

## **Tanks Focus Area**

# **Savannah River Site Salt Processing Project Research and Development Program Plan**

**Revision 0**

**May 2000**

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*operated by*  
BATTELLE  
*for the*  
UNITED STATES DEPARTMENT OF ENERGY  
*under Contract DE-AC06-76RLO 1830*

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**Savannah River Site Salt Processing Project**  
**Research and Development Program Plan**

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

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## **Executive Summary**

The Department of Energy's (DOE) Savannah River Site (SRS) high-level waste (HLW) program is responsible for storage, treatment, and immobilization of HLW for disposal. The Salt Processing Project (SPP) is the salt (soluble) waste treatment portion of the SRS HLW cleanup effort. The overall SPP encompasses the selection, design, construction and operation of treatment technologies to prepare the salt waste feed material for the site's Saltstone Facility and vitrification facility (Defense Waste Processing Facility [DWPF]). Major constituents that must be removed from the salt waste and sent as feed to DWPF include actinides, strontium, and cesium.

SRS successfully demonstrated the In-Tank Precipitation (ITP) process for salt waste treatment both on a moderate and full-scale basis with actual SRS salt waste in the 1980s. The ITP process separates the cesium isotopes from the non-radioactive salts by tetraphenylborate precipitation. By 1995, the site's contractor, Westinghouse Savannah River Company (WSRC), completed design and construction activities for the ITP facility. During radioactive startup of ITP in 1995, higher than predicted releases of benzene occurred. The contractor initiated additional laboratory and facility tests to determine the cause of the escalated benzene generation and to return the facility to a safer status by removing the benzene contained within the facility. In August 1996, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1. The DNFSB recommended that operations and testing in the ITP Facility not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release.

WSRC conducted studies of the chemical, physical, and mechanical properties of the ITP process to investigate and explain benzene generation, retention, and release. Conclusions from the WSRC test program showed that the benzene release rates associated with ITP facility operation could exceed the capability of the current plant hardware and systems. On February 20, 1998, DOE-Savannah River (SR) concurred with the WSRC evaluation of the ITP chemistry data and directed WSRC to perform an evaluation of alternatives to the current system configuration for HLW salt removal, treatment, and disposal. These were included in the cesium removal studies.

An extensive systems engineering evaluation over 140 alternative of cesium removal processes reduced the list of candidates to four. Crystalline Silicotitanate Non-Elutable Ion Exchange Caustic Side Solvent Extraction, Small Tank Tetraphenylborate Precipitation, and direct grouting (with no cesium removal). Further review eliminated direct grouting as an option, and the remaining three alternative processes are currently being pursued in an extensive research and development program:

In 1999, DOE-Headquarters asked the National Academy of Sciences (NAS) to independently review the Department's evaluation of technologies to replace ITP. As a result of the NAS review, DOE agreed that further research and development on each alternative was required to reduce technical uncertainty prior to a down-select. In March 2000, DOE-Headquarters

requested the Tanks Focus Area (TFA) to assume management responsibility for the SPP technology development program at SRS. The TFA was requested to review and revise the technology development roadmaps, develop down-selection criteria, and prepare a comprehensive Research and Development Program Plan for the three candidate cesium removal technologies, as well as the alpha and strontium removal technologies that are part of the overall SPP.

This Research and Development Program Plan describes the technology development needs for each process that must be satisfied to reach a down-selection decision, as well as continuing technology development required to support conceptual design activities for the SPP. Previous results are summarized, ongoing Fiscal Year (FY) 2000 work is described, and plans for FY01 work are presented. In addition, TFA's roadmap reviews identified initiatives outside the current baseline that are recommended for addition to the FY00 and FY01 program.

The SPP Research and Development Program is funded jointly by the DOE Offices of Science and Technology (EM-50) and Project Completion (EM-40). Participants in the program include WSRC's Savannah River Technology Center, Oak Ridge National Laboratory, Argonne National Laboratory, Sandia National Laboratories, Pacific Northwest National Laboratory, and various universities and commercial vendors. Combined program funding for FY00 totals \$14.6 million and total projected funding for FY01 is \$17.7 million.

A detailed integrated schedule of all research and development tasks has been prepared and is being used by all program participants to manage and to report status on their activities. The program is focused on resolving high-risk areas for each alternative cesium-removal process by mid-FY01 in order to support a DOE down selection decision by June 2001.

## **Acknowledgements**

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## **Acronyms and Abbreviations**

AOP	Annual Operating Plan
CSSX	Caustic Side Solvent Extraction
CST	crystalline silicotitanate
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DSS	decontaminated salt solution
DTA	differential thermal analysis
DWPF	Defense Waste Processing Facility
EM	Office of Environmental Management
EM-40	Office of Project Completion
EM-50	Office of Science and Technology
EPA	U.S. Environmental Protection Agency
ES-MS	electrospray mass spectrometry
ETF	Effluent Treatment Facility
FFA	Federal Facilities Agreement
FTIR	Fourier transform infrared (spectroscopy)
FY	fiscal year
GC-MS	gas chromatograph-mass spectrometry
HFIR	High Flux Isotope Reactor
HQ	Headquarters (DOE)
HLW	high-level waste
HM	H modified (SRS enriched uranium solvent extraction process)
HPLC	high pressure liquid chromatography
ITP	In-Tank Precipitation
IWO	Internal Work Order
Mm	millimolar
MTZ	Mass Transfer Zone
NAS	National Academy of Sciences
NMR	nuclear magnetic resonance

PEG	Program Execution Guidance
PHA	precipitate hydrolysis aqueous
QA	quality assurance
R&D	research and development
SCDHEC	South Carolina Department of Health and Environmental Control
SEIS	Supplemental Environmental Impact Statement
SEM	scanning electron microscope
SME	Slurry Mix Evaporator
SOWM	Statement of Work Matrix
SPP	Salt Processing Project
SRAT	Slurry Receipt Adjustment Tank
SRS	Savannah River Site (DOE)
SRTC	Savannah River Technology Center
STP	Site Treatment Plan (SRS)
STTP	Small Tank Tetraphenylborate Precipitation
TCLP	toxicity characteristics leach procedures
TCR	Technical Change Request
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TTP	Technical Task Plan
TFA	Tanks Focus Area
TRU	transuranic
TWB	Technical Working Group
WSRC	Westinghouse Savannah River Company
ZAM	Zheng-Anthony-Miller (CST equilibrium model)

## **1.0 Introduction**

The Department of Energy's (DOE) Savannah River Site (SRS) high-level waste (HLW) program is responsible for storage, treatment, and immobilization of HLW for disposal. The Salt Processing Project (SPP) is the salt (soluble) waste treatment portion of the SRS HLW cleanup effort. The overall SPP encompasses the selection, design, construction and operation of treatment technologies to prepare the salt waste feed material for treatment at the site's Saltstone Facility and vitrification facility (Defense Waste Processing Facility [DWPF]). Major radionuclides that must be removed from the salt waste and sent as feed to DWPF include actinides, strontium (Sr), and cesium (Cs).

In March 2000, DOE-Headquarters (HQ) requested the Tanks Focus Area (TFA) to assume management responsibility for the SPP technology development program at SRS. The TFA was requested to conduct several activities, including review and revision of the technology development roadmaps, development of down-selection criteria, and preparation of a comprehensive research and development (R&D) Program Plan for three candidate Cs removal technologies, as well as the alpha and Sr removal technologies that are part of the overall SPP. The three Cs removal candidate technologies are Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange, Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP).

This plan describes the technology development needs for each process that must be satisfied to reach a down-selection decision, as well as a subset of continuing technology development to support conceptual design activities. Previous results are summarized, ongoing FY00 work is described, and plans for FY01 work are provided in Section 7.0. Funding requirements and project schedules for the R&D workscope are presented in Section 8.0. TFA's roadmap reviews identified initiatives outside the current baseline that are recommended for addition to the FY00 and FY01 program and are reflected as proposed modifications in Appendix A of this plan; recommendations are provided in Section 8.2.

## **2.0 Background**

The SRS Site Treatment Plan (STP) and Federal Facilities Agreement (FFA) call for emptying the site's HLW tanks and closing the "old style" tanks. All waste tanks must be empty of existing waste by 2028 to comply with the STP and FFA. To complete this mission, the HLW system at SRS must retrieve the tank waste and convert the HLW into solid waste forms suitable for disposal. Both the long-lived and short-lived radioisotopes in the waste will be incorporated into borosilicate glass, (vitrified) in the DWPF as a precursor to transporting the material for disposal to the national HLW repository. To make this program economically feasible, the SRS implementing technology must limit the volume of HLW glass produced by removing a significant portion of the non-radioactive salts as incidental wastes for subsequent on-site LLW disposal.

To achieve this mission, the SRS contractor, Westinghouse Savannah River Company (WSRC) successfully demonstrated the In-Tank Precipitation (ITP) process both on a moderate and full-scale basis with actual SRS waste in the 1980s. The ITP process separates the Cs isotopes from the non-radioactive salts to enable disposal of the decontaminated salt solution (DSS) in a grouted low-level waste (LLW) form at the Saltstone Facility. By 1995, WSRC completed design and construction activities for the ITP facility.

During radioactive startup of ITP in 1995, higher than predicted benzene releases occurred. The contractor initiated laboratory and facility tests to determine the cause of the escalated benzene generation and to return the facility to a safer status by removing the benzene contained within the facility.

In August 1996, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1. The DNFSB recommended that operations and testing in the ITP Facility not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In response to DNFSB Recommendation 96-1, WSRC conducted studies of the chemical, physical, and mechanical properties of the ITP process to investigate and explain benzene generation, retention, and release. This research lasted from August 1996 through March 1998.

In January 1998, conclusions from the test program showed that benzene release rates associated with ITP facility operation could exceed the capability of the current plant hardware and systems. On January 22, 1998, WSRC informed the DOE that the chemistry testing demonstrated that the existing system configuration could not cost-effectively meet the safety and production requirements for the ITP facility. WSRC recommended that a systems engineering team conduct a study of alternatives to the current system configuration.

On February 6, 1998, the DOE Assistant Secretary for Environmental Management (EM) approved a DOE-Savannah River (DOE-SR) plan-of-action to suspend startup-related activities and undertake a systems engineering study of alternatives to ITP. On February 20, 1998, DOE-SR concurred with the WSRC evaluation of the ITP chemistry data, instructed WSRC to suspend

ITP startup preparations, and directed WSRC to perform an evaluation of alternatives to the current system configuration for HLW salt removal, treatment, and disposal.

On March 13, 1998, the WSRC HLW Management Division chartered the Systems Engineering Team (Team) to systematically develop and recommend an alternative method and/or technology for disposition of HLW salt waste. DOE approved the WSRC-selected Team on March 31, 1998. Team members provided expertise in systems engineering, process engineering, operations, waste processing, science, safety and regulatory engineering, chemistry, and chemical processes. Team members also provided viewpoints from other DOE Complex facilities with large radioactive waste disposal programs, international radioactive waste disposal programs, and industry. Resources dedicated to and managed by the Team included the WSRC engineering personell and an administrative support staff. R&D support and management came from the Savannah River Technology Center (SRTC). Additional R&D support came from the DOE national laboratories – including Oak Ridge and Argonne National Laboratories – and several universities

The system engineering studies evaluated over 140 alternatives processes and reduced the list of alternatives to four candidates: CST, CSSX, STTP, and direct grouting (with no Cs removal). Further review eliminated direct grouting as an option and RD efforts have focused on the CST, CSSX and STTP.

On April 13, 1998, the DOE-HQ chartered an additional group, the Independent Panel for Evaluation, to assess the progress and direction of the systems engineering effort. The Systems Engineering Team integrated feedback from the Independent Panel for Evaluation into the definition of research activities.

In 1999, DOE-HQ asked the National Academy of Sciences (NAS) to independently review the evaluation of technologies to replace ITP. NAS issued a letter report in October 1999 and their final report is planned to be completed in June 2000. As a result of the interim NAS review, the DOE Under Secretary and the Assistant Secretary for EM jointly agreed that further research and development on each alternative was required to reduce technical uncertainty prior to a down-select. Accordingly, DOE postponed plans to issue a draft Request for Proposal to the private sector seeking input on design and construction of the needed treatment facilities. DOE-SR also held back the issuance of the Draft Supplemental Environmental Impact Statement (SEIS) on SRS HLW treatment alternatives pending further development of salt processing technology alternatives.

In March, 2000, DOE-HQ requested the TFA to assume management responsibility for the SPP technology development program at SRS. The TFA was requested to conduct several activities including review and revision of the SPP technology development roadmaps, development of down-selection criteria, and preparation of a comprehensive R&D Program Plan for the three candidate Cs removal technologies, as well as the alpha and Sr removal processes that are a part of the overall SPP.

### **3.0 High-Level Waste System Overview**

Any new salt processing system will be required to interface with existing facilities. The ease or difficulty of successful implementation of an alternative technology is governed by how well it will integrate into the existing HLW System.

The SRS HLW System is a set of seven different interconnected processes operated by the HLW and Solid Waste Divisions. These processes function as one large treatment plant that receives, stores, and treats HLW at SRS and converts these wastes into forms suitable for final disposal.

These processes currently include:

- HLW Storage and Evaporation (F and H Area Tank Farms)
- Salt Processing (ITP and Late Wash Facilities)
- Sludge Processing (Extended Sludge Processing [ESP] Facility)
- Vitrification (DWPF)
- Wastewater Treatment (Effluent Treatment Facility[ETF])
- Solidification (Saltstone Facility)
- Organic Destruction (Consolidated Incineration Facility [CIF])

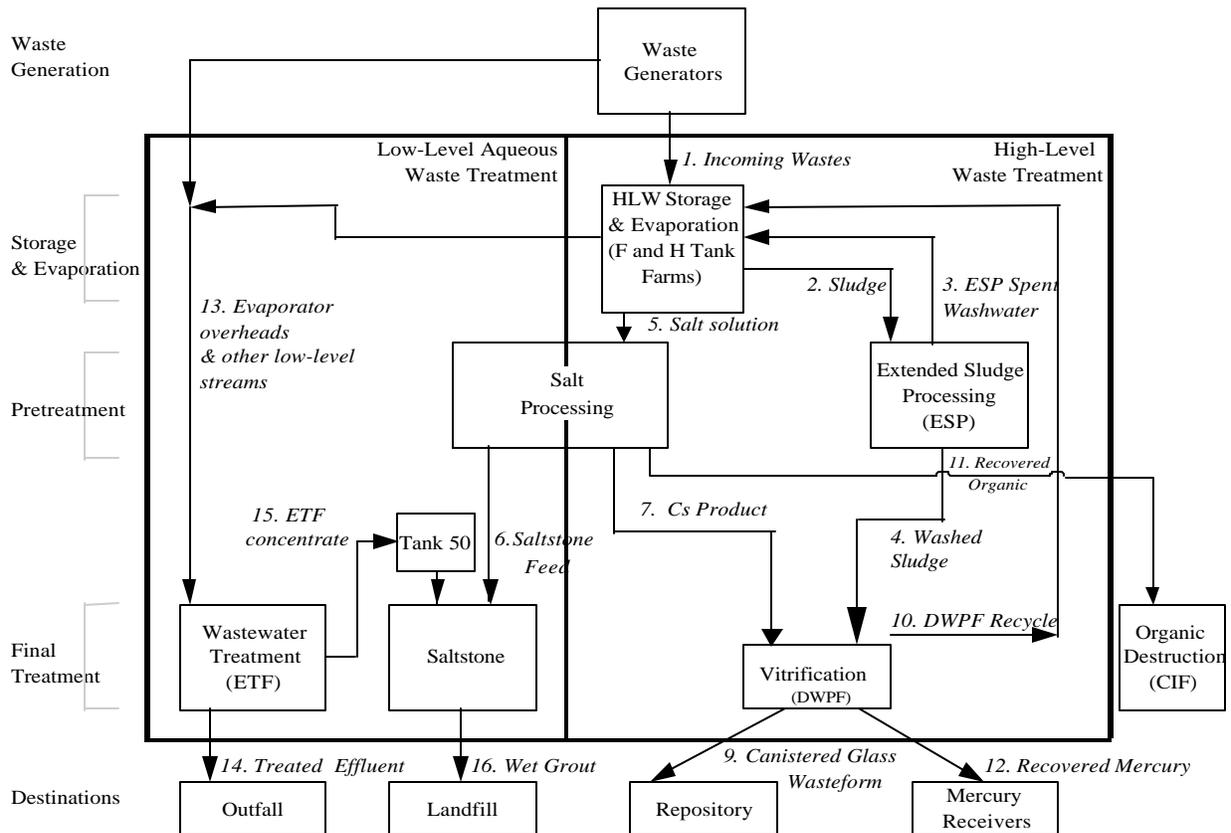
The F and H Area Tank Farms, ESP Facility, DWPF, ETF, Saltstone Facility, and CIF are all operational. ITP facility operations are limited to safe storage and transfer of materials. The Late Wash Facility has been tested and is in a dry lay-up status.

The mission of the SRS HLW System is to receive and store HLW in a safe and environmentally sound manner and to convert these wastes into forms suitable for final disposal. The planned disposal forms are:

- borosilicate glass to be sent to a federal repository
- saltstone to be disposed on site
- treated wastewater to be released to the environment.

Also, the storage tanks and facilities used to process the HLW must be left in a state such that they can be decommissioned and closed in a cost-effective manner and in accordance with appropriate regulations and regulatory agreements.

**Figure 3.1 High-Level Waste Major Interfaces**



All HLW in storage at SRS is regulated as Land Disposal Restriction waste, which prohibits it from permanent storage. Because the planned processing of this waste will require considerable time and therefore continued storage of the waste, DOE has entered into a compliance agreement with the Environmental Protection Agency (EPA) and South Carolina Department of Health and Environmental Control (SCDHEC). This compliance agreement is implemented through the STP, which requires processing of all the HLW at SRS according to a schedule negotiated between the parties.

Figure 3.1 schematically illustrates the routine flow of wastes through the SRS HLW System. The various internal and external processes are shown in rectangles. The numbered streams identified in italics are the interface streams between the various processes. The discussion below describes the SRS HLW System configuration as it will exist in the future with the proposed Salt Processing Facility.

Incoming HLW is received into HLW Storage and Evaporation facilities (F and H Area Tank Farms) (Stream 1). The function of HLW Storage and Evaporation is to safely concentrate and store these wastes until downstream processes are available for further processing. The decontaminated liquid from the evaporators are sent to ETF (Stream 13).

The insoluble sludges that settle to the bottom of waste receipt tanks in HLW Storage and Evaporation are slurried and sent to ESP (Stream 2). In ESP, sludges high in aluminum (Al) are processed to remove some of the insoluble Al compounds. All sludges, including those processed to remove Al, are washed with water to reduce their soluble salt content. The spent washwater from this process is sent back to HLW Storage and Evaporation (Stream 3). The washed sludge is sent to DWPF for feed pretreatment and vitrification (Stream 4).

Saltcake is redissolved using hydraulic slurring techniques similar to sludge slurring. As originally designed, the salt solutions from this operation, and other salt solutions from HLW Storage and Evaporation, were intended for feed to ITP (Stream 5). In the proposed Salt Processing Facility, the salt solution will be processed to remove radionuclides (i.e., actinides, Sr, and Cs). These concentrated radionuclides will be prepared for transfer to DWPF. Depending on the process chosen, the Cs stream (Stream 7) will be either loaded CST sorbent, dilute nitric acid from CSSX, or a precipitate hydrolysis aqueous (PHA) stream from STTP. The actinide and Sr sorbent (e.g., monoNa titanate [MST]) will be transferred to DWPF either as a separate stream or combined with the Cs stream, depending upon the process.

For the STTP process, 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 organics are stored and eventually transferred to CIF (Stream 11). The aqueous stream is transferred to DWPF where it is combined with the washed sludge from ESP - which has undergone further processing - and the 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 (Hg) is removed, purified, and sent to Hg receivers (Stream 12). The aqueous Cs product from the Salt Processing Facility 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 stainless-steel canister. The canistered glass waste form is sent to on-site interim storage, and will eventually be disposed in a federal repository (Stream 9).

The water vapor driven off the melter is condensed and combined with other aqueous streams generated throughout the DWPF. The combined aqueous stream 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 LLW is sent to the ETF (Stream 13).

In the ETF, LLW is 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), for storage prior to transfer to the Saltstone Facility (Stream 6). In the Saltstone Facility, the liquid waste is combined with cement formers and pumped as a wet grout to a vault (Stream 16). In the vault, the cement formers hydrate and cure, forming a saltstone monolith. The Saltstone Facility vaults will eventually be closed as a landfill.

## **4.0 Functional Requirements for the Salt Processing Process**

As described in Section 3.0 above and in the Final Supplemental Environmental Impact Statement (SEIS) (DOE/EIS-0082-S), the existing SRS HLW System consists of seven interconnected facilities operated for the DOE by the HLW and Solid Waste Divisions of the WSRC. These separate facilities function as one large waste treatment plant.

As an integral part of the mission, the SRS HLW System must immobilize the key radionuclides in the salt for final disposition in support of environmental protection, safety, and current and planned missions. In 1994, the SEIS projected Salt Processing using ITP and Late Wash facilities to yield a precipitate slurry containing  $^{137}\text{Cs}$  suitable for transfer to and processing in the DWPF. Plans also called for the ITP process to produce a decontaminated salt solution (DSS) for conversion to saltstone, a solid LLW, for disposal at the SRS.

Although any alternative process to ITP would be specifically developed to enable HLW salt disposition, the impact on all HLW facilities and processes at SRS must also be addressed. Functionally, the selected alternative must interface safely and efficiently with the processing facilities within and outside of the HLW System. The timing for selection of an alternative needs to support tank farm space and water inventory management, the STP, and the FFA for tank closure. Table 4.1 summarizes key functional requirements and the schedule to recover HLW storage space and meet the FFA/STP that any alternative must fulfill.

**Table 4.1. Key Functional Criteria**

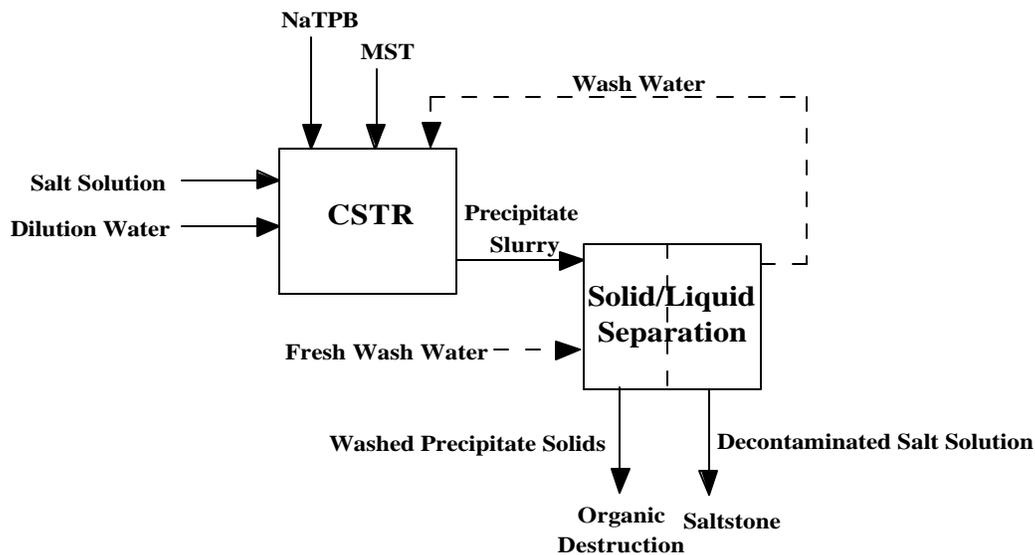
<b>FOCUS AREA</b>	<b>FUNCTIONS</b>
Safety Hazard Assessment (HAD)	Provide a facility that meets the requirements of a non-reactor nuclear hazard category 2 and low chemical hazard category.
Interface Streams DWPF Recycle DWPF Glass Saltstone Tank 49H Tank 50H New Waste Form	<p>Support tank farm space management and DWPF recycle evaporator strategy.</p> <p>Provide a Cs-containing product that supports glass waste form requirements relative to durability, crystallization temperature, Na content, and viscosity.</p> <p>Provide a Decontaminated Salt Solution (DSS) product that meets Waste Acceptance Criteria relative to producing a non-hazardous saltstone waste form suitable for disposal as low-level solid waste at the SRS.</p> <p>Support Tank Farm space management strategy to recover Tank 49H for HLW storage.</p> <p>Support Tank Farm space management strategy to recover Tank 50H for HLW storage.</p> <p>Comply with DOE-RW HLW repository requirements.</p>
Nominal DF Sr DF TRU DF Cs DF	<p>Provide a Sr DSS concentration of <math>\leq 40</math> nCi/g, which equals a nominal DF = 5 (overall average).</p> <p>Provide a TRU DSS concentration of <math>\leq 18</math> nCi/g, which equals a nominal DF = 12 (overall average).</p> <p>Provide a Cs DSS concentration that enables conversion to a solid low-level waste form suitable for near-surface disposal at the SRS.</p> <ul style="list-style-type: none"> <li>• for processes that remove Cs, Cs-137 <math>\leq 45</math> nCi/g is required to enable processing and disposal in the existing saltstone production and disposal facilities, which equals a nominal DF = 8000 (overall average).</li> <li>• For processes that do not remove Cs, Cs-137 must be within NRC Class C limits.</li> </ul>
Schedule HLW Storage FFA STP	<p>Support Tank Farm space management strategy to support site missions (timely startup of new process by 2010).</p> <p>Support readiness for closure of all waste tanks by 2028.</p> <p>Support readiness for closure of old style tanks by 2020, and an average glass canister production rate of 200 canisters/yr.</p>

## 5.0 Description Of Radionuclide Cs Removal Processes

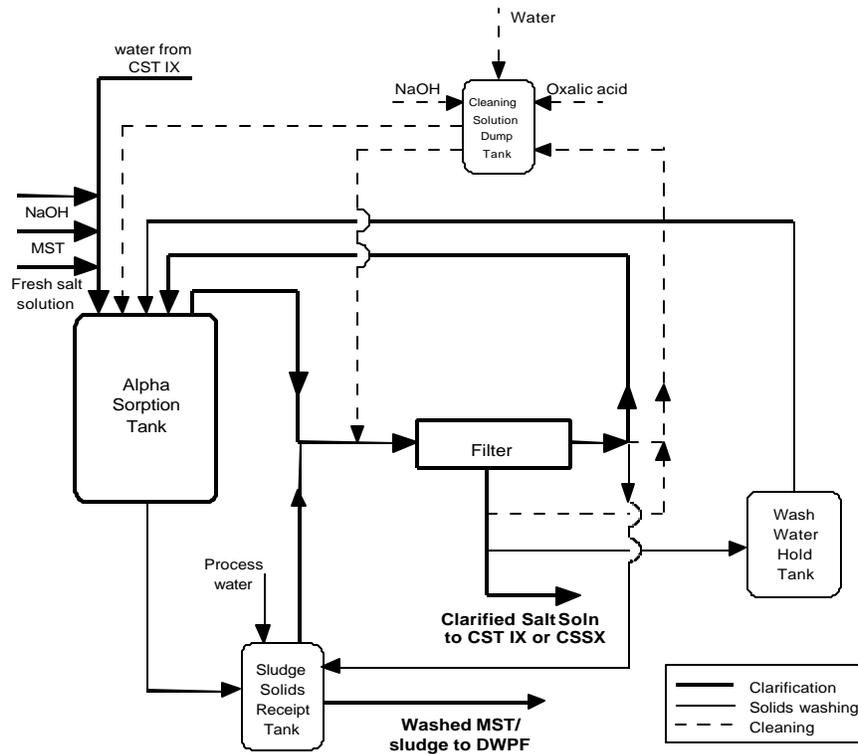
### 5.1 Alpha and Sr Removal

For STTP, alpha (i.e., selected actinides) and Sr removal occurs simultaneously with precipitation of Cs (see Figure 5.1). In contrast, the CST Non-Elutable Ion Exchange alternative – using the sorbent IONSIV™ IE-911 – and the CSSX alternative both require removal of these actinide and transuranic (TRU) radionuclides in advance of removing Cs from the solution (see Figure 5.2). In addition to the process complexity added through extra equipment, the latter two options also require an additional solid-liquid separation. Previous studies showed a low filtration flux during solid-liquid separation step.<sup>1,2,3</sup> Because of the lower fluxes, the CST and CSSX processes require larger filtration equipment, process vessels and storage vessels to maintain the desired waste processing rate.

**Figure 5.1 Actinide and Sr Removal Flow Diagram for Small Tank Tetraphenylborate Precipitation**



**Figure 5.2. Actinide and Sr Removal Flow Diagram for CST Non-Elutable Ion Exchange and Caustic Side Solvent Extraction**

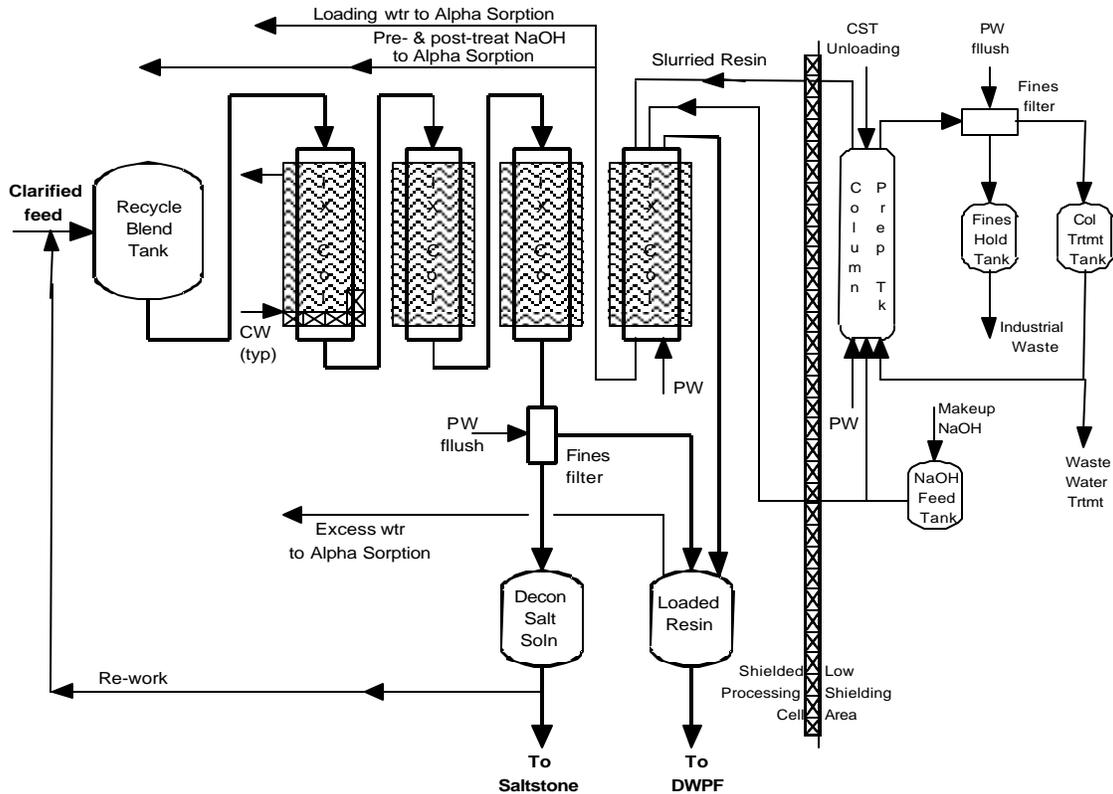


## 5.2 CST Non-Elutable Ion Exchange

In the proposed CST Non-Elutable Ion Exchange process (see Figure 5.3), salt solution (6.44 M sodium [Na]) is combined with dilution caustic and spent solutions from filter cleaning and other aqueous streams generated from resin loading and unloading operations in the Alpha Sorption Tank (AST) within the shielded facility. Soluble alpha contaminants and  $^{90}\text{Sr}$  are sorbed on monosodium titanate (MST) solids that are added as a slurry to the salt solution in the AST. The solution is diluted to  $\sim 5.6$  M Na in the AST in the combined waste stream that is fed to filtration.

After sampling to confirm the soluble alpha and Sr concentration is reduced to an acceptably low level, the resulting slurry is filtered to remove MST and entrained sludge solids that may have accompanied the salt solution to the AST. Clarified filtrate is transferred to the Recycle Blend Tank, which serves as the feed tank for ion exchange column operation. Combining these streams yield  $\sim 5.6$  M Na solution. The combined stream is stored until it can be processed through the ion exchange column train loaded with CST.

Figure 5.3. Combined Stirred Tank Non-Elutable Ion Exchange Flow Diagram



The ion exchange train consists of three operating columns in series, identified as lead, middle and guard columns, where the Cs is sorbed onto the CST. A fourth standby column is provided to allow continued operation while Cs-loaded CST is removed and fresh CST is added to the previous lead column. The effluent from the guard column is passed through a fines filter to prevent Cs-loaded fines from contaminating the salt solution. The filtered salt solution flows to one of two Product Holdup Tanks and the activity is measured to ensure it meets the saltstone limit for Cs. These two tanks are sized to allow sufficient hold time for secular equilibrium to be re-established between residual Cs and its decay daughter, barium, before the salt solution is analyzed to determine if it has been adequately decontaminated. After analysis confirms adequate decontamination, the DSS is transferred to one of two DSS Hold Tanks and stored until it can be transferred to Z Area for processing and disposal as saltstone.

When the lead column in the train is close to saturation (expected to be >90% Cs loading), that column is removed from service, the middle column becomes the lead column, the guard column becomes the middle column, and the fresh, standby column becomes the guard column. The Cs-loaded CST from the first column is then sluiced

with water into one of two Loaded Resin Hold Tanks where it is combined with the fines from the fines filter. Excess sluicing water is removed to produce a 10 wt% CST slurry in water. The excess water is sent to the alpha sorption tank. The CST slurry is stored in the Loaded Resin Hold Tank until it can be transferred to the DWPF for incorporation into HLW waste glass.

Before being loaded into a column, the CST resin must undergo two treatments. First, the CST is loaded into the Column Preparation Tank, similar in dimensions to an ion exchange column bed. The CST is then backflushed with water to remove 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 in the hydrogen form. The resin is converted to the Na form by circulating a sodium hydroxide (NaOH) solution through the Column Preparation Tank for 24 hours. The material is then loaded into an empty standby column by sluicing with water.

After loading the column, sufficient water must be retained in the column to cover the resin bed and exclude air which might cause channeling in the bed. Prior to placing the loaded standby column in service, the water must be displaced by a 2 M NaOH solution. If this is not done, Al may precipitate from the initial salt solution feed as the pH is reduced by mixing with the residual water. A similar NaOH flush is required after the bed is removed from service and before the CST loaded with Cs is sluiced from the bed with water. As noted above, these flushes are sent to the Alpha Sorption Tank and combined with clarified salt solution.

### 5.3 Caustic Side Solvent Extraction

The basic principle of solvent extraction is to use a sparingly soluble diluent material that carries an extractant that will complex with the Cs ions in the caustic solution. The decontaminated aqueous stream (raffinate) is then sent to Saltstone for disposal. The Cs contained in the organic phase (solvent) is then stripped into an aqueous phase ready for transfer to DWPF. The solvent is recycled.

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

The CSSX process utilizes a novel solvent made up of four components: calix[4]arene-bis-(*tert*-octylbenzo-crown-6) known as BOBCalixC6, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-secbutylphenoxy)-2-propanol, known as modifier Cs7SB, trioctylamine known as TOA, and Isopar<sup>®</sup> L, 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 Cs 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 Cs to the aqueous

phase. The aqueous strip effluent is transferred to the DWPF. Figure 5.4 contains a schematic representation of the proposed solvent extraction flowsheet.

In the extraction stages, Cs and nitrate are extracted into the solvent phase. The Cs is stabilized in the solvent phase by the calixarene molecule while the nitrate ion is stabilized by the modifier molecules. Due to the complimentary geometry and electronic environment in the cavity of the calixarene molecules, Cs is removed in dramatic preference to other cations, in particular Na and potassium. This selectivity is more than two orders of magnitude versus potassium and more than four order of magnitude versus Na. This high selectivity is required to achieve the desired separation of the Cs ions from the bulk Na ions, resulting in a concentrated stream of Cs nitrate for vitrification.

In the proposed process, the Cs concentration in the organic phase is 3.5 times that in the aqueous feed solution. For a typical HLW feed solution containing 0.14 millimolar (mM) Cs, the concentration in the organic stream leaving the extraction stages is approximately 0.5 mM. Note that this is significantly below the 10 mM concentration of calixarene in the solvent. Thus, a large excess of available calixarene sites are available for extraction. However, due to the high concentrations of Na and K in the feed stream, a measurable quantity of both Na and K are extracted, and thus take up a small portion of the sites. In addition, some Na and K ions are extracted directly by the modifier.

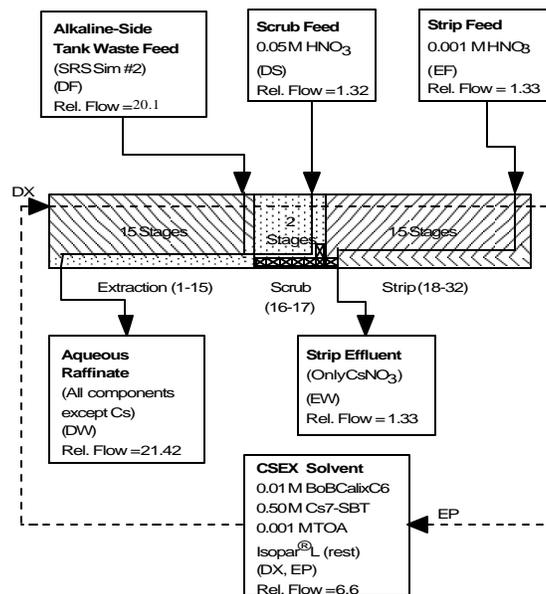
To provide an essentially pure Cs nitrate product stream, the K and Na are scrubbed out of the organic phase using two scrubbing stages between the extraction and strip stages. In addition to removing Na and K from the organic phase, the scrub stages also work to remove Al, Fe and Hg. The scrub stages 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 has the potential to produce greatly reduced stripping performance. Such impurities could possibly come from the waste or from solvent radiolysis. To remedy the potential 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 Cs in the solvent to be stripped by supplying the impurity in the solvent with equivalent cationic charges<sup>4</sup>.

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 in contact with acid solutions. However, the modifier was designed so that the phenolic compounds would distribute preferentially to alkaline aqueous solutions, either the waste itself or NaOH wash solutions. Gradual degradation of the solvent will result in some loss of performance, owing both to loss of the calixarene, modifier, and amine and to buildup of various degradation products. The proposed flowsheet contains two additional unit operations intended to maintain solvent performance.

The two proposed unit operations involve first an acidic wash of the solvent followed by a caustic wash of the solvent. These two wash stages are intended to take out 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 and diluent degradation products. In addition, the proposed flowsheet has also assumed that, to maintain system performance, the solvent will be replaced on an annual basis.

**Figure 5.4 Caustic Side Solvent Extraction Flow Diagram**



After extraction, the aqueous phase will contain either soluble or entrained organics. This may represent an economic problem due to loss of the expensive solvent or a problem in downstream operations. 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 Isopar® 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 Isopar® L) is allowed to float and is decanted. From the settling tank, the raffinate is transferred to one of two hold tanks to allow decay of the short half-life gamma from Ba-133m in the raffinate stream. These two tanks are sized to allow sufficient hold time for sufficient gamma decay to facilitate determination whether the target decontamination has been met to allow transfer of the raffinate material to Saltstone. The wash solutions from the organic clean up process are also transferred to the 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 Isopar® L is introduced into the stages and used to extract any of the solvent from the aqueous phase. The aqueous phase leaves the cleanup stage and is transferred to a settling tank where the Isopar® L is allowed to float and is decanted. The Isopar L® added in the two solvent recovery processes is sent to the CIF.

Note that the feed stream is fed to the process from a 100,000 gallon 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-day capacity). The use of a large tank provides for some decoupling of the solvent extraction process and the DWPF. The solvent extraction process can only operate as long as DWPF is operating or storage volume remains in the tanks between the solvent extraction process and DWPF. Cold chemical feed tanks have generally been designed to provide one day 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 (<1 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 <0.01 M Na, and <0.001 M of other metals.

#### **5.4 Small Tank Tetraphenylborate Precipitation**

In the STTP process, salt solution is received into a Fresh Waste Day Tank located in the new facility. For this continuous precipitation process, salt solution, Na TPB solution, MST slurry, spent wash water and dilution water are continuously added to two Continuous Stirred Tank Reactors (CSTR) located in the new facility. Sufficient dilution water is added to the first CSTR to reduce the Na molarity to ~4.7 M to optimize

conditions for precipitation and MST sorption reactions... The first CSTR feeds a second CSTR in which precipitation is completed. In the CSTRs, soluble Cs and K are precipitated as TPB salts and Sr, U, Pu, Am, Np and Cm are sorbed on the MST solids. The resulting slurry, containing ~1 wt% insoluble solids, is transferred from the second CSTR to the Concentrate Tank from which the slurry is continuously fed to a cross-flow filter to concentrate the solids, which contain most of the radioactive contaminants. DSS filtrate is transferred to a Filtrate Hold Tank from the filter unit and stored until it can be transferred to the existing Saltstone, where it is converted to saltstone for disposal.

After concentrating the slurry to 10 weight percent, and accumulating 4,000 to 5,000 gallons in the Concentrate Tank, the slurry is transferred to the Wash Tank and washed to remove soluble Na salts by adding process water and removing spent wash water by filtration. Na TPB removed in the wash water can be recovered by recycling the spent wash water to the first CSTR. Spent wash water is either recycled to the first CSTR to provide a portion of the needed dilution water or sent to the Filtrate Hold Tank and on to Saltstone for conversion to saltstone for disposal. At the end of the washing operation, 10 wt% slurry is transferred to the Precipitate Storage Tank for staging. The slurry is then processed through the acid hydrolysis unit operation and eventually vitrified. Recovered by-product benzene from acid hydrolysis is transferred to the CIF and incinerated. The aqueous product from acid hydrolysis is combined with sludge feed to the DWPF and incorporated into HLW waste glass.

In the initial proposal for the Small Tank TPB alternative, washed 10 wt% slurry was to be processed using the existing acid hydrolysis process equipment installed in the DWPF Salt Cell. However, a tank farm salt/space management strategy recommends using the DWPF Salt Cell for housing an acid evaporator. This development, coupled with the limiting design capacity of the existing acid hydrolysis processing equipment, led to the acid hydrolysis process being moved to the new SPP facility. The equipment will be sized such that the production rate will match the desired waste removal rate. Moving the acid hydrolysis operation to the new facility offers the advantage of confining the operations involving benzene generation and handling to a single facility, but the footprint of the proposed facility will increase for this alternative.



## 6.0 Technology Development Needs

A large number of technical issues and concerns have been identified in previous phases of the Alternative SPP. Evaluation of these issues and concerns has led to a small number that are believed to represent high technical risks to implementation of the four processes described in this R&D Program Plan. These high risk areas and the technology needs they represent must be resolved satisfactorily prior to Cs removal technology downselection. The key technology needs for each process are summarized below.

### 6.1 Alpha and Sr Removal

The program proposes the addition of MST to remove portions of the soluble U, Pu, Np, and Sr contained in the waste stream. Design efforts require an understanding of the rate and equilibrium loading of these components as a function of temperature, ionic strength and mixing to support both the CSTR and the batch reactor designs. Initial data from batch reactor studies indicates that the MST reaction kinetics require more than the 24 hours assumed the design basis, resulting in larger batch volumes. Also, low filter flux demonstrated in testing indicated the need for large surface area filters and large volume circulation pumps. The program, therefore, requires additional information on the kinetics for radionuclide removal under proposed process conditions.

The original SRS implementation scheme using MST allowed sufficient time to remove the radionuclides. In contrast, the current process options shorten the contact time for the sorbent to 24 hours before filtration occurs. Sr removal occurs rapidly under alkaline conditions with no apparent influence from the presence of competing sorbates such as actinides. Of the actinides, Pu removal proves most important to satisfying the requirements for total alpha activity in the DSS. In general, MST exhibits slower removal rates for Pu and other actinides than observed for Sr. Testing indicates that the actinides compete for sites on the MST. U and Np both exhibit much higher solubility in alkaline solutions than Pu. Consequently, the extent and rate of Pu removal depends strongly on the total actinide concentration. Hence, while the current pre-conceptual designs achieve the requirements for radionuclides, the use of MST does limit the process cycle times and equipment size.

The original process design achieved the solid-liquid separation for the MST concurrently with concentration of the organic precipitate. The precipitate apparently mitigated the tendency of the MST particles to closely pack. Thus, the use of cross-flow filtration for the composite slurry showed good process rates and posed minimal process maintenance issues. In contrast, two of the currently suggested process designs require solid-liquid separation of a stream containing the MST combined with entrained metal OH (i.e., sludge) solids. The cross-flow filtration proves notably slower for these designs.

While MST adequately meets the functional requirements for each process design, the use of alternate sorbents or technologies to remove the radionuclides of interest (i.e., Sr, Pu, and Np) may significantly improve some of the designs. Therefore, a portion of this research effort evaluates the use of alternate chemical means to remove these radionuclides. Similarly, the

program will also investigate means to improve cross-flow filtration performance by using chemical additives as well as alternate solid-liquid separation technologies with MST or the alternate chemicals defined to remove radionuclides.

Finally, the conceptual designs include the use of at-line (or on-line) analytical equipment to verify the removal of the radionuclides. The original process performed this analysis on samples decontaminated from Cs, Sr, and the actinides. In contrast, two of the proposed designs require verifying the removal of Sr and the actinides with radioCs still present in the solution. All three process designs rely on faster analytical response time than the original design. Thus, the program requires development of appropriate analytical monitors to meet these objectives.

In summary, the high priority technology needs that require investigation to support alpha and Sr removal include:

- Alpha and Sr removal performance with MST and alternate sorbents
- Equipment scale
- Solid-liquid separation performance

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

In the CST Non-Elutable Ion Exchange process, MST sorbs alpha contaminants and Sr-90 from the salt solution. The MST resulting slurry is then filtered and the filtrate solution is combined with other aqueous streams for processing through an ion exchange column loaded with CST to remove Cs. The most significant issue with CST is the stability of the CST in highly alkaline solutions. Leaching of excess materials used in manufacturing the resin and column pluggage events have been observed in previous testing. This has led to a desire to re-engineer the resin manufacturing process. Also, loaded CST must be transferred as a slurry to DWPF and the sludge, CST, and glass frit mixture must be homogeneously mixed and accurately sampled prior to feeding the melter. Both of these operations have proven difficult in initial tests. Thus, the two high-risk areas for implementation of the CST process are:

- Resin stability
- Resin handling and sampling.

The ability of CST to remove Cs from aqueous solutions as a function of temperature and waste composition needs to be investigated. K, Sr, nitrate, and OH are known to impact the equilibrium loading of Cs on CST. Mass transfer coefficients and diffusivity as a function of column geometry and velocity are needed to provide sufficient information to size ion exchange columns properly. To avoid potential criticality issues, the ability of CST to sorb Sr, Pu, and U must also be defined. Finally, the thermal characteristics of CST performance including thermal stability of this resin and its potential to desorb Cs in response to thermal fluctuations (in both normal operations ranges and abnormal swings), must also be defined.

### 6.3 Caustic Side Solvent Extraction

Technology needs for CSSX are derived primarily from the immaturity of the solvent extraction process. The CSSX process uses a multi-component solvent that is complex, and poses risks from a chemical stability standpoint that, unmitigated, could destabilize the process and/or impact operations personnel. The performance of CSSX may also be affected by the impacts on the solvent by radionuclides in the treatment stream. Extraction kinetics for solvent mixtures have been studied previously and the reaction kinetics have been found to be more than adequate for application to salt processing. However, bench-scale extraction studies must be run to determine if the dual performance goals (DF of 40,000 and CF of 12) can be simultaneously achieved, particularly with real waste. Thus, technology needs are driven by four primary areas of technical uncertainty:

- Chemical stability
- Radiolytic stability
- Solvent system proof-of-concept
- Real waste performance

Technology development needs also derive from the effect of extractable minor components in the waste feed that could build up in the solvent. These could cause hindered extraction or stripping, third phase formation, slow coalescence, or cruds. Although the sparse initial data suggest that most minor components are innocuous, strongly lipophilic anions, such as those present in detergents, could be a problem if allowed to build up past the tolerance of the TOA. Commercial availability of the reagents must be demonstrated. This will require that issues with synthesis improvements and patent applications be resolved. In addition, the expense of the extractant BOBCalixC6 makes further improvements in synthesis a worthwhile investment.

### 6.4 Small Tank TPB Precipitation

The STTP is a continuous precipitation process that mixes salt solution, Na TPB, a slurry of MST, spent wash water, and dilution water in a CSTR. Under optimum conditions obtained in the CSTR, soluble Cs and K precipitate as TPB salts, and MST sorbs Sr, U, Pu and Cm. The salts and MST solids are readily filtered to achieve the desired DF, but the process has inherent risks due to the catalytic decomposition of TPB (to form benzene) and foaming of the slurry. Foaming can interfere or block flow in the process, while benzene generation poses both exposure and instability (fire) risks to personnel and the potential environmental releases. Therefore, the key technology needs are:

- Catalytic product decomposition
- Foaming

Initial data from batch reactor experiments indicates that MST kinetics will control the size of the reactor. The rate and equilibrium (solubility) of MTPB as a function of temperature, ionic strength, and mixing is required to support reactor design. Researchers must provide physical property data such as density viscosity, yield stress, and consistency of slurry, as a function of

state variables, such as temperature, to support design. Additional studies on TPB decomposition under expected process conditions are required.

## **6.5 Other Technology Development Needs**

Other specific technology development needs have been identified based on technical issues and concerns that were identified in earlier phases of the program. These needs are listed in Appendix B. The technology development activities described in Section 7.0 focus primarily on resolving the high priority issues described above.

## 7.0 R&D Program Description

### 7.1 Alpha And Sr Removal

For the STTP, alpha and Sr removal occurs simultaneously with precipitation of Cs. In contrast, both CST Non-Elutable Ion Exchange using IONSIV™ IE-911 and the CSSX process require removal of these actinides and TRU radionuclides in advance of removing Cs from the solution. In addition to the process complexity added through extra equipment, the latter two options requires an additional solid-liquid separation step. Previous studies showed low filtration flux in the absence of the organic TPB precipitate. The lower fluxes necessitate the use of larger filtration equipment process vessels, and storage vessels for waste to maintain the desired waste processing rate.

#### 7.1.1 R&D Roadmap Summary – Alpha and Sr Removal

To achieve critical project decision milestones, the program must complete several important science and technology activities. Failure to meet the technology milestones in the integrated project schedule will delay startup of the salt removal process. This delay will result in inadequate tank storage space availability, jeopardizing DWPF operations and other SRS missions while significantly impacting the ability for SRS to support potential new missions.

