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Tanks Focus Area

Savannah River Site
Salt Processing Project
Research and Development
Program Plan

Revision 1

November 2000

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

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Executive Summary

The Department of Energy's (DOE) Savannah River Site (SRS) high-level waste (HLW) program is responsible for storage, treatment, and immobilization of HLW for disposal. The Salt Processing Project (SPP) is the salt (soluble) waste treatment portion of the SRS HLW 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.

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

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

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

In 1999, DOE-Headquarters asked the National Academy of Sciences (NAS) to independently review the Department's evaluation of technologies to replace ITP. As a result of the NAS review, DOE agreed that further research and development on each alternative was required to reduce technical uncertainty prior to a down-selection. In March 2000, DOE-Headquarters requested the Tanks Focus Area (TFA) to assume management responsibility for the SPP

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

This Research and Development Program Plan describes the technology development needs, continued effort for each process that must be satisfied to reach a down-selection decision, as well as continuing technology development required to support conceptual design activities for the SPP. Previous results are summarized, and planned Fiscal Year (FY) 2001 work is described and presented.

The SPP Research and Development Program is funded jointly by the DOE Offices of Science and Technology (EM-50) and Project Completion (EM-40). Participants in the program include WSRC's Savannah River Technology Center, Oak Ridge National Laboratory, Argonne National Laboratory, Sandia National Laboratories, Pacific Northwest National Laboratory, and various universities and commercial vendors. Combined program funding for FY00 was $13.1 million and total planned funding for FY01 is $13.4 million.

A detailed integrated schedule of all research and development tasks has been prepared and is being used by all program participants to manage and to report status on their activities. The program is focused on resolving high-risk areas for each alternative cesium-removal process by mid-FY01 to support a DOE down-selection decision by June 2000.

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Acronyms and Abbreviations

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

MTZ	Mass Transfer Zone
NAS	National Academy of Sciences
NMR	nuclear magnetic resonance
PEG	Program Execution Guidance
PHA	precipitate hydrolysis aqueous
PCCS	Product Composition Control System
QA	quality assurance
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
SOWM	Scope of Work Matrix
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)
TCLP	toxicity characteristics leach procedures
TCR	Technical Change Request
TEM	transmission electron microscopy
TFA	Tanks Focus Area
TGA	thermogravimetric analysis
TPB	tetraphenylborate
TTP	Technical Task Plan
TRU	transuranic
TWG	Technical Working Group

WSRC	Westinghouse Savannah River Company
ZAM	Zheng-Anthony-Miller (CST equilibrium model)

1.0 Introduction

The Department of Energy’s (DOE) Savannah River Site (SRS) high-level waste (HLW) program is responsible for storage, treatment, and immobilization of HLW for disposal. The Salt Processing Project (SPP) is the salt (soluble) waste treatment portion of the SRS HLW cleanup effort. The overall SPP encompasses the selection, design, construction and operation of treatment technologies to prepare the salt waste feed material for treatment at the site’s Saltstone 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 March 2000, DOE-Headquarters (HQ) requested the Tanks Focus Area (TFA) to assume management responsibility for the SPP technology development program at SRS. The TFA was requested to conduct several activities, including review and revision of the technology development roadmaps, development of down-selection criteria, and preparation of a comprehensive research and development (R&D) Program Plan for three candidate Cs removal technologies, as well as the alpha and Sr removal technologies that are part of the overall SPP. The three Cs removal candidate technologies are Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange, Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP).

This plan describes the technology development needs for each process that must be satisfied to reach a down-selection decision, as well as a subset of continuing technology development to support conceptual design activities. Previous results are summarized, recent FY00 results are described, and plans for FY01 work are provided in Section 7.0. Funding requirements and project schedules for the R&D workscope are presented in Section 8.0. TFA’s roadmap reviews and other identified initiatives outside the original baseline are incorporated in the roadmaps and logic diagrams shown in Appendix A of this plan.

2.0 Background

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

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

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

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

In January 1998, conclusions from the test program showed that benzene release rates associated with ITP facility operation could exceed the capability of the current ITP hardware and systems to assure safe operations at the production rate needed to support the STP and FAA. On January 22, 1998, WSRC informed the DOE that the chemistry testing demonstrated that the existing system configuration could not cost-effectively meet the safety and production requirements for the ITP facility. WSRC recommended that a Systems Engineering Team conduct a study of alternatives to the current system configuration.

On February 6, 1998, the DOE Assistant Secretary for Environmental Management (EM) approved a DOE-Savannah River (DOE-SR) plan-of-action to suspend startup-related activities and undertake a systems engineering study of alternatives to ITP. On February 20, 1998, DOE-SR concurred with the WSRC evaluation of the ITP chemistry data, instructed WSRC to suspend ITP startup preparations, and directed WSRC to perform an evaluation of alternatives to the current system configuration for HLW salt removal, treatment, and disposal.

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

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

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

In 1999, DOE-HQ asked the National Academy of Sciences (NAS) to independently review the evaluation of technologies to replace ITP. NAS issued a letter report in October 1999 and their final report was issued in August 2000. As a result of the interim NAS review, the DOE Under Secretary and the Assistant Secretary for EM jointly agreed that further research and development on each alternative was required to reduce technical uncertainty prior to a down-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 March 2000, DOE-HQ requested the TFA 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.

3.0 High-Level Waste System Overview

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

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

These processes currently include:

- HLW Storage and Evaporation (F and H Area Tank Farms)
- Salt Processing (ITP and Late Wash Facilities)
- Sludge Processing (Extended Sludge Processing [ESP] Facility)
- Vitrification (DWPF)
- Wastewater Treatment (Effluent Treatment Facility[ETF])
- Solidification 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 operating at the present.

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

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

Also, the storage tanks and facilities used to process the HLW must be left in a state such that they can be 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 STP, 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

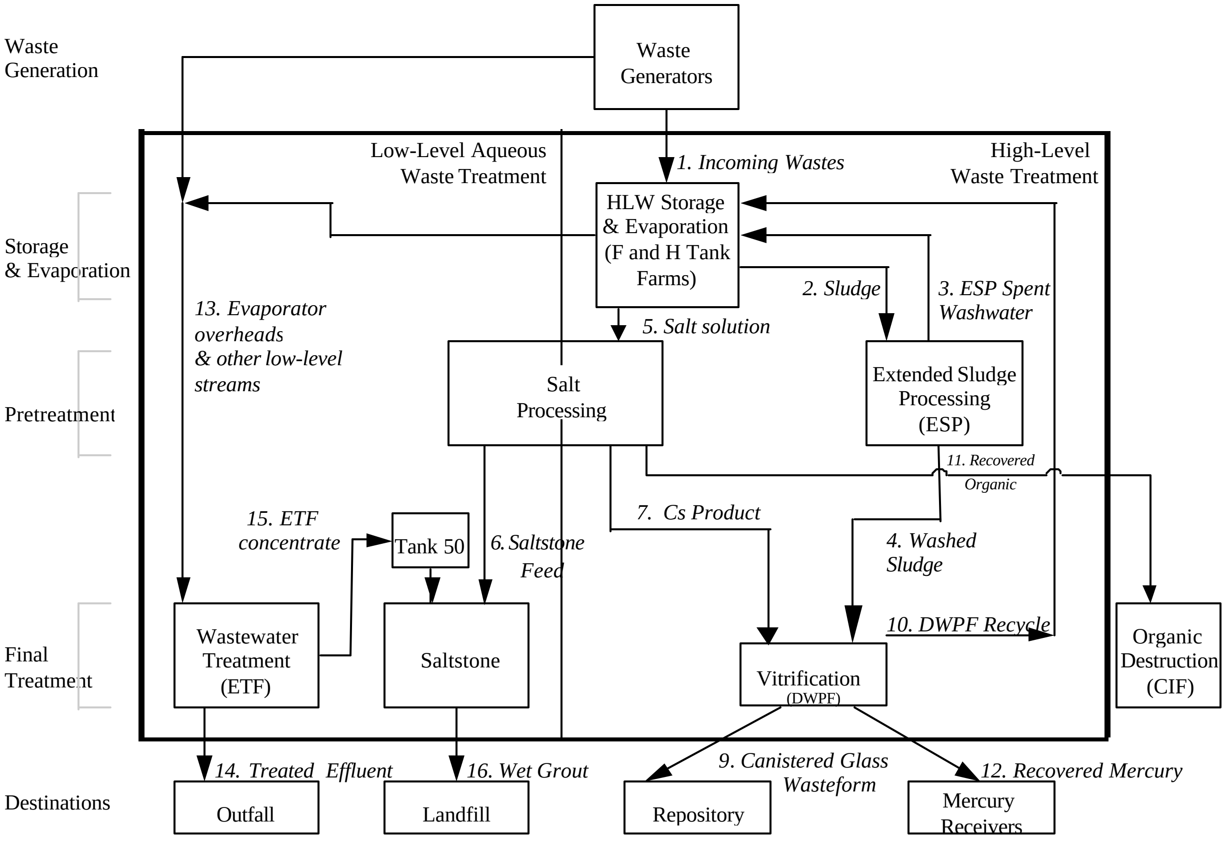


Figure 3.1 schematically illustrates the routine flow of wastes through the SRS HLW System. The various internal and external processes are shown in rectangles. The numbered streams identified in italics are the interface streams between the various processes. The discussion below describes the SRS HLW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

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

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

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

For the STTP process, the precipitate is catalytically decomposed and separated into two streams: a mildly contaminated organic stream and an aqueous stream containing virtually all of the radionuclides. The mildly contaminated organics are stored and eventually transferred to CIF (Stream 11). The aqueous stream is transferred to DWPF where it is combined with the washed sludge from ESP - which has undergone further processing - and the mixture vitrified.

The washed sludge from ESP (Stream 4) is chemically adjusted in the DWPF to prepare the sludge for feed to the glass melter. As part of this process, mercury (Hg) is removed, purified, and sent to Hg receivers (Stream 12). The aqueous Cs product or CST sorbent slurry 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 is sent to on-site interim storage, and will eventually be disposed in a federal repository (Stream 9).

The water vapor driven off the melter is condensed and combined with other aqueous streams generated throughout the DWPF. The combined aqueous stream is recycled to HLW Storage and Evaporation for processing (Stream 10).

Overheads from the HLW Storage and Evaporation evaporators are combined with overheads from evaporators in the F and H Area separations processes and other low-level streams from various waste generators. This mixture of LLW is sent to the ETF (Stream 13).

In the ETF, LLW is decontaminated by a series of cleaning processes. The decontaminated water effluent is sent to the H Area outfall and eventually flows to local creeks and the Savannah River (Stream 14). The contaminants removed from the water are concentrated and sent to Tank 50 (Stream 15), for storage prior to transfer to the SPF (Stream 6). In the SPF, the liquid waste is combined with cement formers and pumped as a wet grout to a vault located in the SDF (Stream 16). 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 Process

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

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

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

Table 4.1 Key Functional Criteria

FOCUS AREA	FUNCTIONS
Safety	
Hazard Assessment (HAD)	Provide a facility that meets the requirements of a non-reactor nuclear hazard category 2 and low chemical hazard category.
Interface Streams	
DWPF Recycle	Support tank farm space management and DWPF recycle evaporator strategy.
DWPF Glass	Provide a Cs-containing product that supports glass waste form requirements relative to durability, crystallization temperature, Na content, and viscosity.
SPF Feed	Provide a Decontaminated Salt Solution (DSS) product that meets Waste Acceptance Criteria relative to producing a non-hazardous saltstone waste form suitable for disposal as low-level solid waste at the SRS.
Tank 49H	Support Tank Farm space management strategy to recover Tank 49H for HLW storage.
Tank 50H	Support Tank Farm space management strategy to recover Tank 50H for HLW storage.
New Waste Form	Comply with DOE-RW HLW repository requirements.
Nominal DF	
Sr DF	Provide a Sr DSS concentration of $\leq$ 40 nCi/g, which equals a nominal DF = 5 (overall average).
TRU DF	Provide a TRU DSS concentration of $\leq$ 18 nCi/g, which equals a nominal DF = 12 (overall average).
Cs DF	Provide a Cs DSS concentration that enables conversion to a solid low-level waste form suitable for near-surface disposal at the SRS. • For processes that remove Cs, Cs-137 $\leq$ 45 nCi/g is required to enable processing in the existing Saltstone Production Facility and disposal in the existing Saltstone Disposal Facility, which equals a nominal DF = 8000 (overall average). • For processes that do not remove Cs, Cs-137 must be within NRC Class C limits.
Schedule	
HLW Storage	Support Tank Farm space management strategy to support site missions (timely startup of new process by 2010).
FFA	Support readiness for closure of all waste tanks by 2028.
STP	Support readiness for closure of old style tanks by 2020, and an average glass canister production rate of 200 canisters/yr.

5.0 Description Of Radionuclide Removal Processes

5.1 Alpha and Sr Removal

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

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

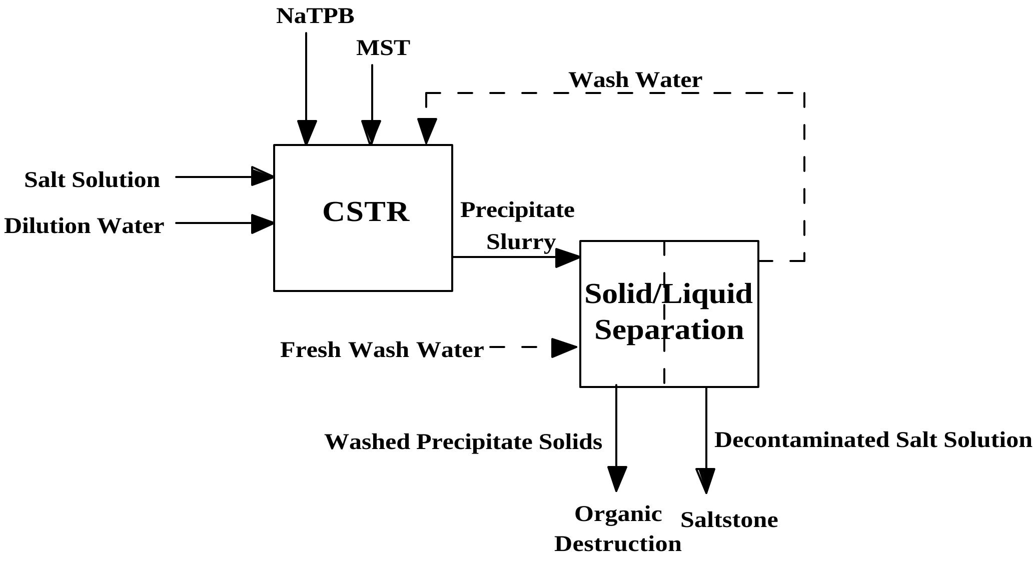
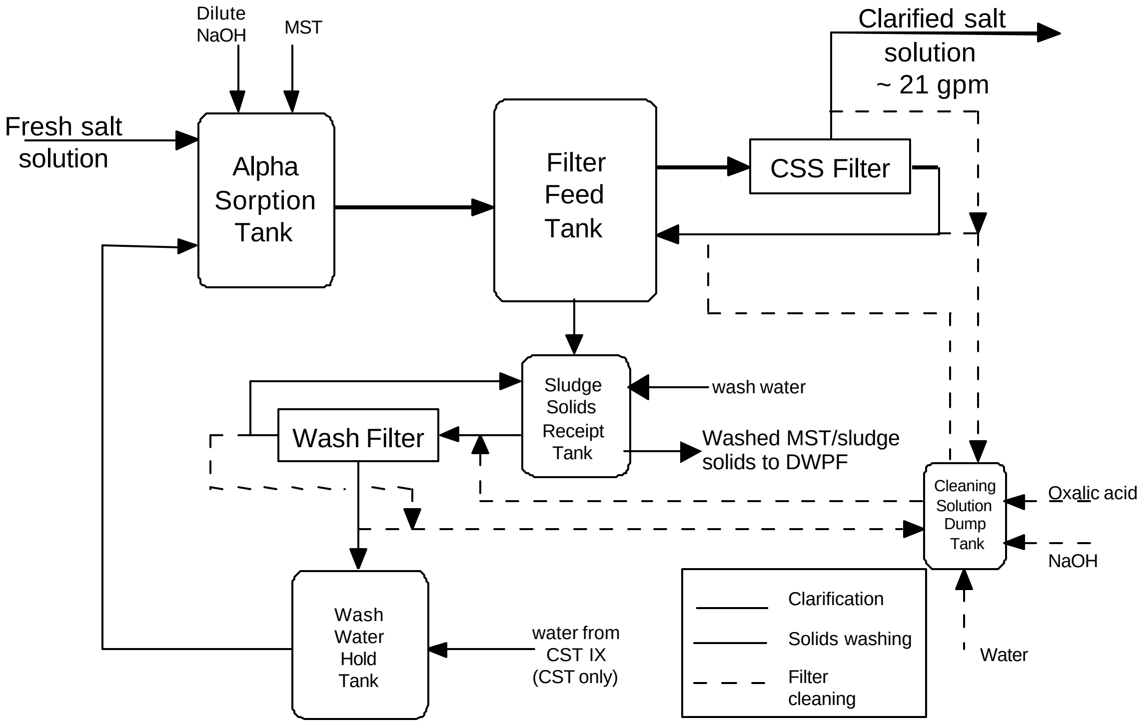


Figure 5.2 Alpha and Sr Removal Flow Diagram for CST Non-Elutable Ion Exchange and Caustic Side Solvent Extraction

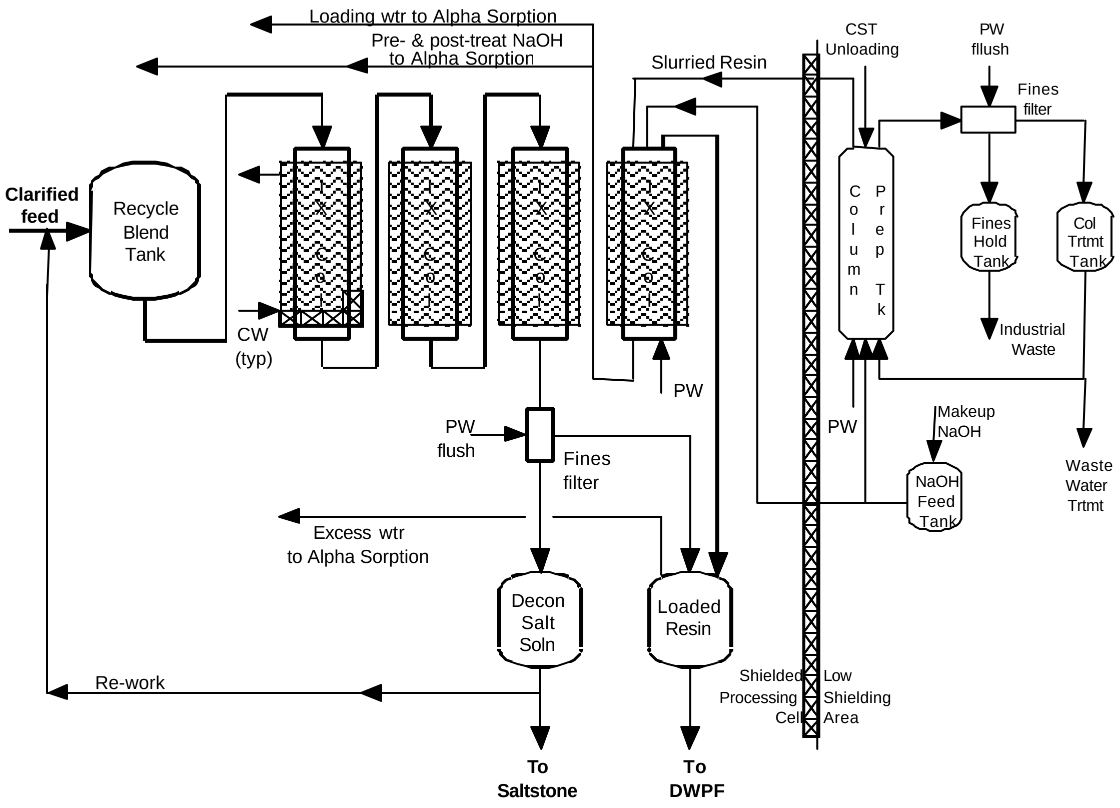


5.2 Cs Removal by CST Non-Elutable Ion Exchange

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

Figure 5.3 CST Non-Elutable Ion Exchange Flow Diagram



Two key aspects of the CST process are the 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 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 Resin 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 Alpha Sorption Tank. The CST slurry is stored in the Loaded Resin Hold Tank until it can be transferred to the DWPF for incorporation into HLW waste glass.

