the granular form of CST has the same  $K_d$  as the powder. Therefore, the  $K_d$ 's and isotherms predicted by the ZAM CST equilibrium model are being used for column modeling.

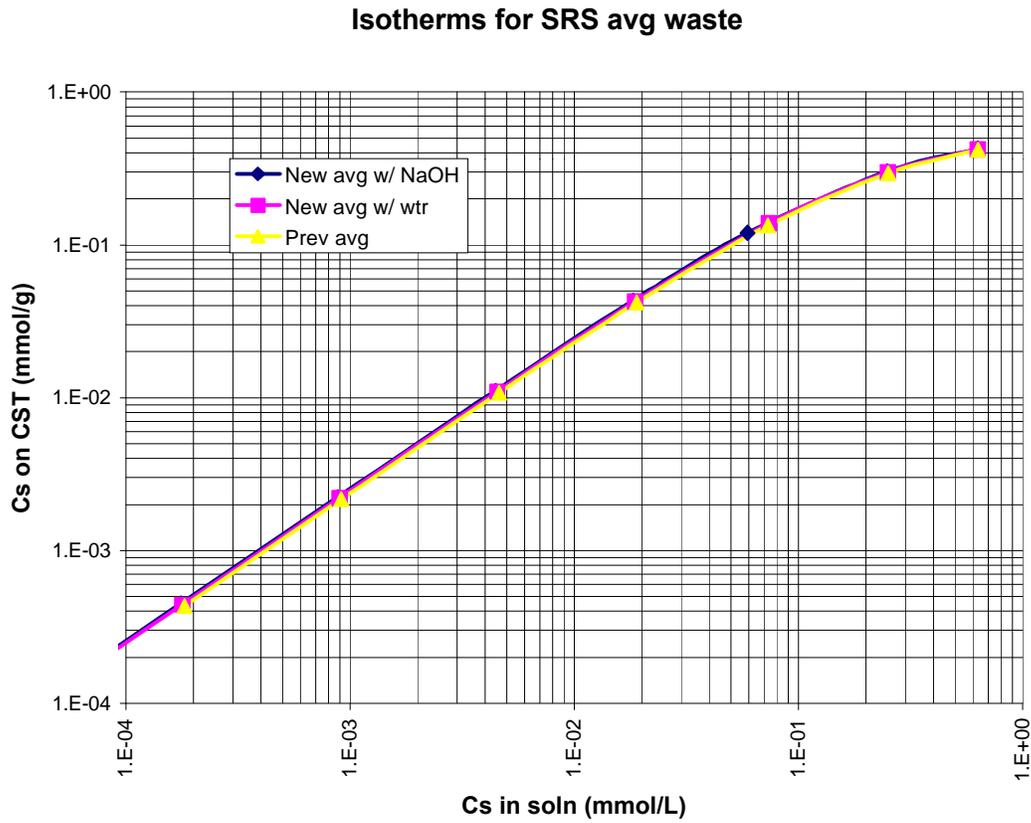
### 3.3.3.3.3 Feed Compositions and Isotherms for Phase III and IV Modeling

For Phase III, numerous waste compositions and isotherms were developed for the model development phase – step 5 (Reference 12). 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 in Section 2.3.2 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 3.3-1 compares the various SRS waste compositions. Figures 3.3-7 and 3.3-8 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 3.3-7).

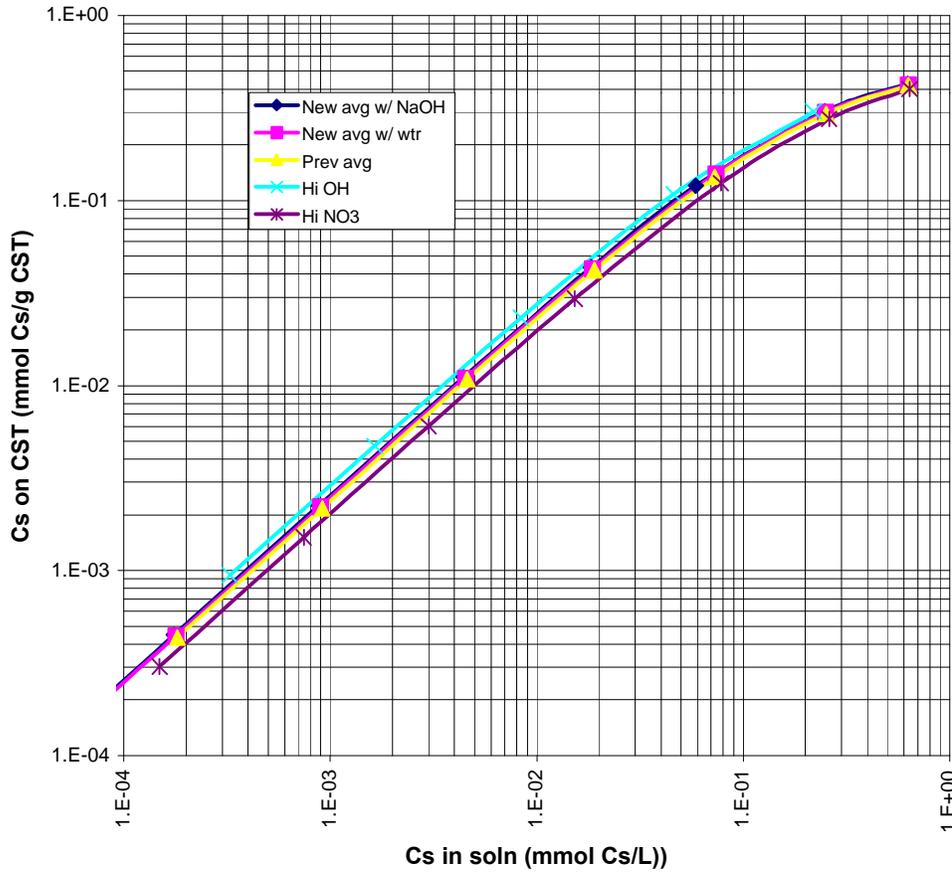
**Table 3.3-1 SRS Waste Compositions**

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



**Figure 3.3-7 SRS Average Waste Isotherms**

### SRS Waste Isotherms



**Figure 3.3-8 SRS Waste Isotherms**

Tables 3.3-2 through 3.3-6 contain the data for the isotherms as calculated from the waste compositions with the ZAM CST equilibrium model.

**Table 3.3-2 SRS Average Waste Isotherm**

<b>Average</b>	
<b>C (mmol Cs/L)</b>	<b>Q (mmol Cs/g CST)</b>
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 3.3-3 SRS High Hydroxide Isotherm**

<b>High Hydroxide</b>	
<b>C (mmol Cs/L)</b>	<b>Q (mmol Cs/g CST)</b>
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 3.3-4 SRS High Nitrate Isotherm**

<b>High Nitrate</b>	
<b>C (mmol Cs/L)</b>	<b>Q (mmol Cs/g CST)</b>
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 3.3-5 SRS New Average Waste Diluted W/ Water Isotherm**

<b>C (mmol Cs/L)</b>	<b>Q (mmol Cs/g CST)</b>
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 3.3-6 SRS New Average Waste Diluted w/ NaOH Isotherm**

<b>C</b> <b>(mmol Cs/L)</b>	<b>Q</b> <b>(mmol Cs/g CST)</b>
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

#### 3.3.3.3.4 Summary of Models Used in Phase III

In Phase III, four ion-exchange models were used to provide information to 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 3.3-7 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 utilizing 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 3.3-7 provides the primary purpose of each model.

**Table 3.3-7 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"> <li>1. “Lumped Resistance” mechanism,</li> <li>2. Linear Isotherm</li> <li>3. Single Long Column</li> <li>4. Constant feed composition</li> <li>5. Zero cesium loaded initially</li> <li>6. Mass transfer coefficient calculated from bench-scale non-SRS wastes.</li> </ol>	<ul style="list-style-type: none"> <li>• Check on preliminary sizing</li> <li>• Compare/validate other models: PU and A&amp;M</li> </ul>
Salt Disposition Modeling Team simulated this model using SpeedUp™. (SDMT)	<ol style="list-style-type: none"> <li>1. “Lumped Resistance” mechanism,</li> <li>2. Non-Linear Isotherm</li> <li>3. 3 Column Carousel</li> <li>4. Variable feed composition</li> <li>5. Calculates cycle time for partially loaded column.</li> <li>6. Mass transfer coefficient calculated from bench-scale non-SRS wastes.</li> </ol>	<ul style="list-style-type: none"> <li>• Provide material balances</li> <li>• Compare/validate other models: PU and A&amp;M</li> </ul>
Purdue University has developed the numerical techniques required to solve this system of equations. (PU)	<ol style="list-style-type: none"> <li>1. Various mass transfer mechanisms,</li> <li>2. Non-Linear Isotherm</li> <li>3. 3 Column Carousel</li> <li>4. Variable feed composition</li> <li>5. Mass transfer coefficient calculated from pilot-scale non-SRS wastes.</li> </ol>	<ul style="list-style-type: none"> <li>• Perform column sizing evaluation</li> <li>• Cross check WSRC models: HLW Process Engineering and SDMT</li> </ul>
Texas A&M University has developed the numerical techniques required to solve this system of equations. (A&M)	<ol style="list-style-type: none"> <li>1. Various mass transfer mechanisms,</li> <li>2. Non-Linear Isotherm</li> <li>3. Single Long Column</li> <li>4. Variable feed composition</li> <li>5. Mass transfer coefficient calculated from pilot-scale non-SRS wastes.</li> </ol>	<ul style="list-style-type: none"> <li>• Perform column sizing evaluation</li> <li>• Cross check WSRC models: HLW Process Engineering and SDMT</li> </ul>

### 3.3.3.3.5 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 3.3-10.

The ion exchange column arrangement for Phase III consisted of a single train with 3 columns. Each column was 5 feet in diameter and 16 feet long. Based on Purdue report (Reference 72), 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 3.3-8 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 3.3-8 Summary of Purdue and Texas A&M Modeling Results including Scaling to 5 ft Diameter and 20 gpm**

Feed Type	Flow Rate (GPM)	Column Diameter (ft)	Column Length (ft) Texas A&M (Ref.90)	Column Length (ft) Purdue (Ref. 91)
High OH <sup>-1</sup>	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 <sub>3</sub> <sup>-1</sup>	15	4	18.6	18.3
	25	4	31.0	30.5
<b>High OH<sup>-1</sup></b>	<b>20</b>	<b>5</b>	<b>6.3</b>	<b>6.2</b>
<b>Average</b>	<b>20</b>	<b>5</b>	<b>13.9</b>	<b>13.3</b>
<b>High NO<sub>3</sub><sup>-1</sup></b>	<b>20</b>	<b>5</b>	<b>15.9</b>	<b>15.6</b>

### 3.3.3.3.6 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. As has been shown, the Cs concentration on the CST is a strong function of the Cs concentration and the salt composition. The waste removal study performed during Phase III provided a projection of the year-by-year composition of the salt solution feed (Reference 12). Table 3.3-9 shows among other things, the year-by-year estimates of cycle times, Cs loading on CST, CST quantities to the DWPF, CST

concentration in the glass, and total TiO<sub>2</sub> in the glass (from CST and MST). The assumptions are: 0.4 g/L MST at 5.6 M Na<sup>+</sup>, no binder dilution factor, 98% loading on the CST, and 0.85 calcine factor for CST in the melter.

**Table 3.3-9 CST Cycle Times and Loadings**

<b>CST IX - Year by Year and Life Cycle Totals</b>												
<b>INPUTS</b>	<b>2007</b>	<b>2008</b>	<b>2009</b>	<b>2010</b>	<b>2011</b>	<b>2012</b>	<b>2013</b>	<b>2014</b>	<b>2015</b>	<b>2016</b>	<b>2017</b>	<b>2018</b>
<i>Salt soln supply vol - k gals</i>	4690.6	6441.2	6293.8	6051.7	6128.3	5464.4	5866.0	6505.6	6791.8	4955.6	5234.0	4707.5
<i>Salt soln supply [Na+] - M</i>	6.60	6.62	6.55	6.41	6.58	6.53	6.55	6.59	6.60	5.95	5.72	5.91
<i>Salt soln vol @ 5.60 M Na+ - k gals</i>	5765.4	7950.7	7680.8	7224.1	7509.7	6653.3	7165.4	7993.8	8353.2	5492.6	5581.7	5187.9
<i>Density of 5.6 M salt soln - lbs/gal</i>	10.43	10.34	10.54	10.53	10.29	10.34	10.49	10.24	10.47	10.41	10.41	10.42
<i>Wtr in 5.6 M Na+ salt soln - lbs/gal</i>	7.28	7.36	7.35	7.32	7.41	7.34	7.31	7.34	7.32	7.30	7.41	7.39
<i>Canister production</i>	225	225	225	225	225	225	225	225	225	225	225	225
@ 5.60 M Na+:												
<i>K+ - M</i>	0.0118	0.0122	0.0091	0.0103	0.0213	0.0190	0.0136	0.0179	0.0177	0.0172	0.0121	0.0098
<i>Cs+ - M</i>	0.000094	0.000097	0.000069	0.000066	0.000143	0.000149	0.000115	0.000090	0.000061	0.000205	0.000175	0.000165
<i>Cs+ - Ci/gal</i>	0.932	0.961	0.685	0.656	1.418	1.475	1.142	0.894	0.609	2.036	1.741	1.636
<b>VALUES FOR YEAR</b>												
<b>CST IX (5.60 M Na+ feed)</b>												
<i>Cs in salt soln - mg/L</i>	12.58	12.97	9.24	8.86	19.13	19.90	15.41	12.07	8.22	27.48	23.50	22.08
<i>Cs ldg on CST - mg Cs/g CST</i>	18.19	21.82	14.97	14.11	26.69	27.37	21.11	20.96	12.78	32.04	29.94	30.01
<i>column cycles during year</i>	1.70	2.01	2.02	1.93	2.29	2.06	2.23	1.96	2.29	2.01	1.86	1.63
<i>cycle time - hours</i>	3870	3266	3254	3402	2867	3190	2951	3353	2873	3277	3523	4043
<i>Cs ldg in column - M Ci</i>	3.26	3.89	2.67	2.52	4.78	4.91	3.78	3.74	2.28	5.77	5.38	5.38
<i>CST IX feed rate @ 75% util - gal/min</i>	15.04	20.66	19.98	18.80	19.61	17.38	18.72	20.76	21.75	14.42	14.62	13.56
<i>CST usage - k lbs</i>	33.28	39.43	39.59	37.86	44.92	40.37	43.64	38.41	44.83	39.31	36.56	31.86
<b>DWPF</b>												
<i>CST slurry activity - Ci/gal (10 wt %)</i>	142.6	171.1	117.4	110.6	209.3	214.6	165.5	164.3	100.2	251.2	234.7	235.3
<i>CST in glass - wt % (calcinced)</i>	3.14%	3.72%	3.74%	3.58%	4.24%	3.81%	4.12%	3.63%	4.23%	3.71%	3.45%	3.01%
<i>MST usage - k lbs</i>	19.2	26.5	25.6	24.1	25.1	22.2	23.9	26.7	27.9	18.3	18.6	17.3
<i>[TiO<sub>2</sub>] in glass - wt %</i>	2.74%	3.57%	3.50%	3.31%	3.61%	3.22%	3.47%	3.55%	3.86%	2.84%	2.78%	2.52%
<i>Fraction TiO<sub>2</sub> from CST</i>	0.375	0.340	0.348	0.352	0.383	0.386	0.387	0.333	0.358	0.426	0.405	0.389
<i>Watts per canister</i>	116	164	113	102	229	211	176	154	109	241	209	183

These calculations, including K<sub>d</sub>'s, are specific for the average annual salt compositions and quantities. Cs loading on CST ranges from 12.5 to almost 32 mg Cs/g CST. The number of column cycles per year runs from 1.7 to 2.3 – or about 5 to 7 months when 75% utility is included. The concentration range for CST in glass is from 3.0 to 4.3 wt %. At the Cs on CST loadings and the column cycle times, the Cs contained in the lead column ranges from 2.5 to 5.8 M Ci.

3.3.3.3.7 Use of VERSE in Phase IV Modeling

As previously discussed (see Section 3.3.2, 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<sub>p</sub> and R<sub>p</sub>) 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 CST IX were performed with a modified version of the HLE Process Engineering model (see Section 3.3.3.3.4). For the Phase IV SpeedUp™ modeling, a computational method similar to the VERSE and Texas A&M models is being used to perform the CST IX calculations (see SpeedUp™ Model Description in Section 3.3.3.3.8).

### 3.3.3.3.8 Description of SpeedUp™ Model for CST IX and DWPF

#### SpeedUp™ Model Functionality

1) The feed composition is the average salt composition SpeedUp™ vector as shown in Section 2.3.2. The feed composition will be diluted to ~5.6 M Na<sup>+</sup> and the TRU and sludge components removed by Alpha Sorption (see Section 3.2.3.3). Including the water and NaOH added to the feed by CST IX 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 back to Alpha Sorption to prevent CST fines from plugging the lead column while the NaOH is added at the RBT. For material balance purposes, the water is added in equal-sized batches at the AST and the NaOH 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/cycle \*

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 3.3.3.3.3. 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 diameter by 16-ft long (314.16 ft<sup>3</sup>). (There is a fourth column that is filled with fresh resin and 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.

5) A cycle begins when feed is started to a column that has been rotated from the second position to the first. A cycle ends when the Cs concentration in the liquid at the exit of the second column reaches 1.3 micrograms Cs/L (or 20 nCi/g).

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) with the rest of the water diverted as described in (2).

---

\* Based on 20 col vols less the water 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  $\text{Cs}^+$  is exchanged for a  $\text{Na}^+$ , which then goes with the decontaminated salt solution. A small amount of  $\text{K}^+$  exchanges onto the resin and goes with the CST 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 portion of the SpeedUp™ model requires additional inputs.

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

The washed, average sludge rate and frit rate/composition will be supplied based on a DWPF recipe developed by HLW-PE. He will also supply the CST composition with the proprietary component designated as X1O and X2O. The molecular weights and free energies of hydration for X1O and X2O will also be specified.

10) 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  $\text{TiO}_2$  in the glass, should be turned off.

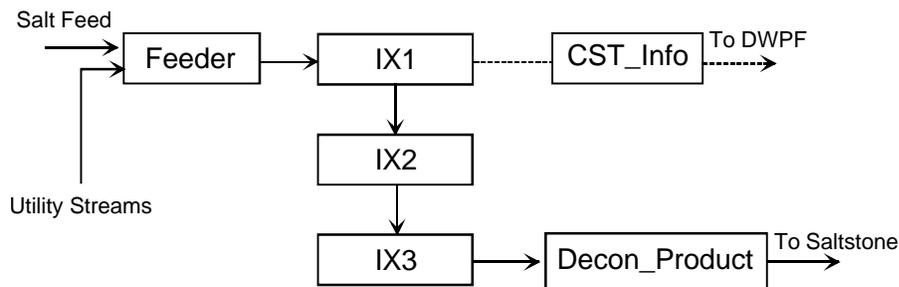
11) The following SpeedUp™ outputs are required including stream compositions:

- 5.6 M CST IX 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
- $\text{TiO}_2$  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 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 3.3-9, the entire SpeedUp™ CST IX 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 Salt Stone. **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 out of 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 3.3-9 Schematic of SpeedUp™ Flow Diagram of CST IX Process**

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Unit	Description
Feeder	Combine the salt solution and utility streams to a single feed stream to the first CST IX column, and convert the 51-component feed stream into a 2-component stream.
IX1	Model the CST IX 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	Model the CST IX second column. Functions similar to IX1.
IX3	Model the CST IX third (guard) column. Functions similar to IX1 and IX2.
Decon_Product	Convert the 2-component product stream at the outlet of the third IX column back to a 51-component decontaminated salt solution stream.
CST_Info	Provide 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 out of service at the end of a cycle. In addition to the slurry information, cycle time and total Cs loading are also given.