This science and technology roadmap for alpha and removal (Figure 7.1), a subset of the overall SPP roadmap, defines needs in the following two basic categories:

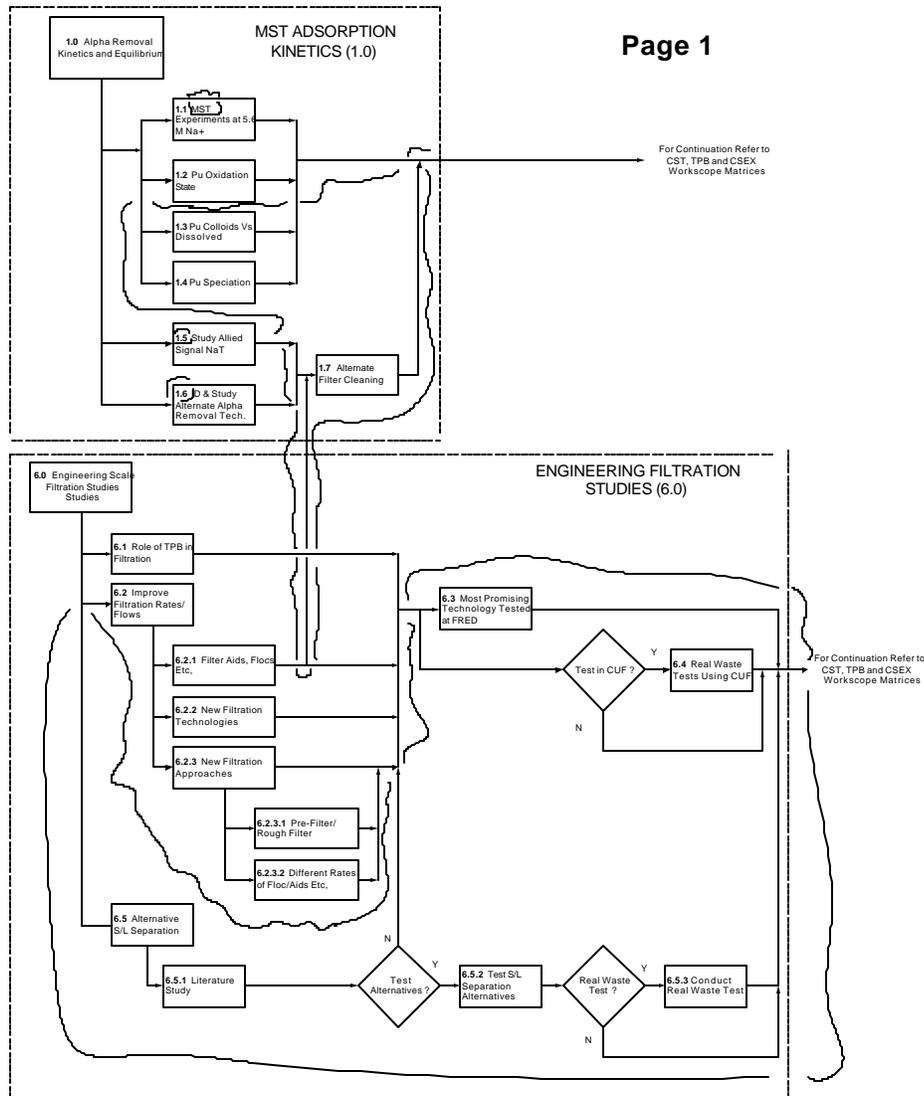
- MST adsorption kinetics, and
- Engineering filtration studies.

Process chemistry needs related to alpha and Sr removal includes collection of data on the thermal and hydraulic transport properties, reaction kinetics and mass transfer properties necessary to finalize the conceptual design. These data establish the physical and engineering property basis for the project and detailed design. Examples of key decisions resulting from these activities include selecting tank mixing technology, filtration technology, and reactor design, and finalizing the process flowsheet.

The program will develop physical property and process engineering data from engineering-scale, or pilot-scale tests during conceptual design. Performance data will come from unit operations testing using pilot-scale equipment to support preliminary design. These data will help to resolve issues related to equipment sizing, specific equipment attributes, material of construction and operational parameters such as pressure drop and requirements for temperature control. A key deliverable for this phase involves demonstrating that the individual components will function as intended in support of establishing the design input for the final design stage of the project.

Figure 7.1 depicts the technology roadmap for the Sr and actinide removal portions of the program. The diagram shows each work element defined for the current and future work scope.

**Figure 7.1. Science and Technology Roadmap for Alpha and Sr Removal Cs Removal Process (\*clouded areas indicate recommended changes to roadmap)**



Integrated pilot-scale operations will be completed during final design to confirm operation under upset conditions. This will establish the limits of operation and recovery, define the limits of feed composition variability, and confirm design assumptions. This testing also directly supports development of operating procedures, simulator development, and operator training.

Appendix A contains detailed logic diagrams that illustrate the various R&D activities, their interactions, and decision points. Note that "clouded" areas are currently under consideration as R&D scope as part of the TFA Roadmap Assessment effort.

## **7.1.2 Monosodium Titanate (MST) Kinetics and Equilibrium**

### **7.1.2.1 Previous Results**

Based on previous SRTC work, MST serves as an adequate removal agent for Sr, U and Pu under equilibrium conditions. However, those studies did not evaluate the kinetics of the reactions.<sup>5,6</sup> Hence, researchers completed a statistically designed set of experiments as a function of a number of parameters to determine the extent and kinetics of actinide and Sr removal.

The results from Hobbs et al.<sup>7</sup> indicate the more important parameters affecting the kinetics of sorption include initial sorbate concentration, MST concentration, ionic strength and temperature. This work examined the statistical concentration bounds expected for these actinides, rather than trying to match the expected ratios of actual tank waste. Testing results indicated that at the target Na molarity for operation of the STTP process (4.5 M Na), addition of 0.2 g/L of MST adequately reduced the <sup>90</sup>Sr, total alpha activity, and <sup>237</sup>Np. However, the removal rates from more concentrated wastes – such as proposed for the ion exchange and solvent extraction technologies – proved too slow to achieve the desired decontamination within the 24 hours allotted for the proposed design bases.

Hobbs et al.<sup>8</sup> next examined the extent and rate of Sr, Np and U removal from 4.5 M Na and 7.5 M Na solutions at two levels of MST addition. In this second group of tests, the authors altered the waste compositions to more nearly reflect the expected process concentrations.

Results proved the addition of 0.4 g/L of MST sufficient to decontaminate the salt solution relative to Sr, Np and Pu. Note that the process does not require decontamination of the solution with respect to uranium because of its low specific activity. Rather, U competes for the sorption sites needed to remove Pu and Np for regulatory purposes. However, the addition of 0.2 g/L of MST proved insufficient to achieve the required Np decontamination. The kinetics of sorption in the 7.5 M Na solution proved too slow to support the needed processing rate, indicating the need to dilute the waste before treating with MST. Personnel used this information to set the size of the alpha sorption batch tanks for the ion exchange and solvent extraction processes.

These experimental studies notably advanced the understanding of process efficiency for MST in these applications. However, the DOE judged this work inadequate to demonstrate the required process for the mission objectives.<sup>9</sup>

#### **7.1.2.2 FY00 - Current Work**

The current phase of research will examine the MST sorption kinetics using 0.2 and 0.4 g MST/L in a 5.6 M Na waste.<sup>10</sup> Personnel will also complete physical characterization of MST particles (e.g., SEM, BET, and XRD) to provide baseline data for comparison with alternative actinide removal technologies. The data collected in this phase will primarily serve to provide an improved understanding of kinetics of sorption for the ion exchange and solvent extraction process designs. The added data will also address, in part, the uncertainty of whether the technology adequately addresses the process requirements.

The TFA review recommended that the program should also seek opportunities to characterize any actual waste samples that become available this FY for insight as to the actinide species present. In particular, studies should examine whether sequential filtration of the waste through finer ultra-filters yields lower reported concentrations of the actinides. Such a finding would suggest the presence of colloidal material that may prove resistant to removal by MST. Because routine protocol for most analyses of the waste samples do not include filtration prior to characterization, the existing database may typically reports total suspended radionuclides. (The most frequent sample analyses only seek to understand the concentration of the soluble species.) Thus, the total amount of soluble radionuclides requiring removal may prove significantly less than assumed in current design calculations.

#### **7.1.2.3 FY01 - Future Work**

Prior test results indicated a change in the Pu removal kinetics after about 10 hours upon contact with the MST. These results suggest that two or more Pu species may exist that react with the MST at different rates. Literature data indicate plutonium exhibits multiple oxidation states in alkaline aqueous solutions.<sup>11,12</sup> Existing studies do not provide definitive identification of Pu oxidation states in the range of solution compositions that will exist during salt solution processing. Identifying the Pu oxidation states and determining the extent and rate of removal of each oxidation state would decrease the uncertainty in predicting Pu removal behavior under varying waste compositions. Work during this fiscal year will include studies of the influence of Pu oxidation state on performance for MST and any alternate sorbent deemed appropriate at the time of work scope authorization. The program will also attempt to leverage funding with any related basic sciences programs – such as those funded through the Environmental Management Science Program – that seek insight into oxidation states of radionuclides in HLW.

An empirical mathematical formula developed from the above work showed limited ability to reliably predict performance even within the existing data set.<sup>7,8</sup> The lead investigators attribute this limitation to two factors. First, the previous experiments investigated removal of multiple radionuclides from a mixture. Incomplete fundamental isotherm studies for single sorbates leads to a lack of understanding of the basic chemistry involved for competing species. Second, the mathematical tools used in these studies derived from simplistic regression software as opposed to evaluating the existing data against multiple component theories. Future work will seek a more fundamental, first-principle interpretation of the behavior.

Current knowledge in this area resorts to empirical formulas to predict behavior due to a lack of fundamental understanding of the nature of chemical binding of radionuclides to the MST. The collective data suggests – but does not definitively show – that Sr sorption occurs through an ion exchange mechanism while the actinides attach via a sorption process. Work will proceed in measuring isotherms for single radionuclides and MST. Studies will examine the influence of solution composition – and particularly the dependence of sorption on the relative concentrations of OH, carbonate, nitrate, nitrite, and aluminate in the waste. Measurements will look for changes in MST structure and the form of sorbed species. This information will provide insight necessary for any efforts to develop improved sorbents.

Similarly, vendors have produced only a limited number of batches of the sorbent resulting in a sparse data set for actinide loading. Work will examine the batch-to-batch variation in actinide sorption by MST.

### **7.1.3 Alternative Alpha Removal Technologies**

#### **7.1.3.1 Previous Results**

To date, the HLW program has relied exclusively on process options that use MST to achieve the required removal of Sr and actinides. The program considered alternative sorbents to MST only in general reviews of available process options. Recently, the DOE judged such reliance upon MST as the sole technology as an unacceptable technical risk.<sup>9</sup> For example, use of alternate sorbents or technologies open the potential of alternate engineered designs, perhaps using existing equipment, to achieve the required decontamination.

#### **7.1.3.2 FY00 - Current Work**

Because of the inherent kinetic limitation of MST removal process, the program will examine the available literature for data related to a number of other actinide and Sr removal technologies. These technologies include ferric flocculation,<sup>13</sup> permanganate reduction,<sup>14</sup> and Na diuranate formation – which SRTC researchers are currently examining for another DOE programs.

On April 10-11, 2000, members of the TFA's Technical Advisory Group (TAG) reviewed the technology roadmap for the program. The participants recommended that studies of alternate technologies also consider in situ formation of magnetite as a means for decontaminating the waste. Similarly, the program will also evaluate the available information concerning the use of IONSIV™ IE-911 or calixarene to remove the radionuclides of interest.

The current scope of work includes initial experimental studies with Na nonatitanate (developed by Honeywell).<sup>10</sup> To support the program schedule, the vendor can provide only a limited number of samples for evaluation. Discussions with vendor representatives indicate that these samples will likely provide less than optimal performance but may provide insight into performance relative to MST for both radionuclide removal and solid-liquid separation. The vendor representatives recommend conducting initial screening tests to assess relative performance and suggest possible alterations in the synthesis of the Na nonatitanate to address the specific composition ranges of SRS wastes. Assuming comparable or only slightly poorer performance for the available samples, program management may elect to pursue additional work with synthesized samples from Honeywell that are formulated for SRS wastes.

#### **7.1.3.3 FY01 - Future Work**

The program will contract university participants to assist in the formulation of improved sorbents for actinide removal. The academic partners will examine variants of the MST formulation and synthesize other titanate compounds for evaluation. Also, the university partners will assist by providing structural analyses and measuring equilibrium isotherms for the sorbents.

One program option worth future consideration involves modifying the synthesis of the IONSIV™ IE-911 sorbent to include added chemical functionality to remove actinides as well as Cs and Sr. Discussion with the lead researcher for a current program funded within the Environmental Management Science Program suggest such an option merits investigation.<sup>15</sup> This approach resembles the approach implemented successfully for the HCW treatment purpose at the West Valley Demonstration Project in New York. In this project a titanate coating on zeolite added the needed functionality to remove actinides. An analogous approach exists for the solvent extraction system based on calixarene.<sup>16</sup> A similar approach would use vendor technology for manufacture of engineered sorbents to prepare a composite of MST for use in column applications. Program management will decide on future testing in this area following the review of available data and completion of FY00 tests with MST and Na nanotitanate.

#### **7.1.4 MST Filtration and Settling**

##### **7.1.4.1 Previous Results**

Each process option requires an operation that separates solids from the liquid. The precipitation process removes the Sr and actinide sorbent concurrently with the organic, Cs-bearing solids during filtration. Extensive information exists related to the use of cross-flow filter technology for the separation of TPB solids, with entrained MST and sludge. The testing information extends from small laboratory equipment to full-scale process equipment used during processing of nuclear waste at SRS. The recent publication of Peterson et al. indicates the depth of knowledge in this area, and includes fundamental discussions of transport phenomenon and filter cake formation.<sup>17</sup> The continuing program requires no additional studies related to solid-liquid separation for the precipitation process.

The extensive core competency and existing process facilities at SRS led in part to the decision to use cross-flow filtration to achieve the solid-liquid separation in the ion exchange and solvent extraction process options. Previous studies throughout the DOE complex also identified this technology as the best option for removing sludge from HLW.<sup>18</sup> Numerous studies demonstrated the efficacy of the technology to treat sludge wastes for several radioactive wastes at sites such as the Oak Ridge Reservation, Hanford Site, Idaho National Engineering Laboratory, and within Russia.<sup>19,20,21,22,23,24</sup> Hence, the program selected cross-flow filtration as the technology to achieve solid-liquid separation in all three process alternatives. Research concentrated on understanding the settling and suspension behavior of mixtures of the MST combined with simulated sludge. Studies examined gravity settling and suspension characteristics of the solids as well as cross-flow filtration of the slurry.

Tests by ORNL staff examined the rheology, settling, and resuspension characteristics of MST/sludge slurries in both laboratory and pilot-scale experiments.<sup>25</sup> The tests demonstrated the relative ease for resuspending settled slurry at pilot scale after settling for 14 days, although the data suggested that not all the MST suspended during these tests. In contrast, after 60 days settling time, personnel could not suspend all of the slurry even at an impeller tip-speed of 300 m/min. Storage of MST/sludge mixtures at 80°C for as little as three days dramatically increased yield stress and consistency. After 60 days of storage at 80°C, the yield stress increased by a

factor of 300 and the consistency by a factor of 30. These results indicate the need to cool the settled MST/sludge to assure subsequent suspension for further processing. As a result of these findings, the program altered the conceptual designs for the downstream tanks (i.e., pump pit tanks and processing tanks). The design added coils and high powered/high tip-speed agitators to ensure suspension of settled MST/sludge solids.

Personnel developed a Computational Fluid Dynamics model to simulate the suspension of sludge and MST tests run at ORNL. The test design facilitated the modeling by including a velocity meter positioned in the tank near the intersection of the side and bottom walls. In steady state, the model provides good agreement between the calculated velocity and that measured during the test. This finding gives confidence that the calculation adequately represents the physical phenomena in the tank. The calculated velocities in the tank appear rather low, raising substantial doubt that this design would provide adequate suspension in a large tank. Previous analyses of the large waste tanks in the HLW System demonstrated that even with 150 hp slurry pumps the in-tank velocities were too low to suspend an MST sludge.<sup>26</sup> This experimental evidence points to the impracticality of using an existing waste tank as the actinide removal facility with MST as the sorbent.

Previous work also investigated the influence of the relative concentration of MST to sludge as well as the use chemical additives on the filter flux observed for sludge slurries.<sup>27,28</sup> The tests with additives attempted to increase the low processing rate observed for cross-flow filtration in the absence of the tetraphenylborate solids by adding selected flocculating reagents or filter aids. The testing demonstrated only marginal success and, based on results to date, the ion exchange designs and solvent extraction processes each require a larger filtration surface area.

#### **7.1.4.2 FY00 - Current Work**

This current phase of research includes further experiments to examine the use of flocculating agents or filter aids to improve separation efficiency.<sup>29</sup> The studies will evaluate individual additives and blends based in part on past experiments. A series of bench-scale tests will test various aids with some optimization of concentration. Personnel will also perform a theoretical investigation of the role of tetraphenylborate as a filter aid to gain insight into possible candidates for experimental testing. Some experimental measurements may prove beneficial in this regard. Furthermore, the program will enlist an independent academic consultant to provide technical guidance and recommendations.

A separate activity will systematically examine applicability of other solid-liquid separation techniques for the ion-exchange and solvent extraction process designs. This study will identify promising technologies for future testing.

Testing will be performed at larger scale at the University of South Carolina to pursue enhanced cross-flow filtration performance for slurries containing MST and sludge. The work will examine the influence of axial velocity, transmembrane pressure, and solids concentration on filter performance.

Testing will also examine the filter performance for sludge slurries containing Honeywell's Na nonatitanate. Testing will first examine the separation on the bench scale using dead-end filtration to establish relative performance for these slurries and those slurries containing MST. If improved fluxes are obtained with the Na nonatitanate, the testing would then advance to using bench-scale cross-flow filters.

#### **7.1.4.3 FY01 - Future Work**

The current process designs require removal of MST and sludge solids to the same criteria used in the original ITP process. Since both the CST and CSSX processes perform the solid-liquid separation in an earlier step in the process, less stringent removal criterion may prove acceptable. Operation of centrifugal contactors may prove acceptable with a limited amount of solids present. Similarly, while ion exchange columns can plug or exhibit prohibitive pressure drops due to the presence of solids, some concentration of particles may not challenge operation. Testing in FY01 will attempt to define the concentration range of solids that prove problematic, thus establishing firm technical criteria for the solid-liquid clarification need.

To date, all sludge filtration studies used simulated wastes. A key element of the FY01 program will perform testing with actual waste using a cross-flow unit installed in the Shielded Cells at SRTC. This testing will reduce the perceived technical risk of implementing either the ion exchange or solvent extraction process options.

If the work with Honeywell's Na nonatitanate appears promising, the program may elect to contract with the vendor to provide sufficient sorbent for larger scale filtration tests. These tests would use either the SRTC filtration unit or the filtration unit available at the University of South Carolina. A similar approach would hold for any other alternate Sr and actinide removal sorbents selected for further evaluation in FY01. Filter aids or flocculating reagents that prove beneficial in bench-scale testing during FY00 will also receive consideration for testing at USC.

### **7.1.5 Feed Clarification Alternatives**

#### **7.1.5.1 Previous Results**

The DOE requested that the SRS HLW program perform a feasibility study to examine the use of current site facilities for implementation of the Sr and actinide removal process. WSRC performed a study to examine the economics associated with using the existing filters from the ITP or Late Washing Facilities for this option, as well as the use of in-tank processing for the MST sorbent.<sup>30</sup> The study deemed the existing infrastructure and slurry transport equipment inadequate to achieve the process objectives in any viable fashion. The DOE judged the study as unnecessarily limited in scope because it did not consider the use of alternate sorbents.<sup>9</sup>

#### **7.1.5.2 FY00 - Current Work**

The current work scope will investigate alternatives in the design concepts for the ion exchange and solvent extraction processes that may allow better utilization of filters. Such alternate facility layouts and production strategies may significantly reduce the volume of waste storage required to satisfy the processing rate for the Cs separation operation.

#### **7.1.5.3 FY01 - Future Work**

Pending encouraging results from the studies on alternate Sr and actinide sorbents or removal technology, the program will revisit the option to use existing equipment and infrastructure to perform this operation.

Program management will decide on the value of testing any promising solid-liquid separation technologies suggested by the studies and consultant during the FY00 work. This testing will enlist vendor laboratories where practicable. Options that may merit further consideration and testing include sequential use of settling, decanting, and dead-end filters to achieve the needed separation. Also, studies will evaluate the design option of performing the Sr and alpha removal in a column configuration.

## 7.1.6 On-Line Effluent Monitor

### 7.1.6.1 Previous Results

The various process options will use an at-line (or on-line) monitor to verify that radionuclide concentrations in treated streams satisfy regulatory requirements for final disposition of the decontaminated HLW.

Table 7.1 presents a predicted clarified salt solution composition based on feed solution and the estimated process effectiveness. For the ion exchange and solvent extraction process options, the clarified salt solution from Sr and actinide removal operation serves as feed to the Cs removal process. In contrast, the precipitation process generates the DSS defined in Table 7.1. In the CSSX process, small amounts of organic solvent to enter the DSS as a result of carry over of the organic phase from the stripper operation.

**Table 7.1. Radionuclide Concentrations**

Radionuclide	Average Soluble Feed (Ci/gal)	Decontaminated Salt Solution nCi/g (SPF WAC Limits)	Clarified Salt Solution (Ci/gal)
<sup>90</sup> Sr	3.28E-02	4.00E+01	5.60E-04
<sup>137</sup> Cs	1.34E+00	4.50E+01	1.12E+00
<sup>232</sup> U	3.79E-8		1.76E-08
<sup>234</sup> U	2.44E-08		1.14E-08
<sup>235</sup> U	1.96E-09		9.12E-10
<sup>236</sup> U	3.34E-09		1.55E-09
<sup>238</sup> U	1.26E-07		5.86E-08
<sup>237</sup> Np	6.50E-08	3.00E-02	5.44E-08
<sup>238</sup> Pu	8.439E-04		3.50E-05
<sup>239</sup> Pu	7.40E-05		3.07E-06
<sup>240</sup> Pu	1.82E-05		7.54E-07
<sup>241</sup> Pu	3.73E-04	2.00E+02	1.55E-05
<sup>242</sup> Pu	9.68E-09		4.01E-10
<sup>241</sup> Am	1.48E-04		1.24E-04
<sup>242m</sup> Am	1.84E-07		1.54E-07
<sup>244</sup> Cm	3.16E-05		2.65E-05
<sup>245</sup> Cm	2.107E-9		1.76E-09
<b>Total Soluble Alpha</b>	7.55E-03	2.00E+01	6.32E-03

**Notes:**

- <sup>137m</sup>Ba and <sup>90</sup>Y exist at equilibrium concentrations in the feed, but may exist at other relative concentrations in the other process streams.
- The Saltstone Processing Facility Waste Acceptance Criteria specifies concentrations in nCi/g; the higher density of decontaminated salt solution from the IONSIV<sup>TM</sup> IE-911 and CSEX processes allows higher volumetric concentration limits for these two processes.

Note that the Sr removal and alpha sorption process inherently sorbs various elements at different efficiencies and will change the relative distribution of radioactive elements. However, none of the proposed processes affect the isotopic distribution of any element. Also, the barium daughter product from radioactive decay of Cs and the Y daughter of Sr decay exist at equilibrium concentrations in the feed solution. The Cs removal operation will not likely remove these elements to any significant degree. For MST, previous findings at Sandia National Laboratory on related compounds show some affinity for Cs and Y. Additional research and testing will eventually determine how these process steps affect these contaminants.

Previous work at PNNL developed the technology for the analytical monitor and provided initial prototypes of equipment for testing at the Melton Valley demonstration, Oak Ridge National Laboratory. This program seeks to adapt that technology to the more rigorous industrial standards needed for the longer term, higher-risk mission at SRS.

#### **7.1.6.2 FY00 - Current Work**

The current work scope limits the effort to solicitation of interest from various commercial vendors to manufacture and provide a monitor for testing within a pilot-scale facility for the program.

#### **7.1.6.3 FY01 - Future Work**

Work in the next fiscal year, or later, would proceed with procurement of a prototype unit for deployment within a technical demonstration facility.

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

The proposed ion exchange process employs CST adsorbent to remove Cs from the salt solution. In this process, slurry of MST is first added to the waste to sorb Sr, Pu, and other actinides. The resulting slurry is then filtered to remove insoluble MST and any entrained sludge in the waste. The insoluble solids is washed and an aqueous slurry of the solids are then transferred to the DWPF for incorporation into borosilicate glass. The clarified salt solution (from filtration) flows through a series of CST columns to remove the Cs. Because Cs cannot be easily recovered by elution, CST will be transferred to the DWPF. There it is combined with the MST/sludge slurry, washed sludge from the Tank Farm, and frit, to produce borosilicate glass. The DSS is transferred to Saltstone Facility and processed into a solid LLW for on-site disposal.

### **7.2.1 R&D Roadmap Summary – CST Non-Elutable Ion Exchange**

For each process alternative, science and technology questions and issues exist. These questions must be answered and issues must be resolved to complete the design and construction activities in a time frame that allows HLW tanks to be decommissioned in accord with compliance agreements with the State of South Carolina and the EPA. SRS personnel worked closely with the DOE Office of Science & Technology through the TFA to develop the Science and

Technology Roadmap. Development of these roadmaps incorporated inputs from subject matter experts using the Team's Selection Phase Work Scope Matrix, Selection Phase Science and Technology Reports, Pre-conceptual Phase Risks/Uncertainties, and Process Engineering Fundamentals. This roadmap outlines the technical studies and demonstrations necessary to provide to the designers, operators, and DOE management the information necessary to proceed through key decision points of the project for the CST Non-Elutable Ion Exchange process.

For CST Ion Exchange, the key issues are Cs removal kinetics as a function of temperature and waste composition, column design parameters, and glass requalification. The large columns defined in the preliminary facility design (5-ft diameter by 16-ft high) result in the accumulation of large quantities of radioactive Cs (up to 5 MCi), which requires extensive shielding to protect personnel. Hydrogen, oxygen and other gases are generated, posing potential safety and operational concerns. Immobilization of the loaded CST in borosilicate glass occurs in the DWPF. This new glass formulation requires re-qualification for the higher TiO<sub>2</sub> loading, revision of the existing glass durability correlation, and potential modification of the feed preparation slurry sampling and agitation systems to maintain feed homogeneity.

Achieving critical project decision milestones requires completion of the science and technology activities. Failure to meet technology insertion milestones in the integrated project schedule will delay startup of the salt removal process. This will result in inadequate tank storage space availability, jeopardizing operation of the DWPF and other SRS missions along, with significantly impacting the ability for SRS to support the complex relative to new missions.

This science and technology roadmap (Figure 7.2), a subset of the overall SPP roadmap, defines needs in the following three basic categories:

- Process chemistry,
- Process engineering, and
- HLW System interface.

Process chemistry includes the data on the thermal and hydraulic transport properties, reaction kinetics, and mass transfer properties that are needed to finalize the conceptual design. These data are used to establish the physical and engineering property basis for the project and detailed design. Examples of key decisions resulting from these activities include selecting tank mixing technology, selecting filtration technology, selecting reactor design, and finalizing the process flowsheet.

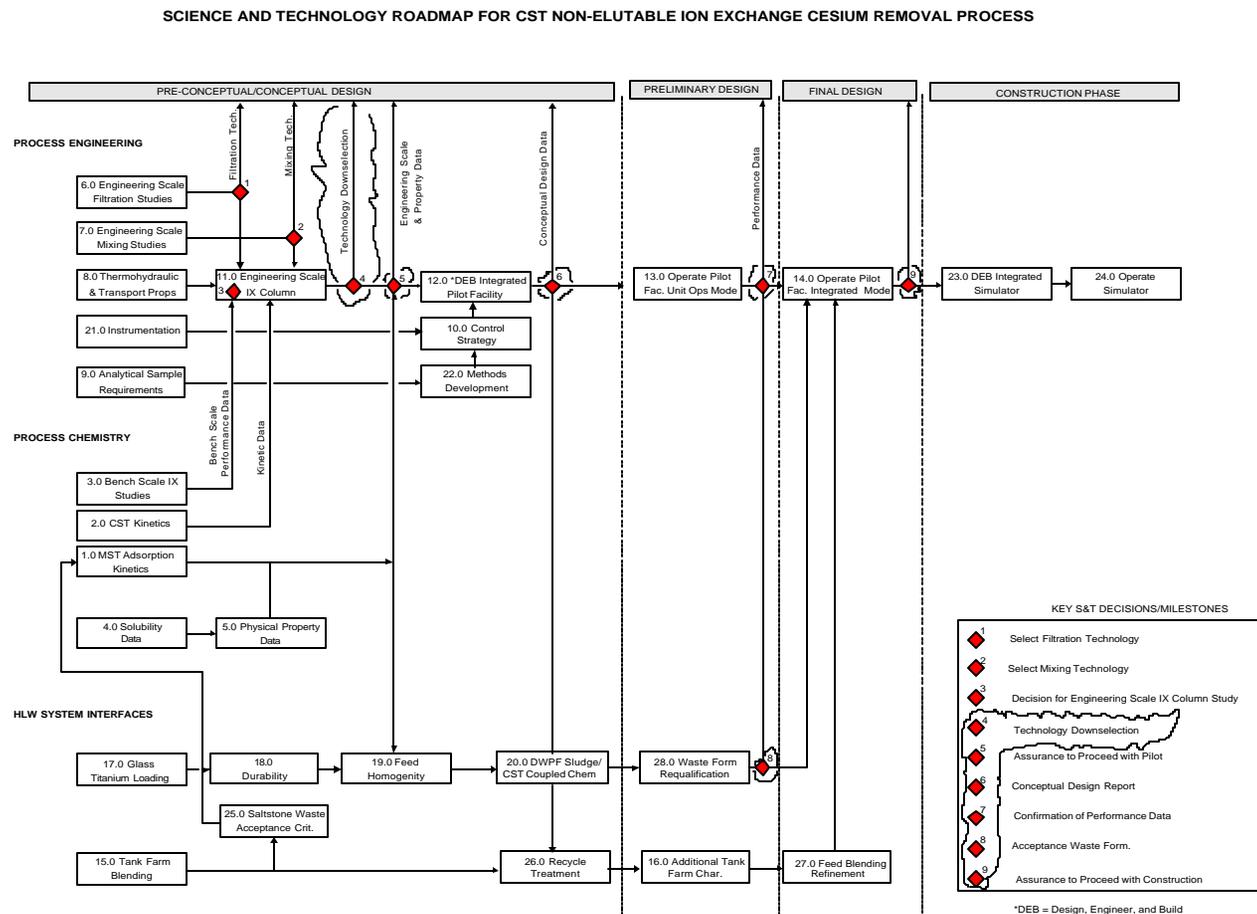
Physical property and process engineering data from engineering scale tests will be developed during the conceptual design. Phase Confirmatory performance data will be developed during unit operations tests to support preliminary design. These data are needed to resolve issues related to equipment sizing, specific equipment attributes, material of construction, and operational parameters such as pressure drop and requirements for temperature control. A key deliverable for this phase is demonstrating that the individual components will function as intended in support of establishing design input for the final design stage of the project.

Integrated pilot facility operations will be completed during final design to confirm operation under upset conditions. This will establish the limits of operation and recovery, the limits of feed composition variability, and will confirm design assumptions. This testing directly supports development of operating procedures, simulator development and operator training.

Additional development and testing during the conceptual design phase will help assure proper feed and product interfaces of the Cs-removal process with the HLW Tank Farm, DWPF and Saltstone. The issues of concern include assurance of glass, waste feed blending and characterization and waste acceptance. Note that "clouded" areas are currently under consideration as R&D scope as part of the TFA Roadmap Assessment effort.

Detailed logic diagrams that illustrate the various R&D activities, their interactions, and decision points are presented in Appendix A.

Figure 7.2. Science and Technology Roadmap for CST Non-Elutable Ion Exchange Cs Removal Process



## 7.2.2 CST Column Performance

### 7.2.2.1 Previous Results

Researchers from Texas A&M University, Purdue University, ORNL, and SRS used existing information about the performance of CST to predict the expected length of the Mass Transfer Zone (MTZ). Previous studies measured Cs distribution on CST samples of the powder form<sup>31</sup> and the engineered form.<sup>32</sup>

Research<sup>33</sup> was performed to determine the performance of CST in column application using SRS simulated waste to determine agreement with computer modeling. Results of the tests indicated that Cs removal in two column tests at moderately rapid flow rates (0.98 and 4.1 cm/min superficial velocities) matched Texas A&M predictions. However, the Texas A&M model incorporated a 30% reduction in Cs capacity at the higher flow rate to match the data. While the observed Cs removal surpassed model predictions at a lower flow rate (0.27 cm/min).

The mathematical model utilized in the simulations is a model of flow through a porous medium takes into account competitive adsorption, bulk convection, axial dispersion, film mass transfer, and pore diffusion. Since surface diffusion effects are not evident from the available data, the pore diffusion model is used in this analysis. The numerical solutions of the governing equations and boundary conditions are performed by the VERSE simulation package.<sup>34</sup> This model has been validated in many previous studies.<sup>35</sup> The pore diffusion model assumes uniform spherical adsorbent particles, local equilibrium within the adsorbent and constant diffusivities.

Walker et al.<sup>36</sup> performed ion exchange experiments at three different superficial velocities in small (1.5 cm x 10 cm) columns. Experimental data agreed with the predicted column performance from a VERSE computer model with the exception of the column run at a superficial velocity of 4.1 cm/min. In this comparison, the experimental breakthrough of Cs was much faster, reaching 95% of the feed concentration after only 120 hours. The best computer fit to this data was obtained by reducing the capacity of the CST by 30%. Extrapolated at the expected plant flow rate, this result significantly increases plant operating costs and represents a technology uncertainty. In review of the experimental design, personnel noted that the CST resin did not receive the entire vendor recommended pretreatment. The recommended pretreatment includes a 24 hour moist air equilibration, fines removal by up-flowing water, and NaOH conditioning. Walker et al. used a reduced length of time in the moist air conditioning. This could potentially reduce the effective capacity of the CST by trapping air in the pores of the CST that blocks Cs ions from the CST binding sites.

Testing by Wilmarth et al.<sup>37</sup> evaluated a number of the possible sources of the discrepancy between model predictions and experimental results obtained by Walker et al. Tests examined the effect of contact with humid air during pretreatment, lot-to-lot variance, aspect ratio and superficial velocity. The most conclusive evidence suggests lot-to-lot variance as the leading cause of the deviation. CST lot # 96-4 shows a dynamic capacity approximately 30% below other lots of CST. Additionally, results from collective tests of column performance indicate the VERSE model can adequately predict full-scale column performance.

Two additional column experiments showed CST performance degraded at only slightly higher superficial velocities. At velocities 75% higher than expected plant velocities, measured Cs breakthrough showed a 15-40% deviation from VERSE model predictions. Lastly, the presence of organic constituents exhibited little or no effect on column performance over the limited duration tested. Laboratory tests indicate a small decrease in capacity but not to the magnitude observed in equilibrium testing by Fondeur.

Another major aspect of prior research evaluated the adequacy of the column design for real waste application. Walker et al.<sup>38</sup> verified column capacity and kinetic data obtained using simulated waste with radioactive waste. Testing of radioactive waste also allowed confirmation of model predictions for a full-length column.

Testing indicated that IONSIV<sup>®</sup> IE-911 effectively removes Cs from SRS radioactive waste. All of the treated waste met Saltstone process requirements for Cs-137 (<45 nCi/g). Cs-137 loading in this test reached 376 Ci/L on the loaded IONSIV<sup>®</sup> IE-911, producing an estimated dose rate of 0.12 Mrad/h, or 15% of that expected in process operations. Comparison of test data to model predictions of IONSIV<sup>®</sup> IE-911 performance suggests intra-particle diffusivity may exceed previous estimates. Cs-137 removal exceeded predictions through most of the test at sampling points located 10, 85, and 160 cm down the 160-cm column. Additionally, Cs-137 removal after 10 cm exceeded predictions for the first 50 hours of the test and lagged the prediction for the remainder of the test.

Radiolysis by absorbed Cs-137 did not generate gas bubbles in the column during loading (i.e., when liquid flowed through the column). At the end to the test, personnel terminated flow and gas bubbles accumulated at a rate of 0.034 mL/h. One observation was that leaching and precipitation of a proprietary component of IONSIV<sup>®</sup> IE-911 posed a problem with column plugging. During NaOH pretreatment of the packed column, the leached material plugged the test column. Personnel removed the blockage by back flushing the column.

The predictions and regression of the ion exchange performance using the VERSE model, and the equilibrium data from the ZAM (Texas A&M) model, suggest the need for additional studies of the pore diffusivity for IONSIV<sup>®</sup> IE-911. The value of diffusivity required in this study to improve agreement between predictions and measurements exceeds that expected based upon viscosity measurements and literature correlation.

### **7.2.2.2 Refinement of the Model**

#### **7.2.2.2.1 FY00 - Current Work**

Data obtained from measurements of the equilibrium of alkaline-earth metals, carbonate, oxalate, and peroxide ions with a column of IE-911 will be used to refine the mathematical coefficients for the ZAM model describing the influence of various ionic constituents upon passage through a column of IE-911. These measurements will enable the refinement of the model used to describe the column performance. This work will be done at SRTC in collaboration with Prof. Ray Anthony of Texas A&M University, who will also assist UOP in refinements of the manufacturing process, consult on other aspects of the testing, and participate in periodic reviews of collected experimental data (see sections below).

#### **7.2.2.2.2 FY01 - Future Work**

The revised ZAM model will be evaluated versus the compiled column data. A report will be drafted, reviewed and approved. A decision will be made about whether additional model changes are needed. Additionally, an evaluation of various tank wastes will be performed during the next several FYs. The purpose of these tests is to catalogue the Cs removal efficiencies of the currently marketed CST versus the chemical composition of F- and H-Area wastes. The results will be compared with those predicted by the refined model.

### **7.2.2.3 Column Configuration**

#### **7.2.2.3.1 Previous Results**

Some questions and concerns about the CST inorganic ion-exchange process are related to equipment design and operation. Among these are the design and operation issues associated with a large CST ion-exchange column which, when fully loaded with Cs, will produce substantial quantities of decay heat and radiolytic gases that require removal.

The design strategy for the CST process stipulates an array of three operating columns with a fourth column held in reserve. Feed from the alpha-removal process is fed into the first (lead) column. The sorbent removes Cs until it becomes fully loaded, creating a saturated region at the top of the column, a MTZ that travels down the column, and fresh sorbent at the bottom of the column. The effluent from the first column is fed into the second (middle) column. The second column begins to adsorb Cs when the MTZ reaches the end of the first column and stretches into the second column. The first column is removed from the train when it becomes nearly fully saturated (to 90% breakthrough), at which point the second column becomes the first column, the third (guard) column becomes the second column, and the fourth (reserve) column becomes the third column. The first column has the loaded CST removed by water sluicing and is reloaded with fresh CST. This column remains in standby until needed.

This design strategy (first column to 90% break-through) minimizes the amount of CST required to be incorporated in the borosilicate glass, minimizing the number of canisters of glass produced. The length of the column results from the removal characteristics of the CST (MTZ) and the diameter from the required waste throughput. Some trade-off exists in these three parameters.

#### **7.2.2.4 Alternative Column Design**

##### **7.2.2.4.1 FY00 – Current Work**

Many questions and concerns about the CST process are related to equipment design and operation. These have not been previously addressed and have been carried as uncertainties and risks. Savannah River Design Engineering (SRDE) will evaluate different column designs and configurations with the goal of minimizing complexity and cost while providing for optimum performance of CST. The design strategy for column configuration will be re-examined to determine if the 16X5 ft column can be replaced by a different configuration that provides for a shorter service lifetime and a smaller volume for the columns.

WSRC will also be responsible for design of cooling systems for the column system to remove heat associated with the high radiation fields of Cs-loaded ion exchanger. In support of this activity, ORNL will perform tests and calculations to determine heat-transfer coefficients for fixed beds of Cs-loaded CST. The thermal conductivity of CST and a mixture of CST with waste simulant will be measured with a Hot Disk Thermal Constants analyzer. Using these thermal conductivity values along with literature data and column design information, the heat transfer coefficients for various combinations of CST, liquid, and gases can be calculated.

##### **7.2.2.4.2 FY01 – Future Work**

The proposed facility at SRS uses a traditional carousel arrangement of large, fixed-bed ion-exchange columns. Alternate column configurations using designs such as the Higgins Loop or simulated moving beds, offer potential reductions in safety source term but at the expense of added equipment complexity. Evaluation of alternative column designs and configurations will continue as needed. Criticality issues related to any new column configurations will be addressed.

### **7.2.3 CST Adsorbent Stability**

#### **7.2.3.1 Previous Results**

The fundamental chemical and thermal stability of the IONSIV<sup>®</sup> IE-911 (engineered sorbent consisting of CST particles and binder) in the highly alkaline environment of the SRS supernate is important for understanding processing lifetime and downstream effects of leached components. Results of the stability tests indicate that silicon and Proprietary Material 1 (PM1) leached from the IONSIV<sup>®</sup> IE-911 along with minor amounts of titanium and Proprietary

Material 2 (PM2). Discussions with members of the UOP staff indicated that silicon and PM1 exist in excess in the CST particles (IONSIV<sup>®</sup> IE-910) at levels of 4 wt% and 1 wt%, respectively. The quantity of silicon and PM1 leached from the IONSIV<sup>®</sup> IE-910 in each of the salt solutions from the samples of IONSIV<sup>®</sup> IE-911 do not exceed the excess in the IONSIV<sup>®</sup> IE-910 precursor. The results of these tests suggest negligible leaching of elements from the microstructure of the IONSIV<sup>®</sup> IE-911.

SRS and ORNL testing suggests that CST is interacting with some SRS waste streams. There have been examples of discoloration of some waste streams and in one particular case, a column plug developed on top of the column during pretreatment with circulating NaOH. Material was discovered in the feed line during pretreatment of an IONSIV<sup>®</sup> IE-911 column for a test using actual waste contained PM1. Observed solid deposits in a test that irradiated IONSIV<sup>®</sup> IE-911 in the presence of high nitrate solution showed similar elevated concentrations of PM1.

During FY99 testing at SRS and ORNL, personnel observed instances of column plugging which were attributed to post-precipitation of aluminates from the simulant. Also, others (UOP and ORNL) have stated that dilution of real wastes must be performed with NaOH to avoid gibbsite and alumino-silicate precipitation. It is necessary to develop an understanding of simulant preparation and waste dilution that prevents post-precipitation that could cause column plugging.

Exposure of the IONSIV<sup>®</sup> IE-911 to salt solutions at elevated temperatures (25°-120°C) and for long duration (2 months) resulted in a loss of Cs sorption capability. When the slurry cooled to room temperature, Cs did not adsorb to the IONSIV<sup>®</sup> IE-911 as well as before heating. Interpretation of the data suggests precipitation of salts from the solution or CST phase change as the most probable cause of this behavior.

The chloride content in CST raises potential concerns regarding corrosion and glass chemistry. Chloride measurements of CST demonstrate that water rinsing or caustic washing of the CST prior to loading the CST columns reduces the chloride content, and hence the corrosion risk. This washing step could occur at the vendor facility or in a non-radiological portion of the processing facilities. Measurements for CST from small-scale Cs removal columns show insufficient chloride content to adversely affect glass chemistry.

### **7.2.3.2 Alternative Pretreatment of IE-911**

#### **7.2.3.2.1 FY00 – Current Work**

One method of avoiding downstream problems caused by leached components of IE-911 is to pretreat the absorbent prior to use. An effective pretreatment regime would remove from IE-911 before it is loaded into the columns those leachable components that could possibly precipitate or mineralize during column operation. It is believed that the observed column plug likely resulted from the amphoteric behavior of one (or more) metal oxides over the pH range likely to have been experienced during the course of the CST pretreatment with NaOH. This hypothesis needs to be confirmed. An alternative pretreatment process that is not considered prohibitive must be

developed. The effectiveness of this alternative process should be confirmed using materials leaching and simulant-column testing.

SNL personnel will review SRS and ORNL leaching results for the chloride form of IE-911. One or more columns of CST will be prepared at SNL upon receipt of CST materials from SRS or ORNL. The columns will be pretreated with NaOH. Solids and liquids will be removed and characterized periodically during the pretreatment process. Particular attention will be paid to the leaching of PM1 and other components.

#### **7.2.3.2.2 FY01 – Future Work**

Knowledge gained from the FY00 activities will provide a basis for scoping laboratory experiments leading to a proposed alternative CST pretreatment process. SRS personnel will be consulted to ensure that the proposed process is compatible with the CST treatment process flow sheet. Samples of the nitrate form of IE-911 will be tested as they become available.

SNL will perform laboratory leaching and simulant column testing to confirm the effectiveness of the recommended treatment process. A report of the work at SNL will be drafted, reviewed and approved.

#### **7.2.3.3 CST Chemical and Thermal Stability**

##### **7.2.3.3.1 FY00 – Current Work**

The aim of this work is to examine the role of salt solution on CST degradation and its effect on the third column performance. Recall that the third column, according to the current design strategy basis, will be exposed to DSS for 6 to 12 months before it is actually placed in service as the primary Cs-removal column. Testing to date has only examined 120-day exposures. The time-temperature and waste-composition operating regime that provides acceptable CST performance must be characterized better. The underlying mechanism(s) responsible for the non-absorption of Cs, two candidates for which are phase changes of the CST and pore blockage by precipitation, should be elucidated.

ORNL staff is presently leaching samples of IE-911 in both the chloride and nitrate forms in both batch and flow-through column tests with average simulants at temperatures from 25-80°C. Column plugging will be studied in more detail to determine the cause. There are several suspected agents for this plugging, the most probable of which is  $\text{NaAlSO}_4$ . Therefore, experiments will be conducted to examine the effect of soluble silicon and Al. The leaching and precipitation of proprietary materials of manufacture during NaOH pretreatment and exposure to SRS waste will also be examined at SRS.

Long-term (12 month) batch leaching tests using the average supernate simulant and high-pH salt solution are being conducted to determine the effect of temperature and solution composition on the leaching behavior of the CST. Samples are stored at temperatures of 25, 30, 35, 50 and 80°C. Samples of the solutions are analyzed periodically for dissolved metals to measure CST

leaching and precipitation of simulant components. Samples of the CST are removed periodically and tested for Cs sorption, porosity, surface area, particle size and elemental composition. Batch 98-5 CST (chloride form) is being used for all of these test conditions with the CST nitrate form and IE-910 powder also tested at 25 and 80°C. A room-temperature leaching test using average simulant and CST batch 98-5 that was started in June 1999 continues.

Average concentration supernate simulant and high-pH salt solution are being recirculated through small PVC columns containing pretreated CST batch 98-5 at room temperature. The solution is being continuously filtered before it enters the column. Samples of the solutions are analyzed periodically for dissolved metals to measure CST leaching and precipitation of simulant components. The solutions are replaced whenever the concentration of any component changes by more than 10% or by more than 200 mg/L, whichever is larger. Any solids collected in the feed tank are quantified and analyzed before fresh solution is placed in the tank. Samples of the CST are removed from the top, middle and bottom of the column periodically and tested for Cs sorption, porosity, surface area, particle size and elemental composition.

At SRS, heat treatment of CST (IE-911) in the range 25-80°C has revealed that Cs from simulants is desorbed at the higher temperatures and only partially resorbed after the temperature is returned to ambient. The reasons for this behavior will be studied.

Leached and heat-treated samples will be examined by analytical methods such as SEM-EDS, TEM, bulk elemental analyses by ICP, powder x-ray diffraction, thermal testing (TGA/DTA), FTIR, surface area analyses (BET), porosity determination, and solid state NMR. Test solutions will be analyzed for the presence and composition of precipitates. These studies will provide insight into processes that may be leading to leaching of excess materials from the IE-911, precipitation of mineralized materials in the interparticle fluid or growth of mineralized materials on the surface or in the pores of IE-911 particles, or causing phase changes of the CST. The PIs will develop a small-column test program to evaluate CST stability by measuring the effluent cation profile for Na, K, Sr, Cs, Al, Si, and other cations of interest as a function of feed composition. In addition,  $K_d$  values of these samples will be measured in order to judge empirically the effect of various treatment regimes on the performance of IE-911. The mechanism for Cs binding of IE-911 and TAM-5 for SRS wastes will be examined.

The Leaching and elution studies are in progress at ORNL. ORNL will perform long-term exposure testing to evaluate the stability of CST to the highly caustic salt solutions. SRS will study column plugging. Test solutions will be analyzed at ORNL. Leached samples will be examined at ORNL, SNL, or PNNL, depending on the expertise available at each laboratory.

#### **7.2.3.3.2 FY01 – Future Work**

The long-term flow-through column studies using NaOH and nitrate solutions will continue at ORNL. Selected samples of CST from the batch-leaching and flow-through tests will be sent to selected laboratories for additional analyses. A report on CST stability (batch-leaching and flow-through) will be drafted, reviewed and approved.

Studies of the effect of heat treatment on Cs desorption and resorption will continue. A report on the thermal stability of CST will be drafted, reviewed and approved.

The examination of leached and heat-treated CST samples by various analytical methods will continue at SNL, PNNL and ORNL.

#### **7.2.3.4 Waste/CST Precipitation Studies**

##### **7.2.3.4.1 FY00 – Current Work**

A combination of bench-top experiments and high-ionic strength solution modeling will be used to develop an understanding of and prevent of post-precipitation in waste simulants. The effect of carbonate, oxalate and peroxide on the capacity and Cs-removal kinetics will be determined. Adsorption isotherms for a range of Cs starting concentrations will be measured. New coefficients for the ZAM model will be developed. Measurements of  $K_d$  will be performed with different anion concentrations to determine the magnitude of CST fouling.

Thermodynamic equilibria calculations are being performed using SolGasMix software and a thermodynamic property database compiled at ORNL from available literature data at ORNL. Initial calculations are being performed to confirm a recent finding<sup>39</sup> for a system containing  $\text{Na}^+$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{SiO}_3^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{HS}^-$ . While that system does not contain all the ions of interest in this study, it will be a good starting point to confirm the reliability of the ORNL database. Following confirmation of the database and the reproducibility of the literature data, the calculations will be expanded to include the full range of those ions listed in the literature<sup>40</sup>. Conditions (concentration of ions, temperature, etc.) under which precipitation is possible will be delineated from the thermodynamic calculations. Because it has been proven to be reliable even at high molarities<sup>41</sup>, Pitzer's activity coefficient method will be used to calculate the activity of water and the activity coefficients of the ions. The model at this stage will not use any parameters correlated from precipitation data. Following the calculation of the ion concentrations, temperature, etc., necessary for precipitation, and subsequent to review by selected SRS personnel and approval of the experimental matrix, laboratory experiments will be performed to recreate the exact solutions and test for precipitation. Any precipitates formed will be collected and analyzed to obtain information on the constituents. Any unusual results obtained in this step will be fed back into the modeling to fine-tune it.

Standard laboratory equipment is used in tests performed to confirm the results of the thermodynamic analyses. Simulant solutions are prepared using a recipe supplied by SRS personnel. Samples are analyzed to confirm the presence of cations and anions in the correct amounts and ratios.