Before being loaded into a column, the CST resin must undergo two treatments. First, the CST is loaded into the Column Preparation Tank, similar in dimensions to an ion exchange column bed. The CST is then backflushed with water to remove the fines. These fines are removed by a filter for disposal as industrial waste. The second treatment involves a 24-hour caustic soak. The as-received CST is in the hydrogen form. The resin is converted to the Na form by circulating a sodium hydroxide (NaOH) solution through the Column Preparation Tank for 24 hours. The material is then loaded into an empty standby column by sluicing with water.

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

5.3 Cs Removal by Caustic Side Solvent Extraction

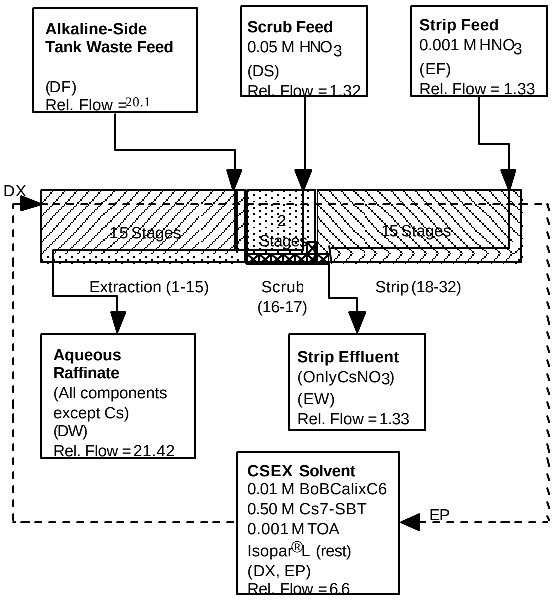
The basic principle of solvent extraction is to use a sparingly soluble diluent material that carries an extractant that will complex with the Cs ions in the caustic solution. The decontaminated aqueous stream (raffinate) is then sent to the SPF for disposal. The Cs contained in the organic phase (solvent)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

Prior to treatment by solvent extraction, actinides and Sr are removed from the waste by sorption with MST. 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 Cs7SB, trioctylamine known as TOA, and Isopar® L, as a diluent. The solvent is contacted with the alkaline waste stream in a series of countercurrent centrifugal contactors (the extraction stages). The resulting clean aqueous raffinate is transferred to the SPF for conversion to saltstone. Following Cs extraction, the solvent is scrubbed with dilute acid to remove other soluble salts from the solvent stream (the scrub stages). The scrubbed solvent then passes into the strip stages where it is contacted with a very dilute (0.001 M) acid stream to transfer the Cs to the aqueous phase. The aqueous strip effluent is transferred to the DWPF. Figure 5.4 contains a schematic representation of the proposed solvent extraction flowsheet.

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

Figure 5.4 Caustic Side Solvent Extraction Flow Diagram



In the proposed process, the Cs concentration in the organic phase is 3.5 times that in the aqueous feed solution. For a typical HLW feed solution containing 0.14 millimolar (mM) Cs, the concentration in the organic stream leaving the extraction stages is approximately 0.5 mM. Note that this is significantly below the 10 mM concentration of calixarene in the solvent. Thus, a large excess of available calixarene sites are available for extraction. However, due to the high concentrations of Na and K in the feed stream, a measurable quantity of both Na and K are extracted, and thus take up a small portion of the sites. In addition, some Na and K ions are extracted directly by the modifier. Section 7.3 describes this technology in greater detail and identifies other issues (e.g., solvent preparation, solvent cleanup, and organic waste) that are involved in implementation of it.

To provide an essentially pure Cs nitrate product stream, the K and Na are scrubbed from the organic phase using two scrubbing stages between the extraction and strip stages. The scrub solution joins the aqueous phase in the extraction section of the contactor cascade. In addition to removing Na and K from the organic phase, the scrub stages also remove Al, Fe and Hg. The scrub stages also neutralize any caustic carryover from the extraction stages. The neutralization is essential to control precipitation and to allow stable operation of the stripping stages. Since the strip stages employ a weak acidic solution, introduction of caustic into the strip stages would likely result in significant pH shifts and thereby diminish process operability.

In the strip stages, the presence of lipophilic anionic impurities (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.[4]

Over long periods of time, either the modifier or the calixarene may degrade. The most likely degradation is that of the modifier to form a phenolic compound that is highly soluble in the organic phase in contact with acid solutions. However, the modifier was designed so that the phenolic compounds would distribute preferentially to alkaline aqueous solutions, either the waste itself or NaOH wash solutions. Gradual degradation of the solvent will result in some loss of performance, owing both to loss of the calixarene, modifier, and amine and to buildup of various degradation products. The proposed flowsheet contains two additional unit operations intended to maintain solvent performance.

The two proposed unit operations involve first an acidic wash of the solvent followed by a caustic wash of the solvent. These two wash stages are intended to remove any acidic or caustic impurities that may accumulate in the solvent system over time. In particular, the caustic wash is known to remove many of the modifier and diluent degradation products. In addition, the proposed flowsheet has assumed 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 will contain either soluble solvent components and/or entrained organic phase. This may represent an economic concern due to loss of the expensive solvent components or a problem in downstream operations. The proposed process contains two additional contactor stages designed to remove soluble organics and in particular to remove solvent from the exiting raffinate stream. A small amount of Isopar® L is introduced into these stages and used to separate the solvent from the aqueous phase. 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. From the settling tank, the raffinate is transferred to one of two hold tanks to allow decay of the short half-life gamma from Ba-137m in the raffinate stream. These two tanks are sized to allow sufficient hold time for gamma decay to facilitate determination of whether the target decontamination has been met to allow transfer of the raffinate material to the SPF. The wash solutions from the organic clean up process are also transferred to the SPF.

A similar solvent recovery process has been designed for the strip effluent. The proposed process contains two additional contactor stages designed to remove soluble organics from the exiting strip effluent. Again, a small amount of Isopar® L is introduced into the stages and used to extract any of the solvent from the aqueous phase. The aqueous phase leaves the cleanup stage and is transferred to a settling tank where the Isopar® L is allowed to float and is decanted. The Isopar® L added in the two solvent recovery processes is sent to the CIF.

Note that the feed stream is fed to the process from a 30,000 gallon tank. Decoupling of the actinide removal section of the flowsheet is provided by the 111,000 gallon filter feed tank. The aqueous strip effluent leaves the settling tank and is sent to a large storage tank (60-day capacity). The use of a large tank provides for some decoupling of the solvent extraction process and the DWPF. The solvent extraction process can only operate as long as DWPF is operating or storage volume remains in the tanks between the solvent extraction process and DWPF. Cold chemical feed tanks have generally sized to provide one day of process operation. These feed tanks are fed from larger feed makeup tanks that will provide a buffer in operations to allow for limited (less than a week) outages of process water and other input chemicals.

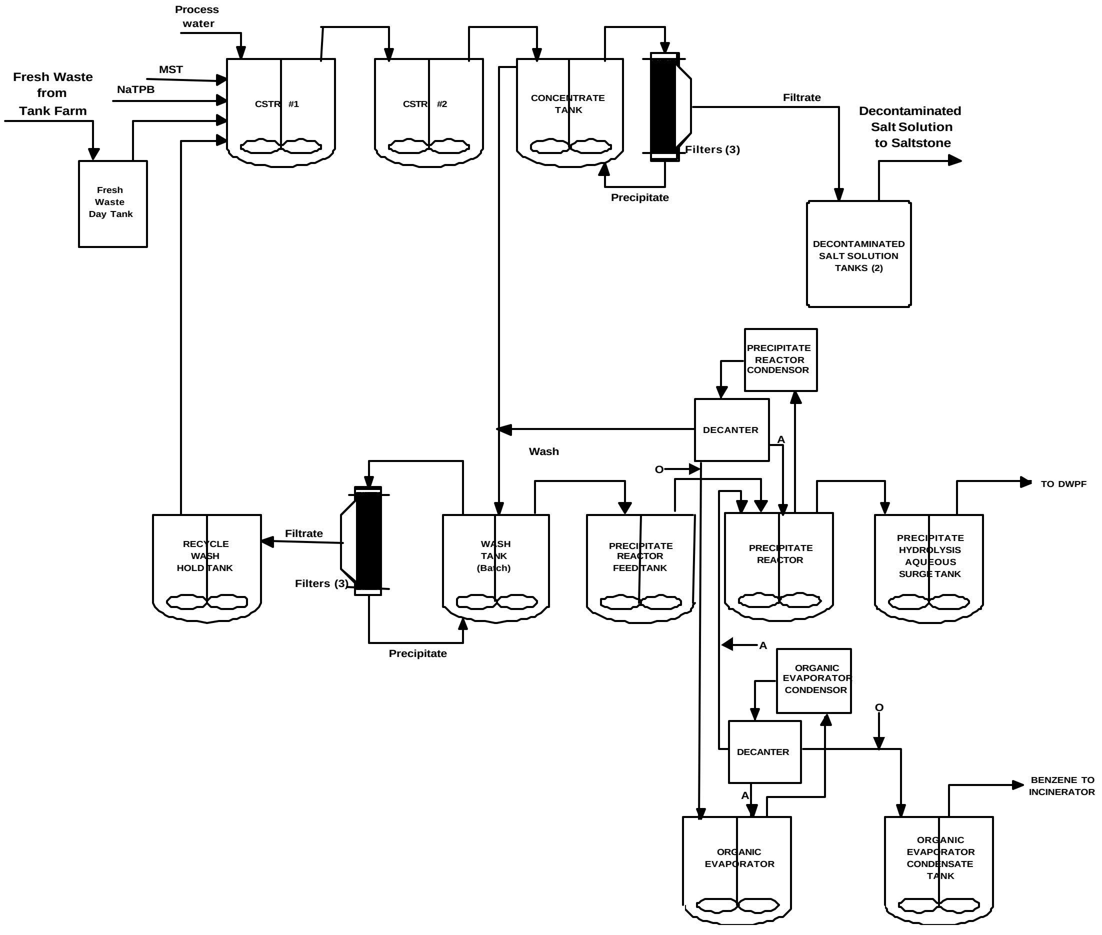
Strip effluent storage is provided to accommodate the differences in cycle times for the SRAT in DWPF and to allow for disengagement of any organic carry-over from the extraction process. Strip effluent will be provided at a rate of 1.5 gpm, thereby eliminating the need for an evaporator. The strip effluent transferred to DWPF is assumed to contain the diluent at the saturation limit (<1 mg/L). The strip effluent is evaporated in the DWPF SRAT where the nitric acid content is used to offset the nominal nitric acid requirement. The effluent would contain <0.01 M Na, and <0.001 M of other metals.

5.4 Cs Removal by Small Tank Tetraphenylborate Precipitation

In the STTP process (see Figure 5.5), salt solution is received into a Fresh Waste Day Tank located in the new facility. For this continuous precipitation process, salt solution, Na TPB solution, MST slurry, spent wash water and dilution water are continuously added to the first of two Continuous Stirred Tank Reactors (CSTR) located in the new facility. Sufficient dilution water is added to the first CSTR to reduce the Na molarity to

~4.7 M to optimize conditions for precipitation and MST sorption reactions. The first CSTR feeds a second CSTR in which precipitation is completed. In the CSTRs, soluble Cs and K are precipitated as TPB salts and Sr and actinides (U, Pu, Am, Np and Cm) are sorbed on the MST solids. The resulting slurry, containing ~1 wt% insoluble solids, is transferred from the second CSTR to the Concentrate Tank from which the slurry is continuously fed to a cross-flow filter to concentrate the solids, which contain most of the radioactive contaminants. DSS filtrate is transferred to a Filtrate Hold Tank from the filter unit and stored until it can be transferred to the existing SPF, where it is converted to saltstone for disposal in the SDF.

Figure 5.5 Small Tank Tetraphenylborate Precipitation Flow Diagram



After concentrating the slurry to 10 w%, and accumulating 4,000 to 5,000 gallons in the Concentrate Tank, the slurry is transferred to the Wash Tank and washed to remove soluble Na salts by adding process water and removing spent wash water by filtration.

Na TPB removed in the wash water can be recovered by recycling the spent wash water to the first CSTR. Spent wash water is either recycled to the first CSTR to provide a portion of the needed dilution water or sent to the Filtrate Hold Tank and on to 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 Storage Tank for staging. The slurry is then processed through the acid hydrolysis unit operation and eventually vitrified. Recovered by-product benzene from acid hydrolysis is transferred to the CIF and incinerated. The aqueous product from acid hydrolysis is combined with sludge feed in the DWPF and incorporated into HLW waste glass.

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

6.0 Technology Development Needs

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

Tests to resolve these issues are generally conducted first with simulated wastes, but final confirmation of key parameters and flowsheet demonstrations will be conducted with real waste samples. Three standard SRS waste simulants are normally used to bound SRS HLW compositions (see Table 6.1). These compositions, and preparation instructions, are provided to all participating laboratories as documented in D. D. Walker, "Preparation of Simulated Waste Solutions", WSRC-TR-99-00116, March 15, 1999. In certain experiments, other components (like lipophilic organic anions for solvent extraction tests) may be added or concentrations of individual components may be varied to examine specific effects.

Table 6.1 Composition of Simulated Waste Solutions

	Concentrations (molar)		
Component	**Average**	**High OH^-**	**High NO_3^-**
Na^+	5.6	5.6	5.6
K^+	0.015	0.030	0.0041
C_s^+	0.00014	0.00037	0.00014
OH^-	1.91	3.05	1.17
NO_3^-	2.14	1.10	2.84
NO_2^-	0.52	0.74	0.37
$Al0^{2-}$	0.31	0.27	0.32
CO_3^{2-}	0.16	0.17	0.16
SO_4^{2-}	0.15	0.30	0.22
Cl^-	0.025	0.010	0.040
F^-	0.032	0.010	0.050
PO_4^{3-}	0.010	0.008	0.010
$C_2O_4^{2-}$	0.008	0.008	0.008
SiO_3^{2-}	0.004	0.004	0.004
MoO_4^{2-}	0.0002	0.0002	0.0002

The key technology needs for each process are summarized below.

6.1 Alpha and Sr Removal

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

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

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

While MST adequately meets the functional requirements for each process design, the use of alternate sorbents or technologies to remove the radionuclides of interest (i.e., Sr, Pu, and Np) may significantly improve some of the designs. Therefore, a portion of this research effort evaluates the use of alternate chemical means to remove these radionuclides. Similarly, the program will also investigate means to improve cross-flow filtration performance by using chemical additives as well as alternate solid-liquid separation technologies with MST or the alternate chemicals defined to remove radionuclides.

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

- Alpha and Sr removal performance with MST and alternate sorbents,
- Size of equipment, and
- Solid-liquid separation performance.

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

6.2 CST Non-Elutable Ion Exchange

In the CST Non-Elutable Ion Exchange process, MST sorbs alpha contaminants and Sr-90 from the salt solution. The MST resulting slurry is then filtered and the filtrate solution is combined with other aqueous streams for processing through an ion exchange column loaded with CST to remove Cs. The most significant issue with CST is the stability of the CST in highly alkaline solutions. Leaching of excess materials used in manufacturing the resin and column pluggage events have been observed in previous testing. This has led to a desire to re-engineer the resin manufacturing process. In addition, the baseline design calls for a series of three ion-exchange columns each with a bed of CST 16 ft tall by 5 ft in diameter. Fully loaded CST is expected to generate gas through radiolysis of the waste solution passing over it. This gas could potentially block access of Cs-containing waste solution to the CST pores or coalesce into bubbles that interfere with fluid flow through the columns. Thus, the effect of gas generation on the performance of the CST downstream of the fully loaded portion becomes an issue. Also, loaded CST must be transferred as a slurry to DWPF and the sludge, CST, and glass frit mixture must be homogeneously mixed and accurately sampled prior to feeding the melter. Both of these operations have proven difficult in initial tests. Thus, the three high-risk areas for implementation of the CST process are:

- Resin stability
- Gas generation, and
- Resin handling and sampling.

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

6.3 Caustic Side Solvent Extraction

Solvent extraction is a proven technology in the nuclear industry as shown by the world-wide use of the PUREX process. Equipment, such as pulse columns, mixer settlers, and centrifugal contactors, has a long history of successful operation in the remote environments required to process radioactive materials. The technology development needs for CSSX are derived primarily from the immaturity of the solvent. The CSSX solvent is a multi-component solvent that is complex, and poses risks from a chemical stability standpoint that, unmitigated, could destabilize the process and/or impact operations personnel. The performance of CSSX may also be affected by the impacts on the solvent by radionuclides in the treatment stream. Extraction rates for solvent mixtures have been studied previously and the rates have been found to be more than adequate for application to salt processing. However, bench-scale extraction studies must be run to determine if the dual performance goals of raffinate stream decontamination and Cs product concentration (DF of 40,000 and a minimum CF of 12) can be simultaneously achieved, particularly with real waste. Thus, the CSSX technology development needs are driven by five high risk areas of technical uncertainty:

- Chemical and thermal stability,
- Radiolytic stability,
- Resistance to impurity effects,
- Flowsheet solvent system proof-of-concept, and
- Real waste performance.

Technology development needs are also driven by the need to demonstrate the commercial availability of the CSSX solvent components. This will require that issues with synthesis improvements and patent applications for the BOBCalixC6 and modifier be resolved.

6.4 Small Tank TPB Precipitation

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

- Catalytic product decomposition, and
- Foaming.

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

6.5 Other Technology Development Needs

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

7.0 R&D Program Description

7.1 Alpha And Sr Removal

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

7.1.1 R&D Roadmap Summary – Alpha and Sr Removal

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

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

- Monosodium titanate sorption kinetics, and
- Engineering filtration studies.

