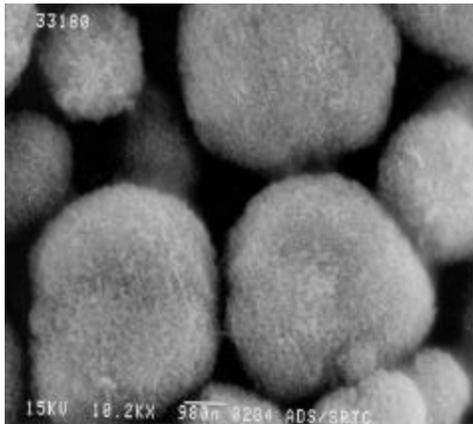


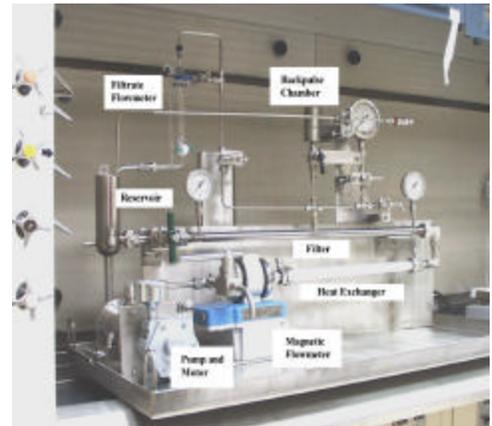


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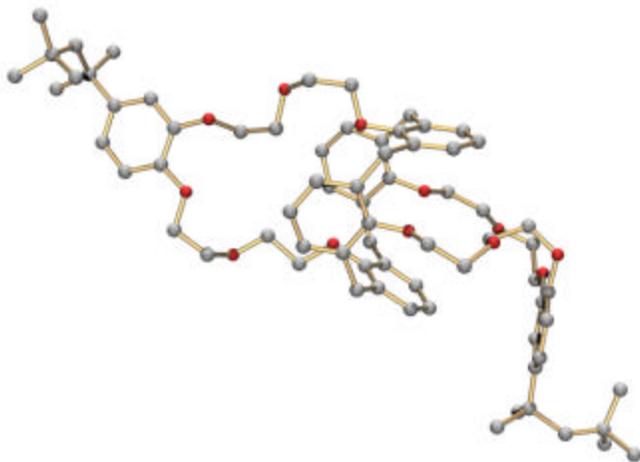
FY 2002 Research and Development Program Plan, Revision 0



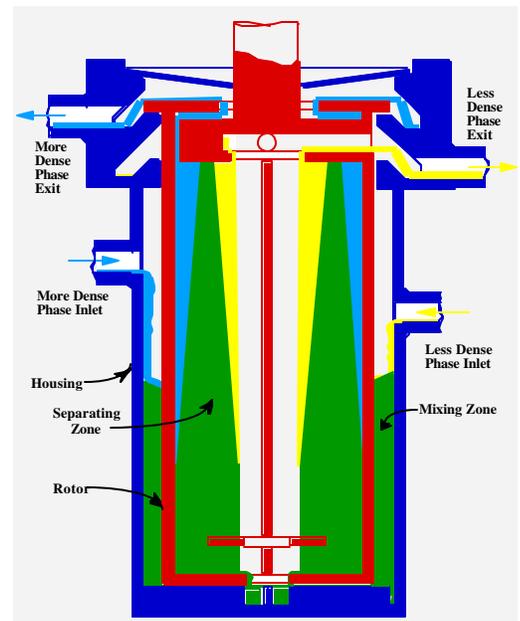
Monosodium Titanate Particles



Small-Scale Cross-Flow Filter



BOBCalixC6



Centrifugal Contactor

October 2001

**Savannah River Site Salt Processing Project:
FY 2002 Research and Development Program Plan**

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October 2001

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

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Richland, Washington 99352

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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 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 Production Facility (SPF) 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.

In April 2000, DOE-Headquarters (DOE-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 TFA issued a revised R&D program plan¹ in November 2000 for the three Cs removal candidate technologies — Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange, Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP) — and the associated alpha and Sr removal technologies.

The goal of these efforts was to conduct testing and evaluation of the three Cs removal technologies to obtain enough information to support a June 2001 technology down selection. Based on the R&D results and subsequent management recommendations^{2,3,4} DOE-HQ selected CSSX as the preferred Cs removal technology. This selection was documented in the SRS Supplemental Environmental Impact Statement and Notice of Availability was published in the Federal Register on July 20, 2001^{5,6}. Selection of a backup technology was deferred pending the results of additional R&D on Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange and Small Tank Tetraphenylborate Precipitation (STTP) processes.

A large number of technical issues, concerns, and uncertainties were identified during the previous phases of the SPP. Evaluation of these issues and concerns led to identification of a small number of areas that represent high technical risks to implementing the four processes described in this R&D Program Plan. These high-risk areas and the technology needs they represent were the focus of previous technology development efforts leading to down selection. Some of these high-risk areas were resolved or reduced to low-risk status during the FY00 and FY01 R&D program effort. Other areas remained as moderate or high risk, and continued R&D effort is required for those areas.

The nature of the R&D work on the Alpha and Sr Removal and CSSX processes has transitioned from technology development for down selection to providing input for conceptual and preliminary design of the Salt Waste Processing Facility (SWPF). This work will include laboratory studies, bench-scale tests, and prototype equipment development. Limited R&D activities are expected to continue on the CST or STTP backup technology(ies), and additional direction will be provided by DOE regarding scope of the desired R&D activities for the backup technology. Finally, recommendations from independent review groups, such as NRC committees, identified technology development needs that are being incorporated into the ongoing R&D 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 FY02 program include WSRC's Savannah River Technology Center, Oak Ridge National Laboratory, Argonne National Laboratory, Pacific Northwest National Laboratory, and various universities and commercial vendors. Additional participants will be identified after the response to the R&D solicitation (TFA's Salt Processing Project Call for Proposals) have been evaluated and awarded. Combined program funding for FY01 was \$13.4 million and total planned funding for FY02 is \$10.7 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 R&D program is focused on continued technical maturity, risk reduction, engineering development, and design support as the program moves toward DOE's selection of engineering, procurement, and construction contractor(s) for the SWPF.

Acknowledgments

The Tanks Focus Area acknowledges the significant contributions of the following individuals as writers and/or reviewers of the Fiscal Year 2002 Salt Processing Project Research and Development Program Plan.

All Sections

Jimmy Bell, Bell Consultants, Inc.
Wally Schulz, W2S Company, Inc.
Larry Tavlarides, University of Syracuse
George Vandegrift, Argonne National Laboratory
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Leon Klatt, Oak Ridge National Laboratory
Bruce Moyer, Oak Ridge National Laboratory
Ralph Leonard, Argonne National Laboratory

The TFA and all individuals above express their particular appreciation to Shari Clifford (WPI) who compiled and edited several draft versions, and to Lynne Roeder-Smith and Mary Ann Showalter (Pacific Northwest National Laboratory) who edited the final draft of Revision 0 of the Research and Development Program Plan. These individuals skillfully incorporated countless rounds of comments. The Plan could not have been issued on schedule without their dedication and personal sacrifice. Also, we appreciate the support of Mitch Peel (Savannah River Technology Center) who assisted with the schedule development and integration for the program.

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Acronyms and Abbreviations

For this report abbreviations for chemical names and compounds, or measurement units are not listed. They are spelled out where first used.

ANL	Argonne National Laboratory
AOP	Annual Operating Plan
AST	Alpha Sorption Tank
CF	Contamination Factor
CIF	Consolidated Incineration Facility
CSSX	Caustic Side Solvent Extraction
CST	crystalline silicotitanate
CST	CST Non-Elutable Ion Exchange
CSTR	Continuously Stirred Tank Reactor
DF	Decontamination Factor
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE-HQ	U.S. Department of Energy-Headquarters
DSS	decontaminated salt solution
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
ESP	Extended Sludge Processing Facility
ETF	Effluent Treatment Facility
FFA	Federal Facilities Agreement
FY	fiscal year
HLW	high level waste
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LLW	low level waste
ITP	In-Tank Precipitation
IWO	Internal Work Order
MST	monosodium titanate
NMR	nuclear magnetic resonance
NRC	National Research Council
ORNL	Oak Ridge National Laboratory
PCCS	Product Composition Control System
PEG	Program Execution Guidance
PHA	precipitate hydrolysis aqueous
PNNL	Pacific Northwest National Laboratory
R&D	research and development
SCDHEC	South Carolina Department of Health and Environmental Control
SDF	Saltstone Disposal Facility
SEIS	Supplemental Environmental Impact Statement
SEM	scanning electron microscope
SME	Slurry Mix Evaporator
SNL	Sandia National Laboratories
SPF	Saltstone Production Facility
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
SWPF	Salt Waste Processing Facility (proposed SPP facility)
TCR	Technical Change Request
TEM	transmission electron microscopy
TFA	Tanks Focus Area

TPB	tetraphenylborate
TTP	Technical Task Plan
TRU	transuranic
TWG	Technical Working Group
UFMB	Up-Flow Moving Bed
USC	University of South Carolina
WAC	Waste Acceptance Criteria
WSRC	Westinghouse Savannah River Company
XAFS	X-ray Absorption Fine-Structure
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 (water soluble) waste treatment portion of the SRS HLW cleanup effort. The overall SPP encompasses the selection, design, construction and operation of technologies to prepare the salt waste feed material for immobilization at the site's Saltstone Production Facility (SPF) 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 April 2000, DOE-Headquarters (DOE-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 TFA issued a revised R&D program plan¹ in November 2000 for the three Cs removal candidate technologies — Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange, Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP) — and the associated alpha and Sr removal technologies.

The goal of these efforts was to conduct testing and evaluation of the three Cs removal technologies to obtain enough information to support a June 2001 technology down selection. Based on the R&D results and subsequent management recommendations^{2,3,4} DOE-HQ selected CSSX as the preferred Cs removal technology. This selection was documented in the SRS Supplemental Environmental Impact Statement and Notice of Availability was published in the Federal Register on July 20, 2001^{5,6}.

This R&D program plan (Plan) describes the technology development program for CSSX and alpha/Sr removal in FY02. CST and STTP are discussed as possible backup technologies.

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 (incidental wastes) for subsequent on-site low-level waste (LLW) disposal.

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. During radioactive startup of ITP in 1995, higher than predicted releases of benzene occurred. Based on subsequent studies of the chemical and physical properties of the ITP process, Westinghouse Savannah River Company (WSRC) concluded they could not simultaneously meet process throughput requirements while maintaining process safety. On February 20, 1998, DOE-Savannah River (SR) concurred with the WSRC evaluation of the chemistry data and WSRC began a system engineering evaluation of alternative salt processing methods. The system engineering studies evaluated over 140 alternative processes and reduced the list to four candidates: CST, CSSX, STTP, and Direct Grouting (with no Cs removal). Further review eliminated Direct Grouting as an option; thus R&D efforts focused on the CST, CSSX, and STTP.

In 1999, DOE-HQ asked the National Research Council (NRC) to independently review the evaluation of technologies to replace ITP. NRC issued a letter report⁷ in October 1999 and their final report⁸ was issued in August 2000. As a result of the interim NRC review, the DOE Under Secretary and the Assistant Secretary for Environmental Management jointly agreed that further R&D on each alternative was required to reduce technical uncertainty prior to a down-selection decision. 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 delayed the issuance of the draft Supplemental Environmental Impact Statement (SEIS) on SRS HLW treatment alternatives pending further development of salt processing technology alternatives.

In April 2000, DOE-HQ established the Technology Working Group to manage the R&D program and to make a recommendation to the Assistant Secretary for Environmental Management on a preferred salt processing technology for implementation at SRS. In support of the Technical Working Group, the TFA was requested to assume management

responsibility for the SPP technology development program at SRS. The TFA was requested to review and revise the SPP technology development roadmaps, develop down-selection criteria, and prepare 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. The TFA issued the first integrated R&D Program Plan⁹ in May 2000 and it was revised for FY 2001¹ in November 2000. The R&D program focused on resolving high-risk areas for alpha/Sr removal and each alternative cesium removal process by mid-FY 2001 to support a DOE down-selection decision by June 2001. The Salt Processing Project Research and Development Summary Report⁴ issued in May 2001 documented the technology development results for each process.

A second NRC Committee was formed in May 2000 to support the technology down-selection decision. This committee was requested to evaluate the adequacy of the decision criteria, to evaluate the progress and results of the R&D efforts, and to assess whether technical uncertainties were sufficiently resolved to proceed with down selection. This committee issued an interim report on the down-selection criteria in March 2001¹⁰ and a final report in May 2001¹¹.

The SPP Technology Down Selection Technical Working Group and Management Review Board meetings were held May 21-24, 2001 at SRS. Presentations on the progress of the program were given by the TFA SPP Technology Development Manager and SPP System Leads, WSRC, and DOE-SR. The NRC reports and the presentations provided the Technical Working Group and the DOE-HQ with information needed to make a recommendation on the technology down selection. The Technical Working Group's Final Report² and the Management Review Board Report³ are available on the SRS SPP Website <<<http://www.srs.gov/general/srtech/spp/techsel.htm>>>. The selection of CSSX as the preferred cesium-removal alternative was documented in the Final SEIS⁵. The Notice of Availability was published in the Federal Register on July 20, 2001⁶.

3.0 High-Level Waste System Overview

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 Facility and Late Wash Facility)
- Sludge Processing (Extended Sludge Processing [ESP] Facility)
- Vitrification (DWPF)
- Wastewater Treatment (Effluent Treatment Facility [ETF])
- Solidification and Disposal (Saltstone Production Facility [SPF] and Saltstone Disposal Facility [SDF])
- Organic Destruction (Consolidated Incineration Facility [CIF])

The F and H Area Tank Farms, ESP Facility, DWPF, ETF, SPF, and SDF are all operational. The ITP facility operations are limited to safe storage and transfer of materials. The Late Wash Facility has been tested and is in an uncontaminated dry lay-up status. CIF is not presently operating.

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, and
- 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 closed and decommissioned in a cost-effective manner and in accordance with appropriate regulations and regulatory agreements.

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 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 Site Treatment Plan, which requires processing of all the HLW at SRS according to a schedule negotiated between the parties.

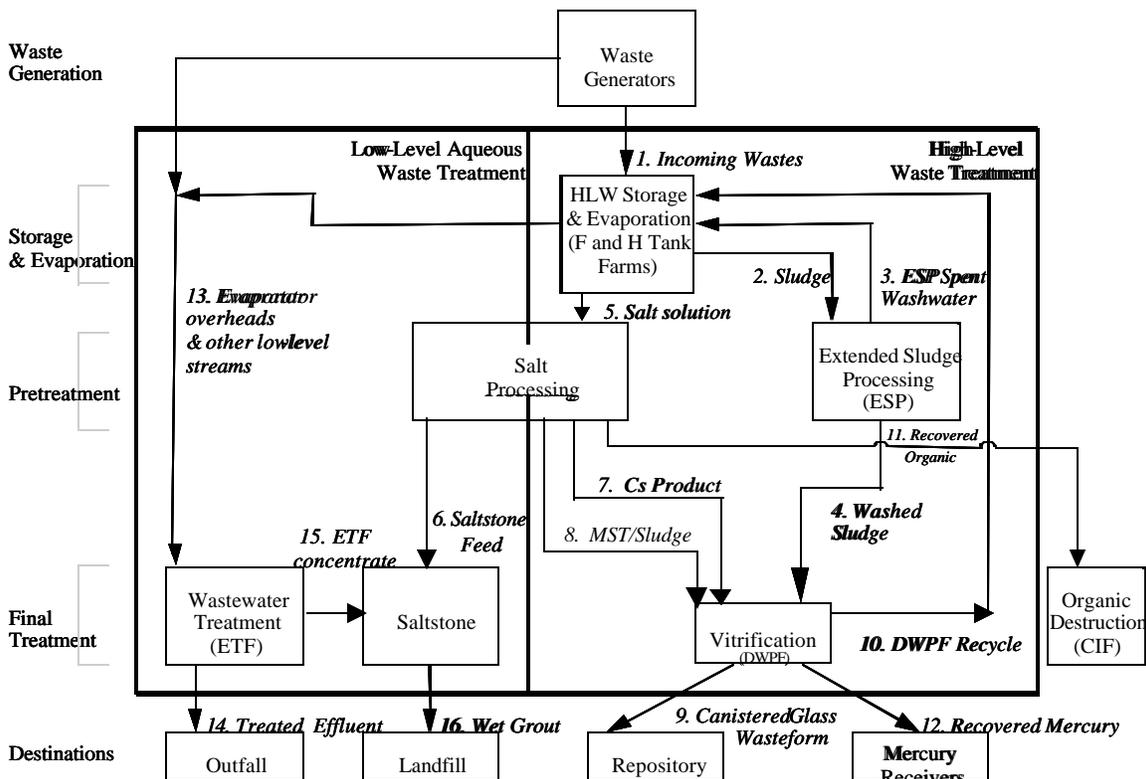


Figure 3.1 High-Level Waste Major Interfaces

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 Waste Processing Facility.

Incoming HLW (Stream 1) is received into HLW Storage and Evaporation facilities (F and H Area Tank Farms). 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 (Stream 13) is sent to ETF.

The insoluble sludges that settle to the bottom of waste receipt tanks in HLW Storage and Evaporation (Stream 2) are slurried and sent to ESP. 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 (Stream 3) is sent back to HLW Storage and Evaporation. The washed sludge (Stream 4) is sent to DWPF for feed pretreatment and vitrification.

Saltcake is redissolved using hydraulic slurring techniques similar to sludge slurring. As originally designed (Figure 3.1), the salt solutions from this operation, and other salt solutions from HLW Storage and Evaporation (Stream 5), were intended for feed to ITP. In the proposed Salt Waste Processing Facility, the salt solution is processed to remove radionuclides (i.e., actinides, Sr, and Cs). These concentrated radionuclides are then prepared for transfer to DWPF. For the CSSX process, actinides and Sr are removed by sorption with monosodium titanate (MST), and the slurry is filtered to remove MST and entrained sludge solids. The MST and sludge solids are transferred to DWPF as a separate stream (Stream 8). Cs contained in the organic phase (solvent) is stripped to an aqueous phase for transfer to DWPF and the solvent is recycled. The decontaminated aqueous stream (raffinate) is sent to SPF for disposal.

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 Waste 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 (Stream 9) is sent to on-site interim storage, and will eventually be disposed in a federal repository.

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 (Stream 10) and transferred to HLW Storage and Evaporation for processing.

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 (Stream 13) is sent to the ETF.

In the ETF, LLW is decontaminated by a series of cleaning processes. The decontaminated water effluent (Stream 14) is sent to the H-Area outfall and eventually flows to local creeks and the Savannah River. The contaminants removed from the water are concentrated (Stream 15) and sent to the SPF. In the SPF, the liquid waste (Streams 6 and 15) is combined with cement formers and pumped as a wet grout (Stream 16) to a vault located in the SDF. In the vault, the cement formers hydrate and cure, forming a saltstone monolith. The SDF will eventually be closed as a landfill.

4.0 Functional Requirements for the Salt Processing Project Process

As described in Section 3.0 and in the Final Supplemental Environmental Impact Statement Defense Waste Processing Facility,¹² 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 site's waste management mission, the SRS HLW System must immobilize key radionuclides in the salt waste for final disposition in support of environmental protection, safety, and current and planned missions. Any salt waste treatment process must be specifically developed to enable HLW salt disposition, and the impact to existing HLW facilities and processes at SRS must also be addressed. Functionally, the CSSX and any backup alternative technology must interface safely and efficiently with the processing facilities within and outside of the HLW System. The Cs and alpha/Sr removal activities 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 that SPP must fulfill to recover HLW storage space and comply with the FFA/STP.

Table 4.1 Key Functional Criteria

Area	Functions
Hazard Assessment Document	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 Salt Waste Processing Facility Feed Tank 49H Tank 50H New Waste Form	Support tank farm space management and the evaporator strategy for addressing DWPF recycle. Provide a Cs-containing product that supports glass waste form requirements relative to durability, crystallization temperature, sodium content, and viscosity. Provide a 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. Support Tank Farm space management strategy to recover Tank 49H for HLW storage. Support Tank Farm space management strategy to recover Tank 50H for HLW storage. Comply with DOE-RW* HLW repository requirements. (*Office of Civilian Radioactive Waste Management Program)
Nominal Decontamination Factor (DF) Strontium DF Alpha DF Cesium DF	Provide a strontium DSS concentration of ≤ 40 nCi/g, which equals to a nominal DF = 5 (overall average). Provide an alpha DSS concentration of ≤ 18 nCi/g, which equals to a nominal DF = 12 (overall average). Provide a cesium DSS concentration that enables conversion to a solid low-level waste form suitable for near-surface disposal at the SRS. <ul style="list-style-type: none"> • For processes that remove cesium, cesium-137 ≤ 45 nCi/g is required to enable processing in the existing SPF and disposal in the existing SDF, which equals a nominal DF = 8000 (overall average).
Schedule HLW Storage Federal Facility Agreement Saltstone Treatment Plant	Support Tank Farm space management strategy to support site missions (timely startup of new process by 2010). Support readiness for closure of all waste tanks by 2028. Support readiness for closure of old style tanks by 2020, and an average glass-canister production rate of 200 canisters per year.

5.0 Description Of Radionuclide Removal Processes

5.1 Alpha and Sr Removal

The current preconceptual design for the CSSX alternative requires removal of Sr and transuranic (TRU) radionuclides in advance of removing Cs from the solution (see Figure 5.1). The selected technology involves addition of an inorganic sorbent, monosodium titanate (MST) and subsequent removal of solids by cross-flow filtration. The MST shows a very high affinity for Sr and also effectively removes soluble actinides such as plutonium (Pu) and uranium (U) from solution. The MST also sorbs lesser amounts of neptunium (Np) and other alpha emitting radionuclides. The treated liquid (filtrate) is processed by solvent extraction to remove Cs (described in the next section). The collected solids require washing to reduce the concentration of soluble salts of sodium (Na) prior to transfer to the DWPF. The process requires an analysis to verify adequate removal of alpha emitters and Sr prior to release of any treated waste to the SPF.

Previous studies showed a low filtration flux during the solid-liquid separation step.^{13,14,15} Because of the lower fluxes, the CSSX process requires larger filtration equipment, process vessels, and storage vessels to maintain the desired waste processing rate.

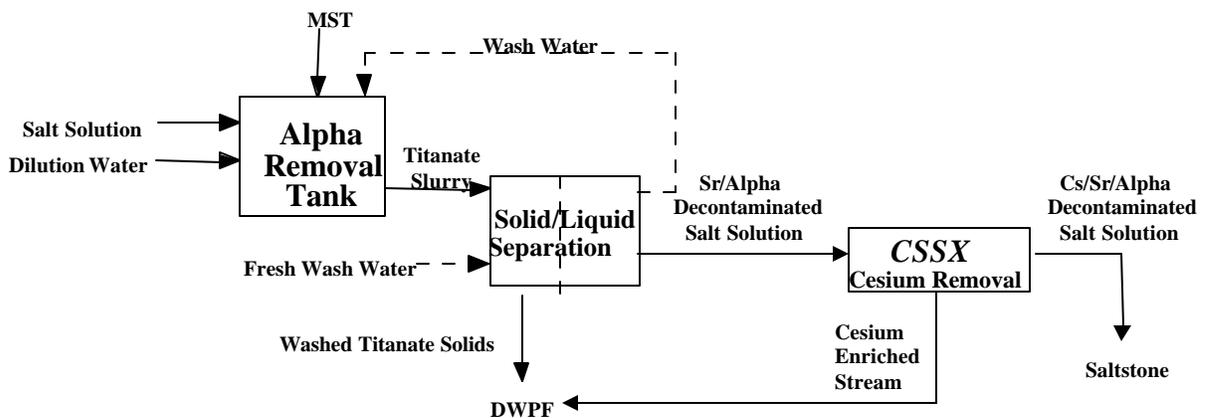


Figure 5.1 Alpha and Sr Removal Flow Diagram for Caustic Side Solvent Extraction

5.2 Cs Removal by Caustic Side Solvent Extraction

In solvent extraction, a sparingly soluble diluent material containing an extractant (to complex the Cs ions) is mixed with the aqueous caustic solution to remove Cs. The decontaminated aqueous stream (raffinate) is then sent to the SPF for treatment and subsequent disposal in the SDF. The Cs contained in organic solution is then stripped into an aqueous phase ready for transfer to DWPF. The solvent is cleaned to remove impurities and recycled.

Prior to treatment by solvent extraction, actinides and Sr are removed from the waste by sorption with MST as shown in Figure 5.1. The resulting slurry is then filtered to remove the MST and sludge solids.

The CSSX process uses a novel solvent system 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 Cs-7SB, trioctylamine known as TOA, and Isopar[®] L, the diluent. The solvent is contacted with the alkaline waste stream in a series of countercurrent centrifugal contactors (the extraction stages) where Cs and nitrate are extracted into the solvent phase. The resulting clean aqueous raffinate is transferred to the SPF for conversion to saltstone. Following Cs extraction, the solvent is scrubbed with dilute acid to remove other soluble salts, particularly Na and potassium (K) from the solvent stream (the scrub stages). The scrubbed solvent then passes into the strip stages where it is contacted with a very dilute acid stream to transfer the Cs to the aqueous phase. The aqueous strip effluent containing pure Cs nitrate (which is 15 times more concentrated than in the salt waste), is transferred to the DWPF for vitrification. Figure 5.2 contains a schematic representation of the solvent extraction flowsheet.

In the strip stages, the presence of lipophilic anionic impurities (e.g., dibutylphosphate, dodecylsulfate) has the potential to greatly reduce 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 salt remains in the organic phase and allows the final traces of Cs in the solvent to be stripped by supplying any anionic impurities in the solvent with equivalent cationic charges.¹⁵

Over long periods of time, either the modifier, the TOA, or the calixarene may degrade either chemically or radiolytically. The most likely degradation is that of the modifier to form a phenolic compound that is soluble in the organic phase in contact with acid solutions. However, the modifier was designed to enable the phenolic compounds to distribute preferentially to alkaline aqueous solutions, in either the waste itself or in sodium hydroxide (NaOH) wash solutions. Gradual degradation of the solvent results in some loss of performance, owing both to loss of the calixarene, modifier, and amine, and to the buildup of various degradation products. The flowsheet contains first an acidic wash of the solvent,

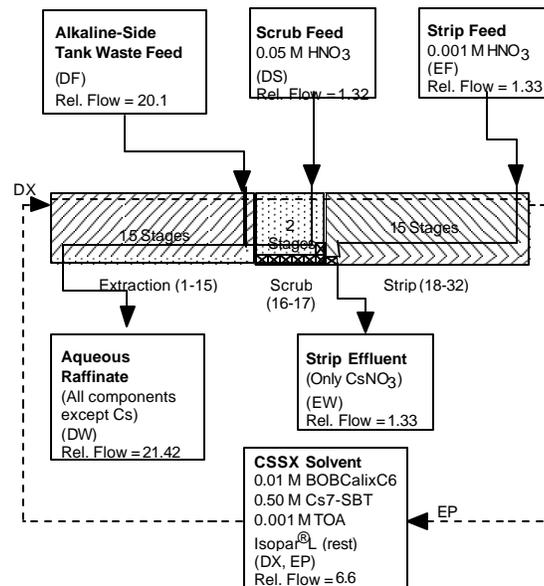


Figure 5.2 Caustic Side Solvent Extraction Flow Diagram

followed by a caustic wash of the solvent to maintain solvent performance. These two wash stages are intended to remove any acidic or caustic impurities that may accumulate in the solvent system over time. In particular, the caustic wash is known to remove the modifier degradation products. In addition, the flowsheet assumes the solvent will be replaced on an annual basis to maintain system performance. Spent solvent will be incinerated.

The aqueous output streams from the CSSX process may contain either soluble solvent components and/or entrained organic phase. This potential loss may represent an economic concern due to the expensive solvent components or a problem in downstream operations. The process contains solvent recovery processes for the aqueous effluent streams. Additional contactor stages are provided to remove soluble organics and, in particular, to remove solvent from the exiting streams with a small amount of Isopar[®] L. The aqueous phase from these stages is then sent to a settling tank where any remaining entrained organic (mostly the Isopar[®] L) is allowed to float and is decanted. The Isopar[®] L (containing the solvent) is distilled to recover the extractant and modifier. The Isopar[®] L added in the two solvent recovery processes is sent to the CIF.

Strip effluent storage is provided to accommodate the differences in cycle times for the Slurry Receipt Adjustment Tank (SRAT) in DWPF and to allow for disengagement of any organic carry-over from the extraction process. Strip effluent, provided at a rate of 1.5 gpm, eliminates the need for an evaporator. 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.

5.3 Backup Technology Alternatives

5.3.1 Alpha and Sr Removal

In the STTP process, alpha (i.e., selected actinides) and Sr removal occurs simultaneously with precipitation of Cs. The CST alternative requires removal of Sr and TRU radionuclides prior to Cs removal from the solution. As in CSSX process, lower fluxes required the CST process to have larger filtration equipment, process vessels and storage vessels to maintain the desired waste processing rate.

Investigation of alternatives aim at improving process throughput through a combination of demonstrating an improved solid-liquid separation technology and evaluating alternate sorbents to replace MST. For instance, use of rotary microfilters or centrifuges may offer promises of smaller equipment and space savings. Similarly, other inorganic sorbents – such as SrTreat™ or Sodium Nonatitanate – may perform better than MST. Another chemistry option involves addition of non-radioactive strontium, as strontium nitrate, to achieve isotopic dilution of the radioactive isotope. Coupled with addition of sodium permanganate, which strips soluble actinides from the waste, the chemical additives may achieve the same process objectives without adding a titanium burden to the glass.

5.3.2 Cs Removal by CST Non-Elutable Ion Exchange

In the proposed CST Non-Elutable Ion Exchange process (see Figure 5.3), salt solution (6.44 M Na) is combined with dilute caustic and spent solutions from filter cleaning and other aqueous streams generated from sorbent loading and unloading operations in the Alpha Sorption Tank (AST) within the SWPF. Soluble alpha contaminants and Sr-90 are absorbed on MST solids that are added as a slurry to the salt solution in the AST. The solution is diluted to ~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.

Two key aspects of the CST process are: loading CST into the train of ion exchange columns; and rotation of the columns as they become loaded with Cs. 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 (not shown) and the activity is measured to ensure it

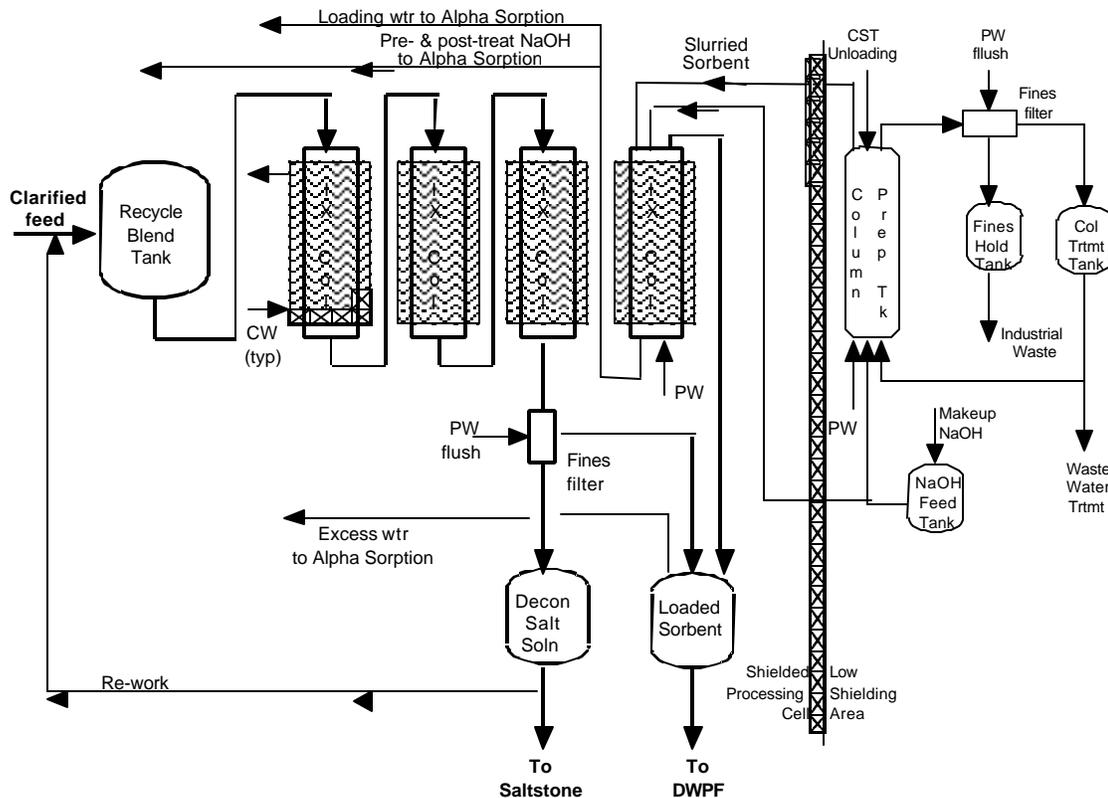


Figure 5.3 CST Non-Elutable Ion Exchange Flow Diagram

meets the saltstone limit for Cs. 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.