The best method for diluting waste solutions to prevent precipitation and post-precipitation of aluminates, alumino-silicates, and any other insoluble salts that may form due to dilution will be determined. Tests will be performed to examine the chemistry of species leached from IE-911. Effects of chemistries on the  $K_d$  values of IE-911 desorption/resorption will be measured at two

temperatures. CST surfaces will be examined by solid characterization techniques (XRD, BET, SEM, IR, and Raman).

#### **7.2.3.4.2 FY01 – Future Work**

Studies of waste precipitation and CST kinetics issues will continue at SRTC on a larger scale with simulated waste containing tracer amounts of Cs-137. The kinetics of Cs removal will be measured using real waste.

The stability of simulated waste solutions will be examined at SRTC. Feed specs and dilution requirements will be proposed.

Studies of waste and simulant precipitation will continue at ORNL. Thermodynamic equilibria modeling calculations will be continued in order to expand the understanding of precipitation in waste solutions. Laboratory confirmation tests will be carried out at ORNL after review and approval by SRS.

#### **7.2.3.5 Revised Manufacturing Process**

##### **7.2.3.5.1 FY00 – Current Work**

Incidents of column plugging have been noted during experiments with IE-911. Solids isolated from the columns were analyzed to determine which chemical elements are contained in the precipitates. The analytical results indicate that the simulants themselves might be unstable with respect to precipitation and that excess materials used in the manufacturing process of IE-911 are leaching during pretreatment and subsequently precipitating. Thus, of IE-911 would be the production of a material that contains little, if any, excess materials.

In addition,  $K_d$  values for different lots of IE-911 can vary as much as 20%. Experimental results suggest that this variation is due to variations in the performance of IE-911 itself.

The combined resources of the SRTC, ORNL, SNL, Texas A&M University and UOP will examine revised manufacturing processes to improve the CST product. The bulk of this work will be performed at UOP. Proprietary testing will be conducted by UOP to examine the chemistries that are necessary to produce the IONSIV® IE-911 without the excess materials of manufacturing and to reduce attrition of material. Details of the work may not be readily available owing to concerns about trade secrets and intellectual property. However, the newly formulated IE-911 will be supplied by UOP to the program in quantities sufficient to characterize fully its performance. Establishment of cross-laboratory comparisons is currently underway. UOP recognizes the importance of reducing the variation of product performance, and has entered into a contract for delivery of a pilot-scale lot of revised material.

#### 7.2.3.5.2 FY01 – Future Work

Collaboration with UOP to develop an engineered form of CST (IE-911) compatible with SRS waste will continue. Test batches will be examined using the methods described in other sections of this plan. Depending on evaluation of test batches, a pilot-scale production batch of IE-911 may be produced.

A manufacturing revision that improves the ability of CST to adsorb alpha-emitters will be sought from UOP. The resulting material will be tested at SRS to confirm the data and to evaluate its chemical stability. The impact on the engineering scale column will be assessed.

### 7.2.4 Gas Generation

#### 7.2.4.1 Previous Results

A previous study<sup>42</sup> measured the impact of CST solids on the rate of formation and composition of radiolytically generated gases in simulated SRS liquid waste. The tests used IONSIV™ IE-911, the engineered form of CST. The test results show that radiolytically generated gas bubbles form rapidly at expected process dose rates. Bubbles near the surface of the resin bed can move by displacing IONSIV™ IE-911 particles.

Irradiation of IONSIV® IE-911 slurries produces hydrogen, oxygen, and nitrous oxide (N<sub>2</sub>O). Oxygen is the major product from irradiation of high-nitrate waste while hydrogen is the major product from irradiation of high OH waste. Researchers measured total radiolytic gas generation rates lower than those used in a preliminary gas generation calculation<sup>43</sup> for a full-scale process column. High-nitrate waste solutions yield the largest gas generation rates. The previous calculation for total gas generation remains bounding because test results showed less oxygen formation (G values up to 0.15 molecules/100 eV) than assumed in the calculation (0.3 molecules/100 eV). Since the high radiation field associated with a loaded column will originate from approximately five million curies of Cs-137 per column, a gas generation rate of approximately 35 L/h is expected.

Additional work investigating the effect of gas generation was performed on a larger scale. To conduct the gas behavior test, a method to simulate radiolytic gas generation in the CST column was developed. After evaluating several alternatives, oxygen production by the decomposition of hydrogen peroxide was selected. Hydrogen-peroxide decomposition-reaction rate data needed to plan the tall-column gas tests were determined from batch and small-column laboratory experiments. In addition to catalyzing the hydrogen peroxide decomposition reaction, CST also adsorbs hydrogen peroxide. Titanium stabilizes hydrogen peroxide. Fortuitously, this method not only simulates gas generation, it also allows simulation of the gas generation front movement due to Cs loading in an actual system by the movement of the peroxide wave front as it loads on the CST. In the course of the laboratory studies, it was determined that peroxide leaches metals from the CST. These findings may have implications in an actual system, since one of the products of radiolysis is hydrogen peroxide.

The gas generation test was conducted to provide information on bed retention and release of gas produced in the column. The target gas generation rate was 82 cc/h based on the maximum expected gas generation in an actual system with high-nitrate SRS supernatant. However, a gas generation range of 40 cc/h to 320 cc/h was used in planning the test to allow for the range of Cs concentrations expected in the real waste. Gas was generated by the decomposition of hydrogen peroxide. Column differential pressures, the volume of gas generated, and the column bed heights were measured. The bed was also monitored for bubble formation and gas accumulation. The test was run at a nominal superficial liquid velocity of 4.1 cm/min. Hydrogen peroxide loaded on the bed relatively quickly. Approximately 9.5 hours after peroxide was introduced at the top of the bed via a modified feed configuration, the first measurable volume of gas was observed in the effluent. Gas bubbles seen at the inside surface of the column wall gave a visual indication of the gas wave progress down the column.

Gases generated in the column were swept out with the effluent at both low and high gas generation rates. Gas did not coalesce and rise in the column, nor did the bed expand while the column was operated in down flow, even at gas evolution rates 16 times the target rate of 82 cc/hr. Gas accumulation in the bed is estimated to be less than 3% of the bed volume and it resulted in a bed pressure drop 2 to 2.5 times the pressure drop without gas. The bed pressure drop at a superficial velocity of 4.1 cm/min with gas was in the 8-9 psig range, compared to 3.5-4.5 psig without gas. After a gas inventory has been established in the column (i.e., once gas voids form in the column) the pressure drop is only weakly affected by the generation rate. After shutdown, part of the gas inventory disengages from the bed and bubbles in streams from the top of the bed. The axial gas inventory upon shutdown remains to be determined. The column was able to eliminate 16 times the design-basis maximum gas generation rate without apparent disruption of the bed.

In a three-column processing train, the gases swept from the lead column will likely accumulate in the head-space of the next column in series. The accumulation of these gases (hydrogen and oxygen) creates a hazard due to the potentially explosive nature of this mixture. It has been proposed that the gas entrained with the effluent be separated from the liquid prior to feeding downstream columns. Methods for removing this gas between columns need to be evaluated and demonstrated. The effect of entrained gas on downstream columns needs to be understood.

#### **7.2.4.2 Gas Disengagement**

##### **7.2.4.2.1 FY00 - Current Work**

Encouraging information indicating that gas generated in the column escapes through the bottom of the column without causing flow disruptions shifts the emphasis of gas generation research into different areas. Hydraulic aspects can now address gas disengagement issues. Tall-column apparatus at ORNL will be used to test prototypical equipment to perform gas disengagement. A variety of industrial equipment will be tested for this purpose. The use of hydrogen peroxide for non-radioactive examination offers potential benefits over a test under irradiation. Many questions and concerns about the CST process are related to equipment design and operation. These have not been previously addressed and have been carried as uncertainties and

risks. A number of these questions and concerns must be addressed. SRDE will evaluate different column designs and configurations (see above) with the goal of minimizing complexity and cost while providing for optimum performance of CST. The design specifications for gas-disengagement equipment resulting from this evaluation will be provided by SRDE to this task as input for equipment procurement by ORNL.

The existing pilot-scale tall column used in FY99 to evaluate CST physical stability, CST handling properties, and gas behavior will be fitted with gas-disengagement equipment. This gas-disengagement equipment will be tested for effectiveness using waste simulants and hydrogen peroxide addition to generate gas. PIs will modify and improve the tall-column design characteristics to adapt it for this task. The CST fixed-bed support screen design will be improved to better simulate full-scale flow-through column operation. Instrumentation and control systems will be slightly modified and upgraded. Column-effluent piping will be modified for installation of the gas-disengagement device. After installing the gas-disengagement device, the system will be tested and operated under various conditions to fully evaluate the performance of the device.

#### **7.2.4.2.2 FY01 - Future Work**

WSRC will develop the gas-disengagement Preconceptual Design Package (PCDP).

ORNL will evaluate the performance of the gas-disengagement equipment. A report on the performance of this equipment will be drafted, reviewed and approved. ORNL will provide technical support to evaluate the alternate column configurations. If warranted, a prototype column will be procured. Testing of the prototype will begin in FY02 to evaluate operating conditions.

#### **7.2.4.3 Cs Loading Under Irradiation**

##### **7.2.4.3.1 FY00 - Current Work**

An overall technical understanding of the CST Non-Elutable Ion-Exchange process is needed to design, construct, and deploy a full-scale facility for treatment of high-level salt waste. One of the concerns associated with deployment of CST is the effect of gas generation from radiolysis of water within the operating CST flow-through column. Calculations and testing are needed to determine the effect of gas generation on the performance of CST in a flow-through column.

SRTC and ORNL will collaborate to study the effect of radiolytic gas generation on the Cs-removal performance of CST. The calculation of gas generation in large columns will be improved. The rate and location of bubble formation during Cs loading will be defined. Diffusion rate of gases out of CST particles will be estimated and compared with experimental results.

Batch tests performed by SRTC in FY99 indicated that a loss of CST capacity can be expected when irradiated under expected conditions. Additional testing will examine the aspect of Cs-

removal performance in the presence of gas generation. The use of the HFIR for a radiation exposure test is being planned. This test offers a number of attributes for study but can also confound the study of the Cs ion exchange. Currently, a team of researchers from SRTC and ORNL are examining the benefits of each test.

A test capsule containing a small flow-through column packed with ~20 mL of CST has been designed and will be fabricated for insertion and irradiation in a spent fuel element of the HFIR test facility. The column will be connected to simulant feed and coolant transfer lines that are routed vertically upward through and out of the pool via an access port to the feed station transfer pumps and holding vessels. Simulant containing cold Cs will be pumped to the CST column using low-pulsation gear pumps in order to load the Cs onto the CST. The performance of this column system will be carefully characterized under a range of operating conditions prior to irradiation. The radiation dose received by the column of CST will be representative of what is expected for treatment of SRS HLW supernate. The test system will be designed for continuous feed of simulated HLW supernate containing nonradioactive Cs and will include a cooling system to maintain the temperature of the column below 35°C. The coolant (ethylene glycol solution) will be chilled and transferred to the column using gear pumps. Samples of the supernate will be collected every 4 h for Cs analysis and a Cs-loading curve will be generated from the data. The loading curve will be compared to baseline column performance data to determine the effect of radiolytic gas generation on CST loading capacity and mass-transfer zone length.

#### **7.2.4.3.2 FY01 - Future Work**

SRS will draft an interim report on the gas-generation calculations. The interim report will be reviewed and approved. The calculations will include temperature effects on Cs loading. A final report will be drafted, reviewed and approved.

ORNL will continue HFIR in-pool tests of the test capsule. After the tests, the test rig will be removed and decontaminated. An identical Cs-loading test will be performed in the absence of radiation to compare with the data obtained from the HFIR test. These data will ascertain if the gases generated in the pool experiment impaired the CST loading characteristics. Data from the tests will be collected. A report will be drafted, reviewed and issued.

### **7.2.5 CST Hydraulic Transfer**

#### **7.2.5.1 Previous Results**

Pumping tests conducted during prior research in a recirculating loop showed that a 24 wt% slurry of CST in water can be transported at fluid velocities of 4.3 ft/s (45 gpm in a 2-in. pipe) with no visible settling of the CST particles. A 5 wt% slurry will stay suspended at a velocity of 3.8 ft/s. The CST was easily mobilized after purposely plugging sections of pipe. The CST particles were rapidly broken up in a centrifugal pump into very small particles (<150 micron). A progressing cavity (Moyno) pump caused less damage to the CST particles.

Additionally, slurries of CST in water showed low abrasivity to 304L stainless steel and moderate abrasivity to A106 carbon steel. However, results indicated that supernate-containing slurries were less abrasive to A106 carbon steel. Of importance to the CST flowsheet, mixtures of received CST and SRS sludge simulants showed minimal tendency to cause caking or hard layers.

CST was easily sluiced into and from the ion exchange column using water and air. The as-received CST is slightly acidic and contains fines that are generated during shipping. The CST is pretreated by stabilizing the pH with dilute NaOH, then backwashing with water to remove any fines. The CST had been pretreated for the ORNL Cs Removal Project. The CST was added to the column in three batches, and the column was backwashed after each batch to remove any fines generated during sluicing. The column was backwashed with tap water at flow rates up to 1.2 L/min after the first and second batches of CST were added to the column, and up to 0.6 L/min after the third batch was added. The CST bed was expanded by at least 50% during the first and second backwashes, but by only 20% during the third backwash due to lack of space in the column.

Hydraulic tests were conducted during the previous studies to obtain data useful for column operation. Pressure drop through the column, across the Johnson screen, and the effect of flow rate on pressure drop were measured. The column-pressure drops for the first four tests ranged from 17 to 23 psig. The pressure drop at the top of the bed where a layer of fines and fragments of CST and other materials existed accounted for 60% to 70% for the pressure drop. After the bed was expanded to redistribute these layers, the pressure drop stabilized in the 7 psig range at 5 cm/min superficial velocity. The pressure drop across the column calculated by the Blake-Kozeny equation of 6.7 psig is in good agreement with the 7.4 psig pressure drop observed in Hydraulic Test 6. The pressure drops in the bed at the nominal flow rate were relatively constant and varied from 0.35 psig/ft to 0.45 psig/ft. The pressure drop across the Johnson Screen remained constant throughout the six tests, ranging from 0.45 psig to 0.55 psig. No channeling was detected. The pressure drop across the Johnson Screen did not increase, indicating no accumulation on the screen.

Prior to sluicing the CST from the column, the supernate simulant in the column was displaced with 2 M NaOH, and then the NaOH was displaced with deionized water. Water, rather than supernate simulant, was used to sluice the CST and facilitate handling of the spent CST. The two-step displacement process was used to avoid possible precipitation of Al(OH)<sub>3</sub> from the supernate simulant if the pH of the solution was lowered during mixing with the water.

The column was pressurized, and then the bottom sluice valve was opened. The CST and water flowed up through the 1-inch-sluice line to the level of the top of the column and then back down into a plastic tank. Because of the restricted air supply, the CST and water flowed rather slowly from the column into the collection tank. The water interface moved slightly faster than the CST interface, leaving about 17 cm of CST in the bottom of the column after the first sluicing. The sluicing took 2.3 minutes, so the average flow rate was 10 L/min, and the average velocity in the sluice line was 33 cm/sec.

Another aspect of DWPF operation is accurate slurry sampling using the Hydragard sampler. The particle size of the as-received CST ranges from 200 – 800 micron, significantly larger than the borosilicate glass formers (frit). This raises two technical issues regarding homogeneity and sampling of CST slurries of DWPF. A series of tests were conducted to address these issues.<sup>44</sup> Four tests used batches of aqueous slurries of 10 wt% CST and the remaining tests used three different batches of sludge-based slurries.

Sampling studies of the mixture of CST, frit and sludge using the Hydragard<sup>®</sup> sampler did not show uniform results when compared with grab sample taken from the feed tank. The Hydragard<sup>®</sup> samples exhibited 12% frit depletion. As expected, the sludge-frit slurry with large as-received CST particles repeatedly plugged the Hydragard<sup>®</sup> sampler.

The CST has been engineered into material with an average particle diameter of around 500 microns for use as packing in the ion exchange columns. Smaller particles would give excessive pressure drop through the column. However, as noted above, preliminary testing<sup>[44]</sup> has shown that the DWPF Hydragard valve is not capable of sampling sludge with as-received CST. Previous work during the DWPF startup configured the Hydragard sampling system to accurately sample sludge with frit particles that are nominally about 175 microns in diameter (acceptable size range 80-200 mesh). Therefore, we assume that if the CST particles can be reduced to the size of frit particles or smaller they will be representatively sampled by the Hydragard system.

Size reduction of the spent CST resin introduces another unit operation into the proposed flowsheet. To select the best method for accomplishing CST particle size reduction, literature was reviewed and other DOE sites were contacted about their experience with similar processes. In particular, personnel at the Hanford Site's K Basin were contacted about their experience at that site in grinding sludge particles and personnel at the West Valley Demonstration Project were contacted about their experience in grinding zeolite. The results of these reviews are summarized below.

Criteria selected for evaluating a method of particle-size reduction are: (1) the method must be capable of processing a wet slurry of CST solids in water. Preliminary flowsheet estimates are based on a 10 wt% slurry of CST in water; (2) It would be highly desirable to accomplish the size reduction in a single pass through the equipment; (3) The process should offer good control over maximum particle size; (4) The equipment must be capable of remote operation for radioactive service and have low maintenance requirements.

A preliminary literature review quickly showed that numerous particle-size reduction methods exist using process equipment of various designs. One particularly attractive piece of equipment is the Dispax-Reactor marketed by IKA Works. IKA Works is an international company known as a leader in the high shear mixing and dispersing industry. The company is based in Germany with a subsidiary IKA Works USA located in Wilmington, North Carolina. The Dispax-Reactor is designed to uniformly disperse a solid material in a liquid flow stream and is capable of wet grinding to provide a specified maximum particle size. The equipment contains a series of rotors with controlled gear tooth clearances. West Valley Demonstration Project (WVDP) personnel

tested IKA Works equipment and found it unsuitable for their application. The WVDP zeolite slurry waste is contaminated with sand and rust; metal particles in the slurry damaged the gear teeth in the IKA equipment.

A kinetic grinding system from Micro Grinding Systems, Inc., was one of the most promising technologies identified for reducing particle size of 105-K East Basin sludge on the Hanford site and was the technology chosen for processing contaminated zeolite stored in a waste tank at WVDP. The zeolite must be slurried out of the waste tank and pumped into another tank as part of the processing operations. The raw zeolite has a particle size distribution very similar to that of the CST. This grinder passes the slurry through a cylinder containing steel or ceramic balls or cylinders that are continuously vibrated. The impact from the objects in the cylinder crushes the particles in the feed slurry providing the grinding action. Tests at WVDP showed that 800-900 micron size particles were ground 98-100% below 200 microns and about 90% below 100 microns.

### **7.2.5.2 Develop And Test Size-Reduction Method**

#### **7.2.5.2.1 FY00 - Current Work**

Grinding tests will be contracted to both IKA Works and Micro Grinding Systems. The IKA equipment best meets the process selection criteria. It is anticipated that the spent ion-exchange resin will be significantly cleaner than the WVDP zeolite slurry. The spent resin should not contain tramp metal and should therefore be more suitable for size reduction with the IKA equipment. However, based on WVDP experience, it is also highly desirable to evaluate the Micro Grinding equipment for CST particle size reduction. It is anticipated that it will be more difficult to control the particle size with the Micro Grinding system and that additional work will be required to establish optimum operating parameters such as slurry concentration and flow. However, WVDP has successfully ground zeolite with very similar specifications to the SRS CST application using this equipment. This equipment is mechanically very simple which may facilitate its use in radioactive service.

The CST tests will grind approximately 50 pounds of solids. With the IKA equipment, a nominal 10 wt% slurry can be used as feed. At 10 wt%, about 50 gallons of slurry can be made. This should provide sufficient data for a preliminary evaluation of the equipment. SRTC personnel will observe the test and make a subjective evaluation of equipment operability. The size distribution of the ground CST will be determined.

Because the Micro Grinding system is most efficient at higher slurry concentrations, it may not be possible to test a 10 wt% slurry on this equipment. The vendor will be consulted and their experience with WVDP zeolite will be used to estimate the desirable slurry concentration. Preliminary indications are that 50 pounds of CST would provide sufficient material for a test grind. Micro Grinding is located in Little Rock, Arkansas.

Size reduced CST from both tests will be returned to SRTC for evaluation of mixing, settling and resuspension characteristics. The material will also be available to make additional melter feed

slurries that can be used to help determine the cause for previous non-representative sampling. Resuspension and homogenization of size-reduced CST will be investigated. A report on CST size reduction will be drafted, reviewed and approved.

#### **7.2.5.2.2 FY01 - Future Work**

The technology to perform on-line measurements of CST slurry concentrations will be assessed and the literature on this topic will be reviewed. Sampling and measurement of CST concentrations prior to size reduction would be difficult because as-received CST settles very quickly. On-line measurement would eliminate the need for this sampling and analysis.

Further testing of CST size reduction will take place. From the preliminary testing in FY00 we plan to select one technology for further evaluation. At a relatively modest cost a small-scale grinder can be leased or purchased. The grinder will be installed at SRS and used to demonstrate long term grinding and possible process configurations. CST on-line particle-size and concentration analysis will also be evaluated in this system. The transfer line from the CST accountability tank to the DWPF SRAT will be constructed and tested. Quantitative transfer of CST/water slurries, as-received and size-reduced, from the DWPF feed tank will be demonstrated.

#### **7.2.5.3 Develop Representative Sampling of CST/Sludge/Frit Slurry**

##### **7.2.5.3.1 FY00 - Current Work**

The operation of the Hydragard sampler with slurries of size-reduced CST will be tested and compared to operation with sludge/frit slurries in order to determine minimal size distributions for adequate CST slurry sampling.

##### **7.2.5.3.2 FY01 - Future Work**

Testing will continue with additional Hydragard experiments at various flow rates with size-reduced CST. CST reduced in size to both 175 microns (frit particle size) and 20 microns will be tested. Modification of the Hydragard sampler will be examined if sampling of size-reduced CST is not acceptable. Tests of themixing technology required to obtain a homogeneous slurry of CST in water and enable material accountability in the feed tank will continue.

### **7.2.6 Coupled DWPF Operation**

#### **7.2.6.1 Previous Results**

Processing within the DWPF would include the addition of IONSIV<sup>TM</sup> IE-911, loaded with Cs, to the sludge and frit slurry prior to vitrification. This addition would occur in the Slurry Receipt Adjustment Tank (SRAT). The DWPF process then adds chemicals – including formic acid – to adjust the redox potential of the mixture. The presence of noble metals catalyzes the formation of hydrogen gas, which poses a safety control concern for operations. The total gas

release also can promote foaming in the process vessels. Little information existed on the ability of IONSIV™ IE-911 to sorb noble metals and alter the amount of gases formed. Hence, personnel conducted process simulations at bench scale and at small pilot scale (1/240<sup>th</sup> DWPF) to examine this risk.<sup>45,46</sup>

Major conclusions from the testing included the following. The maximum observed SRAT hydrogen generation rate was 0.0034 lb/hr (scaled to a 6000 gallon DWPF sludge batch) and occurred during the sludge-only run without CST present. The maximum hydrogen generation occurred at the end of the SRAT reflux cycle and is about 0.5% of the current DWPF limit of 0.65 lb/h. The maximum SME hydrogen generation rate was 0.012 lb/h (based on a 6000-gallon DWPF sludge batch), which occurred in the size-reduced CST run. This maximum hydrogen generation occurred at the beginning of the SME dewater cycle and is about 5% of the current DWPF limit of 0.23 lb/h. The size-reduced CST runs produced slightly more hydrogen than the as-received CST but still far below DWPF limits.

Since these studies suggested no significant concerns, the program deemed that no additional work was necessary in this area before selection of a preferred process.

## **7.2.7 DWPF Melter Operation**

### **7.2.7.1 Previous Results**

A variability study addressing the compositional changes in sludge and frit was examined with a statistical designed approach.<sup>47</sup> The sludge, frit and CST loading were varied in order to assess the operating window for glass composition in DWPF. The existing models were used to predict the processing and product properties for each of the compositions. Due to the large difference in composition, it was unclear whether the models were applicable in this compositional region.

The results indicate that the viscosities and liquidus models for the CST/sludge glasses appeared adequate to cover the different compositional regions. Glasses at reasonable loadings of CST and sludge had durabilities acceptable for DWPF. However, the durability model under-predicts the measured PCT values.

In this phase of research, twenty-two glasses containing Purex sludge and three glasses containing HM sludge were fabricated and tested.<sup>48</sup> The fabricated glasses were tested for durability using the 7-day Product Consistency Test (PCT) and characterized by measuring the viscosity at 1150°C and by determining an approximate, bounding liquidus temperature. The current models used by Defense Waste Processing Facility (DWPF) for predicting durability, viscosity, and liquidus temperature were applied to all 25 glasses. The goal of this work was to identify any major problems from a glass perspective, within the scope of this effort, which could potentially preclude the use of CST at DWPF. As part of this study, product and property model predictions were made using targeted, measured, and bias-corrected measured compositions of the glasses. It was demonstrated that the results were essentially insensitive to the type of composition used in these models. This provides evidence that the glasses produced

were close to the targeted compositions, and that the analytical measurements were of high quality.

The results indicated all 25 glasses were very durable as measured by the PCT. The PCT values clustered within the interval from 0.64 to 0.91 g/L for boron for all of the Purex glasses except one and ranged from 0.37 to 0.43 g/L for boron for the HM glasses. The values for the other elements were similar. For comparison, the reference Environmental Assessment (EA) glass has a boron rate of 16.7 g/L. A remarkable finding from this study was the highly clustered nature of the results. The 22 Purex-loaded glasses clustered tightly in one region, whereas the HM glasses clustered at an even lower value for boron release.

The DWPF's Product Composition Control System (PCCS) durability model predicted values for boron release that were generally greater than the upper 95% prediction limit of the model. This type of behavior has been observed before for a range of glasses predicted to be very durable. The highly clustered nature of the results suggests that model revisions could be made to ensure glass durability. The DWPF homogeneity constraint was not developed for glasses within the compositional region defined for these 25 glasses. The results from this study reveal that the measured durabilities are not correlated to the values of this homogeneity constraint for these glasses. This is evident from the tightly clustered PCT results.

For this study, the liquidus temperature was bounded by performing 24-hour isothermal holds (as required) for the glass melts at 900°, 950°, 1000°, and 1050°C. X-ray diffraction (XRD) was used to detect crystallization, in this case Trevorite. For the 22 wt% Purex glasses, no crystals were detected in the bulk at 900°C or at the top surface of the glasses. For the 26 wt% Purex glasses, only two of the six glasses had bulk crystals after 24 hours at 900°C, and crystallization was no longer evident after the 24 hour hold at 950°C. For the 30 wt % Purex glasses, crystals were evident at higher temperatures but below the XRD detection limit at 1000°C. Given the fact that liquidus temperatures were only bounded, the 30 wt% loading of Purex may be near or at the edge of acceptability for liquidus. Surface crystallization was evident on top of the glass surface near the glass-crucible interface after some of the heat treatments. This crystallization was not considered as evidence in the determination of the approximate liquidus temperature. For HM glasses, no crystals were detected in the bulk or on the surface after 24 hours at 900°C.

The melt viscosity for many of these glasses was measured and the results reported at 1150°C (nominal temperature of the glass within the DWPF melter). For the Purex containing glasses, all viscosities were well within the DWPF range of 20 to 100 poise. The viscosity model, in general, over-predicted the measured viscosities. This is not surprising given the fact that the model was not developed for glasses incorporating CST elements. On the other hand, the HM sludge-containing glasses had, as predicted, viscosities at 1150°C (~160 poise) that were far above the 100 poise limit. Thus, the HM sludge-containing glasses fabricated for this study are not acceptable for processing in the DWPF. Although no Blend sludge glasses were fabricated, viscosity predictions for these glasses suggest that viscosity values may be close to 100 poise, or the upper limit for DWPF operations.

Test results indicated the aqueous slurry of as-received CST could not be mixed effectively with an agitator speed representative of DWPF processes. However, the slurry can be easily re-suspended by the agitator. The agitator system could not reduce the CST particle size. Prolonged repeated pumping of the slurry through a centrifugal pump did show evidence of particle size reduction.

#### **7.2.7.2 FY00 - Current Work**

No work in this area is funded currently.

#### **7.2.7.3 FY01 - Future Work**

Transfer of CST/sludge/frit slurry from the melter feed tank to the melter without separation of CST or frit from the slurry will be demonstrated. A fresh batch of melter feed material will be prepared in the Glass Feed Prep System (GFPS) using new size-reduced CST and frit specific for the CST process. A mock up of the melter feed loop will be constructed and tested to demonstrate that CST/water slurries can be fed to the DWPF melter without material segregation.

In the area of glass chemistry, properties and issues related to crystal growth kinetic effects will be examined. The glasses would be characterized by PCT and XRD. The aim of this work would be to ensure that amorphous phase separation would not occur with centerline cooling, for example, since this could have a deleterious effect on the durability of the glass. This work is required since the previous variability study looked only at rapidly quenched glasses.

A second area would be to investigate the effect independent variation of chemical constituents of the sludge or frit. In a major variability study, ranges are established for each element, and a statistically designed set of glasses is identified which not only covers a larger region of compositional space, but also provides the potential for revealing (or confirming) relationships between the properties and the glass compositions. A statistically generated set of glasses that will provide more evidence on the size of the operating window is required.

A third research scope would examine non-bounding measurements of the liquidus temperatures. ASTM liquidus temperature measurements need to be performed on those glasses showing the greatest propensity towards crystallization. The new liquidus model needs to be tested for these systems (Spinel formers).

A fourth area would include a thorough search (beyond scanning electron microscopy) for phase separation. This type of investigation requires use of transmission electron microscopy (TEM) and/or other high-resolution techniques. Although the strategy used in work to date assumes HM and Purex containing glasses would cover the extremes, a Blend sludge (a combination of the HM and Purex sludges) glass must be prepared and tested to verify these glasses based on extremes of composition bound the range of glass properties. The variability study was performed only with rapidly quenched glasses. Since the homogeneity discriminator indicated that most of the glasses would be phase separated, this apparent discrepancy needs to be resolved.

The kinetic effects above will provide one set of data from PCT tests to help resolve this, but additional tests to search for phase separation should be performed. No Blend sludge glasses were fabricated as part of the previous study and glasses should be fabricated and tested with this sludge type as (1) confirmation that acceptable glasses can be fabricated and (2) for use in the items identified above. In addition, experiments would be performed to determine if there is a solution to the high viscosity problem encountered with HM sludge. This involves use of models to adjust the frit, reduce the viscosity, and still meet the other requirements. Several glasses would then be fabricated and tested based on the results of the model calculations.

### **7.3 Caustic Side Solvent Extraction**

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

The CSEX process utilizes a novel solvent made up of four components: calix[4]arene-bis-(*tert*-octylbenzo-crown-6) known as BOBCalixC6, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-secbutylphenoxy)-2-propanol known as modifier Cs7SB, trioctylamine known as TOA, and Isopar L<sup>®</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 Cs 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 Cs to the aqueous phase. The aqueous strip effluent is transferred to the DWPF.

#### **7.3.1 R&D Roadmap Summary – Caustic Side Solvent Extraction**

Achieving critical project decision milestones requires completion of important science and technology activities. Failure to meet technology insertion milestones into the integrated project schedule will delay startup of the salt removal process. This will result in inadequate tank storage space availability, jeopardizing DWPF operations and other SRS missions, along with significantly impacting the ability for SRS to support the complex relative to new missions.

The Science and Technology Roadmap (Figure 9), a subset of the overall Salt Disposition Project roadmap, defines needs in the following three basic categories:

- Process chemistry,
- Process engineering, and
- HLW System interface.

The data resulting from these activities and the uses of the data in each phase of the project are discussed in Section 7.2.1. Process chemistry includes data on the thermal and hydraulic transport properties, reaction kinetics and mass transfer properties that are needed to finalize the conceptual design. These data are used to establish the physical and engineering property basis

for the project and detailed design. Examples of key decisions resulting from these activities include selecting tank mixing technology, selecting filtration technology, selecting reactor design, and finalizing the process flowsheet.

Physical property and process engineering data from engineering scale tests will be developed during the conceptual design phase. Confirming performance data will be developed during unit operations testing to support preliminary design. These data are needed to resolve issues related to equipment sizing, specific equipment attributes, material of construction and operational parameters such as pressure drop and requirements for temperature control. A key deliverable for this phase is demonstrating that the individual components will function as intended in support of establishing the design input for the final design stage of the project.

Integrated pilot facility operations will be completed during final design to confirm operation under upset conditions to establish the limits of operation and recovery, the limits of feed composition variability, and confirm design assumptions. This testing directly supports development of operating procedures, simulator development and operator training.

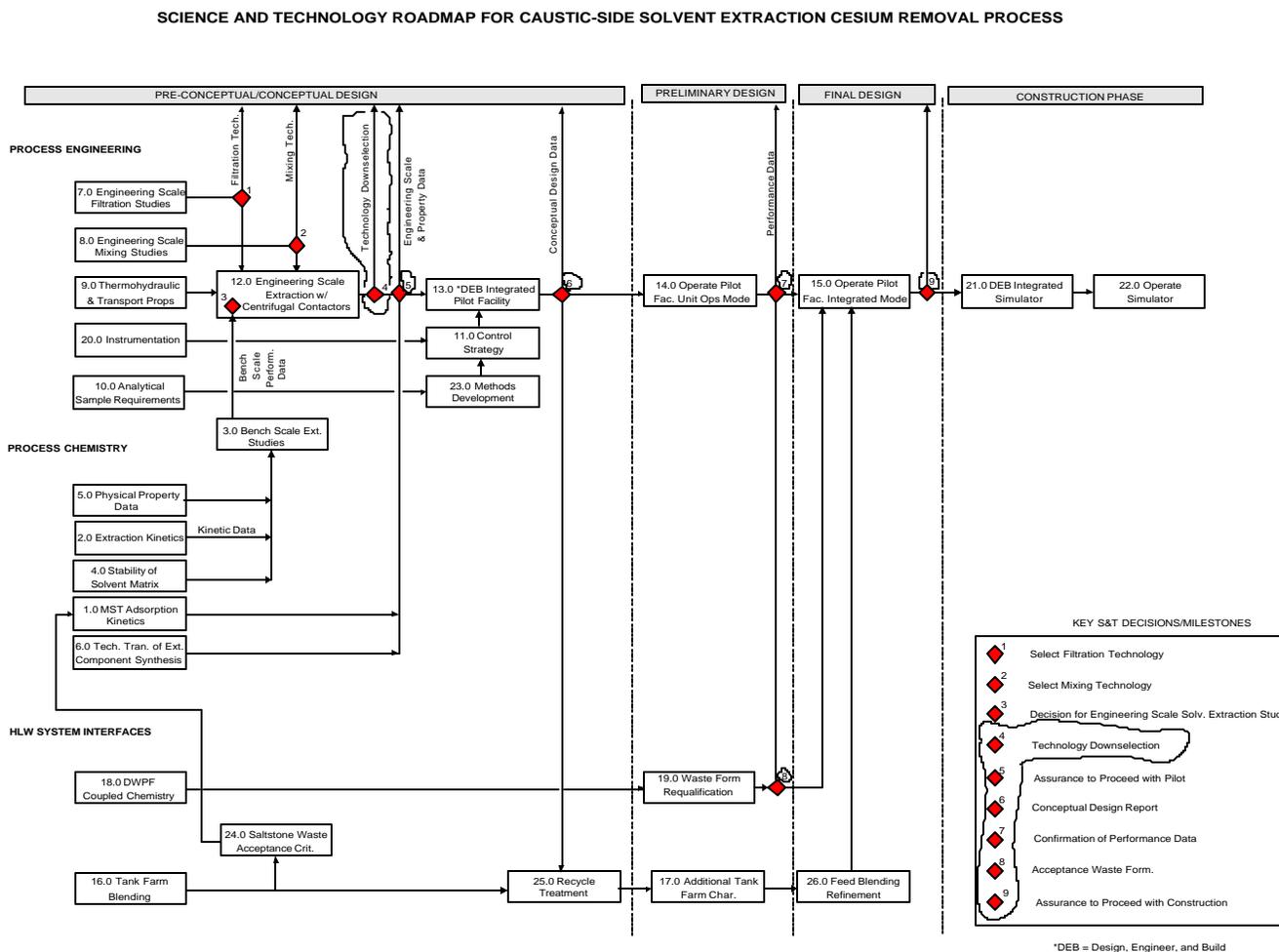
Additional development and testing during the conceptual design phase will help assure proper feed and product interfaces of the Cs removal process with the HLW Tank Farm, DWPF and the Saltstone Facility. The issues of concern include assurance of glass, waste feed blending and characterization and waste acceptance. Note that items in the "clouded" areas of the roadmap are currently under consideration as R&D scope, as part of the TFA Roadmap Assessment effort.

This roadmap was developed in order to answer technology questions and resolve issues in order to complete the design and construction activities of this facility in a time frame that allows HLW tanks to be decommissioned in accord with the compliance agreements with the State of South Carolina and the EPA. The development of this roadmap incorporated inputs from Subject Matter Experts, the Work Scope Matrix developed at the request of DOE, Preconceptual Risks and Uncertainties, and Process Engineering Fundamentals.

For CSSX, the key issues center on the maturity of the solvent system. These issues include the stability of the solvent (both radiolytic and chemical) the impact of minor solvent decomposition products and/or impurities on system performance and efficiency, and commercialization of the production of the extractant and modifier. Initial testing indicated that stripping efficiencies could be impacted by trace impurities. To address concerns related to trace impurities, a second generation solvent was developed. Preliminary data indicates the effect of trace impurities has been substantially reduced, if not eliminated.

Detailed logic diagrams that illustrate the various R&D activities, their interactions, and decision points are presented in Appendix A.

Figure 7.3. Science and Technology Roadmap for Caustic Side Solvent Extraction Cs Removal Process



## **7.3.2 Solvent Preparation**

### **7.3.2.1 Previous Results**

The initial solvent optimization work was completed as a part of the work conducted in FY-98 as a part of the Alternative Salt Disposition Program. The optimum solvent at that time was chosen to be the BoBCalixC6 (previously described), a modifier, 1-(1,1,2,2-tetrafluoroethoxy)-3-[4-(t-octyl)phenoxy]-2-propanol designated as Cs3, and Isopar L®. A complete description of this work is found in Reference <sup>49</sup>. Work during FY98 indicated that the Cs3 modifier showed significant radiolytic decomposition.<sup>50</sup> Work was conducted at ORNL to develop a more stable modifier. The new modifier Cs7SBT, previously described, was developed and indicates a greater stability than the Cs3.<sup>51</sup> In addition, previous work indicated that cold Cs may have to be added to the strip stream or TOA be added to the solvent matrix to maintain the stripping efficiency.<sup>50</sup> Adding cold Cs was not desirable. Subsequent work has demonstrated that the TOA addition to the solvent matrix results in more effective stripping with impurities present<sup>52</sup>.

### **7.3.2.2 FY00 - Current Work**

In order to standardize the solvent matrix being used in the FY00 CSSX program, the work scope matrix designated that all of the solvent would be prepared by ORNL. The primary work for this FY00 will be to synthesize the modifier and makeup the required solvent for all R&D work being conducted this FY and in early FY01. This will include the purchase of additional extractant and the chemicals required to synthesize the modifier. In addition, ORNL will develop a QA procedure to ensure the effectiveness of solution performance in batch tests. The R&D program for FY00 is aimed at finalizing the solvent matrix prior to the real waste test planned in early FY01.

The complete scope of work is described in Reference <sup>53</sup>.

### **7.3.2.3 FY01 - Future Work**

The solvent matrix will be chosen for the real waste tests planned in FY01. Additional optimization of the solvent matrix may be completed if required.

## **7.3.3 Batch Equilibrium With Internal Irradiation Of Solvent**

Solvent stability (chemical and radiological) is not completely understood. The degradation products could impact the extraction capabilities of the solvent matrix. These degradation products need to be identified. The ability to remove these degradation products from the solvent matrix may be required for this process to operate efficiently. The stability of the solvent, and the ability to clean it up to prolong its useful lifetime, will be investigated.

### 7.3.3.1 Previous Results

SRTC personnel performed a test to determine the extraction, scrubbing and stripping performance of the solvent system with a sample of SRS HLW. This test employed two extraction, one scrub and three strip contacts. SRTC 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.

### 7.3.3.2 FY00 - Current Work

The impact of internal radiation R&D will be conducted at both SRTC and ORNL.

#### 7.3.3.2.1 SRTC Scope

A number of limitations existed in the initial tests described above. These tests did not identify any minor components extracted by the solvent system. In addition, as has been previously reported, the solvent has been modified to include a new modifier compound.<sup>54</sup> Also, no attempt was made to determine the impact of self-irradiation of the samples. Furthermore, previous testing only explored the performance of material from a single source. Therefore, HLW process engineering personnel requested the Savannah River Technology Center to explore the performance of the new solvent system for both Cs and other trace components with HLW under a complete range of conditions representative of the various types of waste stored in the SRS tank farm.<sup>55</sup> These tests were also directed to explore the impact of self-irradiation on solvent performance.

The first phase of this testing will investigate the proclivity of the solvent system to extract species from the aqueous phase. Experiments will use samples obtained from at least six HLW tanks. Current plans propose the use of samples from Tanks 13H, 30H, 35H, 33F, and 46F. These tanks include the Waste Removal, Concentrate Receipt and Canyon Receipt Tank. These samples will all be filtered prior to testing. The tests will initially contact the solvent with HLW. Subsequently, SRTC personnel will contact the solvent with scrub and strip solutions. The scrub solution will contain 0.05 M nitric acid and the strip solution will contain 0.001M nitric acid. SRTC personnel will analyze the aqueous phase following each of these contacts. This sequence will be conducted twice. Following the last strip contact, SRTC personnel will analyze the organic phase to determine the presence of any components accumulated in the solvent system by ICP-MS and other appropriate methods.

A second set of tests will expose these solvents to internal radiation from <sup>137</sup>Cs while continuously agitating. SRTC personnel will sample the organic phase after approximately ¼ and ½ the anticipated annual doses for each of the aqueous/organic mixtures. Analysis will include determination of the D<sub>Cs</sub> (distribution coefficient for Cs) after contacts, measurement of the concentration of the various solvent species and determination of the concentrations of any detectable degradation products. SRTC will develop and implement an HPLC technique for

measuring solvent. Other potential analytical techniques include gas chromatograph-mass spectroscopy (GC-MS).

A complete description of these tests is found in Reference <sup>56</sup>.

#### **7.3.3.2.2 ORNL Scope**

The ORNL internal exposure tests will use a simulant solution spiked with <sup>137</sup>Cs. The experimental protocol will mirror the SRTC tests so that direct comparisons can be made between the simulant tests and real waste tests. Since the ORNL tests will be using simulants instead of real waste, the aqueous volumes will be larger. A complete description of these tests can be found in Reference <sup>57</sup>.

#### **7.3.3.3 FY01 - Future Work**

Some of the work described above will continue into and be completed in FY01. Additional work may be required depending on the results of the current experimental program.

### **7.3.4 Batch Equilibrium With External Irradiation Of Solvent**

Batch-equilibrium hot cell tests will be conducted with SRS high activity waste (internal Cs-137 exposure) with following variables:

- Modifier alkyl group structure
- Diluent structure
- Temperature and mixing

#### **7.3.4.1 Previous Results**

External radiation testing was conducted at SRTC during FY98 as a part of the Alternative Salt Disposition Program and is described completely in Reference 58. These experiments indicated that the extractant and modifier were stable at an exposure equivalent to three years of radiation from processing. The modifier degraded approximately 3% and the extractant only 1%. These experiments indicated no significant impact on stripping, extraction or scrubbing from the irradiation. Additional testing indicated that the stripping  $D_{Cs}$  became unacceptable above 4 Mrad exposure.

Proton NMR analysis of solvent Cs3B/120L exposed to 1, 4, 8, and 25 Mrad gamma radiation (<sup>60</sup>Co source) shows that while the Cs3 modifier appears to be intact, the BoBCalixC6 appears to break down.<sup>50</sup> Note: Reid Petereson presented data to show that calix degradation was minor.

The performance of solvent Cs3B/150L following irradiation showed  $D_{Cs}$  on extraction to first decrease at low radiation exposures before increasing at higher exposures, indicating that smaller BoBCalixC6 fragments (possibly phenols or catechols) may have formed which can enhance Cs

extraction. The  $D_{Cs}$  on scrubbing was surprisingly unchanged as a function of radiation exposure, but on stripping was observed to increase with increasing radiation exposure, reaching an unacceptable level by 4 Mrad exposure.

#### 7.3.4.2 FY00 - Current Work

The preliminary tests described above were performed with simulated waste solution. These preliminary tests determined the susceptibility of a calixarene based solvent system to radiation damage.<sup>58</sup> A number of limitations existed in these preliminary tests. These tests did not continuously agitate the solutions. Also, irradiation exposure only occurred in the presence of simulated waste solution. In addition, the solvent matrix has been modified by the introduction of a new modifier compound.<sup>54</sup> Therefore, HLW Engineering requested SRTC to explore the stability of the new solvent system under a complete range of conditions representative of the expected conditions in the proposed process.<sup>55</sup> These tests will examine the impact of the following variables modifier alkyl group structure, diluent, and mixing.

Four different solvents will be studied in these experiments. All of these solvents will employ calix[4]arene-bis(t-octylbenzo-crown-6) (BOBCalixC6) as the extractant. Other components of the solvent will likely include the proprietary CS-7SB modifier, trioctylamine, as a suppressor and Exxon Isopar L® as diluent. Another solvent will consist of BOBCalixC6, the proprietary CS-6 modifier and the Exxon Norpar® diluent. Testing will also use two solvent systems; the first will consist of the proprietary CS-6 modifier and Norpar™

These tests will involve exposure of these solvents to external radiation from a  $^{60}\text{Co}$  gamma source with samples continuously agitated. The base test will expose the samples to ¼, ½, 1 and 2 times the annual exposure for each aqueous phase. For the next two solvent systems, experiments will use ¼ and 1 times the annual exposure. The final examination will use the annual exposure. Also, each of the O/A ratios present in each test will represent the O/A ratio anticipated in the proposed process. Each extraction test will employ approximately 25 mL of solvent (with measurements performed in triplicate) while the tests with the scrub and strip solutions will employ 50 mL of solvent. The Co source will be cooled. Previously, this has limited temperatures in the source to between 30 and 40°C. At these temperatures, little degradation of the solvent should occur for the short periods of time that the solvent is in the source.

At the completion of each irradiation, SRTC personnel will analyze the samples. Analysis will include determination of the  $D_{Cs}$  after irradiation, measurement of the concentration of the various solvent species, and determination of the concentrations of any detectable degradation products. Analyses will occur in parallel at both SRTC and ORNL. SRTC will develop and implement an HPLC technique for measuring solvent quality while ORNL will likely use NMR to determine solvent quality. Other potential analytical techniques include GC-MS, Fourier Transform Infrared (FTIR) and electrospray mass spectroscopy. Physical properties of the exposed solvent will also be measured. One potential measurement will be determination of break times for the solvent/aqueous mixtures.

Based on the results obtained from this initial set of tests, it may prove necessary to perform additional tests to further investigate the impact of irradiation exposure of some of the alternative solvent systems. In addition, results obtained from this test program may identify potential solvent cleanup processes.

This work is described in more detail in Reference <sup>59</sup>.

#### **7.3.4.3 FY01 - Future Work**

Some of the work described above will continue into FY01. Additional work may be defined as a result of the work described above.

### **7.3.5 Solvent Physical/Chemical Properties**

Physical property data for the solvent matrix must be determined. A better understanding of process equilibrium and chemistry fundamentals, such as the distribution and impact of minor components, and the solubility behavior of components and degradation products as a function of temperature, must be determined. Experiments will be conducted to determine this information.

#### **7.3.5.1 Previous Results**

##### **7.3.5.1.1 Chemical Stability**

No degradation of the BoBCalixC6 was observed following continuous contact with alkaline SRS#2-1 simulant for up to 570 hours at  $53 \pm 2^\circ\text{C}$ . However, the Cs3 modifier was degraded by 50%, causing a reduction in the  $D_{\text{Cs}}$  on extraction. The  $D_{\text{Cs}}$  on stripping was observed to increase slightly. The Cs3 degradation products are as yet unidentified, and cannot be washed out with 0.5 M NaOH. However, their presence does not strongly impair the functioning of the solvent. Refreshing the degraded solvent by replacing the Cs3 modifier that was decomposed with fresh Cs3 results in a near restoration of the  $D_{\text{Cs}}$  obtained on extraction and scrubbing with pristine solvent. However, the  $D_{\text{Cs}}$  on stripping were somewhat higher (0.045, 0.098, 0.109, respectively for the first, second, and third stripping contacts) than those obtained for the pristine solvent control (0.024, 0.032, 0.124).

By NMR, the solvent appears to be stable to 43 days of continuous contact with 50 mM nitric acid scrub solution at  $53 \pm 2^\circ\text{C}$ . No degradation of either the BoBCalixC6 or the Cs3 modifier was observed.

Stability studies conducted at  $25^\circ\text{C}$  between the solvent and the SRS#2-1 simulant reveal the same type of degradation as observed at  $53^\circ\text{C}$ , only at a much slower rate. The solvent retained 88% ( $D_{\text{Cs}} = 10.52$  vs. 11.93) of its extraction power after 360 hours continuous contact at  $25^\circ\text{C}$ , and 80% ( $D_{\text{Cs}} = 9.575$ ) after 648 hours (27 days) continuous contact.

##### **7.3.5.1.2 Feed Impurities**

Researchers at ORNL<sup>60</sup> prepared simulated salt solution saturated with 0.1 mM mercury, 0.1mM lead, 0.01 mM iron, and 0.011 M silicate. An additional test was performed using perchlorate concentrations up to 0.01 M. They contacted this simulant with the solvent system and measured the extraction, scrub and strip performance. The distribution coefficients for this simulant system proved statistically identical to those obtained from simple simulant systems that did not contain these impurities. In addition, measurements of the concentrations of these species in the scrub and strip solutions found no Al, Cr or Fe in the strip solution. A small quantity of Hg transferred to the strip solution but most of the Hg (80%) remained in the first scrub solution. In contrast, Al distributed in nearly equal amounts in the first scrub and the first strip solutions.

Testing at ORNL and ANL indicates that feed impurities can impact the stripping performance. Tests with simulant prepared at ANL provided stripping distribution coefficients of approximately 0.2 following extraction. However, tests with simulant prepared at ORNL tests performed at ANL that had only contacted the strip solution both gave distribution coefficients of approximately 0.02. These results suggest that an unidentified feed impurity in the ANL simulant provided a mechanism for shifting the equilibrium to the right, either by introducing an anionic species that facilitated the extraction of Cs or by introducing an organic extractant for Cs. However, pilot-scale testing (discussed below) indicates that this feed impurity did not concentrate in the solvent phase upon multiple contacts, showing that distribution coefficients of 0.2 will result for planned operations. The impurity was later identified as a surfactant mixture of undecyl- and dodecylsulfonate, common in detergents used to clean glassware.