#### 3.3.3.3.9 Results of CST IX Model

This model also produces two streams: the decontaminated salt solution that flows to Z Area and the Cs-loaded CST that is another of the input streams to the DWPF. 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  $\sim 2930$  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  $\sim 220$  Ci/gal.

### 3.3.3.4 DWPF Vitrification

#### 3.3.3.4.1 Technical and Modeling Bases

The Technical Bases for the operation of the DWPF and flowsheet modeling bases are the same as those used in Phase III.

#### Bases for HNO<sub>3</sub> / HCOOH addition and F-N basis

Technical Bases - Acid adjustment in the SRAT is partially completed by adding nitric acid to yield an acid pH. Also, formic acid (HCOOH) is added to reduce mercury(II) compounds to mercury(0). The mercury is then steam-stripped from the sludge slurry to minimize the quantity sent to the melter. Only those reactions that involve a species in the salt solution are included, since reactions of sludge components are not generally affected by the various alternatives.

<u>Reactants</u>	<u>Products</u>
NaOH + HNO <sub>3</sub>	NaNO <sub>3</sub> + H <sub>2</sub> O
NH <sub>4</sub> OH + HNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub> + H <sub>2</sub> O
NaAlO <sub>2</sub> + 4 HNO <sub>3</sub>	Al(NO <sub>3</sub> ) <sub>3</sub> + NaNO <sub>3</sub> + 2 H <sub>2</sub> O
CsOH + HNO <sub>3</sub>	CsNO <sub>3</sub> + H <sub>2</sub> O
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> + 6 HNO <sub>3</sub>	2 UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> + 2 NaNO <sub>3</sub> + 3 H <sub>2</sub> O
SrCO <sub>3</sub> + 2 HNO <sub>3</sub>	Sr(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O + CO <sub>2</sub>
CoO + 2 HNO <sub>3</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O (70%)
HgO + HCOOH	Hg + H <sub>2</sub> O + CO <sub>2</sub> (99%)
2Ag <sub>2</sub> O + 2 HCOOH	2 Ag + H <sub>2</sub> O + CO <sub>2</sub> (99%)
PdO + HCOOH	Pd + H <sub>2</sub> O + CO <sub>2</sub> (99%)
RhO <sub>2</sub> + 2 HCOOH	Rh + 2H <sub>2</sub> O + 2CO <sub>2</sub> (99%)

The method for calculating acid addition and the balance between formate ion and nitrate ion are based on laboratory work (Reference 55) and DWPF cold runs and operating experience.

- 1 Calculate the total acid required to neutralize or to react with materials in the feed. One mole acid is needed for each mole of HgO, NaOH, and KOH. Two moles of acid are needed for Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, Mg(OH)<sub>2</sub> and carbonate (CO<sub>3</sub>)<sup>--</sup>. One-quarter mole is needed for each mole of nitrite (NO<sub>2</sub><sup>-</sup>) and 0.4 moles are needed for each mole of MnO<sub>2</sub>.
- 2 Multiply this “stoichiometric” amount by 1.25. This is the **total** amount of acid to be added.
- 3 Assume that 40% of the formic acid is lost in the SRAT cycle. Based on this, calculate how much formic acid is required such that the [formate]-[nitrate] (“F minus N”) will be 0.4 M in the SME – normalized to 45 wt% solids in the SME.

Assume that 100 gallons 90% formic acid will be added to the SME to provide part of the formate needed.

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

200 gallons of 50 wt% nitric acid

150 gallons of 90 wt% formic acid

In each SME batch 100 gallons of 90 wt % formic acid are added. The F-N redox value is calculated in the SME using the equation:

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

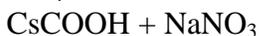
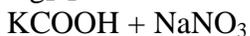
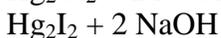
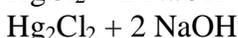
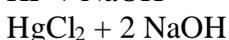
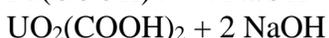
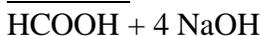
Some formic acid will be removed in the SRAT cycle during the evaporation. The amount of acid lost is calculated by an ideal solution estimate of the vapor composition and may not be the nominal 40%.

Mercury is removed from the solution in the SRAT and collected as a side stream. The mercury is tracked as HgO throughout the process.

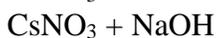
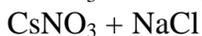
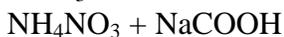
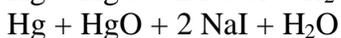
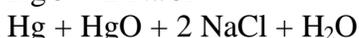
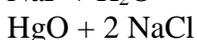
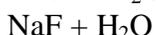
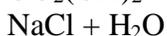
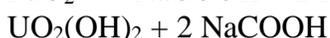
### **Bases for NaOH and NaNO<sub>2</sub> to RCT**

#### Technical Bases

##### Reactants



##### Products



The quantities of caustic and nitrite added to the RCT are based on the Waste Acceptance Specification and operating experience. This is to assure that the inhibitors required to prevent corrosion of the carbon steel waste tanks are present.

Modeling Bases - Caustic and inhibitor are added to the RCT to produce a recycle solution that is



Water evaporated in the SRAT, SME and melter goes directly to the RCT in the simplified Speedup model.

**Bases for NO<sub>x</sub> Produced in the Melter**

Technical Bases - In the melter, 50 % of the nitrate salts and all of the nitrite salts react with sodium formate to form nitric oxide (NO). The balance of the nitrate salts react to form nitrogen (N<sub>2</sub>). Subsequently, the NO reacts with oxygen in the air to form nitrogen dioxide (NO<sub>2</sub>).

Reactants	Products
4 NaNO <sub>3</sub> + 8 NaCOOH	6 Na <sub>2</sub> O + 2 NO + N <sub>2</sub> + 8 CO <sub>2</sub> + 4 H <sub>2</sub> O
4 NaNO <sub>2</sub> + 2 NaCOOH	3 Na <sub>2</sub> O + 4 NO + 2 CO <sub>2</sub> + H <sub>2</sub> O (100 %)
4 Al(NO <sub>3</sub> ) <sub>3</sub> + 24 NaCOOH	2 Al <sub>2</sub> O <sub>3</sub> + 12 Na <sub>2</sub> O + 6 NO + 3 N <sub>2</sub> + 24 CO <sub>2</sub> + 12 H <sub>2</sub> O

Modeling Bases - The reactions shown below as the Modeling Bases for Vitrification, closely approximate the NO<sub>2</sub> emission. Since complete oxidation is assumed, carbon monoxide and hydrogen in the melter off-gas are not accounted for.

**Bases for Vitrification in the Melter**

Technical Bases

In addition to reactions with nitrate and nitrite salts, formate salts either react with other 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., CaC<sub>2</sub>O<sub>4</sub>, HgO).

Reactants	Products
4 Al(NO <sub>3</sub> ) <sub>3</sub> + 18 NaCOOH	2 Al <sub>2</sub> O <sub>3</sub> + 9 Na <sub>2</sub> O + 12 NO + 18 CO <sub>2</sub> + 9 H <sub>2</sub> O
2 Na <sub>2</sub> SO <sub>4</sub> + 2 NaCOOH	3 Na <sub>2</sub> O + 2 SO <sub>2</sub> + 2 CO <sub>2</sub> + H <sub>2</sub> O
4 Fe <sub>2</sub> O <sub>3</sub> + 2 NaCOOH	4 FeO + Na <sub>2</sub> O + 2 CO <sub>2</sub> + 7 H <sub>2</sub> O
2 NaCOOH	Na <sub>2</sub> O + CO + CO <sub>2</sub> + H <sub>2</sub>
2 KCOOH	K <sub>2</sub> O + CO + CO <sub>2</sub> + H <sub>2</sub>
4 NH <sub>4</sub> COOH + 3 O <sub>2</sub>	2 N <sub>2</sub> + 8 H <sub>2</sub> O + 2 CO + 2 CO <sub>2</sub> + 2 H <sub>2</sub>
Mn(COOH) <sub>2</sub>	MnO + CO + CO <sub>2</sub> + H <sub>2</sub>
Ni(COOH) <sub>2</sub>	NiO + CO + CO <sub>2</sub> + H <sub>2</sub>
Ca(COOH) <sub>2</sub>	CaO + CO + CO <sub>2</sub> + H <sub>2</sub>

<u>Reactants (Cont'd)</u>	<u>Products (Cont'd)</u>
$\text{UO}_2(\text{COOH})_2 + \text{O}_2$	$\text{U}_3\text{O}_8 + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Cu}(\text{COOH})_2$	$\text{CuO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Co}(\text{COOH})_2$	$\text{CoO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Zn}(\text{COOH})_2$	$\text{ZnO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Mg}(\text{COOH})_2$	$\text{MgO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Sr}(\text{COOH})_2$	$\text{SrO} + \text{CO} + \text{CO}_2 + \text{H}_2$
$2 \text{CsCOOH}$	$\text{Cs}_2\text{O} + \text{CO} + \text{CO}_2 + \text{H}_2$
$\text{Na}_2\text{C}_2\text{O}_4$	$\text{Na}_2\text{O} + \text{CO}_2 + \text{CO}$
$\text{CaC}_2\text{O}_4$	$\text{CaO} + \text{CO}_2 + \text{CO}$
$\text{CaF}_2 + \text{Na}_2\text{O}$	$\text{CaO} + 2 \text{NaF}$
$\text{Sr}(\text{OH})_2$	$\text{SrO} + \text{H}_2\text{O}$
$\text{HgO}$	$\text{Hg}(\text{v}) + \text{O}_2$
$\text{Hg}$	$\text{Hg}(\text{v})$
$\text{Cs}_2\text{O}$	$\text{Cs}_2\text{O}(\text{v})$ (10%)
$2 \text{MnO}_2$	$\text{MnO} + \text{O}_2$
$\text{Pd}(\text{NO}_3)_2$	$\text{Pd} + 2 \text{NO} + 2 \text{O}_2$
$2 \text{PuO}_2(\text{NaTi}_2\text{O}_5)_2$	$2 \text{PuO}_2 + 8 \text{TiO}_2 + 2 \text{Na}_2\text{O} + \text{O}_2$
$\text{Sr}(\text{NaTi}_2\text{O}_5)_2$	$\text{SrO} + 4 \text{TiO}_2 + \text{Na}_2\text{O}$
$2 \text{H}(\text{NaTi}_2\text{O}_5)$	$\text{H}_2\text{O} + 4 \text{TiO}_2 + \text{Na}_2\text{O}$

Modeling Bases - The following simplified oxidation reactions were used to convert metal salts and other compounds into oxides in the glass melter:

<u>Reactants</u>	<u>Products</u>
$2\text{B}(\text{OH})_3$	$\text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$
$2\text{C}_6\text{H}_6 + 15 \text{O}_2$	$12\text{CO}_2 + 6\text{H}_2\text{O}$
$2\text{CsCOOH} + \text{O}_2$	$\text{Cs}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O}$
$2\text{KCOOH} + \text{O}_2$	$\text{K}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O}$
$2\text{NaCOOH} + \text{O}_2$	$\text{Na}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O}$
$2\text{NH}_4\text{COOH} + \text{O}_2$	$2\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O}$
$2\text{Cu}(\text{NO}_3)_2$	$2\text{CuO} + 4\text{NO}_2 + \text{O}_2$
$4\text{HNO}_3$	$4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$
$2\text{HCOOH} + \text{O}_2$	$2\text{CO}_2 + 2\text{H}_2\text{O}$
$2\text{NaOH}$	$\text{Na}_2\text{O} + \text{H}_2\text{O}$
$4\text{NaNO}_3$	$2\text{Na}_2\text{O} + 4\text{NO}_2 + \text{O}_2$
$4\text{NaNO}_2 + \text{O}_2$	$2\text{Na}_2\text{O} + 4\text{NO}_2$
$2\text{NaTi}_2\text{O}_5\text{H}$	$\text{Na}_2\text{O} + 4\text{TiO}_2 + \text{H}_2\text{O}$

### **Bases for Water additions and Recycle:**

Modeling Bases - Water evaporated from SRAT and SME is collected in the SMECT and transferred to RCT.

All water fed to the melter goes to the Offgas Condensate Tank and thence to the RCT

Steam Atomized Scrubbers and Film Cooler add 1000 pph water to offgas stream. This water is condensed and recycled. Decontamination waste adds another 340 pph of water to the RCT.

### **Phase IV DWPF Model Feed Streams**

The feed streams modeled in the flowsheet were based on average sludge and a CST rate reduced to that produced with average salt and no CST granular dilution factor. The CST rate matched 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 reduced the quantity of each oxide sent to DWPF by 15%. The washed CST feed stream modeled has the composition shown in the table below, on an oxide basis. The proprietary ingredients (X1O and X2O) are shown in the DWPF stream vector as BaO and ZrO<sub>2</sub>.

**Table 3.3-10 Washed CST Composition Modeled**

<b>Oxide</b>	<b>Weight %</b>
Al <sub>2</sub> O <sub>3</sub>	0.3
"BaO"	17.0
B <sub>2</sub> O <sub>3</sub>	0.2
CaO	0.6
CuO	0.3
Fe <sub>2</sub> O <sub>3</sub>	0.1
H <sub>2</sub> O	15.0
K <sub>2</sub> O	1.1
MgO	0.2
Na <sub>2</sub> O	9.9
PbO	0.2
SiO <sub>2</sub>	15.3
TiO <sub>2</sub>	27.7
ZnO	0.1
"ZrO <sub>2</sub> "	12.2

Glass formers are introduced into the DWPF as ground up glass or frit. The composition of frit used for modeling purposes is shown in Table 3.3-11 below.

**Table 3.3-11 CST Frit Composition Modeled - Weight %**

Oxide	CST Frit
B <sub>2</sub> O <sub>3</sub>	10
Li <sub>2</sub> O	9
Na <sub>2</sub> O	6
SiO <sub>2</sub>	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.

#### 3.3.3.4.2 R&D Impacts on DWPF Operation

Several of the R&D results, discussed in Section 3.3.2, have impact on the operability of the DWPF vitrification of CST.

*Sampling* - The as-received CST resin plugs the slurry samplers of the DWPF design. Size reduction of the CST would be required because representative samples (and their reliable analysis) are required for process control AND acceptance of the DWPF waste form, glass contained in sealed canisters. DWPF does not sample glass frequently, but depends on a tested, qualified system of sampling of the feed to its melter to demonstrate compliance with Waste Acceptance Product Specifications. This system was reviewed in great depth and at a high level by DOE and it is unlikely that it will be modified. Further, the sized reduced CST samples were lower than expected in frit. This result would not be acceptable, so improved sample system design requires development and demonstration.

*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 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.

#### 3.3.3.4.3 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:

CST composition, including a placeholder called “X1O” and “X2O” used to represent proprietary materials. These materials were introduced to the model using the vector positions normally used for BaO and ZrO<sub>2</sub>, materials not present in the CST calculation. A nominal molecular weight and free energy were provided for the proprietary constituents.

The modeling of Alpha Sorption and CST IX provided input to the DWPF model. This included two source vectors: a CST slurry containing adsorbed cesium from the ion exchange column and an MST/sludge slurry including alpha constituents stripped from the source salt stream.

A special CST frit composition was used for the glass calculation.

The high titanium content from both the CST and the MST input vectors required disabling the titanium limit in the PCCS calculation.

Results from the DWPF model are given as yearly average values. The 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 including startup effects in the yearly averages.

#### 3.3.3.4.4 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 3.0 % CST (calcined basis), 2.2 % MST, and ~ 30 % sludge oxides. The total TiO<sub>2</sub> from CST and MST is 2.7 %. The MST concentration is within the range tested in the CST glass variability study (Reference 89). 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 (cst16: 3 % CST, 2.5 % MST, 30 % sludge) had the following properties: ΔGp 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 89, 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.

### **3.3.3.5 Saltstone Product Basis**

Saltstone is a solid waste form that is the product of chemical reactions between a salt solution and a blend of cementitious materials (slag, flyash, 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 3.3-12 (Reference 48). The demonstrated range of acceptability for each component with respect to physical properties and resistance to contaminant leaching is shown in Table 3.3-13 (Reference 49). 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 substitute for the cement to function as a lime source 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.

Saltstone grout is formulated to minimize bleed water from the grout during curing. An acceptable saltstone product, from the standpoint of physical properties, has been demonstrated with salt solution ranging from about 20 wt % to 32 wt % salt, corresponding to a specific gravity ranging from about 1.18 to 1.32 with a sodium molarity of ranging from about 4 M to 6 M. Bleed water is controlled by controlling the water-to-premix mass ratio in the range of 0.52 to 0.60 (presently set at 0.57). The density of cured saltstone ranges between 1.70 and 1.80 kg/L (References 50 and 51).

**Table 3.3-12 Composition of Saltstone Cementitious Materials**

Component	Cement Type II Santee (Wt%)	Slag Grade 120 NEWCEM <sup>a</sup> (Wt%)	Fly Ash Class F Low CaO (Wt%)
SiO <sub>2</sub>	21.10	34.70	52.17
Al <sub>2</sub> O <sub>3</sub>	4.66	10.70	27.60
TiO <sub>2</sub>	0.23	0.51	1.98
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.11	0.25	0.26
K <sub>2</sub> O	0.34	0.55	1.53
P <sub>2</sub> O <sub>5</sub>	0.31	<0.05	0.12
SO <sub>3</sub>	2.25		0.33
SrO			0.04
LOI (900° C)	1.35	1.34 <sup>b</sup>	9.92
Totals	100.40	100.36	100.00

<sup>a</sup> Also referred to as Atlantic

<sup>b</sup> The loss-on-ignition (LOI) values for slag is negative indicating the existence of sulfur as free sulfur or metal sulfides (i.e., FeS) rather than SO<sub>3</sub> (i.e., samples gained weight on heating).

**Table 3.3-13 Demonstrated Range of Acceptability**

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

<sup>a</sup> Either Portland Class II cement or Ca(OH)<sub>2</sub>.

### 3.3.3.6 Material Balance Results

The results of the material balances are summarized in Table 3.3-14. All rates are at 100 % attainment. Included for comparison are the results from the Phase III material balance (year 2016).