Rotation of the columns and processing of the Cs-loaded CST occurs as follows. 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 Sorbent Hold Tanks where it is combined with the solids 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 AST. The particle size of the CST will be reduced by grinding to facilitate slurry transfer and to ensure representative sampling in DWPF. The CST slurry is stored in the Loaded Sorbent Hold Tank until it can be transferred to the DWPF for incorporation into HLW glass.

5.3.3 Cs Removal by Small Tank Tetraphenylborate Precipitation

In the STTP process (see Figure 5.4), salt solution is received into a Fresh Waste Day Tank located in the new facility. For this continuous precipitation process, salt solution, sodium tetraphenylborate (NaTPB) solution, MST slurry, spent wash water and dilution water are continuously added to the first of two Continuous Stirred Tank Reactors (CSTR), also located in the new facility. Sufficient dilution water is added to the first CSTR to reduce the Na molarity to ~4.7 M and 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 tetraphenylborate (TPB) salts, while Sr and actinides (U, Pu, americium, Np, and curium) 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 the Concentrate Tank, the slurry is continuously fed to a cross-flow filter to concentrate the solids, which contain most of the radioactive contaminants. DSS filtrate from the cross-flow filter unit is transferred to a Filtrate Hold Tank and stored until it can be transferred to the existing SPF, where it is converted to saltstone for disposal in the SDF.

After concentrating the slurry to 10 wt%, and accumulating 4,000 to 5,000 gallons in the Concentrate Tank, the slurry is transferred to the Wash Tank. There, the concentrated slurry is washed to remove soluble Na salts by adding process water and removing spent wash water by filtration. NaTPB removed in the wash water is 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 the SPF for conversion to saltstone for disposal in the SDF. At the end of the washing operation, 10 wt% slurry is transferred to the Precipitate Reactor Feed Tank for staging. The slurry is then processed through the acid hydrolysis unit operation and eventually vitrified at DWPF. The recovered benzene by-product from acid hydrolysis is transferred to the CIF and incinerated. The aqueous product from precipitate hydrolysis is combined with sludge feed in the DWPF and incorporated into HLW waste glass.

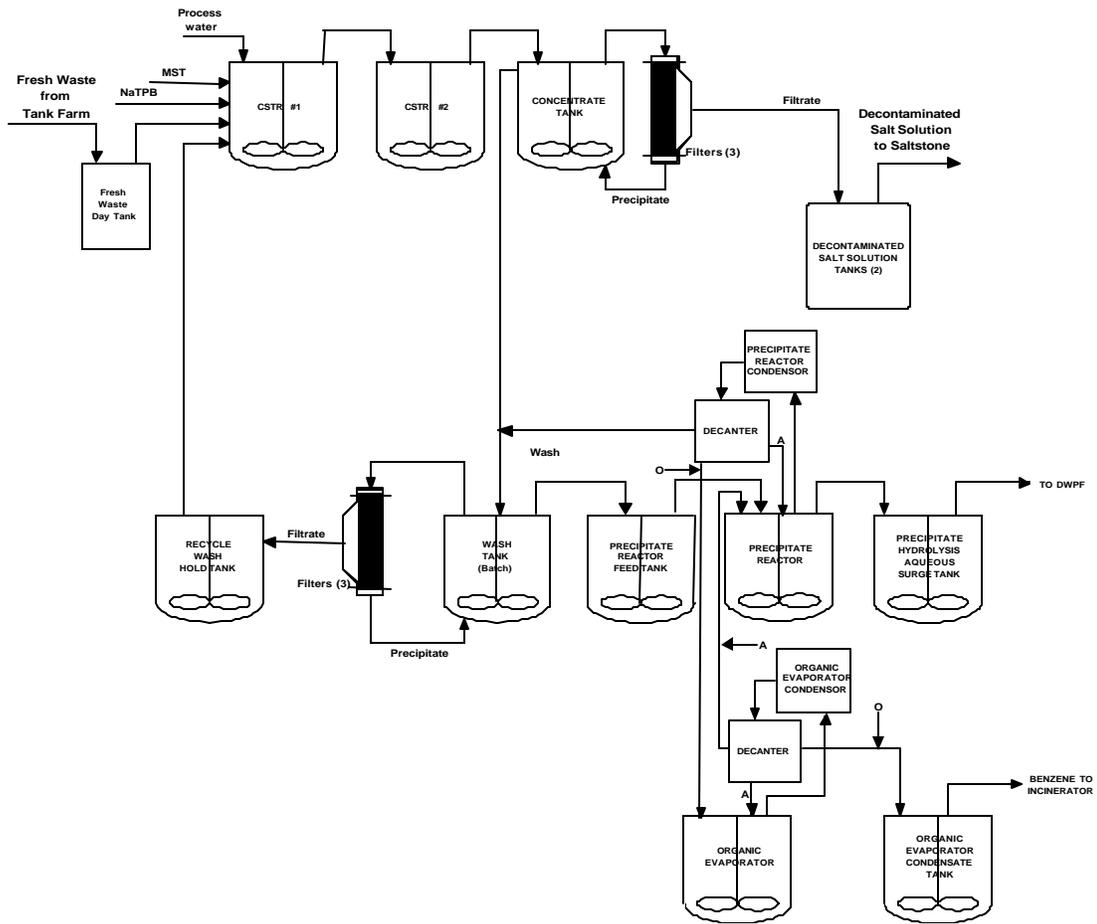


Figure 5.4 Small Tank Tetraphenylborate Precipitation Flow Diagram

6.0 Technology Development Needs

A large number of technical issues, concerns, and uncertainties were identified during the previous phases of the SPP. Evaluation of these issues and concerns led to discovery of a small number of areas that represent high technical risks to implementing the four processes described in this R&D Program Plan. These high-risk areas and the technology needs they represent were the focus of technology development efforts leading to down selection. Some of these high-risk areas were resolved or reduced to low-risk status during the FY00 and FY01 R&D program effort. Other areas remained as moderate or high risk, and continued R&D effort is required for those areas. In addition to the moderate- to high-risk areas, pre-conceptual and conceptual design activities have identified uncertainties that must be addressed to support future design efforts. Finally, recommendations from independent review groups, such as NRC committees, identified technology development needs that are being incorporated into the ongoing R&D program.

6.1 Alpha and Sr Removal

A previous risk assessment⁴ identified two high-risk areas for the Alpha/Sr Removal process: (1) MST Plutonium Removal Performance and (2) MST/Filtration. In addition, deployment of this technology requires additional work to define the analytical instrumentation needed to verify performance.

MST Plutonium Removal Performance: During the past several years, SPP examined the sorption of plutonium – and other radionuclides – by MST under prototypical conditions for the process options. These studies included numerous experiments with actual HLW, tests with simulated waste containing added actinides and strontium, and plutonium and Sr removal as part of flowsheet demonstrations for each of the cesium removal process options using both simulated and actual wastes. The accumulated data demonstrated successful operation across a variety of waste compositions while meeting process requirements defined for the proposed facility. While the rate of plutonium sorption limits the nominal processing capacity for this process option, little doubt exists that MST adequately removes plutonium with an acceptable efficiency for the majority of the waste. Studies in FY01 demonstrated that relative to plutonium removal, MST performs comparably to the principal competing inorganic sorbents either currently available at commercial scale or in final stages of development. However, feasibility tests with permanganate additions and with several of the inorganic sorbents show equal or superior removal of the radionuclides as compared to sorption on MST. The research efforts for these alternatives continue in a manner such that the baseline design could readily incorporate the alternate chemistry option as it matures.

The research program also provided researchers with added confidence that the project will realize continued improvements in this technology. Basic structural studies will provide

insight into the surface chemistry of the actinides on MST. The data will provide the needed information to either improve the synthesis of MST to enhance removal efficiency for plutonium or to replace that sorbent with a superior material. Development efforts for inorganic sorbents will also continue via funding obtained from the Environmental Management Science Program (EMSP), as will efforts to incorporate actinide removal directly within the solvent extraction process.

The confidence in deployment of this process technology will increase as the site continues efforts to expand the available analytical data for the contents of the waste tanks. Demonstration of the use of centrifugal filters to test for colloids of plutonium stands as an example of efforts to improve the understanding of the fundamental waste chemistry. Likewise, research in late FY01 investigated the chemistry required for removal of plutonium and neptunium present in different oxidation states. These compositional variations appear to pose no additional challenge for MST.

With continued research efforts of comparable stature during the design, piloting, and construction phases of the facility, the likelihood of this technology failing appears limited. Furthermore, the most probable recovery from any failure will simply require addition of more MST and will only result in a brief interruption of operations. As a result of existing studies, a lower probability for failure is perceived for this process chemistry. Thus, the overall risk is judged to be low.

Initial feasibility tests show that addition of permanganate with a reducing agent (e.g., peroxide or formate) also removes these radionuclides from solution under the conditions studied. Similarly, personnel continue to explore the use of selected inorganic materials designed to decontaminate the waste. Some of these materials equal or surpass MST in performance.

Sorbent Performance

The defined baseline process for removing soluble Sr and alpha radiation-emitting radionuclides (i.e., the Alpha and Sr Removal process) retains risks that restrict the processing rate for the facility.⁴ Specifically, the rate of sorption for plutonium on MST defines the ultimate processing rate. The R&D tasks to be performed in FY02 to address sorbent performance include the following:

- Continue studies of the baseline technology using MST, emphasizing collection of additional actual-waste data and developing a fundamental understanding of the chemistry.
- Evaluate the use of permanganate to selectively remove alpha emitters and Sr.
- Develop and test novel sorbents designed specifically to remove Sr and selected actinides. This effort will be funded by EMSP.

The NRC committee¹¹ believes that continued R&D on the alternate process to using MST for removal of actinides and Sr is essential until MST processing can be demonstrated to meet saltstone, DWPF throughput, and DWPF glass requirements.

MST/Filtration: The research on the cross-flow filtration technology used as the baseline design for each process option includes both pilot-scale demonstration of the technology using simulated waste and successful experiments using actual HLW samples. For the STTP process option, previous work demonstrated filtrate flow rate using actual waste in full-scale equipment – in the In-Tank Precipitation facility. Thus, low risk is perceived for implementation of this technology. Previous demonstrations also included full-scale implementation of chemical cleaning and backpulsing - the two process steps necessary to ensure prolonged operation at the desired capacity.

However, for both the CST and CSSX process options, the measured performance shows notably lower processing rates for simulated wastes without the presence of the tetraphenylborate precipitate. Also, comparative analysis shows reasonably good agreement between the pilot-scale tests using simulated waste and laboratory-sized experiments using actual waste, with the former apparently providing a slightly conservative margin for facility design efforts. The pilot-scale demonstrations yielded acceptable filtrate flow rate, but showed relatively poor performance with slurries containing the maximum concentration of solids expected for the facility. At these higher concentrations, acceptable equipment performance was reliably achieved only with high transmembrane pressure (i.e., 60 psi). Thus, the complete research data provide the information needed to select pumps and filter equipment for the facility. However, the data suggest that the equipment will only marginally achieve the target performance and may well require frequent outages for cleaning. Thus, this technology may well force an extension of the operating lifetime for the facility and still represents a moderate technology risk.

To reduce the risk, the project continues to pursue alternate means of solid-liquid separation. The options under investigation include use of a centrifuge or a high-shear, rotary cross-flow filter. Initial vendor testing of the latter equipment using simulated waste shows significant promise of improved performance. Similarly, investigations continue on alternate process configurations that, for instance, use chemical additives to achieve enhanced sedimentation in advance of the process facility. Such approaches may reduce the burden for the cross-flow filter, thereby substantially reducing the implementation risk.

Solid-Liquid Separation Technology

The use of cross-flow filtration in the baseline process to separate the MST and entrained sludge prior to solvent extraction for cesium removal requires the use of relatively large pumps. The potential for frequent cleaning of the filters and maintenance for the pumps may

also pose risk for timely completion of the waste treatment mission. The R&D tasks in FY02 to address solid-liquid separation technology include the following:

- Continue studies of use of conventional cross-flow filtration to separate solids from waste using new samples of HLW sludge.
- Evaluate the use of a rotary microfilter to separate solids from the waste with demonstrations on actual waste samples and equipment reliability testing at the pilot scale.
- Complete evaluation of alternate technologies, including centrifugation and use of flocculants in a settling and decant application.

Characterization and Analytical Monitoring

Although not explicitly identified by the SPP as a significant risk, the project still needs to define the analytical method for use in confirming that the treated waste meets the required efficiency for the Alpha and Sr Removal process. The R&D tasks in FY02 to address characterization and monitoring include the following:

- Conduct additional actinide characterization in actual-waste samples.
- Identify a preferred (baseline) analytical approach for determining concentrations of Sr and total alpha emitters.
- Develop an online or at-line technology that provides real-time determination of the concentrations in the filtered waste following treatment with MST.

6.2 CSSX

A previous risk assessment⁴ identified four high-risk areas for CSSX: (1) Flowsheet Solvent System Proof-of-Concept; (2) Chemical and Thermal Stability; (3) Radiation Stability; and (4) Actual-waste Performance. Of these four high-risk areas, only actual-waste performance was judged to represent a moderate risk. Thus, R&D in FY02 will continue to focus on reducing risk in the area of actual-waste performance and also move toward engineering development with the focus on process chemistry, engineering tests of equipment, and chemical and physical properties relevant to safety.

Flowsheet Solvent System Proof-of-Concept: During FY00 and FY01, the flowsheet solvent system was demonstrated in three tests using 2-cm centrifugal contactors at ANL with CSSX simulant solutions spiked with radioactive cesium-137 (Cs-137). Results from testing showed that the requirements for waste and solvent decontamination (40,000) and the concentration factor (CF) for cesium from feed to cesium product (15) were met or exceeded. In addition, the first test demonstrated the need for control of the temperature in the extraction section of the centrifugal contactor cascade to assure the highest waste decontamination. The solvent was recycled four times during the second test with no adverse

effects on the process. These very successful demonstrations of the flowsheet solvent system makes the probability of failure of the flowsheet low and results in the risk being reduced to low.

Chemical and Thermal Stability: The solvent system for the CSSX process consists of four chemicals: the extractant, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6); a modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy) -2-propanol (Cs-7SB); trioctylamine to aid stripping; and the diluent, Isopar[®] L. The extractant and modifier are new chemicals. The chemical and thermal stability of this four-component solvent had not been tested previously to determine the products of reaction or their effects on processing, which led to a high risk rating. Laboratory studies during FY00 and FY01 were aimed at understanding the chemistry of the solvent and any effects on the process as a result of chemical reactions or thermal degradation. The overall conclusion of these studies was that chemical and thermal processes slowly degrade solvent, but effects on the solvent were easily corrected by caustic washing and periodic additions of trioctylamine. Thus, the probability that chemical and thermal effects on the solvent will affect plant operation is low, resulting in a low-risk rating.

Radiation Stability: The risk for radiation stability was judged to be high in the earlier assessment because the solvent had not been tested to determine the products of reaction or their effects on processing. Dose calculations showed that the solvent would receive an annual dose of only 0.092 Mrad per year, assuming 100% plant use; a baseline solvent inventory of 1000 gallons; and an application of the MST process prior to the CSSX process. The relatively low dose is the result of the short residence time of the solvent in the centrifugal contactor cascade, the large inventory of solvent in the plant, and the nuclides contributing to the solvent dose (Cs-137 and barium-137m). Both external and internal radiation studies showed essentially the same results: production of 4-*sec*-butylphenol from modifier degradation, and dioctylamine from degradation of trioctylamine (TOA). External radiation tests involved irradiation of solvent and simulant with a Co-60 gamma source to doses exceeding the life of the plant by ten-fold. No significant degradation of the primary solvent components was observed for doses typical of the proposed facility lifetime.

Internal radiation studies were performed with both actual-waste solutions and simulant spiked to SRS-average waste Cs-137 concentration with total radiation doses from 1 to 13.5 years of plant operation. Neither the actual waste nor the spiked-simulant tests showed any effect of radiation on extraction or scrubbing, but stripping effectiveness was reduced due to high distribution coefficients. Washing the solvent with 0.01-M NaOH and replenishing the TOA concentration restored good stripping performance.

The radiation studies show the solvent to be quite stable to radiation, with TOA being most sensitive to radiation-induced degradation. As a result of these studies, the probability and, consequently, the risk that radiation effects will cause problems during plant operation are considered to be low.

Actual-Waste Performance: At the time of the earlier risk assessment, very little actual-waste testing had been conducted, which increased the technological risk that the process might not be viable. Efforts in FY01 focused on actual-waste testing with both batch equilibration studies with waste from several different F and H area tanks, and a 48-hour flowsheet test using 2-cm centrifugal contactors similar to those that were used for the flowsheet proof-of-concept tests. Batch equilibration studies with samples from five different tanks showed that the distribution coefficients of cesium for extraction all meet or exceed the minimum required value of 8. Distribution coefficients for scrub and the first strip are generally higher than expected.

During the flowsheet test, 105 liters of waste from Tanks 37H and 44F were treated using 1.5 liters of solvent. The solvent was recycled continuously (~25 times) to the process after passing through a single centrifugal-contactor stage of NaOH wash solution. A composite of samples taken throughout the test showed a DF of 40,000 versus a requirement of 13,000 to meet the saltstone Waste Acceptance Criteria and a target of 40,000. The overall average DF for the spent solvent was 154,000 versus a target of 40,000. Problems were encountered in measuring the flow rate of the waste feed stream, resulting in low feed flow rate in the first 24 hours of the test. Consequently, the CFs averaged only 12.8 during that part of the test, which is lower than the target value of 15. Flow rate adjustments to the feed and strip streams resulted in varied, but higher, CFs during the remainder of the test. Thus, the actual-waste test proved flowsheet viability, but the evaluation of the technology risk was lowered only to moderate because only one contactor test has been conducted and limited batch equilibration test results with actual waste are available. Also, the NRC Committee¹¹ concluded that successful bench-scale demonstration of the complete CSSX process with actual tank waste is critical. These demonstrations are needed to clarify any residual risks.

The residual risk will be further lowered in FY02 by increasing the work performed with actual waste. Additional batch distribution and 2-cm centrifugal contactor studies will be performed with both dissolved salt cake and waste supernatant solutions. Additional internal irradiation studies using waste supernatant solutions will also be performed. Studies of feed stability will be continued to examine post-precipitation after dilution. Additional characterization of the organic compounds in the actual waste and in solutions from flowsheet testing will be conducted.

Process Chemistry: During FY02, the solvent will be optimized to improve performance, and the flowsheet will be demonstrated with the optimized solvent. Solvent stability and solvent cleanup studies will be continued, and the need for solvent recycle will be evaluated for potential cost reduction. Work will continue on modeling cesium distribution and comparing calculations with actual-waste test results. Solvent will be prepared for all testing performed in FY02.

Engineering Development: Engineering tests of equipment will include contactor studies with solids, hydraulic performance of optimized solvent, performance testing related to contactor design, and use for organic removal from aqueous effluents.

Chemical and Physical Properties Relevant to Safety: Studies in the area of chemical and physical properties relevant to safety will include effect of nitrite on cesium stripping, nitration of solvent with high nitrite solutions, vapor pressure measurements for solvents, and criticality in the CSSX process.

6.3 Backup Technologies

The current status of technology development needs for the backup technologies (CST and STTP) is described in the R&D Summary Report.⁴ The principal technology development needs (that will be addressed if DOE requests TFA to pursue the backup technologies) are summarized below:

CST

- Conduct additional alternative column studies (e.g., Up-Flow Moving Bed Column).

STTP

- Conduct additional actual-waste batch tests to further define the tetraphenylborate decomposition mechanism.
- Repeat the 20-Liter Continuous Stirred Tank Reactor closed loop test to verify long-term, steady-state performance when recycling the wash water.

7.0 R&D Program Description

The U. S. Department of Energy (DOE) selected CSSX as the preferred Cs removal process in July 2001. The decision followed a period of R&D that largely emphasized evaluating the technical uncertainties and risks of the various technologies. A technology roadmap, implemented through a R&D Program Plan,¹ documented the investigative path for each technology area.

Selection of a backup technology was deferred pending the results of additional R&D on the CST and STTP processes. After the down-selection decision, the nature of the R&D work on the Alpha and Sr Removal and CSSX processes has transitioned from technology development for down selection to providing input to any pilot plant design and generating data needed for conceptual and preliminary design of the SWPF. This work will include laboratory studies, bench-scale tests, and prototype equipment development. Limited R&D activities are expected to continue on the CST or STTP backup technology(ies), and additional direction will be provided by DOE regarding scope of the desired R&D activities for the backup technology.

7.1 Alpha and Sr Removal

The defined baseline process for removing soluble Sr and alpha-emitting radionuclides (i.e., Alpha and Sr Removal) retain risks that restrict the processing rate for the facility.⁴ Specifically, the rate of sorption for Pu on MST defines the ultimate processing rate for the facility. In some potential processing scenarios, MST also fails to provide required neptunium removal. Similarly, the use of cross-flow filtration in the baseline process to separate the MST and entrained sludge prior to solvent extraction for Cs removal requires the use of relatively large pumps. The potential for frequent cleaning of the filters and maintenance of the pumps may also pose risk for timely completion of the waste treatment mission. Finally, although not explicitly identified by the SPP as a significant risk, the project still needs to define the analytical method for use in confirming that the treated waste meets the required efficiency for Alpha and Sr Removal process. R&D tasks in Fiscal Year 2002 (FY02) address each of these three areas: sorbent performance, solid-liquid separation, and analytical methods.

7.1.1 R&D Roadmap Summary – Alpha and Sr Removal

Appendix A shows the logic diagrams for the R&D tasks. The following sections detail the generic research areas for all three needs. Some of the recommended R&D tasks address design needs for a pilot facility for the baseline process. Other recommended tasks provide a suggested balance of the immediate design needs against evaluation of process alternatives that appear likely to mature in sufficient time to be implemented in the planned SWPF.

7.1.2 Alpha and Sr Removal Chemistry

The technology roadmap has three focal areas relative to development of the chemistry for Alpha and Sr Removal process:

- Continue studies of the baseline technology using MST, emphasizing collection of additional actual waste data and developing a fundamental understanding of the chemistry.
- Evaluate the permanganate process to selectively remove alpha emitters and Sr.
- Develop and test novel sorbents designed specifically to remove Sr and selected actinides.

7.1.2.1 MST R&D Tasks

Existing data suggest that MST may not meet the project requirements for all of the waste in storage when deployed at conditions already evaluated in laboratory studies.¹⁷ Prediction of actinide removal based on the existing data suggests insufficient removal of Pu for five of the projected macrobatches of waste to meet the Saltstone acceptance criteria for total alpha emitters. (Note that if the blend plan changes, scenarios also exist in which predictions indicate MST will not adequately remove Np as well.) However, this preliminary study included assumptions specific to the use of TPB precipitation when defining the projected composition of the 67 macrobatches (i.e., nominally one million gallons of waste prepared for process facility) of waste for treatment. The project should revise the waste blending profile, assuming use of the solvent extraction and MST chemistry. The revised study may still identify a number of batches that will require variations from the demonstrated operational conditions for MST. The revision should occur early in FY02 to support the proposed schedule.

After identification of the bounding wastes, researchers will conduct experiments to examine the performance of MST in treating samples from these bounding batches of HLW. Testing will include characterization of the waste to ascertain the accuracy of the predicted compositions. Furthermore, the direct measurements for these wastes eliminates any uncertainty due to predicting behavior based on the current limited understanding of the fundamental chemistry. Sample collection efforts should begin immediately with testing for at least one batch completed by mid-FY02. Testing will continue in FY03 and beyond for additional batches of waste.

Research will continue to develop sufficient understanding of the fundamental chemistry to reliably predict performance. During FY01, researchers used X-ray absorption fine structure analyses (XAFS) to examine the effects of MST surface chemistry on Sr sorption.¹⁸ The work demonstrated that Sr associates with the MST primarily by undergoing partial dehydration and specific adsorption. Structural incorporation of Sr into the MST lattice may

occur to a limited extent, but Sr does not bind via ion exchange with sodium. The Sr coordination environment – or speciation – does change upon sorption.

Similar measurements examined plutonium, uranium, and neptunium interaction with MST.¹⁹ Uranium(VI) sorbs via an inner sphere/specific adsorption mechanism. Plutonium [added as Pu(IV)] exhibits inner sphere/specific adsorption as polymeric (colloidal) Pu species—with a local environment that is consistent with Pu(IV). Plutonium [added as Pu(VI)] exhibits inner sphere/specific adsorption as monomeric species on MST. Apparently, Pu(VI) has a limited stability in the waste – either in solution or sorbed on the solids – as demonstrated by its persistence over the several-week test. Neptunium [from salt solutions spiked with a Np(IV) stock solution] exhibits outer sphere/electrostatic sorption as monomeric Np. Neptunium [from salt solutions spiked with a Np(V) stock solution] exhibits inner sphere/specific adsorption as polymeric Np species. The studies could not differentiate whether between the final oxidation states for the Np in the two studies. As evidenced by the studies, sorption of actinides is site specific and probably occurs on distorted and perfect Ti octahedra (if present) on the MST.

During FY02, Scanning Transmission Electron Microscopy (STEM/TEM) will be used to complement the findings from the earlier XAFS work. The combined information will help develop a first-principles model to predict the performance by MST in removing key radionuclides. Without such a model, the project remains hindered by the limited ability of empirical predictions from past experiments to reliability estimate behavior for a diverse range of waste compositions. Development of such a model will progress only to a limited extent in FY02, restricted in large part by the limited extent of the XAFS and STEM/TEM studies.

Lacking demonstration of the use of MST to successfully treat the entire waste inventory for SRS at baseline operating conditions, the project needs to select and evaluate a mitigation path. One option involves the use of additional MST for these select batches. Evaluation of that alternative would require additional glass studies. Other approaches include dilution of the waste or slower process cycle times. These approaches imply greater project costs or extended process schedule. If selected, the project should alter the planning documents to reflect these delays and costs. Regardless of the selected mitigation path, the planned use of MST requires revision of the projected glass composition profiles for the additional titanate content. This change in composition necessitates additional work on glass qualification. The timing of these tasks remains uncertain as preparation of this plan nears completion, but likely falls into FY03.

7.1.2.1.1 Develop MST Qualification Test to Support Procurements (*Not Presently Funded*)

The ultimate deployment of the MST technology requires establishing a new vendor supply of material. Analysis of the existing supply indicates a limited shelf life for the material. Over time, the MST shows a loss in the ability to sorb Sr as well as a change in particle size

due to agglomeration. Also, results from tests in late FY01 show variability in Sr removal performance from different manufacturing lots.²⁰

While these attributes do not threaten process viability, they do limit the reliability of predictions for performance. Obtaining a new supply also requires establishment of procurement specifications and qualification test protocols for the material. Specifications and protocols exist from the previous plan to use this sorbent for the In-Tank Precipitation process. However, both tools need to be reviewed and potentially revised to reflect current project plans. Sufficient progress must occur in FY02 on these procurement issues to provide adequate supplies for completion of scheduled R&D activities.

Procurement of MST for the pilot and operating facilities will require development of a standard qualification test. The qualification involves a combination of criteria (i.e., particle size, Sr removal efficiency, and actinide removal efficiency) with available data insufficient to finalize the criteria. After a complete evaluation of the alternatives for solid-liquid separation, a particle size requirement will be developed. A test will be defined for removal efficiency for Sr and actinides derived in part from the revised production schedule for processing the waste.

7.1.2.1.2 Perform MST Test on “Bounding Waste”

During FY01, the projected blending plan for the facility defining 67 macrobatches was developed and MST performance for removing Sr and Pu from those batches was estimated. The projections identified five batches that failed to meet process objectives at the proposed operating conditions. This FY02 task will provide experimental evaluation of MST efficiency for the limiting wastes. The study will involve developing a revised blend profile, based on selection of the CSSX process; collecting tank samples for the most limiting waste; and performing the experiments.

7.1.2.1.3 Larger-Scale (100-L) MST Test with Actual Waste

The SPP proposes use of MST to remove Sr and selected radionuclides from HLW. Previous studies provided the technical bases for the conceptual design of a pilot facility and a final processing facility. The testing only included a single evaluation of the influence of mixing and only in small volumes. The demonstration of the process using solvent extraction included verification of the MST performance.²¹ The efficiency for removal of Sr proved marginal, presumably due to poor mixing. The waste treated required no removal of plutonium. A parallel demonstration of MST in conjunction with the tetraphenylborate process using the same supply of MST showed better performance.²²

Presumably the improved performance resulted from the superior mixing conditions. The Savannah River Technology Center (SRTC) will examine MST efficiency using a larger (~100 L) actual waste sample under mixing conditions that approximate those anticipated in the process facility. The test will serve as the largest demonstration on the process to date and will provide insight as to the influence of mixing of performance. (The demonstration of

the CSSX process at approximately this scale showed lower-than-expected removal efficiency for Sr, presumably due to inadequate mixing.) The test will likely use a supernatant from dissolved salt cake proposed for collection from Tank 37H.

7.1.2.1.4 Larger-Scale MST Test: Spike-Simulated Waste (TFA Call – Not Presently Funded)

To complement the examination of the influence on mixing on sorption performance using actual waste, the program will also conduct tests using simulated wastes. These tests will allow studies at a range of mixing conditions using different agitators. The data will help provide design guidance and insights on process efficiency upon increases in the size of equipment.

The current funding profile anticipates this task proceeding only through equipment preparation in FY02 with testing occurring in early FY03. The TFA will select the performing organization for this test in early FY02 based upon competitive proposals.

7.1.2.2 Permanganate Process R&D Tasks

Preliminary results show that use of sodium permanganate in combination with both sodium formate, or a similar reductant, and isotopic dilution via addition of non-radioactive Sr provide similar performance to MST. However, this technology avoids issues of manufacturing variability and shelf life. In addition, the technology likely also avoids any need to alter current glass qualifications.

The permanganate process chemistry requires significant additional study prior to deployment including successful completion of the tasks initiated in FY01 to screen optimal conditions for use of permanganate with SRS waste.²³ This work will lead to a selection of hydrogen peroxide, sodium formate, or formic acid as the preferred reductant and will provide a preliminary understanding of the influence of waste concentration (i.e., ionic strength) on performance. Tests will determine whether use of significantly less – or complete elimination – of non-radioactive Sr achieves acceptable performance. Also, these studies will include an initial demonstration with actual waste. The remaining FY01 work scope (described in Section 7.1.3, Solid-Liquid Separation Technology) provides data related to the separation of the solids from the resulting waste slurries.

In addition to successful completion of the FY01 tasks, this project should demonstrate the permanganate process chemistry and filtration at larger scale prior to selecting the technology as a replacement for use of MST. This testing should occur in FY02 to accommodate the earliest possible decision on replacing MST with the permanganate process.

Note that this same minimal data set would in principle allow consideration of a hybrid process that incorporates both MST and permanganate process in appropriate ratio to achieve the required separations. A hybrid process could combine the rapid Sr sorption kinetics and high loading of MST with similar permanganate characteristics for actinide removal. The

combined rapid kinetics offers a potential to reduce the cycle time for the process, easing filter burden provided that the use of both materials results in an equivalent or lower net solids concentration in the slurry to assure no penalty in filter performance. Use of a hybrid recipe also offers the potential of maintaining titanate content within existing glass qualification limits. An evaluation will be conducted of the hybrid process early in FY02 based on data.

Reliable deployment of the permanganate process requires a full understanding of the sorption chemistry. As with MST, direct measurements related to the surface chemistry will be made using XAFS and SEM/TSEM to allow development of a first-principles model for predicting performance. This project will obtain cost savings by conducting these measurements in conjunction with those for MST to the maximal extent possible. Also, the data obtained serve as useful baseline data for the River Protection Program at Hanford proposes use of permanganate process for the same processing objectives.

7.1.2.2.1 Permanganate Process: Ionic Strength, Formate, and Multiple Strike Variations

Existing studies, already completed or in progress, will be extended to evaluate the effectiveness of permanganate process in removing soluble Sr and alpha radionuclides from simulated SRS HLW. The proposed testing further examines the role of formate as a reductant for permanganate ion in this matrix. Also, initial evaluations will be conducted of the influence of lower ionic strength (i.e., at 4.6 M Na) for the solution as well as the relative efficiency of using multiple additions of permanganate — as opposed to a single addition.