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

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

Figure 7.1 Science and Technology Roadmap for Alpha and Sr Removal Process

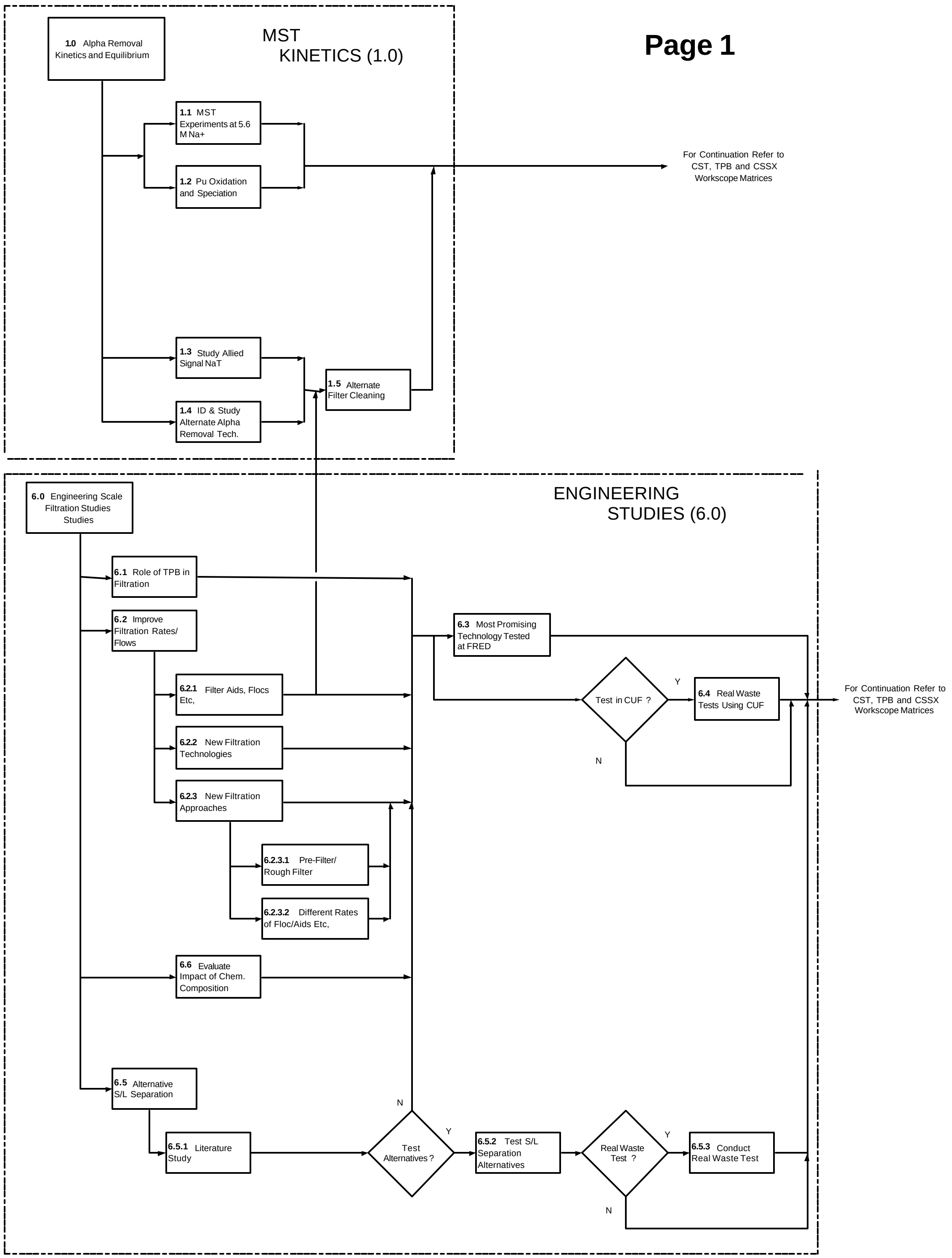


Figure 7.1 depicts the technology roadmap for the Sr and actinide removal portions of the program. The diagram shows each work element defined for the current and future work scope. Integrated pilot-scale operations will occur during final design to confirm operation under upset conditions. This will establish the limits of operation and recovery, define the limits of feed composition variability, and confirm design assumptions. This testing also directly supports development of operating procedures, simulator development, and operator training.

Appendix A contains detailed logic diagrams that illustrate the various R&D activities, their interactions, and decision points.

7.1.2 Monosodium Titanate (MST) Kinetics and Equilibrium (Alpha SOWM 1.1, 1.2)*

7.1.2.1 Previous Results

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

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

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

Results proved the addition of 0.4 g/L of MST sufficient to decontaminate the salt solution relative to Sr, Np and Pu at the concentrations tested. Note that the process does not require decontamination of the solution with respect to uranium because of its low specific activity. Rather, U competes for the sorption sites needed to remove Pu and Np for regulatory purposes. However, the addition of 0.2 g/L of MST proved insufficient to achieve the required Np

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* SOWM refers to the Scope of Work Matrix provided in Appendix A. The numbers link to that document and provide the reader with additional reference materials.

decontamination. The kinetics of sorption in the 7.5 M Na solution proved too slow to support the needed processing rate, indicating the need to dilute the waste before treating with MST. This information was used to set the size of the Alpha Sorption Tanks for the ion exchange and solvent extraction processes.

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

7.1.2.2 FY00 – Results

Research during FY00 examined MST sorption kinetics using 0.2 and 0.4 g MST/L in a 5.6 M Na waste.[10] Results indicated intermediate sorbate removal from a 5.6 M Na solution compared to that observed for a 4.5 M and a 7.5 M Na solution. The Sr and Pu removal produced equilibrium concentrations that met process requirements under certain conditions, indicating that feed-blending strategies must consider the isotopic distribution of Sr and Pu. For Np, process requirements were not met at either MST concentration, although the addition of 0.4 g/L MST nearly achieved the limit. These results demonstrated that Sr and Pu removal rates decreased with increased Na concentration (i.e., ionic strength). The Np and U removal proved lower from the 5.6 M Na solution than the 7.5 M Na solutions. These results provided additional data for sizing CSTRs for the STTP process and processing tanks for alpha and Sr removal unit operations in the CSSX and CST Non-Elutable Ion Exchange processes.

7.1.2.3 FY01 – Current Work

The previous experimental data confirms the current cost estimates for the proposed options. Furthermore, the limited ability to remove Np by addition of MST requires blending of wastes from selected tanks prior to treatment. This engineering approach provides an acceptable level of confidence for successfully processing the wastes. Additional data on MST sorption for individual radionuclides is needed to develop increased confidence in predicting the behavior of the baseline sorbent. Also, characterization data on actual waste is needed to provide a better understanding of the state of Pu and Np in the waste.

Late in FY00, actual waste samples were obtained to conduct FY01 characterization studies focused on determining whether the actinides exist in part as colloidal species. This work will examine whether sequential filtration of the waste through finer ultra-filters yields lower measured concentrations of the actinides. Such a finding would suggest the presence of colloidal material that may prove resistant to removal by MST. Because routine protocol for most analyses of the waste samples do not include filtration prior to characterization, the existing database may report total suspended radionuclides. (The most frequent sample analyses only provide the concentration of the soluble species.) Thus, the total amount of soluble radionuclides requiring removal may prove significantly less than assumed in current design calculations. By conducting these studies, researchers will refine the understanding of the required performance for any sorbent.

Research in FY01 will also shift to examining the sorption behavior for individual radionuclides (e.g., Sr, U, Np and Pu). Modeling conducted in FY00 using an empirical mathematical formula showed limited ability to reliably predict radionuclide performance even within the existing data set.[7,8] The lead investigators attribute this limitation to two factors. First, the previous experiments investigated removal of multiple radionuclides from a mixture. Incomplete fundamental isotherm studies for single sorbates lead to a lack of understanding of the basic chemistry involved for competing species. Second, the mathematical tools used in these studies derived from simplistic regression software as opposed to evaluating the existing data against multiple component theories. Future work will seek a more fundamental, first-principle interpretation of the behavior.

Due to the lack of fundamental understanding of the nature of chemical binding of radionuclides to the MST, current knowledge in this area resorts to empirical formulas to predict behavior. The collective data suggests – but does not definitively show – that Sr sorption occurs through an ion exchange mechanism while the actinides attach via a sorption process. Work will focus on measuring isotherms for single radionuclides and MST. Studies will examine the influence of solution composition – particularly the dependence of sorption on the relative concentrations of hydroxide, carbonate, nitrate, nitrite, and aluminate in the waste.

In addition, personnel will examine loaded sorbents using fine structure x-ray spectroscopy techniques to gain an understanding of the nature of the mechanism that governs sorption for each radionuclide. The combined data will allow researchers to further develop “first-principles” models to correlate sorption behavior. These data will increase the reliability of estimating facility performance for a variety of wastes with compositions that differ from those previously examined. An understanding of the binding mechanism will also help guide researchers in efforts to identify superior sorbents for this application.

To date, vendors have produced only a limited number of batches of the MST sorbent resulting in a sparse data set for actinide loading. The FY01 work will examine the batch-to-batch variation in actinide sorption by MST.

Prior test results indicated a change in the Pu removal kinetics after about 10 hours upon contact with the MST. These results suggest that two or more Pu species may exist that react with the MST at different rates. Literature data indicate Pu exhibits multiple oxidation states in alkaline aqueous solutions.[11,12] One expects Np to also exist in multiple oxidation states with differing removal efficiency through sorption on MST. Existing studies do not provide definitive identification of Pu and Np oxidation states in the range of solution compositions that will exist during salt solution processing. Identifying the Pu and Np oxidation states and determining the extent and rate of removal of each oxidation state would decrease the uncertainty in predicting removal behavior under varying waste compositions. Future work will include studies of the influence of Pu and Np oxidation state on performance for MST and any alternate sorbent deemed appropriate at the time of work scope authorization. Similarly, studies will also examine – in a screening fashion – the ability of reducing agents to improve performance.

7.1.3 Alternative Alpha and Sr Removal Technologies (Alpha SOWM 1.3 and 1.4)

7.1.3.1 Previous Results

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

7.1.3.2 FY00 – Results

During FY00, Hobbs conducted a review of available literature for data related to a number of actinide and Sr removal technologies.[13] This evaluation recommended the following sorbent materials for further testing to determine the rate and extent of removal: sodium nonatitanate in the form under development by Honeywell Performance Polymers and Chemicals (Morristown, NJ); SrTreat produced by Selion OY (Finland); CST in various forms; and pharmacosiderites as developed by Abe Clearfield (Texas A&M University). The report also recommended evaluating precipitation with $Sr^{2+}/Ca^{2+}/NaMnO_4$. The study recommended not pursuing any testing of liquid/liquid extraction and polymer filtration methods in FY01.

A review of the use of sodium nonatitanate began in FY00. Hobbs evaluated the performance of three samples of the material relative to Sr and actinide removal.[14] Poirier evaluated the same samples to determine the influence on cross-flow filter performance.[15]

Physical and chemical characterization indicated that the three samples exhibited similar particle volume distributions, which proved larger than that measured for the reference MST material. In Sr and actinide removal testing, the samples exhibited lower removal capacities than MST. Removal rates appeared similar after 24 hours. Review by Clearfield of the x-ray analyses for the ST suggests that the Honeywell samples represent a poor conversion of the sorbent to the desired structure and appear atypical of the material that the Honeywell production should yield. Based on these data Hobbs recommended additional testing to measure removal kinetics during the first eight hours of contact between the solution and sorbent. He also recommended that further testing of ST samples proceed only upon documented evidence that future samples exhibit the structure expected for the synthesized sorbent as determined by x-ray diffraction.

Bench-scale dead-end filtration tests used 5.6 M sodium, average salt solution containing 0.6 g/L simulated sludge, and 0.55 g/L MST or sodium nonatitanate. Testing identified no correlation between MST or sodium nonatitanate particle size and filter flux. Any potential filtration gains from differences in particle size between the MST and sodium nonatitanate appeared offset by changes in filter cake porosity. The dispersion of the particle size for these samples likely contributes to this behavior. The sodium nonatitanate particles produced marginal improvement in filter flux (~30%). The rate of improvement in filter flux proves less than previous gains obtained through the addition of chemical additives to improve performance. The marginal improvement would not appreciably reduce equipment size.

7.1.3.3 FY01 – Current Work

During FY01, the SPP alpha and Sr removal program will contract Abe Clearfield (Texas A&M University) to assist in the formulation of improved sorbents for actinide removal. Clearfield will examine variants of the MST formulation and synthesize other titanate compounds for evaluation. The study will also include structural analyses and measuring equilibrium isotherms for the sorbents.

Hobbs (SRTC) will perform batch tests contacting newly developed sorbents with simulated waste containing the radionuclides of interest. This testing will continue and expand upon testing of sorbents and alternate technologies recommended in the FY00 evaluation.[13]

By mid-FY01, the program should collect sufficient information to determine whether an alternate sorbent or technology appears viable as a replacement to the baseline material (MST). If no promising candidates exist, the program may elect to pursue development of an engineered form of the MST suitable for application in an ion exchange column configuration. The engineered MST will be synthesized using various techniques commonly employed for this purpose. The approaches will use the combined expertise of resources available to the program to select the most promising synthesis routes. Researchers will conduct screening tests on the selected materials.

Depending upon final definition of scope, a portion of this work may include collaborative efforts by Dr. Jack Collins (ORNL).[16] Collins previously attempted development of an engineered form of MST and the program may elect to continue those earlier studies.

7.1.4 MST Filtration and Settling (Alpha SOWM 6.2.1, 6.3, 6.5.3)

7.1.4.1 Previous Results

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

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

Tests by ORNL staff examined the rheology, settling, and resuspension characteristics of MST/sludge slurries in both laboratory and pilot-scale experiments.[25] The tests demonstrated the relative ease for resuspending settled slurry at pilot scale after settling for 14 days, although the data suggested that not all the MST suspended during these tests. In contrast, after 60 days settling time, ORNL personnel could not suspend all of the slurry even at an impeller tip-speed of 300 m/min. Storage of MST/sludge mixtures at 80ºC for as little as three days dramatically increased yield stress and consistency. After 60 days of storage at 80ºC, the yield stress increased by a factor of 300 and the consistency by a factor of 30. These results indicate the need to cool the settled MST/sludge to assure subsequent suspension for further processing. As a result of these findings, the program altered the conceptual designs for the downstream tanks (i.e., pump pit tanks and processing tanks). The design added coils and high powered/high tip-speed agitators to ensure suspension of settled MST/sludge solids.

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

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

7.1.4.2 FY00 – Results

Cross-flow filter testing in FY00 included tests at the University of South Carolina (USC) with equipment representing about ~1/20th scale – (based on filter area) – of the filter used in the ITP facility at SRS.[29] The testing measured flux rate using a slurry consisting of simulated sludge – representing a blend of SRS wastes – and MST. The investigation studied the influence of axial velocity, transmembrane pressure, and concentration of solids on cross-flow filter flux. In general, the measured flux equaled or exceeded the value determined in smaller scale tests. The authors used the data from the entire range of operating conditions studied to develop a model for predicting performance. The model includes three terms representing pressure driven flow, resistance of slurry concentration gradient to transport, and resistance of the filter media. The simple three-term equation reliably reproduced the data from widely divergent operating conditions.

Late in FY00, Poirier started additional experiments to examine the use of flocculating agents or filter aids to improve separation efficiency.[30] The studies examined individual additives and blends based in part on past experiments and using recommendations from various consultants. Testing late in the fiscal year (not yet formally documented) identified six promising additives coming from two different commercial suppliers. In dead-end filtration tests to screen effectiveness, flux increased as much as fourfold with minor amounts of additives. Flocculation proved rapid and highly effective.

7.1.4.3 FY01 – Current Work

Work to date has established that cross-flow filtration can achieve satisfactory performance rates for the CST and CSSX options, but at the cost of greater filter area, larger tanks, and more powerful pumps. In contrast, the filtration equipment for the STTP option falls well within the range of equipment previously deployed at SRS for treatment of radioactive waste. The program focus for cross-flow filtration will thus include work to increase the confidence in the previous data set by collecting additional information for a variety of simulated and actual sludge wastes.

Testing will continue at USC during FY01. The tests will examine the filter flux for two sludges with varying amounts of MST. The two sludges will simulate the two primary types of waste stored at SRS. Testing will also include experiments without any added MST. This option represents the process configuration should alternate sorbent development or in-tank application of MST with subsequent settling and decanting proves viable. Finally, testing will examine the improvement gained by adding the most promising flocculating agents based on laboratory testing.

The contract with USC also provides funds to procure and install a device that allows in situ measurements of particle size. The size and attrition of particles during filtration partially determines filter performance. Researchers will attempt to correlate flux with particle size data.

All existing filtration data for MST and sludge slurries (absent TPB) come from tests with simulated wastes. During FY01, Poirier will conduct filtration tests using several actual waste samples. The tests will measure flux rates at the range of anticipated solids content for the processes. One experiment will examine the influence of the most promising flocculating agent on flux. These tests will also measure the rheology of the slurries and perform thermal analyses to understand the behavior of solids as a result of radiolytic heating during extended storage. (An FY99 study by Taylor and Mattus[25] demonstrated that under such conditions the viscosity and yield stress of simulated slurries increased.) The thermal analyses will provide insight into the nature of the chemical interactions if this behavior also occurs with real waste.

Another activity will continue the investigation of chemical additives to improve the settling and filter performance for mixtures of MST and sludge. Researchers will examine the improvements gained in flux for cross-flow filters. The work will include a university or industrial contract to develop and identify promising chemical additives. SRTC personnel will examine the most promising candidates by measuring filter performance or settling with simulated or real waste as deemed appropriate. The real waste test will occur after completing an evaluation of the chemical additive for compatibility within the vitrification process. Also, SRTC personnel will perform initial radiolytic stability measurements of any selected organic reagents. Compatibility studies for the additives within the integrated waste processing system will start as appropriate.

7.1.5 Feed Clarification Alternatives (Alpha SOWM 6.2.3, 6.5.1, 6.5.2)

7.1.5.1 Previous Results

The DOE requested that the SRS HLW program perform a feasibility study to examine the use of current site facilities for implementation of the Sr and actinide removal process. WSRC performed a study to examine the economics associated with using the existing filters from the ITP or Late Washing Facilities for this option, as well as the use of in-tank processing for the MST sorbent.[31] The study deemed the existing infrastructure and slurry transport equipment inadequate to achieve the process objectives in any viable fashion. The DOE judged the study as unnecessarily limited in scope because it did not consider the use of alternate sorbents.[9]

7.1.5.2 FY00 – Results

During FY00, Poirier conducted an evaluation of alternate methods for achieving the required separation of solids from liquid.[32] The TFA-funded solid-liquid separation study conducted in 1995 was used as a starting point for conducting the review of technical literature. The review also included discussions with vendors, as well as soliciting guidance from researchers at SRTC and within the DOE complex who possess extensive experience in solid-liquid separation. Finally, the author coordinated a workshop with representatives from SRTC, SRS HLW, SRS Solid Waste, and the academic community on the specific application of interest. Based on the findings, Poirier recommended evaluation of several alternate solid-liquid separation technologies for removing sludge and MST from HLW salt solutions. In continuing work in this area, primary focus should remain on identification of chemical additives (e.g., flocculating agents) that will improve the performance of the cross-flow filters. Other work should investigate settling and decanting followed by polishing filtration (both cross-flow and dead-end). This testing requires a large volume of continuous fresh feed and will examine improvements in filtration by combination with the addition of flocculating additives. If flocculation with cross-flow filtration proves ineffective, SRTC should investigate high shear filtration (using a centrifugal filter or VSEP filter) as well as flocculation in combination with centrifugation.