**Table 3.3-14 Summary of Material Balance Results**

	Average Waste	Year 2016*
Fresh waste feed – gal/min	17.5	17.5
Na <sup>+</sup> in fresh waste – M	6.44	5.94
Sludge in feed – lbs/hr	5.8	5.9
MST added (dry basis) – lbs/hr	4.2	0.4
Washed MST/sludge – lbs/hr total	186	103
Fraction sludge in MST/sludge solids	0.52	0.93
IX column feed – gal/min	20.7	19.6**
Na <sup>+</sup> in Saltstone feed – M	5.61	5.33
Decon salt soln to Saltstone – gal/min	20.9	19.6**
Grout production – gal/min	34.7	32.6**
Cs concentration – Ci/gal @ 5.6 M	1.37	2.21
Granular CST dilution factor	1.0	0.7
Cs loading on CST – mg Cs/g CST ***	28.5	20.1 (28.7)
Column cycle time – hours	2932	1562 (2230)
CST rate to DWPF – lbs/hr	6.70	12.55 (8.79)
Activity of CST slurry – Ci/gal	220	161 (230)
Glass production rate – lbs/hr	191.4	170.6
CST (calcined) in glass – wt %	2.98	6.13 (4.29)

	Average Waste	Year 2016*
Total TiO <sub>2</sub> in glass – wt %	2.71	2.09 (1.59)
Fraction of TiO <sub>2</sub> from CST	0.36	0.96 (0.88)
Sludge oxides – wt %	30.2	30.5
Glass Properties	Ref 89	PCCS
Durability – ln NL(B) g/L	-10.84	-5.52
Viscosity – poise	25 – 35	50.1
Liquidus - °C	< 950	1007

\* Values in parentheses are for granular dilution factor = 1.0

\*\* Note that fresh waste feed is dilute

\*\*\* Assuming 10 wt % slurry of CST in water

The material balances are quite similar with the exception of results associated with the granular dilution factor. For example, the cycle times, the CST production rate (in lbs/hr), and the CST concentration in the glass.

In Phase III, the year 2016 was chosen because it would produce the highest CST usage and thus the bounding CST concentration in glass. If the granular dilution factor for Phase III had been 1.0 (instead of 0.7), then the CST production rate would have much closer to the rate for average salt solution. Therefore, the average CST in glass is predicted to be about 3.0 % with a maximum of about 4.3 %.

Note that the 2016 fresh feed is dilute – 5.94 M. As a consequence, less water is added to dilute to the CST IX feed conditions and year 2016 makes less grout. If the feeds started with the same Na molarity, they would make almost exactly the same amount of grout.

In the case of the average feed, diluting with NaOH adds approximately 1 gal/min to the quantity of solution fed to Saltstone. At 6.9 M gallons of 6.44 M salt workoff per year (75% utility), the extra saltstone produced is 650 kgal/yr.

Using a granular dilution factor of 1.0 has three other 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 2900 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 M Ci. Third, the 10 wt % CST slurry is “hotter”. It is estimated the slurry would be about 220 Ci/gal.

Note the total TiO<sub>2</sub> in the glass is higher for the average salt even though the CST concentration is lower. This is because the 2016 salt solution had such a low MST demand according to the waste removal study. The material balance for average salt solution reflects the use of 0.4 g/L MST (at 5.6 M) – thus the MST to DWPF is 10X higher. Since MST is 80 % TiO<sub>2</sub>, it has a large impact on total TiO<sub>2</sub>.

### 3.3.4 Conclusions

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

#### 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 H<sub>2</sub> generation, temperature control/heat removal, and accident scenarios and recovery.

Experimentation with CST revealed the impacts (or lack thereof) of many parameters. It was found that organics, 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. However, concerns and issues were raised in the area of CST production variability, long term stability and leaching in SRS waste, rapid desorption of Cs at moderate temperature (50 °C), and strong temperature dependence of  $K_d$  in IE-911.

#### CST in the DWPF

Further experiments indicate CST is not a H<sub>2</sub> generation concern and only slightly exacerbates the foaming problems in the Chemical Processing Cell. The CST glasses were very durable although not predictable. Viscosity and liquiduses were within required ranges with the exception of HM sludge which produced a viscosity of ~ 160 poise (versus the DWPF limit of 100 poise). However, there is a significant engineering challenge associated with CST homogeneity and sampling. As-received CST plugged the Hydragard<sup>®</sup> and size-reduced CST was not sampled representatively by the Hydragard<sup>®</sup> sampler. Also, CST was difficult to suspend homogeneously in a water/ CST slurry.

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 produce between 4.5 and 7.5 lb/hr of CST to DWPF with the average waste producing 6.7 lbs/hr.
- The performance of the ion exchange depends primarily on deviations in SRS waste from nominal composition.

- *Ci/gal in CST slurry to DWPF* – The Ci/gal Cs-137 ranges from 100 to 250 with the average waste at 220 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 the batch cycle ranges from 2.5 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 34 to 47 k lbs per year with the average waste using 46 k lbs in a year.
- *CST loading in glass* – Loading in glass is shown to be from 3.0 to 4.5 wt % with the average waste at 3.0 wt %.
- *TiO<sub>2</sub> in the glass* – The total TiO<sub>2</sub> in the glass ranges from 2.5 to almost 4 wt % with the average waste at 2.7 wt %. The contribution from CST to this total is ~ 40 %.
- *Sludge oxides and glass properties* – The sludge oxide concentration is ~ 30 wt % and the CST concentration is 3.0 %. These are at the limit of current glass variability testing. Tests show the durability is acceptable and the viscosity is borderline low at 25 to 35 poise. The liquidus is < 950 °C.

### **3.3.5 Equipment**

#### **3.3.5.1 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 3.3-15. 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 3.3-15 Non-Elutable Ion Exchange**

	DWPF	CST	CST %DWPF
AREA (SQ.FT)			
SHIELDED	16,278	9,795	60%
UNLOADING WELL	2,175	2,100	97%
LOW SHIELD		2,100	
OPERATING CORRIDOR	59,029	32,400	55%
CRANE OPERATING	18,457	16,800	91%
TOTAL	95,939	63,195	66%
VOLUME(CU.FT)			
SHIELDED	640,344	440,775	69%
UNLOADING WELL	86,348	94,500	109%
LOW SHIELD		94,500	
OPERATING CORRIDOR	1,081,583	980,100	91%
CRANE OPERATING	700,261	890,400	127%
TOTAL	2,508,536	2,500,275	~100%

**3.3.5.2 Tanks**

**Table 3.3-16 Tanks for Non-Elutable Ion Exchange Alternative**

<b>Tank</b>	<b>Tank Size</b>	<b>Sizing Assumption</b>
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 Saltstone Waste Acceptance Criteria. The tanks also allow hold-up of material during the time that the Saltstone Facility is de-staffed and somewhat de-couple the Saltstone Facility from the CST 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 CST Facility. This five days of product is less than two days of operation of the Saltstone Facility 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 approximately four weeks of storage.
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 and 10,000 gallons for solids accumulation.
Recycle Blend Tank	88,000 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.

<b>Tank</b>	<b>Tank Size</b>	<b>Sizing Assumption</b>
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 <sup>137</sup> 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.
Ion Exchange Columns	4 columns each 5' diameter with 16' bed length	

### 3.3.6 Trade Study Results

#### 3.3.6.1 Use of Alternative Facilities for Feed Clarification

Part of the CST Ion Exchange facility is used to prepare the salt solution for feeding to the CST columns. This is done by adding solid monosodium titanate (MST) to the solution. MST sorbs soluble alpha contamination and strontium. The solution is filtered, separating the column feed (the filtrate) from the MST solids and residual sludge. These steps are called Alpha Sorption.

The current pre-conceptual design shows the feed clarification as a portion of the new CST Ion Exchange facility. Using some existing facility to do this may save some of the cost of the new facility and make economically sound use of parts of the In-Tank Precipitation Facility or Late Wash. This was studied as part of Phase IV (Reference 92).

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, potential 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 value added to risk not meeting 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 CST Ion Exchange Facility.

### **3.3.7 Supplemental Environmental Impact Statement (SEIS)**

SEIS for the salt disposition facility is drafted to include 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. (Reference 59) Accidental releases are based on historical information on similar processes and facilities. (Reference 60) The resulting population doses from these emission estimates are calculated by modeling the environmental dispersion of the emission. (Reference 61)

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 no action is less desirable than any the other process alternatives. Under the “no action” alternative, SRS will not be able to meet the commitments of the Federal Facilities Compliance Agreement. Each of the two process alternatives produces only minor environmental changes.(Reference 61)

### 3.4 Caustic-Side Solvent Extraction

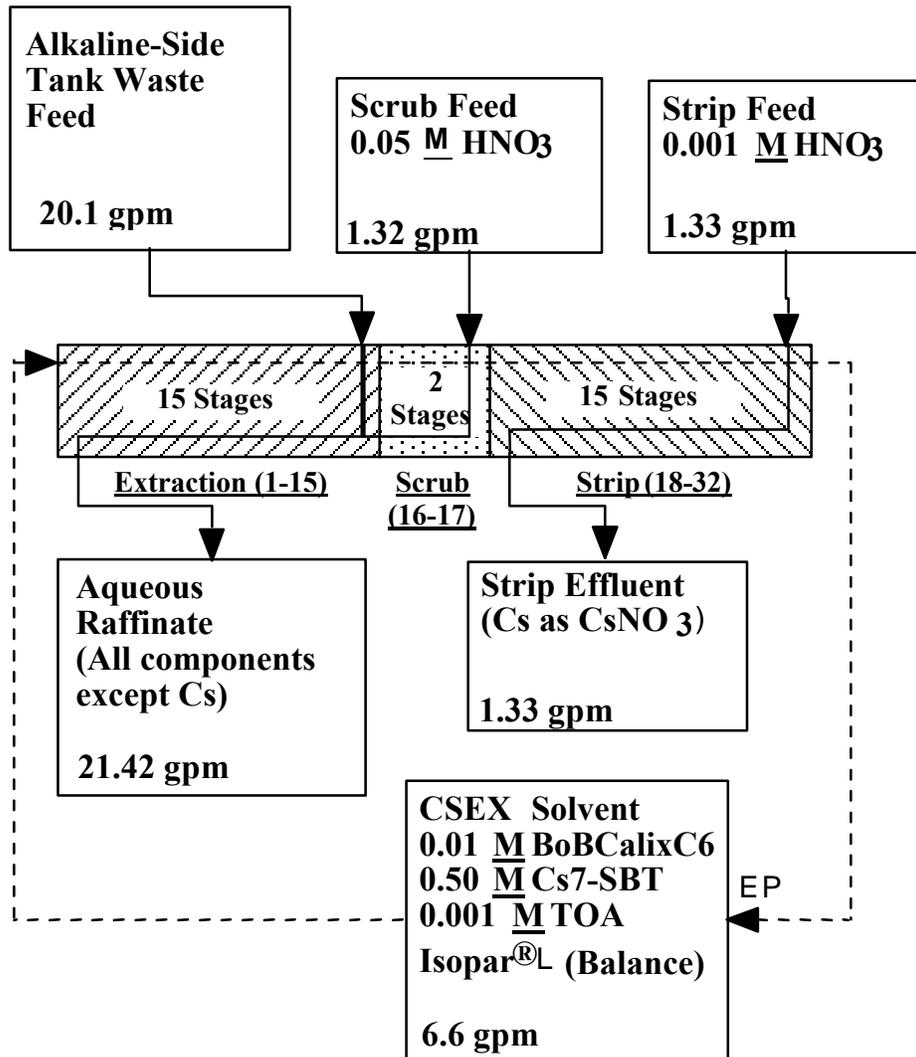
#### 3.4.1 Alternative Description

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 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 then recycled.

Prior to treatment by solvent extraction, actinides are removed from the waste by absorption with monosodium titanate. The resulting slurry is then filtered to remove the MST and sludge solids.

The Caustic Side Solvent Extraction (CSEX) process utilizes a novel solvent made up of four components: calix[4]arene-bis-(*tert*-octylbenzo-crown-6) known as BOBCalix6, 1-(4-*tert*-octylphenoxy)-3-(1,1,2,2-tetrafluoroethoxy)-2-propanol known as modifier Cs7, trioctylamine known as TOA, and Iso-par<sup>TM</sup>, as a diluent. The solvent is contacted with the alkaline waste stream in a series of countercurrent centrifugal contactors (the extraction stages). The resulting clean aqueous raffinate is transferred to Saltstone for disposal. 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. The CSSX flow sheet is shown in Figure 3.4-1.

**Figure 3.4-1 CSSX Flowsheet**



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 small size of the opening in the calixarene molecules, cesium is removed in dramatic preference to other cations, in particular sodium and potassium. This selectivity is more than two orders of magnitude versus potassium and more than four orders of magnitude versus sodium. This high selectivity is required to achieve the desired separation of the cesium ions from the bulk sodium ions.

In the proposed process, the cesium concentration in the organic phase is 4.3 times that in the aqueous feed solution. For a typical high level waste feed solution containing 0.27 millimolar (mM) cesium, the concentration in the organic stream leaving the extraction stages is approximately 1 mM. Note that this is significantly below the 10-mM concentration of calixarene in the solvent. Thus, a large excess of available calixarene sites is 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 out of the organic phase using two scrubbing stages between the extraction and strip stages. In addition to removing sodium and potassium from the organic phase, the scrub stages also work to remove aluminum, iron and mercury. The scrub stages also work to neutralize any caustic carryover into the scrub stages. The neutralization of these species is essential to control precipitation and to allow stable operation of the stripping stages. Since the strip stages employ a weak acidic solution, introduction of caustic into the strip stages would likely result in significant pH shifts and thereby diminish process operability.

In the strip stages, the presence of lipophilic anionic impurities will produce greatly reduced stripping performance. To remedy the effects of these impurities, TOA is added to the solvent. This amine remains essentially inert in the extraction section of the process but converts to the trioctylammonium nitrate salt during scrubbing and stripping. This lipophilic salt remains in the organic phase and allows the final traces of cesium in the solvent to be stripped by supplying the impurity in the solvent with equivalent cationic charges. (Reference 93)

Over long periods of time, degradation of either the modifier or the calixarene may occur. The most likely degradation is that of the modifier to form a phenolic compound that is highly 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.

The two proposed unit operations involve washing the solvent first 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 is known to remove many of the modifier degradation products. In addition, the proposed flowsheet has also assumed that to maintain system performance the solvent will be replaced on an annual basis.

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 raffinate stream. 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 from this stage is then sent to a settling tank

where any remaining entrained organics (mostly the Iso-par L<sup>®</sup>) is allowed to float and is then decanted. From the settling tank, the raffinate is transferred to one of two hold tanks to allow decay of the short half-life beta in the raffinate stream. These two tanks are sized to allow sufficient hold time for sufficient beta decay to facilitate determination whether the target decontamination has been met to allow transfer of the raffinate material to the saltstone facility. The scrub solutions from the organic clean up process are also transferred to saltstone.

A similar solvent recovery process has been designed for the strip effluent. 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<sup>®</sup> is introduced into the stages and used to extract any of the solvent from the aqueous phase. The aqueous phase leaves the clean-up stage and is transferred to a settling tank where the Iso-par L<sup>®</sup> is allowed to float and is decanted.

Since Iso-par L<sup>®</sup> was added in the two solvent recovery processes, removal of this additional diluent is required. This material is sent to CIF. The cleaned and solvent stream is sent back to service in the solvent hold tank.

Note that the feed stream to the process comes from a 110,000 gallon filter feed tank to a 30,000 gallon salt solution feed tank. The use of a relatively large tank provides approximately 4 days of feed storage and some decoupling of the solvent extraction process from the up stream actinide removal process. Also note that the aqueous strip effluent leaves the settling tank and is sent to a large storage tank (60 days capacity). The use of a large tank provides for some decoupling of the solvent extraction process and the DWPF. Also 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). However, the solvent extraction process can only operate as long as DWPF is operating or storage volume remains in the tanks between the solvent extraction process and DWPF. 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 differences in cycle times for the SRAT in 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 content is used to offset the nominal nitric acid requirement. The effluent would contain < .01 M Na, < 0.001 M of other metals.

The feed to the extraction units comes from the alpha sorption portion of the flowsheet previously described.

## 3.4.2 Results

### 3.4.2.1 R&D Results

An extensive experimental program was completed in support of phase III evaluation. The results of these investigations have been evaluated to determine the potential impacts on the proposed process. The following is a summary of those impacts.

#### High Level Waste Performance

SRTC personnel completed a test to determine the extraction, scrubbing and stripping performance of the solvent system with a sample of SRS High Level Waste (Reference 94). This test employed two extraction, one scrub and three strip contacts. Personnel determined distribution coefficients for each of these contacts. The distribution coefficient for extraction exceeds 11, versus the design basis value of 8. In addition, the stripping distribution coefficients proved 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 proposed process likely contains a significant amount of over design. Modification of the proposed process based on these values could result in the elimination of as many as 16 contactor stages from the proposed process.

#### Temperature Control

The cesium equilibrium between solvent and aqueous phase is strongly dependent upon the temperature of the system. Under extraction and stripping conditions typical of expected plant operations, the equilibrium distribution coefficients will change by at least a factor of 2 for every 10 °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  $\geq 30$  °C for the strip stages (to obtain  $D_{CS} \geq 8.0$ ) and  $\leq 25$  °C in the extraction stages (to obtain  $D_{CS} \leq 0.2$ ).

In addition, more stringent temperature controls, such as setting the strip temperature to  $> 37$  °C could greatly decrease the number of stages required for operation. At a stripping temperature of  $> 37$  °C (to obtain  $D_{CS} \leq 0.06$ ), the number of required processing stages could be reduced to 20 (Reference 95). Such a reduction in the number of required stages would eliminate 2 six-packs of contactor stages and their associated jumpers.

Similarly, the addition of  $1 \times 10^{-4}$  M trioctylamine (TOA) to the solvent has been shown to decrease the stripping distribution coefficient by 10 fold (Reference 96). If TOA is used, the temperature controls indicated above could be relaxed. Furthermore, addition of TOA to the solvent could reduce the required number of processing stages to 20.

The revised flowsheet has eliminated the cesium nitrate addition to the strip solution. The TOA has removed the temperature limitations discussed above. However, subsequent work has shown that third phase formation (Reference 97) could be a problem at temperatures less than 20 °C. The temperature of the process will be controlled above this temperature.

### Solvent Recovery

Testing has shown that calixarene and the modifier are sparingly soluble in aqueous solutions (Reference 103). 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 would eliminate the need for four solvent recovery stages, a kerosene still, and a kerosene condensate tank.

### 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 (Reference 103). The primary products of decomposition were p-(t-octyl)phenol and fluorinated alcohols. Under these conditions, no detectable decomposition of the calixarene was observed (Reference 103). The modifier planned for use Cs-7SB has not exhibited this decomposition. (Reference 98) No measurable decomposition of the solvent under simulated process conditions up to 60 °C has occurred.

Based on an average concentration of  $3.5 \times 10^{-5}$  M  $^{137}\text{Cs}$  in the organic phases, the solvent is expected to receive about 8 Mrad of dose. Note that this dose rate does not credit residence time outside of the contactor stages (i.e., residence time in the solvent hold tank). 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 (Reference 99). Additional tests with the proposed modifier, Cs-7SB, indicate the new modifier is much more stable than the previous modifier. (Reference 100) The primary decomposition product is 4-sec-butylphenol (4-SBP).

This data suggests 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 (based on 100 % replacement per year).

Testing at ORNL showed that a 0.5 M caustic scrub will be moderately effective in controlling the concentration of degradation products in the solvent system (Reference 103 and 107). The 4-SBP is expected to be washed out in the extraction section of the flowsheet and will not build up in the solvent. Partitioning coefficient information has not been fully developed at the writing of this document.

### 3.4.2.2 Model Results

#### Solvent Extraction Material Balance Model

Figure 3.4-1 shows a schematic diagram of the Solvent Extraction Material Balance. The alpha decontamination and grout production parts of this model are identical to those discussed in the CST Ion Exchange model. The solvent extraction process adds a continuous counter-current solvent extraction process to remove cesium from the salt solution in the SSHT prior to grouting. 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 scrubber 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.