#### **7.3.5.1.3 Solvent Recovery**

Researchers at ORNL determined the partition coefficients for the calixarene and the modifier when the solvent contacts various aqueous phases. The partition coefficient for the calixarene exceeded the detection limit ( $10^6$ ) of the test. The partition coefficient for the modifier measured approximately  $5 \times 10^4$  (i.e., less than 4 M modifier in the aqueous phases). Based on these values, the proposed system would lose less than 15% of the low cost modifier and less than 1% of the calixarene in a year. Thus, if all losses are due to partitioning of the extractant and modifier to the aqueous phases, a simple decantation of the raffinate and the effluent should prove sufficient means for solvent recovery for the purpose of limiting the organic carryover to downstream processes. Use of decantation would then eliminate the need for four solvent recovery stages, a kerosene still, and a kerosene condensate tank. However, losses of the solvent due to entrainment of the solvent as fine droplets in the aqueous phases are expected to be much more important than partitioning losses. Thus, the question of solvent recovery remains an important one to resolve in FY01.

#### **7.3.5.2 FY00 - Current Work**

The work planned for FY00 is described below and is more completely described in Reference 13.

##### **7.3.5.2.1 Phase behavior of primary solvent components**

The solubility of BOBCalixC6 will be measured as a function of modifier and amine concentration. This will be done neat and in the presence of flowsheet and other aqueous solutions. Third-phase formation will be taken as a solubility limit for extraction complexes upon loading. The distribution of the primary solvent components to flowsheet aqueous phases and wash solutions will be determined by contacting experiments followed by pre-concentration (disk or back-extraction) and organic analysis by HPLC, NMR, or GC as appropriate.

#### **7.3.5.2.2 Partitioning and migration of solute species**

Experiments will include the standard batch extract/scrub/strip contacting protocol and may also include systematic batch tests as a function of compositional variables. Analytical methods are discussed in Reference 13. The objective is to learn how various inorganic and organic solute species partition between the solvent and relevant aqueous solutions, migrate through the flowsheet, and possibly accumulate in the solvent.

Primary solvent degradation products will be examined. Selection of degradation products will be made according to results of organic analysis, their likely importance, and whether they can be readily obtained by purchase or synthesis. Some limited synthesis of primary solvent degradation products will be performed. Certain phenols, including the starting material for the modifier, will be included here. Cations will include all the major cations in the simulant and trace metals. Major and important minor inorganic anions will be examined.

Lipophilic organic anions will also be examined. These anions may be present in the waste, such as dibutylphosphate, TPB, dodecylsulfonate, and others as recommended by SRTC. This must also be done as a function of Cs and K concentrations. Preventative or remediative measures such as solvent washing and anion exchange will be investigated. Partitioning of anions to a range of alkaline or other wash solutions and to off-the-shelf or synthesized anion-exchange resins will be systematically examined.

#### **7.3.5.2.3 Effect of major and minor components in waste feed**

This work will span FY00 and FY01. In FY00, examination of the effect of lipophilic anions will be initiated (but not completed), as these directly influence extraction and stripping and pose a significant degree of risk. Effect on Cs extraction performance, including selectivity, will be tested using a standard batch extraction/scrub/strip protocol and systematic batch tests as a function of compositional variables.

The effect of lipophilic anions such as dibutylphosphate, TPB, dodecylsulfonate, phenoxides, and others as recommended by the SRTC will be examined. If an effective remediation method is available, solvent rejuvenation will be demonstrated.

#### **7.3.5.2.4 Batch contacting demonstration with high-activity**

The purpose is to demonstrate that realistic activity levels (0.325 Ci/L) can be fully decontaminated ( $DF > 40,000$  or  $A < 20$  nCi/mL) and that the loaded solvent can also be fully stripped without an intervening spike. The hot-cell phase of this work will be conducted in the ORNL Chemical Technology Division and has been described previously. When solution activity is sufficiently low for radiochemical hood operation, solutions will be transferred to the Chemical Analytical Sciences Division laboratories, where the remaining contacts will be performed. Contacts will be performed in crosscurrent batch mode. No attempt will be made to simulate counter-current conditions. If needed, stripped solvent will be subjected to solvent-performance evaluation and diagnostics.

#### **7.3.5.2.5 Performance behavior as a function of feed composition variability**

We will initiate measurement of the Cs distribution ratio as a function of the concentration of the major ions in the simulant to support design of the flowsheet to be tested on real waste in FY01 and to predict performance over a range of dilutions of the waste with NaOH. The major ions will be Na, K, Cs, Al,  $N_3$ , and OH.

#### **7.3.5.2.6 Solvent Stability, Analysis, and Cleanup of Degraded Solvent**

Samples from several SOWM items will be received and subjected to analytical procedures and performance assessment. It should be noted that this work is exploratory and highly dependent upon the extent of solvent degradation and performance. Analyses and tests will be prioritized according to the apparent severity of degradation and to the type of information needed to diagnose and remediate any identified problems. Thus, the plan below is used as a guide and may be subject to modification in the course of the work.

#### **7.3.5.2.7 Analysis**

Samples will be submitted for organic analysis and may be further subjected to other diagnostic experiments such as electrospray mass spectrometry (ES-MS), FTIR, or NMR as warranted. There is potential for overlap with planned the work at SRTC, as noted below for the  $^{60}\text{Co}$  section. The intent in those cases will be to complement the SRTC data in cooperation with SRTC staff and to validate data where desirable.

#### **7.3.5.2.8 Performance Assessment**

QA procedures to be used on pristine solvent include: standard batch extract/scrub/strip protocol (if not part of the QA); third-phase formation; break time; interfacial tension; and selectivity.

Remaining issues regarding chemical stability of the solvent will be addressed. These include thermal stability over waste simulants containing noble metals, over nitric acid as a function of concentration, over strip solution, and over other solutions (e.g., wash solutions).

On receipt of a sample of spent solvent (> 100 mL) from the flowsheet test at ANL, QA tests will be performed that were performed on the pristine solvent shipped to ANL originally. Further analysis, extract/scrub/strip protocol, and diagnostics may be performed, if needed, according to the nature of the results from the test.

In cooperation with SRTC, certain analyses will be performed upon receipt of aqueous and degraded solvent samples from <sup>60</sup>Co tests. These will include HPLC, GPC, ES-MS, and NMR on the solvent samples. Aqueous samples will be analyzed for organic degradation products. Performance tests will be performed upon receipt of degraded solvent samples from <sup>60</sup>Co tests. These will include interfacial tension, break time, batch extract/scrub/strip protocol, third-phase formation, and extraction selectivity. Partitioning of degradation products to selected aqueous phases will be determined and solvent washing with selected aqueous phases will be tested. Anion exchange will be investigated as a possible solvent cleanup method upon receipt of degraded solvent samples from <sup>60</sup>Co tests.

On receipt of stripped samples of degraded samples from batch internal radiolysis tests at ORNL-CTD, selected performance tests, diagnostic experiments, and cleanup procedures will be tested.

#### **7.3.5.3 FY01 - Future Work**

Methods to evaluate (e.g., HPLC-MS, EM-MS, NMR, distribution behavior, etc.) solvent quality will continue to be studied in order to specify the baseline (pristine solvent) quality assay, in-process monitoring requirements, and post-process monitoring (solvent meets disposal criteria). The efforts to evaluate the effect of major and minor components expected to be present in actual waste will continue. Partitioning behavior of organics (e.g., surfactants, TBP degradation products) other inorganics (heavy metals; chromate, etc.) in waste will also be studied.

Additional work is planned to provide increased understanding of the process chemistry such as the effect of organics on extraction behavior and the effect of minor components on distribution behavior. Planned work will include investigation of extraction equilibria throughout the various sections (scrub, strip) of the flowsheet.

Development of a model to help predict performance as a function of variation of major components in the waste feed solutions will begin.

#### **7.3.6 Solvent Decomposition and Contactor Hydraulic Performance**

Solvent stability (chemical and radiological) is not completely understood. Degradation products could impact the extraction capabilities of the solvent matrix. These degradation products need to be identified. The ability to remove these degradation products from the solvent matrix may be required for this process to operate efficiently. The stability of the solvent, and the ability to clean it up to prolong its useful lifetime, need to be investigated.

### 7.3.6.1 Previous Results

The radiolytic and chemical stability of the solvent matrix are discussed in the above sections. Hydraulic performance of the solvent system is outlined below.

#### 7.3.6.1.1 Precipitate and Rag Layer Formation

Researchers at ANL performed a pilot-scale solvent extraction test.<sup>61</sup> This test consisted of two segments. The first segment involved a single pass of the solvent through the process. This test lasted 90 minutes. At the conclusion of this segment, ANL personnel drained the stages and inspected the fluids for either precipitates or a rag layer. No significant precipitation or rag layer formation occurred.

Following the first segment, a second segment of the test recirculated the solvent through the contactors for a period of 3 hours. Again, at the conclusion of this segment, ANL personnel drained the stages inspected for the buildup of either precipitates or a rag layer. No significant precipitation or rag layer formation occurred.

#### 7.3.6.1.2 Phase Separation

The ANL researchers performed three measures of phase separation.<sup>61</sup> The first of these measures determined the dispersion number for the solvent/aqueous systems of interest. These tests show that, except for low O/A ratios in the strip section, very good to excellent performance (i.e., dispersion numbers greater than  $8 \times 10^{-4}$ ) were obtained. Note that the process design does not include operation at low O/A ratios in the strip section.

The second measure involved single stage hydraulic performance tests. These tests employed a single stage contactor operated at various flow rates and O/A ratios for the extraction, scrub and strip stages. Performance ranged from very good to excellent (i.e., less than 1 % other phase carryover) for all tests with the scrub and strip stages. For the extraction stages, performance degraded at high O/A ratios with other phase carry over reaching 20 % in some cases. Note that the process design does not include operation at these high O/A ratios in the extraction stages. Performance also suffered at low O/A in the extraction stages when the organic phase serves as the initial continuous phase. While typical operation would start with the aqueous phase continuous, upset conditions might result in the organic phase becoming the continuous phase. Thus, recovery from such upset should attempt to first establish the aqueous phase as continuous.

The proposed solvent extraction process has been demonstrated on miniature (2 cm nominal diameter) centrifugal contactors.<sup>61</sup> In that work, testing was first performed with a single stage contactor and then in a multi-stage array similar to the proposed CSSX flow sheet. The modifier is different from that currently proposed used in these tests (Cs-3). In the strip tests, cold Cs nitrate was added to facilitate Cs removal from the solvent. With the currently proposed modifier, addition of cold Cs is not necessary.

### **7.3.6.1.3 Single-stage Testing**

The 2 cm centrifugal contactors were designed for 98% stage efficiency. To evaluate the actual efficiency, tests were run in a single-stage 2 cm contactor using the proposed solvent with various aqueous phases, including simulated SRP waste as feed. For extraction with the simulated waste, the measured efficiency averaged 97.1%. The scrub and strip tests averaged 80.9% and 99.7% respectively. When flow rates were much lower than normal, or when O/A ratios were furthest from one, the efficiency dropped as low as 79%.

### **7.3.6.1.4 Multi-stage Testing**

Multi-stage tests were run with two different configurations of contactors. In the first configuration, there were ten extraction stages, two scrub stages, and six strip stages. The second configuration contained ten extraction stages, two scrub stages, eleven strip stages and one rinse stage. The solvent was not recycled in the first series of tests but was recycled in the second. The rinse stage provided a caustic wash of the solvent before it re-entered the extraction section.

### **7.3.6.1.5 Results**

In general, the hydraulic and chemical performance demonstrated in these tests were good. There were some hydraulic problems associated with the small size of the contactors used and with the effects of trace surfactants present in the hardware. As a result of the surfactant problem, the solvent was later modified by the addition of trioctylamine (TOA).

## **7.3.6.2 FY00 - Current Work**

### **7.3.6.2.1 ORNL - Contactor Tests using SRS Simulant Waste and Internal <sup>137</sup>Cs Irradiation**

#### *Throughput and phase separation*

Initial hydraulic testing will be performed using a single centrifugal contactor stage. Relative organic and aqueous volumetric flowrates (O/A ratios) will be established at values consistent with CSSX flowsheet conditions. At each combination of organic and aqueous flow rates, the contactor speed will be varied until cross-phase contamination is observed in either or both phases. The onset of cross-phase contamination will establish a point defining the contactor operating envelope for the specific test condition. Testing will be performed at a sufficient number of flow conditions to establish operating envelopes applicable to the extraction, scrubbing, and stripping sections of the CSSX flowsheet. During this test, effluents from the contactor will be returned to the appropriate feed vessel, thereby facilitating extended continuous operation.

#### *Single-stage mass transfer*

Testing will involve contacting a solute-containing phase with an opposing phase in a single, 5.5-cm centrifugal contactor. Solution compositions and flow conditions representative of those expected in the extraction, scrubbing, and stripping sections of the flowsheet will be applied. Flowrates and contactor speeds used in testing will be based on the results of the throughput/phase separation test. Both flowrates and contactor speeds will be varied to investigate possible residence time effects on mass transfer performance. Prior to testing, samples of both feed solutions will be collected and equilibrated under controlled conditions. Solute concentrations in the equilibrated phases will be used to determine equilibrium distribution coefficients. These values will be compared against results from contactor testing in order to determine stage efficiency values.

#### *Four-stage mass transfer*

The test configuration will be identical to that used in the single-stage mass transfer test, except that the single-stage contactor will be replaced with an assembly of four contactor stages. Testing will be performed at conditions approximating those present in the extraction, scrubbing, and stripping sections of the CSSX flowsheet. Samples of aqueous and organic effluents will be collected from the inlets and outlets of each stage. Organic and aqueous inlet samples from each stage will be equilibrated in the correct volume ratios. Samples of equilibrated and separated aqueous and organic phases will be collected and analyzed for Cs and HNO<sub>3</sub> (when applicable). Comparison of equilibration sample results with outlet samples will be used to determine individual stage efficiencies and the overall efficiency of the four-stage unit.

These tests are more fully described in Reference <sup>62</sup>.

#### **7.3.6.3 FY01 - Future Work**

A test is planned for the second quarter of FY01 in which the results from simulant testing will be confirmed by operating the proposed flow sheet with actual SRS HLW feed.

Tests of the equipment and flow sheet on simulated waste will provide most of the data needed for scale-up and final process design. The results from these tests must be confirmed with real waste to be sure that there is no unexpected perturbation of system behavior due to the presence of minor components in the waste. These are components that might not have been present in adequate quantities in the simulant to effect test results. In addition to this confirmation of the simulant test data, testing on real waste will provide data on potential chemical damage that might not be fully explored in the simulant testing. The solvent damage data will be used to determine the best solvent recovery and cleanup process as well as provide an indication of solvent life before necessitating complete changeout. It is expected that this test will be conducted in small-scale equipment so that total operating time can be maximized while minimizing the total amount of HLW needed for the test. Due to the high levels of radiation associated with the real waste, the test will be conducted in a shielded facility. The exact test conditions for the real waste test are under development.

### **7.3.7 Waste Simulant and 2-cm Contactor Flowsheet**

#### **7.3.7.1 Previous Results**

The proposed solvent extraction process has been demonstrated on miniature (2 cm nominal diameter) centrifugal contactors.<sup>61</sup> In that work, testing was first performed with a single stage contactor and then in a multi-stage array similar to the proposed CSSX flow sheet. The modifier (Cs-3) used in these tests is different from that currently proposed but similar to it. In the strip tests, cold Cs nitrate was added to facilitate Cs removal from the solvent. With the currently proposed modifier, addition of cold Cs is not necessary.

#### **7.3.7.2 FY00 - Current Work**

Prior work performed at ANL in FY98 showed that Cs can be extracted from caustic aqueous solutions representative of the HLW at the SRS using solvent extraction processes carried out in centrifugal contactors. The tests showed that, while the process worked, the solvent needed improvement and the stage efficiency in the 2-cm centrifugal contactor was less than desired. The solvent was subsequently improved at ORNL in FY99. In the scheduled test, the stage efficiency of the contactor will be improved and stages will be added. Then, with the improved solvent, the process flowsheet required for removing Cs from HLW at SRS will be demonstrated using a waste simulant. The goal is to demonstrate the entire process while achieving a DF of at least 40,000 and CF of 12. The test will use simulant with Cs-137 spike as feed. Solvent will be recycled three to four times during the test. The waste simulant will be spiked with enough Cs-137 so that a decontamination factor of 40,000 can be measured accurately. These tests are described in Reference 15.

The basis and composition of the waste simulant to be used in all testing in FY00 are described in Reference <sup>63</sup>. The simulant composition is similar to previous simulants but includes more compounds. The new simulant was developed to stress the solvent system and to reduce the differences between the simulant and real waste.

#### **7.3.7.3 FY01 - Future Work**

Centrifugal contactor tests will be conducted with a 32-stage bank of 2-cm contactors housed in a glovebox at ANL. Tests will be conducted using solvent and waste simulant. The goal is to show that DF of 40,000 and CF of 12 can be simultaneously achieved. The following activities were completed in FY99: optimum solvent formulation developed for the test lab-scale batch-equilibrium tests of the flowsheet with waste simulant at 15°, 25°, and 45°C conducted at ORNL; and the flowsheet for the 2 cm centrifugal contactor test constructed at ANL.

A real waste test will be conducted in early FY01. This test may be conducted using 2-cm contactors. This test has been described above.

## **7.3.8 Solvent Commercialization**

### **7.3.8.1 Previous Results**

The extractant BOBCalixC6 has been provided in small batches (<50) of high-quality material by a well-known commercial vendor since 1998. The Cs-7SB modifier has only been produced at ORNL and is not commercially available. The Commercialization Plan or Technology Transfer Plan includes protecting intellectual property by way of patents and non-disclosure agreements. The associated scope of work is part of Technical Task Plan, TTP-ORNL-CASD-3 “Technical Task Plan for Technology Transfer for Caustic-Side CSSX”<sup>64</sup>.

### **7.3.8.2 FY00 – Current Work**

An invention disclosure covering the synthesis and use of the 2<sup>nd</sup> generation modifiers will be submitted to ORNL’s Office of Technology Transfer. The DOE will file a patent application for these modifiers, most likely as a continuation-in-part of a previous filed patent application covering the CSSX process (Reference <sup>65</sup>, “Solvent and Process for Extracting Cs from Alkaline Waste Solutions”). ORNL will draft a patent application for the Cs-7SB modifier and submit it to DOE patent attorneys, from which the full application will be written.

A synthesis procedure written by ORNL for preparing the BOBCalixC6 was written as part of a Technical Test Plan, TTP-CASD-1, “Technical Task Plan for Solvent Preparation for Caustic-Side CSEX”<sup>5</sup>. ORNL will convert this procedure into an invention disclosure, and submit it to the ORNL’s Office of Technology Transfer in FY00.

Procurement personnel at both ORNL and SRS will contact candidate chemical producers and custom synthesis companies, and transfer the technology under non-disclosure agreements written by ORNL’s Office of Technology Transfer and Office of General Counsel. Plans are to identify several producers for both the modifier and BOBCalixC6 by the end of FY00.

Documentation for the technology transfer aspects will entail an Invention Disclosure, the draft file patent application, followed by the final application to the US Patent and Trademark Office.

### **7.3.8.3 FY01 – Future Work**

A Procurement Plan was written to obtain 44 kg of BOBCalixC6 and a like amount of Cs-7SB modifier within specification by the SWPF start-up phase. The Request for Information will be continued and a Request for Quotation issued in April 2001.

It is necessary to identify at least one potential vendor for each solvent component to ensure viability of the solvent extraction option. If a vendor capable and willing to produce the solvent components can not be found, the program would be severely impacted. The solvent would have to be manufactured in-house, either at ORNL or at SRS.

## **7.4 Small Tank TPB Precipitation**

The proposed process employs NaTPB to remove Cs from the salt solution. In this process, removal of Sr, and Pu occurs through the MST addition concurrently with Cs removal. The precipitation process occurs in two sequential reactors – Continuous Stirred Tank Reactors (CSTR) to concentrate the solids (NaTPB and MST). Cross-flow filtration provides for the separation of the solids. The DSS is transferred to Saltstone to produce a solid waste form. Subsequently, the process washes the solids to remove the bulk of the remaining soluble salts and returns the wash water to the front end of the process for use as dilution water.

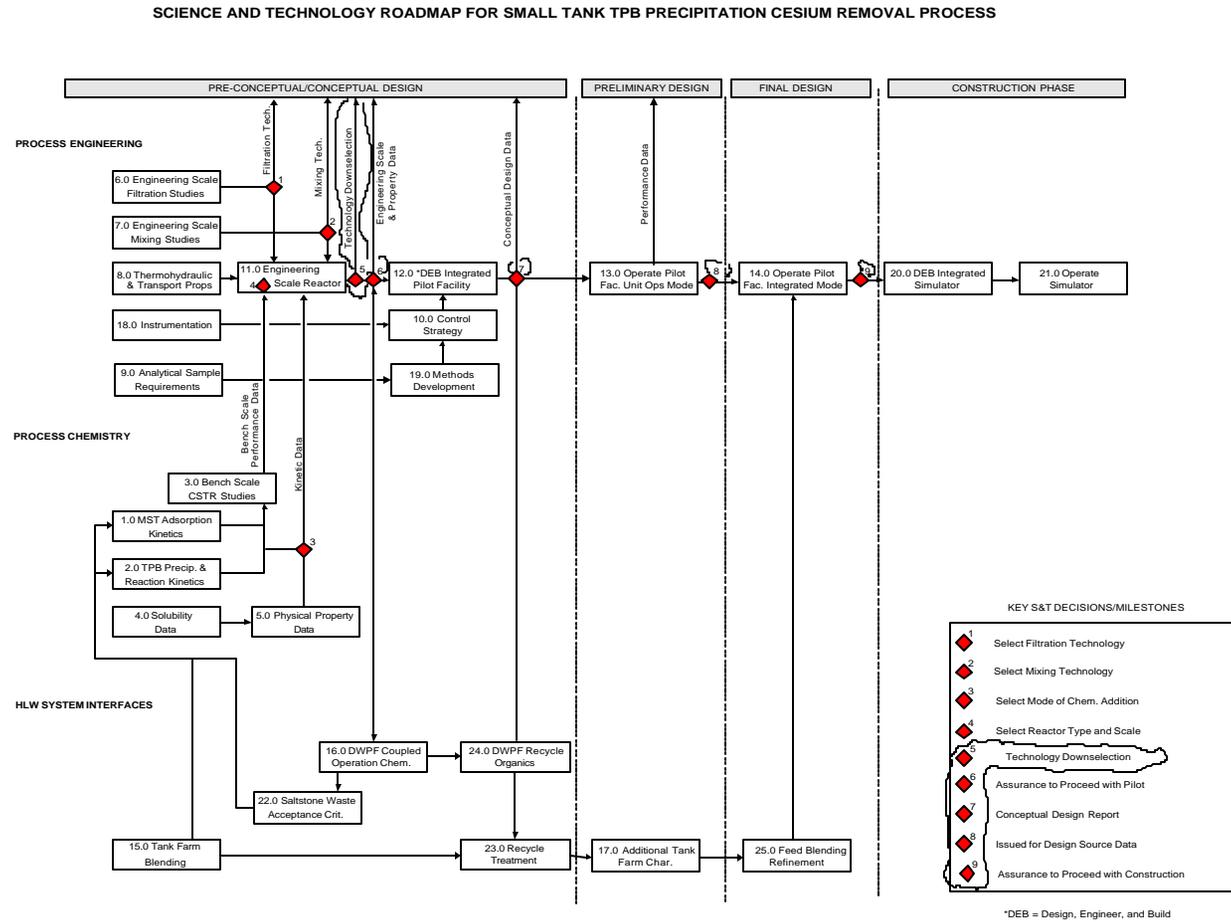
### **7.4.1 R&D Roadmap Summary – Small Tank TPB Precipitation**

Achieving critical project decision milestones requires completion of important science and technology activities. Failure to meet technology insertion milestones into the integrated project schedule will delay startup of the salt removal process. This will result in inadequate tank storage space availability, jeopardizing of the DWPF operations, and other SRS missions along with significantly impacting the ability for SRS to support the complex relative to new missions.

This Science and Technology Roadmap (Figure 7.4), a subset of the overall SPP roadmap, defines needs in the following three basic categories:

- Process chemistry,
- Process engineering, and
- HLW System interface.

Figure 7.4. Science and Technology Roadmap for Small Tank TPB Precipitation Cs Removal Process



Process chemistry includes data on the thermal and hydraulic transport properties, reaction kinetics, and mass transfer properties that are needed to finalize the conceptual design. These data are used to establish the physical and engineering property basis for the project and detailed design. Examples of key decisions resulting from these activities include selecting tank mixing technology, selecting filtration technology, selecting reactor design, and finalizing the process flowsheet.

Physical property and process engineering data from engineering scale tests will be developed during conceptual design. Confirming performance data will be developed during unit operations testing to support preliminary design. These data are needed to resolve issues related to equipment sizing, specific equipment attributes, material of construction and operational parameters such as pressure drop and requirements for temperature control. A key deliverable for this phase is demonstrating that the individual components will function as intended in support of establishing the design input for the final design stage of the project.

Integrated pilot facility operations will be completed during final design to confirm operation under upset conditions. This will establish the limits of operation and recovery, the limits of feed composition variability, and confirm design assumptions. This testing directly supports development of operating procedures, simulator development and operator training.

Additional development and testing during conceptual design will help assure proper feed and product interfaces of the Cs removal process with the HLW Tank Farm, DWPF and Saltstone. The issues of concern include assurance of glass, waste feed blending and characterization and waste acceptance. Note that “clouded” areas are currently under consideration as R&D scope, as part of the TFA Roadmap Assessment effort.

For each process alternative, Science and Technology questions and issues exist. These questions require resolution to complete the design and construction activities in a time frame that allows HLW tank decommissioning in accordance with compliance agreements with the State of South Carolina and the EPA. SRS personnel worked closely with the DOE Office of Science & Technology through the TFA to develop the Science and Technology Roadmap. Development of these roadmaps incorporated inputs from Subject Matter Experts using the Team’s Selection Phase Work Scope Matrix, Selection Phase Science and Technology Reports, Pre-conceptual Phase Risks/Uncertainties, and Process Engineering Fundamentals. This document outlines the needed technical studies and demonstrations necessary to provide to the designers, operators, and DOE management the information necessary to proceed through key decision points of the project for the STTP.

For STTP the key issues include understanding TPB precipitation kinetics, TRU adsorption kinetics, reactor mixing, and excess TPB to support washing and to allow proper precipitation reactor sizing. While engineered features will address the key benzene safety concerns, catalytic decomposition of TPB at lower temperatures remains

an issue relative to environmental release rates and operability. Similarly, operation at a smaller scale than used in the original precipitation prompts questions related to potential foam formation and the need to mitigate the impact of system hydraulics.

Detailed logic diagrams that illustrate the various R&D activities, their interactions, and decision points are presented in Appendix A.

## **7.4.2 Tetraphenylborate Decomposition Studies**

### **7.4.2.1 Previous Results**

Prior to the decision to open the search for a new salt processing alternative, extensive testing of the degradation of NaTPB was performed. This testing investigated the nature of the catalyst and the requirement for decomposition. Investigations into catalyst decomposition indicate that both copper and palladium are active catalysts in alkaline waste conditions. Palladium is significantly more reactive with TPB, than copper. The palladium catalyst species is believed to be palladium (0) metal supported on tetraphenylborate solids. Mercury, oxygen, temperature, benzene, and phenylborate intermediates affect catalyst activation. Copper catalyzes all four phenylborate species. Copper is a better catalyst than palladium for decomposition of the last two intermediates in the decomposition chain (i.e., diphenylborinic acid and phenylboronic acid). Continuing research into the decomposition reaction was primarily directed at resolving open questions raised by the Defense Nuclear Safety Board (DNFSB) 96-1 recommendation. In addition, research was needed to address the validity of the assumed benzene generation rate used in the preconceptual design basis. This research focused on two primary areas.

The first area of emphasis was to establish conditions under which the decomposition reaction could be effectively inhibited. The first set of tests used inhibiting agents to reduce the reaction rate.<sup>66</sup> These tests were based on previous tests that identified potential inhibiting agents. The primary focus of these tests was to investigate the impact of elevated temperature and exposure to radiation on the performance of inhibiting agents. These tests indicated that the use of a proprietary oxidizing agent at higher temperatures was less effective than at reduced temperatures. Another inhibiting agent (Na sulfide) showed only modest ability to mitigate reaction rates at elevated temperatures while a third (dimethylglyoxime) provided good performance as an inhibitor. However, the impact of radiation on inhibitor performance is inconclusive at this time.

The second set of tests examined the use of low temperature to slow reaction rates.<sup>67</sup> Previous testing indicated that very little decomposition occurred at 25°C. Thus, testing was initiated to determine the impact of temperature on catalyst activity. This data indicated that the decomposition reaction for TPB exhibited an activation energy of ~ 47 kJ/mole. However, these tests did indicate that the presence of oxygen at low temperatures can prevent the activation of the catalyst. However, increased temperature

can significantly decrease the incubation period for this reaction. These tests also indicated that the total quantity of soluble Pd(II) added to the system had very little impact on the final decomposition rate. Also, the addition of Pt(IV) resulted in significantly lower catalytic activity relative to Pd(II).

The final step in testing the proposed methods for inhibiting the decomposition reaction was measuring their efficacy with HLW from the SRS tank farm.<sup>68</sup> A series of tests were performed to determine the performance of these inhibitor methods with a composite of material from Tank 43H and 38H. These tests also evaluated simple removal of entrained solids as a potential inhibitor method. These tests indicated that reduction in temperature was the most effective method of reducing catalytic activity. However, even under conditions in which no inhibitor was added, the observed reaction rates were relatively low. This low activity was attributed to the absence of suspected catalyst species; in particular the absence of Pd. As such, the observed lack of efficacy of the selected inhibiting agents is expected.

While the above testing did not indicate a significant decrease in catalytic activity following filtration of the salt solution prior to introduction of the TPB, additional testing indicated that filtration following precipitation (and significant decomposition reaction), significantly decreased the catalytic activity of the filtrate.<sup>69</sup> These results suggest that the catalytically active species may well enter the system as a soluble species but may be converted to an insoluble species upon exposure to TPB (in a reactive system).

Additional testing explored the catalytic mechanism for the activation of Pd.<sup>70</sup> As indicated above, significant speculation on the role of oxygen in the activation of Pd catalyst had been strongly suggested. These tests indicated that the presence of oxygen at low temperatures (25°C) prevented the decomposition of NaTPB. However, at elevated temperatures (45°C) the presence of oxygen proved insufficient to eliminate catalytic activity.

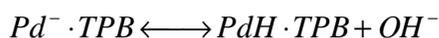
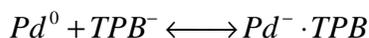
Additional tests indicated that Pd on BaSO<sub>4</sub> was a more effective catalyst for the decomposition of TPB than Pd(0) on activated carbon or Pt(IV) on activated carbon. (Note that Pd(II) reduced in TPB slurries was more reactive than Pd on Ba D04). An additional study searched for spectrophotometric evidence of phenylborate – palladium complexes.<sup>71</sup> These UV-visible measurements were unable to detect the presence of any such complexes.

#### 7.4.2.2 FY00 – Current Work

One of the most significant issues associated with the small tank precipitation process involves closure of the open DNFSB 96-1 issues. The workscope to address these issues contains three primary elements. The first element continues the development of understanding of the catalyst system. The second element continues evaluation of the catalytic activity in HLW samples. The third element involves the demonstration of the performance of the CSTR system in the presence of a significant decomposition reaction based system.

To develop an increased understanding of the catalyst system, testing is being performed to investigate the role of degradation products in the activation of the Pd catalyst. Previous testing has indicated that the presence of one or more of the degradation products plays a significant role in the activation of the catalytic species. These tests explore this interaction. A second set of tests is exploring potential synergism between the catalytic activity of Cu and Pd (both of these are known catalysts for the decomposition process). Also, the potential for a synergism between Pd and Hg is being explored. Previous testing indicates that mercury may play some role in the catalytic cycle, and the exact nature of that interaction is being investigated.

Additional testing explores the fundamental form of the Pd responsible for the catalytic process; in particular, the oxidation state, state of the catalyst (homogeneous or heterogeneous) and type of support material. Varying forms of palladium are being employed (supported, organometallic, reduced) and TPB surrogates. In addition, these tests examine the potential mechanism for Pd catalysis suggested by a panel of experts.<sup>72</sup>



Another aspect of testing employs a variety of both solid state and liquid phase characterization techniques. NMR studies are being performed to potentially provide a simpler technique for measurement of reaction kinetics. In addition, NMR offers the potential to identify organometallic Pd species. Another method of exploring the Pd speciation involves the use of electrochemical and spectroscopic techniques to evaluate the state of the aqueous phase Pd species. Tests will determine the oxidation states and behavior of potential catalytic metals in alkaline waste. These studies will employ available analytical tools such as cyclic voltametry and FT-IR in simplified salt solutions. In addition to Pd, a number of other potentially catalytic metals are being explored including Ru and Rh. Potentially useful characterization techniques, such as x-ray photoelectron spectrometry, electron microprobe and x-ray absorption, are being tested to determine the state of the solid phase catalyst.

The second aspect of this work continues to examine the catalytic activity of real waste. These tests will not only provide insight into the potential reaction rates that would be observed with the real waste, but would also provide insight into the catalytic mechanism based on extensive analysis of the waste composition. In FY00, additional tanks will be sampled for characterization and testing in FY01. In addition, a feasibility study will be conducted to evaluate the technical value, and estimate the cost and time required for performing a bench-scale CSTR experiment with actual waste. Bench-scale 1-liter CSTR tests conducted in FY99 were terminated due to foaming difficulties. Though sufficient Cs removal was achieved, the tests fell short of demonstrating sustained, steady state performance in maintaining sufficient Cs removal in a catalytically active system.

The third aspect of the testing involves a 1/4000 scale demonstration of the precipitation process in the presence of a significant decomposition reaction. The intent of this segment of testing will be to demonstrate that the proposed precipitation process will continue to provide DSS even in the presence of a significant decomposition reaction. The 1/4000 scale 20-L CSTR system used in FY99 testing will be upgraded in FY00 to correct deficiencies and enhance automation and data acquisition. Information from laboratory-scale catalyst testing will be used to design experiments to demonstrate the ability to maintain the required decontamination factor and system performance while TPB is actively decomposing.

#### **7.4.2.3 FY01 – Future Work**

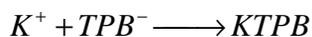
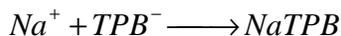
FY01 work will focus on using additional HLW tank waste samples collected in FY00 to verify the relationship between waste composition and TPB decomposition during treatment. The rate of TPB decomposition will be determined for several waste samples identified with different catalyst systems. Additional testing to further define and validate the decomposition mechanism may be required. To accomplish this, academic institutions may be contracted and tasked with refining mechanistic steps and exploring alternative steps. For example, additional detail or insight into the nature of the Pd intermediate species may be required. Information as to the form of this species and its interaction with diphenylmercury may be further elucidated by continued research through academic involvement.

Demonstration testing will be continued in FY01 using the 1/4000 scale system. Tests will be designed to demonstrate the improved understanding of the catalyst system by operating the 20-L system in a fully integrated mode, including washing, recovery, and recycle of NaTPB while TPB is actively decomposing.

If the feasibility study conducted in FY00 indicates significant technical value associated with an additional bench scale CSTR test with actual waste, this task will be planned for execution following the completion of 1/4000 scale CSTR testing in FY01.

### 7.4.3 Cs Precipitation Kinetics

The ITP process was designed to operate as a batch process. Prior work established the required kinetics and solubility information for the batch precipitation process.<sup>73,74,75,76</sup> The fundamental steps of interest for the precipitation reaction follow.



These tests were unfortunately not designed to provide the data required for predicting the performance of a continuous process. Therefore, a significant research effort was established to investigate the precipitation chemistry under more representative conditions.

#### 7.4.3.1 Previous Results

The first segment of this work extended existing basic batch data under conditions approaching those of the continuous process. Kinetic precipitation data was obtained exploring a number of potential process variables.<sup>77</sup> These variables included the quantity of excess reagent employed, the ratio of K and Cs in the waste stream, the Na molarity of the solution and the degree of agitation employed. The most significant impact was associated with the degree of mixing employed. Both the quantity of excess reagent employed and the Na molarity moderately impacted the precipitation kinetics.

Earlier results indicated that a significant portion of the excess reagent was immediately precipitated as NaTPB and was not readily available for precipitation of K and Cs. The next segment of testing evaluated the extent of this phenomenon.<sup>78</sup> These tests indicated that NaTPB precipitation occurs by co-precipitation and also occurs by exceeding the local solubility limit during the mixing of the feed stream with the bulk reactor material. The amount of co-precipitation that occurs is a strong function of the Na molarity of the salt solution. The tests confirmed that the amount of soluble TPB<sup>-</sup> in solution increased as the quantity of Na in the crystal lattice increased. These results further indicated that the precipitation of Cs<sup>+</sup> and K<sup>+</sup> effectively forms an isomorphous substituted crystal consisting of KTPB with CsTPB and NaTPB mixed throughout the crystalline lattice. Based on these results, a simplified model of the mixing that occurs during the precipitation reaction was developed.<sup>79</sup>

Based on the previous batch precipitation work, tests were performed to examine the performance of the precipitation process using the proposed CSTR configuration.<sup>80</sup> The primary goal of these tests was to demonstrate the ability to achieve the desired DF in the desired reactor configuration. Testing explored the impact of a number of variables on the achieved DF. These variables included the agitator type, the quantity of excess reagent employed, residence time in the reactors, concentration of NaTPB added, and the

bulk solution Na molarity. These tests indicated that using of longer residence time and adding dilute NaTPB feedstocks resulted in the highest DFs. Conversely, use of different agitator types did not significantly alter the system performance.

The next stage of work was to demonstrate the continuous precipitation process using larger scale equipment.<sup>81</sup> A 1/4000<sup>th</sup> scale continuous precipitation system was fabricated, including concentration and washing stages. Two demonstrations were performed with this equipment. The first demonstration involved only the concentration step. The second demonstration also employed the washing step and recycled the wash water to the reactors (as required by the proposed design). The required Cs removal was demonstrated during both tests. The required Sr and U removal were demonstrated in the first test, feed solution preparation prohibited determination in the second test. However, only a limited quantity of the excess NaTPB was recovered during the washing.

The final element of the precipitation demonstration involved the continuous precipitation process using HLW from the SRS tank farm.<sup>82</sup> During this test, the Cs and Sr were removed from solution to below 1 nCi/mL. However, the formation of foam posed a significant problem during the performance of this test element. One test was prematurely terminated due to the formation of foam and a second test was interrupted due to foam formation.

#### **7.4.3.2 FY00 – Current Work**

Due to funding constraints and the high priority of catalyst activation and antifoam studies, additional work in evaluation of Cs removal kinetics was deferred to FY01.

#### **7.4.3.3 FY01 – Future Work**

The first segment of testing during the technical demonstration phase will be to provide fundamental data pertaining to the rate of precipitation of the species of interest. Differential Scanning Calorimetry (DSC) will be explored as a potential tool to provide fundamental measurements of the rate of precipitation of NaTPB, KTPB and CsTPB. These tests will attempt to measure the heat of crystallization from TPB solutions for the species of interest. The rate of evolution of heat will then be used to calculate precipitation rates. This data will provide a fundamental understanding of the rates involved in the precipitation reactions of interest. Subsequent work would explore the rate of precipitation of mixed crystalline phases.

Testing will be performed to further evaluate the phenomenon of co-precipitation of NaTPB. These tests will focus on the impact of a number of parameters on the extent of NaTPB precipitation, including the agitation energy employed, the bulk Na molarity, the concentration of the TPB ion in the feed stock and the K concentration in the waste feed. In addition, these tests will use available analytical tools such as XRD to illuminate the fundamental nature of the crystals formed. Additional studies will investigate the mixing achieved during the precipitation reaction through the use of radiotracers; such as Na<sup>22</sup>.

Further testing will attempt to produce mixed crystals of known stoichiometry and to determine the nature of these crystals; both by XRD and by determining the solubility of these crystals. These tests will likely provide insight into the optimal conditions for operations of the precipitation process. It is anticipated that results from these tests will be incorporated in to a 1/4000<sup>th</sup> scale demonstration of the precipitation process.

#### **7.4.4 Washing And Filtration Studies**

The performance of the filtration and washing stages of the proposed continuous precipitation process had not been previously explored. Previous work had focused on the ability to filter and wash material prepared by batch processing. Also, due to the scale of the In-Tank Precipitation process, the previously proposed washing process was of a significantly longer duration. Additional work was required to examine the shorter duration washing required for the continuous process.

##### **7.4.4.1 Previous Results**

Tests were performed to examine the filtration rates for TPB slurries both with and without sludge present. The concentrated material was then washed to determine the efficacy of the proposed washing steps. The results from this work indicated that filtration performance was similar to previous work with precipitate prepared by batch processing. However, recovery of excess NaTPB during the washing stage was less effective than previous testing, recovering only 62% to 77% of the precipitated NaTPB.

Additional rheology measurements of both washed and unwashed slurries indicated that the materials produced during this testing had significant lower yield stress values. However, these lower yield stresses could not be directly attributed to the formation route for the precipitate material due to a number of other impacts, including the presence of an antifoam agent and the prior shear history of the material.

##### **7.4.4.2 FY00 – Current Work**

Due to funding constraints and the high priority of catalyst activation and antifoam studies, additional work in evaluation of slurry washing and TPB recovery was deferred to FY01.

#### 7.4.4.3 FY01 – Future Work

The next phase of testing will investigate the rate of dissolution of NaTPB from the mixed crystalline phase. As noted above, the dissolution of TPB plays an important role in achieving the decontamination of the waste stream and in the recovery of the TPB during washing. Tests will be performed to measure the rate of dissolution of NaTPB from the mixed crystalline phase. These studies will examine a number of experimental variables including the agitation employed, the total solids loading of the precipitate, the composition of the precipitate (ratio of Na to K in the mixed crystal), the impact of antifoam agents, time, and metal OHs on dissolution rates. These tests will also explore the impact of Na molarity on the dissolution rate. These results will then be assembled to provide a simple model of the dissolution process. This model will then be used to produce the conditions to be employed in a demonstration of the washing process. Scale demonstrations of the washing process will be performed.

#### 7.4.5 Antifoam Development

As indicated above, one of the prime needs for the STTP process is the development of a new antifoam. The severity of foam development during FY99 testing at SRS led to the recommendation to develop an improved antifoam as one of two strategic research needs for the STTP. This was recommended by several outside review panels including a National Academy of Science panel. The formation of foam proved to be a significant operational issue during the demonstration of CSTR performance with HLW.

##### 7.4.5.1 Previous Results

SRS has over a decade of experience with the TPB precipitation process. However, prior testing was accomplished in a million-gallon waste tank where there was sufficient volume to accommodate foam. Addition of antifoam was only planned to support DWPF processing of the TPB precipitate. During testing in SRS pilot facilities, 5 or 6 ft of stable foam was produced in a 12 ft precipitate storage tank. This foam was controlled by the addition of 2000 ppm (2000 ppm is an extremely high antifoam concentration but was necessary to control foam in this process) of Surfynol 104E antifoam. In testing of the STTP process with Surfynol 104E, the antifoam agent was ineffective in controlling foam. This is probably because Surfynol 104E is ineffective in high ionic strength salt solutions.

In the STTP process, there is the potential for foaming in three different processing vessels, the precipitation vessel, the concentration vessel and the washing vessel. Each of these vessels has a very different chemical composition.

- **Precipitation tank** - NaTPB is added to a 5-8 molar Na salt solution. Many antifoam agents are ineffective in this high salt solution. Agitation of the slurry is necessary

for the mixing needed for a rapid precipitation rate in a CSTR. The slurry is a high ionic strength caustic slurry but has a low concentration of K TPB solids (0.5 - 1 wt % insoluble solids).

- Concentration tank - The dilute TPB solution is filtered to concentrate the slurry to approximately 10 wt% insoluble solids. A crossflow filter is used for this concentration step. The slurry is now both high ionic strength and has a high concentration of potassium TPB solids.
- Wash tank - The concentrated slurry is washed to remove as many of the non-radioactive salts as practical. Washing reduces the soluble salt concentrations by a factor of 16. The endpoint for the washing is 0.01 molar nitrite as required for hydrolysis processing. The slurry becomes a low ionic strength caustic slurry with a high concentration of K TPB solids.

The three processing vessels each use agitation to produce a well mixed slurry and pumping to allow recirculating the slurry and transferring the slurry to the next processing vessel. Both agitation and pumping can lead to the entrainment of gas (nitrogen). Solids with trapped gas are lower in density than the slurry, allowing the foam to float. The foam remains separate from the slurry unless intense agitation is applied (intense agitation was accomplished using "mashing" tools in non-radioactive pilot plant experiments). Attempts to reslurry the foamy mixture often lead to the incorporation of more air into the slurry and aggravating the foaming. Unless the mixture is uniform in the processing vessels, it is likely that the foam layer will build up in the vessels over time and will lead to more problems in long term processing than can be experienced in typical precipitation experiments.

There are several other processing problems that aggravate foaming in the STTP process. Chemical decomposition of TPB by catalysts produces benzene, an oil that can stabilize the foam and lead to severe foaming problems. This will be present during all processing with TPB. Radiolytic decomposition of TPB produces a wide variety of different organics including diphenylamine, phenol, aniline, biphenyl, terphenyl, etc. These are more likely to be a concern in the concentration and washing steps where the precipitate has been exposed to the radiation for a longer time. These organic byproducts may stabilize the foam and lead to processing problems.

#### **7.4.5.2 FY00 – Current Work**

The primary objective of this work is to identify a more effective antifoam agent to mitigate foaming during precipitation, concentration, and washing in the CSTRs. A research contract has been established with the Illinois Institute of Technology (IIT) and Dr. Darsh Wasan, a known expert in the field of foam formation. IIT has identified two potential antifoam agents and a third material has shown promise. The efficacy of these antifoam agents is being evaluated in bench-scale tests with simulated waste. Additional

tests with HLW material will also be conducted. Potential effects the antifoam may have on Cs removal efficiency, TPB degradation, filtration, washing, and other aspects of the process will be determined. The material that shows superior performance will be recommended for testing in the 1/4000<sup>th</sup> CSTR system.

Past experience also indicated that pure solutions of TPB have a tendency to foam upon agitation. Laboratory scoping tests will be conducted to investigate this behavior and determine if additional testing is warranted.

#### **7.4.5.3 FY01 – Future Work**

An analytical method to detect the antifoam must be developed to assure proper concentration of the antifoam is present in the reaction vessels.

#### **7.4.6 Saltstone Facility**

Saltstone will immobilize the DSS from the small tank precipitation process. However, previous testing has not explored the higher concentrations of phenylborate species that might be present in the feed to saltstone from the proposed TPB process.

##### **7.4.6.1 Previous Results**

Testing was performed to determine the impact of higher than previously tested concentration of TPB degradation products on the benzene evolution rates from Saltstone,<sup>83</sup> the benzene TCLP results from Saltstone,<sup>84</sup> and benzene generation rates from Saltstone<sup>85</sup>. The results of these tests indicate that between 18% and 27% of the theoretical conversion of phenylborates occurs during the curing of Saltstone. The maximum release rate increased as a function of curing temperature. Also, the presence of 3PB in the feed is the dominant source of benzene in the Saltstone. The benzene concentration in the TCLP extract is nearly two orders of magnitude below the regulatory limits for Saltstone cured at ambient temperatures and is an order of magnitude below the limit for Saltstone cured at 85 °C.

##### **7.4.6.2 FY00 – Current Work**

None at this time.

### **7.4.6.3 FY01 – Future Work**

Removal of dissolved TPB from decontaminated supernate will be considered for further evaluation in FY01. This treatment could reduce the quantity of benzene that would otherwise be released to the environment. Promising technologies will be considered for additional testing.

### **7.4.7 Hydrolysis Testing**

Prior to immobilization of the concentrated waste stream, the K and Cs are returned to solution through acid hydrolysis of the TPB solids. Prior studies explored the ability to convert aged material. However, the proposed process will involve the production of freshly precipitated material.

#### **7.4.7.1 Previous Results**

Testing was performed to determine precipitate exposed to either no dose or to 65.6 Mrad could be processed.<sup>86</sup> These tests indicated that acceptable product was produced under both conditions. Furthermore, potential areas for further work were illuminated including optimizing reaction conditions and the extent of nitrite growth at lower proposed dose rates.

#### **7.4.7.2 FY00 – Current Work**

Due to funding constraints and the high priority of catalyst activation and antifoam studies, additional work in evaluating the hydrolysis process was deferred to FY01.

#### **7.4.7.3 FY01 – Future Work**

As indicated above, the hydrolysis process can be improved significantly by optimizing the reaction conditions. Additional work will explore ways to minimize the Cu catalyst concentration and determining the corresponding maximum acceptable range of formic acid addition. Testing will also develop a relationship between nitrite and nitrate concentration in the product stream and the absorbed dose. The identified optimum process parameters will be validated with a complete bench-scale hydrolysis process. This testing will also investigate the impact of the proposed antifoam agent on the hydrolysis process (see previous section on antifoam development). Work in future years will likely explore variations of the proposed hydrolysis process including exploration of the use of other catalysts, other forms of the Cu catalyst (such as supported Cu) or recovery of the Cu from the product stream (to minimize the impact of Cu on glass quality).

## **7.4.8 Glass Formulation Studies**

### **7.4.8.1 Previous Results**

As indicated above, testing in the evaluation phase indicated that higher levels of MST would be required to achieve the necessary Sr and actinide removal. As a result, the impact of this higher MST loading on glass properties was investigated.<sup>87</sup> In addition, these tests also explored varying levels of PHA on the glass properties. Three different glasses were formulated for these studies<sup>88,89,90</sup> All of the glasses formulated during these tests were very durable as measured by the PCT. In addition, performing 24-hour isothermal holds for the glass melts bound the liquidus temperature. This testing did indicate, however, that for Purex sludge, 30wt % loading of Purex in glass may be near or at the edge of acceptability for liquidus. The viscosities of approximately half of the glasses formulated were measured. Again, when 30 wt% loading of Purex was tested, the viscosities were very near the lower viscosity limit.

However, crystal formation kinetics work was not explored during this work. Based on the data available, the majority of glasses failed the phase sorption discriminator model.

### **7.4.8.2 FY00 – Current Work**

Due to funding constraints and the high priority of catalyst activation and antifoam studies, additional work in evaluation of crystal formation kinetics for the vitrifier operation was deferred to FY01.

### **7.4.8.3 FY01 – Future Work**

Further work (including kinetics studies) will be required to resolve the apparent inconsistency in the phase sorption discriminator model. Such studies would also investigate the potential for amorphous phase separation during centerline cooling.