7.1.2.2.2 Test of the Permanganate Process with Actual Waste

The relative performance of MST and permanganate process will be evaluated for removal of soluble Sr and alpha-emitting radionuclides from a single sample of SRS HLW supernate. Final details to define test conditions remain under development. However, testing will use archived supernatant samples currently available at SRTC. Selected radionuclides including Pu-238, americium, curium, and Np-237 will be added to provide a challenging test matrix.

7.1.2.3 Novel Sorbent R&D Tasks (EMSP Funding and Schedule)

Results from FY01 tests with SrTreat[®], sodium nonatitanate, and a pharmacosiderite demonstrated equal or superior performance to MST despite use of larger particle size material.²⁴ These findings, combined with the good performance of solids from permanganate process treatment of waste, strongly suggest that researchers can design a novel sorbent. Based in part on the findings from this project, researchers applied for and received funding for a multi-year investigation from the Environmental Management Science Program (EMSP) starting in FY02. The project plans to evaluate the most promising materials from the EMSP task at the earliest convenient date. When appropriate, the project should supplement funds to accelerate work within the EMSP task aimed at developing the novel sorbents.

7.1.2.3.1 XAFS Studies for Permanganate Process

In FY01, use of X-ray fine structure analyses provided an understanding of the fundamental surface chemistry governing the removal of Sr from (simulated) HLW.¹⁸ Similar studies occurred for Pu, U, and Np, with documentation still being prepared. The collected data defined the mechanism for removal of the elements, providing an understanding of the limitations achievable in the process. The work in FY02 will extend these techniques for samples from the permanganate process.

7.1.2.3.2 TEM/STEM Structural Analyses for MST and Permanganate Process Solids

Recent advances in the use of TEM and STEM methods allow characterization of the local chemistry on solid surfaces. The FY02 work in this area involves a subcontract for such analyses by Georgia Institute of Technology. SRTC will prepare samples of MST with sorbed actinides and Sr for analysis. Also, testing will examine solids obtained from the permanganate process option.

7.1.3 Solid-Liquid Separation Technology

There are three focal areas for the technology roadmap relative to solid-liquid separation methods:

- Continue studies of the use of conventional cross-flow filtration to separate solids from waste.
- Evaluate the use of a rotary microfilter to separate solids from the waste.
- Complete evaluation of alternate technologies – including centrifugation and use of flocculants in a settling and decant application – for the desired separation.

7.1.3.1 Cross-Flow Filtration Tasks

Sufficient confidence exists in the use of cross-flow filtration to allow design efforts for the pilot facility to proceed. The project should complete the large-scale demonstration scope initiated in FY01, including determination of filtrate production rate for slurries containing only MST and the investigation of two simulated sludges. These data will provide baseline data for the pilot facility under a wide range of operating conditions. Work should be completed by the end of FY02 to allow ample time to develop a correlation for predicting filtration in the pilot facility.

The pilot-scale cross-flow filter used during the past several years of testing developed a leak in late FY01. The vendor recommended actions to determine the location – and possibly the cause – of the leak and return the equipment to service. These efforts will be completed in

early FY02; however, should these efforts not provide a definitive cause for the leak, the project will conduct additional diagnostics on the failed filter, including more elaborate actions to identify the leak site and destructive metallurgical analysis to investigate the cause.

While this database provides a sufficient understanding of cross-flow filtration for sludge and MST slurries, the project lacks adequate data needed to deploy the permanganate process chemistry in the pilot facility. Tests conducted late in FY01 evaluated filtration using simulated waste,²⁴ and filtration tests will be conducted in early FY02 using slurries produced to evaluate permanganate for treatment of HLW samples. Assuming encouraging data, the project will fund larger-scale tests at USC to demonstrate filtration rates for simulated waste slurries from permanganate process treatment. These demonstrations will include measurement of the particle size distribution for the solids during the precipitation and under the shear conditions of filtration.

7.1.3.1.1 Cross-Flow Filtration Tests: Permanganate Process

This testing will evaluate the cross-flow filtration of slurries containing simulated HLW sludge and manganese solids resulting from the use of permanganate process proposed to remove soluble Sr and actinides. The proposed testing will provide a direct comparison in filtration performance using the Parallel Rheology Experimental Filter for slurries representing both the proposed permanganate process and the baseline process that uses MST.

7.1.3.1.2 Metallurgical Evaluation of Failed Filter from USC

In FY01, the filter element used at USC showed evidence of solids passing through the media. A second test confirmed the event and USC arranged a subcontract to determine the bubble point (i.e., the pressure at which air bubbles first penetrate the filter media).²⁵ To date the leak site for the filter has not been identified. Late in FY01, Mott Corporation agreed to provide limited diagnostics support without charge and to share data from the analyses. Those analyses suggested that the leak occurred due to damage of the seal face of the O-ring used to assemble the equipment. The speculation is that the abrasion occurred during prolonged service due to flexing of the horizontal filter during backpulsing and operation. The hardened design of the filter – such as that deployed in the In-Tank Precipitation Facility – does not use such O-ring seals, relying instead on welded surfaces. Mott Corporation initiated repair of the seal faces, and will install the filter late in FY01 to assess whether the repairs successfully mitigate the leak. If testing indicates that a leak still exists attempts will be made to locate the leak site through other means such as adapting a housing to allow visual flow testing for identification of the leak site. Following that effort destructive metallurgical examination of the filter tubes will be conducted and porosity measurements to better characterize the failure mode will be made.

7.1.3.1.3 Filter Cleaning Studies (TFA Call)

The baseline process for the SPP assumes use of oxalic acid to clean the cross-flow filters thereby removing residual sludge and MST. The proposed work will examine the use of alternate chemicals for cleaning, including evaluation of cleaning efficiency with simulated waste and actual HLW in the Cells Unit Filter (CUF). Studies will compare the cleaning efficiency obtained using oxalic acid (i.e., as in the baseline flowsheet), nitric acid, and methods using various additives aimed at improving leaching efficiencies for trapped solids. Initial screening tests may use “dead-end” Mott filters under protocols approved by project management.

7.1.3.1.4 Filtration Tests with Actual Waste

During FY01, sludge filtration tests were performed using various archived samples and added MST.²⁶ The proposed studies will extend the database using newly acquired sludge samples. Ideally, the test will use the dissolved salt cake solution proposed for collection from Tank 37H.

7.1.3.1.5 Permanganate Filtration Test with Actual Waste

During late FY01, a test began with actual waste to examine the efficiency of permanganate process for removing Sr and alpha emitters.²³ Also, similar filtration tests were initiated using simulate wastes. The FY02 work extends testing to include filtration studies on actual waste sludge resulting from the application of permanganate process. The test will use the optimized flowsheet developed in testing during the last quarter of FY01 as well as samples from that testing (to the maximum extent practical).

7.1.3.1.6 Pilot-Scale Permanganate Process Precipitation/Filtration Test (Simulated Waste)

The proposed work provides for pilot-scale examination of the permanganate process using simulated waste in conjunction with cross-flow filtration studies. The work will use the facilities available at USC including an installed Lasentec particle size analyzer to evaluate the use of this measurement for process control.

7.1.3.2 Rotary Microfilter Tasks

Vendor testing of a rotary microfilter in FY01 showed significant improvement – two to six times the flux – compared to results from conventional cross-flow filters.²⁷ However, little data exist related to reliability and maintenance of this equipment for radioactive service. A design review occurred with vendor representatives and program researchers in mid-August 2001 to allow preliminary evaluation of the equipment. The review culminated in a decision to extend testing in FY02 to include experiments with actual waste as well as long duration reliability testing of the equipment at pilot-scale.

Each of the research tasks with the rotary microfilter will also include slurries produced from the permanganate process treatment of waste. Conducting the tests with both slurries minimizes the costs associated with setup, disassembly, and waste disposal. The expense of the reliability and maintenance testing prohibits full testing of both chemistry options. Rather, research will include demonstration with both MST and permanganate process solids within the extended test duration, although this adds a complexity to the evaluation of the resulting data.

7.1.3.2.1 Actual Waste Filtration Test Using SpinTek Rotary Microfilter

Tests of the SpinTek Rotary Microfilter at the vendor location in FY01 demonstrated a significant improvement in performance relative to the conventional cross-flow units. This FY02 work will examine the performance using actual HLW samples. Should the project decide to employ the composite ceramic and stainless-steel filter media that show a further improvement in performance, the testing will examine the media for evidence of retention of radionuclides. Testing will also include cleaning of the filter, will use samples from the FY01 filtration studies using the conventional cross-flow filter, and may also employ samples from Tank 37H, if available.

The funds for this task will be released in two portions. The initial release at the start of the fiscal year will provide for procurement of the filter from the vendor. The remaining funds will be released later – nominally in January – to provide for installation and testing of the equipment.

7.1.3.2.2 Rotary Microfilter Test at Pilot Scale with Simulated Waste

This task provides for procurement and testing of a SpinTek rotary microfilter at USC. Testing with limited volumes of waste occurred at the vendor location in FY01 indicating markedly improved performance relative to a conventional cross-flow filter. However, the program requires more extensive and longer duration tests to assess the performance and reliability of the equipment in the proposed service.

These tests will persist for a duration (e.g., 1000 hour) comparable to that used to evaluate the reliability of the equipment. Testing will also include evaluation of cleaning protocol. The standard protocol for cleaning these filters does not include the backpulsing method proposed for the cross-flow filter. Rather, cleaning will involve circulation of cleaning fluids as well as possible disassembly and remote handling. The tests at USC will provide the baseline cleaning information for the technology.

7.1.3.3 Evaluation of Alternative Solid-Liquid Separation Methods

Research tasks in late FY01 include evaluation of the use of a centrifuge for achieving the desired separation of solids.²⁸ This testing will examine performance of the equipment with slurries representing both the MST and permanganate processes. Also, work in progress examines the impact of entrained solids on the solvent extraction process.²⁹ The project should complete both tasks prior to defining any future work using this method of solid liquid separation.

7.1.3.3.1 Centrifuge Testing

The centrifuge tests use an Alfa Laval Charles P600 series decanter centrifuge. The feed for the tests include slurries containing mixtures of simulated SRS HLW supernate, simulated SRS HLW sludge, MST, permanganate process, and commercially available flocculating agents. The testing will provide sufficient data to understand the approximate efficiency of centrifuges for removal of solids from waste and to allow development of conceptual designs using this technology. Vendors will be consulted to identify promising equipment for this application beyond the unit tested.

7.1.4 Analytical Monitoring

There are two important focal areas for the technology roadmap relative to analytical methods:

- Identify a preferred (baseline) analytical approach for determining concentrations of Sr and total alpha emitters.
- Develop an on-line or at-line technology that provides real-time determination of the concentrations in the filtered waste following treatment with MST.

Both tasks should seek to provide a reduction in the analytical response time assumed in the calculations for the facility design.³⁰ Reduction of the response time allows a reduction in the filtration rate and, hence, allows use of smaller pumps.

7.1.4.1 Defining the Baseline Methods for Sr and Alpha Analyses (TFA Call)

Evaluation and selection of a baseline technology should occur in early FY02 to maximize the data provided to the Engineering, Procurement, and Construction (EPC) Contractor for design of the final facility. Start of engineering deployment efforts and verification testing of the selected technology late in FY02 or in FY03 will likely satisfy the EPC needs. However, this timing requires concurrence from that contractor as the earliest practical date.

The preconceptual design for the SWPF assumes use of off-line analyses to measure the Sr and alpha emitter content of waste following treatment with MST. The calculations to date assume a 20-hour response time for this analysis. The FY02 work will survey available

methods, select the most promising candidates, and evaluate performance on simulated and actual wastes.

7.1.4.2 Development of Neutron Counting for On-Line Monitor

In contrast, the on-line or at-line method requires a significant advance in the state of the art for radionuclide monitoring. The preferred candidate technology – following an assessment of several vendor proposals and an independent assessment of available technologies for this application – involves use of neutron counting in the presence of a high gamma radiation field. This technology first requires laboratory demonstration with HLW samples.

A solicitation of vendor bids for on-line analytical equipment to measure Sr and alpha emitters identified no viable candidates as confirmed by an independent assessment. Development on an on-line or at-line analytical method with less than 20-hour response would reduce process cycle time. Previously, the program considered the development of a neutron counting method, but halted that effort when the development cost appeared prohibitive. The independent evaluation identified the neutron counting method as the most probable successful path to support the baseline configuration. The task provides development of a prototypical monitor (at PNNL) and feasibility testing of the equipment using actual HLW (at SRTC).

The SRTC scope involves preparation of the Shielded Cells, or similar facility, for use of the prototype. Samples of HLW will be obtained and prepared for analysis. Parallel analysis using conventional radiochemical methods will serve for validation of the monitor's performance.

7.2 Caustic Side Solvent Extraction

The CSSX process uses 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 Cs-7SB; trioctylamine, known as TOA; and Isopar[®] L, as a diluent. The solvent is contacted with the alkaline waste stream to extract Cs in a series of countercurrent centrifugal contactors (the extraction stages). The resulting clean aqueous raffinate is transferred to SDF for disposal. Following Cs extraction, the solvent is scrubbed with dilute acid (0.05 M) 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. The baseline process also includes washing the aqueous exit streams with diluent to recover solvent, and washing the solvent with base to remove extracted impurities and solvent degradation products.

The basis and composition of the waste simulant to be used in all CSSX testing are described in an SRS position paper.³¹ The simulant composition is similar to previous simulants, but includes more compounds. The new simulant was developed not only to reduce the differences between the simulant and actual waste with regard to most inorganic components,

but to also stress the solvent system with certain minor organic compounds and certain metals that could possibly act as catalysts for solvent decomposition. This simulant is called the CSSX simulant to distinguish it from previous simulants.

7.2.1 R&D Roadmap Summary – Caustic Side Solvent Extraction

The science and technology roadmap for CSSX is shown in Appendix A. The CSSX roadmap defines needs in the following three basic categories:

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

Process chemistry includes data on the thermal and hydraulic transport properties 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 specification of: centrifugal contactor size, solvent clean-up chemistry, solvent recovery technology, and optimizing 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, materials 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 in order to establish limits of operation and recovery, 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 CSSX process with the HLW Tank Farm, DWPF, and SDF. The issues of concern include assurance of glass composition and quality, waste feed blending and characterization, and waste acceptance.

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 indicate the effect of trace impurities has been substantially reduced, if not eliminated.

7.2.2 Process Chemistry

R&D results obtained in FY00 and FY01 point to possible improvements in solvent performance.^{4,32} Optimal concentrations of solvent components could be employed, including a higher modifier concentration, lower extractant concentration, and a higher TOA concentration. Higher modifier concentration provides greater resistance to third-phase formation and lowers the temperature limit of the plant operating window. An economic benefit to plant operation may be gained by lowering the extractant concentration. Current data suggest that increasing the TOA concentration will improve the stripping in the presence of organic components in the waste feed. These aspects of process chemistry as well as others associated with solvent degradation and clean up need to be investigated further during FY02.

7.2.2.1 Solvent Optimization Criteria (*Complete*)

The criteria for defining the optimum solvent composition were developed and formalized in a letter report late in FY01. A test matrix was prepared and used to guide the subsequent experimental program.

7.2.2.2 Basic Data for Optimized Solvent

Analytical support will be provided for solvent component solubility studies to be conducted during the balance of FY01.

7.2.2.3 Chemical/Physical Property Experiments on the Modified Solvent Composition

The solvent composition was optimized late in FY01 by changing the concentrations of the extractant, phase modifier, and the trioctylamine stripping aid. These changes in concentration may affect the physical and possibly the chemical properties of the solvent. Studies are needed to define the changes in physical and chemical properties. The work involves measurement of the properties at the new composition and within a range of compositions around the optimum over the expected process temperature range: density, viscosity, break time, solids precipitation, and phase separation. Any chemical stability tests where the effects cannot be predicted from the studies of the previous solvent composition will be repeated.

Experiments investigating the physical and chemical properties of the optimized solvent, which were initiated in FY01, will be completed in FY02. The work will encompass extraction, scrub and strip (ESS) protocol for the measurement of Cs distribution ratios, studies of third phase formation and BOBCalixC6 solubility, and the measurement of dispersion numbers, solvent viscosity, surface tension, and density. Experiments carried out

in FY01 will have yielded a recommendation regarding the reformulated solvent composition. Because of the potential for fluctuation of the component concentrations in the process plant environment, chemical and physical property data will be obtained for a range of concentrations within an interval defined by the WSRC Process Engineering Group.

Laboratory-scale batch-equilibrium tests will be repeated with waste simulant at temperatures spanning the expected process plant conditions (15°C to 35°C) to perform flowsheet design and to predict performance as a function of temperature. These tests should also include a range of feed compositions to allow the prediction of Cs distribution with actual-waste compositions that do not exactly match that of the SRS waste simulant. Actual waste tests with the new solvent are described in Section 7.2.3.2.3.

Tests involving the distribution behavior of major and minor feed components will be included in this subtask. Particular attention will be devoted to determining the dependence of the strip Cs distribution ratio on the nitrite content of the waste simulant. The concentration of modifier will be higher than the concentration used in FY01, which will have a definite impact on the sodium and, to a lesser extent, the potassium content of the solvent in the scrub and strip stages. Acceptable solvent behavior needs to be verified. Partitioning of some of the minor components will be determined. Emphasis will be placed on those minor components that were previously shown to partition strongly to the solvent; these are likely to include DBP and n-butanol, together with certain lipophilic anions.

The experiments in this task will employ Cs-137 tracer. Analytical methodology will include gamma counting (Cs-137 and Na-22), ICP-AES (Na, K), ICP-MS (metal ions), ion chromatography (anions), HPLC (organic species), GC (organic species), and other techniques, as required. Some of these measurements will be conducted within the CASD Chemical Separations Group; analytical service groups will be employed as needed.

Physical property data, such as dispersion number³³ (a dimensionless number based on the break time and initial thickness of the dispersion layer), viscosity, etc. will be acquired using standard laboratory techniques and commercially available equipment.

7.2.2.4 Check Cesium Distribution Model Against Experimental Results

The Cs distribution model developed in FY01 showed a good agreement between the predicted and experimentally obtained data.³⁴ The optimization of the solvent will produce a new set of concentrations in the organic phase that will have to be taken into account in the model developed in FY01. In order to confirm the set of species included in the current model, more Cs distribution data will be obtained using the new solvent.

Cs will be extracted from simple aqueous systems to provide the required thermodynamic rigor. Simple tracer techniques (Cs-137 and Na-22) and ICP-AES will be employed to generate data points over a range of component concentrations and temperatures. The computer program SXFIT, which uses the Pitzer treatment for activity coefficients and can handle an unlimited number of electrolytes and solvent components, will be used to create a

modified model that accounts for the changes in the organic phase. This task will assess the validity of the revised model for predicting Cs distribution ratios from simulants and actual wastes.

7.2.2.5 Expand ORNL's D-Value Model to Incorporate Optimized Solvent and Waste Compositions

This task is an extension of modeling work performed at Oak Ridge National Laboratory (ORNL) during FY01 in order for the model to cover the optimized solvent composition and to ensure that a wide range of waste compositions can be modeled.³⁴ ORNL will transfer the model to other sites for use in operating models. During FY01, ORNL developed a model to calculate extraction distribution coefficients for Cs from salt solutions using the existing CSSX solvent. Pure salts of sodium including nitrate, nitrite, hydroxide, and chloride were used in tests to develop the model. The new optimized solvent developed late in FY01 requires additional batch extraction data to be collected to modify the model. This task will develop and execute a statistically designed set of measurements of the Cs distribution coefficients (extraction, scrub, and strip) to check and/or update the Cs distribution model for the optimized solvent composition.

The present model does not account for salting by divalent ions such as sulfate and carbonate, which are present in significant concentrations in SRS waste solutions. Batch extraction tests are needed to incorporate effects of these ions into the model. The model will be checked against as wide a variation of waste compositions as possible using data from actual waste tests. These checks are needed to ensure that the model will calculate accurate distribution coefficients for use in material balance calculations for the plant and during operation with different feed batches.

7.2.2.6 Solvent Preparation

The extractant and modifier are new materials first synthesized for use in the process flowsheet and as a result required protection of intellectual property during development of suppliers and transfer of the technology from ORNL to SRS. The Commercialization Plan or Technology Transfer Plan includes protecting intellectual property by way of patents and non-disclosure agreements as necessary. An invention disclosure covering the synthesis and use of the second-generation modifiers was submitted to ORNL's Office of Technology Transfer in FY99. The patent on the base CSSX process was issued in January 2001.

During 1998 and 1999, the extractant BOBCalixC6 was provided in small batches (<50 g) of high-quality material by IBC Advanced Technologies, a small specialty chemical company located in American Fork, Utah. In FY00, IBC Advanced Technologies, Inc. successfully manufactured and delivered on schedule a 1-kg lot of BOBCalixC6; the material was of high purity. IBC Advanced Technologies, Inc. also expressed willingness and confidence in their ability to produce larger quantities of the material.³⁵

In FY00, the Cs-7SB modifier was only produced at ORNL in small quantities. In FY01, the synthesis of Cs-7SB modifier was simplified and scaled up to the 3 kg level by ORNL. ORNL also identified companies possibly interested in producing extractant and/or modifier.³⁶ The information was transferred to SRS to allow ordering of test quantities of extractant and modifier from vendors.^{37,38} A quality assurance test was developed for solvent and demonstrated on both fresh and recycled, washed solvent.³⁹ These activities completed transfer of the technology to SRS.

ORNL prepared and qualified all solvent used in R&D testing at ORNL, Argonne National Laboratory (ANL), and SRTC during FY00 and FY01. The FY02 program includes preparation of another large batch of modifier and preparation and qualification of solvent for all R&D activities. Depending on the quantity of solvent needed for R&D, more extractant may be ordered and additional modifier synthesized at ORNL.

7.2.2.7 Optimized Solvent Flowsheet Modeling

Flowsheet modeling has been performed using the Spreadsheet Algorithm for Stagewise Solvent Extraction program and distribution coefficients measured at ORNL for both prior solvents tested for Cs removal. Similar modeling needs to be performed for the optimized solvent to ensure a workable flowsheet and determine the robustness of the process. Modeling will be performed at ANL after transmittal of the distribution data for ESS data from ORNL. The results will be documented and form the basis of the simulant test in Section 7.2.3.2.

7.2.2.8 Simulant Flowsheet Testing with Optimized Solvent (2-cm Scale)

This task is a continuation and expansion of work performed in FY01. In FY00 and FY01, ANL successfully performed proof-of-concept tests for the CSSX flowsheet with the existing solvent composition.⁴⁰ Such a proof-of-concept test needs to be performed for the optimized solvent composition. This task will examine hydraulic performance, stage efficiency, decontamination factors, and concentration factors for the modified solvent composition in a 32-stage, 2-cm contactor apparatus during a 12-hour test of the CSSX process. Tests at ANL and SRTC during FY01 demonstrated solvent washing and recycle using a single centrifugal contactor stage with 0.01-M NaOH as the wash solution.^{21,41} In the planned test, solvent will be washed in one contactor stage with 0.010 M NaOH, but may include reuse of NaOH recycled to minimize waste. However, these conditions could be changed depending on results of tasks described in Section 7.2.2.11.

7.2.2.9 Organic Decomposition Pathway Study (TFA Call)

Extensive studies on the chemical and thermal stability of the solvent were performed in FY00 and FY01. Tests to date have not shown any decomposition of the extractant and only minor degradation of the modifier due to chemical or radiolytic reactions. Degradation of the modifier essentially involved hydrolysis of the modifier to give expected products. The trioctylamine degradation was greatest with the reaction products agreeing with literature

reports. In order to ensure that there are no reactions that would result in safety problems or process failure, a review of the literature is needed to identify reaction conditions that could decompose or alter the composition of the extractant and modifier.

In FY02, a search of the chemical literature will be made for reaction conditions that decompose the extractant or modifier in the CSSX solvent system. Reaction conditions shall include temperature, radiation, normal operating conditions, and process upset conditions. The reaction conditions include solutions containing high concentrations of nitrate, nitrite and hydroxide as well as nitric acid solutions. A report will be prepared summarizing conditions that pose threats to the stability of the solvent system based on literature information.

7.2.2.10 Analysis of Solvent and Solvent Wash Solutions (*Complete*)

The analysis of solvent and solvent wash solutions from flowsheet testing provides insight into organic compounds that may build up in the solvent or are washed from the solvent. ORNL will complete characterization of the solvent and solvent wash solution from the ANL March 2001 multi-day test, where the solvent was recycled a total of 40 times.⁴¹ Since this test was conducted with waste simulant, the identity of compounds of interest are known; however, method development and or modification will be required to determine the concentrations of the compounds in the respective solutions. This task complements work that SRTC performed on similar solutions obtained from the actual waste test. Characterization of these solutions is relevant to the solvent recycle and cleanup R&D need.

7.2.2.11 Effect of NaOH Concentration on Emulsion Formation

Small quantities of emulsion were observed to form in the solvent wash decanter during solvent extraction tests with both simulant and actual waste solutions.^{10,41} Emulsifiers may be formed as a result of chemical or radiolytic degradation of solvent components. Emulsions could also be a result of the smaller density difference between the liquids and low concentration of NaOH. Studies are needed to identify the cause of emulsion formation and examine the effect of NaOH concentration on emulsion formation and washing effectiveness. Some hydraulic studies are needed to ensure that total hydraulic capacity of the contactor is not being exceeded for these liquids.

7.2.3 Actual Waste Studies

One of the largest unknown concerns for any technology to be used for processing HLW is whether the actual waste solutions will provide the same results as simulants. Additional studies are needed to ensure that actual waste solutions behave in a similar manner to simulants used for process development. Limited testing with SRS actual waste solutions was conducted in FY01.^{21,42,43}

7.2.3.1 Internal Irradiation Test with Actual Waste

Internal irradiation tests were performed with five different actual waste samples during FY01.⁴² However, due to problems with the test protocol and sample analyses especially for the organic samples, the results were scattered. This test would provide for new internal irradiation tests with actual waste using an improved test protocol. The improved protocol will mimic the simulant tests performed at ORNL for internal irradiation with spiked simulant, and will include one or more SRS actual waste samples and the ORNL simulant (as a control). The task will determine solvent decomposition rates and effects on ESS distribution coefficients from internal irradiation.

7.2.3.2 Actual Waste Batch Tests with Dissolved Salt Cake

This task is an extension of previous work on radioactive supernate samples to dissolved salt cake samples. Two dissolved salt cake samples will be obtained from SRS Tanks 37H and 38H. The samples will be dissolved and the solutions characterized. The distribution of Cs between aqueous and solvent phases for extraction, scrubbing and stripping batch tests will be measured in duplicate for each waste sample. The proposed testing will search for adverse distribution coefficients for dissolved salt cake compared to predicted coefficients from the ORNL model. This task does not include costs for solvent (to be provided by ORNL) and distribution coefficient calculations by ORNL. A technical report will be drafted following completion of this work in FY01.

7.2.3.3 ESS Batch Distribution Tests with Actual Waste

Testing in FY01 showed acceptable ESS of Cs from various waste tanks.⁴³ Experimental difficulties associated with remote handling of radioactive waste appear to have affected some results. Carryover of caustic through the single scrub step appears to have caused high scrub and strip results. A new batch test protocol using two scrub tests will be used in future tests. The extraction results were marginal though acceptable for processing, but in some cases did not agree with the predictions of the ORNL model. Additional actual waste data and refinement of the model are planned for FY02. Tests will include SRS HLW samples from various storage tanks, including the 3H Evaporator feed/drop tanks; dissolved salt cake samples; and a sample of HLW treated by the permanganate process for actinide removal. Examination of these samples under processing conditions extends the database for actual waste.

7.2.3.4 Organic Analysis from FY01 Actual Waste Flowsheet Test

Analytical results for organic compounds and minor components in the process streams from the FY01 CSSX actual waste flowsheet test were not available when the final test report was issued. The analyses were completed and reviewed, but were not documented in FY01 due to manpower shortages for the remainder of the fiscal year. This task allows for preparation and review of the written report in FY02.

7.2.3.5 2-cm Contactor Test with Optimized Solvent Composition and Actual Waste From Tanks 37/44

Following optimization, the new solvent system will be tested in a 32-stage, 2-cm contactor apparatus using composite waste from Tanks 37 and 44. This test allows direct comparison with the previous solvent composition that was tested with this waste solution in FY01.²¹ The test will include the determination of the maximum hydraulic capacity of the apparatus using simulated waste and ≥ 24 -hour test using radioactive waste from Tanks 37 and 44. The Cs decontamination factor (DF) for the waste solution, concentration factor of Cs from feed to strip stream, and the DF for the solvent will be determined and compared with earlier tests. The test also involves analyses of the amount of organic in the end streams (including spent 0.01-M NaOH solvent wash solution) and evaluation of the results against the waste acceptance criteria for DWPF and SDF.

7.2.3.6 2-cm Contactor Tests with Actual Dissolved Salt Cake Waste

The first contactor tests with actual HLW solution was performed during FY01 with supernatant solution.²¹ The chemical composition of dissolved salt cake is expected to be different from the supernatant solutions and needs to be tested in contactors. The new solvent system will be tested in a 32-stage, 2-cm contactor apparatus using a radioactive waste sample prepared by dissolving salt cake obtained from the SRS tank farms. (A dissolved salt cake sample will likely contain a high nitrite concentration.) The salt cake will be dissolved by the same flowsheet to be used during plant operation. The test will run a minimum of 12 hours and require approximately 14 kg of damp salt cake. The task also involves analyses of the amount of organic (including chemical and radiation degradation products) in the end streams (the spent 0.01-M NaOH solvent wash solution) and evaluation of the results against the waste acceptance criteria for DWPF and SDF.

7.2.3.7 Actual Waste Stability Studies

In FY01, experimentation were completed to examine the propensity of SRS HLW samples to form precipitates when heated or when seeded with various solids. The collected data will help in efforts at ORNL to spot check a thermodynamic model for predicting solids formation in alkaline waste.

Sample preparation and analytical protocols were developed to measure the amount of organic dissolved or entrained in the aqueous streams from the demonstration of the solvent extraction process with actual waste samples. This task provides funding to complete development of the technical reports. Also, the funding allows for disposal of residue materials from these and other experimental efforts.

7.2.3.8 Identification of Organic Compounds and Actinide Characterization of SRS HLW

Minor concentrations of organic compounds, (i.e., dibutylphosphoric acid) in SRS HLW could impact performance of the CSSX solvent system. Sensitive methods for identifying and quantifying of trace organic compounds in SRS actual waste are needed to provide early warning of potential problems. Knowledge of potential organic compounds will allow for protocol development for testing future waste samples. This task provides for a review and report of potential organic compounds from past SRS operations of the various facilities that discharge to the tank farms (canyons, laboratories, 299-H, etc.) and future use of additives proposed for the Sr/TRU removal and filtration steps of the SPP flowsheet. Initially, SRTC and HLW engineering will screen prospective tanks and develop a list of four to six tanks to be sampled. Samples will be prepared in the shielded cells and submitted for actinide analysis. Additionally, in FY01 SRTC used centrifugal filters to begin examining for the presence of colloidal actinide (Pu) species. These colloids could have an impact on the MST portion of the SPP flowsheet and could potentially impact solvent extraction. This work will be expanded to include these samples. This task provides funding for arranging and shipping the samples of actual waste to the laboratory that performs analyses for organics (see Section 7.2.3.9).

7.2.3.9 Organic and Actinide Characterization (TFA Call)

The HLW at the SRS was generated during processing of nuclear materials by solvent extraction with tributyl phosphate and by ion exchange with both anion and cation exchange resins. Residual portions of these organics as well as gelatin, Alconox[®], (made by Alconox, Inc., White Plains, New York) and potentially other organic complexants were transferred to the HLW tanks along with the aqueous solutions. Subsequent degradation of these organics has produced degradation products such as dibutyl phosphoric acid, trimethylamine, and other organics at very low concentrations. Measurements of organic compounds are limited due to the intense radioactivity of the samples. Identification and quantification of the organic species present are needed to determine if the compounds will interfere with processing of the wastes through the solvent extraction process selected for Cs removal from these wastes.

This task requires the development and testing of analytical procedures suitable for trace organic compounds in SRS HLW. Trace compounds may include methanol, butanol, toluene, n-paraffin, tri-, di-, and mono-butylphosphate, trimethylamine, and dimethyl siloxanes. The procedures may include preconcentration or decontamination activities to obtain low detection limits with highly radioactive samples. After demonstrating the analytical procedures with simulated waste solutions, up to six samples of undiluted SRS HLW will be provided and the analytical procedures used to identify and measure organic compounds present.