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 showed that a solvent flow rate of 6.6 gpm maximized the amount of cesium removed from the salt solution. The scrub flow was set to 20% of the solvent flow and the strip flow was fixed at 1.33 gpm. Cesium was assumed to be the only component extracted from the salt solution.

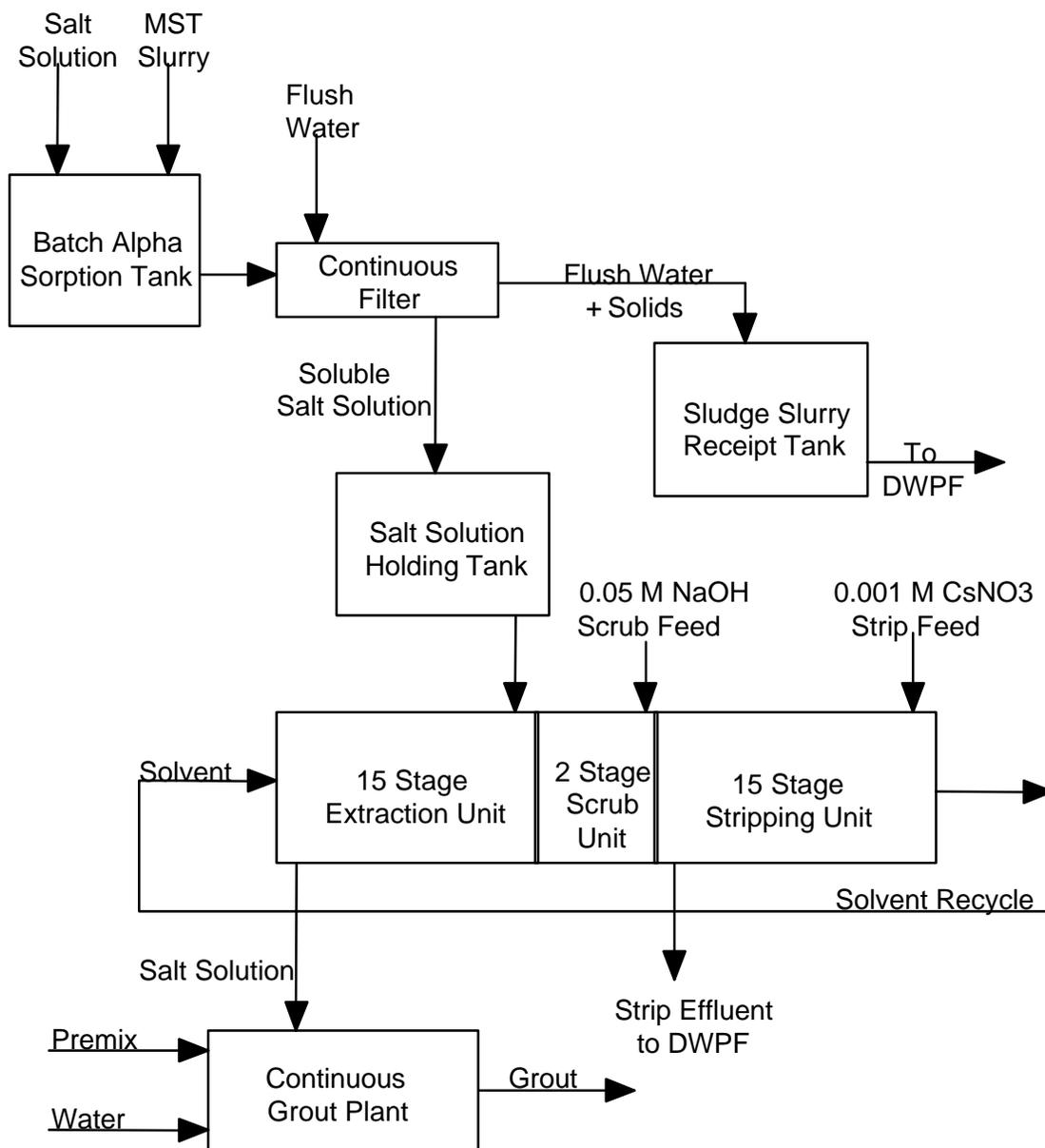
The speedup model was modified to provide material balances for the proposed solvent extraction process. These modifications included increasing the salt flow rate, decreasing the strip flow rate and adding the caustic wash solution. The results of this model are summarized in Table 3.4-1.

**Table 3.4-1 Summary of Solvent Extraction SPEEDUP Model**

Parameter (@ 100 % attainment)	Model Result
Salt Solution Processed (kgal/year)	9,198
Grout Made (kgal/year)	19,815
Strip Solution to DWPF (kgal/year)	699
Canisters (per year)	372
Solvent Used (kgal/year)	1

The raffinate sent to Saltstone from this process contains less than 40 nCi/g of  $^{137}\text{Cs}$  and contains only trace (< 20 ppm) concentrations of organics. This feed stream to Saltstone is approximately 5.7 M sodium. The strip effluent sent to DWPF from this process contains approximately 20 Ci/gallon of  $\text{Cs}^{137}$  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 facility is relatively seamless.

**Figure 3.4-2 Schematic Representation of Solvent Extraction Model.**



### 3.4.3 Bases

The basis for the development of caustic side solvent extraction is laboratory testing from Oak Ridge National Laboratory (References 108, 109, 110, & 111). 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-7SB modifier  
0.001 TOA  
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:

$$D = C_{Sorg}/C_{Saq}$$

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. These measurements were:

	Extraction	Scrub	Strip
D(Cs)	8 (25°C)	0.6 (25°C)	0.16 (30°C)

Using this data, a proposed flowsheet for the extraction of cesium from typical ( $2.7e-4$  molar cesium) waste 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 (with the balance primarily OH, NO<sub>3</sub>, and NO<sub>2</sub>). In addition, the flowsheet targeted a raffinate cesium concentration of less than 40 nCi/g.

The spreadsheet output for the rates for the various streams are:

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 effluent would contain < .01 M Na, < 0.001 M of other metals.

This flowsheet assumed 15 stages of extraction, 2 stages of scrubbing and 15 stages of stripping. This number of stages was employed to achieve an approximate 15-fold increase in the Cs concentration of the effluent over the feed. Use of additional stages can produce an increase in the concentration achieved while use of fewer stages results in lower concentration increases.

This flowsheet was developed under the assumption of equilibrium stages (a relatively accurate assumption for centrifugal contactors as indicated by testing at ANL, Reference 112). 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 SASSE model was rerun using the solvent matrix described above to define the new flowsheet described in Section 3.4.1.

### 3.4.3.1 DWPF Vitrification Technical and Modeling Bases

The Technical Bases for the operation of the DWPF and flowsheet modeling bases are the same as those used in Phase III.

#### Bases for HNO<sub>3</sub> / HCOOH addition and F-N basis

Technical Bases - Acid adjustment in the SRAT is partially completed by adding nitric acid to yield an acid pH. Also, formic acid (HCOOH) is added to reduce mercury(II) compounds to mercury(0). The mercury is then steam-stripped from the sludge slurry to minimize the quantity sent to the melter. Only those reactions that involve a species in the salt solution are included, since reactions of sludge components are not generally affected by the various alternatives.

<u>Reactants</u>	<u>Products</u>
NaOH + HNO <sub>3</sub>	NaNO <sub>3</sub> + H <sub>2</sub> O
NH <sub>4</sub> OH + HNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub> + H <sub>2</sub> O
NaAlO <sub>2</sub> + 4 HNO <sub>3</sub>	Al(NO <sub>3</sub> ) <sub>3</sub> + NaNO <sub>3</sub> + 2 H <sub>2</sub> O
CsOH + HNO <sub>3</sub>	CsNO <sub>3</sub> + H <sub>2</sub> O
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> + 6 HNO <sub>3</sub>	2 UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> + 2 NaNO <sub>3</sub> + 3 H <sub>2</sub> O
SrCO <sub>3</sub> + 2 HNO <sub>3</sub>	Sr(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O + CO <sub>2</sub>
CoO + 2 HNO <sub>3</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O (70%)
HgO + HCOOH	Hg + H <sub>2</sub> O + CO <sub>2</sub> (99%)
2Ag <sub>2</sub> O + 2 HCOOH	2 Ag + H <sub>2</sub> O + CO <sub>2</sub> (99%)
PdO + HCOOH	Pd + H <sub>2</sub> O + CO <sub>2</sub> (99%)
RhO <sub>2</sub> + 2 HCOOH	Rh + 2H <sub>2</sub> O + 2CO <sub>2</sub> (99%)

The method for calculating acid addition and the balance between formate ion and nitrate ion are based on laboratory work (Reference 55) and DWPF cold runs and operating experience.

- 4 Calculate the total acid required to neutralize or to react with materials in the feed. One mole acid is needed for each mole of HgO, NaOH, and KOH. Two moles of acid are needed for Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, Mg(OH)<sub>2</sub> and carbonate (CO<sub>3</sub>)<sup>--</sup>. One-quarter mole is needed for each mole of nitrite (NO<sub>2</sub><sup>-</sup>) and 0.4 moles are needed for each mole of MnO<sub>2</sub>.
- 5 Multiply this “stoichiometric” amount by 1.25. This is the **total** amount of acid to be added.
- 6 Assume that 40% of the formic acid is lost in the SRAT cycle. Based on this, calculate how much formic acid is required such that the [formate]-[nitrate] (“F minus N”) will be 0.4 M in the SME – normalized to 45 wt% solids in the SME. Assume that 100 gallons 90% formic acid will be added to the SME to provide part of the formate needed.

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

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

In each SME batch 100 gallons of 90 wt % formic acid are added. The F-N redox value is calculated in the SME using the equation:

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

Some formic acid will be removed in the SRAT cycle during the evaporation. The amount of acid lost is calculated by an ideal solution estimate of the vapor composition and may not be the nominal 40%.

Mercury is removed from the solution in the SRAT and collected as a side stream. The mercury is tracked as HgO throughout the process.

### **Bases for NaOH and NaNO<sub>2</sub> to RCT**

#### Technical Bases

##### Reactants

HCOOH + 4 NaOH  
Pu(COOH)<sub>4</sub> + 4 NaOH  
UO<sub>2</sub>(COOH)<sub>2</sub> + 2 NaOH  
HCl + NaOH  
HF + NaOH  
HgCl<sub>2</sub> + 2 NaOH  
Hg<sub>2</sub>Cl<sub>2</sub> + 2 NaOH  
Hg<sub>2</sub>I<sub>2</sub> + 2 NaOH  
KCOOH + NaNO<sub>3</sub>  
NH<sub>4</sub>COOH + NaNO<sub>3</sub>  
CsCOOH + NaNO<sub>3</sub>  
CsCl + NaNO<sub>3</sub>  
Cs<sub>2</sub>O + 2 NaNO<sub>3</sub> + H<sub>2</sub>O

##### Products

NaCOOH + H<sub>2</sub>O  
PuO<sub>2</sub> + 4 NaCOOH + 2 H<sub>2</sub>O  
UO<sub>2</sub>(OH)<sub>2</sub> + 2 NaCOOH  
NaCl + H<sub>2</sub>O  
NaF + H<sub>2</sub>O  
HgO + 2 NaCl  
Hg + HgO + 2 NaCl + H<sub>2</sub>O  
Hg + HgO + 2 NaI + H<sub>2</sub>O  
KNO<sub>3</sub> + NaCOOH  
NH<sub>4</sub>NO<sub>3</sub> + NaCOOH  
CsNO<sub>3</sub> + NaCOOH  
CsNO<sub>3</sub> + NaCl  
CsNO<sub>3</sub> + NaOH

The quantities of caustic and nitrite added to the RCT are based on the Waste Acceptance Specification and operating experience. This is to assure that the inhibitors required to prevent corrosion of the carbon steel waste tanks are present.

Modeling Bases - Caustic and inhibitor are added to the RCT to produce a recycle solution that is

0.5 M NaOH and 0.045 M NaNO<sub>2</sub>

Water evaporated in the SRAT, SME and melter goes directly to the RCT in the simplified Speedup model.

## Bases for NO<sub>x</sub> Produced in the Melter

Technical Bases - In the melter, 50 % of the nitrate salts and all of the nitrite salts react with sodium formate to form nitric oxide (NO). The balance of the nitrate salts react to form nitrogen (N<sub>2</sub>). Subsequently, the NO reacts with oxygen in the air to form nitrogen dioxide (NO<sub>2</sub>).

<u>Reactants</u>	<u>Products</u>
4 NaNO <sub>3</sub> + 8 NaCOOH	6 Na <sub>2</sub> O + 2 NO + N <sub>2</sub> + 8 CO <sub>2</sub> + 4 H <sub>2</sub> O
4 NaNO <sub>2</sub> + 2 NaCOOH	3 Na <sub>2</sub> O + 4 NO + 2 CO <sub>2</sub> + H <sub>2</sub> O (100 %)
4 Al(NO <sub>3</sub> ) <sub>3</sub> + 24 NaCOOH	2 Al <sub>2</sub> O <sub>3</sub> + 12 Na <sub>2</sub> O + 6 NO + 3 N <sub>2</sub> + 24 CO <sub>2</sub> + 12 H <sub>2</sub> O

Modeling Bases - The reactions shown below as the Modeling Bases for Vitrification, closely approximate the NO<sub>2</sub> emission. Since complete oxidation is assumed, carbon monoxide and hydrogen in the melter off-gas are not accounted for.

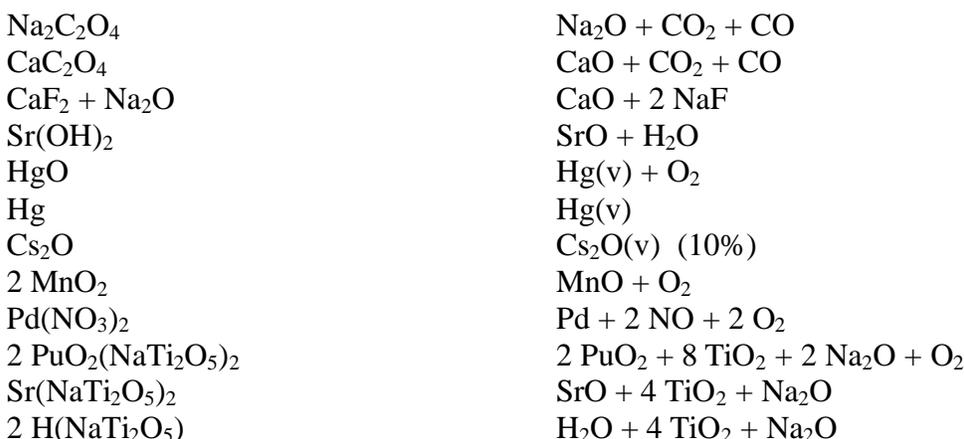
## Bases for Vitrification in the Melter

### Technical Bases

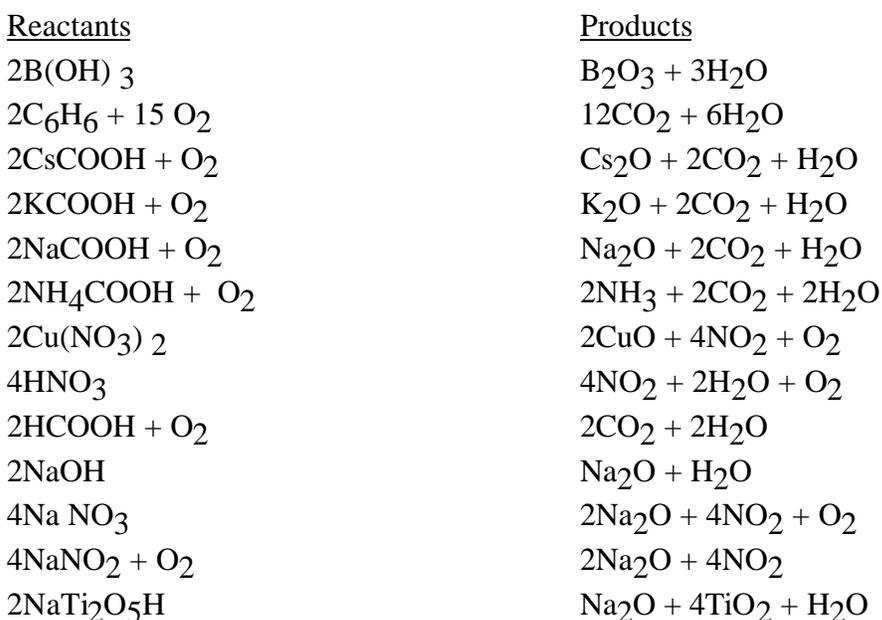
In addition to reactions with nitrate and nitrite salts, formate salts either react with other oxidizing species in the melter feed or thermally decompose to generate carbon monoxide, carbon dioxide, hydrogen, water and oxides of metal ion species. Oxalate salts and other compounds that are thermally unstable at melter temperature also decompose (e.g., CaC<sub>2</sub>O<sub>4</sub>, HgO).

<u>Reactants</u>	<u>Products</u>
4 Al(NO <sub>3</sub> ) <sub>3</sub> + 18 NaCOOH	2 Al <sub>2</sub> O <sub>3</sub> + 9 Na <sub>2</sub> O + 12 NO + 18 CO <sub>2</sub> + 9 H <sub>2</sub> O
2 Na <sub>2</sub> SO <sub>4</sub> + 2 NaCOOH	3 Na <sub>2</sub> O + 2 SO <sub>2</sub> + 2 CO <sub>2</sub> + H <sub>2</sub> O
4 Fe <sub>2</sub> O <sub>3</sub> + 2 NaCOOH	4 FeO + Na <sub>2</sub> O + 2 CO <sub>2</sub> + 7 H <sub>2</sub> O
2 NaCOOH	Na <sub>2</sub> O + CO + CO <sub>2</sub> + H <sub>2</sub>
2 KCOOH	K <sub>2</sub> O + CO + CO <sub>2</sub> + H <sub>2</sub>
4 NH <sub>4</sub> COOH + 3 O <sub>2</sub>	2 N <sub>2</sub> + 8 H <sub>2</sub> O + 2 CO + 2 CO <sub>2</sub> + 2 H <sub>2</sub>
Mn(COOH) <sub>2</sub>	MnO + CO + CO <sub>2</sub> + H <sub>2</sub>
Ni(COOH) <sub>2</sub>	NiO + CO + CO <sub>2</sub> + H <sub>2</sub>
Ca(COOH) <sub>2</sub>	CaO + CO + CO <sub>2</sub> + H <sub>2</sub>

<u>Reactants (Cont'd)</u>	<u>Products (Cont'd)</u>
UO <sub>2</sub> (COOH) <sub>2</sub> + O <sub>2</sub>	U <sub>3</sub> O <sub>8</sub> + CO + CO <sub>2</sub> + H <sub>2</sub>
Cu(COOH) <sub>2</sub>	CuO + CO + CO <sub>2</sub> + H <sub>2</sub>
Co(COOH) <sub>2</sub>	CoO + CO + CO <sub>2</sub> + H <sub>2</sub>
Zn(COOH) <sub>2</sub>	ZnO + CO + CO <sub>2</sub> + H <sub>2</sub>
Mg(COOH) <sub>2</sub>	MgO + CO + CO <sub>2</sub> + H <sub>2</sub>
Sr(COOH) <sub>2</sub>	SrO + CO + CO <sub>2</sub> + H <sub>2</sub>
2 CsCOOH	Cs <sub>2</sub> O + CO + CO <sub>2</sub> + H <sub>2</sub>



Modeling Bases - The following simplified oxidation reactions were used to convert metal salts and other compounds into oxides in the glass melter:



### **Bases for Water additions and Recycle:**

Modeling Bases - Water evaporated from SRAT and SME is collected in the SMECT and transferred to RCT.