## 8.0 R&D Program Funding And Schedule

### 8.1 Funding Summary

The SPP R&D Program is funded jointly by the DOE Offices of Science and Technology (EM-50) and Project Completion (EM-40). Combined R&D program funding for FY00 totals \$14.6 million and total projected funding for FY01 is \$17.7 million. Total funding and funding source for each process is shown in Table 8.1.1 The CSSX program did not begin until mid-FY00, so its funding level is actually greater than STTP and CST if annualized. The increased funding rate in the second half of FY00 for CSSX was required to accelerate the development of its technical maturity relative to the other processes. Also, it is noted that alpha and Sr removal shows a decrease in funding from FY00 to FY01, even though, as described below in Section 8.2, TFA has added funding in this area. It is anticipated that additional funding will be required to review literature studies of alternatives that are currently underway.

The funding allocation is presented in greater detail in Table 8.1.2. Funding for the various performing organizations is shown by work scope area for both FY00 and FY01. The work scope areas follow the outline presented in the R&D Program Description, Section 7.0

**Table 8.1.1. Research and Development Program Funding**

	FY00			FY01		
	EM-40	EM-50	Total	EM-40	EM-50	Total
Alpha and Sr Removal	435	1240	1675	1400	850	2250
CST Non-Elutable Ion Exchange	2957	2255	5212	2800	2700	5500
Caustic Side Solvent Extraction	3876	0	3876	4900	0	4900
Small Tank TPB Precipitation	885	2955	3840	800	4250	5050
<b>Grand Total</b>	<b>8153</b>	<b>6450</b>	<b>14603</b>	<b>9900</b>	<b>7800</b>	<b>17700</b>

**Table 8.1.2 Salt Processing R&D Funding Allocation by Work Area and Performing Organization**

	FY00						Total	FY01						Total
	ORNL	SRTC	ANL	SNL	PNNL	ORNL		SRTC	ANL	SNL	PNNL			
<b>Alpha and Sr Removal</b>														
MonoNa Titanate (MST) Kinetics and Equilibrium		160						500						
Alternative Alpha Removal Technologies		205						750						
MST Filtration and Settling		515						600						
Feed Clarification Alternatives		375						200						
On-Line Effluent Monitor					420			200						
	0	1255	0	0	420	1675	0	2250	0	0	0	2250		
<b>CST Non-Elutable Ion Exchange</b>														
CST Column Performance														
Refinement of the Model		275												
Column Configuration														
Alternative Column Design		150					50	700						
CST Adsorbent Stability														
Alternative Pretreatment of IE-911				75				300		250				
CST Chemical and Thermal Stability	300	1180		200	100		400	750		200	150			
Waste/CST Precipitation Studies	100	110					100	200						
Revised Manufacturing Process	80	740		50			100	500						
Gas Generation														
Gas Disengagement	400	62					300	300						
Cs Loading Under Irradiation	750													
CST Hydraulic Transfer														
Develop And Test Size-Reduction Method		640						500						
Develop Representative Sampling of CST/Sludge/Frit Slurry								400						

	FY00						Total	FY01					
	ORNL	SRTC	ANL	SNL	PNNL	ORNL		SRTC	ANL	SNL	PNNL	Total	
Coupled DWPF Operation													
DWPF Melter Operation								300					
	1630	3157	0	325	100	5212	950	3950	0	450	150	5500	
<b>Caustic Side Solvent Extraction</b>													
Solvent Preparation	481						400						
Batch Equilibrium With Internal Irradiation Of Solvent	527	487					100						
Batch Equilibrium With External Irradiation Of Solvent		538						100					
Solvent Physical/Chemical Properties	426						500						
Solvent Decomposition And Contactor Hydraulic Performance	658						3000						
Waste Simulant And 2-cm Contactor Flowsheet			692						700				
Solvent Commercialization	67						100						
	2159	1025	692	0	0	3876	4100	100	700	0	0	4900	
<b>Small Tank TPB Precipitation</b>													
Tetraphenylborate Decomposition Studies	1740	1440					1900	1300					
Cs Precipitation Kinetics								250					
Washing And Filtration Studies								500					
Antifoam Development		660						300					
Saltstone Facility													
Hydrolysis Testing								500					
Glass Formulation Studies								300					
	1740	2100	0	0	0	3840	1900	3150	0	0	0	5080	
<b>Grand Total</b>	5529	7537	692	325	520	14603	6950	9450	700	450	150	17700	

## 8.2 Recommendations from TFA Roadmap Review

Key personnel from in the SPP technology development program met in a two-day workshop to review the technology development roadmaps for alpha and Sr removal, CST, CSSX, and STTP. Attendees included members of the TFA TAG, TFA SPP Technology Development, TFA Program Management, WSRC HLW Waste Process Engineering, SRTC, and DOE-SR. Members of the WSRC HLW Processing Engineering Group presented detailed descriptions of the technology roadmaps, and extensive discussions covering all the roadmaps occurred. The TFA reviewers concluded that the proposed technology development program and test plans were generally complete. Specific recommendations for additional workscope and the performing organizations are described below. The primary focus of the recommendations is the desire to expand SNL's participation in the CST resin stability program and the belief that greater effort is needed on an alternative alpha removal technologies. If promising alternative processes are identified in laboratory testing, expanded work in alternative solid-liquid separations will be recommended if filtration is no longer the preferred approach.

Recommendations from the roadmap reviews and funding needs are summarized in Table 8.2.1.

### Westinghouse Savannah River Company

- **Analyze HLW real waste samples for colloidal plutonium (FY00 \$10K).** The knowledge of the species and physical state of Pu and other actinides in HLW salt solutions is key to developing an effective alpha removal process. Currently scheduled HLW samples should be filtered and analyzed for colloidal Pu in addition to the currently planned characterization. No additional samples are anticipated.
- **Conduct an engineering study of alternative CST column configurations or designs (FY00 \$150K).** Certain technical concerns (chemical stability, thermal stability, curie loading, etc.) are intensified by the current large column design and long exposure of CST to waste solutions.
- **Provide support to a feasibility study for carrying out an additional STTP real waste test (FY00 \$20K).** This study will be conducted by the TFA System Lead for STTP. The results of previous real waste tests (WSRC-TR-99-00345) cannot be considered conclusive due to foaming and fluid flow difficulties. The desired future test should demonstrate the chosen antifoam agent, overcome fluid-flow difficulties with small-scale equipment, and evaluate the impact of a temperature ramp-up after steady state has been achieved. Hot cell space, requirements for significant volume of real waste and potential interference with

other planned tests must be evaluated before committing to this test as a FY-01 activity.

- **Begin laboratory scoping tests on alternative alpha removal processes (FY00 \$50K).** A paper study of alternative alpha removal technologies is currently underway. Laboratory scoping tests on promising technologies should begin in late FY00, and are expected to continue in FY01.
- **Laboratory confirmation of recommended alternatives CST pretreatment process (FY01 \$TBD).** Confirm the effectiveness of the SNL recommended pretreatment process through performing laboratory leaching and real waste column testing.

#### **Sandia National Laboratory (SNL)**

- **Characterization of CST samples used in SRTC and ORNL studies (FY00 \$200K).** Non-radioactive treated samples of CST, including data on their performance, will be sent to SNL from SRTC and ORNL. SNL will utilize a variety of analytical techniques to determine if and/or when CST phase changes have occurred and to assess if pore blockage might be happening. Once an understanding of the underlying mechanism is obtained, SNL will perform additional analysis of the ORNL and SRTC samples, as necessary, to define the time-temperature, waste composition operability regime (based on phase changes and/or pore blockages) for CST.
- **Develop alternative CST pretreatment process (FY01 \$250K).** Based on results obtained from characterization of CST samples, SNL will perform scoping laboratory experiments leading to a proposed alternative CST pretreatment process. SNL will perform laboratory leaching and simulant column testing to confirm the effectiveness of the recommended pretreatment process.
- **Evaluate SRS and ORNL results on leaching CST with NaOH (FY00 \$75K).** SNL believes the column plug observed at SRS is likely based on the amphoteric behavior of one (or more) metal oxides over the pH range likely to have been experienced during the course of the CST pretreatment process. SNL will utilize non-radioactive treated samples of CST from SRS and ORNL (see task above) to prepare one or more columns of CST, pretreating each with NaOH. Periodically during the pretreatment process, solids and liquids will be removed and characterized.

#### **Pacific Northwest National Laboratory (PNNL)**

- **Examination of temperature effects on CST structure, phase changes, and Cs sorption (FY00 \$100K).** PNNL is in the final year of an EMSP project where

they have performed related CST work. PNNL has performed high temperature (500°-1000°C) experiments on Cs loaded (CsCl) CST to determine sorption, structural and phase changes upon heating. This task will investigate lower temperature (25°-80°C) effects of temperature on CST sorption, structure, and phase changes.

**Table 8.2.1 Worskscope and Funding Recommendations  
 from TFA Roadmap Review**

<b>Task</b>	<b>Performer</b>	<b>FY00</b>	<b>FY01</b>
Analyze HLW real waste samples for colloidal plutonium	WSRC*	10	0
Characterization of CST samples used in SRTC and ORNL studies	SNL	200	200
Examination of temperature effects on CST structure, phase changes, and Cs sorption	PNNL	100	150
Conduct an engineering study of alternative CST column configurations or designs	WSRC	150	0
Develop alternative CST pretreatment process	SNL	0	250
Support a feasibility study for carrying out an additional Small Tank TPB real waste test	WSRC	20	0
Begin laboratory scoping tests on alternative alpha removal processes	WSRC*	50	150
Evaluate SRTC and ORNL results on leaching CST with NaOH	SNL	75	0
Laboratory confirmation of recommended alternative CST pretreatment process	WSRC	0	300
<b>TOTALS</b>		<b>605</b>	<b>1050</b>

### 8.3 Overview of the Salt Processing Program Schedule

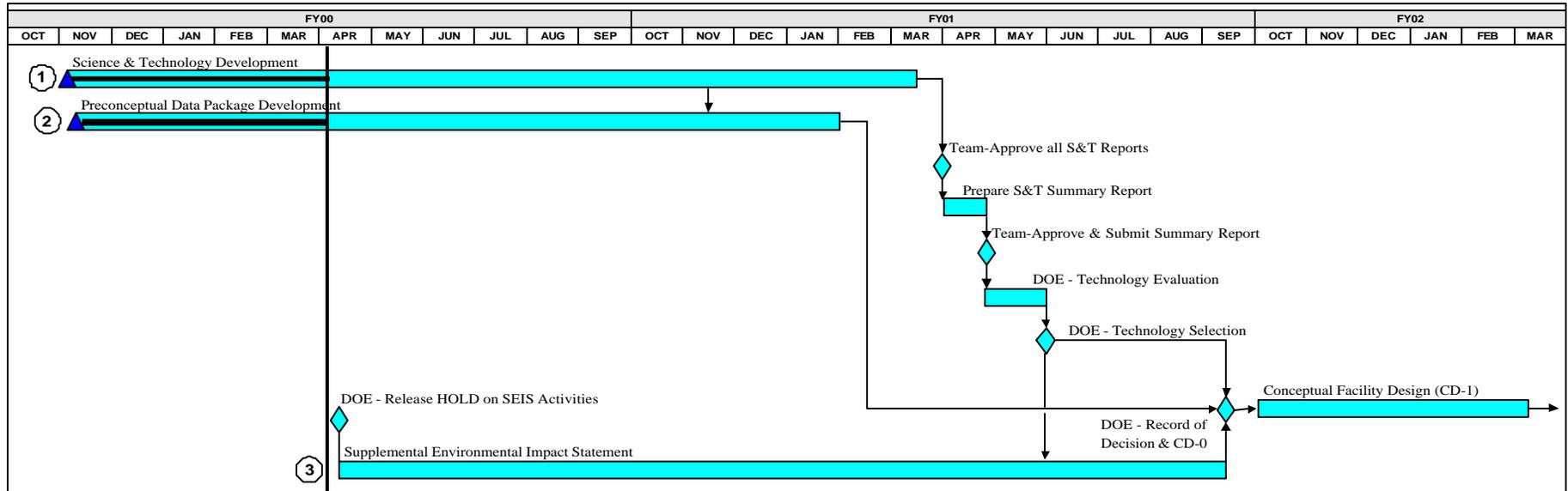
The Level 0 Schedule for the SPP is presented in Figure 8.3.1. Science and technology development will proceed in parallel with preconceptual data package development, and science and technology reports for each Cs removal process will be prepared by March 31, 2001. The alpha and Sr removal approach that optimizes each flowsheet will be addressed in these reports. A science and technology summary report will be provided to DOE in support of the technology down selection. The down selection decision will feed into preparation of the SEIS and a Record of Decision by September 30, 2001.

### 8.4 Research and Development Program Schedule

A detailed schedule has been prepared for all R&D activities and related engineering work. A summary level schedule showing the major activities and their duration is shown in Figure 8.4.1. The complete detailed schedule is shown in Appendix C. The

detailed schedule in Appendix C is used by all program participants to manage their work. Schedule status is presented at a technology development Plan-of-the-Week Meeting and an SPP Plan-of-the-Week Meeting. Schedules are updated weekly. All changes that impact a Technical Task Plan-TTP-approved schedule, scope, or budget must be approved by the Change Control Board (see Section 9.0, R&D Program Controls). The summary (Level 0) schedule (Figure 8.4.1) shows that several R&D activities proceed well into FY01. STTP bench-scale CST studies, CSSX real waste tests, CST manufacturing revisions with UOP, and MST kinetics/Pu oxidation state are examples of long-term activities. The program's goal is to resolve all high-risk technology issues in time to support the down select decision shown in Figure 8.4.1. It is fully anticipated that technology development activities will continue for the selected alternative(s) well into the design phase.

Figure 8.3.1 Salt Waste Processing Level 0 Schedule



**Figure 8.4.1 Summary R&D Program Schedule**

[CST Charts](#) (downloadable PDF format)  
[CSSX Charts](#) (downloadable PDF format)  
[TBP Charts](#) (downloadable PDF format)

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02					
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D			
<b>A-1 CST Stability/Cs Leaching/Manufacturing Rev</b>																																				
ASCST200	98*	123	19NOV99A	04OCT00	DDW	0.00	2.0 Cs Removal Kinetics & Equilibrium (FY00)<HA>																													
ASCST21	203*	18	21FEB00A	08MAR01	WRW	262.48	Cs Resin - Manufacturing Revisions with UOP <HA>																													
ASCST212	4*	217	03JAN00A	22MAY00	WRW	1.84	Effect of NaOH Pretreatment Tests <HA>																													
ASCST23	156*	65	03JAN00A	29DEC00	DDW	209.43	CST Thermal Stability Issues <HA>																													
ASCST24	35*	186	03JAN00A	06JUL00	FF	16.14	Cs Kinetics (Real Waste Tests) <HA>																													
ASCST52	153*	68	03JAN00A	22DEC00	FF	106.00	AlkEarth Metals, Carbonate, Oxalate & Perox <HA>																													
ASORNL2201	140*	83	01OCT99A	05DEC00	TK	0.00	CST Stability and Cs Leaching <HA>																													
ASORNL2202	0*		03NOV99A	18NOV99A	TK	0.00	Plans and Safety Documents <HA>																													
ASORNL2204	0*		22NOV99A	08FEB00A	TK	0.00	Develop TTP <HA>																													
ASORNL2211	74*	543	01OCT99A	31AUG00	TK	0.00	CST Batch Stability Leaching Long Term Test <HA>																													
ASORNL2219	184*	433	12JAN00A	07FEB01	TK	0.00	Long Term Flow Through Column Studies <HA>																													
ASORNL2225	118*	85	01OCT99A	02NOV00	TK	0.00	Data Collection and Reporting <HA>																													
<b>A-2 CST Size Reduction</b>																																				
ASCST1900	122*	99	19NOV99A	07NOV00	FGS	0.00	DWPf Waste Qualification, Feed Homogeneity <HA>																													
ASCST191	110*	111	17JAN00A	20OCT00	FGS	161.19	Develop Representative Sampling SRAT/SME <HA>																													
ASCST1911	110*	111	17JAN00A	20OCT00	FGS	0.00	Cause of NonRepresentative HydraGard Sample <HA>																													
ASCST192	50*	171	17JAN00A	27JUL00	FGS	7.40	Develop and Test Size Reduction Method <HA>																													
ASCST193	35*	528	29SEP00	16NOV00	FGS	0.00	Assess On-Line Particle Size Analyzers <HA>																													
ASCST194	122*	99	17JAN00A	07NOV00	FGS	92.83	Determine How to Suspend CST in DWPf <HA>																													

Start Date 01OCT98  
 Finish Date 16SEP02  
 Data Date 17MAY00  
 Run Date 17MAY00 18:38  
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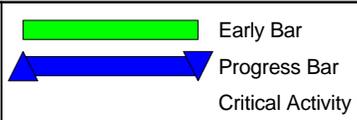
 Early Bar  
 Progress Bar  
 Critical Activity

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02											
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D									
ASCST195	95*	32	29SEP00	15FEB01	FGS	0.00	Demo Feed of CST/Sludge/Frit Slurry to Melter HA																																			
A-3 Engineering Filtration Studies																																										
ASCST600	138*	519	19NOV99A	01DEC00	MRP	0.00	6.0 Engineering Filtration Studies <HA>																																			
ASCST61	26*	511	14FEB00A	22JUN00	MRP	2.69	Role of TPB in Filtration <HA>																																			
ASCST62	138*	519	24JAN00A	01DEC00	MRP	162.11	Improve Filtration Rates & Flows <HA>																																			
ASCST623	60*	477	24JAN00A	10AUG00	MRP	162.98	Cross-flow Filter Optimization FRED Testing <HA>																																			
A-4 Waste CST/Precipitation/Kinetics																																										
ASCST500	178*	479	19NOV99A	31JAN01	DDW	0.00	5.0 CST Precip/Kinetics Issues (Simulant) <HA>																																			
ASCST51	107*	550	03JAN00A	17OCT00	DDW	42.19	Stability of Simulated Waste Solutions <HA>																																			
ASORNL4001	114*	109	03NOV99A	27OCT00	TK	0.00	Waste and Simulant Precipitation Issues <HA>																																			
ASORNL4002	0*		03NOV99A	15FEB00A	TK	0.00	Plans and Safety Documents <HA>																																			
ASORNL4004	0*		22NOV99A	30DEC99A	TK	0.00	Develop TTP <HA>																																			
ASORNL4011	0*		03JAN00A	31MAR00A	TK	0.00	Initial SolGasMix Calculations <HA>																																			
ASORNL4014	18*	170	15FEB00A	12JUN00	TK	0.00	Laboratory Confirmation Tests <HA>																																			
ASORNL4020	27*	136	01MAY00A	23JUN00	TK	0.00	SolGasMix Calculations with CST Components <HA>																																			
ASORNL4023	82*	109	26JUN00	20OCT00	TK	0.00	Laboratory Confirmation Tests <HA>																																			
Alternative Column Config, Gas Disengagement																																										
ASCST8000	134*	523	08NOV99A	27NOV00		0.00	A-5 CST IX - Alternate Column Studies <HA>																																			
ASORNL5001	134*	533	03NOV99A	27NOV00	TK	0.00	Heat Transfer Calcs, Gas Disengagement <HA>																																			
ASORNL5002	0*		03NOV99A	30DEC99A	TK	0.00	ORNL - Plans and Safety Documents <HA>																																			
ASORNL5006	33*	634	17JAN00A	05JUL00	TK	0.00	ORNL - Measure Thermal Conductivity <HA>																																			
ASORNL5015	58*	535	04JAN00A	09AUG00	TK	0.00	ORNL - Prepare Tall Column System <HA>																																			
ASORNL5017	8*	631	04JAN00A	26MAY00	TK	0.00	ORNL - Prepare Design Package <HA>																																			



Activity ID	Activity Description	Rem Dur	Total Float	Early Start	Early Finish	SOW Matrix	Lead	FY00												FY01											
								J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S			
<b>Caustic Side Solvent Extraction</b>																															
<b>CSSX - SRTC FY 2000 Related Activities</b>																															
ASCX41	Solvent Radiolytic & Chemical Stability <HA>	213*	8	12APR00A	22MAR01	B411	RAP	Solvent Radiolytic & Chemical Stability <HA>																							
ASCX411	External Radiation Tests (Co-60 Source) <HA>	71*	125	12APR00A	25AUG00	B411	RAP	External Radiation Tests (Co-60 Source) <HA>																							
ASCX412	Batch Equilibrium Hot Cell Test (Interim Rpt)<HA>	213*	8	12APR00A	22MAR01	B41A	RAP	Batch Equilibrium Hot Cell Test (Interim Rpt)<HA>																							
<b>CSSX- ORNL FY2000 Related Activities</b>																															
ASORN7004	Solvent Extraction Development <HA>	193*	30	07APR00A	20FEB01	CX1	LNK	Solvent Extraction Development <HA>																							
ASORN7005	Solvent Preparation (TTP ORNL CASD-1) <HA>	49*	-7	07APR00A	27JUL00	B313	LNK	Solvent Preparation (TTP ORNL CASD-1) <HA>																							
ASORN7036	Flowsheet Test on Waste Simulant TTP ANL-1 <HA>	126*	97	17MAY00	14NOV00	B310	LNK	Flowsheet Test on Waste Simulant TTP ANL-1 <HA>																							
ASORN7038	Improve Stage Efficiency <HA>	44*	1	03APR00A	20JUL00	B311	LNK	Improve Stage Efficiency <HA>																							
ASORN7043	Contacto Stage Addition <HA>	77*	77	07APR00A	06SEP00	B312	LNK	Contacto Stage Addition <HA>																							
ASORN7048	Contacto Test With 3-4X Solvent Recycle <HA>	126*	97	03APR00A	14NOV00	B314	LNK	Contacto Test With 3-4X Solvent Recycle <HA>																							
ASORN7058	Physical And Chemical Properties <HA>	148*	75	17MAY00	15DEC00	B510	LNK	Physical And Chemical Properties <HA>																							
ASORN7060	Partitioning and migration of solute species <HA>	89*	94	17MAY00	22SEP00	B510	LNK	Partitioning and migration of solute species <HA>																							
ASORN7066	Solvent Thermal Stability <HA>	101*	122	10MAY00A	10OCT00	B511	LNK	Solvent Thermal Stability <HA>																							
ASORN7070	Solvent Stability to External Irradiation <HA>	92*	83	30MAY00	09OCT00	B411	LNK	Solvent Stability to External Irradiation <HA>																							
ASORN7075	Effect of waste feed components <HA>	91*	91	18MAY00	27SEP00	B520	LNK	Effect of waste feed components <HA>																							
ASORN7078	Phase behavior of primary solvent components <HA>	77*	94	05JUN00	22SEP00	B511	LNK	Phase behavior of primary solvent components <HA>																							
ASORN7081	Batch Contacting with Single Cs-137 Spike <HA>	54*	80	03AUG00	18OCT00	B517	LNK	Batch Contacting with Single Cs-137 Spike <HA>																							
ASORN7085	Case 1: No Further Experiments Are Necessary	10*	578	11SEP00	22SEP00	B517	LNK	Case 1: No Further Experiments Are Necessary HA																							
ASORN7088	Case 2: Further Experiments Are Necessary	28*	80	11SEP00	18OCT00	B517	LNK	Case 2: Further Experiments Are Necessary <HA>																							
ASORN7094	Solvent Stability Study, Internal Irradiation	95*	76	16AUG00	29DEC00	B412	LNK	Solvent Stability Study, Internal Irradiation <HA>																							

Start Date 01OCT98  
Data Date 17MAY00  
Run Date 17MAY00 18:12



Activity ID	Activity Description	Rem Dur	Total Float	Early Start	Early Finish	SOW Matrix	Lead	FY00													FY01														
								J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S							
ASORN7099	Project Report <HA>	60*	496	25OCT00	19JAN01	B412	LNK														Project Report <HA>														
ASORN7108	Cs-137 Batch Irradiation with Simulant <HA>	182*	41	17MAY00	05FEB01	B412	LNK														Cs-137 Batch Irradiation with Simulant <HA>														
ASORN7112	Simulant Preparation <HA>	7*	126	10MAY00A	25MAY00	B413	LNK														Simulant Preparation <HA>														
ASORN7117	Hot Cell Batch Contacting with Cs137 Test <HA>	68*	-7	03APR00A	23AUG00	B517	LNK														Hot Cell Batch Contacting with Cs137 Test <HA>														
ASORN7126	Development of Batch Equilibrium Test Plan	23*	12	03APR00A	19JUN00	B412	LNK														Development of Batch Equilibrium Test Plan <HA>														
ASORN7133	Test preparation <HA>	35*	12	12JUN00	01AUG00	B412	LNK														Test preparation <HA>														
ASORN7134	Cs-137 Procurement <HA>	30*	47	12JUN00	25JUL00	B412	LNK														Cs-137 Procurement <HA>														
ASORN7141	Execute Test Protocol CTD-1 <HA>	130*	41	02AUG00	05FEB01	B412	LNK														Execute Test Protocol CTD-1 <HA>														
ASORN7146	Case 1: Terminate Test in 4th Qtr FY 2000 <HA>	38*	129	08AUG00	29SEP00	B412	LNK														Case 1: Terminate Test in 4th Qtr FY 2000 <HA>														
ASORN7151	Case 2: Terminate Test in 1st Qtr FY 2001 <HA>	126*	41	08AUG00	05FEB01	B412	LNK														Case 2: Terminate Test in 1st Qtr FY 2001 <HA>														
ASORN7161	Cs-137 Irradiation Contactor Test <HA>	193*	30	17MAY00	20FEB01	B413	LNK														Cs-137 Irradiation Contactor Test <HA>														
ASORN7163	Development of Test Plan SOW Item 4.1.3 <HA>	15*	54	03APR00A	07JUN00	B413	LNK														Development of Test Plan SOW Item 4.1.3 <HA>														
ASORN7171	Execute Project Test Plan CTD-2 <HA>	209*	458	03APR00A	14MAR01	B413	LNK														Execute Project Test Plan CTD-2 <HA>														
ASORN7186	Case 1: Terminate Test in 4th Qtr FY 2000 <HA>	38*	85	18AUG00	11OCT00	B413	LNK														Case 1: Terminate Test in 4th Qtr FY 2000 <HA>														
ASORN7191	Case 2: Terminate Test in 1st Qtr FY01 CTD-2 <HA>	145*	458	18AUG00	14MAR01	B415	LNK														Case 2: Terminate Test in 1st Qtr FY01 CTD-2 <HA>														
ASORN7203	CSSX Technology Transfer <HA>	94*	12	17MAY00	29SEP00	B600	LNK														CSSX Technology Transfer <HA>														
ASORN7205	Patent disclosure- 2nd generation modifier <HA>	45*	61	03APR00A	21JUL00	B600	LNK														Patent disclosure- 2nd generation modifier <HA>														
ASORN7208	Patent disclosure on calix synthesis <HA>	85*	21	10MAY00A	18SEP00	B600	LNK														Patent disclosure on calix synthesis <HA>														
ASORN7211	Identify Commercial Suppliers	59*	18	28JUN00	21SEP00	B600	LNK														Identify Commercial Suppliers														
ASORN7218	Project Technical & Programmatic Management	116*	541	01JUN00	14NOV00	CX1	LNK														Project Technical & Programmatic Management <HA>														
<b>CSSX - Commercialization &amp; Supply Assurance</b>																																			
ASCX33000	Solvent Commercialization- Assure Supply <HA>	464*	57	10MAY00A	16SEP02	B600	RWB														Solvent Commercialization- Assure Supply <HA>														
ASCX33300	Request For Information <HA>	173*	10	10MAY00A	29MAR01	B600	RWB														Request For Information <HA>														
ASCX33600	Request For Quotation <HA>	133*	57	02APR01	28NOV01	B600	RWB														Request For Quotation <HA>														
<b>CSSX - Operating Chemical Supply &amp; Fabrication</b>																																			
ASCX33900	CSSX - Initial Commercial Manufacture <HA>	150*	57	13DEC01	16SEP02	B600	RWB																												



Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00													FY01													FY02			
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D			
<b>S-1 TPB Precipitation - Catalyst Activation</b>																																				
ASORN2001	55*	168	08DEC99A	04AUG00	TK	0.00	NMR Studies (Work Scope Matrix 2.2.4.1) <HA>																													
ASORN2002	0*		08DEC99A	22DEC99A	TK	0.00	Plans and Safety Documents <HA>																													
ASORN2004	0*		10DEC99A	22DEC99A	TK	0.00	Develop TTP <HA>																													
ASORN2011	8*	173	02FEB00A	26MAY00	TK	0.00	Information Gathering <HA>																													
ASORN2016	32*	171	17MAY00	30JUN00	TK	0.00	Perform Tests <HA>																													
ASTPB200	143*	78	19NOV99A	08DEC00	MJB	89.15	2.0 TPB Reaction Kinetics (FY00) <HA>																													
ASTPB22	108*	113	12JAN00A	18OCT00	MJB	0.00	Define Catalyst / Synergistic Effects <HA>																													
ASTPB2200	53*	23	12JAN00A	01AUG00		0.00	SRTC TPB Catalyst Studies <HA>																													
ASTPB2201	120*	101	30MAR00A	03NOV00	RAP	0.00	X-Ray Absorption Spectroscopy (EXAFS) <HA>																													
ASTPB222	55*	104	26JUN00	12SEP00	MJB	0.00	Role of Intermediates Tests <HA>																													
ASTPB223	108*	113	28JAN00A	18OCT00	MJB	278.36	Synergistic Effects Tests <HA>																													
ASTPB224	30*	191	24JAN00A	28JUN00	RAP	0.00	Mechanistic Pd Tests <HA>																													
ASTPB225	143*	78	24JAN00A	08DEC00	TBP	0.00	Electrochem/Spectroscopic Transition Metals <HA>																													
ASTPB226	65*	104	12JUN00	12SEP00	MJB	0.00	Ru/Rh Activation <HA>																													
ASTPB227	0*		14FEB00A	12MAY00A	LNO	0.00	Expanded Metals Tests <HA>																													
ASTPB228	82*	108	30JUN00	25OCT00	MJB	0.00	Develop and Test New Simulant <HA>																													
ASTPB23	130*	91	01MAR00A	17NOV00	MJB	0.00	Real Waste TPB Kinetics Test #2 <HA>																													
ASTPB233	113*	108	08FEB00A	25OCT00	MJB	118.36	Real Waste TPB Kinetics Test #1 <HA>																													

Start Date 01OCT98  
 Finish Date 16SEP02  
 Data Date 17MAY00  
 Run Date 17MAY00 18:36



FY2K [Page X of Y]  
 Westinghouse Savannah River  
 Salt Waste Disposition Program  
 TPB Precipitation (Summary)

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02											
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D									
<b>S-2 Anti-Foam Development</b>																																										
ASTPB500	100*	121	19NOV99A	06OCT00	DPL	0.00	5.0 Physical Property Data - Antifoam <HA>																																			
ASTPB51	27*	630	19NOV99A	23JUN00	DPL	0.00	IIT Antifoam Study <HA>																																			
ASTPB52	91*	130	31JAN00A	25SEP00	DPL	128.56	Antifoam Test on Simulant Waste (Bench-scale) HA																																			
ASTPB55	45*	121	04AUG00	06OCT00	MRP	37.80	Test Most Efficient Antifoam Agent (PREF) <HA>																																			
ASTPB56	70*	393	26FEB01	05JUN01	RAP	0.00	Real Waste Antifoam Test <HA>																																			
<b>TPB Solubility Data</b>																																										
ASORNL3001	221*	2	01OCT99A	30MAR01	TK	0.00	Bench Scale CSTR Studies <HA>																																			
ASORNL3002	0*		01OCT99A	01FEB00A	TK	0.00	Work Planning <HA>																																			
ASORNL3004	0*		22NOV99A	22DEC99A	TK	0.00	Develop TTP <HA>																																			
ASORNL3010	0*		19NOV99A	19JAN00A	TK	0.00	Develop Schedule <HA>																																			
ASORNL3015	0*		24JAN00A	01FEB00A	TK	0.00	Planning for FY 2001 Pilot Scale CSTR <HA>																																			
ASORNL3018	94*	75	15DEC99A	29SEP00	TK	0.00	Safety & QA Planning <HA>																																			
ASORNL3025	51*	47	04OCT99A	31JUL00	TK	0.00	20 L Hot Cell CSTR Preparations <HA>																																			
ASORNL3047	28*	46	24JAN00A	26JUN00	TK	0.00	Update Control System <HA>																																			
ASORNL3061	0*		29OCT99A	09FEB00A	TK	0.00	20 L Cold CSTR Preparations <HA>																																			
ASORNL3067	48*	24	05JUL00	11SEP00	TK	0.00	ORNL TPB Catalyst Lab Scale Activation <HA>																																			
ASORNL3077	84*	85	04AUG00	01DEC00	TK	0.00	CSTR Cold Open Loop Tests <HA>																																			
ASORNL3106	74*	33	25SEP00	09JAN01	TK	0.00	CSTR Closed Loop Hot Cell Tests <HA>																																			
ASTPB42	153*	410	29SEP00	10MAY01	MRP	0.00	Perform Dissolution Tests <HA>																																			
ASTPB4250	88*	312	27DEC00	05JUN01	RK	0.00	Develop Scale Equipment Design <HA>																																			
<b>Na, K, Cs, TPB Precipitation Kinetics</b>																																										
ASTPB41	205*	350	11OCT00	06AUG01	RAP	0.00	TPB Precipitation Testing <HA>																																			





## **9.0 R&D Program Controls**

The following section outlines the basic premise on which SPP/R&D project management/control procedures will be defined. Existing project procedures and plans will be reviewed and appropriately used as the basis for TFA SPP/R&D project control procedures and management requirements. The TFA SPP/R&D project control procedures and management requirements will define the following:

- requirements for project planning and baseline development
- project evaluation and review criteria
- reporting requirements
- change control procedures/approval process
- performer and contractor roles and responsibilities

These procedures will be documented in an SPP/R&D Project Management and Controls Document and will be communicated to the SPP/R&D team, including the individual performers responsible for execution of the technical activities.

### **9.1 Work Authorization**

Scope, cost, and schedule of SPP/R&D work for the SRS salt disposition alternatives will be documented in performer-developed TTPs, prepared in response to PEG/TTR issued by the TFA SPP/R&D. The TTPs will be concurred on by the appropriate performer, System Lead, TFA SPP/R&D TDM, and DOE-SR SPP Manager, and will be approved by the TFA Program Manager. Funding for SPP/R&D TTPs is provided by EM-50 through the TFA Financial Plan, and by EM-40 through the DOE-SR Financial Plan, Interoffice Work Orders (IWO) and Annual Operating Plan (AOP).

### **9.2 Change Control**

The technical baseline established in the R&D Program Plan will provide the basis on which overall change will be evaluated. Any changes affecting the R&D Program Plan will be approved by the TWG prior to implementation.

TTPs are developed to implement specific technical activities necessary to meet the objectives established in the R&D Program Plan. All changes that impact a TTP's approved scope, schedule, or budget are subject to the review and approval of the CCB prior to formal submission for subsequent approvals or implementation. The CCB will be led by the TFA SPP/R&D TDM, and will include the TFA SPP/R&D Deputy/Project Controls Manager, System Leads, the SRS Pre-Conceptual Engineering Manager, and the DOE-SR SPP Manager.

CCB approved changes with budget impact of greater than \$100K, which affect a TFA level milestone<sup>1</sup>, or require a fin plan or other contractual/budget change will be approved by the TFA Program Manager. The TFA Program Manager (EM-50) and the DOE-SR SPP Manager (EM-40) will be responsible for approving and submitting formal budget/contract changes identified in the TCR according to the requirements of the particular TTP funding type (i.e., fin plan, IWO, AOP). In addition, the CCB and the TFA Program Manager will evaluate all changes for their impact to the technical baseline, to ensure proper coordination and approval of the TWG. Changes expected to meet this criteria, requiring TWG approval, would include TWG directed changes, changes in technology options, changes with a budget impact of greater than \$1M, or changes which impact to a TWG level<sup>22</sup> milestone.

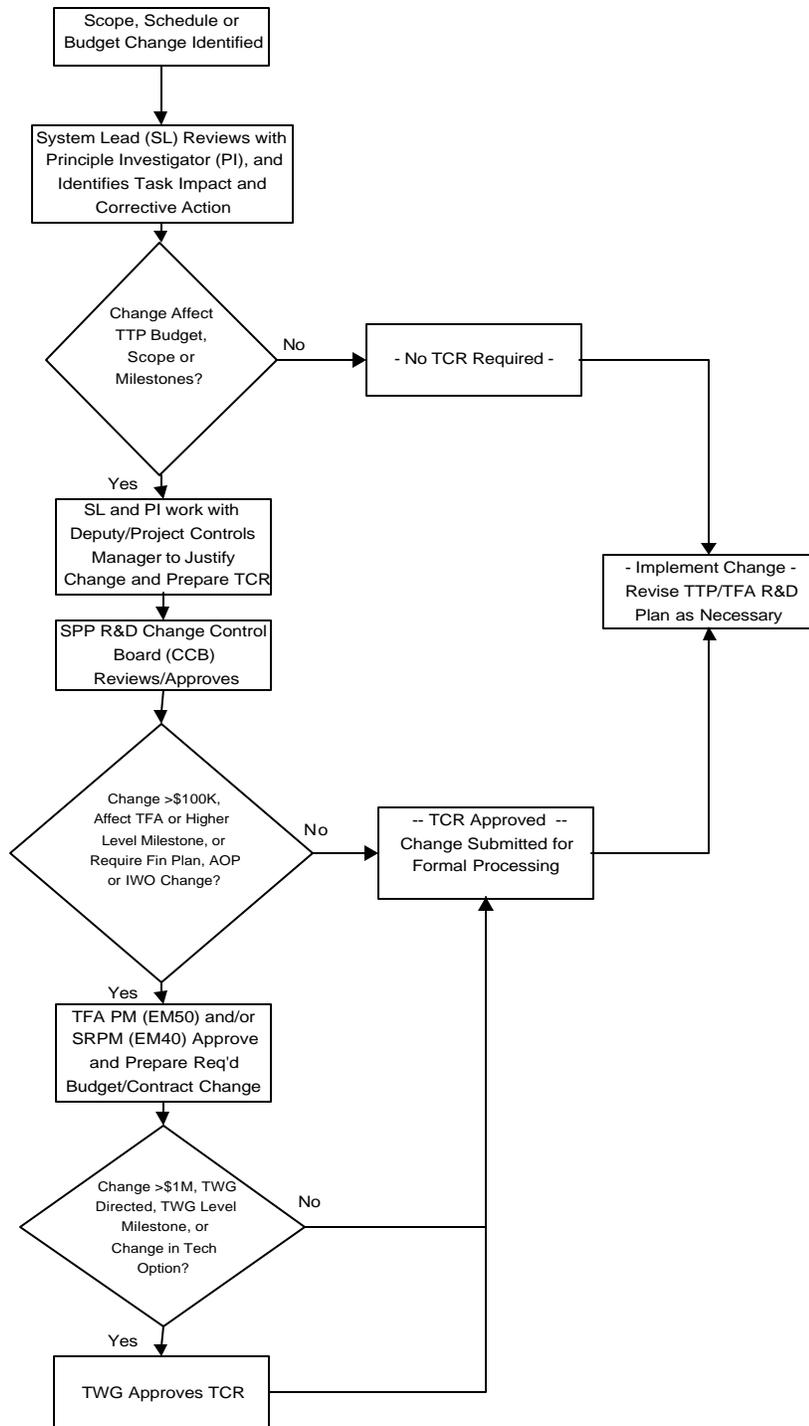
Changes will be submitted via a Technical Change Request (TCR) (see Appendix A.4), and may be initiated by any of the individuals who have concurred on or approved the TTP. All TCRs will be initially sent to the TFA SPP/R&D Deputy/Project Controls Manager for review to ensure that the TCR contains adequate justification. The TFA SPP/R&D Deputy/Project Controls Manager will coordinate the CCB review, as well as additional reviews and approvals required by the type of change. Once fully approved, the TCR will be submitted to the appropriate contract and budget authority for processing.

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<sup>1</sup> TFA and TWG level milestone criteria will be defined in the SPP/R&D Project Management and Controls Document.

<sup>2</sup> TFA and TWG level milestone criteria will be defined in the SPP/R&D Project Management and Controls Document.

Figure 9.1. Change Control Process



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## **Appendix A**

### **Salt Processing Technology Development Roadmaps and Logic Diagrams**

The guiding documents for this Research and Development Program Plan are the Science and Technology Roadmaps for Alpha and Strontium (Sr) Removal, Small Tank Tetraphenylborate Precipitation (STTP), Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange and Caustic Side Solvent Extraction (CSSX). The Science and Technology Roadmaps provide the technology development paths forward towards successful deployment of the three options. The Tanks Focus Area has conducted a review of the existing roadmaps and has recommended additions to the current workscope, including evaluation of alternative processes for alpha and Sr removal. The recommended changes are highlighted ("clouded") on the roadmaps presented herein. If the Technical Working Group approves these changes, they will become part of the Salt Processing Project technical baseline.

Matrix Legend

Item No.	Corresponds to the block number on the Science and Technology Roadmap and Logic Diagrams; provides a tie between documents.
Item	General title of the S&T block; corresponds to block title on the Science and Technology Roadmap and Logic Diagrams.
Considerations	Discusses the considerations pertinent to the completion and resolution of each item; provides details and numbered R&D activities to be performed to resolve the item (numbered R&D activities correspond to numbered activities on logic diagrams). Italicized text is extracted from previous roadmaps and reflects activities previously completed or no longer required.
Scale	Defines the scale at which R&D test will be performed (Lab scale, bench scale, engineering scale or pilot scale).
Lead Org.	Identifies the organization responsible for conducting the R&D activity and hence location where activity will be performed.
Path Forward Doc.	Lists the applicable Technical Task Requests (TTRs) denoted xxxx <sup>1</sup> ; Task Technical and Quality Assurance Plans (TTPs) denoted xxxx <sup>2</sup> and Test Reports (TRs) denoted xxxx <sup>3</sup> which respectively initiate, plan and document the results of R&D activities.
Reference Doc.	Lists reference documents such as previous test results, reviews etc., which relate to the current R&D activity.
Uncertainty	Provides a cross-tie to the cost validation matrix uncertainty statement Ids within the Decision Phase Final Report, WSRC-RP-99-00007.
NA	Not Applicable

Figure A.1 Alpha and Strontium Removal

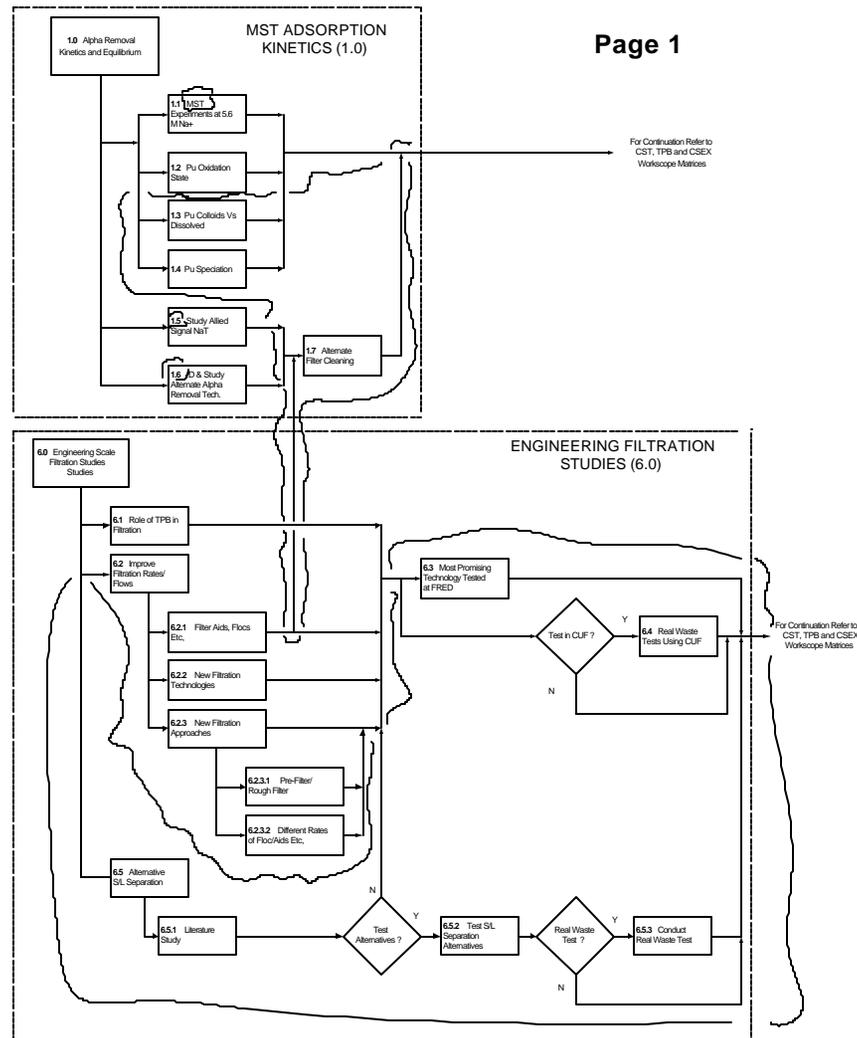
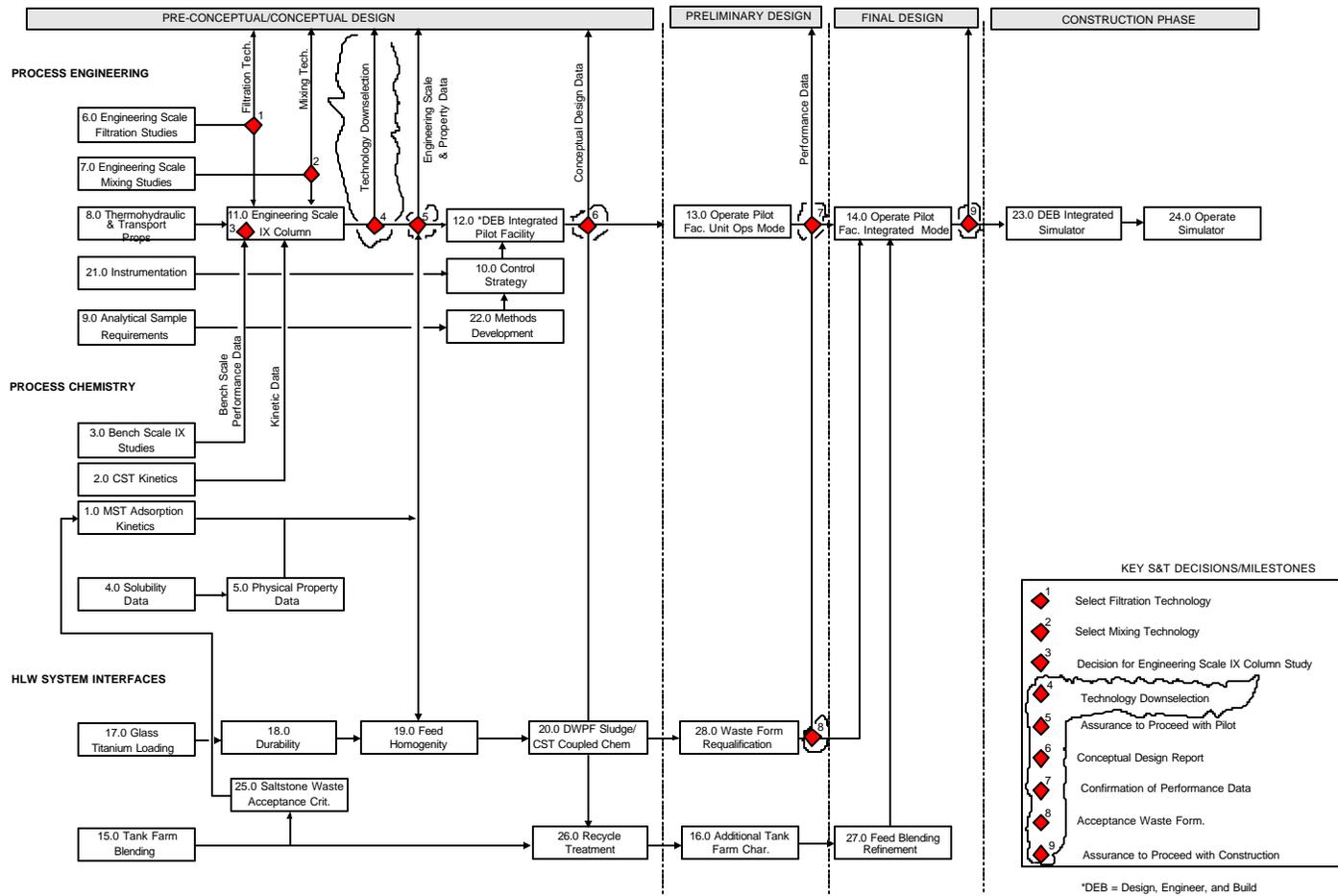
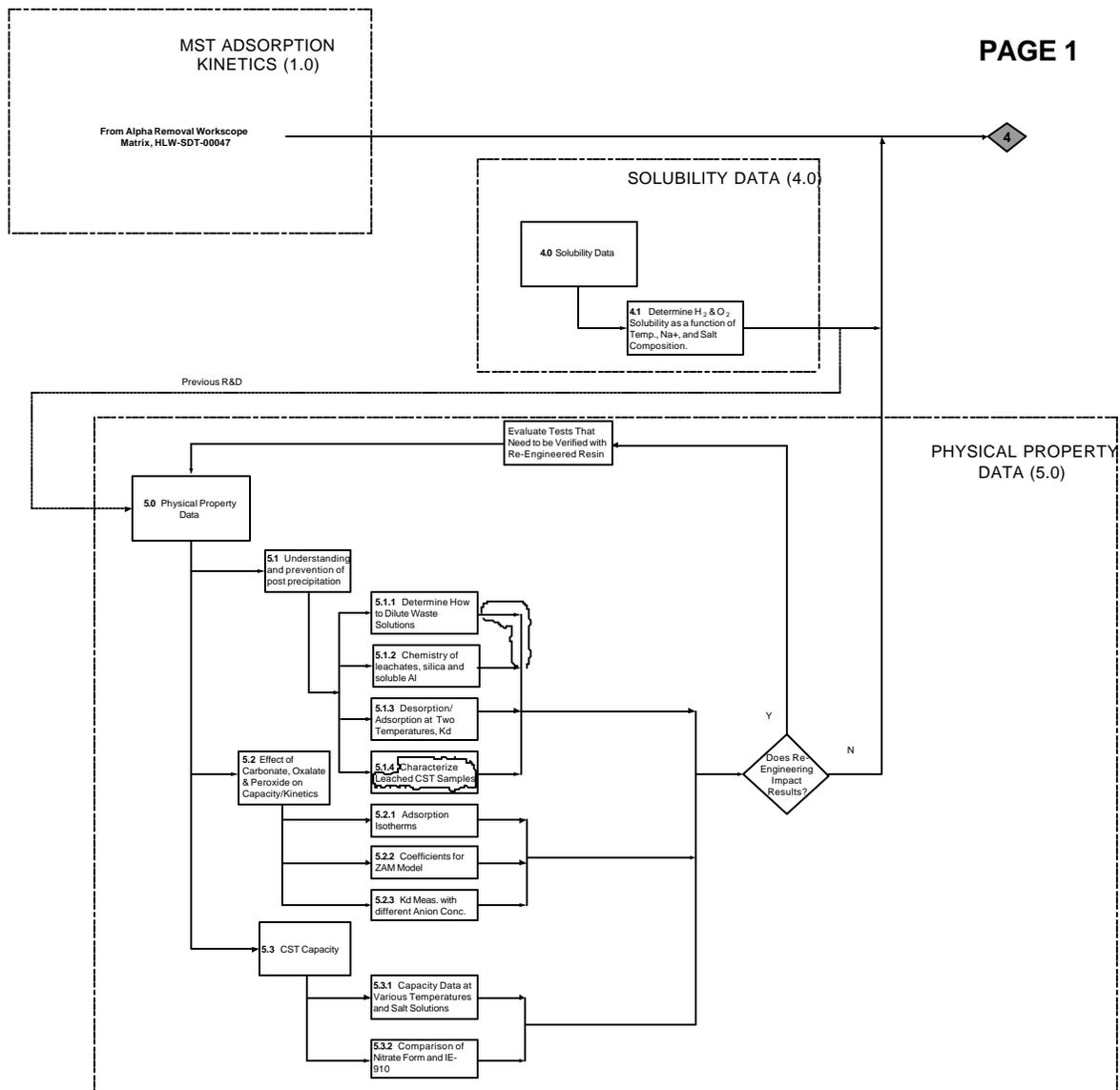
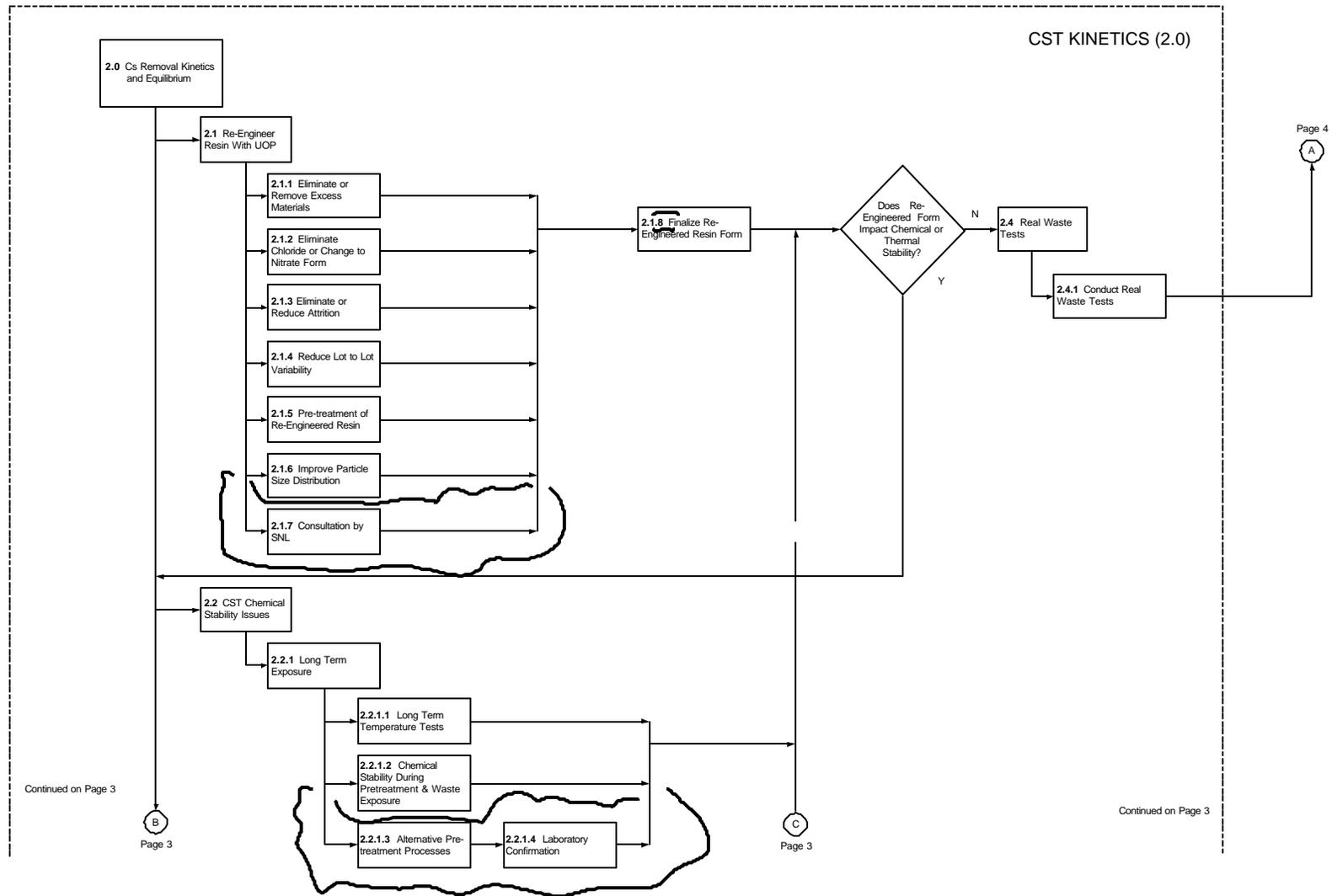