7.2.3.10 Analytical Methods for Cs-137 and Other Radionuclides in Solvent Samples

Analytical characterization of the solvent extraction process suffers from the inability to analyze the organic phase by means of mass spectrometry using the current setup at SRTC. This activity would upgrade the SRTC mass spectrometer to allow the direct injection of the organic phase, which is needed to determine species including noble metals, technetium and actinides. This upgrade will allow the mass flow meters to deliver oxygen to the plasma and a de-solvator before the plasma.

7.2.4 Engineering Tests of Equipment

7.2.4.1 Contactor Solids Performance

The present flowsheet involves removal of alpha and Sr prior to solvent extraction of Cs. This process arrangement is required due to the presence of sludge solids in the feed solutions, which could interfere with the solvent extraction process. The sludge solids are removed along with the MST during alpha/Sr removal. The size of the alpha/Sr removal equipment controls the size of the plant shielded-space and thus affects the cost of the overall SWPF. If the sludge solids pass through the centrifugal contactors, then alpha/Sr removal (and filtration) could follow the contactors, thus requiring less shielding for alpha/Sr/filtration and lower SWPF costs. ORNL completed short-duration contactor tests with simulated sludge solids in late FY01. The results indicated approximately 70% of solids accumulate in the contactors and a small fraction goes to the organic phase. A report documenting the results of this work will be completed and issued in FY02.²⁹

7.2.4.2 Contactor Hydraulic Performance of Optimized Solvent (*TFA Call*)

Studies made in FY01 showed that the BOBCalixC6 in the solvent exceeded its solubility, although solutions stored for as long as one year did not indicate solids. The solvent is being optimized during the last quarter of FY01 by changing concentrations of all three components. The optimized solvent may have different physical properties such as density, dispersion number, surface tension, and viscosity that could affect the hydraulics of the contactor. This task will test hydraulic operation of the contactors for ESS sections using the optimized solvent with CSSX waste simulant. The tests will also measure total hydraulic capacity, mass transfer efficiency, and phase entrainment for both phases using a single centrifugal contactor stage for comparison with similar results obtained during FY01.

This task element will also involve preparation of a large batch of the simulant that will be used in all the other task elements.

7.2.4.3 Test Performance of 5-cm CINC Contactor

A single-stage, 5-cm centrifugal contactor unit, developed by Costner Industries Nevada Corporation (CINC) located in Carson City, Nevada, is available at ANL to establish

hydraulic performance of the contactor. This unit will be tested to obtain (1) hydraulic performance data (other phase carryover, emulsion formation), and (2) maximum throughput information using the aqueous/organic composition and organic to aqueous (O/A) ratio that will be employed in the plant. These same standard tests were performed earlier to evaluate the performance of the 2-cm and 4-cm units. The performance data will be used to benchmark the CINC unit for sizing purposes.

7.2.4.4 Contactor Prototype Development and Testing (*On Hold*)

Testing during FY00 and in FY01 showed that the centrifugal contactors used for the PUREX process must be modified in order to be used for the CSSX process. The changes require hydraulic testing of prototype contactors to assure operation at design flow rates. This task will involve building a test bed and testing prototype contactors. The test bed will contain a test stand, tanks, pumps, and instrumentation for hydraulic testing of one to eight contactor stages in ESS modes of operation. Test solutions consist of CSSX solvent, water, dilute acids, and non-radioactive simulant feed. Up to three prototype contactor designs may be tested during FY02.

7.2.4.5 Evaluate the Performance of the 4-cm 2-Stage Contactor Unit for Organic Removal from the Strip Effluent

The baseline design for the CSSX process included two centrifugal contactor stages on each exiting aqueous stream for recovery of dissolved solvent components. The primary reasons for inclusion of the recovery step were lack of data on solubility and the high cost of the organic extractant. Due to the difference in flow rates, aqueous composition, and O/A ratio between the extraction and strip sections, the performance of the solvent recovery unit must be evaluated for the strip section. Equivalent studies were performed earlier in FY01 for the extraction section effluent and indicated the feasibility of solvent recovery. The test involves contacting the aqueous strip feed with the CSSX solvent in one stage, at flow rates and O/A ratio of the strip section, then using Isopar[®] L to recover the entrained solvent in the aqueous flow in the following two contactor stages. Isopar[®] L samples will then be analyzed at ORNL for solvent components (see Section 7.2.4.6). If the quantity of dissolved solvent is very low, solvent recovery may not be required, resulting in significant cost savings for the plant.

7.2.4.6 Analytical Support for Simplification of Solvent Recovery System

Analytical measurements will be performed in support of the ANL test for organic removal from the strip effluent using a 4-cm, 2-stage contactor (see Section 7.2.4.5). The ANL test involves contacting the aqueous strip feed with the CSSX solvent in one stage, at flow rates and O/A ratio of the strip section, then using Isopar[®] L to recover the entrained solvent in the aqueous flow in the following two contactor stages. ORNL will analyze the Isopar[®] L samples for solvent components. This task includes lowering the detectability limit for the extractant BOBCalixC6 in aqueous solutions by a factor of ten by extraction into a volatile

organic solvent, which will be concentrated prior to analysis by previously developed methods.

7.2.4.7 Establish Settling-Rate Parameters Required for Sizing Decanting Tank for Solvent Recovery

Both the strip product and raffinate will contain dispersed organic solvent that can be removed by settling. Further, if the solvent recovery option using contact with pure Isopar[®] L is chosen, decantation of the dilute solvent is also needed. Therefore, organic-phase settling rates in these four systems must be known to size decanting tanks, and options compared. ANL will obtain the required data by performing measurements of the droplet size distribution of the organic phase dispersed in the aqueous phase. These measurements will be performed over time. These data will be correlated in a manner that will predict adequate settling times and, therefore, allow design engineers to size the tanks. The main goal is to predict if decanting only is sufficient to meet the SDF and DWPF criteria and, therefore, eliminate the need for further recovery steps.

7.2.5 Chemical and Physical Properties Relevant to Safety

7.2.5.1 Impacts of High Nitrite Ion Concentration on Stripping of Cesium

This task investigates a potential inadequate understanding of the chemistry of nitrite ion during stripping of Cs from the CSSX solvent. Nitrite ion was added to SRS HLW solutions to inhibit corrosion of carbon steel; therefore, high concentrations of nitrite ion might be present in some feed solutions. Studies at ORNL during FY01 were performed with pure sodium salts of nitrate, hydroxide, chloride and nitrite. Tests with sodium nitrite indicate a linear relationship between nitrite concentration and strip D values. Batch distribution data for five different tank wastes with nitrite concentrations from 0.5 to 1.24 M did not show a direct correlation between nitrite ion concentration and strip D values, although some strip values were unusually high. Additional batch equilibration studies are needed to confirm the effect of nitrite ion concentrations on stripping and determine if limit must be placed on nitrite concentration in the waste feed solutions. The ESS protocol will be used in these studies with two scrub steps instead of only one.

7.2.5.2 Nitration of Solvent Containing High Concentrations of Nitrite

Nitrated organics are often used as explosives due to the presence of both oxidizing and reducing functionalities in the same compound. Thus, nitration of the CSSX solvent could be a safety issue for the process. Nitration of the solvent for CSSX was studied during FY01 with caustic waste simulant and acid solutions. Nitration was measurable only when the acid concentration was higher than 0.3-M HNO₃ (hydrogen nitrate), which is higher than any acid and HNO₃ concentration in the process. Although nitrite ion was present in the simulant at low concentrations, waste solutions from dissolved salt cake are expected to have much higher nitrite ion concentration. Further study of nitration is needed at nitrite ion concentrations up to 3 M in the waste simulant and also with nitrite ion in scrub and higher

acid concentrations (0.2 M) in order to determine if nitration of solvent components is a significant safety issue.

7.2.5.3 Provide Vapor Pressure Data for CSSX Solvent Components

Safety analyses for the plant must consider the potential for a fire due to ignition of vapor from components of the solvent. Vapor pressures for CSSX solvent components are needed to provide input to a safety evaluation for the potential for fire in a solvent extraction facility. It is anticipated that vapor pressures of the pure components are bounding values (i.e., no credit for vapor pressure lowering in mixtures) that are easily measured and will suffice for the safety analysis. The vapor pressures of Isopar[®] L and trioctylamine are available from the literature. The extractant is a solid with no measurable vapor pressure. Vapor pressure data will be measured for Cs-7SB modifier at temperatures from 15°C to 50°C. The data will be documented for use in the safety evaluation.

7.2.5.4 CSSX Criticality Issues

The CSSX will process radioactive waste from the SRS tank farms. This plant will process sufficient actual waste volume that more than a critical mass of U-235 and Pu-239 will pass through the facility. The nuclear criticality safety evaluation of the proposed facility identifies several potential issues. Studies are needed to address two of the issues. The first issue relates to a potential change in uranium and plutonium solubility in the extraction bank because of the addition of the scrub acid. Previous studies measured the uranium and plutonium solubility under alkaline conditions and developed empirical models for their solubility. In these studies, researchers will use the empirical models to examine the potential for precipitation of actinides due to the pH change when scrub acid mixes with radioactive waste. The second issue relates to the composition of the solvent system and its ability to extract and possibly concentrate actinides. The baseline solvent includes an Isopar[®] L diluent, the BOBCalixC6 extractant, the Cs-7SB modifier, and trioctylamine. Previous ORNL tests showed that the baseline solvent is ineffective at extracting the actinides. However, the specific composition of the solvent system may change before start-up of the plant, and there is the possibility of errors in solvent make-up. Therefore, a series of tests will measure the extraction of uranium and plutonium by Isopar[®] L and mixtures of the diluent with the other solvent components, where the concentration of the solvent components is varied widely.

7.3 Backup Technology

The CST Non-Elutable Ion Exchange (CST) and Small Tank Tetraphenylborate Precipitation (STTP) are the proposed backup technologies for the SPP Cs removal process. The science and technology roadmaps for CST and STTP are shown in Appendix A of Reference 1. DOE-SR is evaluating the potential R&D activities and funding availability to support R&D on the backup technologies. After DOE guidance is received, this R&D Program Plan will be revised as required to incorporate any new work.

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 was \$14.6 million and for FY01 was \$17.7 million. The total projected funding for FY02 is \$10-11 million. Total funding and funding source for FY02 is shown below.

Table 8.1 Research and Development Program Funding

PROCESS	FY02, \$K		
	EM-40	EM-50	Total
Strontium and Alpha Removal	1,166	2,140	3,306
Caustic Side Solvent Extraction	2,485	4,125	6,610
Cs Removal Backup Technology(ies)	800*	0	800*
Grand Total	4,451	6,265**	10,716

*Proposed for funding. DOE-SR has not made a decision on funding for backup technology.

**Only \$5,265K of the \$6,265K is presently funded.

The funding allocation is presented in greater detail in Table 8.2. Funding for the various performing organizations is shown by the work scope area which follows the outline presented in Section 7.0, R&D Program Description.

8.2 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 8.1. The complete detailed schedule is shown in Appendix B. The detailed schedule in the appendix 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-approved schedule, scope, or budget must be approved by the Change Control Board (see Section 9.0, R&D Program Controls). It is anticipated that technology development activities will continue into the final design stage.

Table 8.2 Salt Processing R&D Funding Allocation by Work Area and Performing Organization

SCOPE OF WORK	SRTC	ORNL	ANL	PNNL	Call
Alpha/Sr Removal					
<i>Alpha and Strontium Removal Chemistry</i>					
MST R&D Tasks					
Perform MST Test on "Bounding Waste"	105				
Larger-Scale (100-L) MST Test with Actual Waste	165				
Larger-Scale MST Test: Spike-Simulated Waste					345*
Permanganate R&D Tasks					
Permanganate: Ionic Strength, Formate, and Multiple Strike Variations	97				
Test of the Permanganate with Actual Waste	112				
Novel Sorbent R&D Tasks					
XAFS Studies for Permanganate Process	100				
TEM/STEM Structural Analyses for MST and Permanganate Process Solids	100				
<i>Solid-Liquid Separation Technology</i>					
Cross-Flow Filtration Tasks					
Cross-Flow Filtration Tests: Permanganate Process	93				
Metallurgical Evaluation of Failed Filter from USC	65				
Filter Cleaning Studies					130
Filtration Tests with Actual Waste	75				
Permanganate Filtration Tests with Actual Waste	75				
Pilot-Scale Permanganate Process Precipitation/Filtration Test (Simulated Waste)	280				
Rotary Microfilter Tasks					
Actual Waste Filtration Test Using SpinTek Rotary Microfilter	240*				
Rotary Microfilter Test at Pilot Scale with Simulated Waste	500*				
Evaluation of Alternative Solid-Liquid Separation Methods					
Centrifuge Testing	89				

**Table 8.2 Salt Processing R&D Funding Allocation by Work Area
 and Performing Organization (Continued)**

SCOPE OF WORK	SRTC	ORNL	ANL	PNNL	Call
Alpha/Sr Removal (Continued)					
<i>Analytical Monitoring</i>					
Defining the Baseline Methods for Sr and Alpha Analyses					45
Development of Neutron Counting for On-Line Monitor	90			600	
Caustic Side Solvent Extraction					
<i>Process Chemistry</i>					
Solvent Optimization Criteria		12			
Basic Data for Optimized Solvent		10			
Chemical/Physical Property Experiments on the Modified Solvent Composition		127			
Check Cesium Distribution Model Against Experimental Results		75			
Expand ORNL's D-value Model to Incorporate Optimized Solvent and Waste Compositions		178			
Solvent Preparation		503			
Optimized Solvent Flowsheet Modeling			25		
Simulant Flowsheet Testing with Modified Solvent (2-cm Scale)			400		
Organic Decomposition Pathway Study					66
Analysis of Solvent and Solvent Wash Solutions		53			
Effect of NaOH Concentration on Emulsion Formation		174			
<i>Actual Waste Studies</i>					
Internal Irradiation Tests with Actual Waste	204				
Actual Waste Batch Tests with Dissolved Salt Cake	150				
ESS Batch Distribution Tests with Actual Waste	539				
Organic Analysis from FY01 Actual Waste Flowsheet Test	10				
2-cm Contactor Test with Optimized Solvent and Actual Waste from Tanks 37/44	805				
2-cm Contactor Test with Actual Dissolved Salt Cake Waste	796				
Actual Waste Stability Studies	10				
Identification of Organic Compounds and Actinide Characterization of SRS HLW	46				
Organic Characterization of Actual Waste					291

**Table 8.2 Salt Processing R&D Funding Allocation by Work Area
 and Performing Organization (Continued)**

SCOPE OF WORK	SRTC	ORNL	ANL	PNNL	Call
Caustic Side Solvent Extraction (Continued)					
Analytical Methods for Cs-137 and Other Radionuclides	152				
<i>Engineering Tests of Equipment</i>					
Contactor Solids Performance		200			
Contactor Hydraulic Performance of Optimized Solvent		84			405
Test Performance of 5-cm CINC Contactor			50		
Contactor Prototype Development and Testing	822				
Evaluate the Performance of 4-cm 2-stage Contactor Unit for Organic Removal from the Strip Effluent			45		
Analytical Support for Simplification of Solvent Recovery System		35			
Establish Settling-Rate Parameters Required for Sizing Decanting Tank for Solvent Recovery			60		
<i>Chemical and Physical Properties Relevant to Safety</i>					
Impacts of High Nitrite Ion Concentration on Stripping of Cesium		45			
Nitration of Solvent Containing High Concentrations of Nitrite		100			
Provide Vapor Pressure Data for CSSX Solvent Components		35			
CSSX Criticality Issues	103				
Backup Technology					
<i>CST Non-Eutable Ion Exchange</i>					
CST Column Performance					800**
TOTALS	5,843	1,831	580	600	2,082

*Pending funding availability.

**DOE-SR has not made a decision on the backup technology and the proposed funding has not been approved.

Figure 8.1 Summary Level Schedule

Activity ID	R&D Plan Section Number	Activity Description	Work Days	Early Start	Early Finish	Lead	FY02												FY03						
							OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB		
WAAS130000	7.1.2.1.2	MST Testing on Bounding Waste	105*	05NOV01	08APR02	MJB	Perform MST Test on "Bounding Waste"																		
WAAS140000	7.1.2.1.3	Larger Scale MST (100L) Test <HA>	167*	12NOV01	12JUL02	MJB	Larger Scale (100 L) MST Test with Actual Waste																		
WAPRM27	7.1.2.2.1	Permanganate, Ionic Strength, Formate, Strike Vy	46*	02AUG01A	04JAN02	MCD	Permanganate Process: Ionic Strength, Formate, and Multiple Strike Variations																		
WAPRM25000	7.1.2.2.2	Permanganate Actual Waste Testing <HA>	31*	01AUG01A	12DEC01	MJB	Test of the Permanganate Process with Actual Waste																		
WAAS100000	7.1.2.3.1	XFAS Studies - Permanganate	134*	14NOV01	29MAY02	MCD	XFAS Studies for Permanganate Process																		
WAAS090000	7.1.2.3.2	TEM/STEM Structural Analysis <HA>	146*	02OCT01A	29MAY02	MCD	TEM / STEM Structural Analysis for MST and Permanganate Process Solids																		
WAPRM26000	7.1.3.1.1	Cross Flow Permanganate Testing <HA>	13*	26JUL01A	14NOV01	DDW	Cross Flow Filtration Tests: Permanganate Process																		
WAAS040000	7.1.3.1.2	Metallurgical Eval of Failed Filter	81*	01OCT01A	25FEB02	MRP	Metallurgical Evaluation of Failed Filter from USC																		
WAAS120000	7.1.3.1.4	Filtration Tests with Actual Wastes	157*	03DEC01	17JUL02		Filtration Tests with Actual Wastes																		
WAAS150000	7.1.3.1.5	Permanganate Filtration Test <HA>	56*	11OCT01A	18JAN02	MRP	Permanganate Filtration Test with Actual Waste																		
WAMST23000	7.1.3.1.6	Pilot Filtration Tests (FRED) <HA>	76*	01AUG00A	15FEB02	MRP	Pilot Scale Permanganate Process Precipitation/Filtration Test (Simulated Waste)																		
WAAS050005	7.1.3.2.1	Actual Waste Filtration Test - Spintek <HA>	181*	01NOV01	23JUL02	MRP	Actual Waste Filtration Test Using SpinTek Rotary Microfilter																		
WAAS160000	7.1.3.2.2	Rotary Microfilter Test At Pilot Scale <HA>	181*	23OCT01A	18JUL02	MRP	Rotary Microfilter Test at Pilot Scale with Simulated Waste																		
WAMST20000	7.1.3.3.1	Centrifuge Testing <HA>	13*	18OCT00A	14NOV01	MRP	Centrifuge Testing																		
WAAS070000	7.1.4.2	Development of Neutron Counting for Monitor <HA>	326*	08OCT01A	13FEB03	T_S	Development of Neutron Counting for On Line Monitor																		

Data Date 29OCT01
Run Date 31OCT01 11:19

SPP Research & Development

**FY 2002
Summary Plan**

* TFA Call Activities are NOT Shown

* Activities that are NOT presently funded are NOT shown.

Activity ID	R&D Plan Section Number	Activity Description	Work Days	Early Start	Early Finish	Lead	FY02												FY03							
							OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB			
WAORNA100	7.2.2.2	Basic Data for Optimized Solvent <HA>	16*	10AUG01A	19NOV01	LNK	Basic Data for Optimized Solvent																			
WAORNB240	7.2.2.3	Chemical Physical Experiments <HA>	210*	20NOV01	20SEP02	LNK	Chemical Physical Property Experiments on the Modified Solvent Composition																			
WAORN370	7.2.2.4	Check Cs Distribution Model Against Expemt' <HA>	148*	23MAY02	23DEC02	LNK	Check Cesium Distribution Model Against Experimental Results																			
WAORNB640	7.2.2.5	Expand Cs D Model	167*	20NOV01	22JUL02	LNK	Expand ORNL's D Value Model to Incorporate Optimized Solvent and Waste Compositions																			
WAORNA200	7.2.2.6	Solvent Preparation <HA>	21*	17AUG01A	28NOV01	LNK	Solvent Preparation																			
WAORNA300	7.2.2.7	Optimized Solvent Flowsheet Modelling	52*	07SEP01A	14JAN02	LNK	Optimized Solvent Flowsheet Modelling																			
WABB080000	7.2.2.8	Simulated Flowsheet Test-Optimized Solvent <HA>	195*	23OCT01A	07AUG02	MCR	Simulant Flowsheet Testing with Optimized Solvent (2-cm Scale)																			
WAORNB500	7.2.2.11	Effect of NaOH Concentration on Emulsion For	121*	23OCT01A	23APR02	LNK	Effect of NaOH Concentration on Emulsion Formation																			
WACX412M00	7.2.3.1	Internal Irradiation Tests with Actual Waste<HA>	139*	07SEP00A	17MAY02	WRW	Internal Irradiation Test with Actual Waste																			
WACX25179	7.2.3.2.	Actual Waste Batch Test with Dissolved Salt <HA>	24*	16OCT01A	03DEC01	DDW	Actual Waste Batch Test with Dissolved Salt Cake																			
WABB010000	7.2.3.3.	ESS Batch Distribution w/ Actual Waste <HA>	171*	12NOV01	18JUL02	WRW	ESS Batch Distribution Tests with Actual Wastes																			
WACX24500	7.2.3.4	Organic Analysis from FY01 Actual Waste Test<HA>	18*	12JUL01A	21NOV01	DDW	Organic Analysis form FY 01 Actual Waste Flowsheet Test																			
WABB040000	7.2.3.5	2-cm Contactor Test with Optimized Solvent <HA>	125*	28NOV01	28MAY02	MCT	2-cm Contactor Test with Optimized Solvent Composition and Actual Waste From Tanks 37/44																			
WABB030000	7.2.3.6	2 cm Contactor Test with HLW SaltCake <HA>	203*	29OCT01A	19AUG02	MAN	2-cm Contractor Tests with Actual Dissolved Salt Cake Waste																			
WACST5400	7.2.3.7	Actual Waste Stability Studies <HA>	38*	06JUN01A	21DEC01	TK	Actual Waste Stability Studies																			
WABB050100	7.2.3.8	Identify Organic Compounds in SRS HLW <HA>	204*	10DEC01	30SEP02	DDW	Identification of Organic Compounds and Actinide Characterization of SRS HLW																			
WABB020000	7.2.3.10	Analytical Methods Cs-137	123*	05NOV01	02MAY02	FMP	Analytical Methods for Cs-137 and Other Radionuclides in Solvent Samples																			
WACX41400	7.2.4.1	Contractor Solids Performance <HA>	10*	02OCT00A	09NOV01	LNK	Contractor Solids Performance																			
WAANL75001	7.2.4.3	Test Performance of 5cm CINC Contactor <HA>	15*	01OCT01A	16NOV01	RL	Test Performance of 5cm CINC Contactor <HA>																			

Activity ID	R&D Plan Section Number	Activity Description	Work Days	Early Start	Early Finish	Lead	FY02												FY03				
							OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB
WAANL7300	7.2.4.5	Evaluate Performance of 4 cm Contactor <HA>	45*	04OCT00A	03JAN02	RL	<i>Evaluate the Performance of the 4 cm 2-Stage Contactor Unit for Organic Removal of the Strip Effluent</i> [Gantt bar: Oct 04 - Jan 03]																
WAORNA500	7.2.4.6	Analytical Support - Solvent Simplification <HA>	8*	13AUG01A	07NOV01	LNK	<i>Analytical Support for Simplification of Solvent Recovery System</i> [Gantt bar: Aug 13 - Nov 07]																
WAANL75000	7.2.4.7	Establish Settling Rate Parameters <HA>	8*	01OCT01A	07NOV01	RL	<i>Establish Settling Rate Parameters Required for Sizing Decanting Tank for Solvent Recovery</i> [Gantt bar: Oct 01 - Nov 07]																
WAPLAN610	7.2.5.1	Develop Schedule -High Nitrite Ion Concentration	18	05NOV01*	30NOV01	RL	<i>Develop Schedule - Impacts of High Nitrite Ion Concentration on Stripping of Cesium</i> [Gantt bar: Nov 05 - Nov 30]																
WAPLAN620	7.2.5.2	Develop Schedule -Nitration of Solvent	18	05NOV01*	30NOV01	RL	<i>Develop Schedule - Nitration of Solvent Containing High Concentrations of Nitrite</i> [Gantt bar: Nov 05 - Nov 30]																
WAPLAN630	7.2.5.3	Develop Schedule - Provide Vapor Pressure Data	18	05NOV01*	30NOV01	RL	<i>Develop Schedule - Provide Vapor Pressure Data CSSX Solvent Components</i> [Gantt bar: Nov 05 - Nov 30]																
WACX26000	7.2.5.4	CSSX Criticality Issues <HA>	56*	09NOV01	31JAN02	WRW	<i>CSSX Criticality Issues</i> [Gantt bar: Nov 09 - Jan 31]																
WAPLAN015	Z1	FY 02 Plan for On-Going Work & Performers	3*	16AUG01A	31OCT01	HDH	<i>FY 02 Plan for On Going Work & Performers</i> [Gantt bar: Aug 16 - Oct 31]																
WAPLAN036	Z2	Prepare & Issue FY02 R&D Program Plan (Rv)	3*	17OCT01A	31OCT01	HDH	<i>End Date For Program Plan = 31 Oct 01</i> [Gantt bar: Oct 17 - Oct 31]																
WAPLAN038	Z4	Prepare & Issue FY02 R&D Program Plan (Rv)	26	01NOV01	10DEC01	HDH	<i>(Revision 1 - Includes New Work)</i> [Gantt bar: Nov 01 - Dec 10]																

9.0 R&D Program Controls

This 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 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, and
- Performer and contractor roles and responsibilities.

The change control procedures and contractor roles and responsibilities will be documented in a DOE-SR Salt Processing Project Execution Plan⁴⁴ and will be communicated to the SPP team, as appropriate, 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 processing project will be documented in Principle Investigator (PI)-developed Technical Task Plans (TTPs), prepared in response to Program Execution Guidance issued by the TFA SPP R&D. In addition to the normal standard EM-50 approval process, the TTPs will be concurred on by the appropriate PI, System Lead (SL), TFA SPP R&D Technology Development Manager (TDM), and DOE-SR SPP Division Director, and will be approved by the TFA DOE-RL Program Lead. 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 Plan will be approved by the SPP Change Control Board (CCB) prior to implementation.

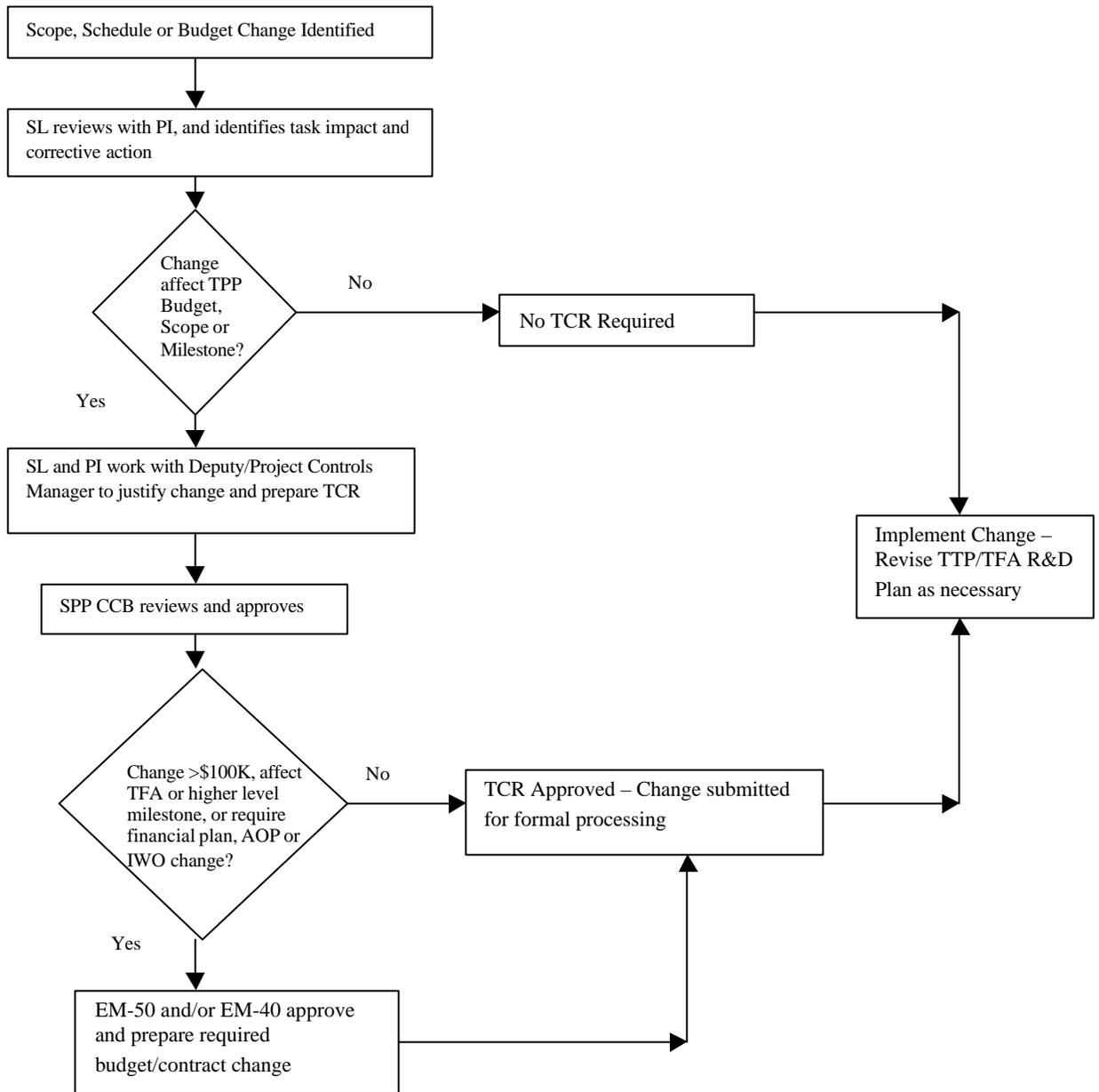
TTPs are developed to implement specific technical activities necessary to meet the objectives established in the R&D Program Plan. All changes that impact a TTP's approved scope, schedule, or budget are subject to the review and approval of the CCB prior to formal submission for subsequent approvals or implementation. The membership and procedures

for the CCB are described in the DOE-SR Salt Processing Project Execution Plan.⁴⁴ Figure 9.1 illustrates the change control process.

CCB approved changes with budget impact of greater than \$100K, which affect a TFA level milestone, or require a financial plan or other contractual/budget change also will be approved by the TFA Program Manager. The TFA DOE-RL Program Lead (EM-50) and the DOE-SR SPP Division Director (EM-40) will be responsible for approving and submitting formal budget/contract changes identified in the Task Change Request (TCR) according to the requirements of the particular TTP funding type (i.e., financial plan, IWO, AOP). In addition, the CCB and the TFA DOE-RL Program Lead will evaluate all changes for their impact to the technical baseline and to ensure proper coordination with all contractors.

Changes will be submitted via TCR 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.