All water fed to the melter goes to the Offgas Condensate Tank and thence to the RCT

Steam Atomized Scrubbers and Film Cooler add 1000 pph water to offgas stream. This water is condensed and recycled. Decontamination waste adds another 340 pph of water to the RCT.

#### **3.4.3.2 Saltstone Product Basis**

Saltstone is a solid waste form that is the product of chemical reactions between a salt solution and a blend of cementitious materials (slag, flyash, 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 3.3-12 (Reference 48). The demonstrated range of acceptability for each component with respect to physical properties and resistance to contaminant leaching is shown in Table 3.3-13 (Reference 49). 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 substitute for the cement to function as a lime source 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.

Saltstone grout is formulated to minimize bleed water from the grout during curing. An acceptable saltstone product, from the standpoint of physical properties, has been demonstrated with salt solution ranging from about 20 wt % to 32 wt % salt, corresponding to a specific gravity ranging from about 1.18 to 1.32 with a sodium molarity of ranging from about 4 M to 6 M. Bleed water is controlled by controlling the water-to-premix mass ratio in the range of 0.52 to 0.60 (presently set at 0.57). The density of cured saltstone ranges between 1.70 and 1.80 kg/L (References 50 and 51).

**Table 3.4-2 Composition of Saltstone Cementitious Materials**

Component	Cement Type II Santee (Wt%)	Slag Grade 120 NEWCEM <sup>a</sup> (Wt%)	Fly Ash Class F Low CaO (Wt%)
SiO <sub>2</sub>	21.10	34.70	52.17
Al <sub>2</sub> O <sub>3</sub>	4.66	10.70	27.60
TiO <sub>2</sub>	0.23	0.51	1.98
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.11	0.25	0.26
K <sub>2</sub> O	0.34	0.55	1.53
P <sub>2</sub> O <sub>5</sub>	0.31	<0.05	0.12
SO <sub>3</sub>	2.25		0.33
SrO			0.04
LOI (900° C)	1.35	1.34 <sup>b</sup>	9.92
Totals	100.40	100.36	100.00

<sup>a</sup> Also referred to as Atlantic

<sup>b</sup> The loss-on-ignition (LOI) values for slag is negative indicating the existence of sulfur as free sulfur or metal sulfides (i.e., FeS) rather than SO<sub>3</sub> (i.e., samples gained weight on heating).

**Table 3.4-3 Demonstrated Range of Acceptability**

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

<sup>a</sup> Either Portland Class II cement or Ca(OH)<sub>2</sub>.

### **3.4.4 Equipment**

#### **3.4.4.1 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 3.4-4. Major process equipment consists of chemical storage and feed tanks, a 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 3.4-4 Building Layout Based On Solvent Extraction**

	DWPF	SOLVENT	SOLVENT %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	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	2,508,536	2,895,360	115%

**3.4.4.2 Tanks**

**Table 3.4-5 Tanks for Caustic Side Solvent Extraction 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.

<b>Tank</b>	<b>Tank Size</b>	<b>Sizing Assumption</b>
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 decoupled 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 approximately four weeks of storage.

Tank	Tank Size	Sizing Assumption
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.
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 Saltstone Waste Acceptance Criteria. The tanks also allow hold-up of material during the time that the Saltstone Facility is de-staffed and somewhat de-couple the Saltstone Facility from the Solvent Extraction 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 Solvent Extraction Facility. This five days of product is less than four days of operation of the Saltstone Facility.
Chemical Additive Tank	100 gallons	Sized to support the make-up of small volumes of additives such as the CsNO <sub>3</sub> .
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	Sized to support makeup of modifier and extractant.
Cleaning Solution Dump Tank	1000 gallons	

<b>Tank</b>	<b>Tank Size</b>	<b>Sizing Assumption</b>
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 <sub>3</sub> 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	110,000 gallons	Sized to hold enough clarified salt solution for five days of processing in the Solvent Extraction Facility.
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.

<b>Tank</b>	<b>Tank Size</b>	<b>Sizing Assumption</b>
Kerosene Vacuum Still		Used to remove the excess kerosene in the solvent extraction process. The excess kerosene 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	Two Stages	These two stages will be used to increase the pH in the solvent after scrubbing.
Strip Organic Removal Stages	Two stages	These two stages are used to remove organic from the aqueous strip stream.
Raffinate Organic Removal Stages	Two stages	These two stages are used to remove organic from the aqueous raffinate stream.

**3.4.4.3 Jumpers**

**Table 3.4-6 Summary of Jumper Usage for Solvent Extraction Alternative**

<b>Jumper Application</b>	<b>Number of Jumpers</b>
Process Jumpers	144
Process Jumpers with MOVs	13
3-way Process Jumpers	5
3-way Process Jumpers w/2 MOVs	1
Electrical Jumpers	95
Instrumentation Jumpers	37
<b>TOTAL</b>	<b>253</b>

**3.4.5 Supplemental Environmental Impact Statement (SEIS)**

The SEIS for the salt disposition facility is drafted to include 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 (Reference 113). Accidental releases are based on historical information on similar processes and facilities (Reference 114). The resulting population doses from these emission estimates are calculated by modeling the environmental dispersion of the emission (Reference 115).

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 "no action" is less desirable than any other process alternative. 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 (Reference 61).

#### **4.0 LIFE CYCLE COMPARISONS**

During the demonstration phase, the start dates for coupled operation for all three flowsheets were changed to March 1, 2010. All three flowsheets were modified to 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 which impact Saltstone production and MST consumption. The quantity of materials consumed and Saltstone produced are shown for each flowsheet on Process Flow Diagrams in the Appendices.

The interface between Extended Sludge Processing (ESP) and the DWPF is 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 materials 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 4.0-1, below. “Average Salt” was used to produce the salt product portion of the blend.

Table 4.0-1 shows the canisters produced for each sludge batch. Revision 11 of the SRS HLW System Plan (Reference 116) assumed a production rate of 225 cans per annum for its “Target Case” after FY 2011 and this 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 1004°C and a melt viscosity of 55 poise, though some blends could not match these parameters). Blends for coupled feeds were made at the salt product loading matched to the nominal salt processing rate of 6 million gallons per year of 6.44M [Na] feed.

Some minor adjustments were made to the order and quantity of sludge removed from HLW tanks versus the current HLW System Plan. These adjustments were made to allow blending DWPF glass within specification for all flowsheets. This DOES NOT constitute a change in HLW planing basis, though these changes were discussed with the responsible managers and were considered plausible. These mismatches between the

system planning and salt disposition bases will be resolved in the next HLW System Plan revision.

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. The canister count is smaller for the "Sludge Only" versus the "Solvent Extraction" case because the "Solvent Extraction" case includes residual sludge associated with stored salt and the MST solids used to remove strontium and alpha contamination. "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) and the magnitude of change (~160 canisters, total change) is correct. PHA produces more coupled canisters, in part, because Sludge Batch 5 material cannot tolerate the nominal PHA feed rate (equivalent to 13.1 % PHA oxides in glass), but must be blended at 9.5 % PHA oxides to meet glass durability limits. This likely can be fixed by revised sludge blending. This will be investigated as input into the next HLW System Plan revision and to this document.

**Table 4.0-1 Canisters Production for the Salt Processing Flowsheets**

Sludge Batch	System Plan Rev. 11 Tanks (Fraction / Al Diss)	This Study Tanks (Fraction / Al Diss)	Sludge Only Cans	Solvent Extraction Cans	Solvent Extraction / Sludge Only Limitation	STTP Cans	STTP Loading Limitation	CST Cans	CST Loading Limitation
1A	51	same	492	N/A	Good Batch, Liquidus Temperature	N/A		N/A	
1B	42	same	625	N/A	High Melt Viscosity	N/A		N/A	
2	8, 40	same	475	N/A	Good Batch, Liquidus Temperature	N/A		N/A	
3	7	same	658	N/A	Good Batch, Liquidus Temperature	N/A		N/A	
4	26, 11(100% / Yes), 18, 19	same	409	N/A	Good Batch, Liquidus Temperature	N/A		N/A	
5 - Sludge	5, 12, 15(100%/Yes)	5, 12, 15 (100%/No)	155	N/A	High Melt Viscosity	N/A		N/A	
5 - Coupled	5, 12, 15(100%/Yes)	5, 12, 15 (100%/No)	465	515	High Melt Viscosity	566	Low Frit (9.5 % PHA Loading)	588	Low Frit
6	13	13(50%), 39(20%), 6(50%), 32(50%), 33(50%), 4(50%)	615	681	Good Batch, Liquidus Temperature	720	Low Frit	712	Low Frit
7	4, 6, 32, 33, 39(40%/No)	13(50%), 39(35%), 6(50%), 32(50%), 33(50%), 4(50%)	634	702	Low Frit	748	Low Frit	740	Low Frit
8	23, 34, 21, 22, 39(60%/No), 43, 47	23, 34, 21, 22, 39(45%/No), 43, 47	599	663	Good Batch, Liquidus Temperature	689	Good Batch, Liquidus Temperature	646	Good Batch, Liquidus Temperature
9	35, heels, residues	same	609	372	Good Batch, Liquidus Temperature	378	Low Frit	247	Low Frit
9 - Sludge	35, heels, residues	same	N/A	274	Good Batch, Liquidus Temperature	268	Good Batch, Liquidus Temperature	397	Good Batch, Liquidus Temperature
<b>Sludge Only Cans</b>			<b>5736</b>	<b>3088</b>		<b>3082</b>		<b>3211</b>	
<b>Cans With Salt Product</b>					<b>2933</b>			<b>2933</b>	
<b>Grand Total</b>			<b>5736</b>	<b>6021</b>		<b>6183</b>		<b>6144</b>	

Table 4.0-2 compares the timing of each batch. This study indicates that there will be enough sludge to blend all processed salt feed.

**Table 4.0-2 Batch Durations**

	<b>System Plan, Revision 11</b>	<b>Sludge Only, This Study</b>	<b>Solvent Extraction</b>	<b>PHA</b>	<b>CST</b>
Start Batch 2	4/20/01	N/A	N/A	N/A	N/A
End Batch 2	1/8/04	N/A	N/A	N/A	N/A
End Batch 3	7/29/07	N/A	N/A	N/A	N/A
End Batch 4	8/13/09	N/A	N/A	N/A	N/A
End Batch 5, Sludge Only	3/1/10	3/1/10	3/1/10	3/1/10	3/1/10
End Batch 5, Coupled	11/11/11	4/28/12	7/18/12	10/9/12	11/14/12
End Batch 6	3/18/15	1/21/15	7/29/15	12/22/15	1/14/16
End Batch 7	7/12/17	11/16/17	9/10/18	4/19/19	4/29/19
End Batch 8	7/5/20	7/15/20	8/22/21	5/12/22	3/13/22
End Batch 9, coupled	11/9/22	N/A	4/18/23	1/15/24	4/18/23
End Batch 9	Salt Only Cans - 12/9/24	3/31/23	7/5/24	3/25/25	1/21/25

Table 4.0-3 shows the annualized canister product. This study and the System Plan assume a 225 canister per year rate. The DWPF model used for the Process Flow Diagrams (PFDs) used the identical processing bases for the salt waste. The model used for the PFDs maximized total waste and was not constrained to make a constant number of canisters. This PFDs also show instantaneous material balances at 100% attainment.

This study uses the nominal 75% attainment and does account for melter change-outs of six months after 2 years melter operation. Solvent Extraction and CST PFDs and rates match quit well when accounting for all these factors. The larger discrepancy for PHA (Small Tank Tetraphenylborate Precipitation – STTP) is due the fact that PHA loading cannot be matched to production rate for Batch 5 Sludge, as noted above.

**Table 4.0-3 Annualized Canister Production**

<b>Canisters Per Year</b>				
	(System Plan Basis	Process Flow Diagrams, 100% Attainment	Process Flow Diagrams, 75% Attainment w/ melter outage	Corrected to This Study's Salt Loading
<b>CSSE</b>	225	391	254	225
<b>STTP</b>	225	475	309	218
<b>CST</b>	225	440	286	227

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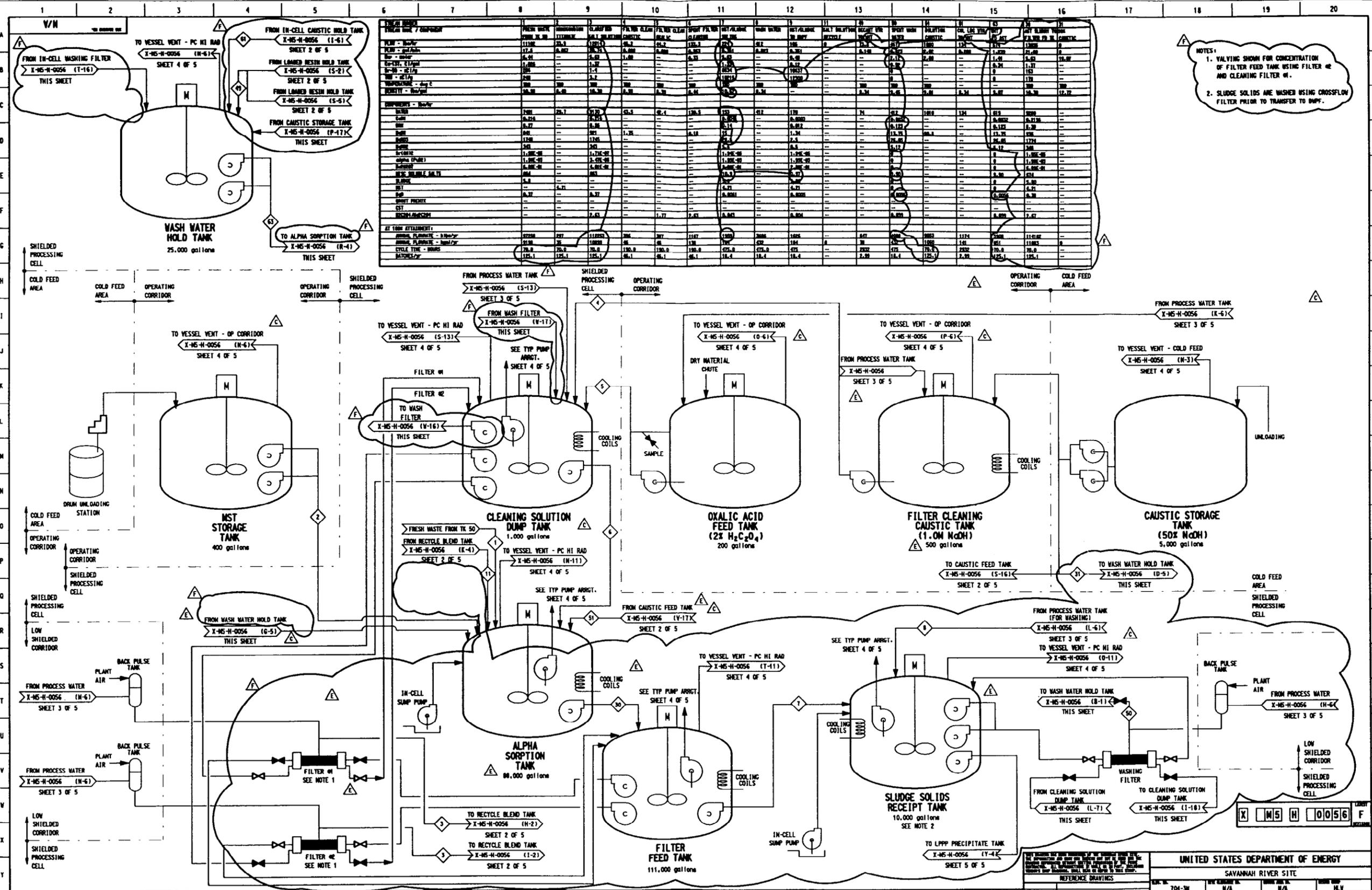
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Appendix A  
WSRC-RP-99-00006, Rev. 1  
CST Ion Exchange Flow Diagrams



ITEM NO.	DESCRIPTION	QTY	UNIT	PRICE	TOTAL	DATE	BY	CHKD	APP'D	REV.	DATE	DESCRIPTION
1	WASH WATER HOLD TANK	1	EA	111.0	111.0	11/13/80	BA	BA	BA	1	11/13/80	ISSUED FOR REVIEW
2	MST STORAGE TANK	1	EA	400.0	400.0	11/13/80	BA	BA	BA	1	11/13/80	REVISIONS AS SHOWN
3	CLEANING SOLUTION DUMP TANK	1	EA	1000.0	1000.0	11/13/80	BA	BA	BA	1	11/13/80	REVISED MATERIAL BALANCE TABLES
4	OXALIC ACID FEED TANK	1	EA	200.0	200.0	11/13/80	BA	BA	BA	1	11/13/80	REVISED MATERIAL BALANCE TABLES SHEET 5
5	FILTER CLEANING CAUSTIC TANK	1	EA	500.0	500.0	11/13/80	BA	BA	BA	1	11/13/80	CURRENT INCORPORATION AND REVISED MATERIAL BALANCE TABLES
6	CAUSTIC STORAGE TANK	1	EA	5000.0	5000.0	11/13/80	BA	BA	BA	1	11/13/80	REVISED TO DISCREPANCY REF. NO. 84-01-0000-0000
7	ALPHA SORPTION TANK	1	EA	80000.0	80000.0	11/13/80	BA	BA	BA	1	11/13/80	
8	FILTER FEED TANK	1	EA	111000.0	111000.0	11/13/80	BA	BA	BA	1	11/13/80	
9	SLUDGE SOLIDS RECEIPT TANK	1	EA	10000.0	10000.0	11/13/80	BA	BA	BA	1	11/13/80	

NOTES:  
 1. VALVING SHOWN FOR CONCENTRATION OF FILTER FEED TANK USING FILTER #2 AND CLEANING FILTER #1.  
 2. SLUDGE SOLIDS ARE WASHED USING CROSSFLOW FILTER PRIOR TO TRANSFER TO DMPP.