During FY00, SRTC performed a systems evaluation study of alternate equipment configurations for the alpha and Sr removal portion of the ion exchange and solvent extraction processes.[33] Their report documents evaluation of nine different processing configurations, all using cross-flow filtration and sorption by MST as the implementing technologies. The team evaluated the relative value of the different configurations using criteria of facility size, process complexity, impact on equipment size, technical maturity, and process flexibility. The study recommended a preferred facility design that adds a filter feed tank and separate filter for washing of sludge and MST solids. This design change allows continuous filter operation and, thus, use of the smaller filters and smaller capacity filter feed pumps.

7.1.5.3 FY01 – Current Work

Based on recommendations from Poirier's survey of available alternate technologies for solid-liquid separation, in FY01 the program will pursue testing of three alternate technologies: centrifugation, vibratory enhanced cross-flow filtration, and dead-end filtration. Centrifuge tests will make use of prototype equipment leased from a vendor. The investigation of vibratory enhanced cross-flow filtration will occur via a subcontract to a commercial vendor of this technology. The dead-end filter tests will likely occur at SRS using procured equipment.

FY99 testing suggested that addition of a settling tank would improve solid removal efficiency, reducing the burden on the cross-flow filters. However, the test data only included short duration tests with a limited total volume of slurry. During longer operation times, the added solids may negate the gains observed. FY01 extended duration tests will use simulated wastes under more typically expected facility conditions.

7.1.6 On-Line Effluent Monitor (Alpha SOWM 9.0)

7.1.6.1 Previous Results

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

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

Table 7.1 Predicted Radionuclide Concentrations

Radionuclide	Soluble Feed (Ci/gal)	Decontaminated Salt Solution nCi/g (SPF WAC Limits)	Clarified Salt Solution (Ci/gal)
Sr-90	3.28E-02	4.00E+01	5.60E-04
Cs-137	1.34E+00	4.50E+01	1.12E+00
U-232	3.79E-8	N/A	1.76E-08
U-234	2.44E-08	N/A	1.14E-08
U-235	1.96E-09	N/A	9.12E-10
U-236	3.34E-09	N/A	1.55E-09
U-238	1.26E-07	N/A	5.86E-08
Np-237	6.50E-08	3.00E-02	5.44E-08
Pu-238	8.439E-04	N/A	3.50E-05
Pu-239	7.40E-05	N/A	3.07E-06
Pu-240	1.82E-05	N/A	7.54E-07
Pu-241	3.73E-04	2.00E+02	1.55E-05
Pu-242	9.68E-09	N/A	4.01E-10
Am-241	1.48E-04	N/A	1.24E-04
Am-242m	1.84E-07	N/A	1.54E-07
Cm-244	3.16E-05	N/A	2.65E-05
Cm-245	2.107E-9	N/A	1.76E-09
Total Soluble Alpha	7.55E-03	2.00E+01	6.32E-03
Co-60	2.27E-05	6.00E+00	2.27E-05
Ru-106	4.84E-04	1.28E+02	4.84E-04
Sb-125	2.88E-04	7.60E+01	2.88E-04
Sn-126	5.30E-05	1.40E+01	5.30E-05
Eu-154	6.50E-05	1.60E+01	6.50E-05

Notes:

1. Ba-137m and Y-90 exist at equilibrium concentrations in the feed, but may exist at other relative concentrations in the other process streams.

2. The Saltstone Processing Facility Waste Acceptance Criteria specifies concentrations in nCi/g; the higher density of decontaminated salt solution from the IONSIV® IE-911 and CSSX processes allow higher volumetric concentration limits for these two processes.

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

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

7.1.6.2 FY00 – Results

Personnel constraints limited work on this task in FY00 to providing a specification to request bids on a prototypical effluent monitor.[34,35] The specification documents provide the requirements for the design of a prototype monitor to meet the requirements of any one of the three Cs-removal process alternatives. The prototypical monitor will receive testing during process demonstration of the selected Cs-removal technology.

7.1.6.3 FY01 – Current Work

In early FY01, the program will solicit vendor bids to design and fabricate a prototype analyzer for testing. Two separate groups, both a contractor-led (i.e., WSRC) team and an independent consultant, will evaluate the bids in parallel. In addition to reviewing the vendor proposals, the consultant will evaluate the design concept and proposed deployment approach for the analyzers. As part of that review, the consultant will assess whether the analyzer technology merits additional research. Based upon the combined reviews, the program will reach a decision whether to proceed with procurement of the prototype analyzer or conduct further research.

7.2 CST Non-Elutable Ion Exchange

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

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

For each salt processing alternative, science and technology questions and issues exist. These questions must be answered and issues must be resolved to complete the design and construction activities in a time frame that allows HLW tanks to be decommissioned in accord with compliance agreements with the State of South Carolina and the EPA. SRS personnel worked closely with the DOE Office of Science & Technology through the TFA to develop the SPP R&D Science and Technology Roadmap. This roadmap outlines the technical studies and demonstrations necessary to provide to the designers, operators, and DOE management the information necessary to proceed through key decision points of the project for the CST Non-Elutable Ion-Exchange process.

For CST Non-Elutable Ion Exchange, the key issues are Cs removal kinetics as a function of temperature and waste composition, gas generation in the ion-exchange columns and column design parameters, sorbent sampling and handling, and glass requalification. The chemical and thermal stabilities of the CST sorbent, in addition to Cs-loading capacity, affect its ability to reduce the Cs concentration in the DSS to that required for disposal in saltstone. The large columns defined in the preliminary facility design (5-ft diameter by 16-ft high) result in the accumulation of large quantities of radioactive Cs (several million curies), which raises issues concerning the effect of gas generation on Cs-sorption and requires extensive shielding to protect personnel. During ion exchange operations, hydrogen, oxygen and other gases are generated, posing potential safety and operational concerns. Potential modification of the feed preparation slurry sampling and agitation systems to maintain feed homogeneity requires that the CST be reduced in size before addition to the slurry. Immobilization of the loaded CST in borosilicate glass occurs in the DWPF. The new glass formulation requires requalification for the higher TiO_2 loading and revision of the existing glass durability correlation.

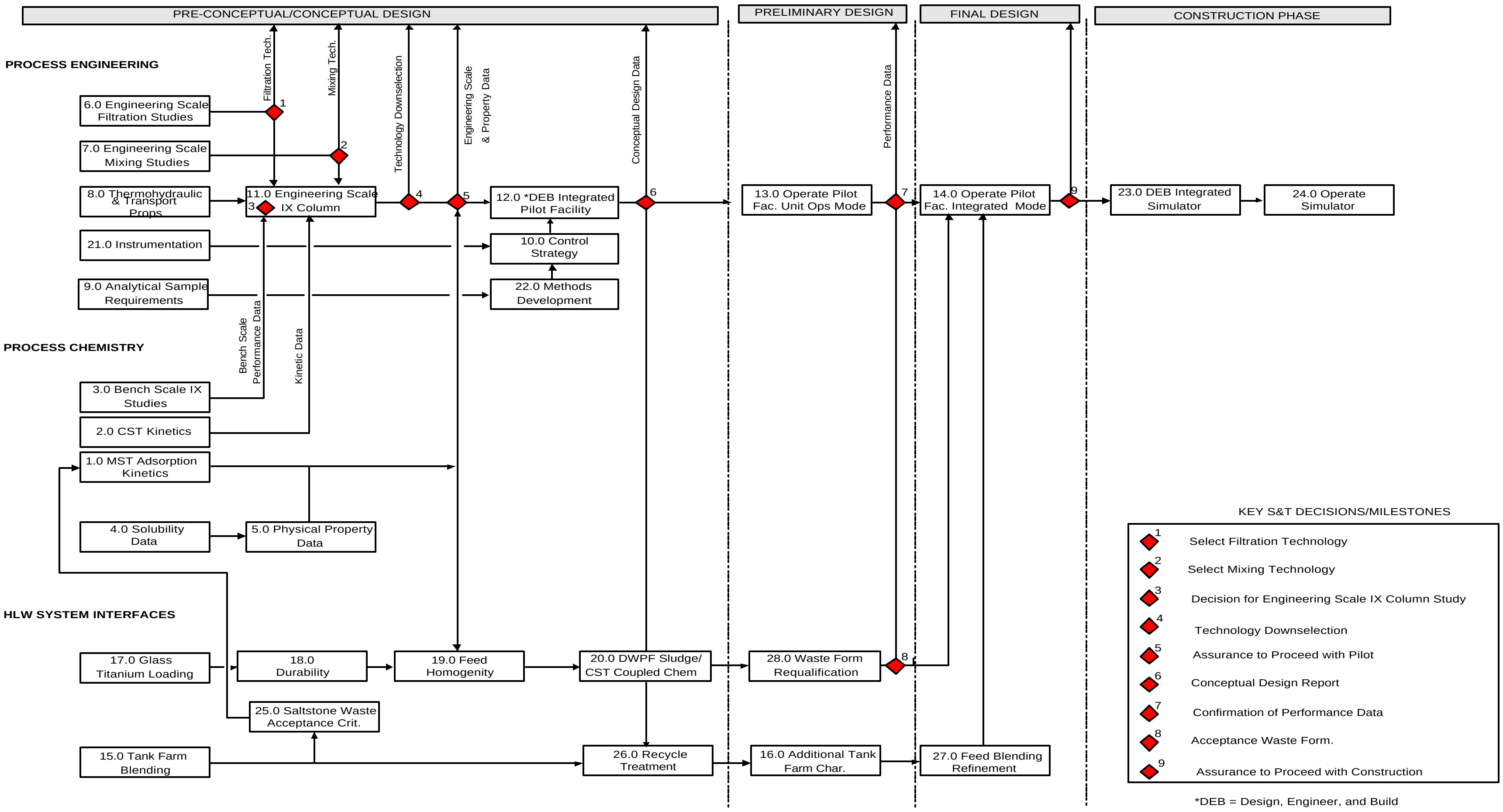
Achieving critical project decision milestones requires completion of the science and technology activities. Failure to meet technology insertion milestones in the integrated project schedule will delay startup of the salt removal process. This will result in inadequate tank storage space, jeopardizing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

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

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

Process chemistry includes data on thermal and hydraulic transport properties, reaction kinetics, and mass transfer properties that are needed to finalize the conceptual design. These data are used to establish the physical and engineering property basis for the project and detailed design. Examples of key decisions resulting from these activities include determining the final composition of the engineered form of the sorbent and developing a pretreatment method for it, confirming the baseline column design, and measuring the chemical and thermal stability of the sorbent. Process engineering includes thermohydraulic transport properties that affect the manner in which the CST particles are transferred from the ion-exchange columns to DWPF,

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



sampled in the CST/sludge/frit slurry, and fed into the melter. HLW system interface refers mainly to ensuring that these steps are carried out properly such that the desired glass quality is maintained.

Physical property and process engineering data from engineering scale tests will be developed during the conceptual design. Confirmatory performance data will be developed during unit operations tests to support preliminary design. These data are needed to resolve issues related to equipment sizing, specific equipment attributes, 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 design input for the final design stage of the project.

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

Additional development and testing during the conceptual design phase will help assure proper feed and product interfaces of the Cs-removal process with the HLW Tank Farm, DWPF and Saltstone. The issues of concern include assurance of glass qualification, waste feed blending and characterization, and waste acceptance.

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

7.2.2 CST Column Performance

7.2.2.1 Refinement of the Model (CST SOWM 5.2)

The purpose of this task is to construct a mathematical model that can be used to predict the performance of a plant-scale column of CST sorbent. The model can then be used to give an accurate indication of the operating parameters required for efficient removal of Cs from the processed salt-waste stream.

7.2.2.1.1 Previous Results

Researchers from Texas A&M University, Purdue University, ORNL, and SRS used existing information about the performance of CST to predict the expected length of the Mass Transfer Zone (MTZ). Previous studies measured Cs distribution on CST samples of the powder form[36] and the engineered form.[37]

Research[38] was performed to determine the performance of CST in column application using SRS simulated waste to determine agreement with the ZAM computer model. Results of the tests indicated that Cs removal in two column tests at moderately rapid flow rates (0.98 and 4.1 cm/min superficial velocities) matched Texas A&M predictions. However, the ZAM model incorporated a 30% reduction in Cs capacity at the higher flow rate to match the data whereas the observed Cs removal surpassed model predictions at a lower flow rate (0.27 cm/min).

The mathematical model utilized in the simulations is a model of flow through a porous medium that takes into account competitive sorption, bulk convection, axial dispersion, film mass transfer, and pore diffusion. Since surface diffusion effects are not evident from the available data, the pore diffusion model is used in this analysis. The numerical solutions of the governing equations and boundary conditions are performed by the VERSE simulation package.[39] This model has been validated in many previous studies.[40] The pore diffusion model assumes uniform spherical sorbent particles, local equilibrium within the sorbent and constant diffusivities.

Walker et al.[41] checked the constructed model by performing ion-exchange experiments at three different superficial velocities in small (1.5 cm x 10 cm) columns. Experimental data agreed with the predicted column performance from a VERSE computer model with the exception of the column run at a superficial velocity of 4.1 cm/min. In this comparison, the experimental breakthrough of Cs was much faster, reaching 95% of the feed concentration after only 120 hours. The best computer fit to this data was obtained by reducing the capacity of the CST by 30%.

Therefore, Wilmarth et al.[42] evaluated a number of the possible sources of the discrepancy between model predictions and experimental results obtained by Walker et al. Tests examined the effect of contact with humid air during pretreatment, lot-to-lot variance, aspect ratio and superficial velocity. The most conclusive evidence suggests lot-to-lot variance as the leading cause of the deviation. CST lot #96-4 shows a dynamic capacity approximately 30% below other lots of CST. Additionally, results from collective tests of column performance indicate the VERSE model can adequately predict full-scale column performance.

Two additional column experiments showed CST performance degraded at only slightly higher superficial velocities. At velocities 75% higher than expected plant velocities, measured Cs breakthrough showed a 15-40% deviation from VERSE model predictions. Lastly, the presence of organic constituents (e.g., dibutylphosphate and tributylphosphate) exhibited little or no effect on column performance over the limited duration tested.

Another major aspect of prior research evaluated the adequacy of the column design for real waste application. Walker et al.[43] verified column capacity and kinetic data obtained using simulated waste with those obtained using radioactive waste. Testing of radioactive waste also allowed confirmation of model predictions for a full-length column.

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

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

7.2.2.1.2 FY00 - Results

In FY00 column experiments, alkaline-earth metals, carbonate, oxalate, and peroxide ions were passed through a column loaded with IE-911 to obtain equilibrium measurement data for various ionic constituents. These measurements enabled the refinement of mathematical coefficients for the ZAM model used to describe the influence of various ionic constituents on column performance. This work was done at SRTC in collaboration with Professor Ray Anthony of Texas A&M University, who also assisted UOP in refinements to the CST manufacturing process, consulted on other aspects of the column testing, and participated in periodic reviews of collected experimental data (see sections below).

Results of these studies showed that Cs loading on IE-911 increased with carbonate content in the simulated salt solution. Over the range of concentrations expected in SRS waste, the Cs loading increased by several percent. The variance likely resulted from a shift in Na activity in the solution due to increasing carbonate concentration. Next, the researcher ran the ZAM model[44] to test if activity coefficient changes brought about by introducing carbonates into the salt solution would replicate the experimental observation. The predicted Cs distribution coefficient (K_d) values increased with the carbonate content in the salt solution. This result is consistent with the ZAM model predictions.

In addition, removing oxalate from simulated “average” salt solution had no effect on Cs loading. Further verification that oxalate has no effect was obtained by performing similar tests with IE-910. Likewise, results from ZAM modeling indicated no effect on Cs loading (2106 versus 2260 mL/g). In fact, increasing oxalate concentration up to 0.1 M in the ZAM model had only a very small effect on Cs loading.

Finally, two sets of experiments conducted simultaneously showed that peroxide decreased Cs loading on IE-911 by several percent. In one experiment (called the “placebo”), researchers injected an “average” salt solution containing 0.005 g/mL of IE-911 every five hours with 100 μL of distilled water. In the other experiment, personnel injected an “average” salt solution containing 0.005 g/mL of IE-911 every five hours with 100 μL of 50 wt% peroxide solution. The peroxide concentration, as determined by permanganate titration, equaled 0.13 M immediately after injection. The peroxide concentration decreased to 0.0034 M five hours later. Both sets of experiments occurred on the same shaker and the experimental measurements were repeated twice. The data for IE-911 indicated a higher Cs loading in the placebo test relative to the peroxide test. However, the estimated peroxide concentration in average SRS waste is 2.6×10^{-6} M. At this concentration level, no peroxide effect is expected on Cs loading.

Solubility studies of carbonate and oxalate anions were also performed. A temperature-composition solubility phase diagram was developed for average, high-nitrate, and high-OH simulants. The current ORNL and OLI model of carbonate-oxalate solubility was updated. The composition of precipitates resulting from the solubility test were determined. The results showed that the carbonate concentration in the wastes could be increased (i.e., saturation in carbonate was not achieved). On the other hand, the oxalate concentration in the wastes was very low compared with other anions and was at the limiting value.

The results of this work, published in a technical report[45] indicate that carbonate, oxalate, and peroxide should have little effect on the performance of the CST columns. Carbonate, which is present in the waste owing to the absorption of CO_2 from air, will enhance Cs sorption if it has any effect at all. Oxalate, which is added to the waste in cleaning solutions, has little effect on CST performance. Finally, peroxide - although it does exert a detrimental effect on CST performance at relatively high concentrations - is expected to be present only at a micromolar level in the actual waste. Therefore, no effect from the presence of such low levels of peroxide is anticipated.

7.2.2.1.3 FY01 - Current Work

In FY01, an evaluation of the ZAM model versus the compiled column data will be published in a technical report. The model will be changed to report activities of ions in order to bring the predictions into better agreement with experimental results. In addition, the water content (15%) of CST will be adjusted in the ZAM model in order to more accurately reflect its measured value (4 - 5%) in CST.

Additionally, an evaluation of various SRS tank wastes will be performed during FY01. The purpose of these tests is to catalogue the Cs removal efficiencies of the currently marketed CST versus the chemical composition of F- and H-Area wastes. The results will be compared with those predicted by the refined ZAM model.

7.2.2.2 Alternative Column Configuration (CST SOWM 8.1, 8.2)

7.2.2.2.1 Previous Results

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

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

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

7.2.2.2.2 FY00 – Results

This work was postponed until FY01.

7.2.2.2.3 FY01 – Current Work

Savannah River Design Engineering (SRDE) will evaluate different column designs and configurations with the goal of minimizing complexity and cost while providing for optimum performance of CST. The design strategy for column configuration will be re-examined to determine if the 16 X 5-ft column can be replaced by a different configuration that provides for a shorter service lifetime and/or a smaller volume for the columns.

The proposed facility at SRS uses a traditional carousel arrangement of large, fixed-bed ion-exchange columns. Alternate column configurations using designs such as the “Higgins Loop” or simulated moving beds and a fluidized bed offer potential reductions in safety source term, but at the expense of added equipment complexity. Evaluation of alternative column designs and configurations will continue as needed, with input from industrial consultants that have extensive experience with such alternative column designs. The industrial consultants will provide technical support to evaluate the alternate column configurations. If warranted, a vendor test for proof of principle will be conducted based on preliminary design(s) and required performance provided by the alternate-column-configuration team.

Removal of heat generated by the decay of sorbed Cs becomes an important issue when the liquid flow to the column is stalled. Industrial consultants will provide assistance in the evaluation of different column designs and configurations that provide good heat management with minimal impact on operational complexity. That is, the design must permit easy CST addition and unloading, minimize accumulation of gases, minimize pressure drop, and avoid plugging of collector systems while providing good heat removal. The general steps are to identify heat removal concepts and systems and evaluate potential impacts to system operability and costs.