Figure 9.1 Change Control Process



10.0 References

1. Savannah River Site Salt Processing Project Research and Development Program Plan, PNNL-13253, Revision 1, November 2000.
2. Technical Working Group's Final Report on the Salt Processing Project Technology Selection, June 2001.
3. Salt Processing Project Management Review Board Summary Report, May 24, 2001.
4. Savannah River Site Salt Processing Project Research and Development Summary Report, TFA-0105, Revision 0, May 2001.
5. "Savannah River Site Salt Processing Alternatives Final Supplemental Environmental Impact Statement", DOE/EIS-0082-S2, June 2001.
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10. Interim Report, "Evaluation of Criteria for Selecting a Salt Processing Alternative for High Level Waste at the Savannah River Site", National Research Council, Committee on Radionuclide Separation Processes for High Level Waste at the Savannah River Site, March 2001.
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16. L. H. Delmau et al., Improved Performance of the Alkaline-Side CSEX Process for Cs Extraction from Alkaline High-Level Waste Obtained by Characterization of the Effect of Surfactant Impurities", ORNL/TM-1999/209, November 1999.
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21. S. G. Campbell, M. W. Geeting, C. W. Kennel, J. D. Law, R. A. Leonard, M. A. Norato, R. A. Pierce, T. A. Todd, D. D. Walker, and W. R. Wilmarth, "Demonstration of Caustic-Side Solvent Extraction with Savannah River Site High Level Waste", WSRC-TR-2001-00223, April 19, 2001.
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APPENDIX A

**Salt Processing Project Roadmaps
and Logic Diagrams**

SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT DISPOSITION
SYSTEMS ENGINEERING TEAM

APPLIED TECHNOLOGY INTEGRATION
SCOPE OF WORK MATRIX
FOR
ALPHA REMOVAL
(Pre-Conceptual/Conceptual Design Phase)

APPROVED: _____ **DATE:** _____
J. T. Carter, SPP Engineering Director

APPROVED: _____ **DATE:** _____
H. D. Harmon, TFA Salt Processing Project
Technology Development Manager

APPROVED: _____ **DATE:** _____
T. J. Spears, DOE-SR, SPP Division Director

Change Control Record

<i>Document Name</i>		<i>Unique Identifier</i>		
Applied Technology Integration Scope of Work Matrix for Alpha Removal (Pre-Conceptual/Conceptual Design Phase)		HLW-SDT-2000-00047		
Summary of Changes				
<i>Revision Date</i>	<i>Matrix Revision</i>	<i>BCF Number(s)</i>	<i>Reasons for change</i>	<i>Items Affected by the change</i>
February 15, 2000	0	NA	Initial Issue	NA
July 10, 2000	1	NA	Incorporates ECF # HLW-SDT-2000-00265 which dispositions comments from the TFA team.	All changes identified with revision bars.
August 23, 2000	2	NA	Incorporates ECF # HLW-SDT-2000-00346, which adds the evaluation of the impact of chemical composition on filter flux rate.	All changes identified with revision bars.
November 9, 2000	3	NA	Incorporates ECF # HLW-SDT-2000-00431 which dispositions comments from the TFA team and updates document with FY00 science and technology results.	All changes identified with revision bars.
October 21, 2001	4	NA	Updates document with FY01 science and technology results and expands logic diagrams.	Work scope matrix and logic diagrams.

Use of Workscope Matrix

This Workscope Matrix has been developed to define the Science and Technology (S&T) development activities to be performed for Alpha Removal during the Pre-Conceptual/Conceptual Design Phase. The S&T Roadmaps provide the technology development path forward towards successful deployment of the technology, in conjunction with Caustic Side Solvent Extraction. This matrix (Attachment 1) expands on the roadmaps by providing the high level details of each segment of Alpha Removal research and development, assigning responsibility for the execution of each segment and documenting the path through each segment of R&D in the form of a logic diagram (Attachment 2). The logic diagram ties to the S&T Roadmaps using S&T item numbers.

In this Pre-Conceptual/Conceptual Design Phase, scale-up will be performed wherever practical and advantageous to the confirmation of technology and application of technology to the full-size facility. The Workscope Matrix provides an additional definition of at which scale the S&T development is to be conducted.

The Scope of Work Matrices (SOWMs) provide a more detailed description of the work summarized in the roadmaps and logic diagrams. These SOWMs were previously used to identify R&D work required to reach a technology down-selection decision. Work also is included in these SOWMs that has been identified as appropriate post-down selection R&D. However, no attempt has been made to compile a comprehensive list of all post-down selection R&D in these documents. Additional R&D planning will be required to support future stages of the project, e.g. preliminary design, final design, and startup support.

ATTACHMENT 1 – Alpha Removal Workscope Matrix

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Chemistry							
1.0	MST Sorption Kinetics	<p><i>The addition of Monosodium Titanate (MST) has been proposed to sorb the soluble U, Pu, and Sr contained in the waste stream. The rate and equilibrium loading of these components as a function of temperature, ionic strength, and mixing is required to support the batch reactor design. Initial data from batch reactor data indicates the MST kinetics require more than the 24 hours assumed in pre-conceptual design resulting in larger reactor batch volumes. Studies will be conducted to determine if the MST strike could be completed in the existing SRS waste tanks. Alternatives to MST will be investigated.</i></p> <p>MST sorption kinetics experiments have been performed at 7.5 M and 4.5 M Na+. In the current flowsheet, the Alpha Sorption step for CST would be performed at 5.6 M Na+. Additional experimentation may be performed at 6.44 M Na+ for CSSX. Also, questions have been raised regarding the oxidation states of Pu (initial, as a function of ionic strength, and equilibrium as Pu is sorbed onto MST) and the effect of oxidation states on MST sorption rates. Since Pu is the primary source of alpha, it is important to assure that experimental results obtained with simulants are representative of performance with real wastes.</p>			<p>HLW-SDT-TTR-99-30.0¹ WSRC-RP-99-01080²</p> <p>Filtration of Sludge and Sodium Nonatitanate Solutions, WSRC-TR-2000-00290³</p> <p>Preparation of Simulated Waste Solutions for Solvent Extraction Testing, WSRC-RP-2000-00361³</p> <p>HLW-SDT-TTR-99-33.0¹ WSRC-RP-99-01080²</p>		<p>CST: 10 TPB: 4 CSSX: 6</p>
		<p>1.1 Repeat prior experiments on Sr, Pu, U, and Np removal with 0.2 and 0.4 g MST/L at 5.6M Na+.</p>	Lab	SRTC		<p>Final Report on Phase III Testing of Monosodium Titanate Adsorption Kinetics, WSRC-TR-99-00134³</p> <p>Phase IV Simulant Testing of Monosodium Titanate Adsorption Kinetics, WSRC-TR-99-00219³</p> <p>Phase IV Testing of Monosodium Titanate Adsorption with Radioactive Waste, WSRC-TR-99-00286³</p>	

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		1.2 Develop an understanding of the sorption mechanism for the radionuclides on MST.	Lab	SRTC	Task Technical and Quality Assurance Plan for FY2001 Strontium and Actinide Removal Testing, WSRC-RP-2001-00188, Rev. 1	Alpha Sorption Process Alternatives Study, HLW-SDT-2000-00296 Characterization of Sorbed Strontium on Monosodium Titanate, WSRC-TR-2001-00245 Characterization of Sorbed Actinides on Monosodium Titanate, WSRC-TR-2001-00467	
		1.2.1 Examine real waste samples for evidence that the radionuclides (and especially the actinides) exist as colloids.				Investigation of Savannah River Site High Level Waste Solutions for Evidence of Colloidal Plutonium, WSRC-TR-2001-00103	
		1.2.2 Measure the kinetics of sorption and capacity for single radionuclides				Evaluation of Alternate Materials and Methods for Strontium and Alpha Removal from Savannah River Site High-Level Waste Solutions, WSRC-TR-2000-00229 ³ Preparation of Simulated Waste Solutions for Solvent Extraction Testing, WSRC-RP-2000-00361 ³ Phase V Simulant Testing of Monosodium Titanate Adsorption Kinetics, WSRC-TR-2000-00142 ³	
		1.2.3 Perform the fine structure x-ray analyses (XAFS) on samples of MST from the experiments individual radionuclide to gain understanding of the binding, or surface chemistry. (post-down select)				Characterization of Sorbed Actinides on Monosodium Titanate, WSRC-TR-2001-00467	
		1.2.4 Examine the influence of oxidation state of the sorption of Pu onto MST.				Characterization of Sorbed Actinides on Monosodium Titanate, WSRC-TR-2001-00467	

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		1.3 Study Allied Signal NaT as a replacement for MST	Lab	SRTC		Filtration of Sludge and Sodium Nonatitanate Solutions, WSRC-TR-2000-00290 ³ Screening Evaluation of Sodium Nonatitanate for Strontium and Actinide Removal from Alkaline Salt Solution, WSRC-TR-2000-00361	
		1.4 Study alternative alpha removal technologies	Lab	SRTC	Task Technical and Quality Assurance Plan for FY2001 Strontium and Actinide Removal Testing, WSRC-RP-2001-00188, Rev. 1		
		1.4.1 Identify Alternative Sorbents 1.4.2 Scoping Test with Simulant 1.4.3 Optimize Process Conditions with Simulant 1.4.4 Test Flowsheet with Real Waste 1.4.5 Evaluate Performance Enhancements 1.4.6 Evaluate Cross-flow Filtration Performance in PREF 1.4.7 Finalize Evaluation of Down Stream Process Impacts 1.4.8 Evaluate Glass Canister Impacts 1.4.9 Confirm Improvement at FRED/Pilot				Screening Evaluation of Alternate Sorbents and Methods for Strontium and Actinide Removal from Alkaline Salt Solution, WSRC-TR-2001-00072	
		1.5 Evaluate alternative filter cleaning methods if new sorbents are chosen. (Preliminary Design) (post-down select)					
Process Engineering							
6.0	Engineering Scale Filtration Studies	<i>Filtration of MST and sludge is required to prevent plugging of the ion exchange column. Initial data indicates low flux rates for the filtration of these solutions requiring large filter areas and high axial velocity for cross flow filtration techniques. Alternative solid/liquid separation techniques and filter aides will be studied, and a selection made. Filtration cleaning studies including the impact of spent cleaning solution will be studied.</i> Tests for MST/sludge filtration (Alpha Sorption step) performed during Phase IV (FY99) indicate low crossflow filter fluxes leading to very large filters. Improvement in filter size and operation is desired.			HLW-SDT-TTR-99-30.0 ¹ Task Technical and Quality Assurance Plan for the Sludge/Monosodium Titanate (MST) Filtration Test Program, WSRC-TR-99-00483 ² HLW-SDT-TTR-2000-00013 ¹	Monosodium Titanate Sludge Filtration, WSRC-RP-2000-00685 ³	CST: 9, 15 TPB: Design Input CSSX: 5

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		6.1 Elucidate role of TPB in filtration	NA	SRTC		Mark Clark Consultation on Role of Tetraphenylborate in Filtration, WSRC-TR-2000-00270 ²	
		6.2 Investigate/test ways to improve filtration rates/fluxes	Lab	SRTC			
		6.2.1 Filter aids, flocculants, etc.				Improving Filtration Rates of Monosodium Titanate (MST) - Treated Sludge Slurry with Chemical Additives, WSRC-TR-99-00343 ³ Improving the Filtration of Sludge/Monosodium Titanate Slurries by the Addition of Flocculants, WSRC-TR-2001-00175	
		6.2.2 Different filtration technologies			Task Technical and Quality Assurance Plan for Filtration Tests with Permanganate, WSRC-RP-2001-00774		
		6.2.3 Different filtration approaches; for example:					
		6.2.3.1 Pre-filter/rough filter					
		6.2.3.2 Different ratios of flocs/aids, etc.					
		6.3 Select most promising technology and run confirmation test with FRED at USC.	Pilot	SRTC		FY2000 FRED Test Report (Filtration Research Engineering Demonstration) USC, WSRC-TR-2001-00035	
		6.4 Perform real waste tests using CUF	Bench	SRTC		Cross-flow Filtration Demonstration for Slurries Containing High Level Waste Sludge and Monosodium Titanate, WSRC-TR-2001-00212	

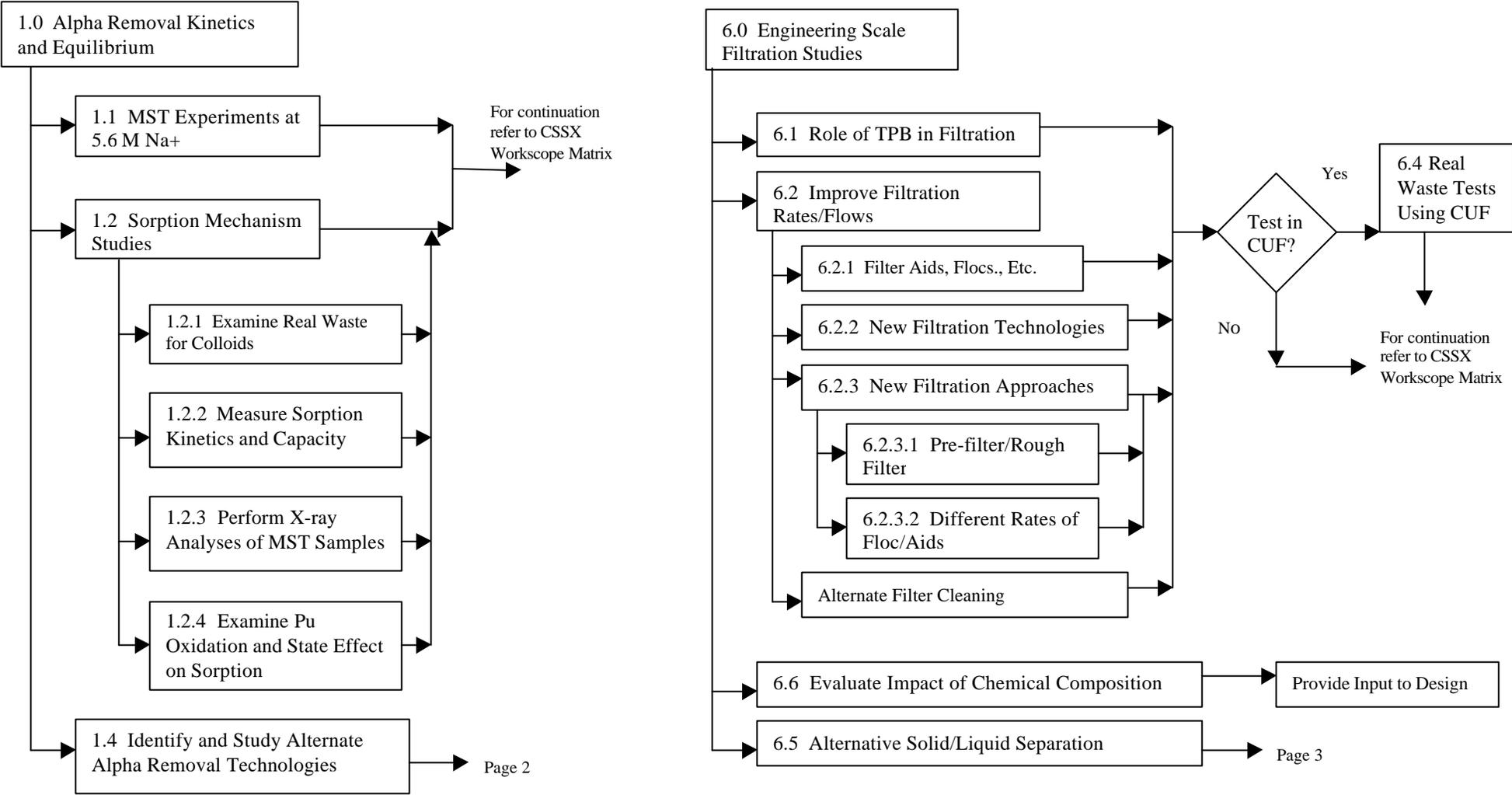
Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		6.5 Evaluate alternative solid/liquid separation technologies	Lab	SRTC			
		6.5.1 Identify alternative solid/liquid separation technology				Evaluation of Solid-Liquid Separation Technologies to Remove Sludge and Monosodium Titanate from SRS High Level Waste, WSRC-TR-2000-00288 Dr. Baki Yarar Consultation on Salt Alternatives Solid-Liquid Separations, WSRC-TR-2000-00287 ³	
		6.5.2 Test promising alternative solid/liquid separation technologies					
		6.5.2.1 Test with Centrifugation			Task Technical and Quality Assurance Plan for Salt Processing Plant Centrifuge Test, WSRC-RP-2001-00737		
		6.5.2.2 Test with SpinTek Filter				Filtration Systems, Inc. Report for SRS SpinTek Rotary Microfilter Testing, WSRC-TR-2001-00214, Rev. 1	
		6.5.2.3 Test with Settle/Decant and Flocculants					
		6.5.2.4 Others					
		6.5.3 Evaluate Impact of Additives				Bubble Test Results from Mott Filter at the Filtration Research Engineering Demonstration Unit (Carolina Filters, Inc.), SRT-LWP-2001-00131	
		6.5.4 Confirm solid/liquid separation with real waste					
		6.5.5 Confirm at FRED/Pilot					
		6.5.6 Define Optimum Plant Design Configuration					
		6.5.6.1 MST with Alternative Solid/Liquid Separation					
		6.5.6.2 Alternate Sorbent with Cross-flow Filtration					
		6.5.6.3 Alternate Sorbent with Alternative Solid/Liquid Separation					
		6.5.7 Conduct Value Engineering and RAMI					
		6.5.8 Evaluate Cost/schedule Impact of Baseline Change					
		6.6 Evaluate the impact of chemical composition on filter flux rate (the evaluation will include the use of an in-line particle size analyzer for pilot filtration facility {FRED})	Pilot	SRTC			

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
9.0	Analytical Sample Requirements	<i>The analytical sample requirements including on-line analysis must be developed to support control strategy development.</i>	Full	PNNL/ Analytical Meas. Lab.			CST: 5 TPB: 7 CSSX: 7
		9.1 Define Needed Analytical Methods/Tools				Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives, WSRC-RP-99-00006, Rev. 3	
		9.2 Develop at-line (or on-line) analyzer for ¹³⁷ Cs, ⁹⁰ Sr, and total alpha.			WSRC Salt Processing, TTP SR01WT21, 9/17/01	Task Requirements and Criteria Salt Waste Processing Facility In-Line/On-Line Radionuclide Detection Monitor (U), G-TC-H-00030	
		9.2.1 Issue request for interest package for vendor solicitation 9.2.2 Conduct independent assessment of vendor bids and technical maturity of analyzer technology 9.2.3 Conduct proof of concept R&D 9.2.4 Test with real waste 9.2.5 Procure Analyzer 9.2.6 Test Analyzer			In Line/On Line Radionuclide Detection Monitor (Technical Bid Evaluation), HLW-SDT-2001-00112 Procurement Specification Salt Waste Processing Facility In-Line/On-Line Radionuclide Detection Monitor, J-SPP-H-00222		
		9.3 Evaluate Off-line Laboratory Analysis Methods					
		9.3.1 Test Selected Methods					
		9.3.2 Adopt Off-line Laboratory Methods					
		9.4 Incorporate in Control Strategy					

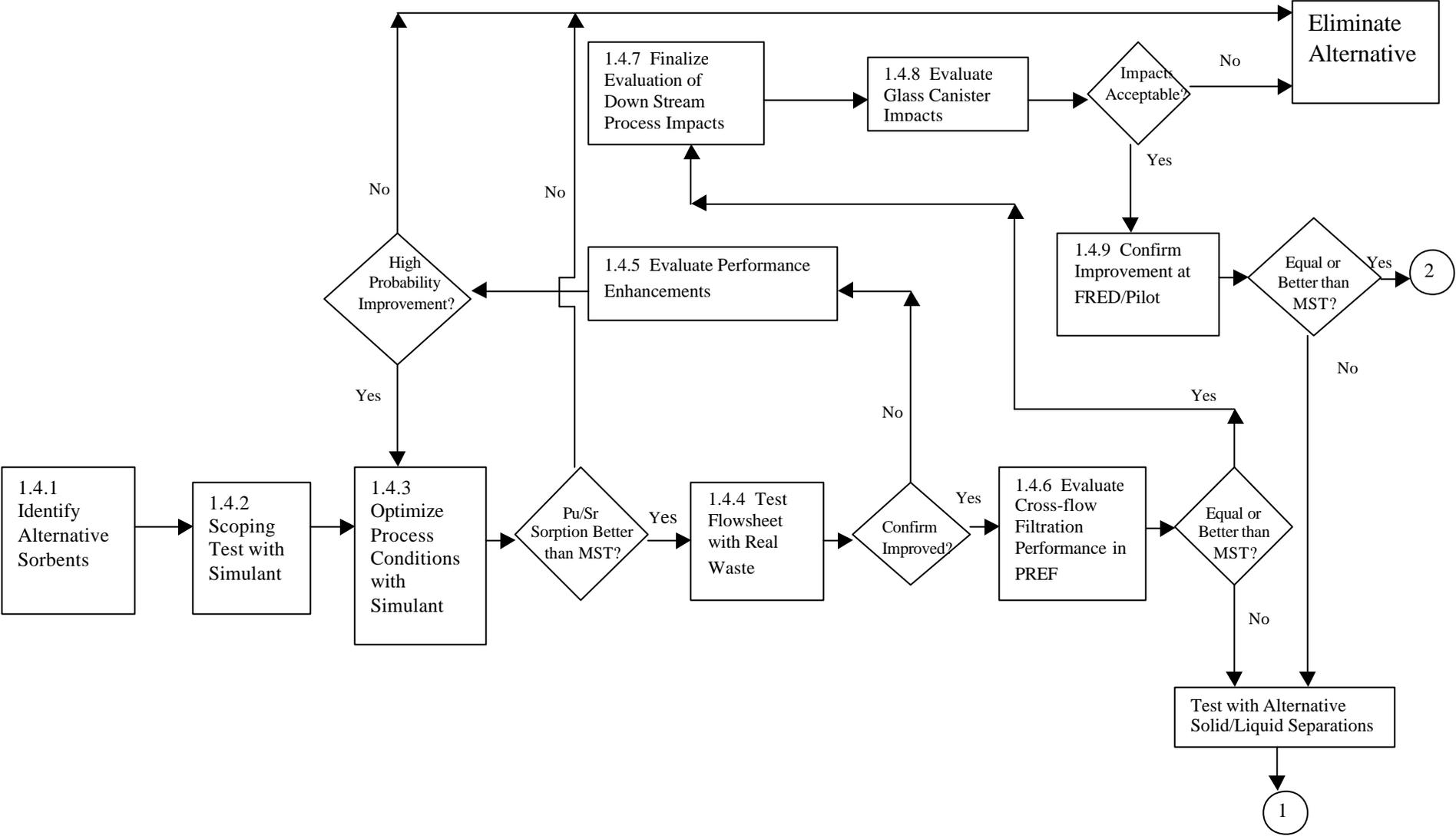
Matrix Legend

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 ¹ ; Task Technical and Quality Assurance Plans (TTPs) denoted xxxx ² and Test Reports (TRs) denoted xxxx ³ 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

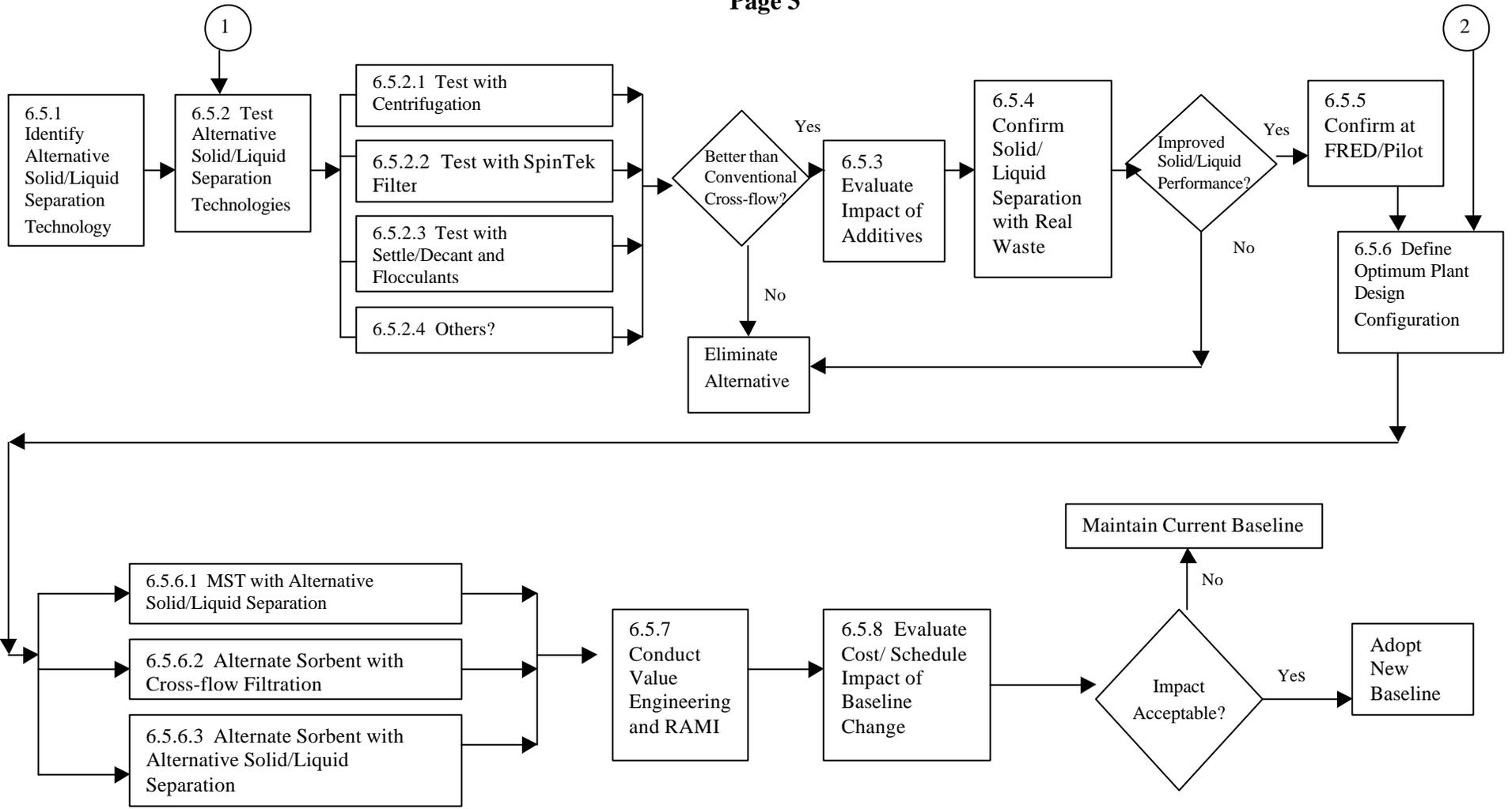
ATTACHMENT 2 – Alpha Removal S&T Logic Diagrams
MST Sorption Kinetics and Cross-Flow Filtration
Page 1



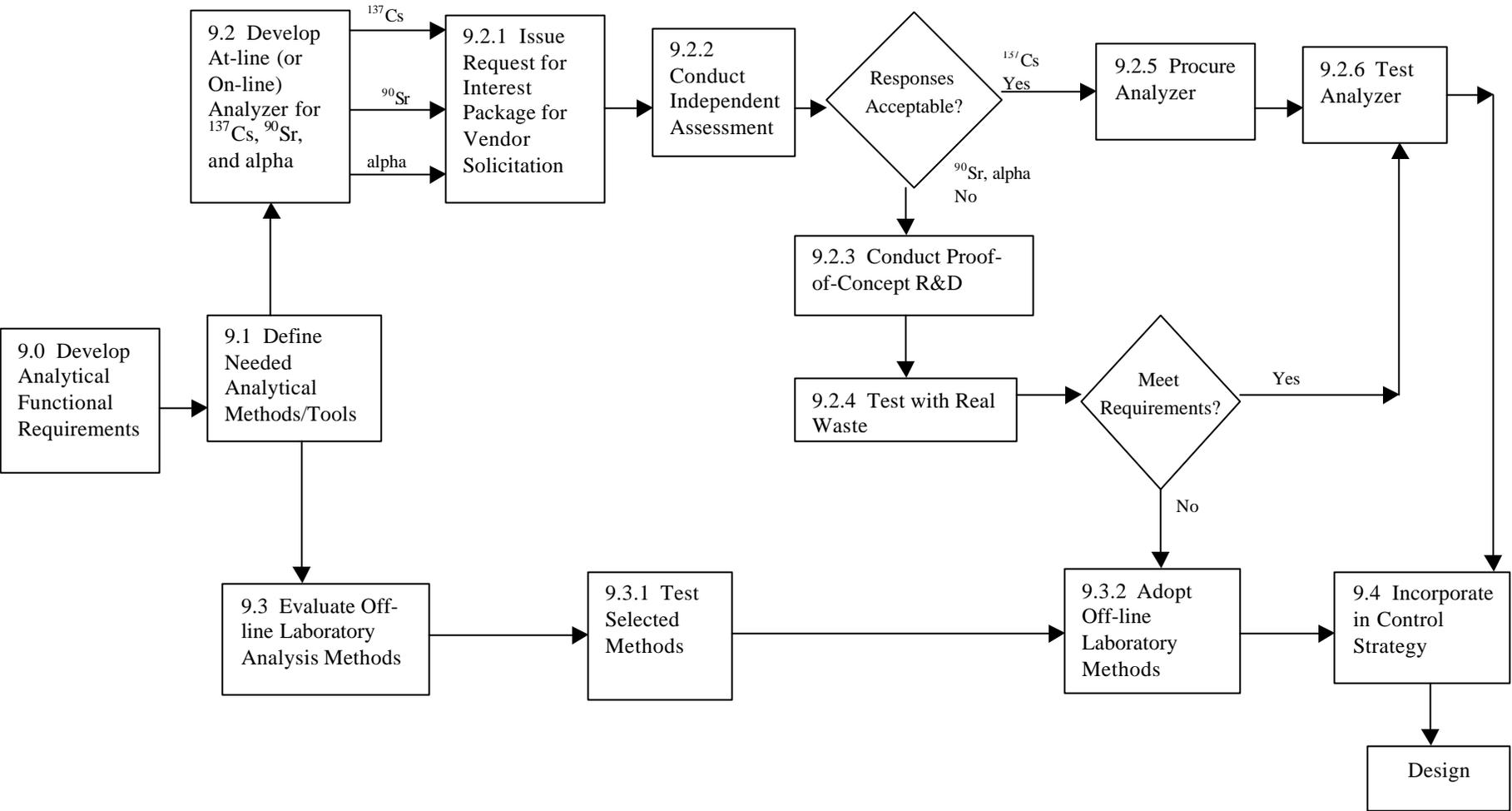
Alpha Removal S&T Logic Diagrams
Alternative Sorbents
Page 2



Alpha Removal S&T Logic Diagrams
Alternative Solid/Liquid Separation
Page 3



Alpha Removal S&T Logic Diagrams
 Analytical Sample Requirements
 Page 4



SAVANNAH RIVER SITE
HIGH LEVEL WASTE SALT DISPOSITION
SYSTEMS ENGINEERING TEAM

APPLIED TECHNOLOGY INTEGRATION
SCOPE OF WORK MATRIX
FOR
CAUSTIC-SIDE SOLVENT EXTRACTION
(Pre-Conceptual/Conceptual Design Phase)

APPROVED: _____ **DATE:** _____
J. T. Carter, SPP Engineering Director

APPROVED: _____ **DATE:** _____
H. D. Harmon, TFA Salt Processing Project
Technology Development Manager

APPROVED: _____ **DATE:** _____
T. J. Spears, DOE-SR, SPP Division Director

Change Control Record

<i>Document Name</i>			<i>Unique Identifier</i>	
Applied Technology Integration Scope of Work Matrix for Caustic-Side Solvent Extraction (Pre-Conceptual/Conceptual Design Phase)			HLW-SDT-2000-00051	
Summary of Changes				
<i>Revision Date</i>	<i>Matrix Revision</i>	<i>BCF Number(s)</i>	<i>Reasons for change</i>	<i>Items Affected by the change</i>
February 15, 2000	0	NA	Initial Issue	NA
April 13, 2000	1	NA	Incorporates ECF # HLW-SDT-2000-00106 which added TTP and TTR references and incorporated ORNL and independent review comments.	All changes identified with revision bars.
May 9, 2000	2	NA	Incorporates ECF # HLW-SDT-2000-00158 which corrects review oversight by adding activity 5.1.7	All changes identified with revision bars.
July 11, 2000	3	NA	Incorporates ECF # HLW-SDT-2000-00268 which dispositions comment from the TFA team and adds editorial designators to references	All changes identified with revision bars.
November 9, 2000	4	NA	Incorporates ECF # HLW-SDT-2000-00425 which dispositions comments from TFA team and updates document with FY00 science and technology results	All changes identified with revision bars.
October 22, 2001	5	NA	Updates document with FY01 science and technology results.	Work Scope Matrix

Use of Workscope Matrix

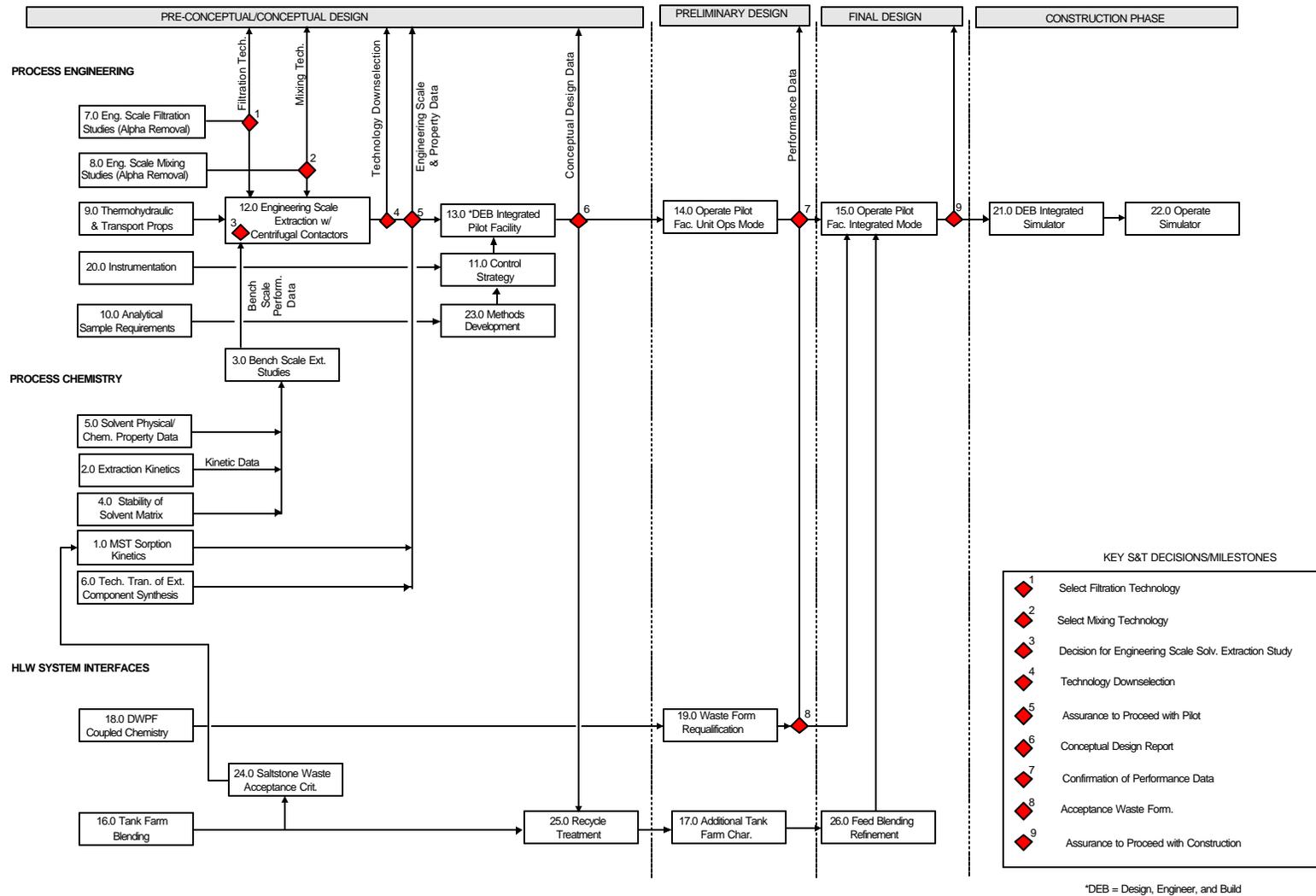
This Workscope Matrix has been developed to define the Science and Technology (S&T) development activities to be performed during the Pre-Conceptual/Conceptual Design Phase. The guiding document for this Workscope Matrix is the HLW Salt Disposition SE Team Science and Technology Roadmap (Attachment 1). This S&T Roadmap is the first issuance of a S&T Roadmap for Caustic-Side Solvent Extraction (CSSX) and provides the technology development path forward towards successful deployment of the CSSX option. This matrix (Attachment 2) expands on the roadmap by providing the high level details of each segment of research and development, assigning responsibility for the execution of each segment and documenting the path through each segment of R&D in the form of a logic diagram(s) (Attachment 3). The logic diagrams tie to the S&T Roadmap using numbered key S&T decisions/milestones.