Figure A.2 Crystalline Silicotitanate Non-Elutable Ion Exchange

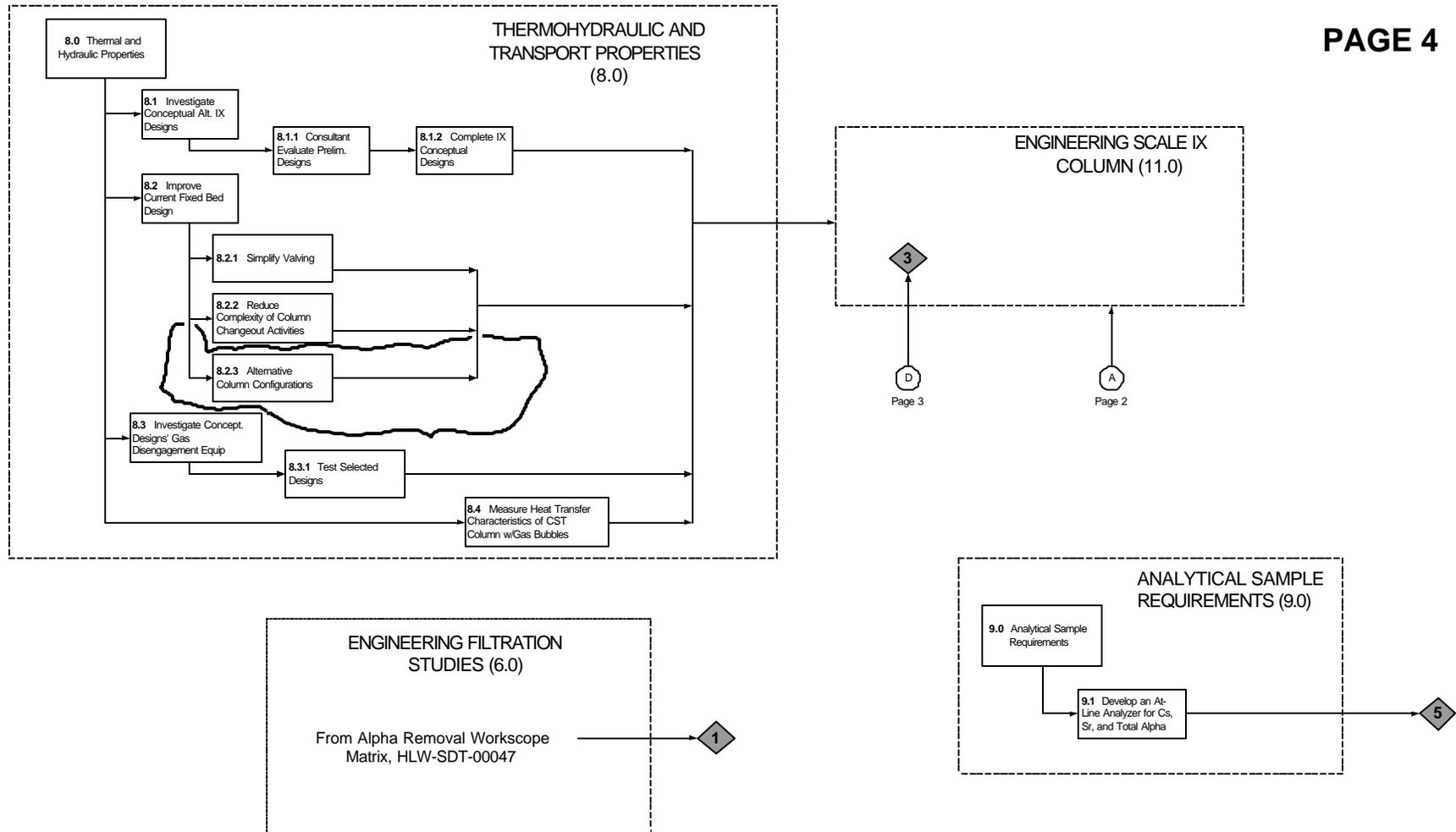
SCIENCE AND TECHNOLOGY ROADMAP FOR CST NON-ELUTABLE ION EXCHANGE CESIUM REMOVAL PROCESS











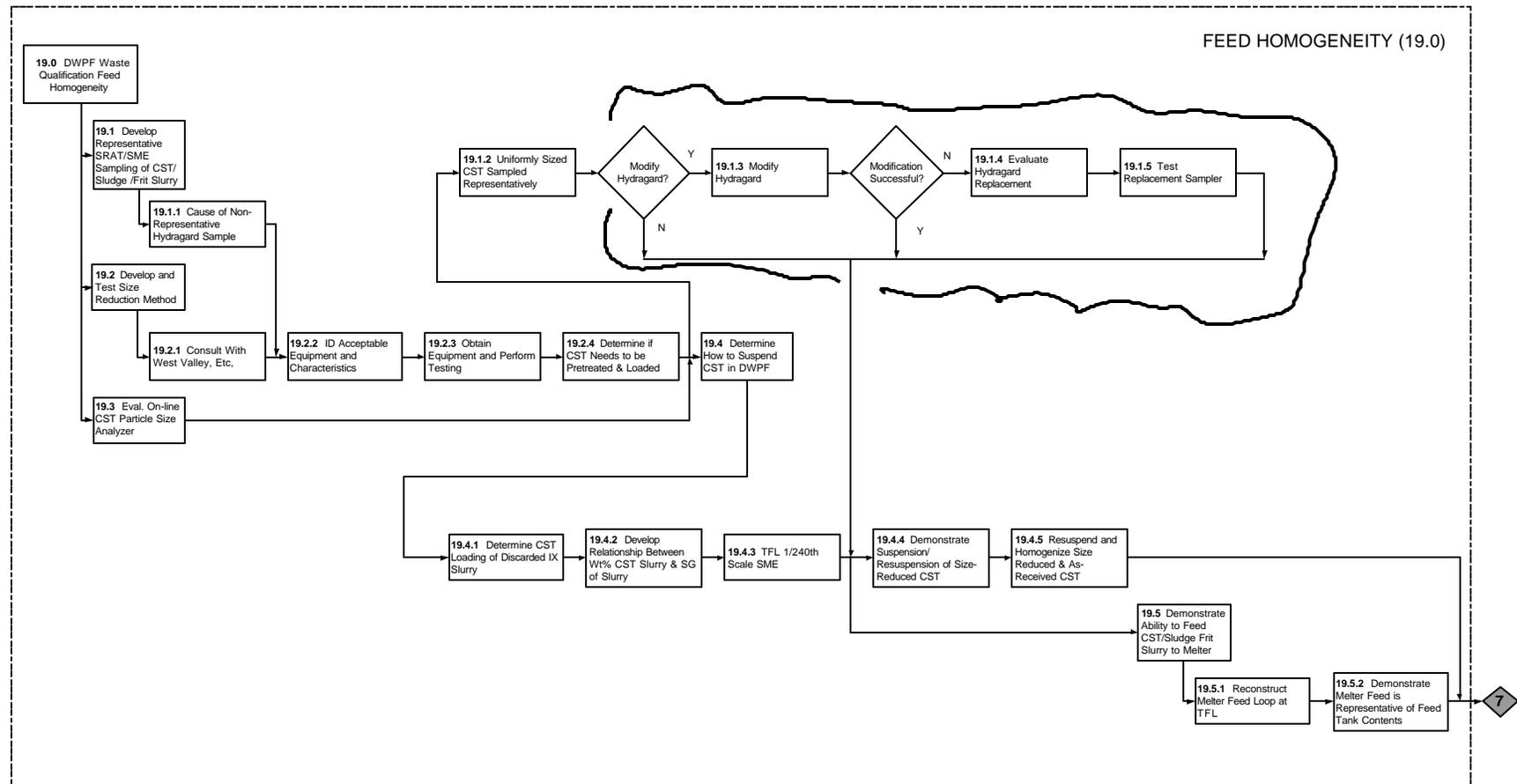
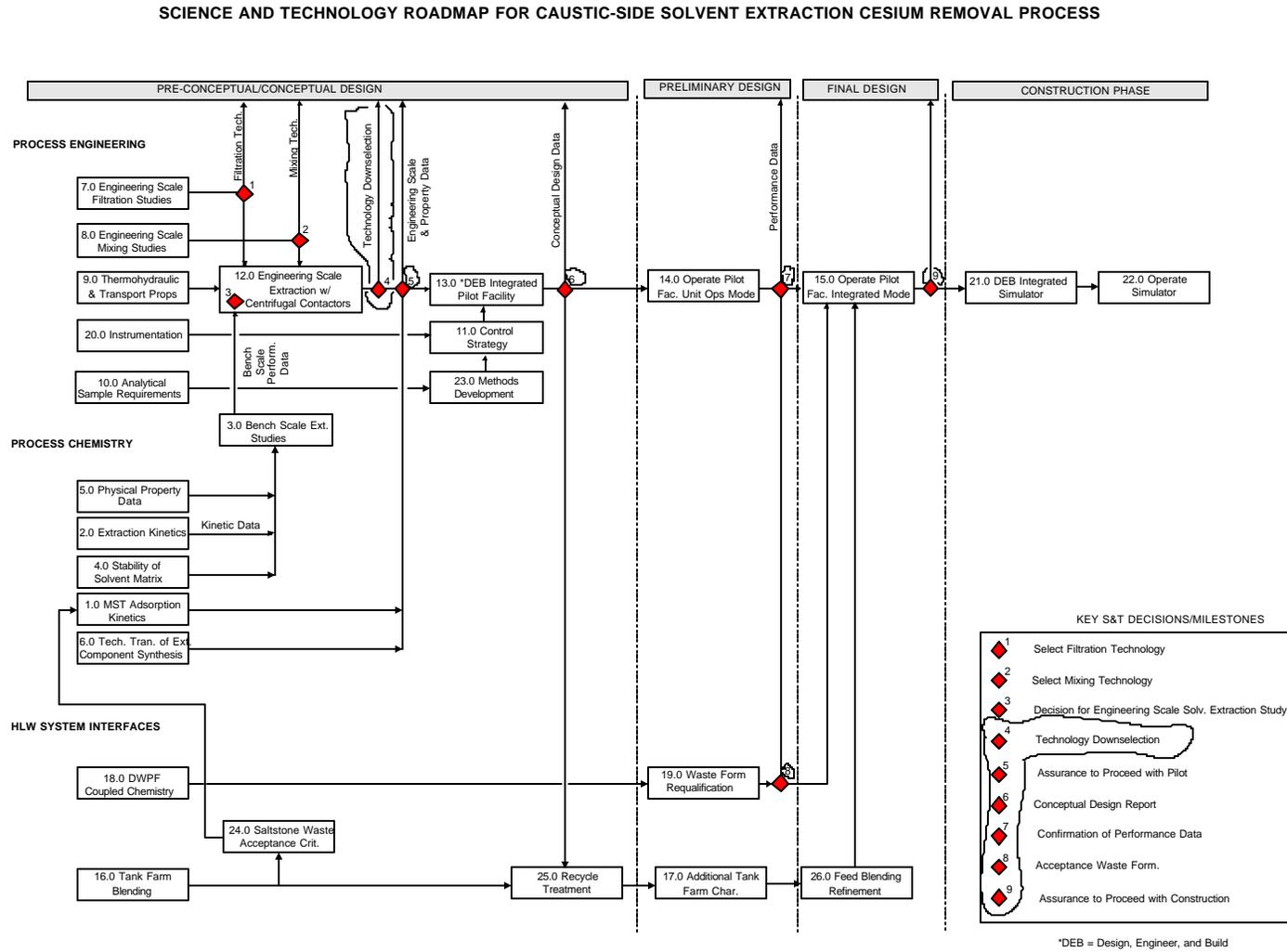
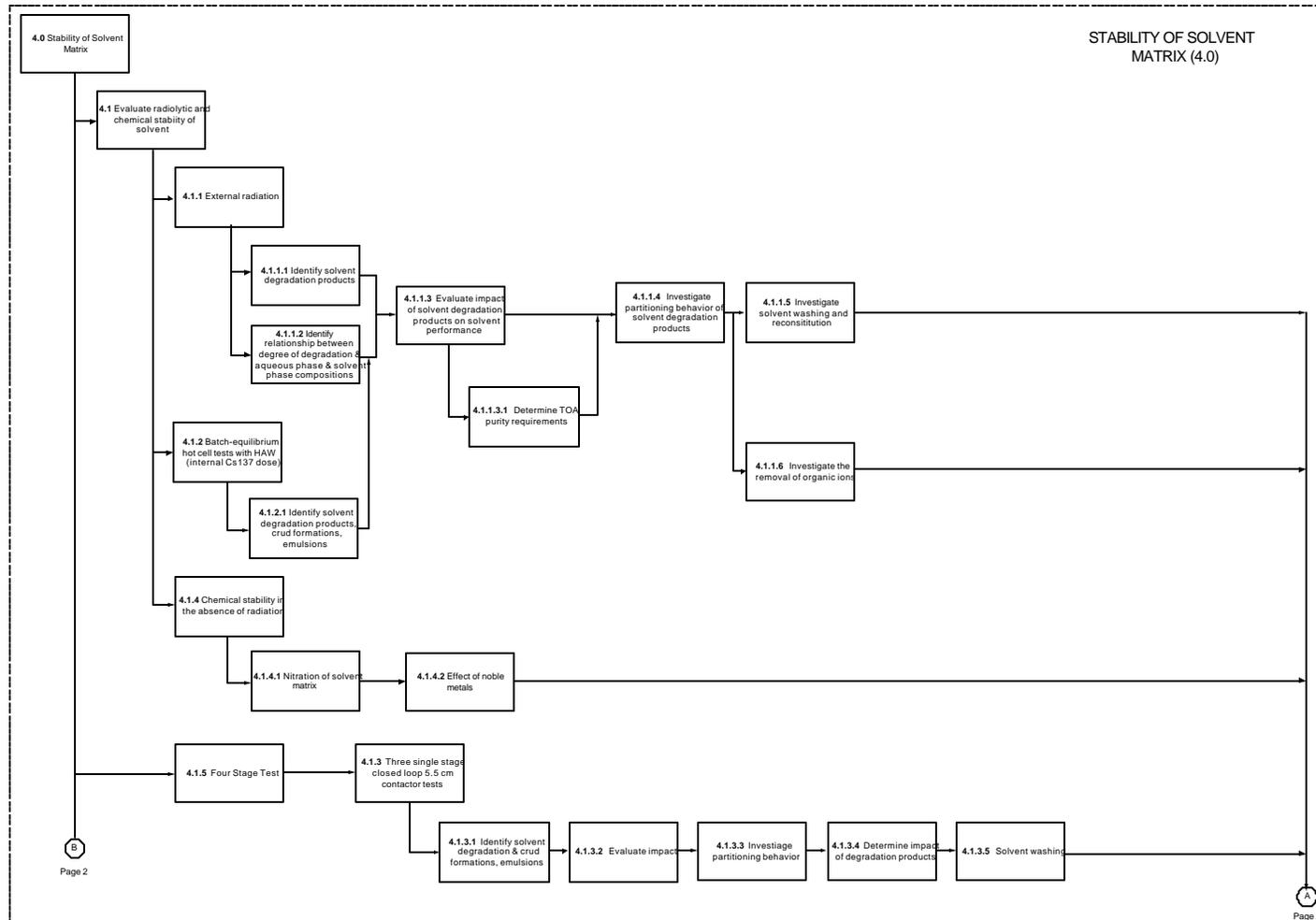
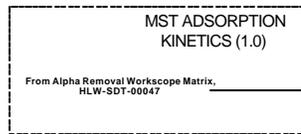


Figure A.3 Caustic Side Solvent Extraction



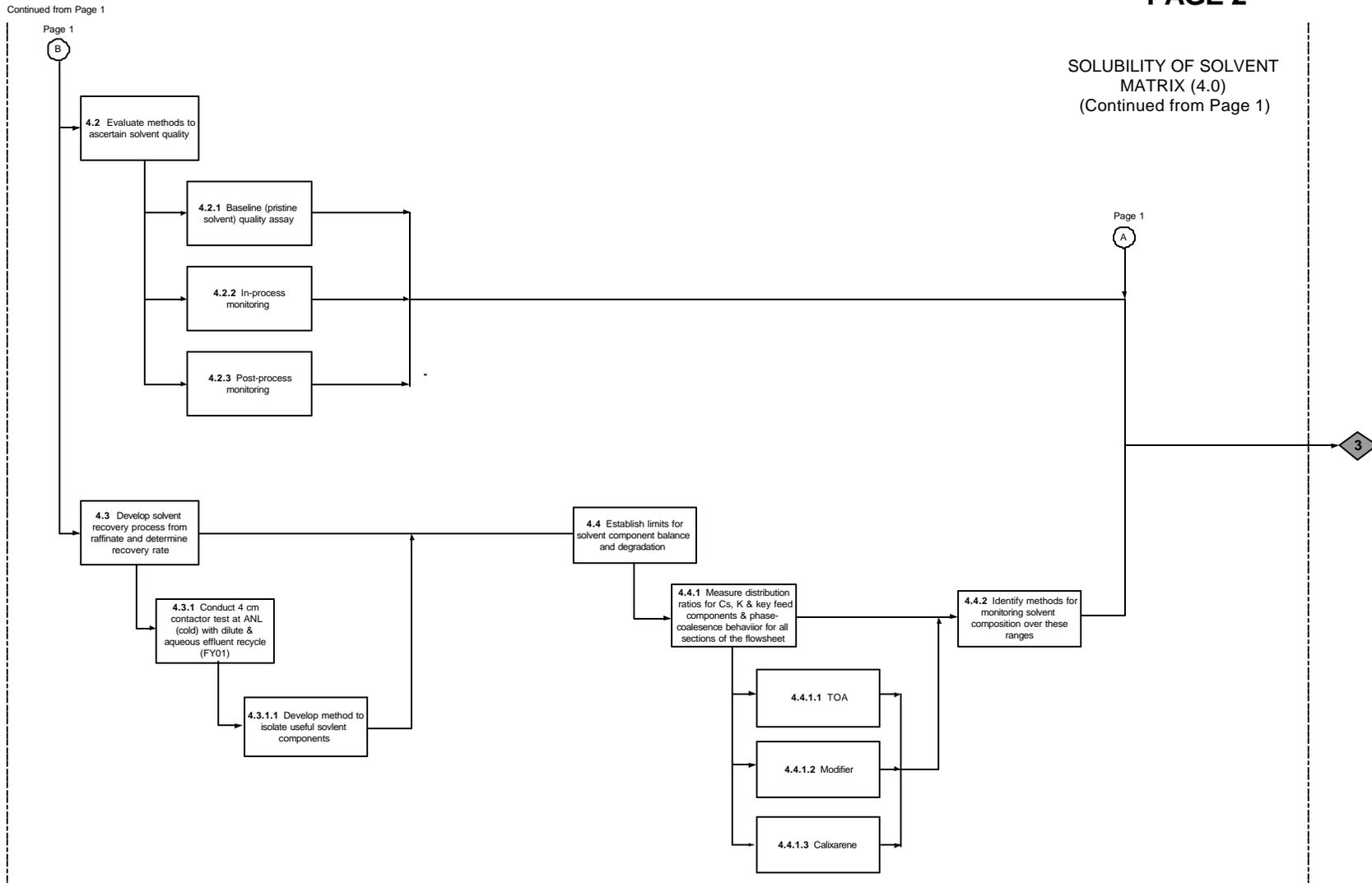


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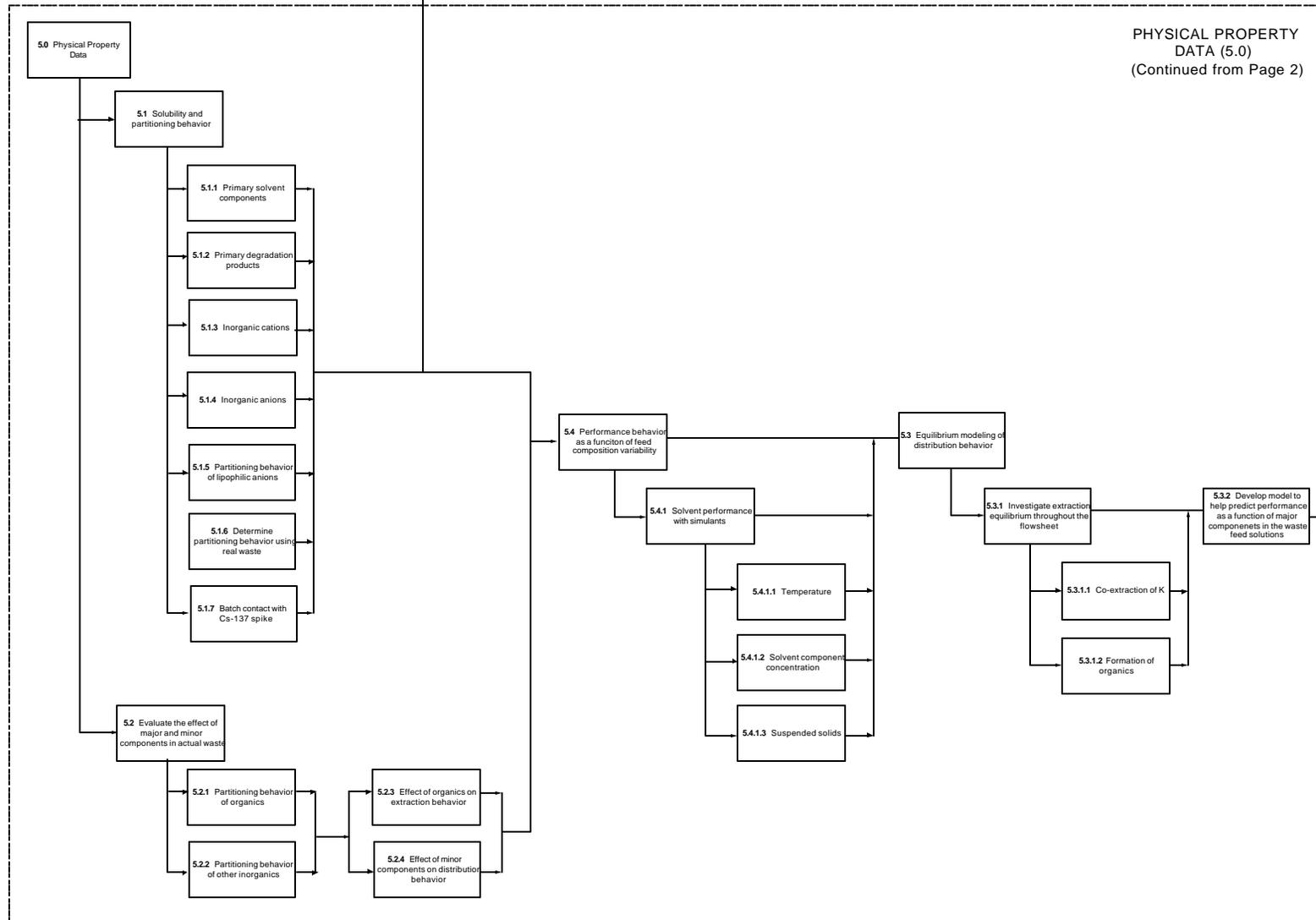
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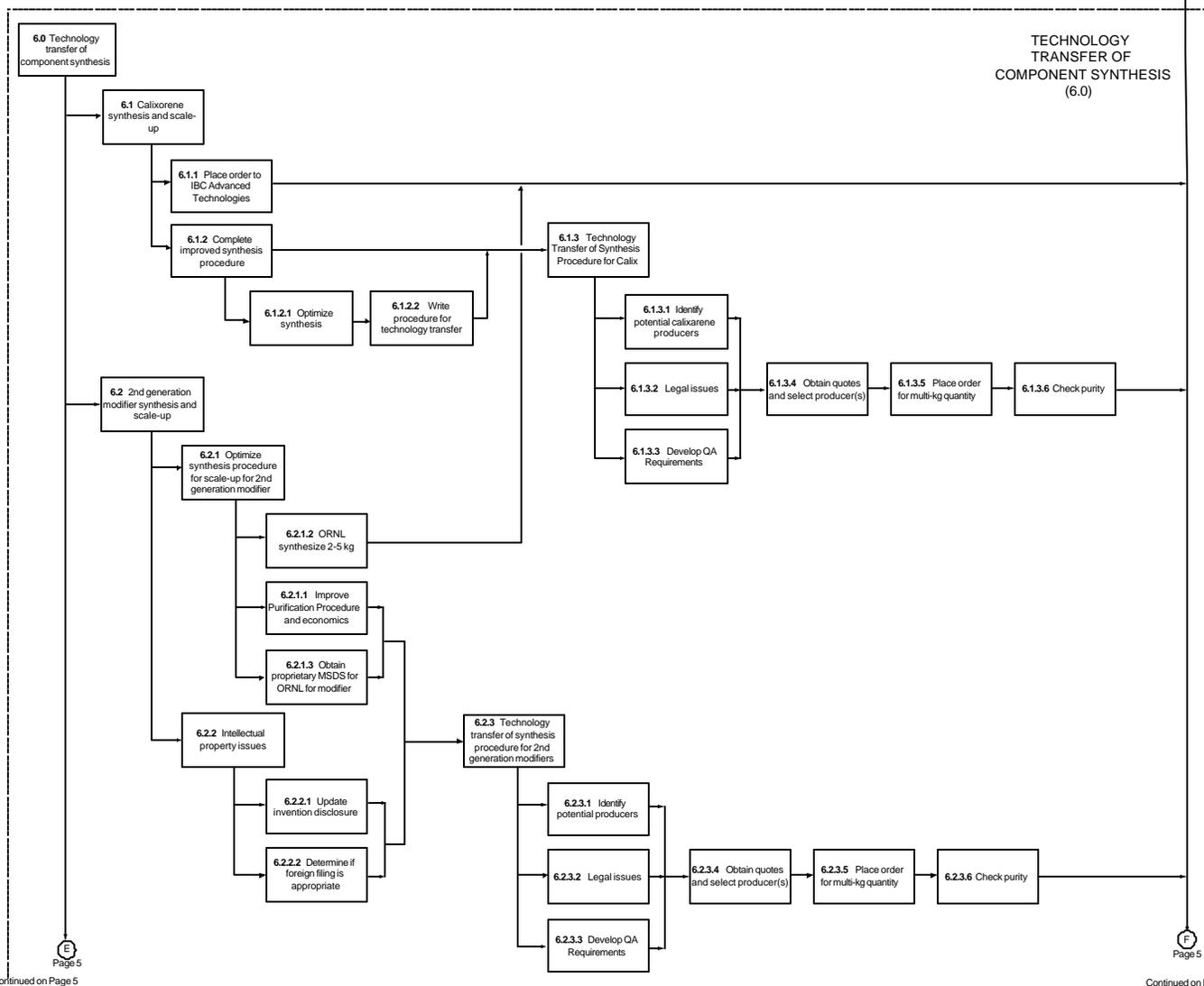
SOLUBILITY OF SOLVENT  
MATRIX (4.0)  
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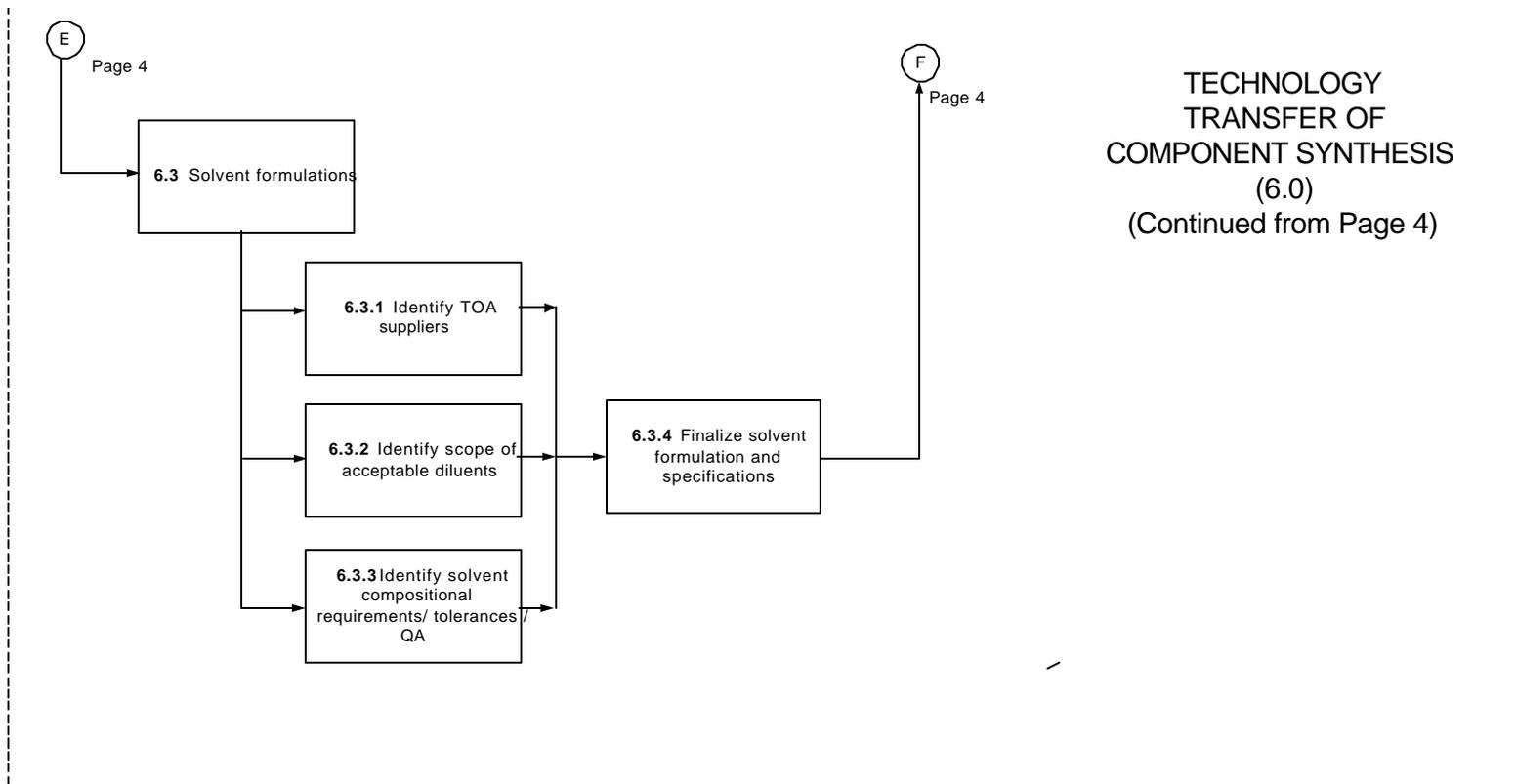


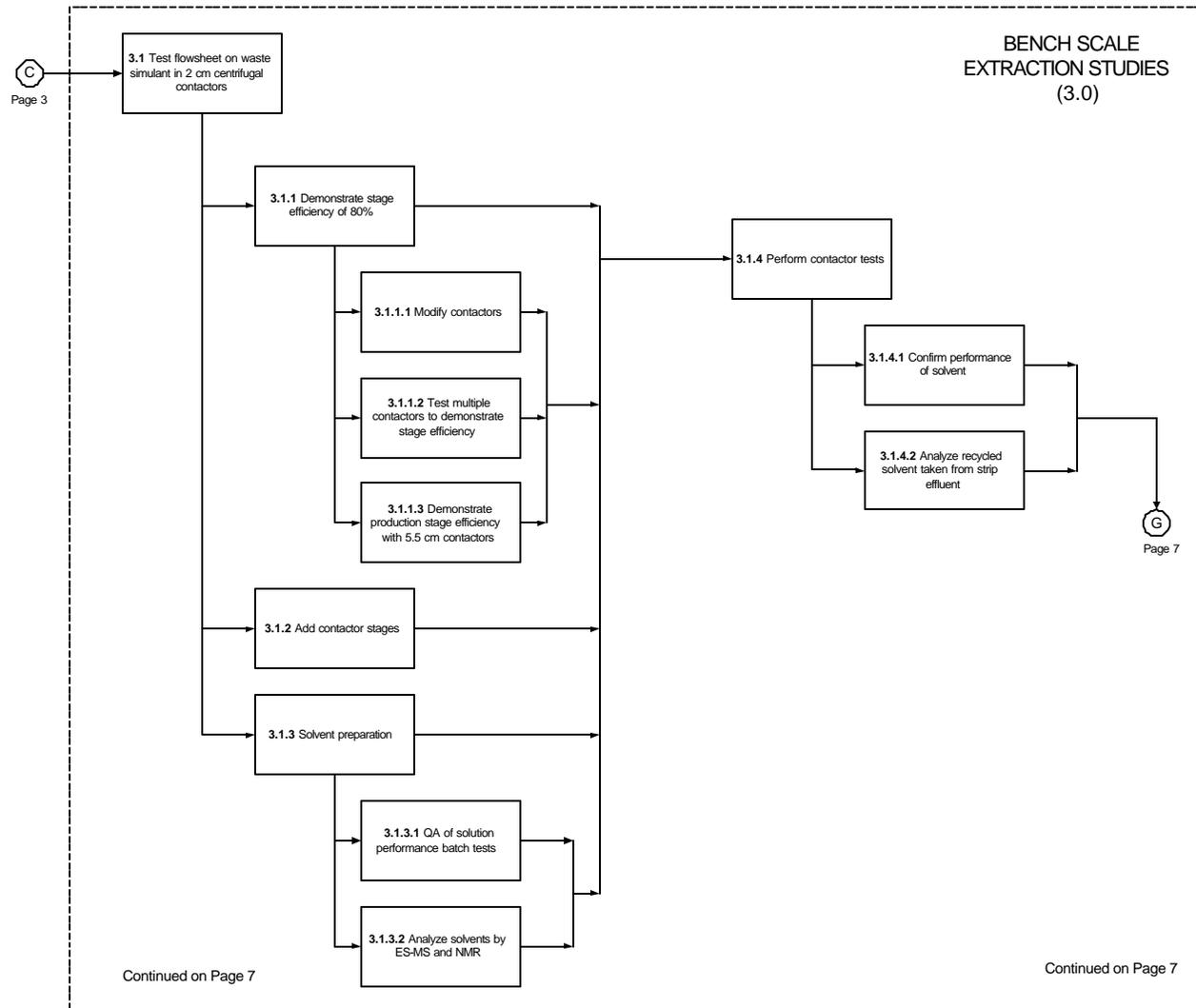


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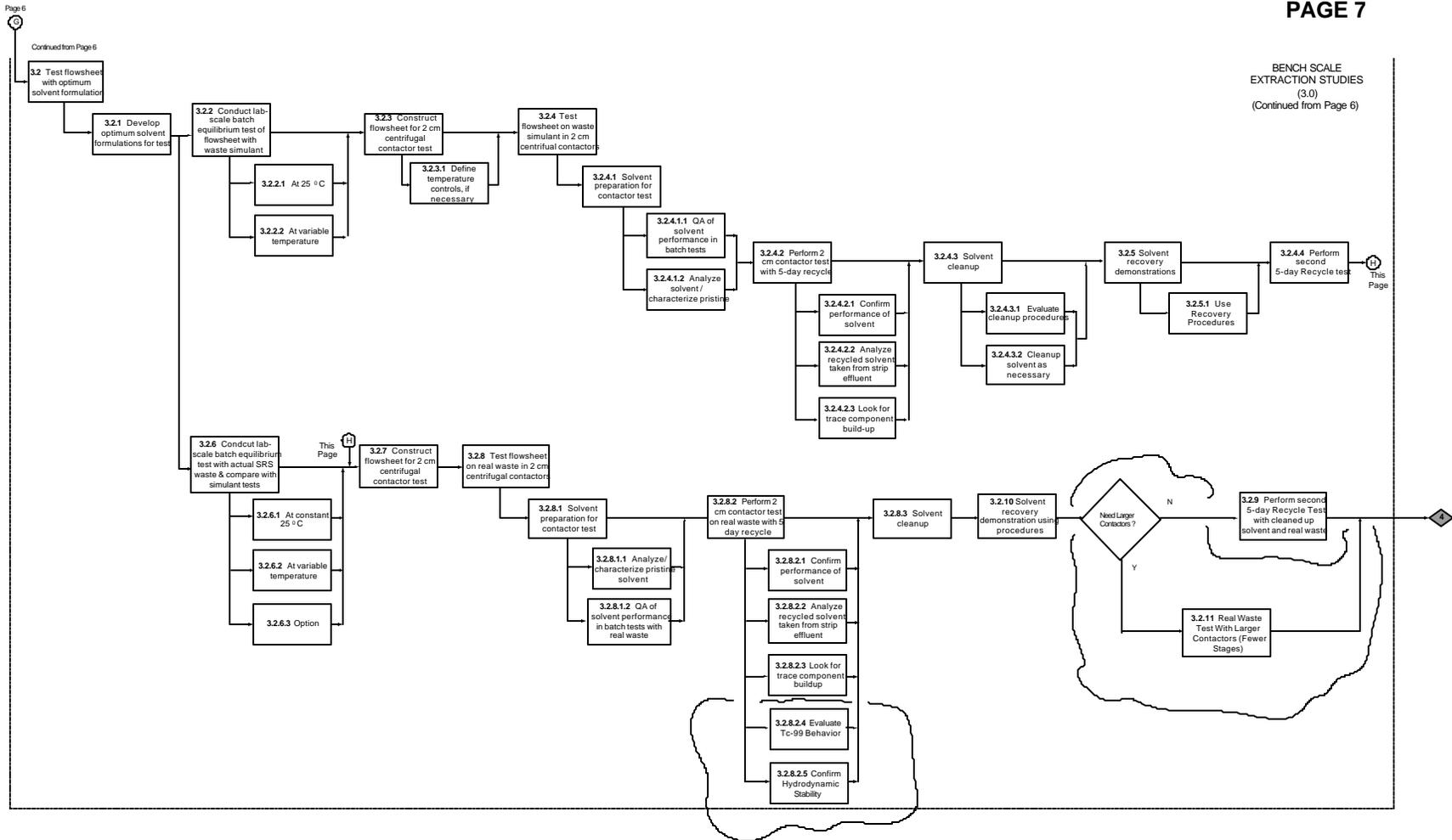
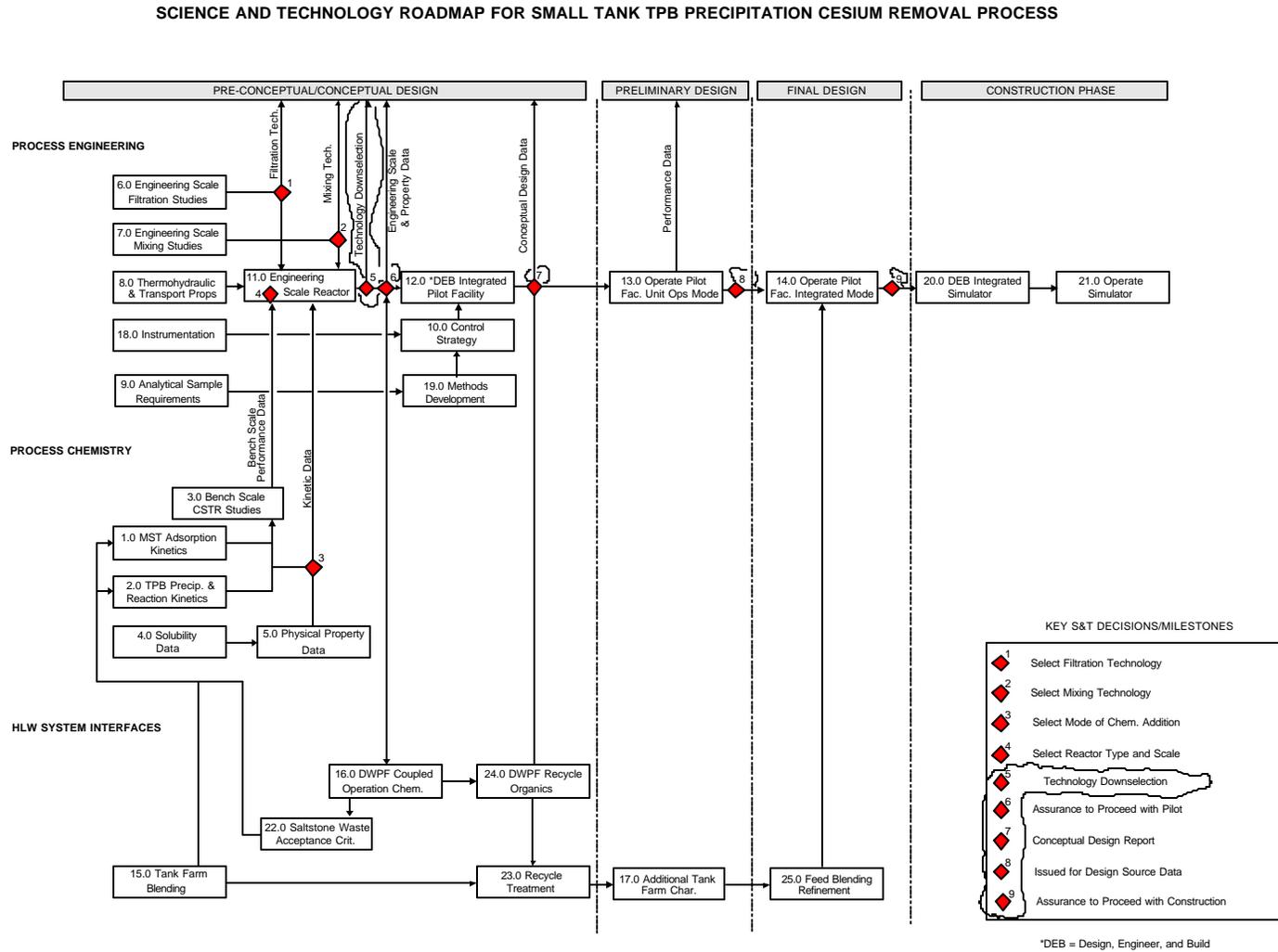
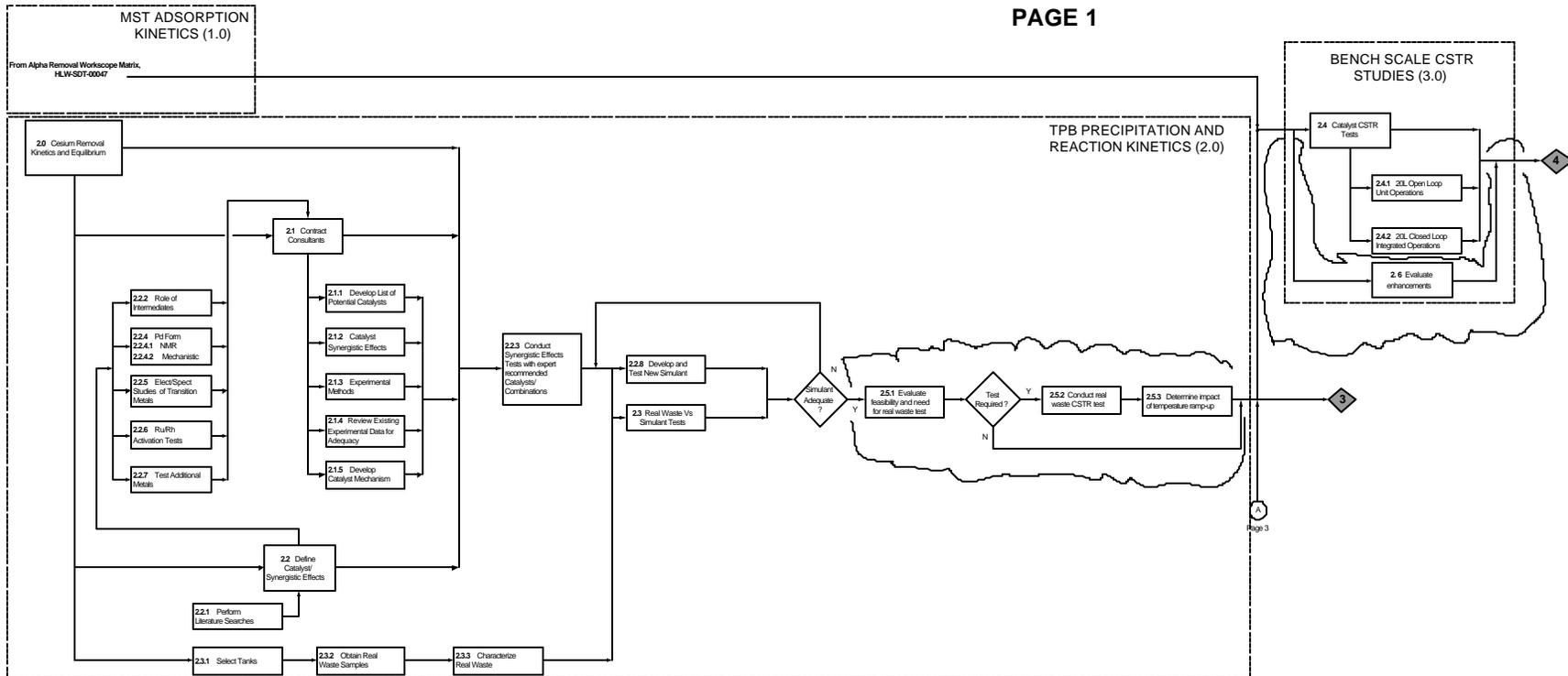
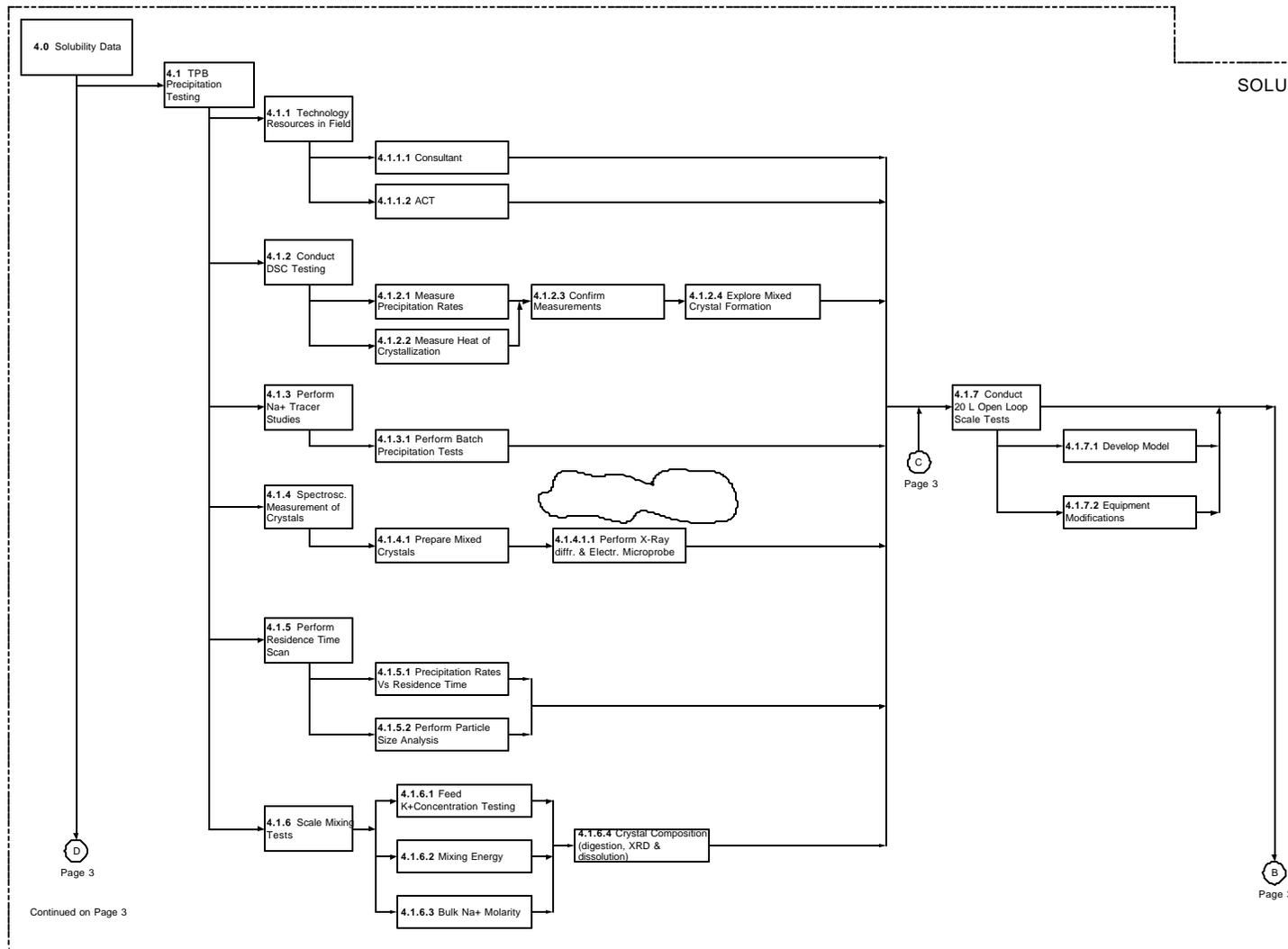
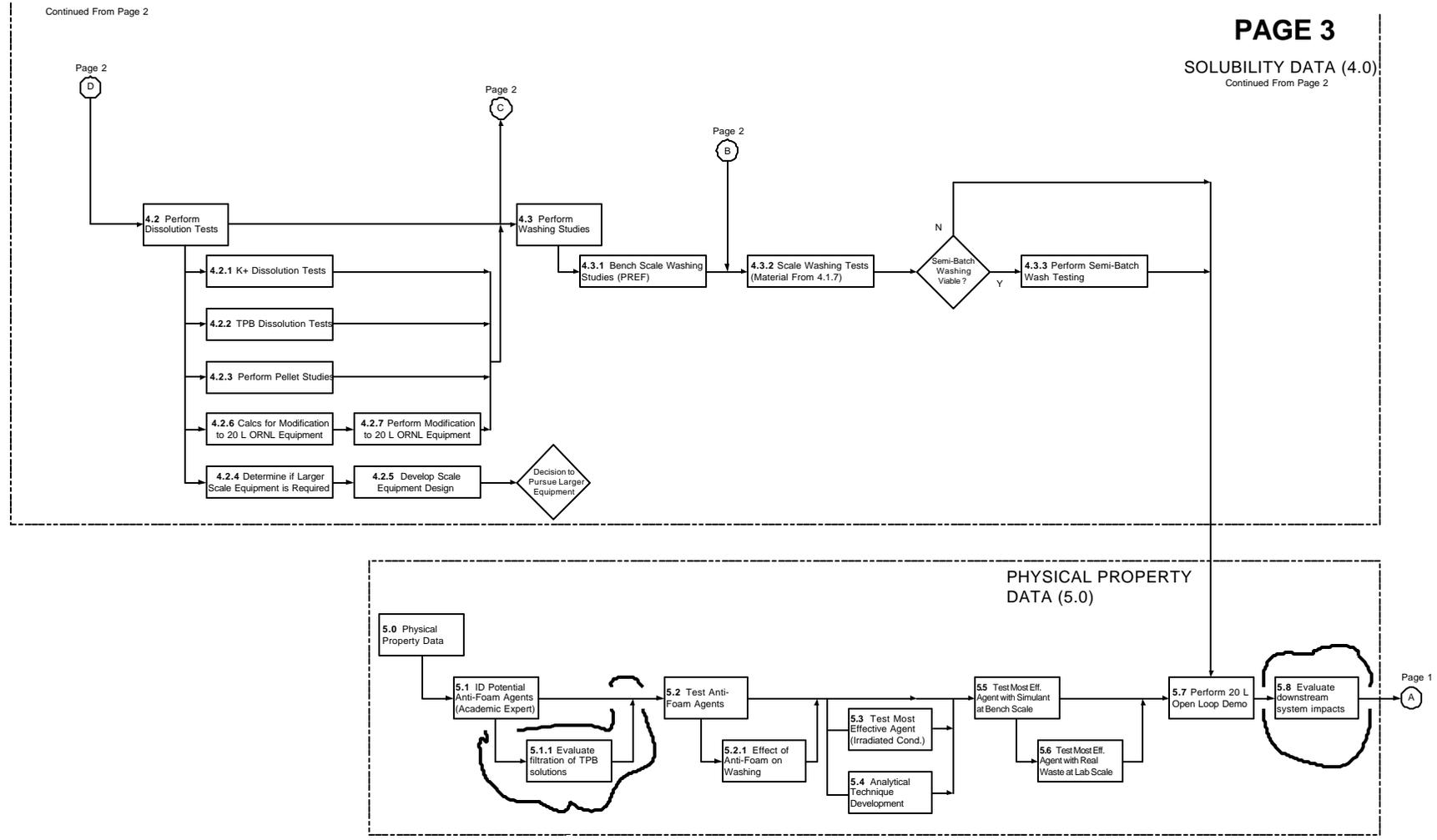