Cooling systems for the column will be designed to remove heat associated with the β-decay of Cs-loaded ion exchanger. In support of this activity, tests and calculations are being performed to determine heat-transfer coefficients for fixed beds of Cs-loaded CST. The thermal conductivity of CST and a mixture of CST with waste simulant will be measured with a Hot Disk Thermal Constants analyzer. Using these thermal conductivity values along with literature data and column design information, the heat transfer coefficients for various combinations of CST, liquid, and gases will be calculated. Thus, thermal conductivities of (a) the equivalent of a settled CST bed immersed in salt solution and (b) the equivalent of a settled CST bed wetted with salt solution and drained of free liquid are being measured. For these measurements, a quantity of CST is being aged in simulated salt solution, and the thermal conductivity of the aged material will be measured. These data will be compared to similar data previously obtained on fresh CST to ensure that no significant differences arise after aging. SRDE will use these results to determine if further measurements are needed.

The results of this work will provide data that are expected to be useful in determining if it is feasible to reduce the risk associated with the operation of relatively large ion-exchange columns by employing columns of a different design. Although the concept of a “Higgins loop” is attractive from the viewpoint of avoiding ion-exchange columns fully loaded with radioactive Cs, the risks of such a design must also be considered. Some risks that have so far been identified are the fate of fines, migration of the mass-transfer zone, and robustness of the CST particles.

In addition, the replacement of the three large columns by several smaller columns was examined. The consensus reached was that smaller columns would reduce the risk associated with their use, but would produce a high degree of equipment complexity, especially during column change-out, and would increase the footprint of the plant, thereby increasing costs.

7.2.3 CST Sorbent Stability (CST SOWM 2.0)

7.2.3.1 Previous Results

Leaching. The fundamental chemical and thermal stabilities of the IE-911 (engineered sorbent consisting of CST particles and binder) in the highly alkaline environment of the SRS supernate are important for understanding processing lifetime and downstream effects of leached components. Results of the stability tests indicate that silicon (Si) and niobium (Nb) are leached from the IE-911 along with minor amounts of titanium and zirconium (Zr). Discussions with members of the UOP staff indicated that Si and Nb exist in excess in the CST particles (IONSIV® IE-910) at levels of 4 wt% and 1 wt%, respectively. The quantity of Si and Nb leached, from the IE-910 in each of the salt solutions from the samples of IE-911, do not exceed the excess in the IE-910 precursor. The results of these tests suggest negligible leaching of elements from the microstructure of the IE-911.

Results from SRS and ORNL tests suggest that CST is interacting with some SRS waste streams. There have been examples of discoloration of some waste streams and in one particular case, a plug developed on top of the column during pretreatment with circulating NaOH. Material discovered in the feed line during pretreatment of an IE-911 column for a test using actual waste contained Nb. A test that irradiated IE-911 in the presence of high nitrate solution showed solid deposits with similar elevated concentrations of Nb.

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

Cs desorption. Exposure of the IE-911 to salt solutions was conducted at elevated temperatures (25º-120ºC) and for long duration (2 months) to simulate severely abnormal process conditions. The exposure resulted in a loss of Cs sorption capability. In addition, Cs desorbed from Cs-loaded CST when heated with simulants at elevated temperature (up to 80°C). When the slurry was cooled to room temperature, Cs sorption by the IE-911 was observed at lower levels than before heating. Interpretation of the data suggests precipitation of salts from the solution or CST phase changes as the most probable cause of the reduced adsorption.

Nitrate form. The chloride content in CST raises potential concerns regarding corrosion and glass chemistry. Chloride measurements of CST demonstrated that water rinsing or caustic washing of the CST prior to loading the CST columns reduced the chloride content, and hence the corrosion risk. This washing step could occur at the vendor facility or in a non-radiological portion of the processing facilities. Measurements for CST from small-scale Cs removal columns showed insufficient chloride content to adversely affect glass chemistry. Ultimately the vendor changed the synthesis of the CST so that chloride was replaced by nitrate, thereby completely eliminating this concern.

7.2.3.2 Alternative Pretreatment of IE-911 (CST SOWM 2.2.1.3, 2.3.1.2)

7.2.3.2.1 FY00 – Results

One method of avoiding downstream problems caused by leached components of IE-911 is to pretreat the sorbent prior to use. An effective pretreatment regime would remove those leachable components from IE-911 that could possibly precipitate or mineralize during column operation. Previous work in this area indicated that the observed column plug likely resulted from the amphoteric behavior of one (or more) metal oxide(s) over the pH range likely to have been experienced during the course of CST pretreatment with NaOH. This hypothesis was confirmed by chemical analysis.

SNL personnel reviewed SRS and ORNL leaching results for the chloride form of IE-911. According to these results, scaled down tests in which 3M NaOH solution was recirculated through a column packed with IE-911 demonstrated that conditioning the ion exchange medium could lead to column plugging. Analysis of the solid produced indicated a preponderance of Nb, though other IE-911 components were detected in the solid as well. Exposing the plug to a fresh 3M NaOH solution caused the plug to dissolve slowly.

A column of CST (nitrate form) was prepared at SNL upon receipt of CST materials from UOP. The column was pretreated with NaOH. Within one day of starting the pretreatment, solids formed in the system and plugged the column. At the time of this writing, the solids are being analyzed.

These results, published in an SRTC technical report[46], clearly indicated that an alternative pretreatment process was required in order to remove excess materials of manufacture before deployment of IE-911 and reduce the risk of column plugging.

7.2.3.2.2 FY01 – Current Work

Solids formed during pretreatment of the CST column will be analyzed to confirm that Nb leaches from the column and precipitates slowly.

Knowledge gained from the FY00 activities provides a basis for scoping laboratory experiments leading to a proposed alternative CST pretreatment process. SRS personnel will be consulted to ensure that the proposed process is compatible with the CST treatment process flowsheet. Existing studies suggest that the underlying cause of column plugging during pretreatment is that recirculating 3M NaOH leaches Nb from the IE-911. Eventually, supersaturation is achieved and a hydrous oxide of Nb precipitates. This task will quantify the degree of supersaturation needed to initiate precipitation, and then monitor the kinetics of the precipitation reaction. It can be expected that the precipitation rate will depend on solution chemistry, in particular the solution pH. Thus, quantifying the pH decrease that results when basic solutions are exposed to “as received” IE-911 will be an important part of developing an overall predictive model for the formation of the plugging material. SNL will perform laboratory leaching and simulant column testing to confirm the effectiveness of the recommended pretreatment process, and will document the work in a technical report.

The results of this work are expected to produce an alternative pretreatment regime that will reduce the amount of leachable Nb to a level at which formation of a column plug will not be an issue. The leaching behavior of Nb will be examined as a function of the pH of the pretreatment solution in order to develop the optimum sequence of treatment. Development of a satisfactory pretreatment regime that removes excess Nb and Si will greatly reduce the risk of using IE-911 in plant-scale operations.

7.2.3.3 CST Chemical and Thermal Stability (CST SOWM 2.2, 2.3)

7.2.3.3.1 FY00 – Results

ORNL

Batch tests. One aim of this work was to examine the possible role of salt solution on CST degradation and its effect on performance of the third (or guard) column. The third column, according to the current design basis, will be exposed to DSS for 6 to 12 months before it is actually placed in service as the primary Cs-removal column. Testing to date has examined 7-month exposures.

Another aim was to improve characterization data for the time-temperature and waste-composition operating regime that provides acceptable CST performance. The underlying mechanism(s) responsible for the non-absorption of Cs after heat treatment of IE-911 should be elucidated; two candidate mechanisms are phase changes of the CST and pore blockage by precipitation.

ORNL staff members treated samples of IE-911, in both the chloride and nitrate form, in batch and flow-through column tests, with simulants at temperatures from 25-80ºC. Experiments were conducted to examine the effect of soluble Si and Al. The leaching and precipitation of proprietary materials of manufacture during NaOH pretreatment and exposure to SRS waste simulants were also examined.

Long-term (12-month) batch leaching tests using the average supernate simulant and high-pH salt solution were initiated at ORNL to determine the effect of temperature and solution composition on the leaching behavior of the CST. Samples were stored at temperatures of 25, 30, 35, 50 and 80°C. Samples of the solutions were analyzed periodically for dissolved metals to measure CST leaching and precipitation of simulant components. Samples of the CST were removed periodically and tested for Cs sorption, porosity, surface area, particle size and elemental composition. Batch 98-5 CST (chloride form) was used for all of these test conditions with the CST nitrate form and IE-910 powder also tested at 25 and 80°C. A room-temperature leaching test using average simulant and CST batch 98-5 was started in June 1999.

After storage for one month at 30, 35, 50 and 80°C, the CST stored in average, high-hydroxide and high-nitrate simulants was weakly cemented together (the cemented CST was easily broken up). All of the samples stored at 25°C, and the CST in the high-pH salt solution at all temperatures, were still free flowing after one month. After two months, the samples stored at 25°C in the average, high-hydroxide and high-nitrate simulants were also cemented together. During subsequent samplings, the CST that had been previously broken up did not reform into clumps. The CST stored in the high-pH salt solution had not formed any clumps at any storage temperature during the seven months testing period. CST fouling, which appeared as nodules on the IE-911 particles, was studied at SRTC in detail to determine the cause. The agent responsible for this fouling was found to be an aluminosilicate.

Cesium-loading tests using CST samples from the batch leaching tests showed a drop of about 30% in distribution coefficient for the samples stored for one month or more at 80°C, compared to samples stored at 25°C, for the average, high-hydroxide and high-nitrate simulant solutions. The ratio did not change as the storage time increased. (Note: all of the Cs loading tests were performed at 25°C using average simulant that initially contained 50 mg/L Cs.) The high-pH salt solution caused less of an effect.

These results indicated an initial (sometime during the first month) degradation in the Cs sorption properties of CST as it contacted with supernate simulants at higher temperatures, but no further change after that. The CST stored at moderate temperatures also shows a drop in K_d compared to the samples stored at 25°C (an average of 15% and 18% reduction at 30 and 35°C, respectively). However, this apparent reduction in Cs sorption can be traced to the effect of the added mass of aluminosilicate to the CST particles, which effectively "dilutes" the amount of active sorbent present.

The results suggest that a column will remain intact when kept in service for a period of months and as it advances from the guard to the middle to the lead column. The deposition of aluminosilicates on the CST particles will be addressed under Waste/Simulant Precipitation Studies. The thermal stability of the CST particles will be investigated further in FY01.

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

The CST in the top of the average simulant column was clumped together when the first sample was taken after one month. The CST throughout the column was lightly cemented together, and tended to move up the column during backwashing. Light tapping on the column helped breakup the clumps of CST and resettle the bed. Photomicrographs showed that smaller CST particles and fragments tended to collect in the upper part of the columns.

The Cs loading capacity of the CST from the column leaching tests was very consistent for the three samples from each column, indicating no change in the Cs capacity of the CST along the length of the columns. The results for the two-month samples were unusually high, and out of line with all of the other results, so these results probably do not represent an actual change in the CST. The CST from the column using the high-pH salt solution did not show any consistent change in the Cs capacity of the samples, but the samples from the average simulant column showed a slight decline over time. The distribution coefficient was 23% lower and the Cs loading on the CST was 12% lower after 6 months exposure to the average simulant.

The ICP results for Al, Si and Nb in the column feed solutions show that the Si concentration for the average simulant column slowly increased and then decreased along with the Al concentration, indicating the precipitation of sodium aluminosilicate. The concentrations were restored when the feed solution was changed, and the Al concentration remained constant since that time. The Si concentration continued to change, but has not shown any consistent trend, so this may just be analytical variation. For the column with high-pH salt solution, the Si concentration increased during the first ten weeks, but dropped back to the starting level when the feed solution was changed. As with the results for the average simulant column, considerable scattering was observed in the Si concentrations. The analysis of the original solution showed 500 mg/L Si, even though there was no Si in the high-pH salt solution, again indicating considerable analytical variation. For both solutions the Nb rapidly leached from the CST, up to an apparent solubility limit, each time new feed solution was introduced.

These results are consistent with those from the batch experiments. The reduced Cs-loading capacity of the CST was demonstrated to result from the deposition of aluminosilicates on the CST particles, which effectively increased their mass, diluted the active material, and caused reduction in the capacity. The results indicate that CST should be stable for long periods in contact with decontaminated salt solution, a situation that would occur if the three-column baseline system were implemented.

SRTC

Heat treatment of CST (IE-911) in the range 25-80°C revealed that Cs from simulants desorbed at higher temperatures and only partially resorbed after returning the temperature to ambient.

The results from tests conducted at temperatures of 35 and 55°C provide a number of conclusions. Pretreating the IE-911 with sodium hydroxide lowers the equilibrium distribution coefficient, K_d, from 2323 ± 72 mL/g to 2117 ± 77 mL/g for average waste simulant starting with a Cs concentration of 18 mg/L. Both of these values compare well with the Texas A&M computer model (ZAM) for Cs removal in the average salt matrix. For the high-hydroxide and high-nitrate solutions, the K_d value averaged 2551 ± 136 mL/g and 1800 ± 60 mL/g, respectively. These agree with the 2500 mL/g and 1850 mL/g ZAM predictions for the high-hydroxide and high-nitrate matrices.

Elevating the temperature to 55°C for a short duration (1 day) lowered the K_d measured at 25°C by 7%. There was no effect on the K_d when the temperature was raised to 35°C. Data from tests conducted with temperature excursion (55°C) of 14 days indicate a detrimental effect (20% reduction) on K_d.

There was no loss in K_d at 35°C for the test conducted in average salt solution that did not contain Si or Al. These data support the theory that the loss in K_d is related to aluminosilicate formation. The losses of K_d were largest in the one-half diluted average waste and in the high nitrate simulant. In these tests, the loss of Cs K_d was 12.8 and 12.6%, respectively. Solid state characterization of the CST surfaces showed formation of sodium aluminosilicate that can be correlated to time at elevated temperature. The sodalite deposition, however, did not correlate with the loss of Cs K_d.

Leached and heat-treated samples were examined at SRTC, SNL and PNNL by analytical methods such as SEM-EDS, TEM, bulk elemental analyses by ICP, powder x-ray diffraction, thermal testing (TGA/DTA), FTIR, surface area analyses (BET), porosity determination, and solid state NMR. Test solutions were analyzed for the presence and composition of precipitates. These studies provided insight into processes that may lead to leaching of excess materials from the IE-911, precipitation of mineralized materials in the interparticle fluid, growth of mineralized materials on the surface or in the pores of IE-911 particles, or causing phase changes of the CST. The results clearly indicated that pretreatment produced cracks in the CST particles and that precipitate filled these cracks, although these phenomena may be artifacts of sample preparation. In addition, CST particles were coated with a layer of aluminosilicate approximately 1 micron thick when stored in SRS waste simulants at elevated temperatures.

SRTC developed a small-column test program to evaluate CST stability by measuring the effluent profile for Al, Si, Nb, and Zr as a function of feed composition. Concentrations of Al and Si were observed to be related in a manner consistent with the precipitation of an aluminosilicate, i.e., an increase in the concentration of one component resulted in a decrease in the concentration of the other. In addition, K_d values of these samples were measured in order to judge empirically the effect of various treatment regimes on the performance of IE-911.

The mechanism for Cs binding of IE-911 and TAM-5 was examined for SRS waste simulants. No significant difference was found, indicating that TAM-5 and the IE-910 used to prepare the IE-911 were essentially the same material. X-ray diffraction patterns of the two materials also revealed no detectable difference. Representatives from UOP, who stated that the synthesis they used to prepare IE-910 was identical to that used at Texas A&M University to prepare TAM-5, supported these findings.

These results are also consistent with an apparent loss of K_d that may be related to the deposition of aluminosilicate on the surface of the CST particles and the dilution of the active material by the added mass. The results also suggest that operating temperatures below 35°C will not have a detrimental effect on CST performance.

7.2.3.3.2 FY01 – Current Work

ORNL

Determinations of the chemical stability of CST continue at ORNL in FY01. Both batch and column leaching tests will be conducted for a full 12 months. These tests will involve contacting samples of CST with four simulant solutions at various temperatures, and analyzing the CST once each month to determine any changes. An interim report on the long-term stability of CST

(P. A. Taylor and C. H. Mattus, "Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent", ORNL/TM-1999/233) has been issued.

The long-term flow-through column studies using NaOH and nitrate solutions will continue until early 2001. Selected samples of CST from the batch-leaching and flow-through tests will be sent to participating laboratories (e.g., PNNL, SNL) for additional analyses.

SRTC

Chemical stability tests of new CST samples generated by UOP will be conducted. These tests will include batch measurement of Cs loading capacity in two simulant solutions (UOP-defined and SRS-average) at ambient temperature. Batch tests of the Cs loading capacity will be performed with real waste using the final material provided by UOP. Column tests will be performed with the pre-production samples at ambient temperature. Leaching tests will measure the amount of leached Si and Nb in batch and column mode. In addition, samples will be characterized with respect to particle size, porosity and surface area. Other measurements will employ vibrational spectroscopy, SEM surface imaging, and thermal analysis. Initiation of tests will depend on when UOP delivers the samples. A final report on the results of these tests will be issued approximately one month after the samples are delivered.

Studies of the effect of heat treatment on Cs desorption and resorption is also continuing. A report on the thermal stability of CST has been drafted and will be issued in FY01.

SNL

NaOH-treated IE-911 samples from ORNL are being characterized by XRD, TGA/DTA thermal analyses, pore volume measurements, SEM/EDS and TEM. In addition, samples of Cs-loaded IE-911 were received from PNNL and are being further analyzed. A final report will be issued documenting the results of the characterization and any relationships between the characterization data and the chemical stability of IE-911. The results from SNL and PNNL testing will be used to propose an operability regime for IE-911.

PNNL

NaOH-treated IE 911 samples are being prepared for batch test exposing the samples to simulated waste at room temperature, 55°C and 80°C. (NaOH treatment procedure and composition of simulant were specified by SRS personnel.) Cs concentrations and IE-911 sample size have been adjusted so that the maximum Cs loading is 2%. Samples of supernate and of the ion exchanger will be removed for analysis after 1 hour and 1, 3, 7, 30 and 60 days.

Solution concentrations of Na, Si, Ti, Al, Nb, and Zr for the supernate samples from the experiments above are being analyzed by ICP. Atomic absorption analysis is being used to determine Cs solution concentrations. The phase content of the samples is being analyzed by x-ray diffraction (XRD). A report on the results of the examination of pretreated CST will be published.

The results of these tests at several laboratories will determine if CST particles (IE-911) are stable to temperatures of at least 35°C and possibly higher. The characterization studies will reveal phases that may form upon heat treatment of Cs-loaded CST particles. The studies of the UOP samples will provide an evaluation of the improvements that have been introduced by the revised manufacturing process (see below).