NO.	REV.	DATE	REVISION	PP/P	LEAD	CHK'D	APP'D	APP'D	APP'D	NO.	REV.	DATE	REVISION	PP/P	LEAD	CHK'D	APP'D	APP'D	APP'D

REFERENCE DRAWINGS			
NO.	REV.	DATE	DESCRIPTION

REFERENCE STANDARDS			
NO.	REV.	DATE	DESCRIPTION

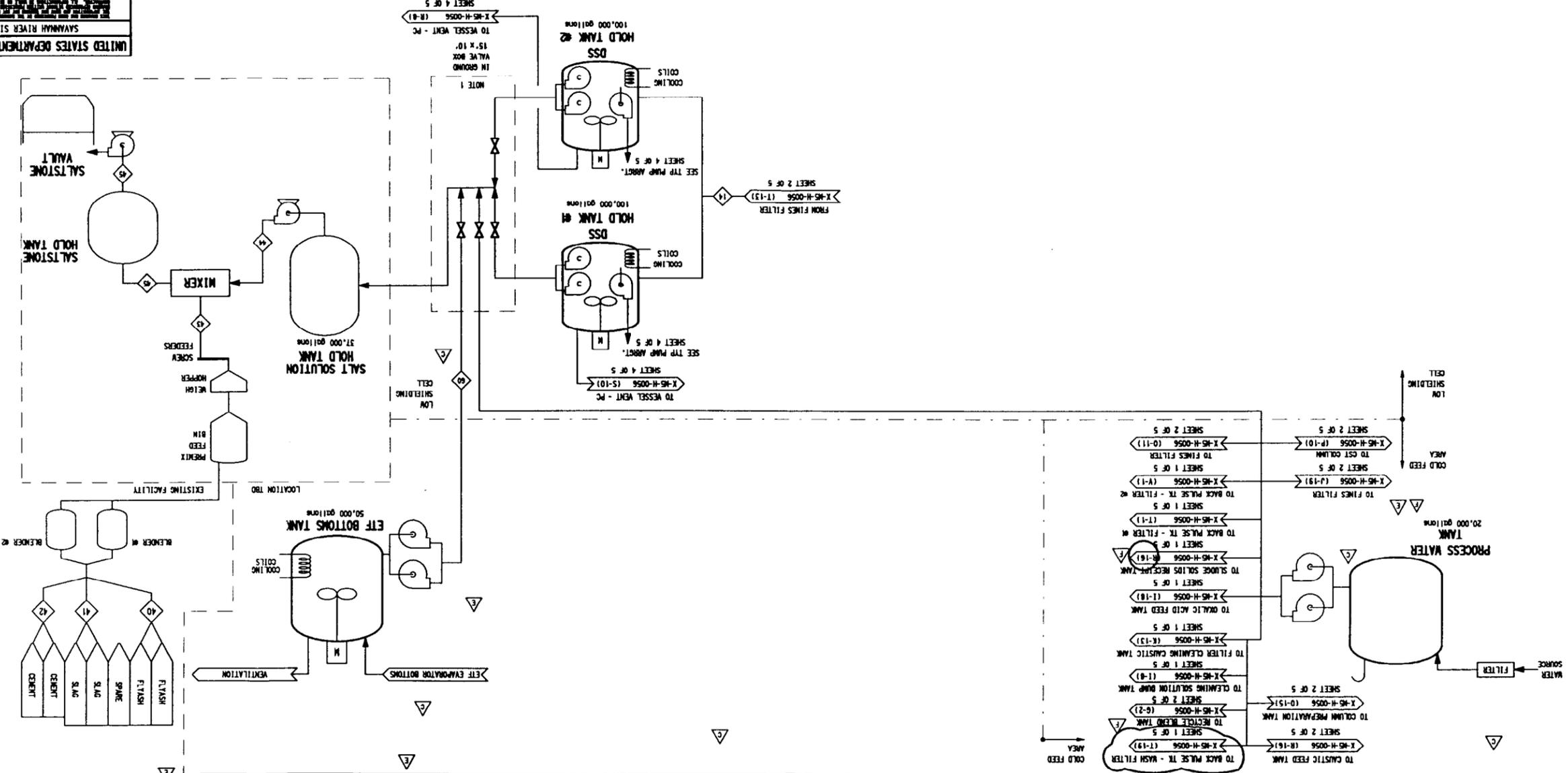
UNITED STATES DEPARTMENT OF ENERGY			
SAVANNAH RIVER SITE			
FORM NO.	REV.	DATE	ISSUED BY
704-34	N/A	N/A	N/A

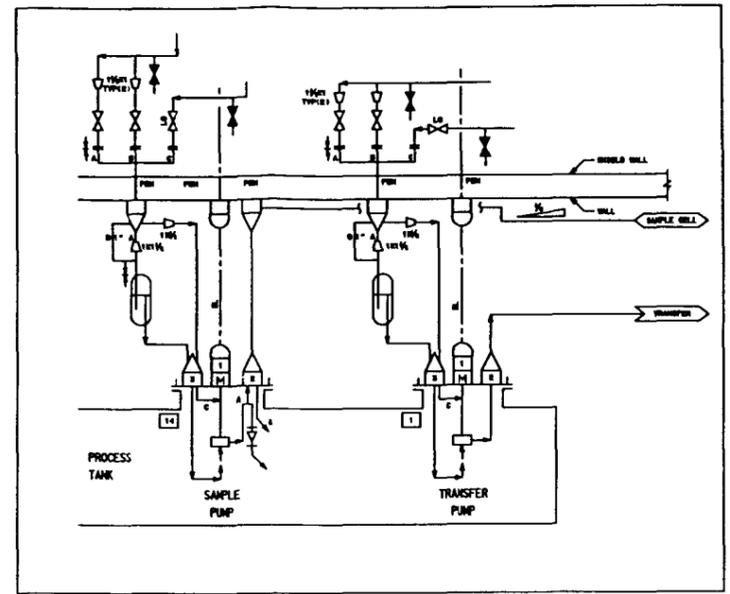
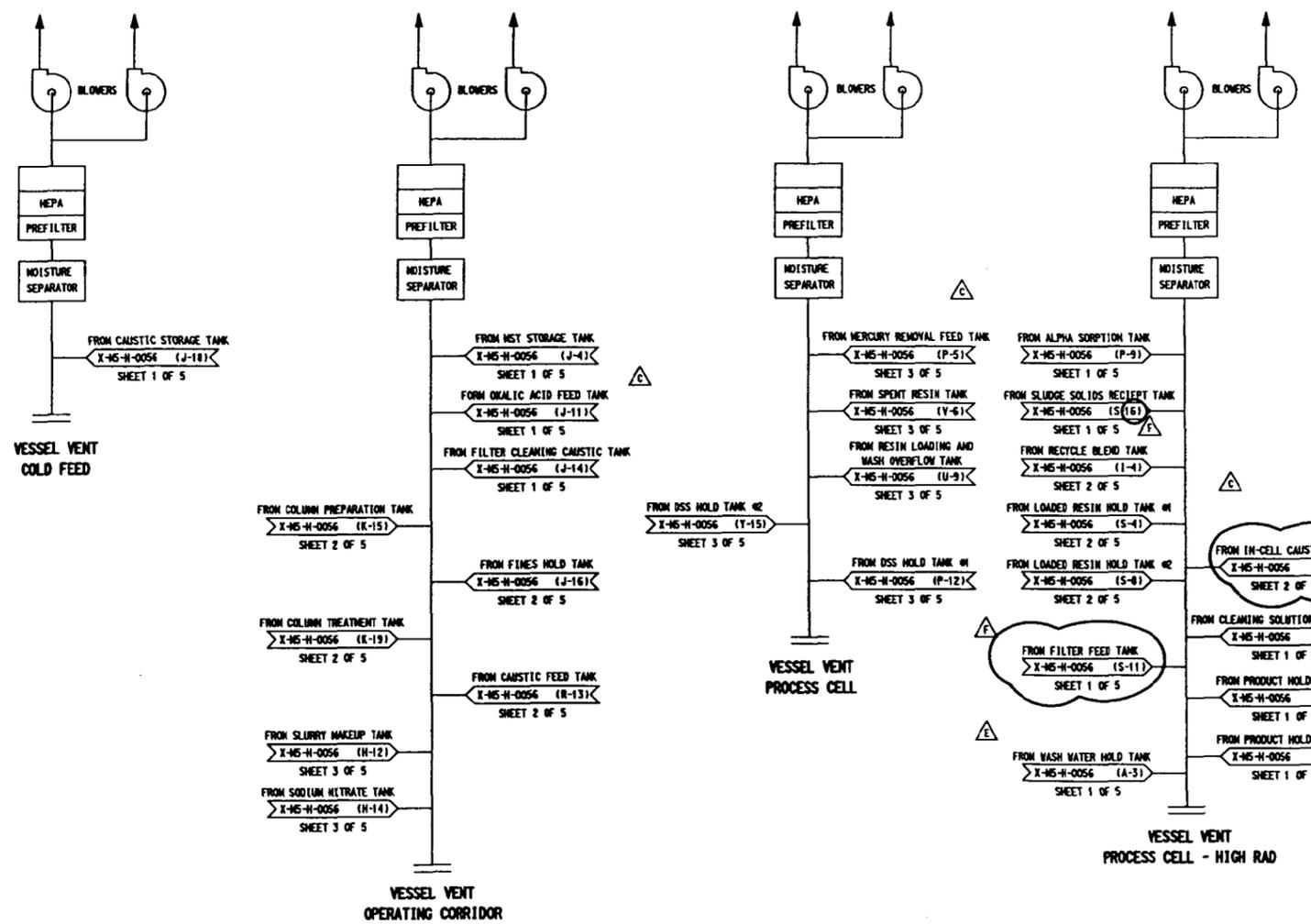
PROJECT TITLE		DATE	REV.
HIGH LEVEL WASTE SALT PROCESSING		11/13/80	1
CST ION EXCHANGE			
(U)			



NOTES:  
 1. ALWAYS TO HAVE HANDWEELS WITH  
 REACH HOOS TO ABOVE CONCRETE  
 COVER.



ITEM NO.	DESCRIPTION	QTY	UNIT	REMARKS
1	FLYASH	1000	TON	
2	SLAG	1000	TON	
3	CEMENT	1000	TON	
4	WATER	20000	GALLONS	
5	SALT SOLUTION	37000	GALLONS	
6	DSS HOLD TANK #1	100000	GALLONS	
7	DSS HOLD TANK #2	100000	GALLONS	
8	PROCESS WATER TANK	20000	GALLONS	
9	MIXER	1	UNIT	
10	SALT SOLUTION HOLD TANK	1	UNIT	
11	VENTILATION	1	UNIT	
12	COOLING COILS	2	SETS	
13	WEIGH HOPPER	1	UNIT	
14	FEED BIN	1	UNIT	
15	PREMIX	1	UNIT	
16	SCREENS	1	UNIT	
17	BLENDER #2	1	UNIT	
18	EXISTING FACILITY	1	UNIT	
19	LOCATION TRD	1	UNIT	
20	VENTILATION	1	UNIT	



TYPICAL PUMP ARRANGEMENT

UNITED STATES DEPARTMENT OF ENERGY  
 SAVANNAH RIVER SITE  
 HIGH LEVEL WASTE SALT  
 PROCESSING - CST ION EXCHANGE  
 (U)

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Appendix B  
WSRC-RP-99-00006, Rev. 1  
CST Ion Exchange General Arrangement Diagrams



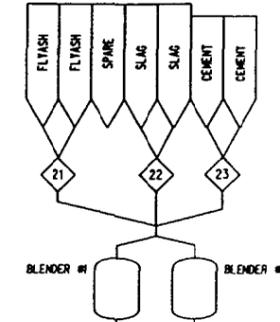
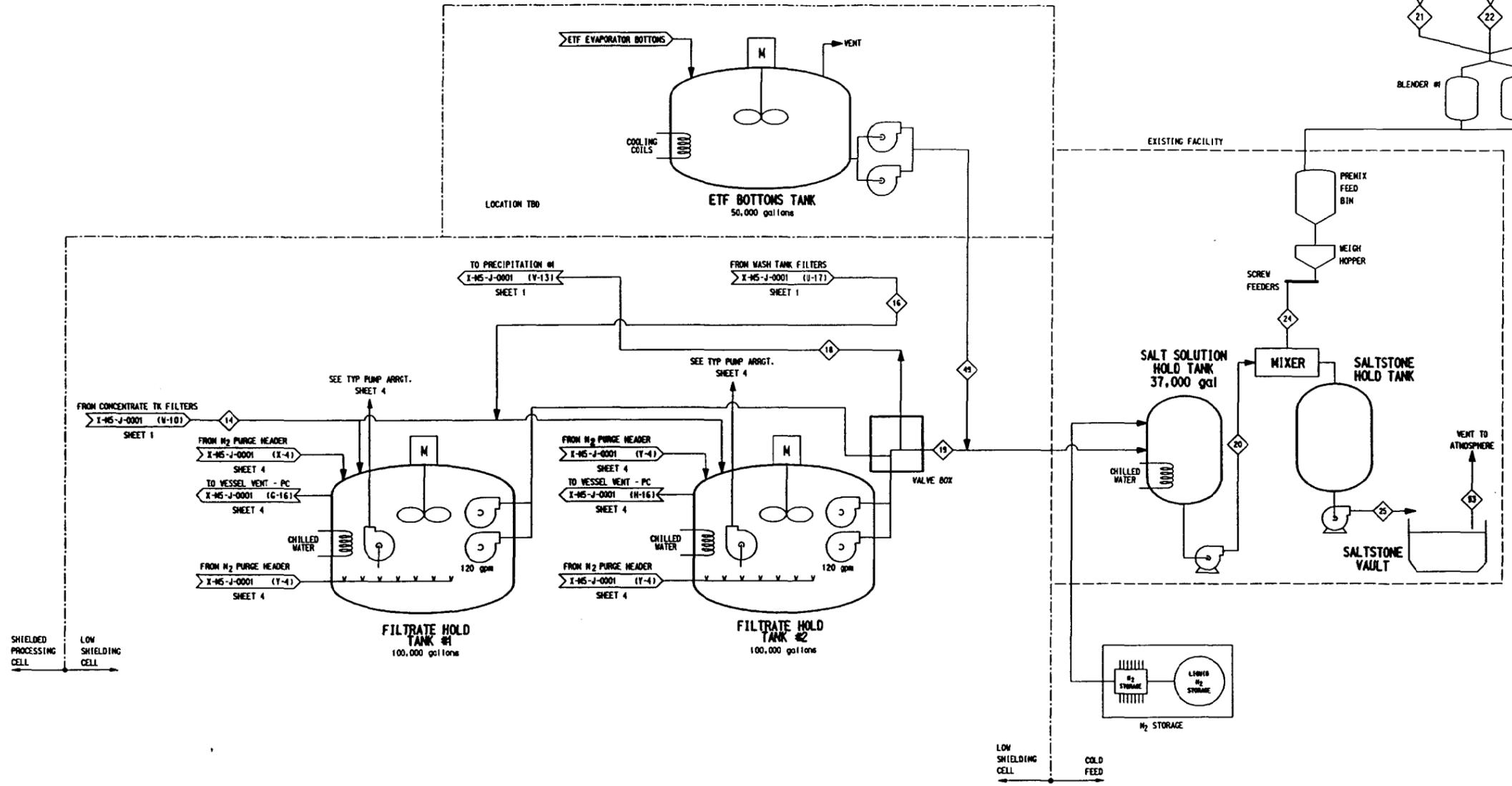




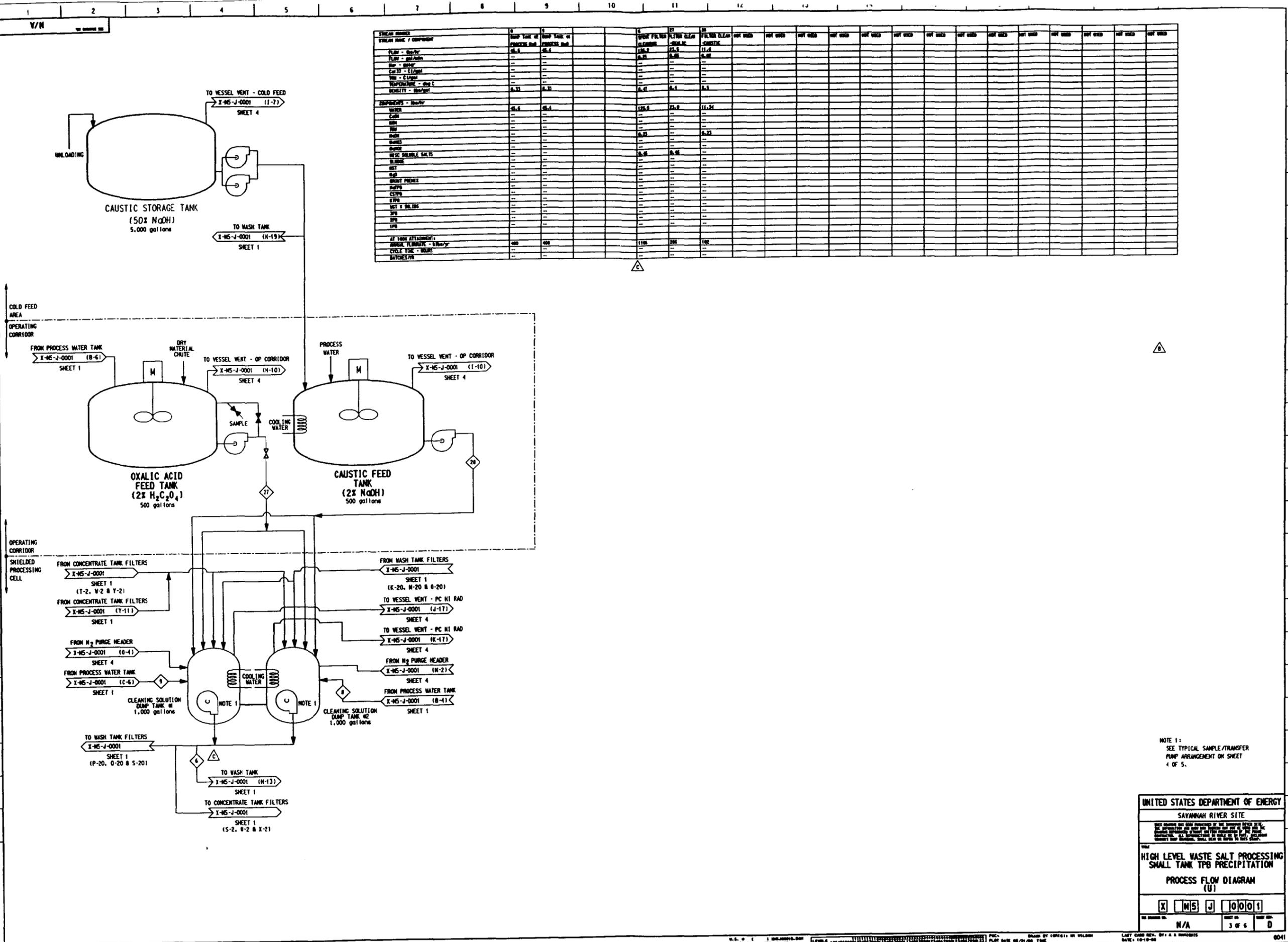
Appendix C  
WSRC-RP-99-00006, Rev. 1  
Small Tank TPB Flow Diagrams