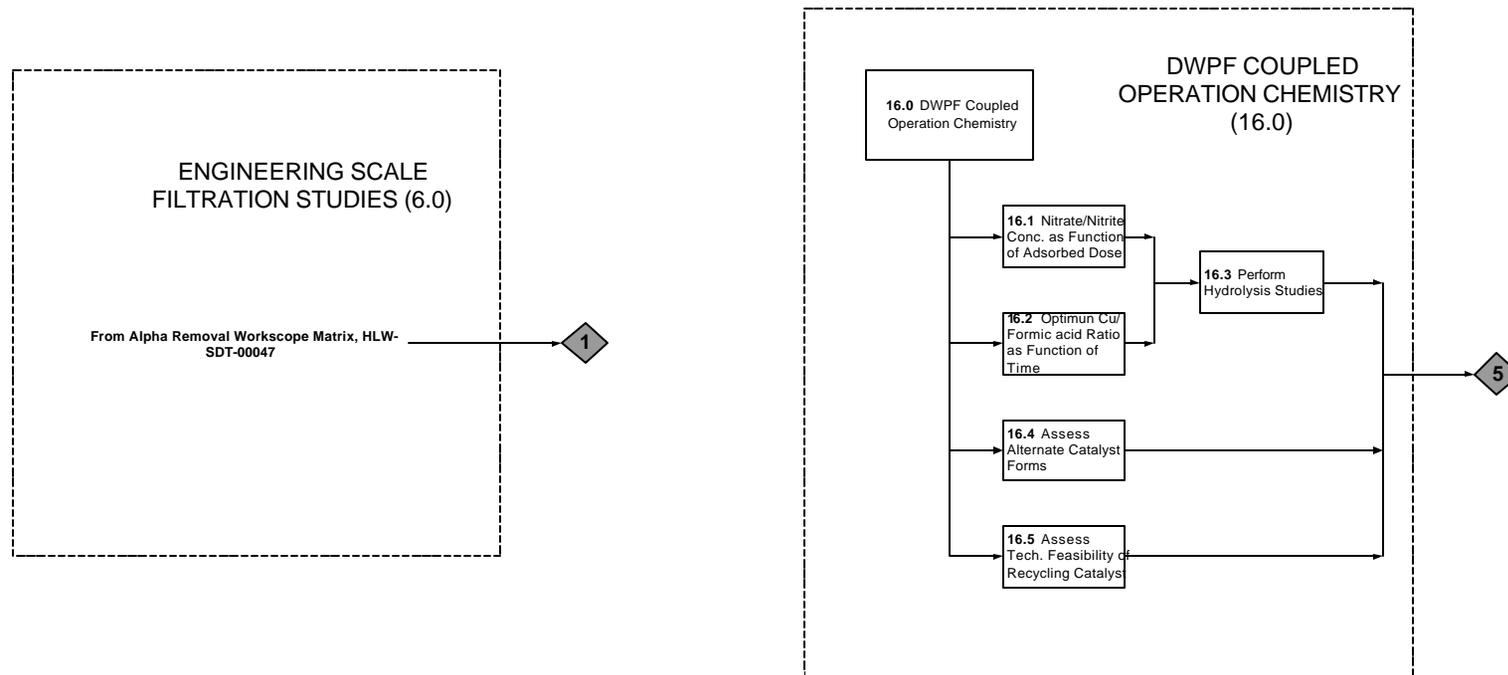
Figure A.5 Small Tank Tetraphenylborate Precipitation











## **Appendix B - Technology Development Needs**

The specific technology development needs listed below are derived from technical issues and concerns that have been identified in previous phases of the Salt Processing Program. Several are related to or are subordinate issues under the high priority needs discussed in previous sections as Technology Development Needs. Other categories, such as "High-Level Waste System Interface Issues" are also used to appropriately organize the other technology development needs.

## **Alpha and Strontium Removal**

### **Actinide and Strontium Removal Performance**

- Define measures to improve actinide decontamination with monosodium titanate (MST) - including slow kinetics for plutonium bonding - to reduce equipment size
- Demonstrate that the designed amounts of MST will provide sufficient decontamination of transuranic elements
- Define the reactions that may be caused by temperature or chemistry changes resulting from the MST strike; define impacts to the process. (Data suggest heating and cooling of the slurry prior to filtration may improve the processing rate.)
- Develop alternative sorbents for alpha and strontium removal
- Define the effect of neptunium content spikes in some tanks to the Performance Assessment and Waste Acceptance Criteria. Define necessary mitigating measures
- Define the effect that the MST strike has on americium disposition
- Identify and confirm the feasibility of required feed blend

### **Equipment Scale**

- Develop new analytical techniques to reduce the delay (1 week) in measuring the decontamination factor for strontium in the MST process
- Define the mechanisms for hydrogen generation in the MST strike process; identify, design and develop methods for hydrogen control
- Define the effect of neptunium content spikes in some tanks

### **Solid-Liquid Separation Performance**

- Evaluate alternative solid/liquid separation technologies
- Develop mitigation measures to address the difficulty inherent in filtration of the composite sludge and MST slurry. The resolution must address low filtrate flow rates and the requirement for cleaning.
- Investigate and recommend a process for dissolving solids from filters

## **Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange**

### **Resin Stability**

- Develop and document an understanding of the process chemistry to satisfy requirements of Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 96-1, especially with respect to stability and leaching
- Define potential for MST and/or sludge solids to breakthrough and transfer to columns.
- Define how the proprietary constituents that have been demonstrated to precipitate and leach from resin will impact the integrated flow sheet
- Define the potential for aluminum precipitation in various operating modes. Develop and demonstrate mitigation measures as needed
- Define the fate of resin and cesium on a loaded column under accident scenario
- Define measures to mitigate deflagration of resin column due to radiolysis of water (H<sub>2</sub> generation)
- Develop and demonstrate a method to degas the resin to prevent resin blinding with H<sub>2</sub>, and O<sub>2</sub>
- Develop methods to mitigate potential for deflagrations/detonations due to hydrogen accumulation in the vapor spaces
- Define a strategy for managing hydrogen in the spent resin vessel
- Define a strategy for managing hydrogen in the spent resin vessel
- Document and validate research and development results that indicate steam pressurization of a resin column results in less H<sub>2</sub> generation than current Authorization Basis (AB) assumptions
- Perform a pilot-scale treatment study to demonstrate that the CST process can meet performance requirements
- Perform a pilot-scale treatment study to demonstrate that the CST process can meet performance requirements

### **Resin Handling and Sampling**

- Determine if the spent resin can be converted from granular engineered form to fine powder with mixing and high shear. Verify that conversion to powder improves transfer, sampling and homogeneity. Demonstrate the conversion process.
- Define requirements for a monitoring system that adequately determines when to verify interface requirements. Develop and demonstrate the system.
- Define disposal method for clean CST fines
- Demonstrate methods to effectively decontaminate process equipment contaminated with fines deposited by the CST process
- Define requirements for process instrumentation to enable detection of process upsets and provide routine monitoring

### **High-Level Waste System Interface Issues**

- Determine if the CST process can produce glass that meets compositional Environmental Assessment standards and processing limit
- Determine if the waste stream can be maintained homogeneous enough (slurry, particle size and sampling) to define specifications for modifying the Defense Waste Processing Facility (DWPF) Hydragard Sampler and assure that it will perform reliably
- Determine if adequate testing can be done to demonstrate the glass composition standards within the limited physical access available to DWPF
- Determine limiting process support requirements, such as tank blending strategies for cesium, that may preclude use of the technology.
- Determine if MST/CST will have a deleterious effect on glass form due to increased concentration of  $\text{TiO}_2$  in glass
- Perform testing to requalify glass form to allow use of CST process
- Develop and demonstrate a method to analyze the composition of CST in conjunction with other DWPF feed components
- Develop/demonstrate means to analyze CST in DWPF
- Complete and validate research results that catalytic  $\text{H}_2$  production rate from formic acid is less than the authorization basis for DWPF feed pretreatment processes

### **General Issues**

- Develop/demonstrate management schemes for large curie inventories in facilities
- Define disposal method for clean CST fines
- Identify or develop sources of sufficient quantity of CST to supply the process (50 ton/yr)

## **Caustic Side Solvent Extraction (CSSX)**

### **Specific System Proof-Of-Concept**

- Develop and document an understanding of the process chemistry to satisfy requirements of DNFSB 96-1
- Provide a sound technical basis for contactor efficiency to separate the organic stream from the aqueous stream (current basis assumes 95%)
- Determine if increasing temperature or adding nitrate improves the DF
- Determine if cold Cs will be used in the stripping stage of the process, and if so, will it occupy active sites
- Define optimal solvent formulation and temperature dependency
- Develop a method to determine the composition of the 4-compound solvent system
- Prevent/minimize CRUD formation at the organic to aqueous interface, thereby increasing stage efficiency and minimizing/reducing number of stages or flow sheet changes
- Define appropriate solvent cleanup method to remove deleterious degradation products (all 4 solvent components)
- Define the disposal routes for spent solvent and the feasibility of implementing the preferred alternative
- Define the CSSX operating window with respect to solvent components and impurities
- Develop understanding to determine if addition of organic removal for raffinate must be added to the process

### **Radiolytic Stability**

- Perform testing process that accurately simulates radiolysis of solvent by Cesium-137
- Determine the potential for radiolysis to nitrate the solvent

### **Chemical Stability**

- Evaluate the potential for nitration of organics in the strip stream; as required, identify and design mitigation measures
- Eliminate the potential for deflagrations/detonations by eliminating hydrogen accumulation in vapor spaces and ignition sources
- Develop measures to mitigate flammability of organic solvent (process and sumps)
- Identify and mitigate potential for fire in the extraction process
- Mitigate the corrosive effects of fluoride from degradation of aromatic modifier

### **Real Waste Performance**

- Confirm solvent performance on real waste (achieve DF of 40,000 at CF of 12)
- Demonstrate the hydraulic performance of CSSX using a real waste mixture
- Determine by analysis of recycled solvent if degradation or polymer products are forming; if so, assess impact
- Determine if trace components are concentrating in recycled solvent; if so, assess impact
- In a 5-day test, demonstrate ability to recover and reuse solvent while maintaining the required DF and CF

### **High-level Waste System Interface Issues**

- Define decomposition/degradation products that affect saltstone grout quality and mitigate these effects
- Determine the range of composition of the cesium product stream that is acceptable in coupling to DWPF
- Identify byproducts and their concentration, determine if they would be carried into saltstone in excess of limits; identify mitigation measures

### **Small Tank Tetraphenylborate Precipitation (STTP)**

#### **Catalytic Product Decomposition**

- Develop and document an understanding of the process chemistry and meet requirements of DFNSB Recommendation 96-1
- Determine if additional (currently unknown) catalytic effects of catalyst buildup through plate-out will increase benzene levels and exceed permit levels and or cause activation greater than the bounding levels (DF decrease).
- Define the procedure for recovering from a batch that decomposes (catalyst activation greater than bounding case resulting in loss of DF)
- Perform radioactive waste tests to provide essential data for equipment design and confirm analytical results from cold tests
- Determine the effects of materials of construction on catalytic effect
- Determine if the slow kinetics of MST and TPB will preclude reaching the required DF; if so, identify mitigation measures

#### **Foaming**

- Identify improved antifoam agents
- Determine if the new antifoam agent will have deleterious effects on downstream processes; if so, identify mitigation measures.

### **High-level Waste System Interface Issues**

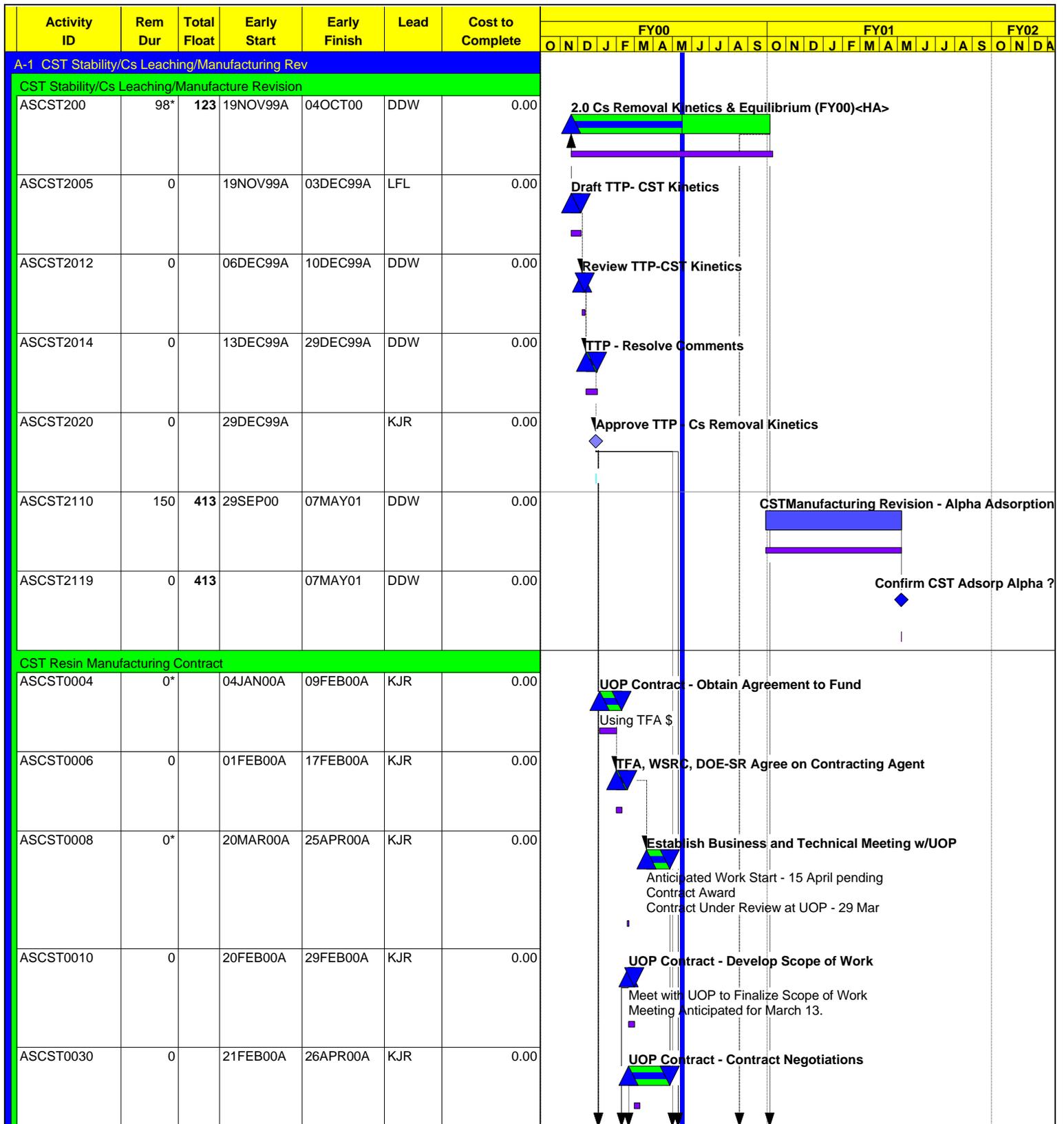
- Determine the limiting process support requirements, such as tank blending strategies for Cs, that may preclude use of the technology
- Determine range of composition of aqueous Cs stream acceptable in DWPF process
- Develop/demonstrate process to facilitate transfer of high viscosity 10 wt % slurry to DWPF

### **General STTP Needs**

- Define method for determining when the process reaches 10% precipitate concentration.
- Determine the storage limit of NaTPB in terms of form, shelf life and benzene release
- Define the conditions that cause material to settle or plate out in tanks and concentrates and define measures to avoid.
- Define all unit operations necessary to assure proper performance and meet requirements to eliminate or minimize adding future unit operations and increasing complexity
- Determine by safety analysis/PHR if a two train design is indicated; assess technology and/or design solutions and identify required path
- Determine if gas entrapment and pressure drop in a filter assembly will cause filter blinding. If so, identify mitigative measures.
- Determine the limiting process support requirements, such as tank blending strategies for Cs, that may preclude use of the technology.

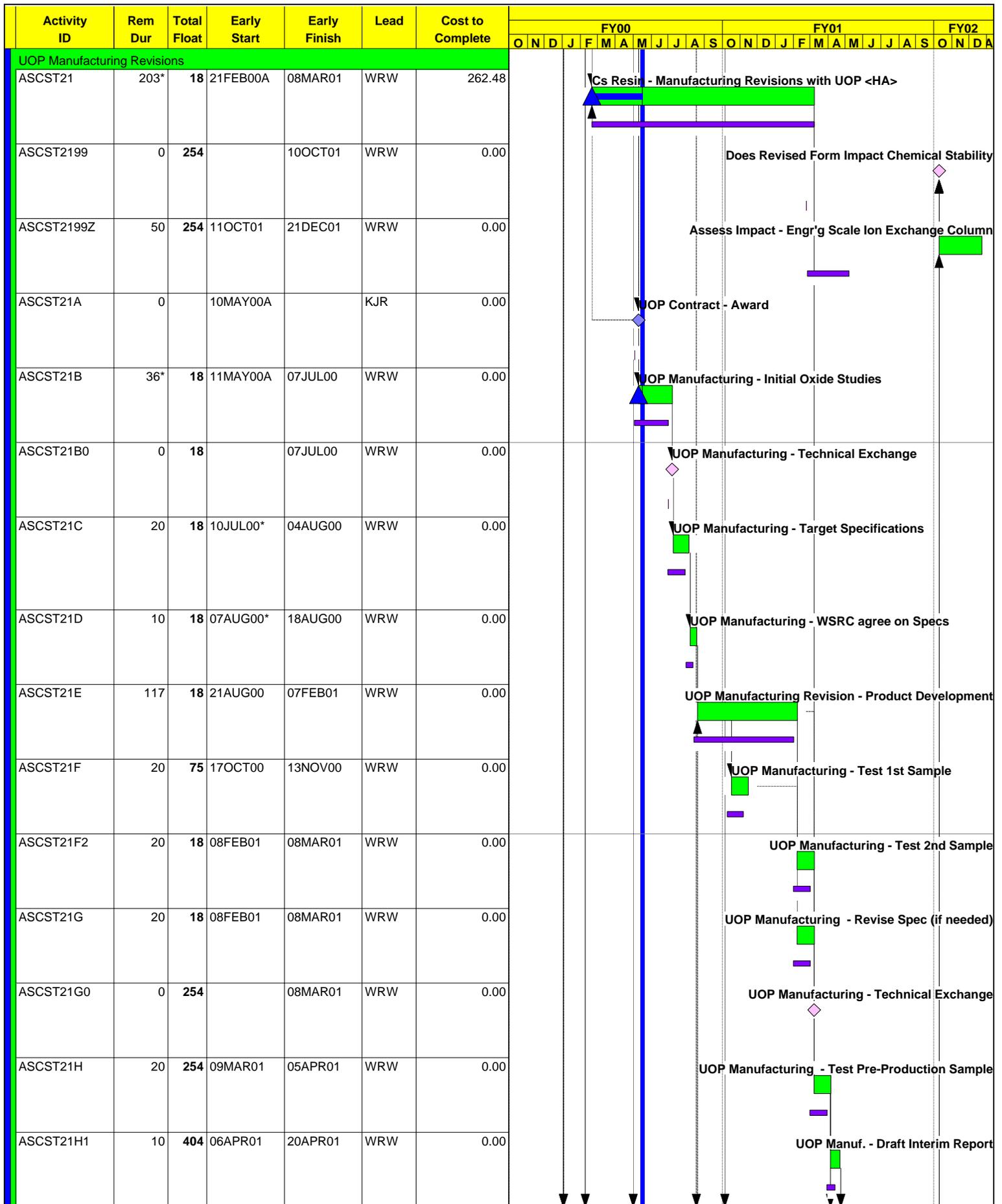
## **Appendix C – Research and Development Program Schedule**

[R&D program schedule](#) (downloadable PDF format)

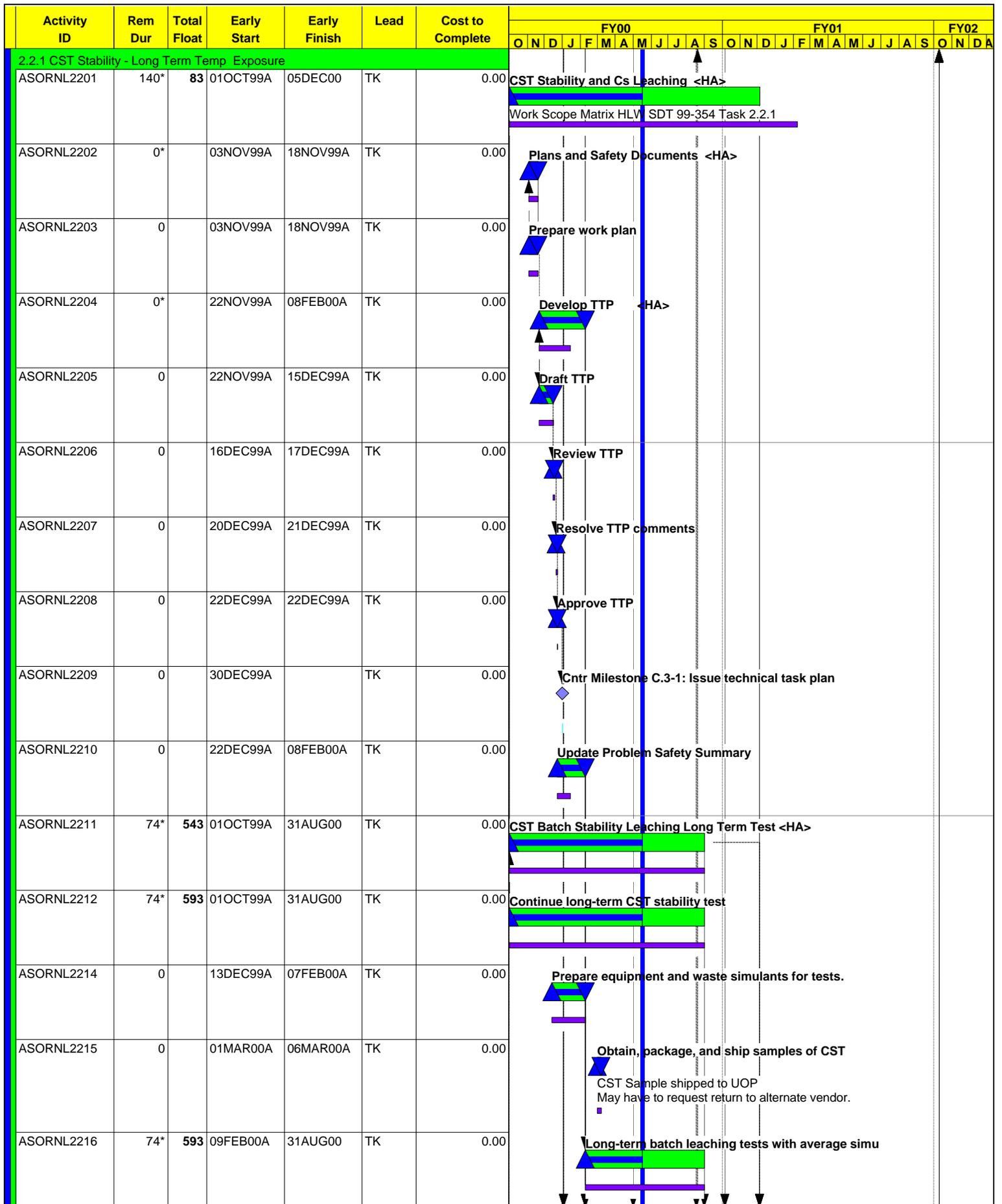


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 Data Date 17MAY00  
 Run Date 24MAY00 13:24

 Early Bar  
 Target (Early Start)  
 Progress Bar  
 Critical Activity



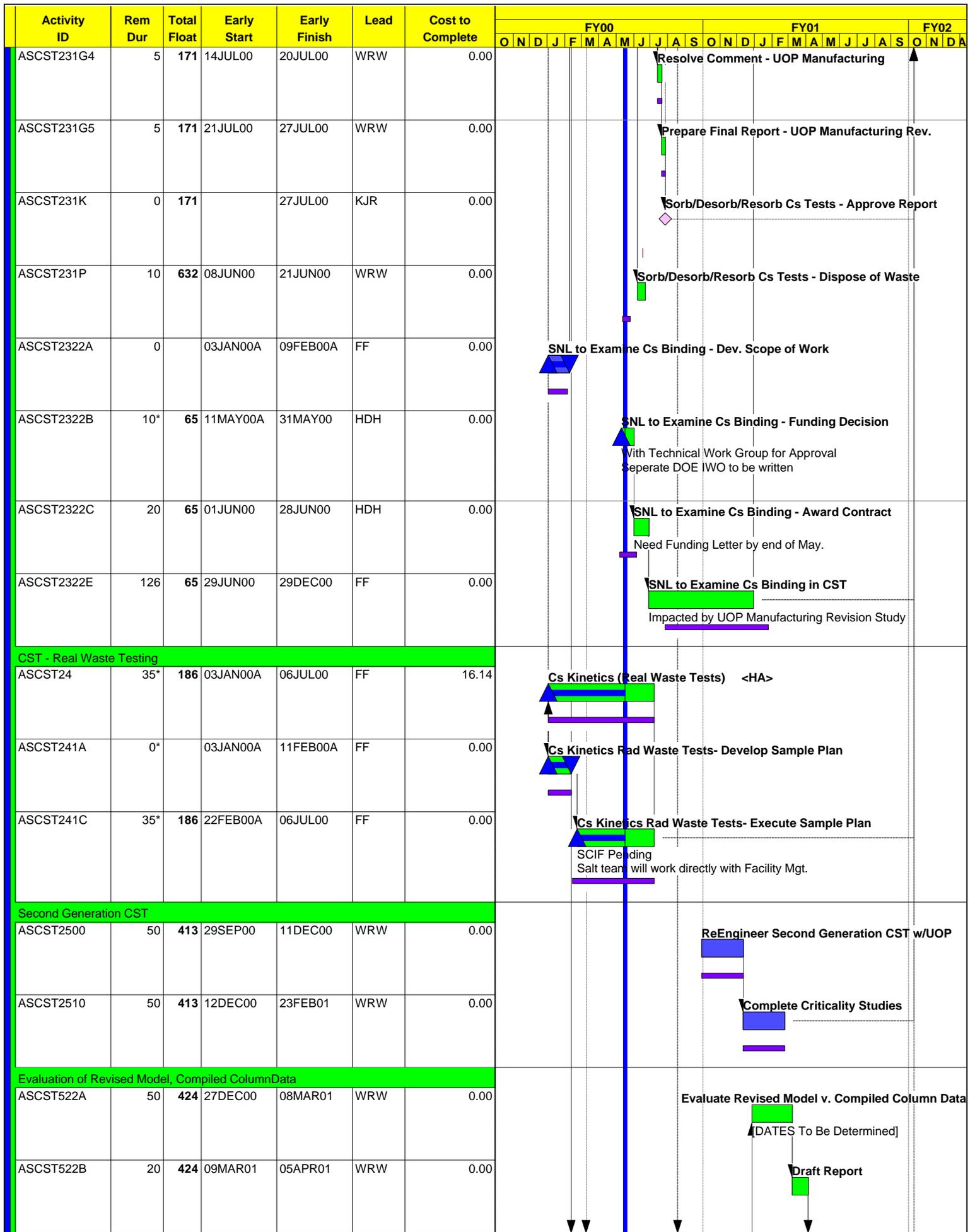


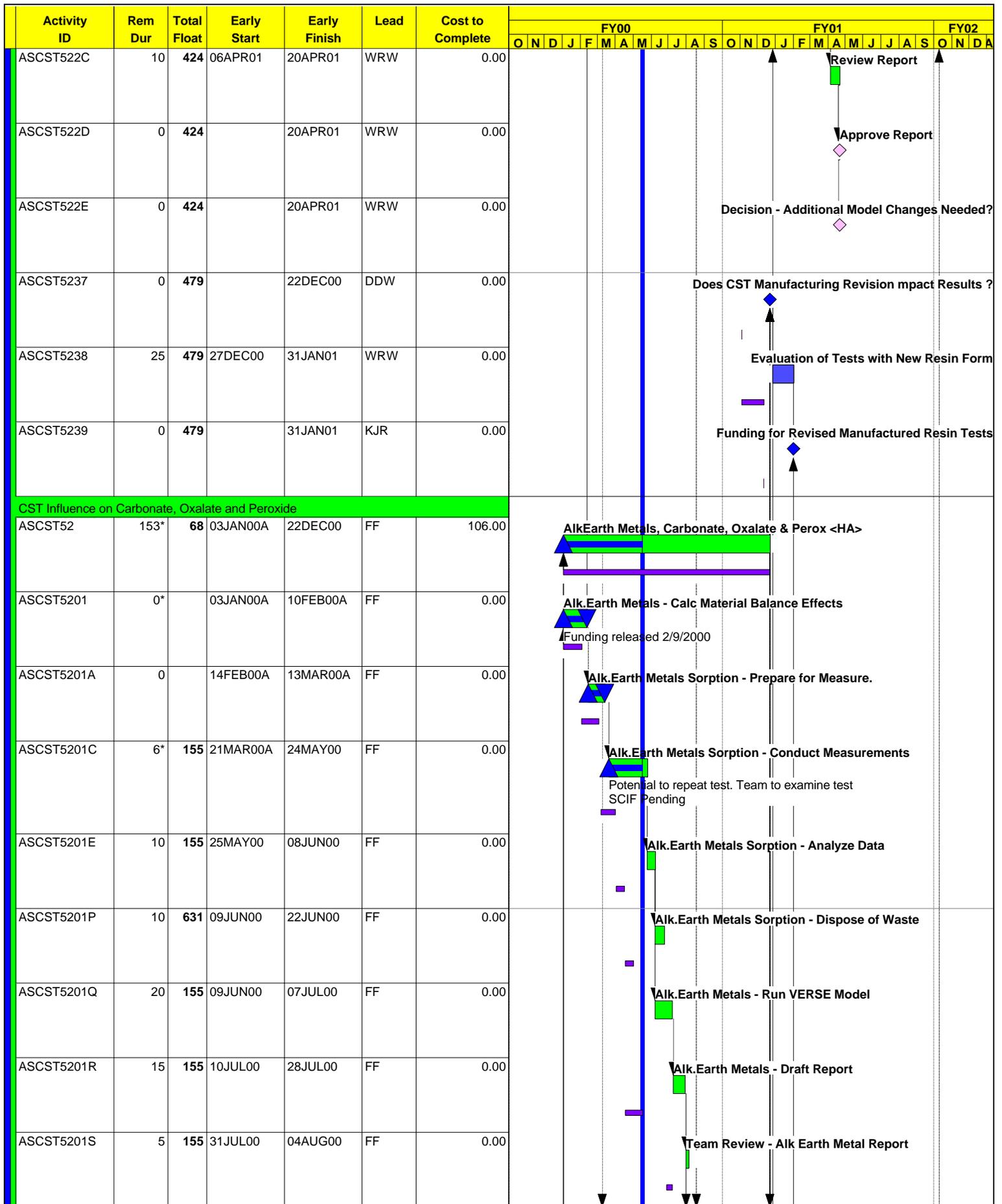




















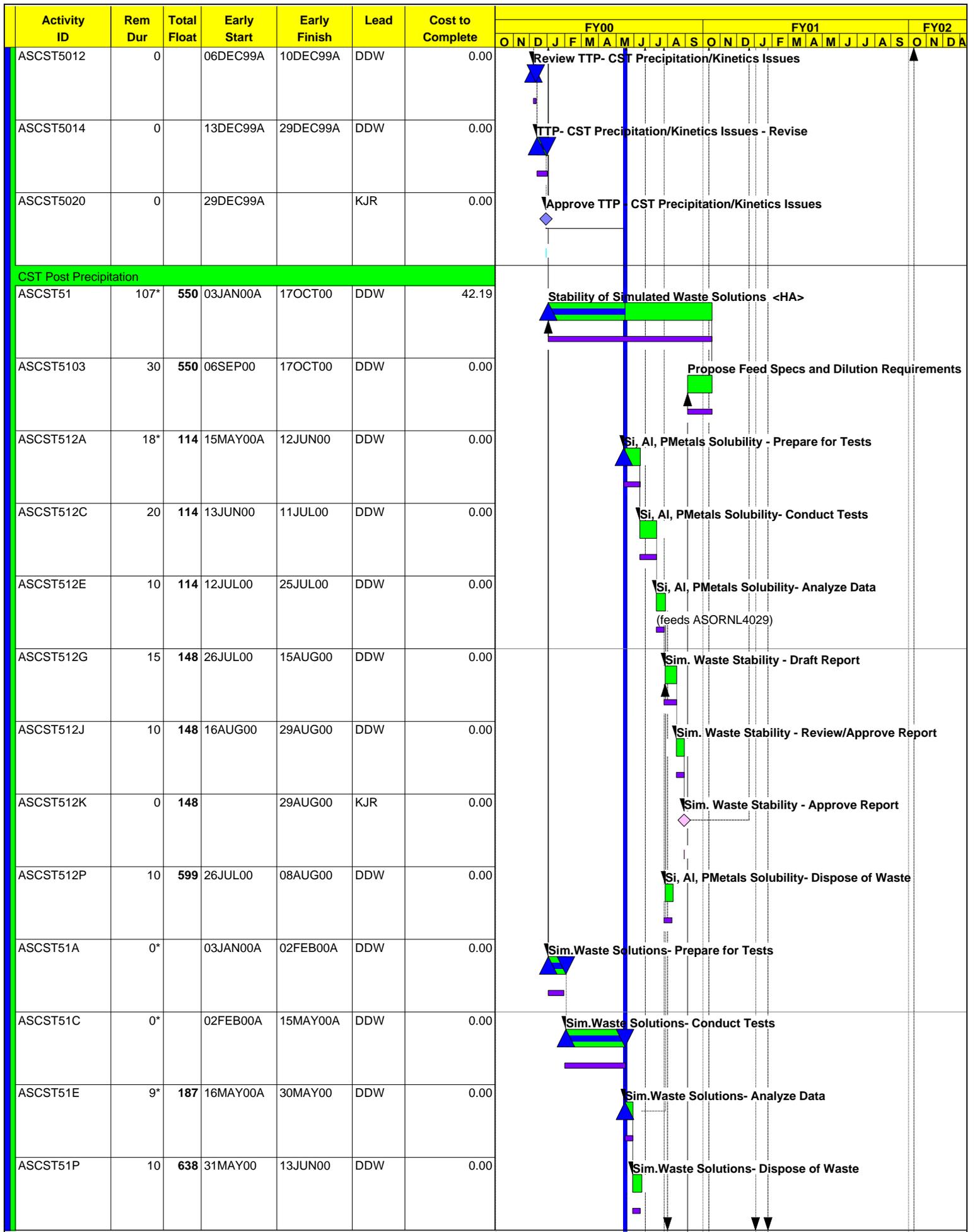


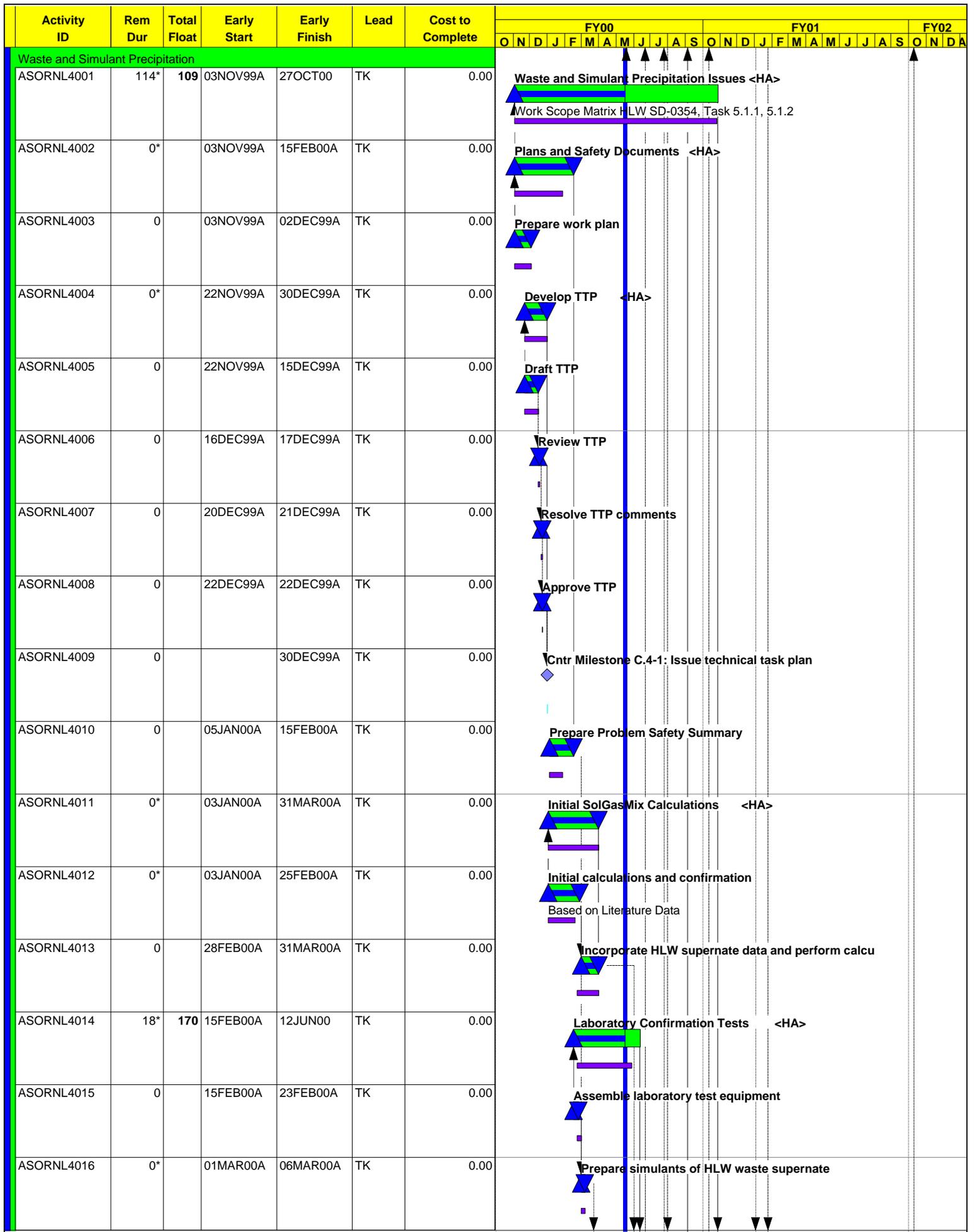




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ASCST623A	0		24JAN00A	02FEB00A	MRP	0.00	▲ Cross-flow Filtr.FRED- Award Contract/Test Prep.																								▲		
ASCST623B	5*	108	03FEB00A	23MAY00	MRP	0.00	Filtration - Prepare Tank 40 Simulated Sludge Need SS Shipping Drums																										
ASCST623B1	16*	125	24MAY00*	15JUN00	MRP	0.00	Filtration - Prepare Tank 8 Simulated Sludge																										
ASCST623C	13	133	03FEB00A	05JUN00	MRP	0.00	Cross-flow Filtr.FRED - Prepare for Tests																										
ASCST623C1	0			24APR00A	MRP	0.00	Decision Point for DWPF Sludge Preparation																										
ASCST623D	20	125	16JUN00	14JUL00	MRP	0.00	Cross-flow Filtr. FRED - Conduct Tests/Eval																										
ASCST623D1	0	125		14JUL00	MRP	0.00	DOE HQ Milestone - Finish Cross Flow Filter Test DOE - HQ TFA Milestone date is 7/30/2000 (No constraint date imposed)																										
ASCST623E	10	477	17JUL00	28JUL00	MRP	0.00	Cross-flow Filtr. FRED - Draft Report																										
ASCST623G	9	477	31JUL00	10AUG00	MRP	0.00	Cross-flow Filtr. FRED - Review/Approve Report																										
ASCST623H	0	477		10AUG00	KJR	0.00	Cross-flow Filtr. FRED - Approve Report Designated as a DOE - HQ, Tank Focus Area Milestone, with a desired end date of 31 July 00 (No imposed end date has been used, to better permit float calculations to technology select.																										
ASCST624A	10	108	26JUL00*	08AUG00	MRP	0.00	Honeywell FRED - Prepare for Tests																										
ASCST624C	20	108	09AUG00	06SEP00	MRP	0.00	Honeywell FRED - Conduct Tests/Eval																										
ASCST624E	15	108	07SEP00	27SEP00	MRP	0.00	Honeywell FRED - Draft Report																										
ASCST624H	8	85	28SEP00	11OCT00	MRP	0.00	Team Comment - Honeywell FRED Report																										
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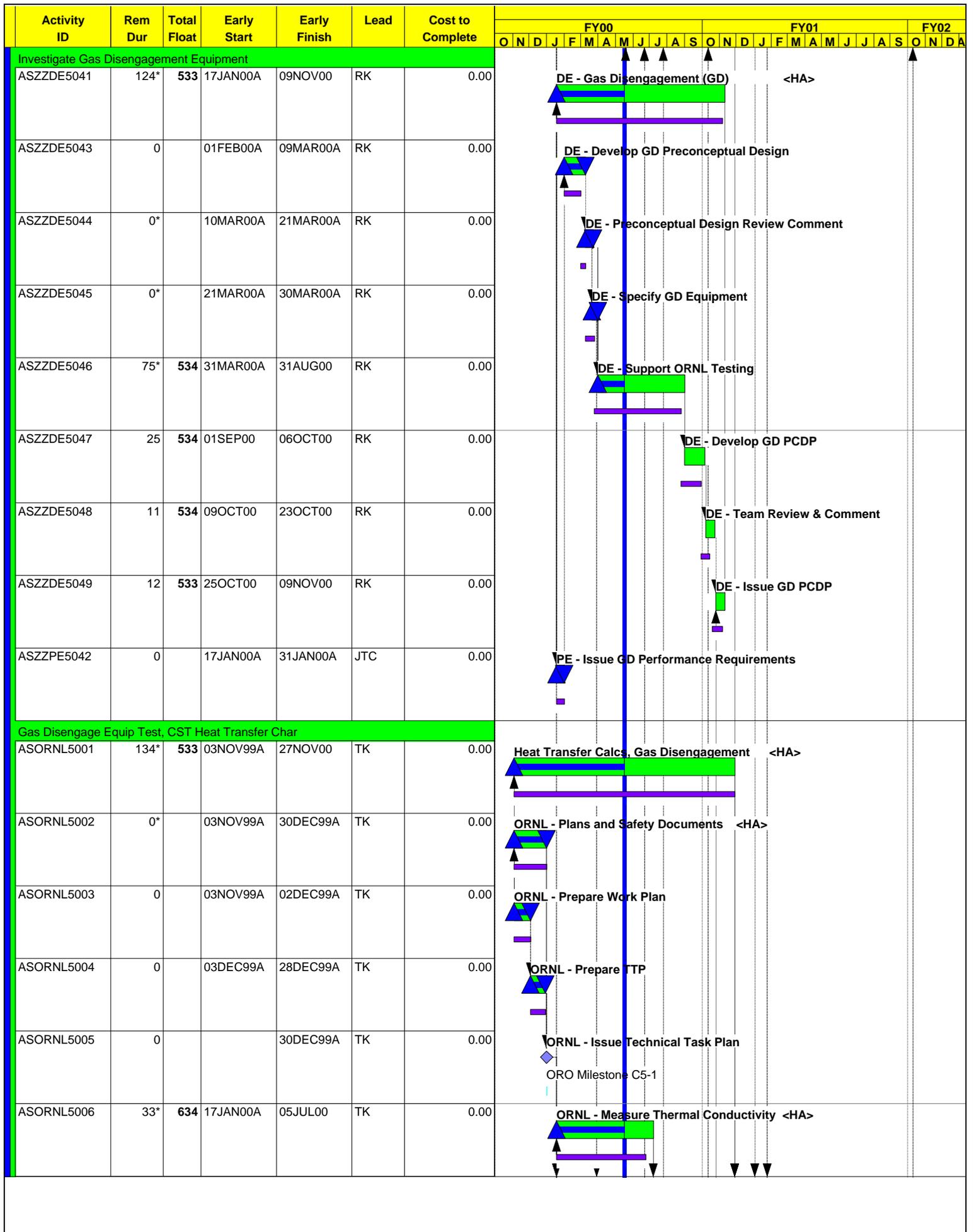