In this Pre-Conceptual/Conceptual Design Phase, scale-up will be performed wherever practical and advantageous to the confirmation of technology and application of technology to the full-size facility. The Workscope Matrix provides an additional definition of the scale which the S&T development is to be conducted.

The Scope of Work Matrices (SOWMs) provide a more detailed description of the work summarized in the roadmaps and logic diagrams. These SOWMs were previously used to identify R&D work required to reach a technology down-selection decision. Work also is included in these SOWMs that has been identified as appropriate post-down selection R&D. However, no attempt has been made to compile a comprehensive list of all post-down selection R&D in these documents. Additional R&D planning will be required to support future stages of the project, e.g. preliminary design, final design, and startup support.

ATTACHMENT 1 – Science and Technology Roadmap

SCIENCE AND TECHNOLOGY ROADMAP FOR CAUSTIC-SIDE SOLVENT EXTRACTION CESIUM REMOVAL PROCESS



ATTACHMENT 2 – Caustic-Side Solvent Extraction Workslope Matrix

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Chemistry							
1.0	MST Sorption Kinetics	<p><i>The addition of Monosodium Titanate (MST) has been proposed to sorb the soluble U, Pu, and Sr contained in the waste stream. The rate and equilibrium loading of these components as a function of temperature, ionic strength, and mixing is required to support the batch reactor design. Initial data from batch reactor data indicates the MST kinetics require more than the 24 hours assumed in pre-conceptual design resulting in larger reactor batch volumes. Studies will be conducted to determine if the MST strike could be completed in the existing SRS waste tanks. Alternatives to MST will be investigated.</i></p> <p>MST sorption kinetics experiments have been performed at 7.5 M and 4.5 M Na+. In the current flowsheet, the Alpha Sorption step for CST would be performed at 5.6 M Na+. Additional experimentation may be performed at 6.44 M Na+ for CSSX. Also, questions have been raised regarding the oxidation states of Pu (initial, as a function of ionic strength, and equilibrium as Pu is sorbed onto MST) and the effect of oxidation states on MST sorption rates. Since Pu is the primary source of alpha, it is important to assure that experimental results obtained with simulants are representative of performance with real wastes.</p>					
2.0	Extraction Kinetics	Extraction kinetics have been previously studied. No additional investigations of the extraction kinetics are planned at this time.	NA	NA	NA	<p>High Level Waste Testing of Solvent Extraction Process, WSRC-TR-98-000368³</p> <p>ANL Report #1, 10/98³</p> <p>Development of an Alkaline-side CSSX Process Applicable to Savannah River HLW Using a Calixarene-crown Extractant - FY98 Report, ORNLFY98 Report³</p>	Design Input
3.0	Bench Scale Extraction Studies	Run centrifugal contactor test with 32-stage bank of 2-cm contactors housed in glovebox at ANL using solvent and waste simulant. Goal is to show that DF of 40,000 and CF of 12 can be simultaneously achieved. The following was completed in FY99: developed the optimum solvent formulation for the test (ORNL); conducted lab-scale batch-equilibrium tests of flowsheet with waste simulant at 15, 25 and 45°C (ORNL); and constructed the flowsheet for the 2-cm centrifugal contactor test (ANL).			Task Technical and Quality Assurance Plan for CSSX Real Waste Batch Tests, WSRC-RP-2001-00772	<p>WSRC-TR-98-000368³</p> <p>ANL Report #1, 10/98³</p> <p>ORNLFY98 Report³</p>	1, 4, 26
		3.1 Test flowsheet on waste simulant in 2-cm centrifugal contactors				Evaluation of an Alkaline-side Solvent Extraction Process for Cesium Removal from SRS Tank Waste Using Laboratory-scale Centrifugal Contactors, ANL-99/14	

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		3.1.1 Demonstrate stage efficiency to >80%	Bench	ANL			
		3.1.1.1 Modify contactors	Bench	ANL			
		3.1.1.2 Test multiple contactors to demonstrate stage efficiency	Bench	ANL			
		3.1.1.3 Demonstrate stage efficiency with 5-cm contactors	Bench	ORNL			
		3.1.2 Add contactor stages (increase from 24 to 32)	Bench	ANL			
		3.1.3 Solvent preparation					
		3.1.3.1 QA of solution performance in batch tests	Bench	ORNL			
		3.1.3.2 Analyze solvents by ES-MS and NMR	Bench	ORNL			
		3.1.4 Perform contactor test with 3-4x recycle					
		3.1.4.1 Confirm performance of solvent	Bench	ANL			
		3.1.4.2 Analyze recycled solvent taken from strip effluent	Bench	ORNL			
		3.2 Test flowsheet with optimum solvent formulation					
		3.2.1 Develop optimum solvent formulation for test (based on stability data)					
		3.2.2 Conduct lab-scale batch-equilibrium test of flowsheet with waste simulant	Lab	ORNL			
		3.2.2.1 At constant 25°C					
		3.2.2.2 At variable temperature					
		3.2.3 Construct flowsheet for 2-cm centrifugal contactor test					
		3.2.3.1 Define temperature controls, if necessary				Temperature Management of Centrifugal Contactor for Caustic-Side Solvent Extraction of Cesium from Tank Waste, ANL-00/31 Caustic-Side Solvent Extraction Batch Distribution Coefficient Measurements for Savannah River Site High Level Wastes, WSRC-TR-2001-00409	
		3.2.4 Test flowsheet on waste simulant in 2-cm centrifugal contactors (see 3.1)	Bench	ANL		Proof-of-Concept Flowsheet Tests for Caustic-Side Solvent Extraction of Cesium from Tank Waste, ANL-00/30 Savannah River Site High Level Waste Salt Process Project (SPP) Design Input – Caustic Solvent Extraction Flowsheet – Proof of Concept Testing, HLW-SDT-2000-00356	
		3.2.4.1 Solvent preparation					
		3.2.4.1.1 QA of solution performance in batch tests					
		3.2.4.1.2 Analyze solvents by ES-MS and NMR					

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		3.2.4.2 Perform contactor test with 5 day recycle				ANL 5-day Test ORR Completion, HLW-SDT-2001-00092	
		3.2.4.2.1 Confirm performance of solvent; monitor decontamination factors (DFs) and concentration factors (CFs); monitor hydraulic performance				Interim Report on a Multi-day Test of the Caustic-Side Solvent Extraction Flowsheet for Cesium Removal from a Simulated SRS Tank Waste, ANL-01/10 (ANL/CMT/CSSX-2001-01)	
		3.2.4.2.2 Analyze recycled solvent taken from strip effluent; look for degradation products and polymer formation				Solvent Inventory in Solvent Extraction Stages, X-CLC-S-00095	
		3.2.4.2.3 Look for trace component buildup					
		3.2.4.3 Solvent cleanup					
		3.2.4.3.1 Evaluate cleanup procedures					
		3.2.4.3.2 Cleanup solvent as necessary					
		3.2.4.4 Perform second 5-day recycle test (post-down select)					
		3.2.5 Solvent recovery demonstration	Bench	ANL			
		3.2.5.1 Use procedures developed from 4.3.2.					
		3.2.6 Conduct lab-scale batch-equilibrium test of flowsheet with actual SRS waste and compare performance with waste simulant (latter from 3.2.2)				Thermal Properties of Simulated and High-Level Waste Solutions Used for the Solvent Extraction Demonstration, WSRC-TR-2001-00240	
		3.2.6.1 At constant 25°C					
		3.2.6.2 At variable temperature					
		3.2.6.3 Option: compare use of real waste that has been treated (e.g., with MST) to remove actinides with waste that has not been treated; examine behavior of actinides and determine if they could buildup in solvent)					
		3.2.7 Construct flowsheet for 2-cm centrifugal contactor test	Bench	ANL			
		3.2.8 Test flowsheet on real waste in 2-cm centrifugal contactors	Bench	SRTC	Task Requirements and Criteria Salt Waste Processing Facility Real Waste Testing for the CSSX Alternative, G-TC-A-000111		

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		3.2.8.1 Solvent preparation for contactor test					
		3.2.8.1.1 Analyze/characterize pristine solvent					
		3.2.8.1.2 QA of solvent performance in batch tests with real waste					
		3.2.8.2 Perform contactor test on real waste with 2-day recycle					
		3.2.8.2.1 Confirm performance of solvent (using distribution coefficient test); monitor DF and CF; monitor hydraulic performance					
		3.2.8.2.2 Analyze recycled solvent taken from strip effluent; look for degradation products and polymer formation					
		3.2.8.2.3 Look for trace component buildup					
		3.2.8.2.4 Evaluate Tc-99 behavior (post-down select)					
		3.2.8.2.5 Confirm hydrodynamic stability					
		3.2.8.3 Solvent cleanup (if required)					
		3.2.9 Solvent recovery demonstration using procedures developed from 3.2.5	Bench	SRTC			
		3.2.10 If required, demonstrate real waste extraction and stripping using larger contactors (post-down select)	TBD	SRTC			
4.0	Stability of Solvent Matrix	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 this 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.				ANL Report #1, 10/98 ³ WSRC-TR-98-00371 ³ HLW-SDT-99-0283 ³ ORNL FY98 Report ³ ORNL/TM-1999/209 ³ Resuspension and Settling of Monosodium Titanate and Sludge in Supernate Simulant for the Savannah River Site, ORNL/TM-1999/166	1, 3, 23
		4.1 Evaluate radiolytic and chemical stability of solvent	Lab	ORNL/SRS	Task Technical and Quality Assurance Plan for Solvent Extraction External Radiation Stability Testing, WSRC-RP-2000-00889		
		4.1.1 External radiation (Co-60) with the following variables: <ul style="list-style-type: none"> • Modifier alkyl group structure • Diluent structure • Aqueous phase composition • Temperature and mixing 				Solvent Extraction External Radiation Stability Testing, WSRC-TR-2000-00413	

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		4.1.1.1 Identify solvent degradation products (at each aqueous phase composition/section of flowsheet)					
		4.1.1.2 Identify relationships between degree of degradation and aqueous phase and solvent phase compositions (do noble metals enhance/catalyze degradation?)					
		4.1.1.3 Evaluate impact of solvent degradation products on solvent performance (use a standard distribution coefficient test to guide efforts)				Irradiation Effects on Phase Separation Performance Using a Centrifugal Contactor in an Caustic-Side Solvent Extraction (CSSX) Process, ORNL/TM-2001/91 Evaluation of 5-cm Centrifugal Contactor Hydraulic and Mass Transfer Performance for Caustic-Side Solvent Extraction of Cesium, ORNL/TM-2001/137	
		4.1.1.3.1 Determine Trioctylamine (TOA) purity requirements					
		4.1.1.4 Investigate partitioning behavior of solvent degradation products					
		4.1.1.5 Investigate solvent washing and reconstitution				Solvent Washing Recommendation, HLW-SDT-2001-00049	
		4.1.1.6 Investigate the removal of organic anions					
		4.1.2 Batch-equilibrium hot cell tests with SRS high activity waste (internal Cs-137 dose) with following variables: <ul style="list-style-type: none"> • Modifier alkyl group structure • Diluent structure • Temperature and mixing 			Test Plan for Hot-Cell Batch Contacting demonstration with High Activity ¹³⁷ Cs in Support of Work Scope Matrix Task 5.1.7 (Test Plan 1), TTP-ORNL-CTD-1 Test Plan for Batch-Equilibrium Hot-Cell Tests with SRS Simulant Waste and Internal ¹³⁷ Cs Irradiation (Experimental Test Plan No. 2), TTP ORNL-CTD-1		

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		4.1.2.1 Identify solvent degradation products, crud formation, emulsions				Solvent Extraction Self-Irradiation Stability Testing, WSRC-TR-2001-00191	
		4.1.2.2 Impact of noble metals on degradation					
		4.1.3 Three single-stage 5-cm closed loop contactor tests, simulating the strip, extraction, and scrub stages with the following variables: <ul style="list-style-type: none"> • High activity Cs-137 waste simulant • Scrub solution 			Throughput and Phase Separation Evaluations of 5-cm Contactors for CSSX Processing (Test Plan 1), TTP ORNL-CTD-2 Test Instruction for One- and Multi-stage CSSX Process Mass Transfer Evaluations in 5-cm Centrifugal Contactors (Test Plan 2), TTP ORNL-CTD-2 Experimental Test Plan for Contactor Loop Tests Using SRS Simulant Waste with 137Cs Internal Irradiation (Test Plan 3), TTP ORNL-CTD-2 Evaluation of 5-cm Centrifugal Contactor Hydraulic and Mass Transfer Performance for Caustic-Side Solvent Extraction of Cesium, ORNL/TM-2001/137		
		4.1.3.1 Identify solvent degradation products and crud formation, emulsions					
		4.1.3.2 Evaluate impact of solvent degradation products on solvent performance					
		4.1.3.3 Investigate partitioning behavior of solvent degradation products					
		4.1.3.4 Determine the impact of the degradation products on the stage efficiency and hydraulic performance of the contactors					
		4.1.3.5 Investigate solvent washing and reconstitution					
		4.1.4 Chemical stability in the absence of radiation	Lab	ORNL			
		4.1.4.1 Nitration of solvent matrix (post-down select)					
		4.1.4.2 Effect of noble metals					

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		4.1.5 Conduct four stage 5-cm contactor test to determine stage efficiencies	Bench	ORNL			
		4.2 Evaluate methods (e.g., HPLC-MS, ES-MS, NMR, distribution behavior, etc.) to ascertain solvent quality	Lab	ORNL	Method for evaluating CSSX Solvent Quality, TTP ORNL-CTD-2		
		4.2.1 Baseline (pristine solvent) quality assay					
		4.2.2 In-process monitoring					
		4.2.3 Post-process monitoring (solvent meets disposal criteria)					
		4.3 Develop solvent recovery process from raffinate and determine recovery rate					
		4.3.1 Conduct 4-cm contactor tests at ANL (cold) with diluent and aqueous effluent recycle	Bench	ANL			
		4.3.1.1 Develop methods to isolate useful solvent components (vac distill diluent; chromatography to recover calix)	Lab	ORNL			
		4.3.2 Conduct larger scale solvent recovery process to measure rate and economics of solvent loss (worked in conjunction with 3.2.5) (post-down select)					
		4.4 Establish limits for solvent component balance and degradation	Lab	ORNL			
		4.4.1 Measure distribution ratios for Cs, K, and key feed components, and phase-coalescence behavior for all sections of the flowsheet for the following components:					
		4.4.1.1 TOA (concentration bracket range from baseline +5% to -50%)					
		4.4.1.2 Modifier (concentration bracket range from baseline +10% to -25%)					
		4.4.1.3 Calixarene (concentration bracket range from baseline +5% to -10%)					
		4.4.2 Identify methods for monitoring solvent composition over these ranges				Analytical Methods Development in Support of the Caustic Side Solvent Extraction System, ORNL/TM-2001/130 (CERS/SR/SX/022)	

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
5.0	Solvent Physical/Chemical Property Data	Physical and chemical property data for the solvent matrix must be determined. 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.			Task Technical and Quality Assurance Plan Supporting CSSX Pilot Plant Criticality Issues, WSRC-RP-2001-00786	ANL Report #1, 10/98 ³ HLW-SDT-99-0283 ³ ORNL FY98 Report ³ Improved Performance of the Alkaline-Side CSEX Process for Cesium Extraction from Alkaline High-Level Waste Obtained by Characterization of the Effect of Surfactant Impurities, ORNL/TM-1999/209 ³	
		5.1 Solubility and partitioning behavior as a function of temperature and aqueous phase composition	Lab	ORNL		Caustic-Side Solvent Extraction Chemical and Physical Properties: Progress in FY 2000 and FY 2001, CERS/SR/SX/019	
		5.1.1 Primary solvent components					
		5.1.2 Primary degradation products (e.g., phenols, products identified in 4.0)					
		5.1.3 Inorganic cations (e.g., Al, Na, K, other trace metals and noble metals) (includes catalytic decomposition)					
		5.1.4 Inorganic anions (e.g., halides, nitrate, nitrite, chromate)					
		5.1.5 Partitioning behavior of lipophilic anions; ways to prevent buildup in solvent					
		5.1.6 Determine partitioning behavior of components using real waste					
		5.1.7 Batch contact with Cs-137 spike				Batch-Equilibrium Hot-Cell Tests of Caustic-Side Solvent Extraction (CSSX) with SRS Simulant Waste and Internal 137-Cs Irradiation, ORNL/TM-2001/49 (CERS/SR/SX/021)	
		5.2 Evaluate the effect of major and minor components that are expected to be present in actual waste	Lab	ORNL	Test Plan for Evaluation of Solids Transfer and Accumulation in 5-cm Centrifugal Contactors, CERS/SR/SX/020		
		5.2.1 Partitioning behavior of organics (e.g., surfactants, TBP degradation products) in waste					

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		5.2.2 Partitioning behavior of other inorganic (heavy metals; chromate, etc.)					
		5.2.3 Effect of organics on extraction behavior					
		5.2.4 Effect of minor components on distribution behavior					
		5.3 Equilibrium modeling of distribution behavior	NA	ORNL		Caustic-Side Solvent Extraction Chemical and Physical Properties: Equilibrium Modeling of Distribution Behavior, CERS/SR/SX/018	
		5.3.1 Investigate extraction equilibria throughout the sections (extraction, scrub, strip) of the flowsheet					
		5.3.1.1 Co-extraction of K					
		5.3.1.2 Formation of aggregates					
		5.3.2 Develop model to help predict performance as a function of variation of major components in the waste feed solutions					
		5.4 Performance behavior as a function of feed composition variability (Note: will be performed here with simulants and in item 12.0 with real waste.)			Task Technical and Quality Assurance Plan for Solvent Extraction Real Waste Contactor Testing, WSRC-RP-2000-00889		
		5.4.1 For concentration range of key species (e.g., K) expected in SRS HLW tanks, monitor solvent and centrifugal contactor performance with simulants as a function of:				Demonstration of Caustic-Side Solvent Extraction with Savannah River Site High Level Waste, WSRC-TR-2001-00223 Real Waste Feasibility Study for Caustic Side Solvent Extraction Alternative, HLW-SDT-2000-00251	
		5.4.1.1 Temperature					
		5.4.1.2 Solvent component concentration					
		5.4.1.3 Suspended solids in feed					
6.0	Technology Transfer of Component Synthesis	Need to establish that solvent components (calixarene-crown ether and modifier) can be produced commercially at the required scale and purity. Synthetic procedures developed at ORNL need to be refined for scale-up, and made ready for technology transfer to suitable companies for production. The technology transfer scope will be initiated in FY00 and be completed in FY01.	NA	ORNL	HLW-SDT-TTR-2000-05 ¹ ORNL-CASD-1 ² ORNL-CASD-3 ²	Alkaline-Side Extraction of Cesium from Savannah River Tank Waste Using a Calixarene-Crown Ether Extractant, ORNL/TM-13704 ORNL FY98 Report ³	9, 22

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		6.1 Calixarene synthesis and scale-up					
		6.1.1 Place order to IBC Advanced Technologies for ca. 200-500g quantity to meet short-term needs.					
		6.1.2 Complete improved synthetic procedure.					
		6.1.2.1 Optimize synthesis					
		6.1.2.2 Write-up procedure for technology transfer; determine if technology is patentable (if so file patent application in US; foreign?)					
		6.1.3 Technology transfer of synthesis procedure for calix				Letter Report on FY00 Technology Transfer Activities for the CSSX Process, CERS/SR/SX/010	
		6.1.3.1 Identify potential calixarene producers				Letter Report on Candidate Calix Producers, CERS/SR/SX/008	
		6.1.3.2 Legal issues/obtain non-disclosure agreements as necessary					
		6.1.3.3 Develop QA requirements and production specifications					
		6.1.3.4 Obtain quotations on bulk manufacture; select producer(s)					
		6.1.3.5 Place order for multi-kg quantity from selected producer(s)					
		6.1.3.6 Check purity; estimate large-scale production cost					
		6.2 2 nd generation modifier synthesis and scale-up					
		6.2.1 Optimize synthesis procedure for scale-up for 2 nd generation modifier family					
		6.2.1.1 Improve purification procedure and economics				Letter Report on Minimum Purity Requirements and Product Specifications for CSSX Solvent Components, CERS/SR/SX/007	
		6.2.1.2 Synthesize 2-5 kg quantity of preferred, modifier family member at ORNL to meet short-term needs					
		6.2.1.3 Obtain proprietary MSDS from ORNL for modifier shipment to ANL					
		6.2.2 Intellectual property issues					
		6.2.2.1 Update invention disclosure; DOE files US patent application on 2 nd generation family					
		6.2.2.2 Determine if foreign filing is appropriate					

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		6.2.3 Technology transfer of synthesis procedure for 2 nd generation modifiers					
		6.2.3.1 Identify potential modifier producers				Letter Report on Candidate Modifier Producers, CERS/SR/SX/009	
		6.2.3.2 Legal issues/obtain non-disclosure agreements as necessary					
		6.2.3.3 Develop QA requirements and production specifications					
		6.2.3.4 Obtain quotations on bulk manufacture; select producer(s) (post-down select)					
		6.2.3.5 Place order for multi-kg quantity from selected producer(s) (post-down select)					
		6.2.3.6 Check purity; estimate large-scale production cost (post-down select)					
		6.3 Solvent formulation					
		6.3.1 Identify TOA suppliers				Letter Report on Acceptable Diluent, Diluent Suppliers, and Tri-n-octylamine Suppliers, CERS/SR/SX/0006	
		6.3.2 Identify scope of acceptable diluents (Are there suitable substitutes for ExxonMobil's Isopar®L?)					
		6.3.3 Identify solvent compositional requirements/tolerances/QA					
		6.3.4 Finalize solvent formulation and specifications				Method for Evaluating CSSX Solvent Quality, CERS/SR/SX/005	
Process Engineering							
7.0	Engineering Scale Filtration Studies (Alpha Removal)	<i>Filtration of MST and sludge is required to prevent the build up of solids in contactors. Initial data indicates low flux rates for the filtration of these solutions requiring large filter areas and high axial velocity for cross-flow filtration techniques. Alternative filtration techniques and filter aides will be studied, and a selection made. Filtration cleaning studies including the impact of spent cleaning solution will be studied.</i> Tests for MST/sludge filtration (Alpha Sorption step) performed during Phase IV (FY99) indicate low cross-flow filter fluxes leading to very large filters. Improvement in filter size and operation is desired.					
8.0	Engineering Scale Mixing Studies (Alpha Removal)	<i>As noted in the kinetic section above, good reactor mixing is essential to proper alpha decontamination batch reactor sizing. Simple mixing by agitation or recirculation may not be adequate. Alternate mixing technologies will be studied. Resuspension criteria must be developed.</i> (Preliminary Design)	NA	NA	NA		27

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
9.0	Thermo-hydraulic and Transport Properties	No issues have been identified at present that will require experimental validation in this area. Identified item will be completed during conceptual design.	NA	NA	NA		Design Input
10.0	Analytical Sample Requirements	<i>The analytical sample requirements including on-line analysis must be developed to support control strategy development.</i> Develop an at-line analyzer for Cs, Sr, and total alpha.					
11.0	Control Strategy	<i>Control strategy must be developed to support the designing, engineering, and building of the pilot facility.</i> Pilot Plant Conceptual Design will be conducted post-down select.	NA	NA	NA		Design Input
12.0	Engineering Scale Extraction with Centrifugal Contactors	Demonstrate viability of SX for achieving desired DF and CF, that is, adequate performance in the extraction and strip sections of the process with solvent recycle. Hydrodynamics; single-stage efficiency; other-phase carry-over, multi-stage single cycle; multi-stage multi cycle. Demonstrate viability of SX for achieving desired DF and CF, that is, adequate performance in the extraction and strip sections of the process with solvent recycle, with real waste. Hydrodynamics; single-stage efficiency; other-phase carry-over, multi-stage single cycle; multi-stage multi cycle. Where contactor test will be performed is to be determined. Need to determine the impact of items 4.0 and 5.0 on process flowsheet for longer contact test and the sensitivity of the process flowsheet to "process upsets".	NA	NA	NA	ANL Report #1, 10/98 ³ ANL Report #2, 10/98 ³ ORNL FY98 Report ³	26
13.0	Design, Engineer, and Build (DEB) the Pilot Facility	<i>A pilot scale (to be determined) facility will be built to support the confirmation of design data and development of operator training.</i> Pilot Facility Conceptual Design will be conducted in parallel with a final technology selection. Pilot Facility design will be conducted on the selected technology.	NA	NA	NA	Pre-conceptual Design Package for the Salt Waste Processing Facility Caustic Side Solvent Extraction, G-CDP-J-00003	Design Input
14.0	Operation of the Pilot Facility in a Unit Operations Mode	<i>The pilot facility testing will include a phase of single unit operations to confirm bench-scale property data, operational parameters, and proof-of-concept component testing.</i> Pilot Facility Conceptual Design will be conducted in parallel with a final technology selection. Pilot Facility design will be conducted on the selected technology.	NA	NA	NA		Design Input

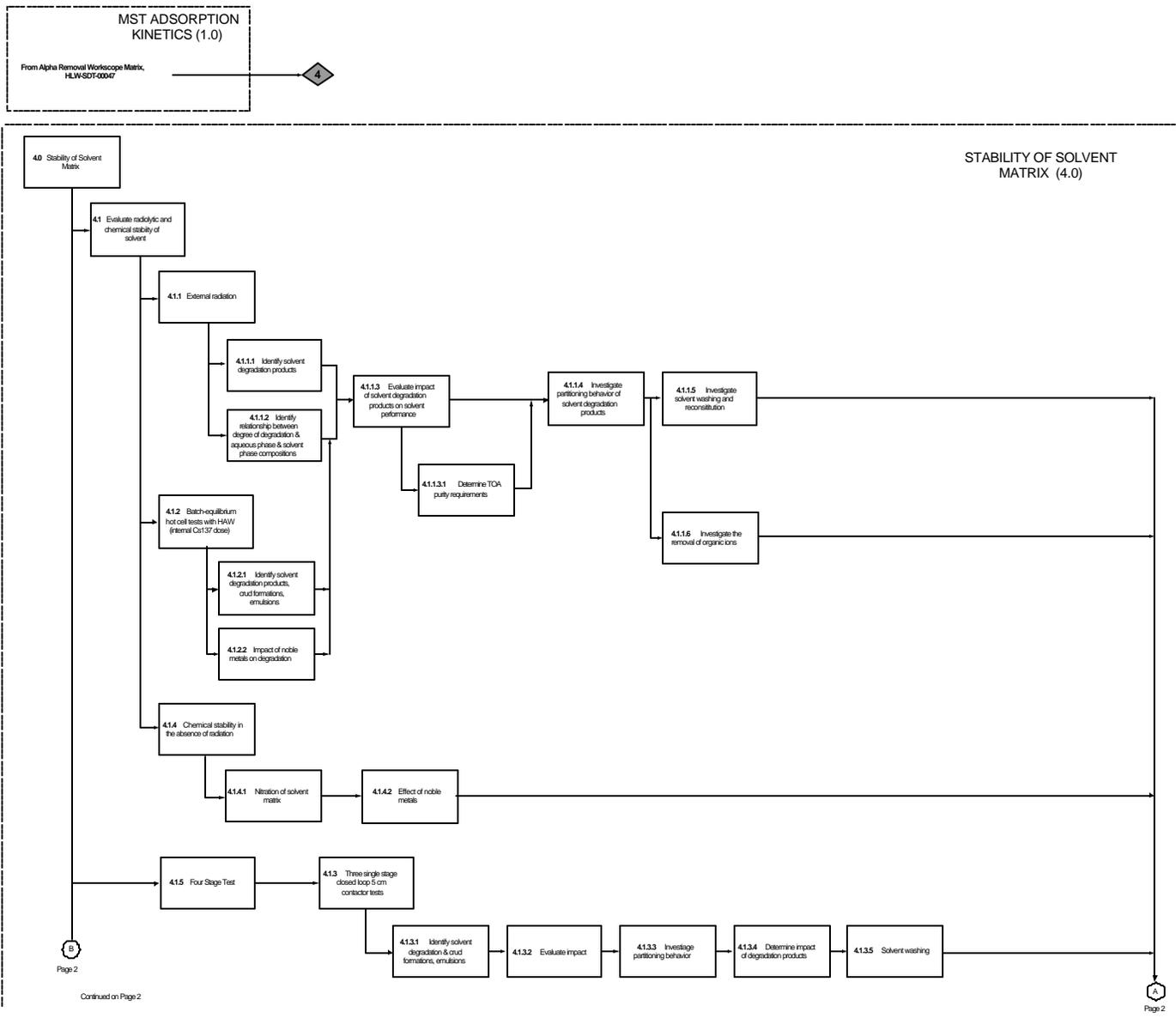
Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
15.0	Operation of the Pilot Facility in an Integrated Operations Mode	<i>The Pilot Facility testing will include a phase of integrated operations to ensure the design will operate under upset conditions, determine the limits of operation to dictate recovery, the limits of feed composition variability, and confirm design assumptions. Investigation of the operating characteristics while varying the velocity, temperature, and waste composition will be conducted. This testing will aid in operator training and simulator development, which in accordance with the overall project roadmap is completed during the construction phase of the project.</i>	NA	NA	NA		Design Input
20.0	Instrumentation	See 13.0.	NA	NA	NA		Design Input
21.0	DEB Integrated Simulator	To be developed during the construction phase of the project.	NA	NA	NA		Design Input
22.0	Operate Simulator	To be developed during the construction phase of the project.	NA	NA	NA		Design Input
23.0	Methods Development	To be developed during Conceptual Design.	NA	NA	NA		Design Input
High Level Waste System Interface							
16.0	Tank Farm Blending	Need to determine whether chemical and radiolytic degradation products that wash into the raffinate and scrub solutions meet the Saltstone Waste Acceptance Criteria. (Decision diamond.) Also, need to determine if "spent" solvent can be incinerated, and whether it meets the CIF Waste Acceptance Criteria.				ORNL FY98 Report ³	
		16.1 Determine whether strip effluent meets DWPF feed requirements (This work performed under Section 3.1.)	NA	SRS			
		16.1.1 Cs concentration factor adequate?					
		16.1.2 Concentration of other species in strip effluent acceptable?					
		16.2 Determine whether raffinate meets Saltstone Facility Waste Acceptance Criteria					
		16.2.1 Solvent components in raffinate		SRS			
		16.2.2 Solvent degradation products in raffinate		ORNL			
		16.3 Determine whether spent solvent meets CIF Waste Acceptance Criteria (post-down select)		SRS			
17.0	Additional Tank Farm Characterization	<i>While the tank farm waste has been characterized, additional characterization may be required to define the range of expected compositions during facility operation.</i> Waste characterizations activities have begun.	NA	NA	NA		4
18.0	DWPF Coupled Chemistry	No needs identified at this time.	NA	NA	NA		Design Input
19.0	Waste Form Requalification	No needs identified at this time.	NA	NA	NA		Design Input