7.2.3.4 Waste/Simulant Precipitation Studies (CST SOWM 5.1)

7.2.3.4.1 FY00 – Results

SRTC

Researchers investigated the stability of SRS simulated waste solutions and the solubility of Nb and Zr in these solutions in laboratory tests. The results support the following conclusions. SRS simulants are unstable towards precipitation of solid phases. Sodium oxalate, sodium aluminosilicate, and aluminum hydroxide form from one or more of the current simulant recipes. SRS simulants supersaturated with Al and Si form easily and reach equilibrium slowly. When Al is present, Si reacts to form an insoluble aluminosilicate. Filtration 24 hours after dissolution does not prevent additional solid formation. Attainment of equilibrium requires weeks or months at ambient temperatures. Seeding SRS simulants promotes crystallization of dissolved components. IE-911 particles and associated fines appear to promote crystallization of aluminum compounds. Addition of $Al(OH)_3$ solids speeds precipitation of dissolved Al. Nb and Zr solubilities are <20 mg/L in simulated waste solutions. Supersaturated solutions form easily and reach equilibrium slowly.

These instabilities may have caused or exacerbated most of the plugging incidents observed in testing of CST. Especially significant was the precipitation of sodium aluminosilicate after heating (boiling at atmospheric pressure for 24 hours in a stainless-steel vessel fitted with a glass condenser) average and high-nitrate simulants (with 7.5 M Na^+). However, modification of the SRS simulant compositions will not be recommended until analyses confirm that tank-farm wastes are at equilibrium with respect to precipitation of solids. If tank-farm wastes contain the same instabilities with respect to $Al(OH)_3$ and aluminosilicates, dilution with NaOH may alleviate the problem.

ORNL

Thermodynamic equilibrium calculations were performed using SolGasMix software and a thermodynamic property database compiled at ORNL from available literature data at ORNL. Initial calculations were performed to confirm a recent finding[47] for a system containing Na^+, $Al(OH)_4^-$, SiO_3^-, OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, and HS^-. While that system does not contain all the ions of interest in this study, it was a good starting point to confirm the reliability of the ORNL thermodynamic property database. Following confirmation of the database and the reproducibility of the literature data, the calculations were expanded to include the full range of those ions listed in the literature.[48] Conditions (concentration of ions, temperature, etc.) under which precipitation could occur were delineated from the thermodynamic calculations. Because of its proven reliability even at high molarities,[49] Pitzer's activity coefficient method was used to calculate the activity of water and the activity coefficients of the ions. The model at this stage did not use any parameters correlated from precipitation data.

The thermodynamic model predicted the precipitation of sodium aluminosilicates and possibly sodium fluorosulfates. Calculations on all three types of waste (i.e., average, high-hydroxide, and high-nitrate) indicated that a precipitate of the aluminosilicate cancrinite ($3Al_2O_3 \cdot 3Na_2O \cdot 6SiO_2 \cdot 1.68NaNO_3 \cdot 4.1H_2O$) would form.

Following the calculation of the ion concentrations, temperature, etc., necessary for precipitation, and subsequent to review by selected SRS personnel, laboratory tests were performed to confirm the results of the thermodynamic analyses. Experiments using standard laboratory equipment were performed to recreate the exact solutions and test for precipitation. Simulant solutions were prepared using a recipe supplied by SRS personnel. Samples were analyzed to confirm the presence of cations and anions in the correct amounts and ratios. Any precipitates formed were collected and analyzed to obtain information on the constituents. Any unusual results obtained in this step were fed back into the model to refine it.

Results were obtained for SRS average, high-hydroxide, and high-nitrate simulants. Average simulant was prepared in two different ways. First, all chemical components were added and a single filtration was performed. Second, each component was added separately and a filtration was performed after 24 hours of stirring. The solids were air-dried and identified by XRD analysis. The first preparation produced solids that included sodium oxalate, sodium nitrate, and sodium carbonate, among others. The second method produced sodium carbonate, aluminum hydroxide, sodium nitrate, and sodium oxalate. Preparation of high-hydroxide simulant by the second method produced the same solids as above; high-nitrate simulant produced the same solids as above, in addition to copious amounts of sodium fluorosulfate. Aluminosilicates did precipitate from the simulants but only after a period of time, which varied from days to weeks for the different simulant preparations. This clearly indicated the simulant was metastable with respect to precipitation of aluminosilicate.

Thermodynamic modeling predicted the precipitation (<1 ppm) of Ti and Nb and a solubility of 14-16 mg/L for Zr in the three simulants. Thermodynamic modeling of possible impurities of Mg, Ca, Sr, Ba, Fe (II and III), Pb, and Zn was also performed. Of these elements, only Sr, Ba, and Pb showed solubilities greater than millimolar levels. The results from these calculations on CST (Ti and Nb) and binder (Zr) components agree with leaching studies carried out at ORNL. Experimental results from SRTC indicated that Nb dissolves (12-18 mg/L) within two weeks in simulants and then precipitated (from 9 in high-nitrate to <3 ppm in average and high-hydroxide) after three weeks. Zirconium exhibited a solubility of 1-16 mg/L in the three simulants.

These results are highly significant because they indicate that the simulants used in virtually all of the experiments with CST are metastable with respect to precipitation of aluminosilicates. Therefore, the deposition of the aluminosilicates on CST particles observed in experiments on the chemical and thermal stability of CST may or may not have any significance with respect to tank waste. The equilibrium state of tank waste should be determined in order to evaluate whether deposition of aluminosilicates represents an actual risk to using CST Non-Elutable Ion Exchange. In addition, the thermodynamic equilibrium calculations can be used to devise a dilution strategy for the tank waste that will create stable solutions.

7.2.3.4.2 FY01 – Current Work

Thermodynamic calculations. ORNL is continuing to build and verify the SolGasMix model in FY01. SRS is working with ORNL and using the ORNL SolGasMix software model to propose feed specifications and a dilution strategy that will create stable conditions in the tank waste.

The dilution strategy and the accuracy of the SolGasMix software model requires experimental confirmation. This is being accomplished at SRS using simulants and radioactive waste samples. SRS will test simulant and real waste samples for precipitation of solids to verify the proposed dilution strategy. SRS simulants are being evaluated for Al and Si content and method of preparation (e.g., heat treatment). The contribution of these factors to post-precipitation and/or CST fouling/resorption problems is being determined. A report on this topic is being prepared.

Studies of waste and simulant precipitation are continuing at ORNL. Thermodynamic equilibrium modeling calculations are continuing in order to expand the understanding of precipitation in waste solutions. Laboratory confirmation tests will be carried out at ORNL after review and approval by SRS. A report summarizing the results of the thermodynamic calculations will be published.

Real waste tests. The kinetics of Cs removal from real waste are being measured by taking tank waste samples at given time intervals and measuring the Cs uptake. Two simulants (UOP and SRS average) are being used as controls. A report on Cs sorption from real waste will be published.

SRS will test five waste samples from different waste tanks during FY01. Tests will yield equilibrium and kinetic data for sorption of Cs on CST in a variety of waste compositions. Ion exchange column sizing and process simulations rely on two computer models. The ZAM model for CST predicts equilibrium sorption isotherms for Cs in waste solutions. A second model uses the ZAM equilibrium data and kinetic information to predict column breakthrough curves. Both models require confirmation against SRS radioactive waste. SRS successfully completed a small-scale ion-exchange column test in FY99 using Tank 44F waste. This test confirmed the length of the mass-transfer zone for a waste composition with high hydroxide concentration. SRS will run another small-scale ion-exchange column tests using either a sample of the re-engineered UOP resin (if available) or using radioactive waste with a composition significantly different from Tank 44F high hydroxide waste (i.e., average waste or high nitrate waste). A report on these studies will be published.

7.2.3.5 Revised Manufacturing Process (CST SOWM 2.1)

7.2.3.5.1 FY00 – Results

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

Results from experiments with the engineered form (IE-911) of the CST crystals (IE-910) clearly indicated that excess materials of manufacture, i.e., Nb and Si, are leached from the particles by the highly alkaline simulants (see previous results in this section). In addition, lot-to-lot variability in the Cs-sorption capacity was noted (see results for Column Performance). Therefore, discussions with UOP LLC were held to determine a path forward to develop an ion-exchange material that could be used with less risk of column plugging or low Cs-sorption capacity.

A contract was signed with UOP to revise the manufacturing process. The contract calls for the elimination of excess materials of manufacture and reduction of the lot-to-lot variability. UOP proposed removing excess materials by post-treatment of IE-911 and reducing lot-to-lot variability by closer control of the manufacturing parameters.

7.2.3.5.2 FY01 – Current Work

Collaboration with UOP to develop an engineered form of CST (IE-911) compatible with SRS waste is continuing in FY01. A schedule for production of test batches of reformulated materials and for holding project review meetings is being followed. Product specifications (target definition) have been defined and agreed to by WSRC. Updates on pretreatment work at SNL are provided to UOP in order to optimize their efforts.

The CST manufacturing process comprises four steps: synthesis of IE-910; post-treatment of IE-910; manufacturing of IE-911; and post-treatment of IE-911. The UOP contract calls for the production of a reference batch of IE-911 against which all subsequent batches will be compared. Manufacturing parameters were tightly controlled during the preparation of the reference batch. In addition, a reference batch of IE-910 will be produced.

Initial efforts to improve IE-911 by UOP are focusing on the post-treatment step. The goal is to reduce the quantity of leachable components from the product. Details of the steps taken by UOP to accomplish this goal are not available due to UOP concerns about the proprietary nature of their work. A test batch of 100 g will be sent to SRTC in mid-November 2000, and will be examined using the methods described in other sections of this plan.

After evaluation of the test batch, a pre-production batch of IE-911 will be produced by mid-December 2000, in sufficient quantity that ORNL, SNL, and PNNL will be able to characterize the material using the methods that have been described in previous parts of this section. The final deliverable in the contract, a 2,000-lb batch of the improved material, will be supplied if the test results indicate that the quality and properties of the material are satisfactory for further testing.

The results of these tests will determine if UOP has produced a material that can be used in the ion-exchange columns with a minimum of pretreatment at SRS. The leaching of Nb from the IE-911 is a necessary step owing to the conditions under which IE-910 must be synthesized. Whether the excess of Nb is leached from the IE-911 at UOP or at SRS is the essential issue. Considering the relative costs of performing operations at UOP or SRS, the willingness of UOP to perform this process at their facility greatly enhances the attractiveness of using IE-911 for CST Non-Elutable Ion Exchange.

7.2.4 Gas Generation (CST SOWM 3.2, 8.3, 8.4)

7.2.4.1 Previous Results

A previous study[50] measured the impact of CST solids on the rate of formation and composition of radiolytically generated gases in simulated SRS liquid waste. The tests used IE-911, the engineered form of CST. The test results showed that radiolytically generated gas bubbles form rapidly at expected process dose rates. Bubbles near the surface of the resin bed can move by displacing IE-911 particles.

Irradiation of IE-911 slurries produced oxygen, hydrogen, and nitrous oxide (N_2O). Oxygen is the major product from irradiation of high-nitrate waste whereas hydrogen is the major product from irradiation of high-OH waste. High-nitrate waste solutions yield the largest gas generation rates. Researchers measured total radiolytic gas generation rates lower than those used in a preliminary gas generation calculation[51] for a full-scale process column. The previous calculation for total gas generation remains bounding because test results showed less oxygen formation (G values up to 0.15 molecules/100 eV) than assumed in the calculation (0.3 molecules/100 eV). Since the high radiation field associated with a loaded column will originate from approximately 5 MCi of Cs-137 per column, a gas generation rate of approximately 35 L/h is expected.

Additional work investigating the effect of gas generation was performed on a larger scale. To conduct the gas behavior test, a method to simulate radiolytic gas generation in the CST column was developed. After evaluating several alternatives, oxygen production by the decomposition of hydrogen peroxide was selected. Hydrogen-peroxide decomposition-reaction rate data needed to plan the tall-column gas tests were determined from batch and small-column laboratory experiments. In addition to catalyzing the hydrogen peroxide decomposition reaction, CST also absorbs hydrogen peroxide. Titanium stabilizes hydrogen peroxide. Fortuitously, this method not only simulates gas generation, it also allows simulation of the gas generation front movement due to Cs loading in an actual system by the movement of the peroxide wave front as it loads on the CST. In the course of the laboratory studies, it was determined that peroxide leaches metals from the CST. These findings may have implications in an actual system, since one of the products of radiolysis is hydrogen peroxide, although it is present at extremely low levels (approximately 10^{-6} M, see Refinement of the Model, 7.2.2.1.2).

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

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

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

7.2.4.2 Gas Disengagement (CST SOWM 8.3, 8.4)

7.2.4.2.1 FY00 - Results

Indications that gas generated in the column escapes through the bottom of the column without causing flow disruptions led to a shift in the emphasis of gas generation research to address the hydraulic aspects of gas disengagement. Tall-column apparatus at ORNL was modified to test prototypical equipment to perform gas disengagement experiments. Locally designed equipment was fabricated and installed for this purpose. The use of hydrogen peroxide for non-radioactive examination offers potential benefits over a radioactive test.

The existing pilot-scale tall column that was used in FY99 to evaluate CST physical stability, CST handling properties, and gas behavior was fitted with gas-disengagement equipment for FY00 testing. ORNL modified and improved the tall-column design characteristics to adapt it for this task. The CST fixed-bed support screen (Johnson) design was improved to better simulate full-scale flow-through column operation. Instrumentation and control systems were slightly modified and upgraded. Column-effluent piping was modified for installation of the gas-disengagement device, supporting FY01 testing and operations under various conditions to evaluate the performance of the device.

7.2.4.2.2 FY01 - Current Work

The gas-disengagement equipment (GDE) is being installed on the existing CST tall-column unit at ORNL for the purpose of removing free gas generated during tall-column testing. The system is designed to operate under varying conditions to establish operating envelope and performance requirements for the CST process. In order to monitor gas generation sufficiently, system process dynamics were previously modeled to properly size valves and ensure that the control strategy allowed for system robustness and disturbance rejection.

The main components of the GDE are a gas-disengagement chamber, a venturi vacuum pump, a system for vapor sweep/sparging, a process pump, and ultrasonic equipment. The gas-disengagement chamber provides the location for free gas disengagement. The venturi vacuum pump provides gas evacuation during GDE operation at or below atmospheric pressure. It is bypassed at pressures greater than atmospheric. The vapor sweep/sparging provides a supply of air or nitrogen to remove the free gas from the simulant during GDE operation. The air or nitrogen introduced into the sparger also assists in the coalescence of smaller bubbles of insoluble gas and the stripping of soluble gas. The process pump maintains the liquid level in the gas-disengagement chamber at or below atmospheric pressure. It may be bypassed during testing at pressures greater than atmospheric. The ultrasonic transducer with acoustic horn and sine generator provides cavitation of the simulant to facilitate the removal of free gas.

Instrumentation and controls (I&C) equipment and materials are comprised of distributed modular microprocessor-based controllers compatible with the existing tall-column communication network (LabVIEW). The GDE also contains a thermocouple, liquid and air flowmeters, pressure and level indicator, pressure transducer, level measurement sensor, flow-control valves and level switch.

Operation of the gas-disengagement chamber will follow one of three modes. Modes A and B involve the simultaneous control of both sweep/sparge air through the chamber vapor space and liquid level control in the chamber. Mode C involves bypassing the gas-disengagement chamber altogether so that no control issues exist. The method of liquid level control differs drastically between Modes A and B. The control of sweep and sparge air differs slightly between Modes A and B.

Results from the ORNL tests will be provided to the SPP team for inclusion in a final report. The results are expected to demonstrate that disengagement of gas between ion-exchange columns can be achieved. Therefore, accumulation of gas at the top of the second (middle) and third (guard) columns is not expected to be an issue during operation of the CST-column carousel. This also is expected to resolve the issue of accumulation of a potentially explosive gas mixture at the top of the columns.

7.2.4.3 Cs Loading Under Irradiation (CST SOWM 3.2.2)

7.2.4.3.1 FY00 - Results

An overall technical understanding of the CST Non-Elutable Ion Exchange process is needed to design, construct, and deploy a full-scale facility for treatment of high-level salt waste. One concern associated with deployment of CST is the effect of gas generation from radiolysis of water within the operating CST flow-through column. Calculations and testing were performed in FY00 to determine the effect of gas generation on the performance of CST in a flow-through column.

SRTC and ORNL collaborated to study the effect of radiolytic gas generation on the Cs-removal performance of CST. The calculation of gas generation in large columns was improved. The rate and location of bubble formation during Cs loading was defined. Diffusion rate of gases out of CST particles was estimated and compared with experimental results. The calculations indicated that the formation of gas bubbles within the small pores of CST (i.e., intraparticle bubble formation) is not likely.

Batch tests performed by SRTC in FY99 indicated that a loss of CST capacity can be expected when irradiated under expected conditions. Additional testing examined this aspect of Cs-removal performance in the presence of gas generation. A spent-fuel element in the HFIR pool was used for a radiation exposure test. This test measured a number of attributes, including Cs absorption in the presence of a radiation field and the rate of gas generation. A team of researchers from SRTC and ORNL examined the results of each test.

A test capsule containing a small flow-through column packed with ~20 mL of CST was designed and fabricated for insertion and irradiation in a spent fuel element of the HFIR test facility. The column was connected to simulant feed and coolant transfer lines routed vertically upward through and out of the pool via an access port to the feed station transfer pumps and holding vessels. Simulant containing non-radioactive Cs was pumped to the CST column using low-pulsation gear pumps in order to load the Cs onto the CST. The radiation dose received by the column of CST was representative of that expected for treatment of SRS HLW supernate. The test system was designed for continuous feed of simulated HLW supernate containing nonradioactive Cs and included a cooling system to maintain the temperature of the column below 35ºC. The coolant (ethylene glycol solution) was chilled and transferred to the column using gear pumps. Samples of the supernate were collected every 4 hours for Cs analysis and a Cs-loading curve was generated from the data. The loading curve was compared to baseline column performance data to determine the effect of radiolytic gas generation on CST loading capacity and mass-transfer zone length. The results indicated no significant effect of the radiation field on Cs loading. The performance of this column system was carefully characterized under a range of operating conditions subsequent to the irradiation.

SRS completed an interim report on the gas-generation calculations including temperature effects on Cs loading. SRTC published two reports documenting their work on the gas generation activities.[52,53]

The results of gas generation tests clearly indicate that gas generation within the CST column does not affect Cs sorption. The sorption closely follows predictions using the VERSE model and sorption measured outside of the radiation field. Thus, CST columns loaded with megacurie quantities of Cs are expected to perform within the baseline requirements.

7.2.4.3.2 FY01 - Current Work

Results from the gas generation experiments conducted in FY00 will be documented in a report. In addition, a final report on the gas-generation calculations is being prepared. The report will include temperature effects on Cs-loading under irradiation.

The test equipment - including the simulant delivery system, the coolant lines, and the moisture detection system - is being decontaminated before removal from the HFIR building for subsequent storage. The equipment will be prepared for storage in such a manner that it can be used again should the need arise after down select.

7.2.5 CST Hydraulic Transfer (CST SOWM 19.1, 19.2, 19.4)

7.2.5.1 Previous Results

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

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

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

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

Prior to sluicing the CST from the column, the supernate simulant in the column was displaced with 2 M NaOH. Then the NaOH was displaced with deionized water. Water, rather than supernate simulant, was used to sluice the CST in order to facilitate handling of the spent CST. The two-step displacement process was used to avoid possible precipitation of $Al(OH)_3$ from the supernate simulant as the pH of the solution was lowered during mixing with the water.

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

Another aspect of DWPF operation is accurate slurry sampling using the Hydragard® sampler. The particle size of the as-received CST ranges from 200 to 800 microns, significantly larger than the borosilicate glass formers (frit, ~170 microns). This raises two technical issues regarding homogeneity and sampling of CST slurries of DWPF. A series of tests were conducted to address these issues.[54] Four tests used batches of aqueous slurries of 10 wt% CST and the remaining tests used three different batches of sludge-based slurries.