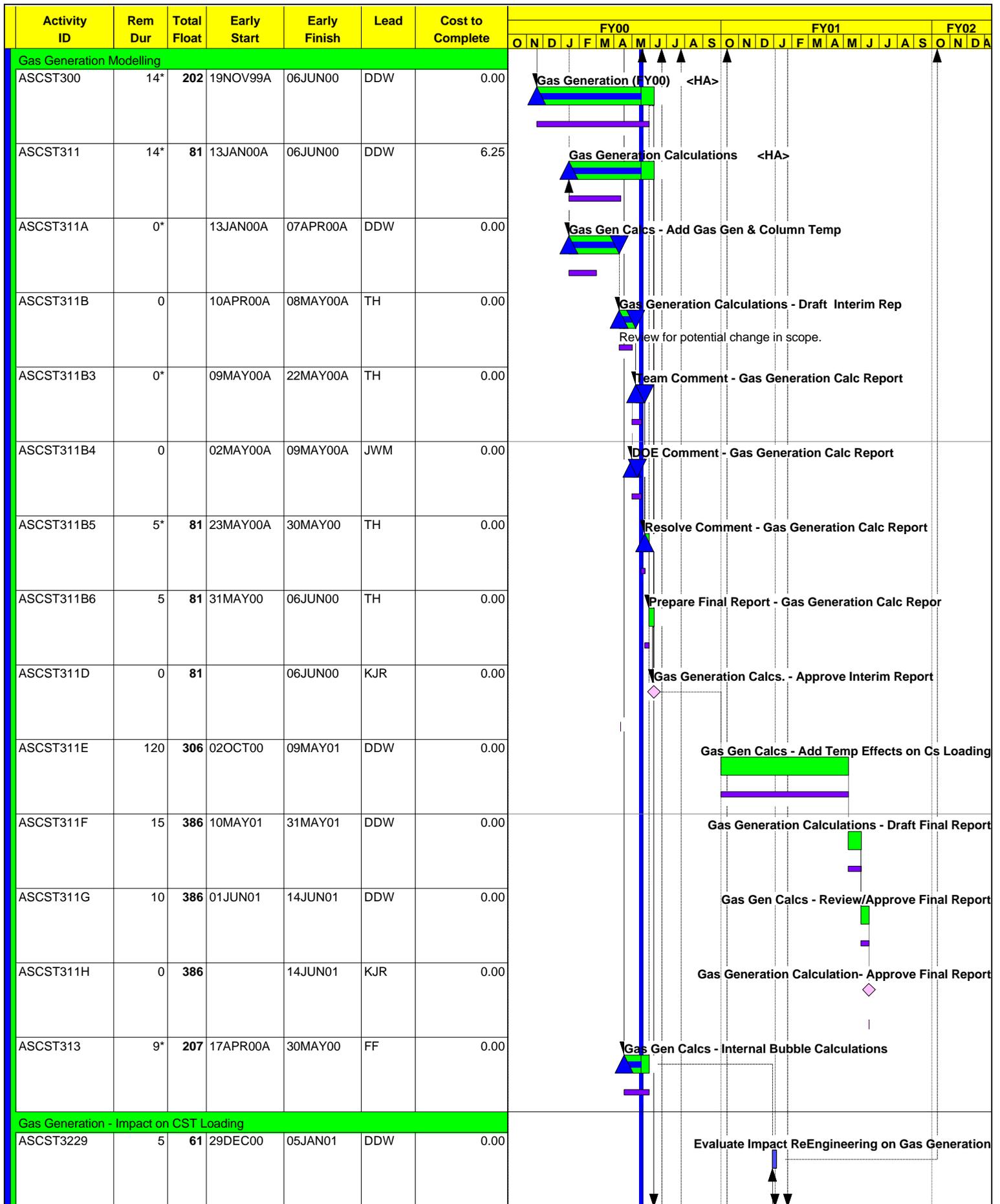


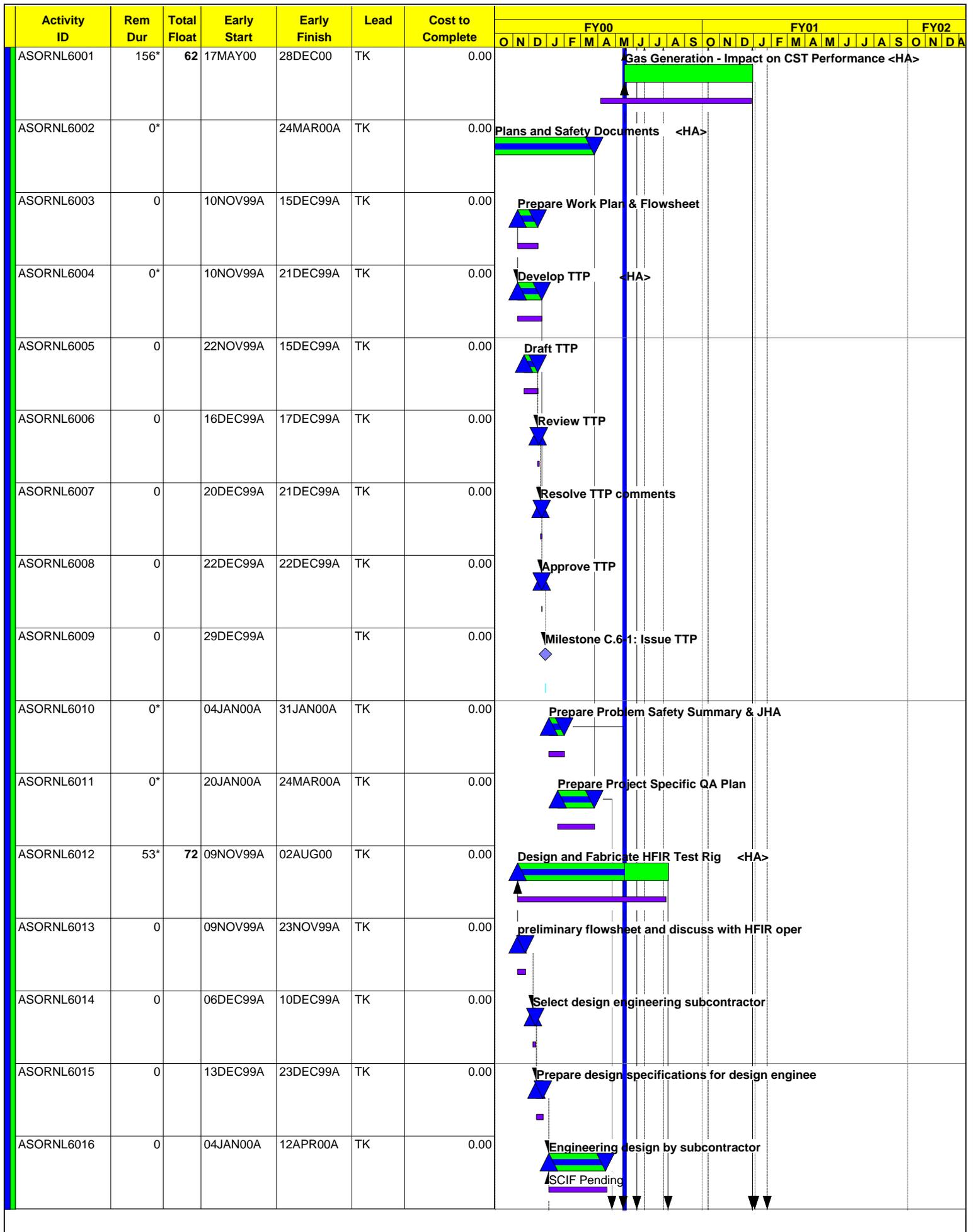










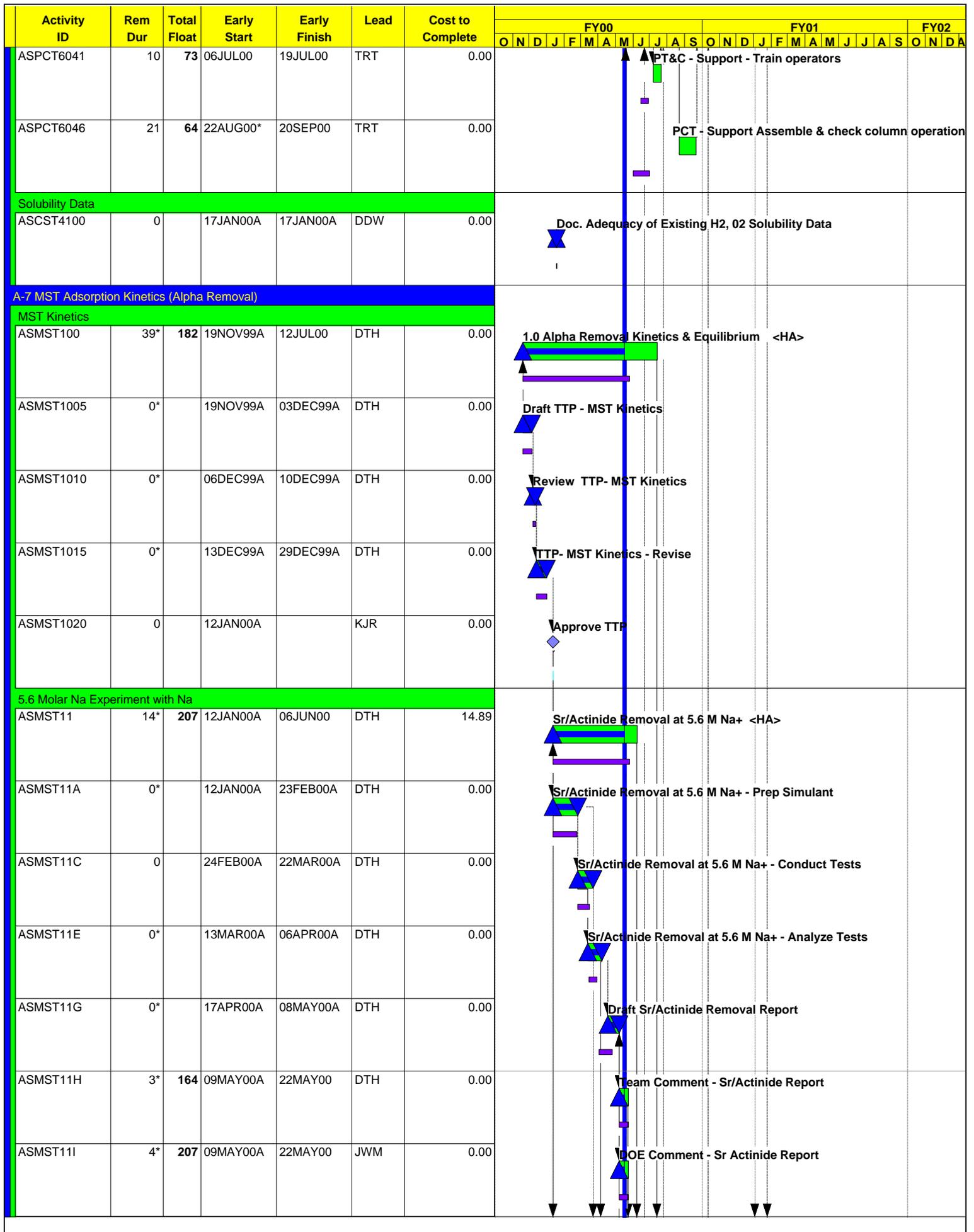










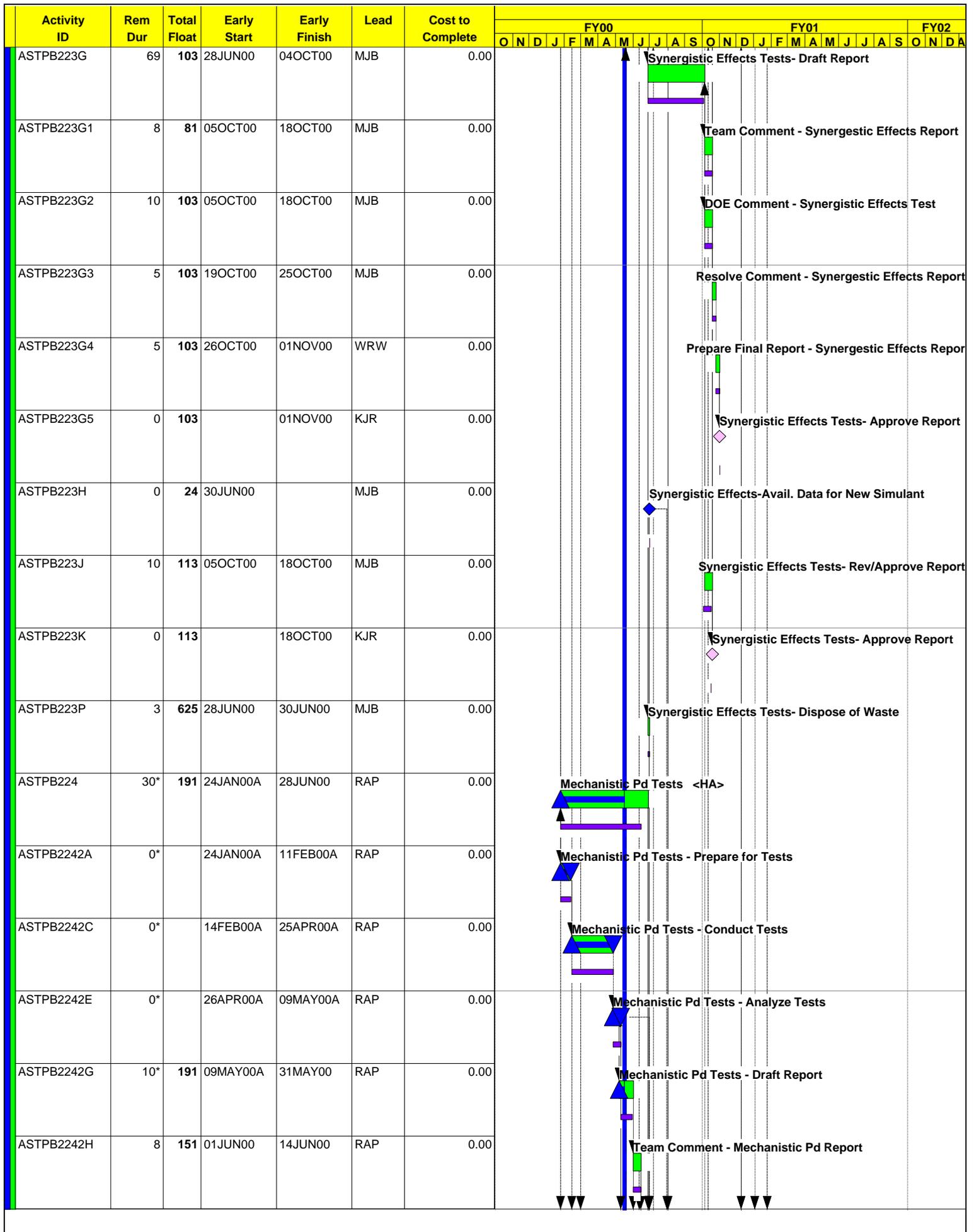














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ASTPB225P	3	551	12OCT00	16OCT00	TBP	0.00													Elect/Spect Transition Metals- Dispose of Waste														
ASTPB226	65*	104	12JUN00	12SEP00	MJB	0.00													Ru/Rh Activation <HA>														
ASTPB226A	15	104	12JUN00*	30JUN00	MJB	0.00													Ru/Rh Activation - Prepare for Tests														
ASTPB226C	40	104	03JUL00	28AUG00	MJB	0.00													Ru/Rh Activation - Conduct Tests														
ASTPB226E	10	104	29AUG00	12SEP00	MJB	0.00													Ru/Rh Activation - Analyze Tests														
ASTPB226P	3	572	13SEP00	15SEP00	MJB	0.00													Ru/Rh Activation - Dispose of Waste														
ASTPB227	0*		14FEB00A	12MAY00A	LNO	0.00	Expanded Metals Tests <HA>																										
ASTPB227A	0*		14FEB00A	22MAR00A	LNO	0.00	Expanded Metals - Prepare for Tests includes reagent delivery, promised ship date 3/8																										
ASTPB227C	0*		23MAR00A	03MAY00A	LNO	0.00	Expanded Metals - Conduct Tests																										
ASTPB227E	0*		03MAY00A	12MAY00A	LNO	0.00	Expanded Metals - Analyze Tests																										
ASTPB227P	6*	651	15MAY00A	24MAY00	LNO	0.00	Expanded Metals - Dispose of Waste																										
ASTPB228	82*	108	30JUN00	25OCT00	MJB	0.00													Develop and Test New Simulant <HA>														
ASTPB2280	0	24	30JUN00		MJB	0.00													Best Simulant Knowledge Available														
ASTPB2281	5	24	30JUN00*	07JUL00	MJB	0.00													Develop New Simulant														
ASTPB228A	5	24	30JUN00	07JUL00	MJB	0.00													Test New Simulant - Prepare for Tests														
ASTPB228C	10	24	10JUL00	21JUL00	MJB	0.00													Test New Simulant - Conduct Tests														

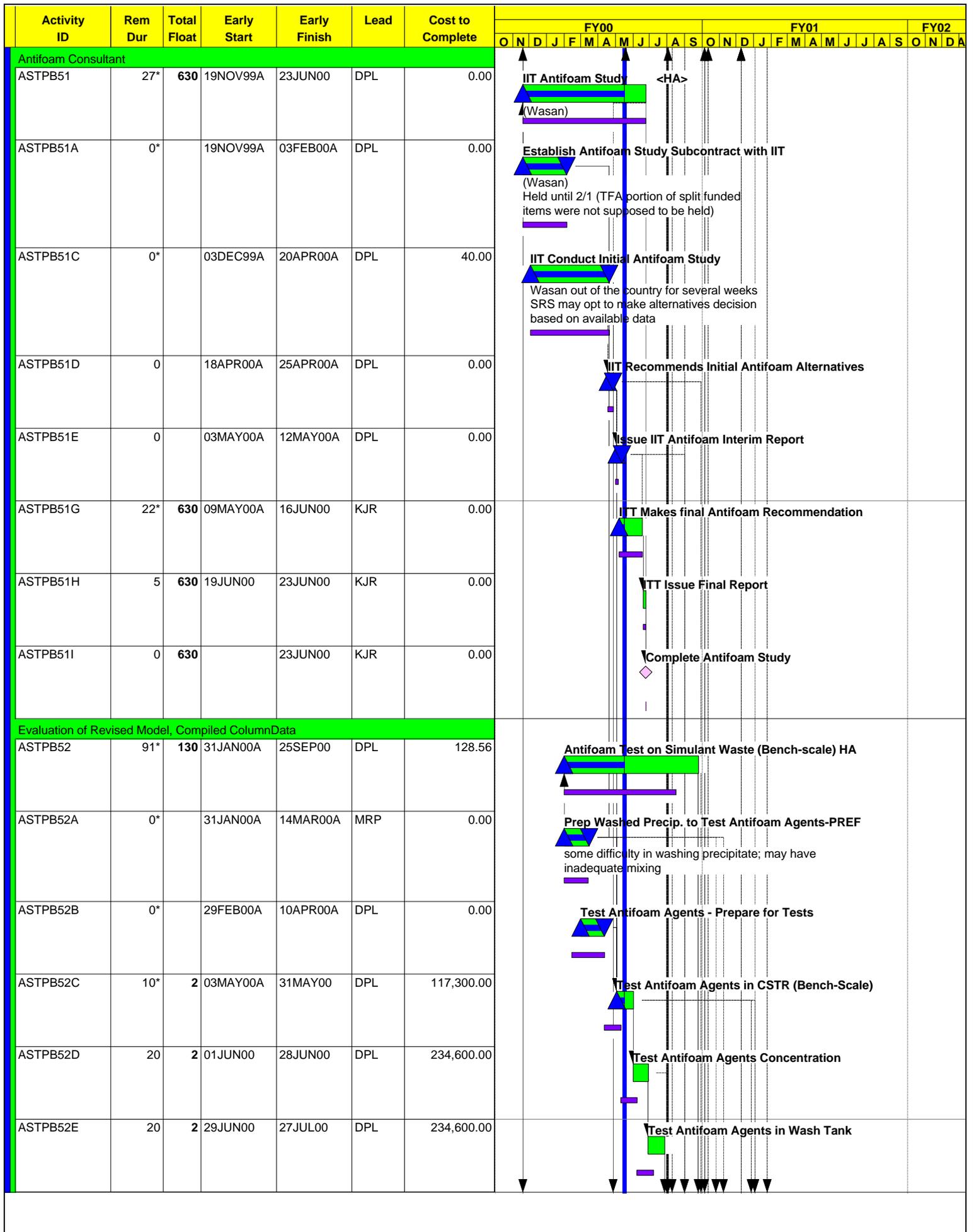




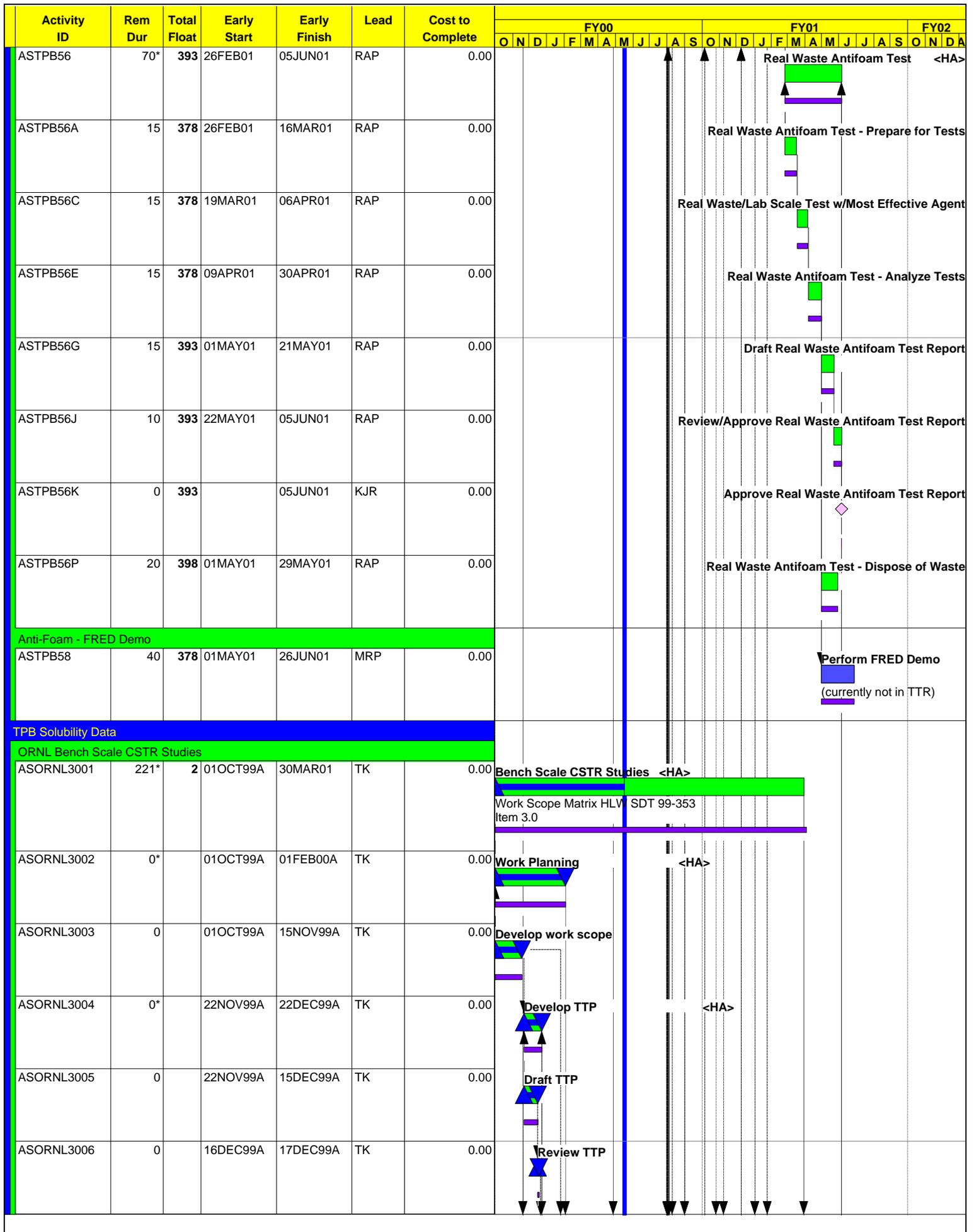














Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02			
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ASORNL3023	94*	75	15DEC99A	29SEP00	TK	0.00	Documentation support - LOE, B. Brock																											
ASORNL3024	94*	75	15DEC99A	29SEP00	TK	0.00	QA support - LOE, G. Chitwood																											
ASORNL3025	51*	47	04OCT99A	31JUL00	TK	0.00	20 L Hot Cell CSTR Preparations <HA>																											
ASORNL3026	0		04OCT99A	28JAN00A	TK	0.00	CSTR decon and waste disposal																											
ASORNL3027	0		31JAN00A	03FEB00A	TK	0.00	Chemical Clean Cross Flow Filters Element																											
ASORNL3028	0*		07FEB00A	10FEB00A	TK	0.00	Removal to Primary Flex Tubing																											
ASORNL3029	0*		28JAN00A	25FEB00A	TK	0.00	Move feed tanks and waste collection system To Cell C																											
ASORNL3030	0		15DEC99A	22FEB00A	TK	0.00	Identify and procure new level instrumentation																											
ASORNL3031	0		06DEC99A	21JAN00A	TK	0.00	Evaluate backpressure control valve problem. Valve Reported as pulled 01 Feb 2000.																											
ASORNL3032	0		24JAN00A	14APR00A	TK	0.00	Order Parts for BackPressure Control Valves Stem Coupling Fabrication in Progress.																											
ASORNL3033	0*		15DEC99A	15FEB00A	TK	0.00	Procure new valve trim for filtrate line																											
ASORNL3034	0		15DEC99A	21JAN00A	TK	0.00	Redesign backpuse system On Both Cross Flow Filters																											
ASORNL3035	0		01FEB00A	10MAR00A	TK	0.00	Procure parts for modified backpuse system Flow Meter Transducer Received.																											
ASORNL3036	0		24JAN00A	15MAR00A	TK	0.00	Choose Benzene Monitoring Option for CSTR Ops and obtain approval																											
ASORNL3037	0		16MAR00A	29MAR00A	TK	0.00	Prepare & Approve Flowsheet CSTR Benzene Monitor and obtain approval																											
ASORNL3038	8*	49	30MAR00A	26MAY00	TK	0.00	Procure & Receive Benzene Monitoring Equipment All Materials ordered, need delivery dates																											





















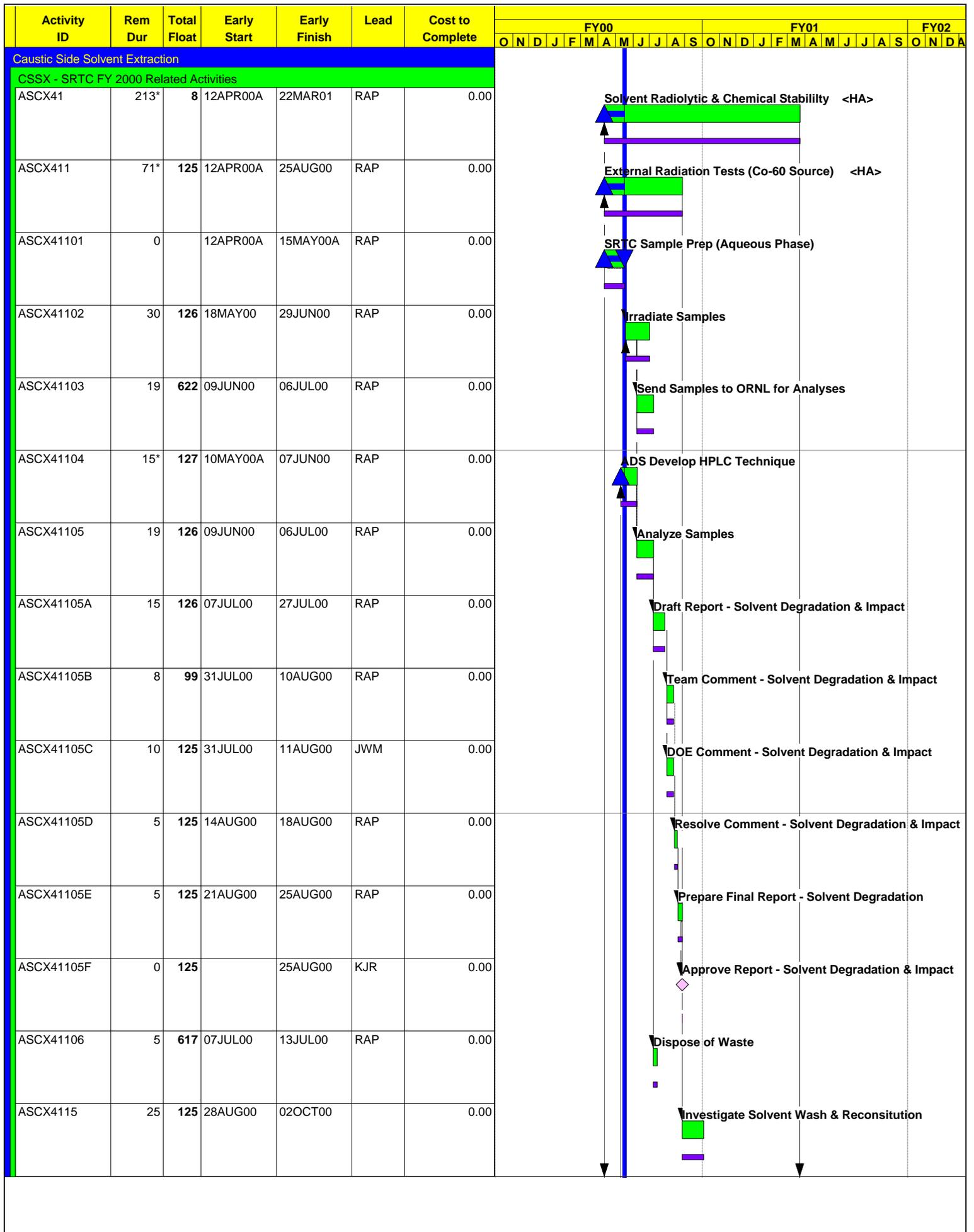




Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02		
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
ASTPB431C	15	350	20APR01	10MAY01	MRP	0.00													PREF Washing Studies - Conduct Tests/Analyze 														
ASTPB431G	10	390	11MAY01	24MAY01	MRP	0.00													PREF Washing Studies - Draft Report 														
ASTPB431J	10	390	25MAY01	08JUN01	MRP	0.00													PREF Washing Studies - Review/Approve Report 														
ASTPB431K	0	390		08JUN01	KJR	0.00													PREF Washing Studies - Approve Report 														
ASTPB431P	5	350	11MAY01	17MAY01	MRP	0.00													PREF Washing Studies - Dispose of Waste 														
ASTPB4320	15	295	07AUG01	27AUG01		0.00													Scale Washing Tests (Mtl From ASTPB4170) 														
ASTPB4322	0	295		27AUG01		0.00													Evaluate Viability of Semi Batch Washing 														
ASTPB4330	40	295	28AUG01	23OCT01		0.00													Perform Semi Batch Wash Testing - PREF 														
ASTPBVIA1	0			25APR00A	KJR	0.00													Assess Viability 														
ASTPBVIA2	0	604		01AUG00*	KJR	0.00													Assess Viability 														
DWPf Coupled Operations Chemistry																																	
Coupled Operations - General Planning																																	
ASTPB1600	195*	368	29SEP00	11JUL01	DPL	0.00													16.0 DWPf Coupled Operation Chemistry <HA> 														
ASTPB16005	0*		19NOV99A	03DEC99A	DPL	0.00	Draft TTP - Hydrolysis Basic Chemistry 																										
ASTPB16012	0		06DEC99A	10DEC99A	DPL	0.00	Review TTP- Hydrolysis Basic Chemistry 																										
ASTPB16014	0		13DEC99A	29DEC99A	DPL	0.00	TTP- Hydrolysis Chemistry - Revise 																										
Nitrate/Nitrite as Function of Absorbed Dose																																	
ASTPB16020	0	418	29SEP00		KJR	0.00													Approve TTP- Hydrolysis Basic Chemistry 														



Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02		
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
ASTPB163E	0	498	29SEP00	28SEP00	DPL	0.00													Hydrolysis Studies - Pilot Preparation														
ASTPB163G	45	363	02APR01	05JUN01	DPL	0.00													Hydrolysis Studies - Pilot Demo														
ASTPB163J	15	368	06JUN01	26JUN01	DPL	0.00													Draft Hydrolysis Studies Report														
ASTPB163L	10	368	27JUN01	11JUL01	DPL	0.00													Review/Approve Hydrolysis Studies Report														
ASTPB163M	0	368		11JUL01	KJR	0.00													Approve Hydrolysis Studies Report														
ASTPB163P	30	363	06JUN01	18JUL01	DPL	0.00													Hydrolysis Studies - Dispose of Waste														
<b>Assess Alternate Catalyst Forms</b>																																	
ASTPB164	60	418	29SEP00	27DEC00	DPL	0.00													Assess Alternate Catalyst Forms														
ASTPB164G	15	478	28DEC00	18JAN01	DPL	0.00													Draft Alternate Catalyst Forms Report														
ASTPB164J	10	478	19JAN01	01FEB01	DPL	0.00													Review/Approve Alternate Catalyst Forms Report														
ASTPB164K	0	478		01FEB01	KJR	0.00													Approve Alternate Catalyst Forms Report														
<b>Technical Feasibility of Recycling Catalyst</b>																																	
ASTPB165	60	418	28DEC00	23MAR01	DPL	0.00													Assess Technical Feasibility of Recycle Copper														
ASTPB165G	15	418	26MAR01	16APR01	DPL	0.00													Draft Recycle Copper Feasibility Report														
ASTPB165J	10	418	17APR01	30APR01	DPL	0.00													Review/Approve Recycle Copper Feasibility Report														
ASTPB165K	0	418		30APR01	KJR	0.00													Approve Recycle Copper Feasibility Report														
<b>Summary Level Science Technologies</b>																																	
ASTEAM1100	264*	393	19NOV99A	05JUN01	DPL	0.00													Science & Technology Development <HA>														

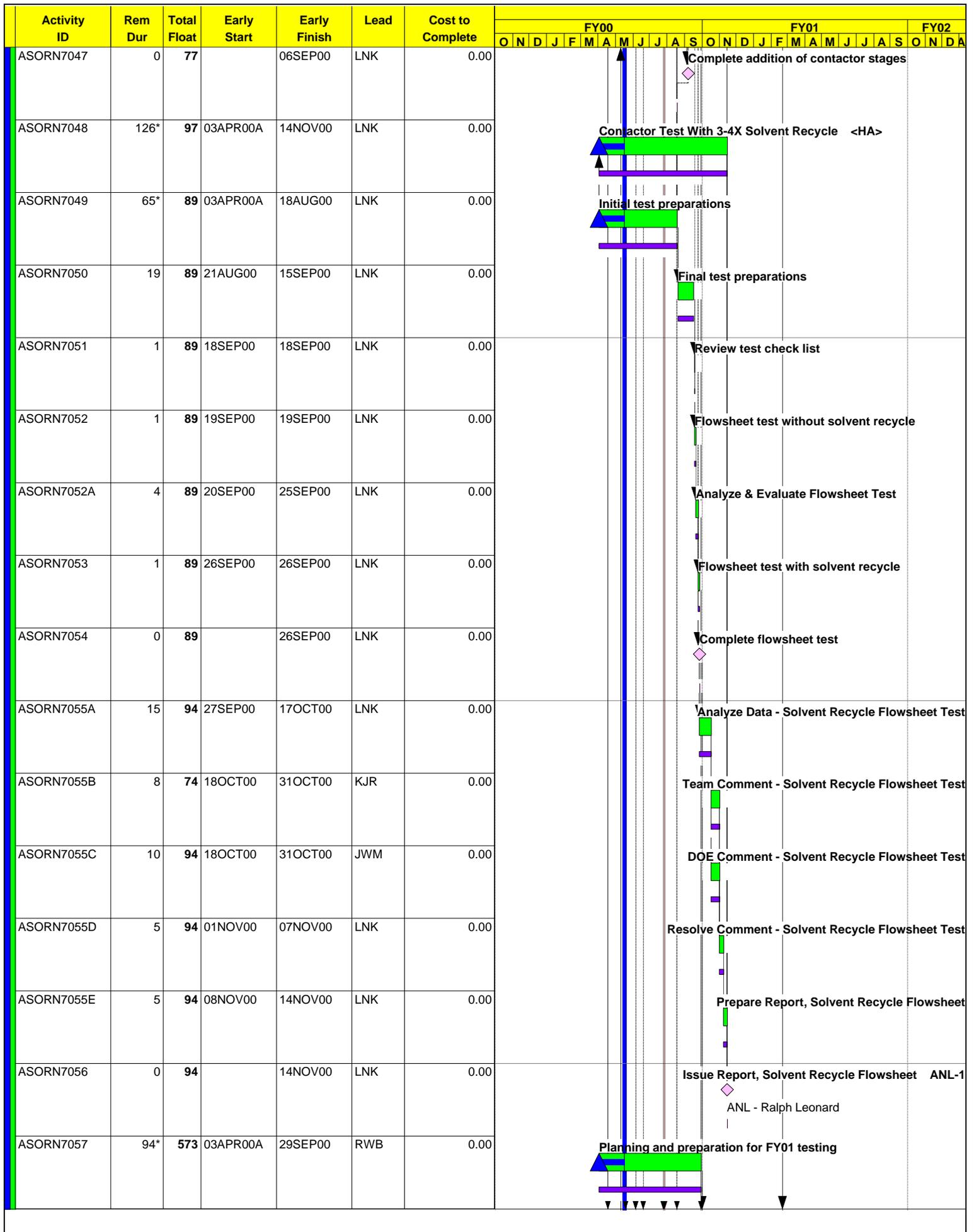


Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02		
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
ASCX412	213*	8	12APR00A	22MAR01	RAP	0.00													Batch Equilibrium Hot Cell Test (Interim Rpt)<HA														
																			HAW (Internal Cs-137 Dose)														
ASCX412A	68*	8	12APR00A	22AUG00	RNH	0.00													Obtain Real Waste Samples from Tank Farm														
ASCX412C	25	79	22AUG00	26SEP00	RAP	0.00													Real Waste Batch Contact Test														
																			(Identify Species Extracted)														
ASCX412E	15	79	27SEP00	17OCT00	RAP	0.00													Analyze Data														
ASCX412E2	8	62	08NOV00	21NOV00	RAP	0.00													Team Comment - Batch Equilibrium Test Report														
ASCX412E3	10	79	08NOV00	21NOV00	JWM	0.00													DOE Comment - Batch Equilibrium Test Report														
ASCX412E4	5	79	22NOV00	30NOV00	RAP	0.00													Resolve Comment - Batch Equilibrium Test Report														
ASCX412E5	5	79	01DEC00	07DEC00	RAP	0.00													Prepare Final Report - Batch Equilibrium Test Report														
ASCX412E6	0	79		07DEC00	KJR	0.00													Approve Report - Batch Equilibrium Test Report														
ASCX412M	5	545	18OCT00	24OCT00	RAP	0.00													Dispose of Waste														
ASCX412N	240	8	23AUG00	07AUG01	RAP	0.00													Conduct In-Cell Exposure Tests														
ASCX412P	225	299	19OCT00	12SEP01	RAP	0.00													Analyze Data														
ASCX412R	15	8	15FEB01	08MAR01	RAP	0.00													Draft In-Cell Exposure Interim Report														
ASCX412T	10	8	09MAR01	22MAR01	RAP	0.00													Review/Approve In-Cell Exposure Interim Report														
ASCX412V	0	8		22MAR01	KJR	0.00													Approve In-Cell Exposure Interim Report														
ASCX412W	15	299	13SEP01	03OCT01	RAP	0.00													Draft In-Cell Exposure Final Report														















Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02			
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	
ASORN7106	17	496	27DEC00	19JAN01	LNK	0.00																												Print test report
ASORN7107	0	496		19JAN01	LNK	0.00																												CASD -2 - Release Test Report
ASORN7108	182*	41	17MAY00	05FEB01	LNK	527,000.00																												Cs-137 Batch Irradiation with Simulant <HA>
ASORN7110	27*	8	03APR00A	23JUN00	LNK	0.00																												Prepare Project Safety Summary - CTD-1
ASORN7111	27*	8	03APR00A	23JUN00	LNK	0.00																												Prepare ALARA plan
ASORN7112	7*	126	10MAY00A	25MAY00	LNK	0.00																												Simulant Preparation <HA>
ASORN7113	0		10MAY00A	10MAY00A	LNK	0.00																												Define simulant volume needs
ASORN7114	0		10MAY00A	10MAY00A	LNK	0.00																												Receive simulant definition from SRS
ASORN7115	0		11MAY00A	16MAY00A	LNK	0.00																												Procure chemicals
ASORN7116	7*	126	10MAY00A	25MAY00	LNK	0.00																												Prepare simulant
ASORN7117	68*	-7	03APR00A	23AUG00	LNK	0.00																												Hot Cell Batch Contacting with Cs137 Test <HA>
ASORN7118	0		03APR00A	15MAY00A	LNK	0.00																												Prepare Draft of Test Plan - SOW Item 5.1.7
ASORN7119	1*	113	16MAY00A	17MAY00	LNK	0.00																												Review Test Plan by ANL, ORNL, & SRS (SOW 5.1.7)
ASORN7120	5	113	18MAY00	24MAY00	LNK	0.00																												CTD-1 Resolve Review Comments
ASORN7121	0	113		24MAY00	LNK	0.00																												CTD-1 Issue test plan
ASORN7122	14	97	19JUN00*	10JUL00	LNK	0.00																												Prepare test samples (SOW 5.1.7)















Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02		
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
ASCX33460	10	13	03NOV00	16NOV00	RWB	0.00													RFI - RDC/RO Review														
ASCX33470	0	10		16NOV00	RWB	0.00													Issue Request for Information to Procurement														
ASCX33480	20	10	20NOV00	28DEC00	RWB	0.00													Procurement - Assemble Package & Issue to Vendor														
ASCX33520	40	10	02JAN01	13MAR01	RWB	0.00													Vendors - Prepare Responses														
ASCX33530	10	10	14MAR01	29MAR01	RWB	0.00													Evaluate Vendor RFI Responses														
ASCX33540	0	10		29MAR01	RWB	0.00													Qualify Operating Chemical Suppliers Assurance of BobCalix & Solvent Supply NB: Restrains Technology Selection														
ASCX33550	89*	28	10MAY00A	21SEP00	LNK	0.00													WORNL - Prepare Product Specifications														
ASCX33600	133*	57	02APR01	28NOV01	RWB	0.00													Request For Quotation <HA>														
ASCX33610	10	156	30MAR01	12APR01	RWB	0.00													Modify Requirements & Synthetic Procedures														
ASCX33620	10	156	16APR01	27APR01	RWB	0.00													Review Modification to Synthetic Procedures														
ASCX33630	0	156		27APR01	RWB	0.00													Approve Modifications - Synthetic Procedures														
ASCX33640	5	156	30APR01	04MAY01	RWB	0.00													Prepare Request For Quotations (RFQ)														
ASCX33650	5	156	07MAY01	11MAY01	RWB	0.00													Review Request for Quotation (RFQ)														
ASCX33660	5	156	07MAY01	11MAY01	RWB	0.00													Incorporate Comments Request for Quotation (RFQ)														
ASCX33670	0	156		11MAY01	RWB	0.00													Approve Request For Quotation														
ASCX33680	10	156	14MAY01	25MAY01	RWB	0.00													RFQ - Intellectual Property Review														

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02			
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	A
ASCX33700	10	156	14MAY01	25MAY01	RWB	0.00																									RFQ - Export Control Review			
ASCX33710	10	156	14MAY01	25MAY01	RWB	0.00																									RFQ - RDC/RO Review			
ASCX33720	0	156		25MAY01	RWB	0.00																									Issued Approved & Cleared RFQ to Procurement			
ASCX33730	5	73	25SEP01	01OCT01	RWB	0.00																									Procurement - Issue RFQ to Vendors NB: Restrained by Record of Decision			
ASCX33740	30	73	02OCT01	12NOV01	RWB	0.00																									Vendors - Respond to Request For Quotations			
ASCX33750	0	73		12NOV01	RWB	0.00																									Procurement - Recieve & Open Responses			
ASCX33760	10	73	13NOV01	28NOV01	RWB	0.00																									Evaluate Response to RFQ			
ASCX33770	0	73		28NOV01	RWB	0.00																									Issue Vendor Recommendation to Procurement			
ASCX33780	10	73	29NOV01	12DEC01	RWB	0.00																									Procurement - Finalize Commercial Terms			
<b>CSSX - Operating Chemical Supply &amp; Fabrication</b>																																		
ASCX33900	150*	57	13DEC01	16SEP02	RWB	0.00																									CSSX - Initial Commerical Manufacture <HA>			
ASCX33910	0	57	13DEC01		RWB	0.00																									Award Operating Chemical Supply Contract(s)			
ASCX33920	60	57	13DEC01	04APR02	RWB	0.00																									Operating Chemical Supplier - Sample Fabrication			
ASCX33930	20	57	08APR02	09MAY02	RWB	0.00																												
ASCX33940	10	57	13MAY02	29MAY02	RWB	0.00																												
ASCX33950	60	57	30MAY02	16SEP02	RWB	0.00																												

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02											
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D									
<b>CSSX - Real Waste Contactor Testing</b>																																										
ASCXS1000	173*	2	10MAY00A	29MAR01	RWB	0.00	Real Waste Testing <HA>																																			
ASCXS1100	45*	1	10MAY00A	07AUG00	RWB	0.00	Real Waste Test - Feasibility & Location <HA>																																			
ASCXS1110	25*	1	10MAY00A	29JUN00	RWB	0.00	Conduct Real Waste Feasibility Study																																			
ASCXS1120	16	1	03JUL00	31JUL00	RWB	0.00	Real Waste - Site Selection																																			
ASCXS1130	4	1	01AUG00	07AUG00	JWM	0.00	Real Waste - DOE Evaluation																																			
ASCXS1140	0	1		07AUG00	JWM	0.00	DOE - Approval of Path Forward																																			
ASCXS1150	5	19	08AUG00	15AUG00	RNH	0.00	Rebaseline Schedule																																			
ASCXS2130	4	57	16AUG00	22AUG00	TBD	0.00	Revise HLW Sampling Plan																																			
ASCXS2140	0	57		22AUG00	TBD	0.00	HLW - Approve Revised Sampling Plan																																			
ASCXS2150	10	57	23AUG00	11SEP00	TBD	0.00	Sample Extraction Planning, Arrange Equipment																																			
ASCXS2160	4	55	14SEP00	20SEP00	TBD	0.00	Extract Tank Sample																																			
ASCXS2170	4	55	21SEP00	27SEP00	TBD	0.00	Transport Sample to Test Site																																			
ASCXS3200	81*	2	24JUL00	14DEC00	TBD	0.00	Real Waste Test - Contactor Equipment <HA>																																			
ASCXS3210	10	0	24JUL00	08AUG00	TBD	0.00	Contactor - Develop Drawings & Specifications																																			
ASCXS3220	10	0	09AUG00	24AUG00	TBD	0.00	Contactor - Finalize Bid Package																																			
ASCXS3230	0	0	28AUG00		TBD	0.00	Contactor - Review & Approve Bid Package																																			

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02		
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
ASCXS3240	30	3	25AUG00	23SEP00	TBD	0.00													Contractor - Vendor Bidding														
ASCXS3250	40	2	25SEP00	05DEC00	TBD	0.00													Contractor - Vendor Fabricate Equipment														
ASCXS3260	2	2	06DEC00	07DEC00	TBD	0.00													Contractor - Witness Factory Acceptance Test														
ASCXS3270	4	2	11DEC00	14DEC00	TBD	0.00													Contractor - Vendor Ship Equipment														
ASCXS6000	77*	2	16AUG00	08JAN01	TBD	0.00													Real Waste Test - Operating Parameters												<HA>		
ASCXS6110	10	19	16AUG00	31AUG00	TBD	0.00													Prepare Functional Test Procedure														
ASCXS6120	10	19	05SEP00	20SEP00	TBD	0.00													Unresolved Safety Question Resolution														
ASCXS6130	10	19	21SEP00	09OCT00	TBD	0.00													Safety Analysis & Reviews														
ASCXS6140	0	19		09OCT00	TBD	0.00													SRS - Review & Approve Test Plans														
ASCXS6160	20	19	10OCT00	13NOV00	TBD	0.00													Prepare Operational Staff														
ASCXS6165	20	19	10OCT00	13NOV00	TBD	0.00													Real Waste Test - Facility Specific Modification														
ASCXS6180	10	2	18DEC00	08JAN01	TBD	0.00													Set-up Rig, Preoperational Testing														
ASCXS7000	0	2		08JAN01	TBD	0.00													DOE - Real Waste Test - Approval to Proceed														
ASCXS7100	22*	2	09JAN01	14FEB01	TBD	0.00													Real Waste Testing												<HA>		
ASCXS7200	10	2	09JAN01	24JAN01	TBD	0.00													Perform Real Waste Testing														
ASCXS7300	15	3	25JAN01	14FEB01	TBD	0.00													Analyze Data - Real Waste, Contactor Test														

Activity ID	Rem Dur	Total Float	Early Start	Early Finish	Lead	Cost to Complete	FY00												FY01												FY02		
							O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
ASCXS7400	5	479	25JAN01	31JAN01	TBD	0.00													Dispose of Wastes														
ASCXS8100	31*	2	15FEB01	30MAR01	TBD	0.00													Test Report												<HA>		
ASCXS8110	10	3	15FEB01	01MAR01	TBD	0.00													Prepare Draft Report														
ASCXS8120	8	2	05MAR01	15MAR01	TBD	0.00													Team Comment - Real Waste, Contactor Test Report														
ASCXS8130	10	2	05MAR01	16MAR01	TBD	0.00													DOE Comment - Real Waste, Contactor Test Report														
ASCXS8140	5	2	19MAR01	23MAR01	TBD	0.00													Resolve Comment - Real Waste, Contactor Test														
ASCXS8150	5	2	26MAR01	30MAR01	TBD	0.00													Prepare Final Report - Real Waste, Contactor Test														
ASCXS8160	0	2		30MAR01	TBD	0.00													Approve Report - Real Waste, Contactor Test														
<b>CSSX - Funding For Planning</b>																																	
ASSX00210	0*		22FEB00A	06MAR00A	KJR	0.00													Draft Oak Ridge Planning MPO														
ASSX00220	0*		22FEB00A	06MAR00A	KJR	0.00													Draft Argonne Planning MPO														
ASSX00230	0		06MAR00A	07MAR00A	KJR	0.00													Negotiate & Place Argonne Planning MPO														
ASSX00240	0		06MAR00A	07MAR00A	KJR	0.00													Negotiate & Place Oak Ridge Planning MPO														
<b>Solvent Extraction, General Planning</b>																																	
ASSX00010	0*		17JAN00A	04APR00A		0.00	CSSX - General Planning												<HA>														
ASSX00020	0		17JAN00A	24JAN00A	KJR	0.00	Complete Draft of RoadMap, Matrix, & Logic																										
ASSX00040	0		31JAN00A	03FEB00A	KJR	0.00	Comment Resolution																										