Item No.	Item	Consideration	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
24.0	Saltstone Waste Acceptance Criteria	No needs identified at this time.	NA	NA	NA		Design Input
25.0	Recycle Treatment	No needs identified at this time.	NA	NA	NA		Design Input
26.0	Feed Blending Refinement	See 17.0, additional activities will be developed during Preliminary Design.	NA	NA	NA		Design Input

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).
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 ¹ ; Task Technical and Quality Assurance Plans (TTPs) denoted xxxx ² and Test Reports (TRs) denoted xxxx ³ 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

ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (1 of 7)

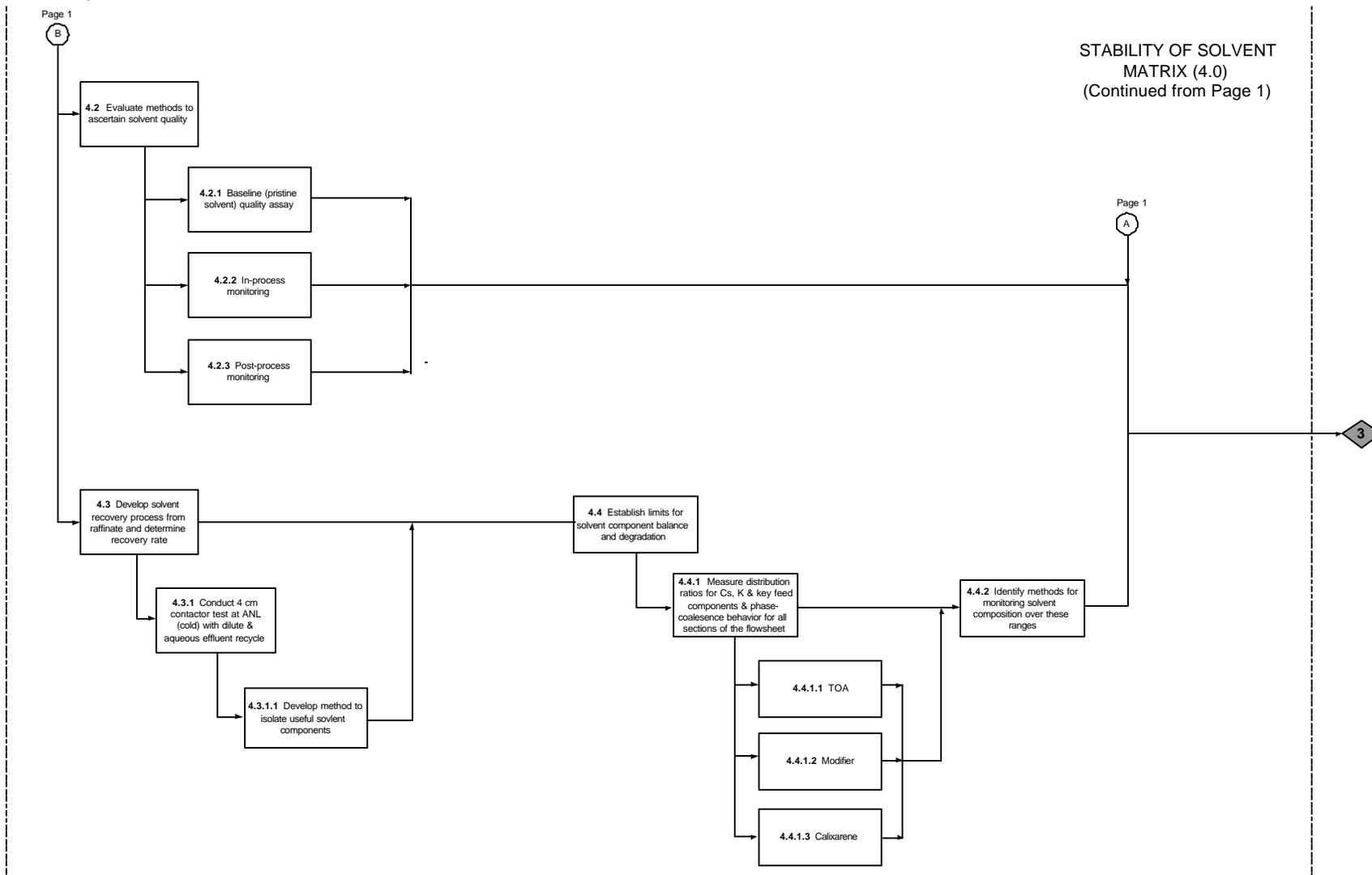


ATTACHMENT 2 - Caustic-Side Solvent Extraction S&T Logic Diagrams (2 of 7)

PAGE 2

STABILITY OF SOLVENT MATRIX (4.0)
(Continued from Page 1)

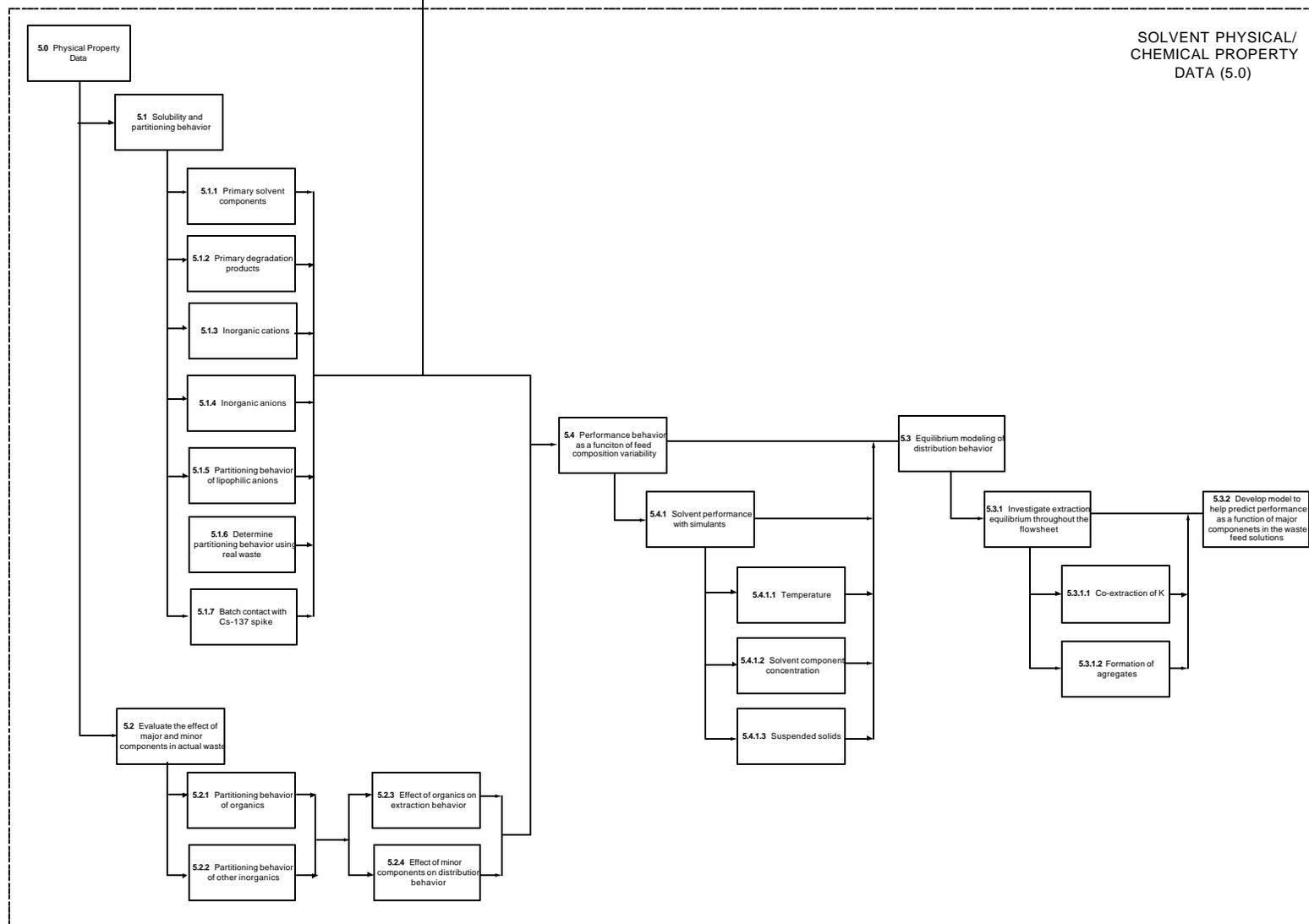
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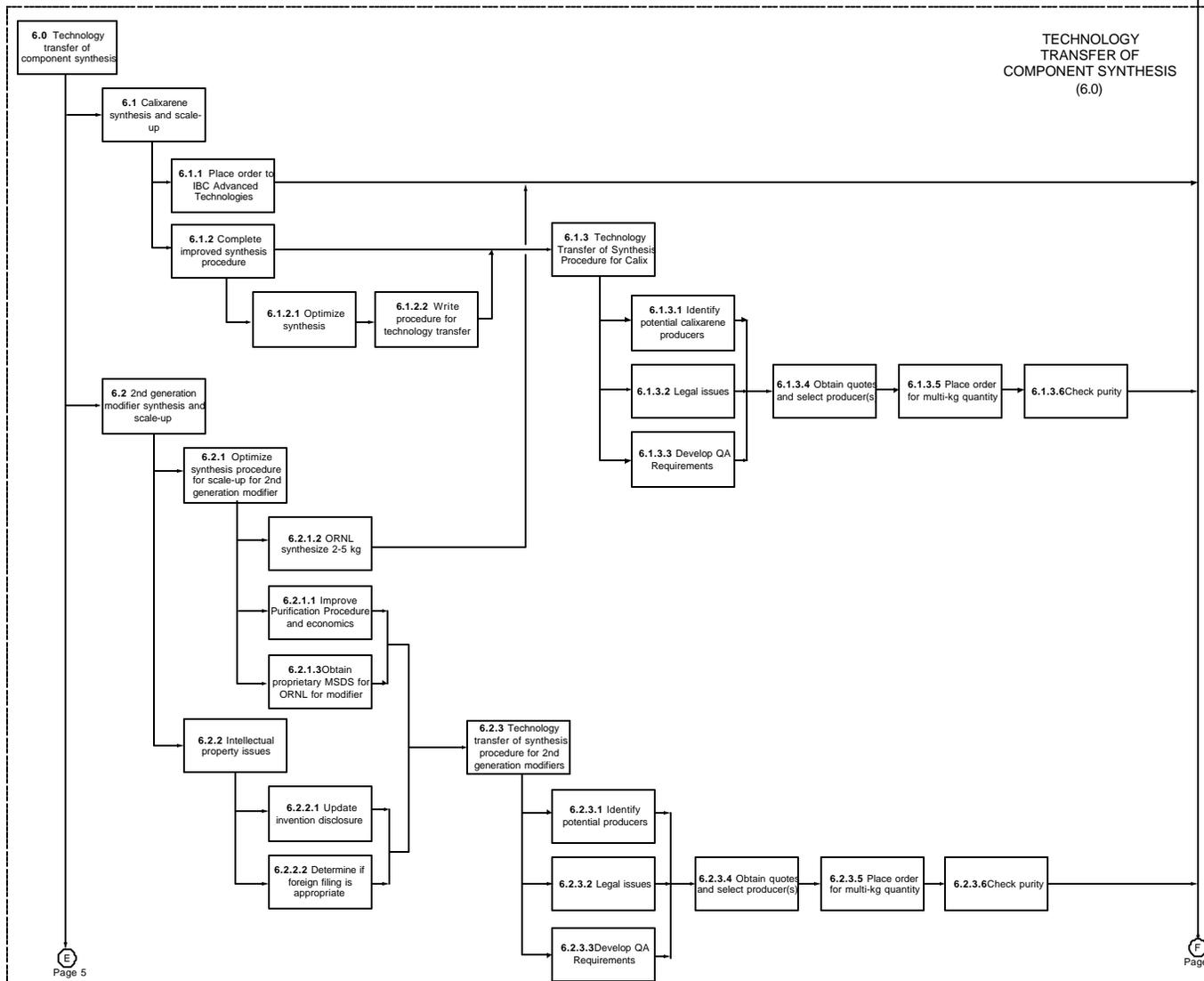
ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (3 of 7)

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PAGE 3



ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (4 of 7)



Continued on Page 5

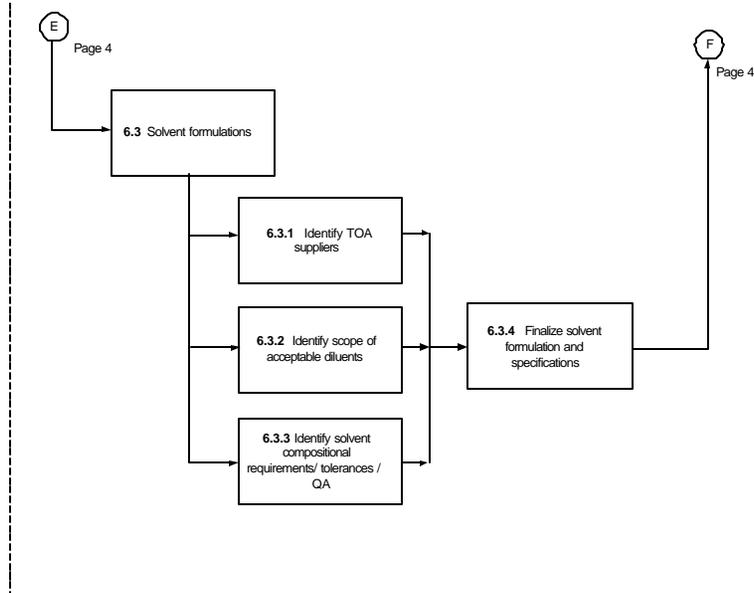
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ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (5 of 7)

PAGE 5

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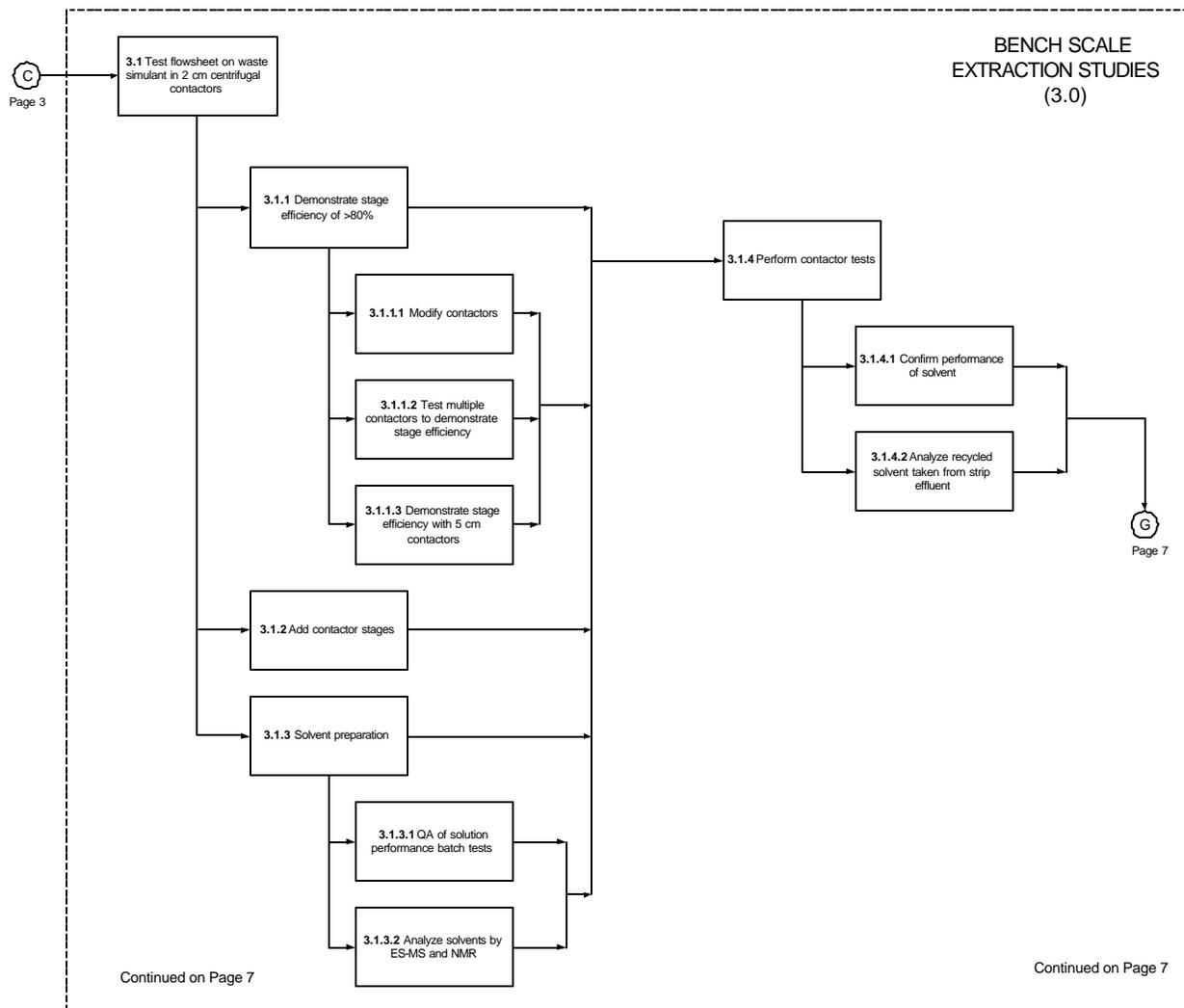
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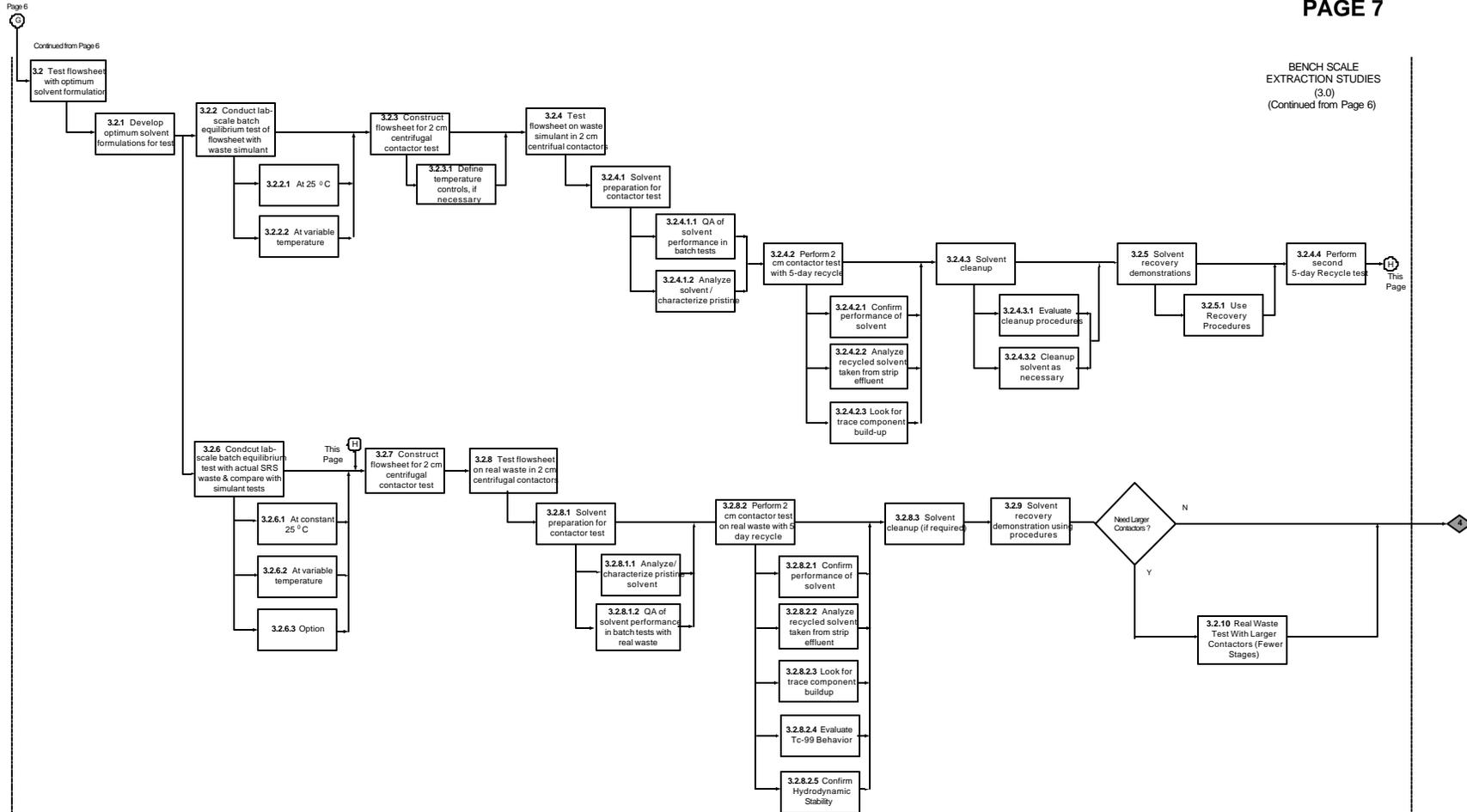
TECHNOLOGY
TRANSFER OF
COMPONENT SYNTHESIS
(6.0)
(Continued from Page 4)

ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (6 of 7)

PAGE 6



ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (7 of 7)



APPENDIX B

Research and Development Program Schedule

The following pages are Salt Processing Program Research and Development schedule (as of October 2001) on the planned work for Alpha and Strontium Removal and Caustic Side Solvent Extraction.

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
Alpha & Strontium Removal																					
Pu Speciation in Waste - XFAS Study																					
WAMST12160	XAFS Approve Pu & Np Final Report	0		22OCT01A	JTC	XAFS Approve Pu & Np Final Report															
Monosodium Titanate Testing																					
WAMST15000	MST Testing <HA>	5*	03NOV00A	02NOV01	DTH	MST Testing <HA>															
WAMST15160	MST Testing- Approve Final Report	0		02NOV01	DTH	MST Testing- Approve Final Report															
Evaluate Alternative Sorbents - TAMU Supplied																					
WAMST17000	Evaluate Alternate Sorbents (TAMU Supplied) <HA>	5*	03NOV00A	02NOV01	DTH	Evaluate Alternate Sorbents (TAMU Supplied) <HA>															
WAMST17130	Alternate Sorbent Evaluate- Approve Final Report	0		02NOV01	DTH	Alternate Sorbent Evaluate- Approve Final Report															
Evaluate Alternative Sorbents & Technologies																					
WAMST16000	Identify Alternate Sorbents & Technologies <HA>	19*	18OCT00A	26NOV01	DTH	Identify Alternate Sorbents & Technologies <HA>															
WAMST16110	Team Review Report - Alternate Sorbents (Rv B)	1	23OCT01A	29OCT01	DTH	Team Review Report - Alternate Sorbents (Rv B)															
WAMST16130	Resolve comments - Alternate Sorbents	16*	16OCT01A	19NOV01	DTH	Resolve comments - Alternate Sorbents															
WAMST16140	Approve Final Report - Alternate Sorbents	0		26NOV01*	DTH	Approve Final Report - Alternate Sorbents															

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Run Date 31OCT01 11:45

**Salt Processing Program FY 2002
Research & Development Activities
(Detail)**

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
Cross-Flow Filtration Tests: Permanganate Process						Cross Flow Permanganate Testing <HA>															
WAPRM26000	Cross Flow Permanganate Testing <HA>	13*	26JUL01A	14NOV01	DDW	Cross Flow Filtration Tests: Permanganate Process															
WAPRM26150	Draft Report - PREF Permanganate Testing	5*	22OCT01A	02NOV01	MRP	Draft Report - PREF Permanganate Testing															
WAPRM26160	DOE Rev Draft Report - PREF Permanganate Testing	4	05NOV01	08NOV01	JWM	DOE Rev Draft Report - PREF Permanganate Testing															
WAPRM26170	Team Review Draft Rpt- PREF Permanganate Testing	4	05NOV01	08NOV01	JTC	Team Review Draft Rpt- PREF Permanganate Testing															
WAPRM26180	Incorporate Comments - PREF Permanganate Testing	3	09NOV01	13NOV01	MRP	Incorporate Comments - PREF Permanganate Testing															
WAPRM26190	Approve Final Report - PREF Permanganate Testing	1	14NOV01	14NOV01	JPM	Approve Final Report - PREF Permanganate Testing															
WAPRM26200	Issue Final Report - PREF Permanganate Testing	0		14NOV01	MRP	Issue Final Report - PREF Permanganate Testing															
Permanganate Ionic Strength, Formate						Permanganate, Ionic Strength, Formate, Strike Vy															
WAPRM27	Permanganate, Ionic Strength, Formate, Strike Vy	46*	02AUG01A	04JAN02	MCD	Permanganate Process: Ionic Strength, Formate, and Multiple Strike Variations															
WAPRM27130	Conduct Tests - Permanganate, Ionic Strength	10	01NOV01*	14NOV01	MCD	Conduct Tests - Permanganate, Ionic Strength															
WAPRM27132	Analysis - Permanganate, Ionic Strength	10	15NOV01	30NOV01	MCD	Analysis - Permanganate, Ionic Strength															
WAPRM27136	Draft Report - Permanganate Ionic Strength,	8	03DEC01	12DEC01	MCD	Draft Report - Permanganate Ionic Strength,															
WAPRM27140	Team Review Draft Report - Permanganate	5	13DEC01	19DEC01	JTC	Team Review Draft Report - Permanganate															
WAPRM27150	DOE Review Draft Report - Permanganate	5	13DEC01	19DEC01	JWM	DOE Review Draft Report - Permanganate															

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
MST Settle, Decant Testing																							
WAMST22000	MST - Settle / Decant Testing <HA>	3*	25OCT00A	31OCT01	MRP	MST - Settle / Decant Testing <HA>																	
WAMST22490	MST Settle Decant - Approve Final Report	0		31OCT01*	MRP	MST Settle Decant - Approve Final Report																	
Test the Permanganate Process with Actual Waste																							
WAPRM25000	Permanganate Actual Waste Testing <HA>	31*	01AUG01A	12DEC01	MJB	Permanganate Actual Waste Testing <HA> Test of the Permanganate Process with Actual Waste																	
WAPRM25210	Analyze Test Samples	10*	08OCT01A	09NOV01	MJB	Analyze Test Samples																	
WAPRM25220	Develop/Issue Draft Report	6	12NOV01	19NOV01	MJB	Develop/Issue Draft Report																	
WAPRM25240	Team Review Draft Report	5	20NOV01	28NOV01	JTC	Team Review Draft Report																	
WAPRM25250	DOE Review Draft Report	5	20NOV01	28NOV01	JWM	DOE Review Draft Report																	
WAPRM25260	Incorporate Comments - Permanganate Tests	5	29NOV01	05DEC01	MJB	Incorporate Comments - Permanganate Tests																	
WAPRM25270	Review/Approve Draft Report - Perman Tests	5	06DEC01	12DEC01	JPM	Review/Approve Draft Report - Perman Tests																	
WAPRM25280	Issue Final Report - Permanganate Real Waste Tes	0		12DEC01	MJB	Issue Final Report - Permanganate Real Waste Tes TFA-HQ Milestone A1.1 of 1/25/2002																	
WAPRM25290	Clean-up/Dispose of Waste	38	17OCT01A	21DEC01	MJB	Clean-up/Dispose of Waste																	
Metallurgical Eval of Failed Filter from USC																							
WAAS040000	Metallurgical Eval of Failed Filter	81*	01OCT01A	25FEB02	MRP	Metallurgical Eval of Failed Filter Metallurgical Evaluation of Failed Filter from USC																	
WAAS040020	USC Test Repaired Filter	0		29OCT01*	MRP	USC Test Repaired Filter																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WAAS040100	Draft Task Plan - Examine Failed Filter Element	10	01NOV01*	14NOV01	MRP	Draft Task Plan - Examine Failed Filter Element																	
WAAS040110	Team Review Task Plan - Examine Failed Filter Element	5	15NOV01	21NOV01	JTC	Team Review Task Plan - Examine Failed Filter Element																	
WAAS040120	DOE Review Task Plan - Examine Failed Filter Element	5	15NOV01	21NOV01	JWM	DOE Review Task Plan - Examine Failed Filter Element																	
WAAS040130	Incorporate Comments - Examine Failed Filter Element	5	26NOV01	30NOV01	MRP	Incorporate Comments - Examine Failed Filter Element																	
WAAS040140	Review/App Task Plan - Examine Failed Filter Element	3	03DEC01	05DEC01	ALL	Review/App Task Plan - Examine Failed Filter Element																	
WAAS040150	Issue Task Plan - Examine Failed Filter Element	0		05DEC01	MRP	Issue Task Plan - Examine Failed Filter Element																	
WAAS040160	Perform Metalurgical Evaluation of Failed Filter	30	06DEC01	18JAN02	MRP	Perform Metalurgical Evaluation of Failed Filter																	
WAAS040170	Analyze Evaluation Data of failed Filter Element	3	21JAN02	23JAN02	MRP	Analyze Evaluation Data of failed Filter Element																	
WAAS040180	Draft Report - Examine Failed Filter Element	7	24JAN02	01FEB02	MRP	Draft Report - Examine Failed Filter Element																	
WAAS040190	Team Review Draft Report - Examine Failed Filter	5	04FEB02	08FEB02	JTC	Team Review Draft Report - Examine Failed Filter																	
WAAS040200	DOE Review Draft Report - Examine Failed Filter	5	04FEB02	08FEB02	JWM	DOE Review Draft Report - Examine Failed Filter																	
WAAS040210	Resolve Comments- Examine Failed Filter	5	11FEB02	15FEB02	MRP	Resolve Comments- Examine Failed Filter																	
WAAS040220	Rev/Approve Final Report- Examine Failed Filter	5	19FEB02	25FEB02	ALL	Rev/Approve Final Report- Examine Failed Filter																	
WAAS040230	Issue Final Report- Examine Failed Filter	0		25FEB02	MRP	Issue Final Report- Examine Failed Filter																	
WAAS040240	Examine Failed Filter Test - Dispose of Waste	20	26FEB02	25MAR02	ALL	Examine Failed Filter Test - Dispose of Waste																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
Actual Waste Filtration Test SpinTek using RMF																					
WAAS050005	Actual Waste Filtration Test - Spintek <HA>	181*	01NOV01	23JUL02	MRP	Actual Waste Filtration Test - Spintek <HA>															
WAAS050010	Develop/Award Procurement Specifications	20	01NOV01*	30NOV01	MRP	Actual Waste Filtration Test Using SpinTek Rotary Microfilter															
WAAS050020	Vendor Fabricate/Deliver Rotary Microfilter	60	03DEC01	27FEB02	MRP	Develop/Award Procurement Specifications															
WAAS050030	SRTC Perform Inspection of Rotary Microfilter	0	02JAN02		MRP	Award of Procurement on HOLD for Funding.															
WAAS050040	SRTC Perform Inspection of Rotary Microfilter	0	28FEB02		MRP	Vendor Fabricate/Deliver Rotary Microfilter															
WAAS050050	Mockup After Receipt of Rotary Microfilter	40	28FEB02	25APR02	MRP	SRTC Perform Inspection of Rotary Microfilter															
WAAS050060	Install Rotary Microfilter	20	26APR02	23MAY02	MRP	SRTC Perform Inspection of Rotary Microfilter															
WAAS050065	Install Rotary Microfilter	0		23MAY02	MRP	Mockup After Receipt of Rotary Microfilter															
WAAS050100	Draft TTP-Rotary Microfilter Test w/Real Waste	10	02JAN02*	15JAN02	MRP	Install Rotary Microfilter															
WAAS050110	Team Review TTP - Rotary Microfilter Test w/Real	5	16JAN02	22JAN02	JTC	Install Rotary Microfilter															
WAAS050120	DOE Review TTP-Rotary Microfilter Test w/Real Wa	5	16JAN02	22JAN02	JWM	Draft TTP-Rotary Microfilter Test w/Real Waste															
WAAS050130	Resolve Comments - Rotary Microfilter Test w/Rea	5	23JAN02	29JAN02	MRP	Team Review TTP - Rotary Microfilter Test w/Real															
WAAS050140	Review/App TTP-Rotary Microfilter Test w/Real Wa	3	30JAN02	01FEB02	ALL	DOE Review TTP-Rotary Microfilter Test w/Real Wa															
WAAS050150	Issue TTP-Rotary Microfilter Test w/Real Waste	0		01FEB02	MRP	Resolve Comments - Rotary Microfilter Test w/Rea															
						Review/App TTP-Rotary Microfilter Test w/Real Wa															
						Issue TTP-Rotary Microfilter Test w/Real Waste															