STREAM NUMBER	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100															
STREAM NAME / COMPONENT	DES SALT	SPENT WATER	FILTRATE TO PRECIP. #1	FILTRATE TO PRECIP. #2	FILTRATE TO PRECIP. #3	FILTRATE TO PRECIP. #4	FILTRATE TO PRECIP. #5	FILTRATE TO PRECIP. #6	FILTRATE TO PRECIP. #7	FILTRATE TO PRECIP. #8	FILTRATE TO PRECIP. #9	FILTRATE TO PRECIP. #10	FILTRATE TO PRECIP. #11	FILTRATE TO PRECIP. #12	FILTRATE TO PRECIP. #13	FILTRATE TO PRECIP. #14	FILTRATE TO PRECIP. #15	FILTRATE TO PRECIP. #16	FILTRATE TO PRECIP. #17	FILTRATE TO PRECIP. #18	FILTRATE TO PRECIP. #19	FILTRATE TO PRECIP. #20	FILTRATE TO PRECIP. #21	FILTRATE TO PRECIP. #22	FILTRATE TO PRECIP. #23	FILTRATE TO PRECIP. #24	FILTRATE TO PRECIP. #25	FILTRATE TO PRECIP. #26	FILTRATE TO PRECIP. #27	FILTRATE TO PRECIP. #28	FILTRATE TO PRECIP. #29	FILTRATE TO PRECIP. #30	FILTRATE TO PRECIP. #31	FILTRATE TO PRECIP. #32	FILTRATE TO PRECIP. #33	FILTRATE TO PRECIP. #34	FILTRATE TO PRECIP. #35	FILTRATE TO PRECIP. #36	FILTRATE TO PRECIP. #37	FILTRATE TO PRECIP. #38	FILTRATE TO PRECIP. #39	FILTRATE TO PRECIP. #40	FILTRATE TO PRECIP. #41	FILTRATE TO PRECIP. #42	FILTRATE TO PRECIP. #43	FILTRATE TO PRECIP. #44	FILTRATE TO PRECIP. #45	FILTRATE TO PRECIP. #46	FILTRATE TO PRECIP. #47	FILTRATE TO PRECIP. #48	FILTRATE TO PRECIP. #49	FILTRATE TO PRECIP. #50	FILTRATE TO PRECIP. #51	FILTRATE TO PRECIP. #52	FILTRATE TO PRECIP. #53	FILTRATE TO PRECIP. #54	FILTRATE TO PRECIP. #55	FILTRATE TO PRECIP. #56	FILTRATE TO PRECIP. #57	FILTRATE TO PRECIP. #58	FILTRATE TO PRECIP. #59	FILTRATE TO PRECIP. #60	FILTRATE TO PRECIP. #61	FILTRATE TO PRECIP. #62	FILTRATE TO PRECIP. #63	FILTRATE TO PRECIP. #64	FILTRATE TO PRECIP. #65	FILTRATE TO PRECIP. #66	FILTRATE TO PRECIP. #67	FILTRATE TO PRECIP. #68	FILTRATE TO PRECIP. #69	FILTRATE TO PRECIP. #70	FILTRATE TO PRECIP. #71	FILTRATE TO PRECIP. #72	FILTRATE TO PRECIP. #73	FILTRATE TO PRECIP. #74	FILTRATE TO PRECIP. #75	FILTRATE TO PRECIP. #76	FILTRATE TO PRECIP. #77	FILTRATE TO PRECIP. #78	FILTRATE TO PRECIP. #79	FILTRATE TO PRECIP. #80	FILTRATE TO PRECIP. #81	FILTRATE TO PRECIP. #82	FILTRATE TO PRECIP. #83	FILTRATE TO PRECIP. #84	FILTRATE TO PRECIP. #85	FILTRATE TO PRECIP. #86	FILTRATE TO PRECIP. #87	FILTRATE TO PRECIP. #88	FILTRATE TO PRECIP. #89	FILTRATE TO PRECIP. #90	FILTRATE TO PRECIP. #91	FILTRATE TO PRECIP. #92	FILTRATE TO PRECIP. #93	FILTRATE TO PRECIP. #94	FILTRATE TO PRECIP. #95	FILTRATE TO PRECIP. #96	FILTRATE TO PRECIP. #97	FILTRATE TO PRECIP. #98	FILTRATE TO PRECIP. #99	FILTRATE TO PRECIP. #100



UNITED STATES DEPARTMENT OF ENERGY  
 SAVANNAH RIVER SITE  
 HIGH LEVEL WASTE SALT PROCESSING  
 SMALL TANK TPB PRECIPITATION  
 PROCESS FLOW DIAGRAM  
 (U)  
 X M5 J 0001  
 N/A 2 OF 6 D



STREAM NUMBER	FROM	TO	TYPE	UNIT	FLOW RATE	TEMPERATURE	DENSITY	PH	OTHER
1	UNLOADING	CAUSTIC STORAGE TANK	LIQUID	50% NaOH	...	...	...	...	...
2	CAUSTIC STORAGE TANK	TO WASH TANK	LIQUID	50% NaOH	...	...	...	...	...
3	FROM PROCESS WATER TANK	OXALIC ACID FEED TANK	LIQUID	...	...	...	...	...	...
4	OXALIC ACID FEED TANK	OXALIC ACID FEED TANK	LIQUID	...	...	...	...	...	...
5	CAUSTIC FEED TANK	CAUSTIC FEED TANK	LIQUID	...	...	...	...	...	...
6	FROM CONCENTRATE TANK FILTERS	CLEANING SOLUTION DUMP TANK #1	LIQUID	...	...	...	...	...	...
7	FROM WASH TANK FILTERS	CLEANING SOLUTION DUMP TANK #2	LIQUID	...	...	...	...	...	...
8	FROM H2 PURGE HEADER	CLEANING SOLUTION DUMP TANK #1	LIQUID	...	...	...	...	...	...
9	FROM PROCESS WATER TANK	CLEANING SOLUTION DUMP TANK #1	LIQUID	...	...	...	...	...	...
10	CLEANING SOLUTION DUMP TANK #1	TO WASH TANK	LIQUID	...	...	...	...	...	...
11	CLEANING SOLUTION DUMP TANK #1	TO CONCENTRATE TANK FILTERS	LIQUID	...	...	...	...	...	...
12	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
13	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
14	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
15	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
16	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
17	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
18	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
19	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
20	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
21	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
22	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
23	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
24	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
25	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
26	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
27	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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31	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
32	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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34	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
35	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
36	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
37	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
38	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
39	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
40	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
41	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
42	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
43	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
44	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
45	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
46	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
47	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
48	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
49	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
50	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
51	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
52	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
53	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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56	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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60	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
61	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
62	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
63	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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83	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
84	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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88	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
89	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
90	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...
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100	FROM WASH TANK FILTERS	TO WASH TANK	LIQUID	...	...	...	...	...	...

NOTE 1:  
SEE TYPICAL SAMPLE/TRANSFER  
PUMP ARRANGEMENT ON SHEET  
4 OF 5.

UNITED STATES DEPARTMENT OF ENERGY  
SAVANNAH RIVER SITE

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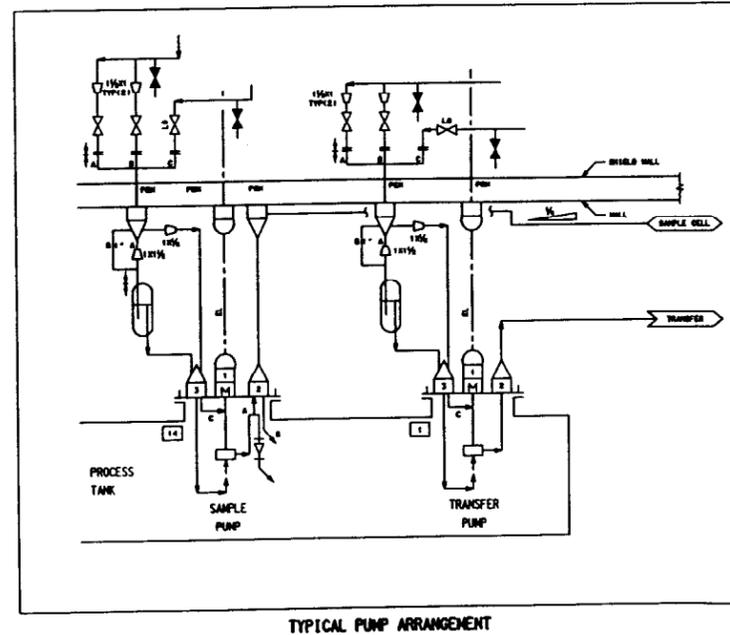
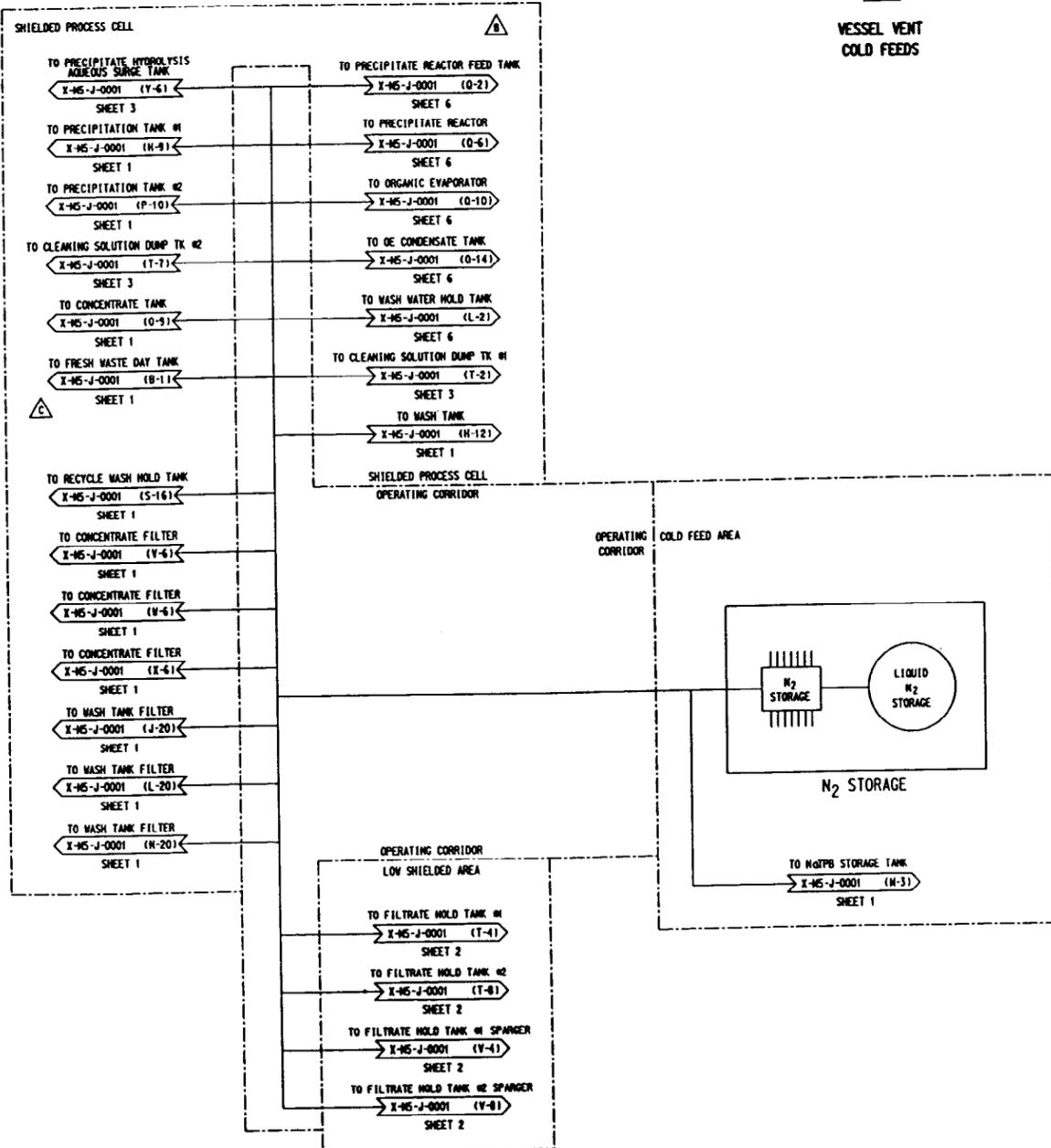
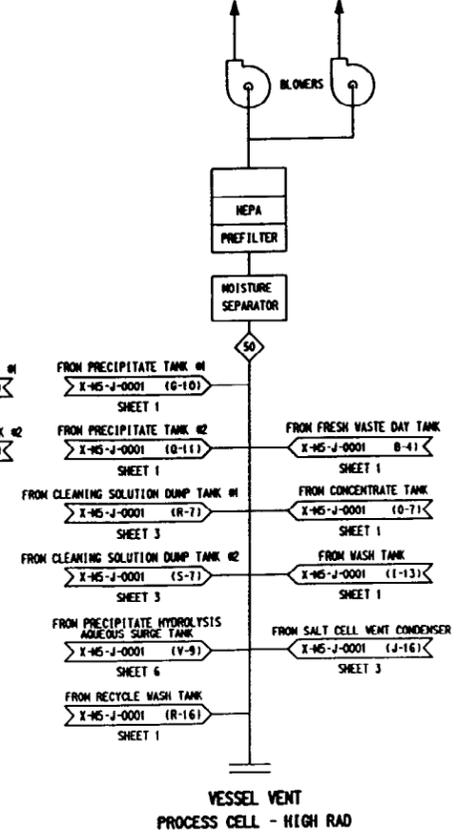
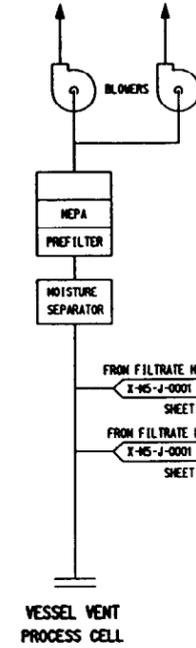
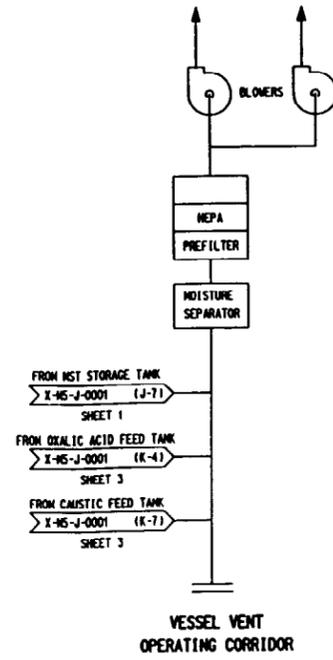
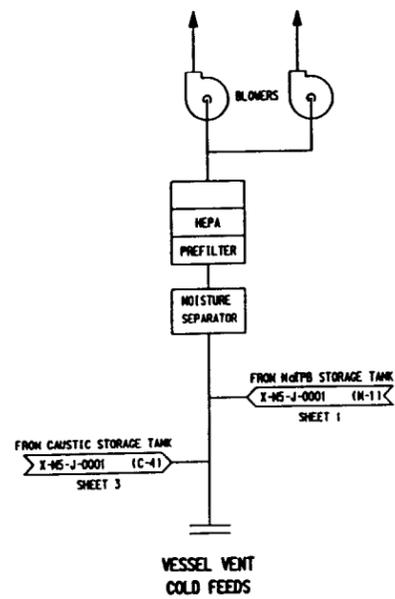
PROJECT  
HIGH LEVEL WASTE SALT PROCESSING  
SMALL TANK TPB PRECIPITATION

PROCESS FLOW DIAGRAM  
(U)

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NO. OF SHEETS: N/A SHEET NO. 3 OF 6 SHEET DATE: D

STREAM NUMBER	SO
STEAM WIRE / COMPONENT <td>MOD/DC</td>	MOD/DC
PLUM - 100psi	...
PLUM - 200psi	...
PLUM - 300psi	...
TEMPERATURE - deg C	...
DENSITY - lb/ft <sup>3</sup>	...
AT 100% ATTACHMENT	...
OTHER PLUMBING - 100psi	...



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PROJECT: HIGH LEVEL WASTE SALT PROCESSING  
SMALL TANK TPB PRECIPITATION  
PROCESS FLOW DIAGRAM (U)

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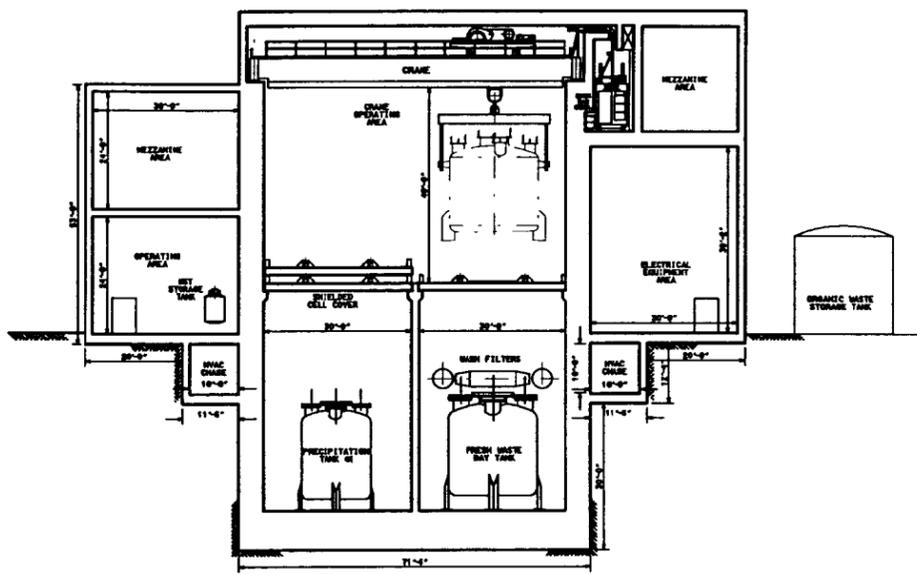
Appendix D  
WSRC-RP-99-00006, Rev. 1  
Small Tank TPB General Arrangement Diagrams





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SECTION B  
SHEET 1

PROCESS TANK	WORKING VOLUME (GALLONS)	HEIGHT (FT)	RADIUS (FT)	CAPACITY	
				CUBIC FEET	GALLONS
PRECIPITATION TANKS #1 & #2	18,000	16	7	2,443	10,423
CONCENTRATE TANK	18,000	15	8	1696	12,670
CLEANING SOLUTION DUMP TANKS #1 & #2	1,000	6	3	179	1,287
RECYCLE WASH HOLD TANK	25,000	16	9	4,871	36,405
WASH TANK	18,000	15	6	1,696	12,670
PRECIPITATE HYDROLYSIS AQUEOUS SURGE TANK	46,000	20	18	6,283	47,800
FILTRATE HOLD TANKS #1 & #2	100,000	30	13	10,520	114,140
NET TANK	400	5.25	2.25	86	493
OA FEED TANK	600	5	2.25	79	695
CAUSTIC FEED TANK	600	5	2	79	664
WATPS STORAGE TANK	20,000	16	8	3,217	24,863
PROCESS WATER TANK	80,000	25	13	13,884	103,254
CAUSTIC STORAGE TANK	6,000	16.5	5	824	6,168
FRESH WASTE DRY TANK	25,000	16	9	4,871	36,405
ANTI-FORM STORAGE TANK	600	5	2.5	98	734
PRECIPITATE REACTOR FEED TANK	18,000	16	6	1818	13,635
PRECIPITATE REACTOR	18,000	16	6	1818	13,635
RP OVERHEADS TANK	7000	12	6	1357	10,198
ORGANIC EVAPORATOR	1750	8	3.5	388	2380
ORGANIC EVAPORATOR CONDENSATE TANK	1800	6	3	170	1289
PRECIPITATE CONDENSER/DECANTER	700 SOFT	N/A	N/A	N/A	700 SOFT
OE CONDENSER/DECANTER	700 SOFT	N/A	N/A	N/A	700 SOFT
SALT CELL VENT CONDENSER	700 SOFT	N/A	N/A	N/A	700 SOFT
ORGANIC WASTE STORAGE TANK	46,000	20	18	6,283	47,800
COPPER NITRATE FEED TANK	600	5	2.25	79	695
FORMIC ACID FEED TANK	600	5	2.25	79	695
CAUSTIC FEED TANK	600	5	2.25	79	695