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

The CST has been engineered into material with an average particle diameter of around 500 microns for use as packing in the ion exchange columns. Smaller particles would give excessive pressure drop through the column. However, as noted above, preliminary testing[26] has shown that the DWPF Hydragard® valve is not capable of sampling sludge with as-received CST. Previous work during the DWPF startup configured the Hydragard® sampling system to accurately sample sludge with frit particles that are nominally about 175 microns in diameter (acceptable size range 80-200 mesh). Therefore, it is assumed that if the CST particles can be reduced to the size of frit particles or smaller they will be representatively sampled by the Hydragard® system.

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

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

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

A kinetic grinding system from Micro Grinding Systems, Inc. (located in Little Rock, Arkansas), was one of the most promising technologies identified for reducing particle size of 105-K East

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

7.2.5.2 Develop And Test Size-Reduction Method (CST SOWM 19.2)

7.2.5.2.1 FY00 - Results

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

The FY00 CST equipment tests ground approximately 50 pounds of solids. With the IKA equipment, a nominal 10 wt% slurry was used as feed. About 50 gallons of slurry were produced at 10 wt%. This provided sufficient data for a preliminary evaluation of the equipment. SRTC personnel observed the test and made a subjective evaluation of equipment operability. The size distribution of the ground CST was determined. About 5% of the CST appeared to pass unchanged through the equipment.

Because the Micro Grinding system is most efficient at higher slurry concentrations, it was not possible to test a 10 wt% slurry on this equipment. The vendor was consulted and their experience with WVDP zeolite was used to estimate the desirable slurry concentration. Preliminary indications were that 50 pounds of CST should provide sufficient material for a test grind. The test was conducted successfully.

Size-reduced CST from both tests was returned to SRTC for evaluation of mixing, settling and resuspension characteristics. The material is also available to make additional melter feed slurries that can be used to help determine the cause for previous non-representative sampling. Resuspension and homogenization of size-reduced CST could also be investigated.

WSRC issued a report on the results of the CST size reduction work.[55]

The results of these preliminary experiments give a clear indication that size-reduction of CST particles presents little risk to their use. According to data, it should be possible to reduce the size of CST particles so that homogeneous slurries can be produced and sampled representatively.

7.2.5.2.2 FY01 - Current Work

Vendor tests completed in FY00 provided results demonstrating that CST can be reduced to a size comparable with the frit or sludge particles. On this basis, no further work in this area is planned for FY01.

7.2.5.3 Develop Representative Sampling of CST/Sludge/Frit Slurry (CST SOWM 19.1)

7.2.5.3.1 FY00 - Results

Operation of the Hydragard® sampler with slurries of size-reduced CST was compared to operation with sludge/frit slurries in order to determine minimal size distributions for adequate CST slurry sampling. Samples taken by the Hydragard® sampler showed a bias toward low frit with or without size-reduced CST present. Thus, the operation of the Hydragard sampler itself will be re-assessed. However, it was concluded that CST was sampled the same as sludge and that a representative sample would be obtained in the DWPF.

During the FY00 study of Hydragard® sampling of melter feed slurry containing CST it was observed that a slurry containing 52 wt% total solids could not be adequately mixed in the 1/240th scale DWPF tank. This slurry, containing 10 wt% CST on an oxide basis in the glass product, appeared to be unusually thick. Historically, DWPF melter feed slurry is typically in the range of 48 to 50 wt% total solids with a maximum observed value of 53 wt%. If melter feed containing CST can not be similarly concentrated, DWPF glass production rates will be reduced. The rheology of melter feed slurry is known to be a strong function of the insoluble solids content.

7.2.5.3.2 FY01 - Current Work

Results of the Hydragard® sampling activities in FY00 will be published in a report in FY01.

7.2.6 Coupled DWPF Operation (CST SOWM 20.0)

7.2.6.1 Previous Results

Processing within the DWPF would include the addition of sized-reduced IE-911 loaded with Cs to the sludge/frit slurry prior to vitrification. This addition would occur in the Slurry Receipt Adjustment Tank (SRAT). The DWPF process then adds chemicals – including formic acid – to adjust the redox potential of the mixture. The presence of noble metals catalyzes the formation of hydrogen gas, which poses a safety control concern for operations. The total gas release also can promote foaming in the process vessels. Little information existed on the ability of IE-911 to sorb noble metals and alter the amount of gases formed. Hence, personnel conducted process simulations at bench scale and at small pilot scale (1/240th DWPF) to examine this risk.[56,57]

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

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

7.2.7 DWPF Melter Operations

7.2.7.1 Glass Titanium Loading (CST SOWM 17.0)

7.2.7.1.1 Previous Results

A variability study addressing the compositional changes in sludge and frit was examined with a statistically designed approach.[58] The sludge, frit and CST loading were varied in order to assess the operating window for glass composition in DWPF. The existing models were used to predict the processing and product properties for each of the compositions. Due to the large difference in composition, it was unclear whether the models were applicable in this compositional region.

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

In this phase of research, twenty-two glasses containing Purex sludge and three glasses containing HM sludge were fabricated and tested.[59] The fabricated glasses were tested for durability using the 7-day PCT and characterized by measuring the viscosity at 1150°C and by determining an approximate, bounding liquidus temperature. The current models used by DWPF for predicting durability, viscosity, and liquidus temperature were applied to all 25 glasses. The goal of this work was to identify any major problems from a glass perspective, within the scope of this effort, which could potentially preclude the use of CST at DWPF. As part of this study, product and property model predictions were made using targeted, measured, and bias-corrected measured compositions of the glasses. It was demonstrated that the results were essentially insensitive to the type of composition used in these models. This provides evidence that the glasses produced were close to the targeted compositions and that the analytical measurements were of high quality.

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

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

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

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

7.2.7.1.2 FY00 - Results

No work in this area was conducted in FY00.

7.2.7.1.3 FY01 - Current Work

In the area of glass studies, the NRC report, "Alternatives for High-Level Waste Salt Processing at the Savannah River Site", lists the influence of glass formulation with higher titanium loadings on waste form performance as a key issue requiring resolution if CST ion exchange were implemented at SRS. In order to resolve this issue, additional studies on centerline cooling are needed to ensure that deleterious phase separation of the CST glasses (as detected by PCT releases) does not occur. These data could also be used should it become necessary to qualify a waste form with a titanium content greater than that now contemplated.

The workscope in this area will include the following tasks: (1) select, batch and melt ~15 glasses for the CST option; (2) rapidly quench the glasses; (3) canister centerline cool (ccc) a portion of each glass; (4) measure the chemical composition of all the glasses; (5) perform the PCT test on all of the quenched and ccc glasses; (6) XRD and SEM on glasses, as necessary; and (7) compare the PCT results of quenched and ccc glasses.

The results of these studies will determine if glass that meets the PCT requirements can be formed from slurries containing CST.

7.2.7.2 Feed Homogeneity (CST SOWM 19.0)

7.2.7.2.1 Previous Results

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

The DWPF melter receives feed from the Melter Feed Tank (MFT). The HLW aqueous slurry in the MFT is pumped through a recirculation loop and a portion of this aqueous slurry is diverted to the melter through a slotted aperture (at a rate of ~1 gpm). In order to produce an acceptable glass product, it is essential that no segregation of any of the feed components occurs using this melter feed system (i.e., the chemical composition of the MFT should be the same as the composition of the feed stream that enters the melter).

7.2.7.2.2 FY01 – Current Work

Because the CST melter feed slurry was first prepared in 1999 and has been used for several Hydragard® tests, it was determined that the best way to obtain representative rheology measurements was to prepare fresh slurry. Because a relatively small amount of material is required for rheology measurements, the preparations can be done on a bench scale (3 to 4 L). In FY01, three bench-scale batches of melter feed slurry will be prepared. One batch will contain 10 wt% CST, size-reduced to less than 177 µm. A second batch will have 10 wt% CST, size-reduced to less than 20 µm. A control batch that does not contain CST will also be prepared. Each batch will contain the same amount of sludge. The sludge used in these tests will be a recently prepared simulant of DWPF Batch 3 sludge. The rheological properties (yield stress and consistency) of these slurries will be measured over the range of total solids from 40 to 50 wt% in 2 wt% increments.

These experiments will provide a sound basis for determining if the presence of CST particles in melter feed slurry has an impact on slurry rheology and thereby imposes an additional operating constraint on the DWPF process.

7.3 Caustic Side Solvent Extraction

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

The CSSX process utilizes a novel solvent made up of four components: calix[4]arene-bis-(*tert*-octylbenzo-crown-6) known as BOBCalixC6; 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-secbutylphenoxy)-2-propanol known as modifier Cs-7SB; trioctylamine known as TOA; and Isopar® L, as a diluent. The solvent is contacted with the alkaline waste stream in a series of countercurrent centrifugal contactors (the extraction stages). The resulting clean aqueous raffinate is transferred to Saltstone for disposal. Following Cs extraction, the solvent is scrubbed with dilute acid to remove other soluble salts from the solvent stream (the scrub stages). The scrubbed solvent then passes into the strip stages where it is contacted with a very dilute (0.001 M) acid stream to transfer the Cs to the aqueous phase. The aqueous strip effluent is transferred to the DWPF.

The basis and composition of the waste simulant to be used in all CSSX testing are described in an SRS position paper.[60] 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 real 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.

7.3.1 R&D Roadmap Summary – Caustic Side Solvent Extraction

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

The Science and Technology Roadmap (Figure 7.3), a subset of the overall Salt Disposition Project roadmap, defines needs in the following three basic categories:

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

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 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, material of construction and operational parameters such as pressure drop and requirements for temperature control. A key deliverable for this phase is demonstrating that the individual components will function as intended in support of establishing the design input for the final design stage of the project.

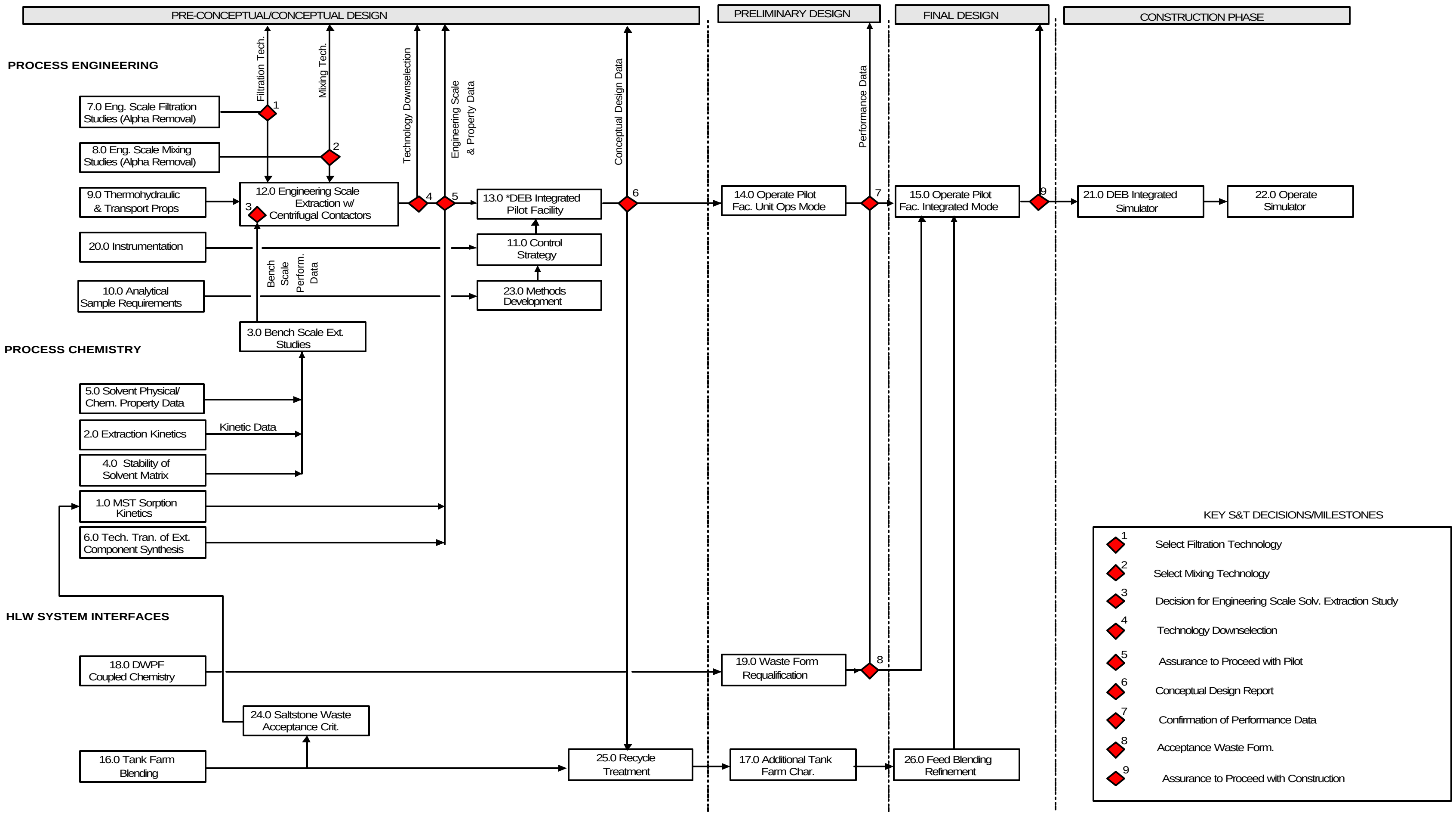
Integrated pilot facility operations will be completed during final design to confirm operation under upset conditions to establish the limits of operation and recovery, the limits of feed composition variability, and confirm design assumptions. This testing directly supports development of operating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

Additional development and testing during the conceptual design phase will help assure proper feed and product interfaces of the CSSX process with the HLW Tank Farm, DWPF and Saltstone Facility. The issues of concern include assurance of glass, waste feed blending and characterization and waste acceptance.

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

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

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



*DEB = Design, Engineer, and Build

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

7.3.2 Solvent Preparation (CSSX SOWM 3.1.3, 3.2)

7.3.2.1 Previous Results

The initial solvent optimization work was completed as a part of the work conducted in FY98 as a segment of the Alternative Salt Disposition Program. The optimum solvent at that time was chosen to be the BOBCalixC6 (previously described), a modifier, 1-(1,1,2,2-tetrafluoroethoxy)-3-[4-(t-octyl)phenoxy]-2-propanol, designated as Cs-3, and the diluent Isopar® L. A complete description of this work is found in the report by Moyer, et al.[61] Work during FY98 indicated that the Cs-3 modifier showed significant chemical and some radiolytic decomposition.[62] Work was conducted at ORNL to develop a more stable modifier. A “second generation” of more stable modifiers was prepared, of which the best performing member was 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, abbreviated Cs-7SBT. In addition, previous work indicated that either cold Cs may have to be added to the strip stream or TOA be added to the solvent matrix to maintain the stripping efficiency.[61] Adding cold Cs was not desirable. Subsequent work has demonstrated that the TOA addition to the solvent matrix results in more effective stripping with impurities present.[63]

The synthesis of BOBCalixC6 was developed at ORNL. Using the synthetic procedure developed at ORNL, IBC Advanced Technologies, Inc., American Fork, UT successfully filled several orders at the level of 2 – 50 grams in FY98 and FY99. The material was delivered on schedule and was of high purity.

7.3.2.2 FY00 - Results

In order to standardize the solvent matrix used in the FY00 CSSX program, all of the solvent was prepared by ORNL. The primary work in FY00 involved synthesis of the modifier and preparation of the required solvent for all R&D work conducted in FY00. This included the purchase of additional extractant and the chemicals required for modifier synthesis. This also included optimization of the synthesis of modifier Cs-7SB, which is a purer version of Cs-7SBT, at multi-kilogram scale. ORNL also developed a QA procedure to ensure the effectiveness of solution performance in batch tests.[64] See Section 7.3.8 for information related to solvent commercialization activities.

7.3.2.3 FY01 - Current Work

In FY01, the ORNL team will prepare about 20 L of solvent to support the testing of CSSX at ANL, ORNL, and SRTC. Such testing will include flowsheet performance using both simulants and real waste in a 32-stage centrifugal contactor cascade. It will also include tests aimed at studying solvent stability and physical properties. If necessary, additional BOBCalixC6 will be purchased. Modifier will either be synthesized or purchased from a custom-synthesis supplier, depending on schedule demands. It is anticipated that solvent required early in FY01 will be prepared at ORNL, and that solvent required later in FY01 will be prepared commercially. However, sufficient modifier will be prepared at ORNL to satisfy all solvent needs. ORNL will prepare the solvent, wash it, perform batch QA tests, and assess purity by NMR and other means (e.g., ES-MS) as necessary. Based on stability and physical property data, additional optimization of the solvent matrix may be completed, if required. This includes the possibility of raising the concentration of the modifier and changing the concentration of the BOBCalixC6.

7.3.3 Batch Equilibrium With Internal Irradiation Of Solvent (CSSX SOWM 4.1.1, 4.1.2)

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

7.3.3.1 Previous Results

SRTC personnel performed a test to determine the extraction, scrubbing and stripping performance of the solvent system with a sample of SRS high level waste. This test employed two extractions, one scrub and three strip contacts. Cesium distribution coefficients for each of these contacts were determined. The distribution coefficient for extraction exceeded 11, versus the design basis value of 8. In addition, the stripping distribution coefficients proved less than 0.1, again an improvement over the design basis value of 0.2.

A number of limitations existed in the tests described above. These tests did not identify any minor components extracted by the solvent system. In addition, as has been previously reported, the solvent has been modified to include a new modifier compound.[65] Also, no attempt was made to determine the impact of self-irradiation of the samples. Furthermore, the testing only explored the performance with waste material from a single source.

7.3.3.2 FY00 - Results

Exposure tests to determine the impact of internal radiation on the solvent were initiated in FY00 at both SRTC and ORNL. The SRTC internal exposure test used HLW while the ORNL internal exposure test uses the average SRS waste simulant spiked with Cs-137. The ORNL and SRTC experimental protocols mirrored each other so that direct comparisons could be made between the simulant and the real waste test data.

SRTC acquired samples from 5 different HLW tanks. Characterization of the samples and batch equilibrium contact protocols were initiated.

SRTC developed and implemented an HPLC technique for measuring the solvent components; this methodology was transferred to ORNL.

The ORNL internal exposure tests used a simulant solution spiked with Cs-137. Experimental test plans were developed and approved.[66] The experiment was set up in hot cells of the Radiochemical Materials Analysis Laboratory. All sample preparations were completed, and the exposures initiated.

ORNL completed dose calculations applicable to the irradiation experimental conditions and to the centrifugal contactor cascade in the proposed process plant. Preliminary results indicated the solvent will receive an annual dose 92K Rad per year assuming 100% plant utilization and the baseline solvent inventory of 1000 gallons. The relatively low dose is the result of the short residence time (~ 8% of the solvent inventory is in the contactor cascade during operation) of the solvent in the centrifugal contactor cascade, the large inventory of solvent in the plant, and Cs-137 and Ba-137m are the nuclides contributing to the solvent dose, assuming the CSSX feed was subjected to the MST Sr and alpha removal process. The dosimetry report is currently undergoing technical peer review; the final report will be published during the early part of FY01.