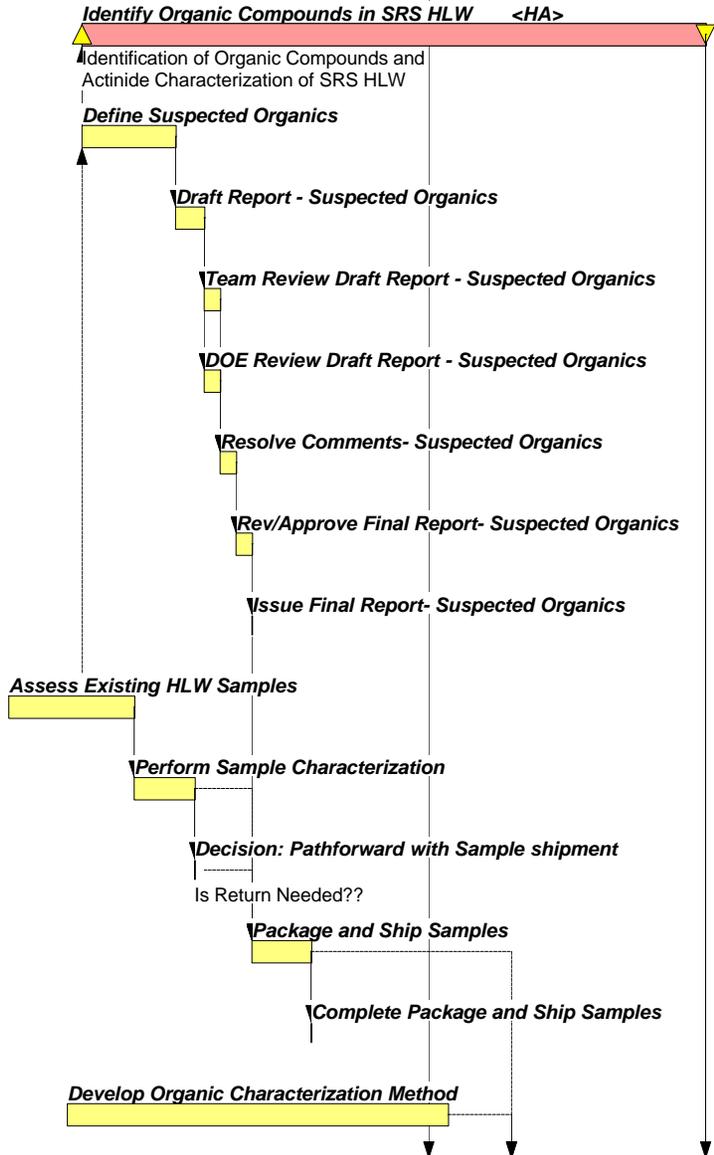
ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WAAS070167	PNNL Draft System Testing Letter Report	10	10OCT02	23OCT02	T_S																		PNNL Draft System Testing Letter Report
WAAS070168	PNNL Pkg and Transport to SRTC	15	10OCT02	30OCT02	T_S																		PNNL Pkg and Transport to SRTC
WAAS070173	Team Review System Testing Letter Report	5	24OCT02	30OCT02	JTC																		Team Review System Testing Letter Report
WAAS070174	DOE Review System Testing Letter Report	5	24OCT02	30OCT02	JWM																		DOE Review System Testing Letter Report
WAAS070175	Resolve Comments- System Testing Letter Report	5	31OCT02	06NOV02	T_S																		Resolve Comments- System Testing Letter Report
WAAS070176	Rev/Approve System Testing Letter Report	5	07NOV02	13NOV02	ALL																		Rev/Approve System Testing Letter Report
WAAS070178	PNNL Issue System Testing Letter Report	0		13NOV02	T_S																		PNNL Issue System Testing Letter Report
WAAS070179	SRTC Install Online Monitor	20	31OCT02	27NOV02	T_S																		SRTC Install Online Monitor
WAAS070180	SRTC Perform Feasibility Testing	30	02DEC02	14JAN03	T_S																		SRTC Perform Feasibility Testing
WAAS070185	Draft Report - Feasibility Testing	7	15JAN03	23JAN03	MJB																		Draft Report - Feasibility Testing
WAAS070190	Team Review Draft Report - Feasibility Testing	5	24JAN03	30JAN03	JTC																		Team Review Draft Report - Feasibility Testing
WAAS070200	DOE Review Draft Report - Feasibility Testing	5	24JAN03	30JAN03	JWM																		DOE Review Draft Report - Feasibility Testing
WAAS070210	Resolve Comments- Feasibility Testing	5	31JAN03	06FEB03	T_S																		Resolve Comments- Feasibility Testing
WAAS070220	Rev/Approve Final Report- Feasibility Testing	5	07FEB03	13FEB03	ALL																		Rev/Approve Final Report- Feasibility Testing
WAAS070230	Issue Final Report- Feasibility Testing	0		13FEB03	T_S																		Issue Final Report- Feasibility Testing

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
WAAS070240	Online Monitor Feasibility - Dispose of Waste	60	14FEB03	13MAY03	ALL	<i>Online Monitor Feasibility - Dispose of Waste</i>															
TEM/STEM Structural Analysis for MST/MNO4 Solids																					
WAAS090000	TEM/STEM Structural Analysis <HA>	146*	02OCT01A	29MAY02	MCD	<i>TEM/STEM Structural Analysis <HA></i>															
WAAS090020	Award Subcontract	12*	16OCT01A	13NOV01	MCD	<i>Award Subcontract</i>															
WAAS090110	Team Review TTP - TEM/STEM/XAFS Studies	4*	26OCT01A	01NOV01	JTC	<i>Team Review TTP - TEM/STEM/XAFS Studies</i>															
WAAS090120	DOE Review TTP-TEM/STEM/XAFS Studies	4*	26OCT01A	01NOV01	JWM	<i>DOE Review TTP-TEM/STEM/XAFS Studies</i>															
WAAS090130	Resolve Comments - TEM/STEM/XAFS Studies	5	02NOV01	08NOV01	MCD	<i>Resolve Comments - TEM/STEM/XAFS Studies</i>															
WAAS090140	Review/App TEM/STEM/XAFS Studies	3	09NOV01	13NOV01	ALL	<i>Review/App TEM/STEM/XAFS Studies</i>															
WAAS090150	Issue TTP-TEM/STEM/XAFS Studies	0		13NOV01	MCD	<i>Issue TTP-TEM/STEM/XAFS Studies</i>															
WAAS090152	Obtain Approval from Subcontractor for Hot Work	0		16NOV01*	MCD	<i>Obtain Approval from Subcontractor for Hot Work</i>															
WAAS090155	Prepare Samples for Testing	42	19NOV01*	21JAN02	MCD	<i>Prepare Samples for Testing</i>															
WAAS090157	Ship MST Samples to Subcontractor	6	04DEC01*	11DEC01	MCD	<i>Ship MST Samples to Subcontractor</i>															
WAAS090160	Perform TEM/STEM Studies w/ MST	27	12DEC01	21JAN02	MCD	<i>Perform TEM/STEM Studies w/ MST</i>															
WAAS090162	Ship Permanganate Samples to Subcontractor	6	22JAN02*	29JAN02	MCD	<i>Ship Permanganate Samples to Subcontractor</i>															
WAAS090165	Perform TEM/STEM Studies w/ Permanganate	18	30JAN02	25FEB02	MCD	<i>Perform TEM/STEM Studies w/ Permanganate</i>															

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WACSTB	Refine ZAM Coefficient & Model <HA>	3*	15FEB01A	31OCT01	FF	Refine ZAM Coefficient & Model <HA>																	
CST Thermal Stability Issue - ORNL																							
WAORN2332	Resolve Comments - CST Thermal Stability Issues	10*	23OCT01A	09NOV01	TK	Resolve Comments - CST Thermal Stability Issues																	
WAORN2333	Approve CST Stability & Thermal Issue Report	5	12NOV01	16NOV01	JTC	Approve CST Stability & Thermal Issue Report (Obtain Approval Signatures)																	
WAORN2334	Issue Report - CST Stability & Thermal Issues	0		16NOV01	TK	Issue Report - CST Stability & Thermal Issues																	
Real Waste Equilibrium - Heated Experiment																							
WACST5400	Actual Waste Stability Studies <HA>	38*	06JUN01A	21DEC01	TK	Actual Waste Stability Studies <HA>																	
WACST5422	Draft Report - Real Waste Heated & Seeded Tests	28*	03OCT01A	07DEC01	DDW	Draft Report - Real Waste Heated & Seeded Tests																	
WACST5431	Team Comment - Real Waste Heated & Seeded Test	5	10DEC01	14DEC01	DDW	Team Comment - Real Waste Heated & Seeded Test																	
WACST5432	DOE Comment - Real Waste Heated & Seeded Tests	5	10DEC01	14DEC01	JWM	DOE Comment - Real Waste Heated & Seeded Tests																	
WACST5434	Resolve Comments - Heated & Seeded Tests	5	17DEC01	21DEC01	DDW	Resolve Comments - Heated & Seeded Tests																	
WACST5436	Issue Report - Real Waste Heated & Seeded Tests	0		21DEC01	JPM	Issue Report - Real Waste Heated & Seeded Tests																	
WACST5437	Dispose of Waste	45	06SEP01A	03JAN02	DDW	Dispose of Waste																	
UOP Manufacturing Revisions																							
WACST21I	UOP Manufacturing - Make 2000 Lb of Product	23*	16MAY01A	30NOV01	WRW	UOP Manufacturing - Make 2000 Lb of Product																	
WACST21K	UOP Manufacturing - Deliver Product	0		30NOV01	WRW	UOP Manufacturing - Deliver Product																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
WACSTK	UOP Manufacturing Revision <HA>	23*	18OCT00A	30NOV01	WRW	UOP Manufacturing Revision <HA>															
Caustic Side Solvent Extraction																					
Test Bed and Prototype Contactor Test - ON HOLD																					
WAAS300000	Contactor Prototype Development ON HOLD <HA>	182*	05NOV01	26JUL02	MAN	Contactor Prototype Development ON HOLD <HA>															
WAAS300100	Draft TTP- Test Bed/ Contactor Testing	10	05NOV01*	16NOV01	MAN	Contactor Prototype Development and Testing Draft TTP- Test Bed/ Contactor Testing (on HOLD)															
WAAS300110	Team Review TTP - Test Bed/ Contactor Testing	5	19NOV01	27NOV01	JTC	Team Review TTP - Test Bed/ Contactor Testing															
WAAS300120	DOE Review TTP-Test Bed/ Contactor Testing	5	19NOV01	27NOV01	JWM	DOE Review TTP-Test Bed/ Contactor Testing															
WAAS300130	Resolve Comments - Test Bed/ Contactor Testing	5	28NOV01	04DEC01	MAN	Resolve Comments - Test Bed/ Contactor Testing															
WAAS300140	Review/App TTP-Test Bed/ Contactor Testing	3	05DEC01	07DEC01	ALL	Review/App TTP-Test Bed/ Contactor Testing															
WAAS300150	Issue TTP-Test Bed/ Contactor Testing	0		07DEC01	MAN	Issue TTP-Test Bed/ Contactor Testing															
WAAS300153	Develop Design for Testing Bed	20	05NOV01	04DEC01	MAN	Develop Design for Testing Bed Ties to TR&C for Pilot Plant Construction															
WAAS300154	Issue Preliminary Design for Testing Bed	0	05DEC01	04DEC01	MAN	Issue Preliminary Design for Testing Bed															
WAAS300155	Team Review of Testing Bed Design	5	05DEC01	11DEC01	JTC	Team Review of Testing Bed Design															
WAAS300156	DOE Review of Testing Bed Design	5	05DEC01	11DEC01	JWM	DOE Review of Testing Bed Design															
WAAS300157	Resolve/Incorp Comment for Testing Bed Design	5	12DEC01	18DEC01	MAN	Resolve/Incorp Comment for Testing Bed Design															
WAAS300158	Rev/Approve Testing Bed Design	5	19DEC01	26DEC01	ALL	Rev/Approve Testing Bed Design															

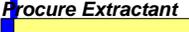
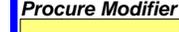
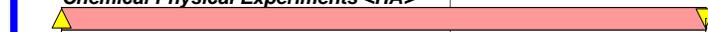
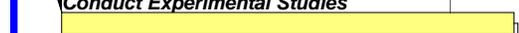
ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
Identify Organic Compounds in SRS HLW																							
WABB050100	Identify Organic Compounds in SRS HLW <HA>	204*	10DEC01	30SEP02	DDW																		
WABB050150	Define Suspected Organics	30	10DEC01*	22JAN02	DDW																		
WABB050151	Draft Report - Suspected Organics	10	23JAN02	05FEB02	DDW																		
WABB050153	Team Review Draft Report - Suspected Organics	5	06FEB02	12FEB02	JTC																		
WABB050154	DOE Review Draft Report - Suspected Organics	5	06FEB02	12FEB02	JWM																		
WABB050155	Resolve Comments- Suspected Organics	5	13FEB02	20FEB02	DDW																		
WABB050156	Rev/Approve Final Report- Suspected Organics	5	21FEB02	27FEB02	ALL																		
WABB050157	Issue Final Report- Suspected Organics	0		27FEB02	DDW																		
WABB050160	Assess Existing HLW Samples	40	05NOV01*	03JAN02	WRW																		
WABB050161	Perform Sample Characterization	20	04JAN02	31JAN02	WRW																		
WABB050162	Decision: Pathforward with Sample shipment	0		31JAN02	WRW																		
WABB050164	Package and Ship Samples	20	28FEB02	27MAR02	WRW																		
WABB050165	Complete Package and Ship Samples	0		27MAR02	WRW																		
WABB050167	Develop Organic Characterization Method	125	03DEC01*	31MAY02	WRW																		



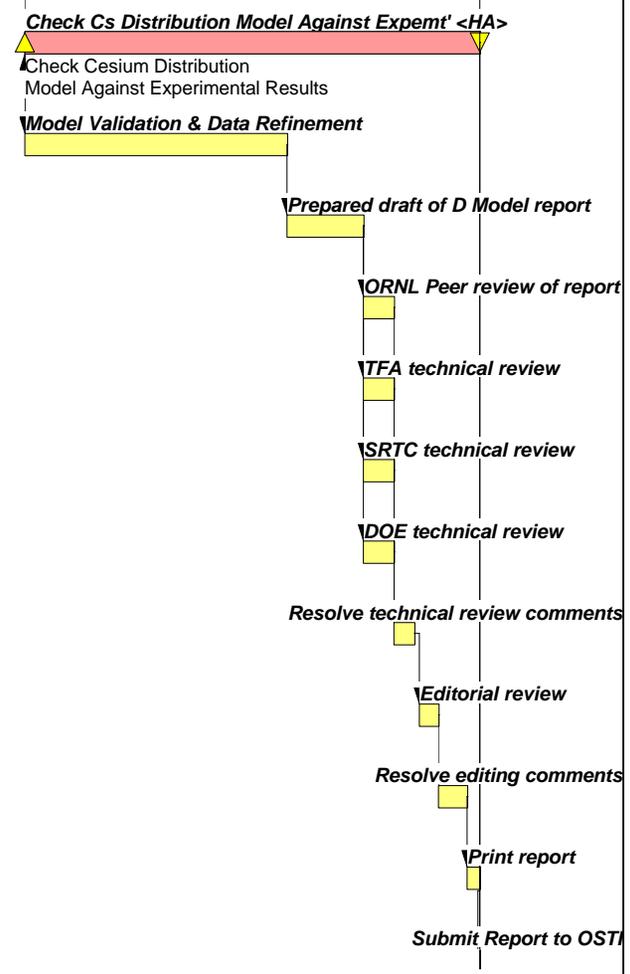
ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WACX414040	Resolve Technical Review Issues	10	29OCT01A	09NOV01	LNK	Resolve Technical Review Issues Convert to ORNL TM Format for Release																	
WACX414070	Issue Test Report - Contactor Thruput	0		09NOV01	REE	Issue Test Report - Contactor Thruput																	
WACX414080	Issue Test Report - Contactor Thruput/Efficiency	0		09NOV01	JTC	Issue Test Report - Contactor Thruput/Efficiency																	
Test Performance of 5 cm CINC Contactor																							
WAANL75001	Test Performance of 5cm CINC Contactor <HA>	15*	01OCT01A	16NOV01	RL	Test Performance of 5cm CINC Contactor <HA>																	
WAANL7513	DOE Review 5cm CINC Contactor and D Value	5	29OCT01A	02NOV01	RL	DOE Review 5cm CINC Contactor and D Value																	
WAANL7514	Team Review Draft 5cm CINC Contactor and D Value	5	29OCT01A	02NOV01	RL	Team Review Draft 5cm CINC Contactor and D Value																	
WAANL7515	Incorporate Comments - 5cm CINC Contactor and D	5	05NOV01	09NOV01	RL	Incorporate Comments - 5cm CINC Contactor and D																	
WAANL7516	Approve 5cm CINC Contactor and D Value	5	12NOV01	16NOV01	RL	Approve 5cm CINC Contactor and D Value																	
WAANL7517	Issue 5cm CINC Contactor and D Value Report	0		16NOV01	RL	Issue 5cm CINC Contactor and D Value Report																	
Establish Settling Rate Parameters																							
WAANL75000	Establish Settling Rate Parameters <HA>	8*	01OCT01A	07NOV01	RL	Establish Settling Rate Parameters <HA> Establish Settling Rate Parameters Required for Sizing Decanting Tank for Solvent Recovery																	
WAANL7530	Incorporate Comments - Decanter Report	5*	29OCT01A	02NOV01	RL	Incorporate Comments - Decanter Report																	
WAANL7535	Approve Decanter Report	3	05NOV01	07NOV01	RL	Approve Decanter Report																	
WAANL7540	Issue Decanter Report	0		07NOV01	RL	Issue Decanter Report																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WAANL7526	Path Forward for Aqueous Strip	0		28OCT01*	RL	Path Forward for Aqueous Strip Yes - Proceed with Activities WAANL7545 - 7575 No - Eliminate Activities WAANL7545 - 7575																	
WAANL7545	Demonstrate Solvent Recovery from Aqueous Strip	40	29OCT01	26DEC01	RL	Demonstrate Solvent Recovery from Aqueous Strip Delete per ANL																	
WAANL7550	Prepare Solvent Recovery Report	10	27DEC01	10JAN02	RL	Prepare Solvent Recovery Report Delete per ANL																	
WAANL7555	DOE Review Draft Solvent Recovery Report	5	11JAN02	17JAN02	RL	DOE Review Draft Solvent Recovery Report Delete per ANL																	
WAANL7560	Team Review Draft Solvent Recovery Report	5	11JAN02	17JAN02	RL	Team Review Draft Solvent Recovery Report Delete per ANL																	
WAANL7565	Incorporate Comments - Solvent Recovery Report	5	18JAN02	24JAN02	RL	Incorporate Comments - Solvent Recovery Report Delete per ANL																	
WAANL7570	Approve Solvent Recovery Report	3	25JAN02	29JAN02	RL	Approve Solvent Recovery Report Delete per ANL																	
WAANL7575	Issue Solvent Recovery Report	0		29JAN02	RL	Issue Solvent Recovery Report Delete per ANL																	
CSSX Real Waste Contactor Testing																							
WACX24500	Organic Analysis from FY01 Actual Waste Test<HA>	18*	12JUL01A	21NOV01	DDW	Organic Analysis from FY01 Actual Waste Test<HA> Organic Analysis from FY 01 Actual Waste Flowsheet Test																	
WACX2451	Revise Draft Report	3*	12JUL01A	31OCT01	DDW	Revise Draft Report																	
WACX2455	Team Comment Interim Draft Report	5	01NOV01	07NOV01	JTC	Team Comment Interim Draft Report																	
WACX2457	DOE Comment Interim Draft Report	5	01NOV01	07NOV01	JWM	DOE Comment Interim Draft Report																	
WACX2459	Resolve Comments - Contactor Test Report	5	08NOV01	14NOV01	DDW	Resolve Comments - Contactor Test Report																	
WACX2461	Approve Revised Final Report - Contactor Test	5	15NOV01	21NOV01	JPM	Approve Revised Final Report - Contactor Test																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
WACX2463	Issue Approved Final Report - Contactor Test	0		21NOV01	JPM	Issue Approved Final Report - Contactor Test															
CSSX Actual Waste Test with Dissolved Salt Cake																					
WACX250180	Draft Report - Real Waste Test w/Dissolute Salt	9*	16OCT01A	08NOV01	DDW	Draft Report - Real Waste Test w/Dissolute Salt															
WACX250190	Team Comment Draft Report - Real Waste Test	5	09NOV01	15NOV01	JTC	Team Comment Draft Report - Real Waste Test															
WACX250200	DOE Comment Draft Report - Real Waste Test	5	09NOV01	15NOV01	JWM	DOE Comment Draft Report - Real Waste Test															
WACX250210	Resolve Comments - Real Waste Test w/Dissolute	5	16NOV01	26NOV01	DDW	Resolve Comments - Real Waste Test w/Dissolute															
WACX250220	Approve Final Report	5	27NOV01	03DEC01	JPM	Approve Final Report															
WACX250230	Issue Approved Final Report	0		03DEC01	DDW	Issue Approved Final Report															
WACX25179	Actual Waste Batch Test with Dissolved Salt <HA>	24*	16OCT01A	03DEC01	DDW	Actual Waste Batch Test with Dissolved Salt <HA>															
CSSX - Criticality Issues																					
WACX26000	CSSX Criticality Issues <HA>	56*	09NOV01	31JAN02	WRW	CSSX Criticality Issues <HA>															
WACX260171	CSSX Criticality Study - DOE Approve AOP Change	0	09NOV01*		WRW	CSSX Criticality Study - DOE Approve AOP Change															
WACX260172	Complete Analyses - CSSX Criticality Study	4	12NOV01	15NOV01	WRW	Complete Analyses - CSSX Criticality Study															
WACX260180	Pathforward- Perform ESS Protocol for Limiting C	0	19NOV01		JTC	Pathforward- Perform ESS Protocol for Limiting C															
WACX260190	Perform ESS Testing- CSSX Criticality Study	17	19NOV01	19DEC01	WRW	Perform ESS Testing- CSSX Criticality Study															
WACX260200	Perform Analyses - CSSX Criticality Study	5	20DEC01	02JAN02	WRW	Perform Analyses - CSSX Criticality Study															

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WAORNB232	Procure Extractant	84*	23OCT01A	20JAN02	LNK	Procure Extractant  Ninety Day Delivery Time Quoted by Vendor																	
WAORNB234	Procure Modifier (3.5 Kg)	50	01NOV01*	15JAN02	LNK	Procure Modifier (3.5 Kg)  Need, Start, Stop dates, from Moyer, Bonnessen -																	
Chemical/Physical Exp on the Modified Solvt Comp																							
WAORNB240	Chemical Physical Experiments <HA>	210*	20NOV01	20SEP02	LNK	Chemical Physical Experiments <HA>  Chemical Physical Property Experiments on the Modified Solvent Composition																	
WAORNB250	Conduct Experimental Studies	147	20NOV01	21JUN02	LNK	Conduct Experimental Studies  Further Detail to be provided by LNK Start Restrained by approval of interim																	
WAORNB270	Prepared draft of Chem/Phys report	21	24JUN02	23JUL02	LNK	Prepared draft of Chem/Phys report 																	
WAORNB280	ORNL Technical review of report	10	24JUL02	06AUG02	LNK	ORNL Technical review of report 																	
WAORNB290	TFA technical review	10	24JUL02	06AUG02	HDH	TFA technical review 																	
WAORNB300	SRTC technical review	10	24JUL02	06AUG02	SDF	SRTC technical review 																	
WAORNB310	DOE technical review	10	24JUL02	06AUG02	JWM	DOE technical review 																	
WAORNB320	Resolve technical review comments	10	07AUG02	20AUG02	LNK	Resolve technical review comments 																	
WAORNB330	Editorial review	6	21AUG02	28AUG02	LNK	Editorial review 																	
WAORNB340	Resolve editing comments	10	29AUG02	12SEP02	LNK	Resolve editing comments 																	
WAORNB350	Print report	6	13SEP02	20SEP02	LNK	Print report 																	
WAORNB360	Submit Report to OSTI	0		20SEP02	LNK	Submit Report to OSTI 																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
Check Cs D Model Against Experimental Results																							
WAORN370	Check Cs Distribution Model Against Expt' <HA>	148*	23MAY02	23DEC02	LNK																		
WAORNB380	Model Validation & Data Refinement	85	23MAY02*	23SEP02	LNK																		
WAORNB400	Prepared draft of D Model report	26	24SEP02	29OCT02	LNK																		
WAORNB410	ORNL Peer review of report	10	30OCT02	12NOV02	LNK																		
WAORNB420	TFA technical review	10	30OCT02	12NOV02	HDH																		
WAORNB430	SRTC technical review	10	30OCT02	12NOV02	SDF																		
WAORNB440	DOE technical review	10	30OCT02	12NOV02	JWM																		
WAORNB450	Resolve technical review comments	8	13NOV02	22NOV02	LNK																		
WAORNB460	Editorial review	5	25NOV02	03DEC02	LNK																		
WAORNB470	Resolve editing comments	10	04DEC02	17DEC02	LNK																		
WAORNB480	Print report	4	18DEC02	23DEC02	LNK																		
WAORNB490	Submit Report to OSTI	0		23DEC02	LNK																		
Effect of NaOH Concentration Emulsion Formation																							
WAORNB500	Effect of NaOH Concentration on Emulsion For	121*	23OCT01A	23APR02	LNK																		



ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WAORNB510	Laboratory Studies	57*	23OCT01A	21JAN02	LNK	Laboratory Studies																	
WAORNB520	Contactor Studies	28	11DEC01*	21JAN02	LNK	Contactor Studies																	
WAORNB540	Prepared draft of emulsion studies report	26	22JAN02	27FEB02	LNK	Prepared draft of emulsion studies report																	
WAORNB550	ORNL technical review of report	10	28FEB02	13MAR02	LNK	ORNL technical review of report																	
WAORNB560	TFA Technical review	10	28FEB02	13MAR02	HDH	TFA Technical review																	
WAORNB570	SRTC technical review	10	28FEB02	13MAR02	SDF	SRTC technical review																	
WAORNB580	DOE technical review	10	28FEB02	13MAR02	JWM	DOE technical review																	
WAORNB590	Resolve technical review comments	8	14MAR02	25MAR02	LNK	Resolve technical review comments																	
WAORNB600	Editorial review	5	26MAR02	02APR02	LNK	Editorial review																	
WAORNB610	Resolve editing comments	10	03APR02	16APR02	LNK	Resolve editing comments																	
WAORNB620	Print report	5	17APR02	23APR02	LNK	Print report																	
WAORNB630	Submit Report to OSTI	0		23APR02	LNK	Submit Report to OSTI																	
Expand ORNL's Cs D Value Model																							
WAORNB640	Expand Cs D Model	167*	20NOV01	22JUL02	LNK	Expand Cs D Model																	
						Expand ORNL's D Value Model to Incorporate Optimized Solvent and Waste Compositions																	
WAORNB650	Measurement of D Values	90	20NOV01	02APR02	LNK	Measurement of D Values																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03					
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	
WAORNB810	Revise to meet ORNL/TM format	26*	29OCT01A	05DEC01	LNK	Revise to meet ORNL/TM format																	
WAORNB820	Editorial review	15	06DEC01	27DEC01	LNK	Editorial review																	
WAORNB830	Resolve editing comments	10	28DEC01	11JAN02	LNK	Resolve editing comments																	
WAORNB840	Print report	8	14JAN02	23JAN02	LNK	Print report																	
WAORNB850	Submit Report to OSTI	0		23JAN02	LNK	Submit Report to OSTI																	
Convert D Model Report																							
WAORNB860	Convert D Model Report <HA>	59*	29OCT01A	23JAN02	LNK	Convert D Model Report <HA>																	
WAORNB870	Revise to meet ORNL/TM format	40*	29OCT01A	26DEC01	LNK	Revise to meet ORNL/TM format																	
WAORNB880	Editorial review	7	27DEC01	07JAN02	LNK	Editorial review																	
WAORNB890	Resolve editing comments	6	08JAN02	15JAN02	LNK	Resolve editing comments																	
WAORNB900	Print report	6	16JAN02	23JAN02	LNK	Print report																	
WAORNB910	Submit Report to OSTI	0		23JAN02	LNK	Submit Report to OSTI																	
Prepare Report-MultiTest of CSSX Flowsheet																							
WAANL7410	Convert Multi-Day CSSX Test Report /OSTI Format	19*	30MAR01A	26NOV01	RL	Convert Multi-Day CSSX Test Report /OSTI Format																	
WAANL7412	Perform Internal Review	5	27NOV01	03DEC01	MCR	Perform Internal Review																	

ACT ID	Description	ToGo Days	Early Start	Early Finish	Lead	FY02												FY03			
						OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN
Bench Scale Test - CSTR Testing (20 L)																					
WAORN3248	CSTR D&D - Chemical Clean Equipment	3	29OCT01*	31OCT01	JW	CSTR D&D - Chemical Clean Equipment On HOLD															
WAORN3249	CSTR D&D - Disassemble Equipment	30	01NOV01	14DEC01	JW	CSTR D&D - Disassemble Equipment															
WAORN3250	Remove Equipment from Cell & Package For Disposal	20	17DEC01	15JAN02	JW	Remove Equipment from Cell & Package For Disposal															
WAORN3251	CSTR D&D - Cell Wipe Down	10	16JAN02	29JAN02	JW	CSTR D&D - Cell Wipe Down															
WAORN3252	CSTR D&D - Transport Package to Disposal Area	5	16JAN02	22JAN02	JW	CSTR D&D - Transport Package to Disposal Area															
TPB Real Waste Test																					
WATPB3620	Dispose of Waste Samples	64*	23APR01A	31DEC01	TBP	Dispose of Waste Samples 18 Weeks Required for Disposal of Organic Wastes															
Research & Development Planning																					
FY 02 Plan for OnGoing Work Performance																					
WAPLAN015	FY 02 Plan for On-Going Work & Performers <HA>	3*	16AUG01A	31OCT01	HDH	FY 02 Plan for On-Going Work & Performers <HA> FY 02 Plan for On Going Work & Performers															
WAPLAN022	Revise, Review, & Approve Detail Planning	3*	17SEP01A	31OCT01	HDH	Revise, Review, & Approve Detail Planning Includes IWO Planning as well															
FY 02 Plan - New Work Scope																					
WAPLAN024	FY 02 Plan New Work Scope <HA>	29*	20AUG01A	10DEC01	HDH	FY 02 Plan New Work Scope <HA>															
WAPLAN027	Review & Evaluate Proposals	3*	10OCT01A	31OCT01	HDH	Review & Evaluate Proposals															
WAPLAN028	Review & Approve Funded Proposals	5	01NOV01	07NOV01	JWM	Review & Approve Funded Proposals															
WAPLAN029	Performers Selected, Funded Transfer Doc Prepare	1	08NOV01	08NOV01	HDH	Performers Selected, Funded Transfer Doc Prepare															
WAPLAN030	New Performers Develop Detail Plan	10	09NOV01	26NOV01	ALL	New Performers Develop Detail Plan															