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HLW SALT PROCESSING  
SMALL TANK TETRAPHENYLBORATE  
PRECIPITATION PROCESS  
GENERAL ARRANGEMENT  
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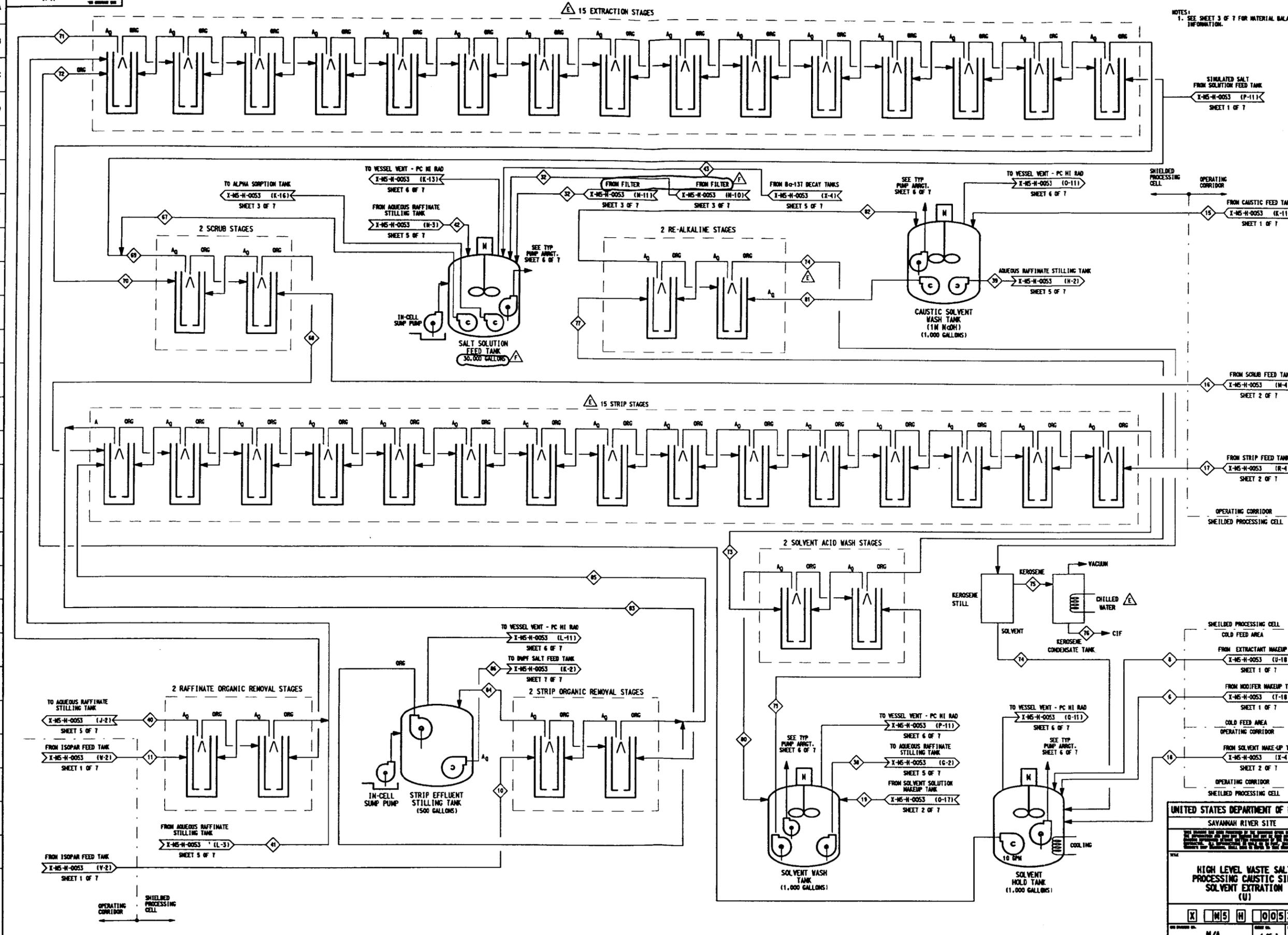
N/A 3 OF 3 A

Appendix E  
WSRC-RP-99-00006, Rev. 1  
CSSX Flow Diagrams









NOTES:  
1. SEE SHEET 3 OF 7 FOR MATERIAL BALANCE INFORMATION.

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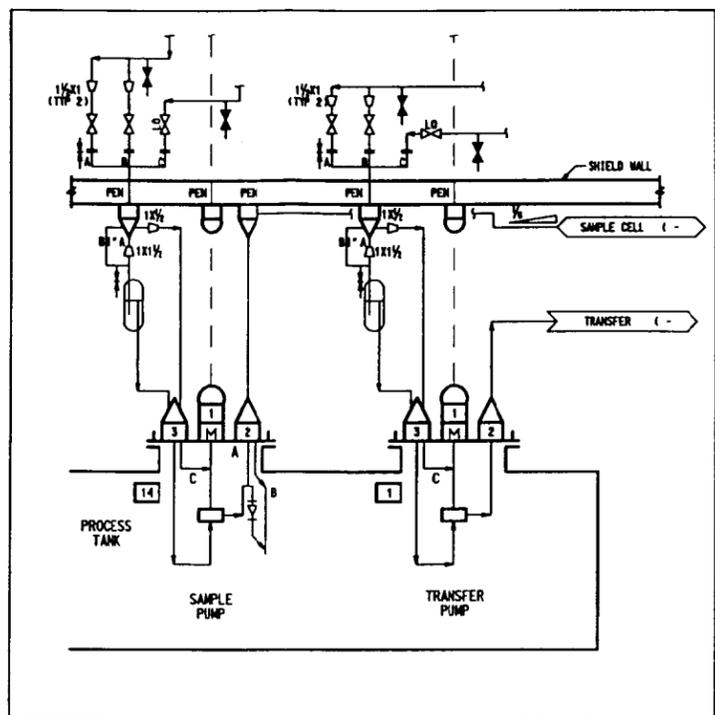
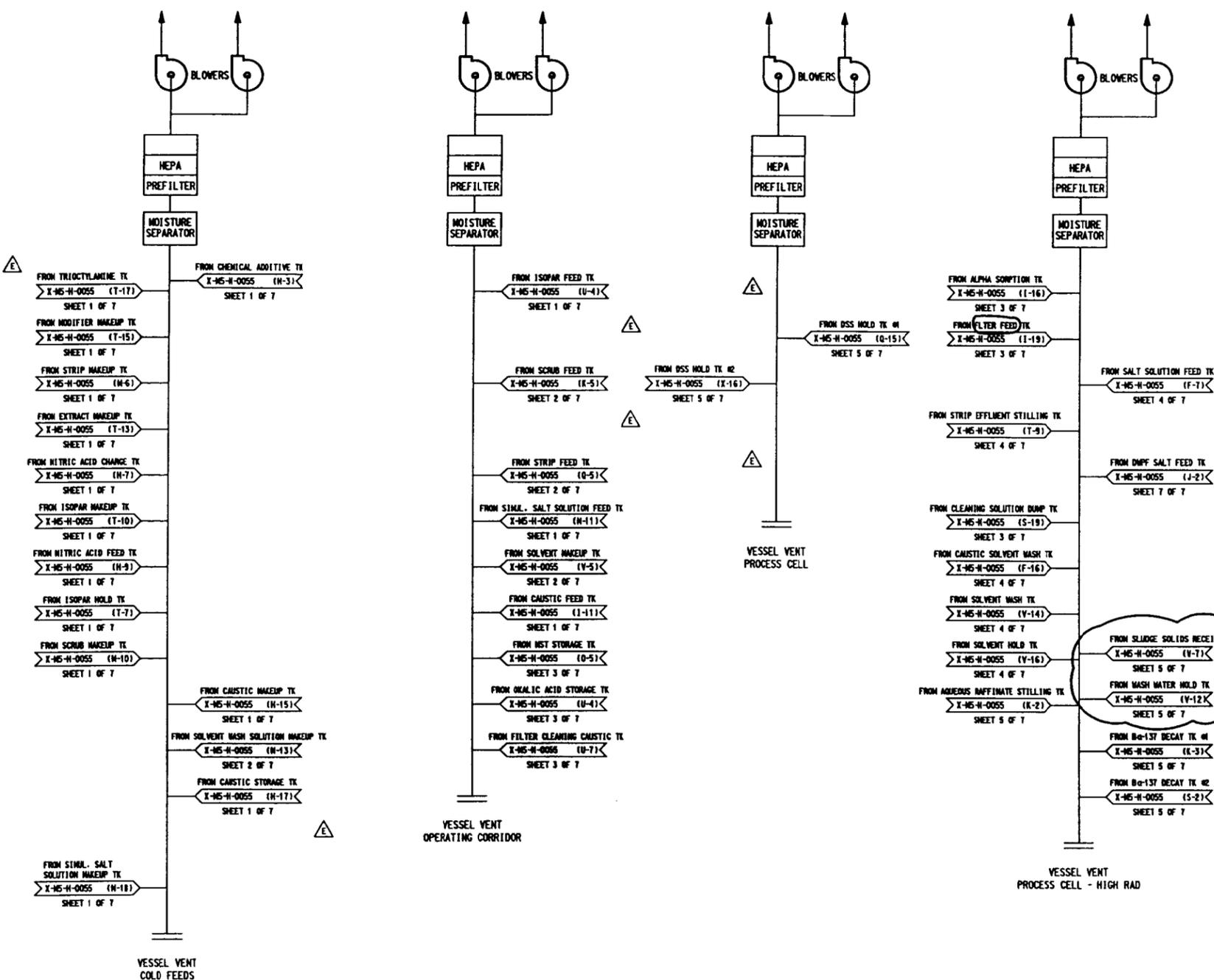
HIGH LEVEL WASTE SALT PROCESSING CAUSTIC SIDE SOLVENT EXTRACTION (U)

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TYPICAL PUMP ARRANGEMENT

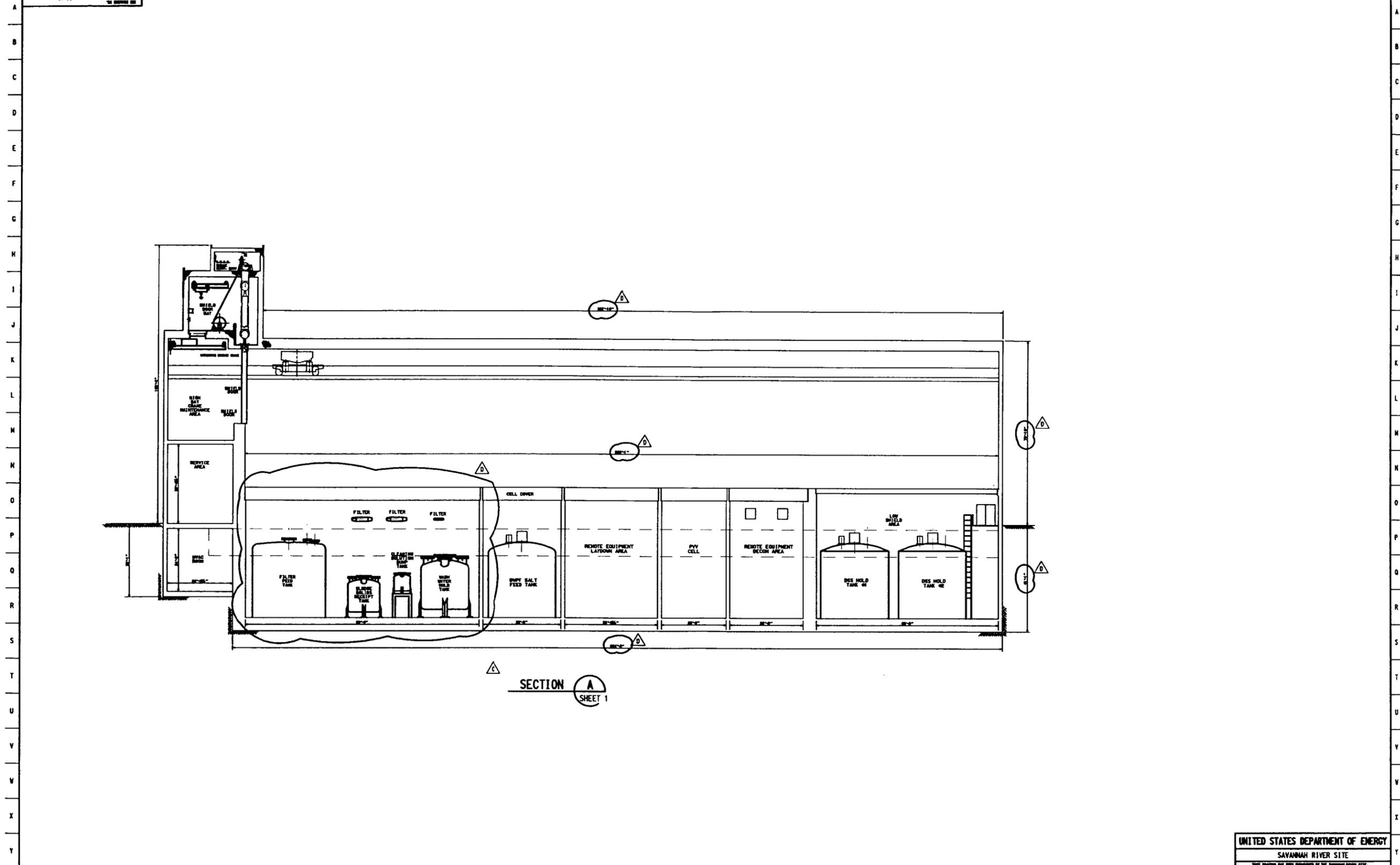
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HIGH LEVEL WASTE SALT PROCESSING CAUSTIC SIDE SOLVENT EXTRACTION (U)			
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Appendix F  
WSRC-RP-99-00006, Rev. 1  
CSSX General Arrangement Diagrams



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20



SECTION A  
SHEET 1

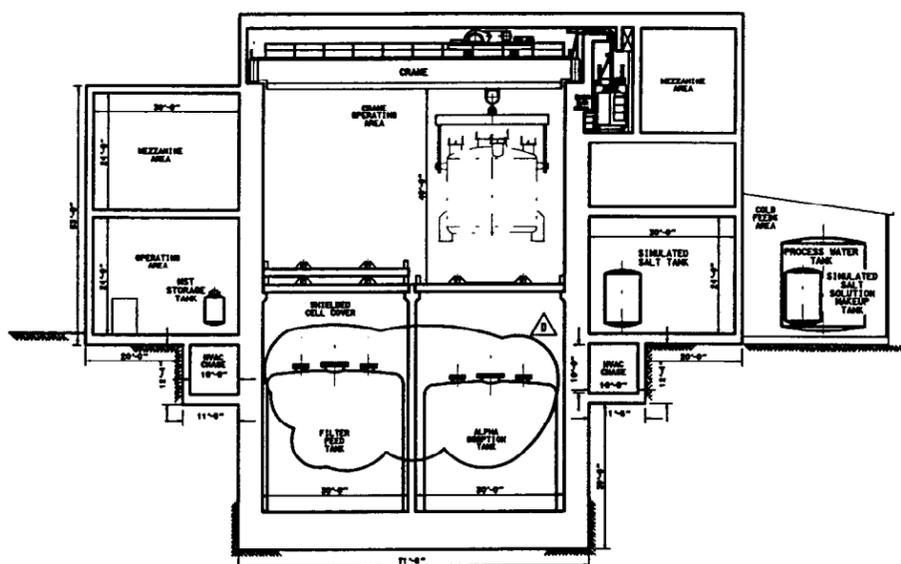


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HIGH LEVEL WASTE SALT PROCESSING CAUSTIC SIDE SOLVENT EXTRACTION			
X	P	G	H
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A B C D E F G H I J K L M N O P Q R S T U V W X Y

V/N



SECTION B SHEET 1 OF 3

PROCESS TANKS	WORKING VOLUME (GALLONS)	HEIGHT (FT)	DIAMETER (FT)	CAPACITY	
				CUBIC FEET	GALLONS
ALPHA SORPTION TANK	88,000	26	26	13,800	103,250
DMPF SALT FEED	100,000	30	26	15,928	119,140
SALT SOLUTION FEED TANK	30,000	18	18	4,580	34,262
DSS HOLD #1	100,000	30	26	15,928	119,140
DSS HOLD #2	100,000	30	26	15,928	119,140
STRIP MAKEUP	25,000	16	16	4,071	30,455
PROCESS WATER	25,000	16	16	4,071	30,455
SCRUB MAKEUP	15,000	16	14	2,463	18,423
CAUSTIC DILUTION FEED TANK	15,000	16	14	2,463	18,423
SLUDGE SOLIDS RECEIPT TANK	10,000	13	12	1,696	12,690
CAUSTIC STORAGE	5,000	10.5	10	824	6,168
ISOPAR HOLD	5,000	10.5	10	824	6,168
SIMULATED SALT SOLUTION MAKEUP	4,000	10	9	636	4,758
SIMULATED SALT	4,000	10	9	636	4,758
STRIP FEED	4,000	10	9	636	4,758
FILTER FEED	111,000	28	28	2,463	18,423
WASH WATER HOLD	25,000	16	16	4,072	30,455
SCRUB FEED	2,500	9	8	452	3,384
Ba-137 DECAY #1	2,500	9	8	452	3,384
Ba-137 DECAY #2	2,500	9	8	452	3,384
ISOPAR MAKEUP	2,000	9	7	346	2,540
CLEANING SOLUTION DUMP	1,000	6	6	170	1,270
NITRIC ACID FEED	1,000	6	6	170	1,270
CAUSTIC FEED	1,000	6	6	170	1,270
CAUSTIC MAKEUP	1,000	6	6	170	1,270
SOLVENT MAKEUP	1,000	6	6	170	1,270
CLEANING SOLUTION DUMP	1,000	6	6	170	1,270
CAUSTIC SOLVENT WASH	1,000	6	6	170	1,270
SOLVENT WASH	1,000	6	6	170	1,270
SOLVENT WASH SOLUTION MAKEUP	1,000	6	6	170	1,270
SOLVENT HOLD	1,000	6	6	170	1,270
AQUEOUS RAFFINATE STILLING	500	5	4.5	79	595
ISOPAR FEED	500	5	4.5	79	595
FILTER CLEANING CAUSTIC	500	5	4.5	79	595
STRIP EFFLUENT STILLING	500	5	4.5	79	595
ISOPAR FEED	500	5	4.5	79	595
MODIFIER MAKEUP	500	5	4.5	79	595
MST STORAGE	400	2.5	4	68	493
OXALIC ACID FEED	200	3	4	38	280
KEROSENE STILL	200	3	4	38	280
KEROSENE CONDENSATE	200	3	4	38	280
CHEMICAL ADDITIVE	100	3.5	2.5	17	130
EXTRACTANT MAKEUP	50	3	1.75	7.2	54



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SAVANNAH RIVER SITE

HIGH LEVEL WASTE  
SALT PROCESSING  
CAUSTIC SIDE  
SOLVENT EXTRACTION

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Appendix G  
WSRC-RP-99-00006, Rev. 1  
HLW Salt Processing  
Salt Disposition Facility  
Mast Plot Plan