7.3.3.3 FY01 - Current Work

This task addresses activities related to the investigation of the effect of internal irradiation on the solvent. The ORNL test uses solvent loaded with Cs-137 from the SRS average simulant. Irradiation of the samples initiated in FY00 will continue into FY01, and the sampling and analysis protocol will continue so as to obtain data ~ 100 - 400% above the expected annual dose the solvent will receive in the proposed process plant.

The tests involve exposing the solvent to internal radiation from Cs-137 while undergoing continuous agitation (see Reference 66). The organic to aqueous phase ratios agree with the latest version of the baseline process flowsheet and represent the current standard test conditions within the program for the extraction, scrub and strip elements within the flowsheet. The single-contact Cs-137 phase distribution material for all of the batches was prepared in a large batch, with subsequent sub-dividing of the phase quantities into individual bottles. This approach was taken to help minimize preparation variations among the batches as one source of experimental error.

At selected time intervals, a set of containers (a control using non-radioactive Cs in the simulant, and samples containing Cs-137 in the simulant) will be removed from the agitation apparatus and subjected to the evaluation protocol. The solutions will be visually inspected and the phase separation time will be determined. After the phases have been separated, the organic and aqueous portions will be analyzed for Cs content (allowing a calculation of D_{Cs}), solvent components, and solvent decomposition products to yield information as a function of dose. Dose calculations for the specific geometry of these irradiations were completed in FY00. The tests is being conducted at ambient temperature, which is being recorded with a computer based data acquisition system.

The experimental results will be summarized in an ORNL technical memorandum report. Upon completion of the experimental plan, effort will be devoted to waste disposal and returning the hot cell to its condition prior to initiation of this task.

SRTC will investigate the impact of radiation dose received from real waste on solvent performance using the samples acquired in FY00. The tests will examine the impact of dose on the extraction, scrub, and strip stages of the process. The extent of loss of key solvent components will be determined and solvent samples will be further examined to determine if any degradation products increase the removal of secondary radionuclides. The test protocol mirrors the ORNL simulant test described in Reference 66.

The results from the SRTC experiments will be published in a report during the 2nd quarter of FY01.

7.3.4 Batch Equilibrium With External Irradiation Of Solvent (CSSX SOWM 4.1.1)

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

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

7.3.4.1 Previous Results

External radiation testing was conducted at SRTC during FY98 as a part of the Alternative Salt Disposition Program and is described completely in Reference 66. Results from these experiments indicated the modifier Cs-3 degraded approximately 3% and the extractant only 1% relative to their original concentrations over the test period in which the solvent accumulated 27 Mrad of dose. These experiments indicated no significant impact on stripping, extraction, or scrubbing from the irradiation. Test results indicated that the cesium distribution coefficient for stripping became unacceptable above 4 Mrad dose.

7.3.4.2 FY00 - Results

The preliminary tests described above were performed with simulated waste solution. These preliminary tests determined the susceptibility of a calixarene-based solvent system to radiation damage.[67] A number of limitations existed in these preliminary tests; the solutions were not continuously agitated, and irradiation exposure only occurred in the presence of simulated waste solution. In addition, the solvent matrix has since been modified by the introduction of a new modifier compound. Therefore, SRTC explored the stability of the new solvent system under a complete range of conditions representative of the expected conditions in the proposed process. These tests examined the impact of the following variables: modifier alkyl group structure, diluent, and mixing.

Four different solvents were studied in these experiments. All of these solvents employed calix[4]arene-bis(t-octylbenzo-crown-6) (BOBCalixC6) as the extractant and trioctylamine. One solvent included the proprietary Cs-7SB modifier, and Exxon Isopar® L as diluent. Another solvent included the related Cs-7SBT modifier and Isopar® L. A third solvent included the proprietary Cs-6 modifier and the Exxon Norpar® 12 diluent, and a fourth solvent employed the Cs-6 modifier in Isopar® L. During the tests, the Cs-6 modifier was found to form a sparingly soluble crystalline dihydrate, and the two Cs-6 solvents were therefore not irradiated.

These tests involved exposing the Cs-7SB and Cs-7SBT solvents to external radiation from a Co-60 gamma source with the samples continuously agitated. Each of the O/A ratios present in each test represented the O/A ratio anticipated in the proposed process. Each extraction test employed approximately 25 mL of solvent (with measurements performed in triplicate) while the tests with the scrub and strip solutions employed 50 mL of solvent. The Co-60 source was cooled. Previously, the lack of cooling has limited experimental temperatures to 30 - 40°C.

At the completion of each irradiation cycle, the samples were analyzed. Analyses included the determination of the D_{Cs}, measurement of the concentration of the various solvent species, and determination of the concentrations of any detectable degradation products. Analyses occurred in parallel at both SRTC and ORNL.

No significant degradation of the primary solvent components was observed for doses typical of the proposed facility lifetime. Less than 10% BOBCalixC6 loss occurred at doses up to 16 Mrad. No statistically significant loss of Cs-7SB modifier occurred at dose of 16 Mrad. Less than 10% of the TOA degraded at a dose of 6 Mrad. At 16 Mrad the concentration of 4-*sec*-butylphenol was ~0.4% of the initial modifier concentration.

The only significant decomposition product identified was 4-*sec*-butylphenol, an expected decomposition product from the modifier. It was readily removed from the solvent by contact with a NaOH solution. Batch testing did not indicate any problems with extraction, scrubbing, or stripping at radiation doses noted above.

7.3.4.3 FY01 - Current Work

Results obtained in FY00 on the SRTC-batch external irradiations will be described in a report scheduled for publication in early FY01.

This subtask is a continuation of work initiated during FY00 at SRTC that will be continued at ORNL in FY01. External irradiation studies using a Co-60 source will focus on issues related to solvent washing and reconstitution. Specific activities will be defined early in FY01 based upon the information obtained from FY00 chemical and thermal stability studies. The impact of radiation-induced solvent decomposition will be determined, and methods to remove compounds deleterious to the solvent performance will be evaluated.

7.3.5 Solvent Physical and Chemical Properties (CSSX SOWM 5.0)

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

Research and development activities in this area involve numerous studies, each with a specific goal. The element of continuity within this research is the collection of the body of information necessary to define and understand the solvent physical and chemical properties. The following subsections contain information for the various studies.

7.3.5.1 Previous Results

7.3.5.1.1 Chemical Stability (CSSX SOWM 4.1)

No degradation of the BOBCalixC6 was observed following continuous contact with alkaline high nitrate simulant for up to 570 hours at 53 ± 2ºC. However, the Cs-3 modifier was degraded by 50%, causing a reduction in the D_{Cs} on extraction. The D_{Cs} on stripping was observed to increase slightly. The Cs-3 degradation products were unidentified, and cannot be washed out with 0.5 M NaOH. However, their presence did not strongly impair the functioning of the solvent. Refreshing the degraded solvent by replacing the Cs-3 modifier that was decomposed with fresh Cs-3 results in a near restoration of the D_{Cs} obtained on extraction and scrubbing with pristine solvent. However, the D_{Cs} on stripping were somewhat higher than those obtained for the pristine solvent control.

By NMR, the solvent appears to be stable after up to 43 days of continuous contact with 50 mM nitric acid scrub solution at 53 ± 2ºC. No degradation of either the BOBCalixC6 or the Cs-3 modifier was observed.

Stability studies conducted at 25ºC between the solvent and the high nitrate simulant reveal the same type of degradation as observed at 53ºC, only at a much slower rate. The solvent retained 88% (D_{Cs} = 10.52 vs. 11.93) of its extraction power after 360 hours continuous contact at 25ºC, and 80% (D_{Cs} = 9.575) after 648 hours (27 days) continuous contact.

7.3.5.1.2 Feed Impurities (CSSX SOWM 5.2)

Researchers at ORNL[68] prepared simulated salt solution containing 0.1 mM mercury, 0.1mM lead, 0.01 mM iron, and 0.011 M silicate. An additional test was performed using perchlorate concentrations up to 0.01 M. They contacted this simulant with the solvent system and measured the extraction, scrub and strip performance. The distribution coefficients for this simulant system proved statistically identical to those obtained from simple simulant systems that did not contain these impurities. In addition, measurements of the concentrations of these species in the scrub and strip solutions found no Al, Cr or Fe in the strip solution. A small quantity of Hg transferred to the strip solution but most of the Hg (80%) remained in the first scrub solution. In contrast, Al distributed in nearly equal amounts in the first scrub and the first strip solutions.

Testing at ORNL and ANL indicates that feed impurities can impact the stripping performance. One such impurity was identified as a surfactant mixture of undecyl- and dodecylsulfonate, common in detergents used to clean glassware. In FY98 and FY99, it was shown that addition of trioctylamine to the solvent nullifies the effect of traces of such detergent impurities. In addition, the surfactants were removed by washing the solvent with NaOH solutions.

7.3.5.1.3 Solvent Recovery (CSSX SOWM 5.1.1)

Researchers at ORNL determined the partition coefficients for the calixarene and the modifier when the solvent contacts various aqueous phases. The partition coefficient for the calixarene exceeded the detection limit of the test, which suggests the partition ratio is $> 10^6$. The partition coefficient for the modifier measured approximately 5×10^4 (i.e., less than 4 micromolar modifier in the aqueous phases). Based on these values, the proposed system would lose less than 15% of the low cost modifier and less than 1% of the calixarene per year of process plant operation. However, losses of the solvent due to entrainment of the solvent as fine droplets in the aqueous phases are expected to be much more important than partitioning losses. Thus, the question of solvent recovery remains an important one to resolve in FY01.

7.3.5.2 FY00 - Results

7.3.5.2.1 Phase Behavior of Primary Solvent Components (CSSX SOWM 5.1.1)

The solubility of BOBCalixC6 was measured as a function of modifier and amine concentration. This was done neat (in the pure form) and in the presence of flowsheet and other aqueous solutions. Third-phase formation was taken as a solubility limit for extraction complexes upon loading. The distribution of the primary solvent components to flowsheet aqueous phases and wash solutions was determined by contacting experiments followed by organic analysis by HPLC, NMR, or GC as appropriate. Although some sample analyses are still outstanding, the following conclusions are evident:

(1) BOBCalixC6 at 97% purity is soluble in the process solvent far above the needed concentration.

(2) Wet solvent is stable to solids formation down to 4°C for at least 2 months on standing. The modifer Cs-6 forms an insoluble solid dihydrate compound, eliminating it as a candidate modifier. Cs-7SB used in the baseline solvent shows no such susceptibility; this is thought to be a result of the multiple isomers that are present in Cs-7SB.

(3) The solvent is only susceptible to third-phase formation on extraction, primarily because of the loading of K, which leaves the solvent on scrubbing. Third-phase formation occurs at approximately 15°C using the full waste simulant. However, if the K concentration in the simulant is increased to the upper limit of its expected range,

third-phase formation can occur at approximately 20°C. Increasing the modifier concentration lowers the temperature for third phase formation. Blending of waste and implementation of the baseline process operating temperature range within the extraction segment of the cascade will prevent third phase formation.

(4) Distribution of the primary solvent components to the aqueous phase represents a negligible source of solvent loss.

7.3.5.2.2 Partitioning and Migration of Solute Species (CSSX SOWM 5.1.2)

FY00 experiments included the standard batch extract/scrub/strip contacting protocol. The objective was to learn how various inorganic and organic solute species partition between the solvent and relevant aqueous solutions, migrate through the flowsheet, and possibly accumulate in the solvent.

The major solvent degradation product, 4-*sec*-butylphenol, was examined, and easily washed out of the solvent by a NaOH wash following the strip section. All the major cations were included in the simulant and the trace metals. Major and important minor inorganic anions were examined. Distribution data were collected for the major and minor inorganic aqueous species in the solvent. K and Na are the ions primarily extracted from the full simulant.

Lipophilic organic anions were examined. These anions, such as dibutylphosphate and trace surfactants, may be present in the waste. Preventative or remediative measures such as solvent washing and anion exchange were investigated. Partitioning of anions to a range of alkaline or other wash solutions and to off-the-shelf or synthesized anion-exchange resins were systematically examined. Dibutylphosphate was shown to distribute partially into the solvent; however, it easily washed out with aqueous NaOH solutions. Surfactant anions extracted from the simulant were found to remain in the solvent through scrubbing and stripping. If allowed to build up past the ability of the trioctylamine to neutralize their effect; however, stripping will be degraded. Certain anion-exchange resins were found to be remarkably effective at removing the surfactant anions ($K_D > 1000$). Solvent washing will be examined more fully in FY01.

7.3.5.2.3 Effect of Major and Minor Components in Waste Feed (CSSX SOWM 5.1.5)

This work spans FY00 and FY01. In FY00, examination of the effect of lipophilic anions was initiated, as these directly influence extraction and stripping and pose a significant degree of process risk. Effect on Cs extraction performance, including selectivity, will be tested in FY01 using a standard batch extraction/scrub/strip protocol and systematic batch tests as a function of compositional variables.

The effect of lipophilic anions, such as dibutylphosphate, tributylphosphate, dodecylsulfonate, phenoxides, and others as recommended by the SRTC, will be examined. If an effective remediation method is available, solvent rejuvenation will be demonstrated. A 5-cycle extraction, scrub, and strip test implied that certain components present in the full simulant (but not in the salts + metals simulant) accumulate in the solvent and degrade stripping performance.

Washing with NaOH solutions restores the solvent to normal performance. Dibutylphosphate is one of the species in the full simulant that may be causing the problem, though other lipophilic anions may also be involved. Dibutylphosphate was observed to degrade stripping efficiency if present in the solvent at sufficiently large concentrations. This was found to be true for 4-*sec*-butylphenol, an impurity in the Cs-7SB modifier and a degradation product. Both dibutylphosphate and 4-*sec*-butylphenol washed out of the solvent on contact with NaOH solutions.

7.3.5.2.4 Batch Contacting Demonstration with High-Activity Waste (CSSX SOWM 5.1.7)

The purpose is to demonstrate that realistic activity levels (0.325 Ci/L) can be fully decontaminated (DF > 40,000) and that the loaded solvent can also be fully stripped without an intervening spike. Contacts will be performed in crosscurrent batch mode. No attempt will be made to simulate counter-current conditions. If needed, stripped solvent will be subjected to solvent-performance evaluation and diagnostics. Solution preparations for this test were completed in FY00. The actual contacting experiments were in progress as this document was being prepared.

7.3.5.2.5 Performance Behavior as a Function of Feed Composition Variability (CSSX SOWM 5.4)

The measurement of the Cs distribution ratio as a function of the concentration of the major ions in the simulant was initiated in FY00. Cs distribution under flowsheet conditions was examined. A significant effect was competition from K, though this is not expected to jeopardize flowsheet performance within the expected feed concentration limits. Cs loading was small, less than 10% of the BOBCalixC6 concentration. This information was required to support design of the flowsheet for the real waste tests scheduled for FY01 and to predict performance over a range of dilutions of the waste with NaOH. The major ions will be Na, K, Cs, Al, NO_3, and OH.

7.3.5.2.6 Solvent Stability, Analysis, and Cleanup of Degraded Solvent (CSSX SOWM 4.1)

Samples from several areas of work in FY00 were received and subjected to analytical procedures and performance assessment. It should be noted that this work is exploratory and highly dependent upon the extent of solvent degradation and performance. Analyses and tests are prioritized according to the apparent severity of solvent degradation and to the type of information needed to diagnose and remediate any identified problems. Samples from the external irradiation experiment were received and analyzed; the results are in agreement with those reported by SRTC (presented in Section 7.3.4.2). Samples from flowsheet tests and the internal irradiations were received at the end of FY00; analysis and evaluation of the data were ongoing as this document was being prepared.

Samples were submitted for organic analysis, with selected samples subjected to other diagnostic experiments such as electrospray mass spectrometry (ES-MS), FTIR, or NMR as warranted.

Activities in this particular area at SRTC and ORNL were designed to complement site capabilities and to validate results where desirable. Conclusions from the analytical work performed at ORNL agree with those performed at the SRTC. Namely, degradation of solvent components out to the equivalent of at least a 10-year dose expected for plant operation were shown to be negligible. The major decomposition product formed with a clear dose response was 4-*sec*-butylphenol, which derived from the Cs-7SB modifier and was easily removed from the solvent by contact with NaOH solutions. NMR experiments also showed that some fluorine-containing organic compounds appeared in the aqueous phase, implying the other fragment from the decomposition of Cs-7SB does not buildup in the solvent.

7.3.5.2.7 Performance Assessment (CSSX SOWM 4.1.4, 5.1.3)

QA procedures to be used on pristine solvent include standard batch extract/scrub/strip protocol[64], third-phase formation, break time, interfacial tension, and selectivity.

Remaining chemical stability issues of the solvent were addressed in FY00. These include thermal stability over waste simulants containing noble metals, over nitric acid as a function of concentration, over strip solution, and over other solutions (e.g., wash solutions). Solvent samples held for 46 days at 60°C still showed acceptable performance in batch extraction behavior and the in-growth of degradation products could be measured by NMR.

In cooperation with SRTC, certain analyses were performed on aqueous and degraded solvent samples from Co-60 external irradiation tests. These included HPLC, GPC, ES-MS, and NMR on the solvent samples. Aqueous samples were analyzed for organic degradation products. As mentioned above, fluorinated compounds appeared to be the major solvent decomposition products reporting to the aqueous phase. Performance tests were performed on degraded solvent samples. These included interfacial tension, break time, batch extract/scrub/strip protocol, third-phase formation, and extraction selectivity. Interfacial tensions and coalescence behavior remained within acceptable limits, and third-phase behavior was normal. Extraction selectivity degraded somewhat with radiation dose in that sodium extraction increases, attributable to the appearance of the 4-*sec*-butylphenol, an expected decomposition product from the modifier. This compound is readily washed from the solvent by contacts with dilute NaOH.

7.3.5.3 FY01 - Current Work

A report summarizing FY00 work related to solvent physical/chemical properties will be published in FY01.

7.3.5.3.1 Distribution Behavior of Major and Minor Feed Components (CSSX SOWM 4.4.1, 5.2, 5.2.1, 5.2.2)

Questions regarding how the major and minor components in the actual waste feed will partition in the extraction, scrub, and strip stages of the flowsheet and their effect on process performance will be addressed in FY01. Major components are important both because of their large effect on the primary Cs equilibria involved in extraction, scrubbing, and stripping and because the flowsheet must be designed to ultimately produce a stream of reasonably clean Cs nitrate for vitrification. Minor components are important because of their potential to build-up in the system to the point where perturbations on system performance are felt through crud formation, impaired phase disengagement, or degraded Cs extraction, scrubbing, and stripping.

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

Partitioning behavior of organic species and inorganic species will be measured using appropriate analytical techniques. Organic species of concern include TBP, TBP degradation products, n-butanol, trimethylamine, and other minor compounds that might be recommended by project participants and stakeholders. Because of their demonstrated potential to cause impaired stripping, certain surfactant species will also be included. Inorganic species include heavy metals, chromate, aluminate, silicate, and other minor constituents known to be present in the waste. Partitioning measurements will be made in standard extract/scrub/strip (“ESS”) batch tests simulating sections of the CSSX flowsheet. Of primary interest is the extraction step. For species that partition significantly to the solvent, additional measurements will be made to examine scrubbing and stripping behavior. For species that survive scrubbing and stripping, tests will be conducted to examine partitioning to typical wash solutions (e.g., NaOH) or, as a last resort, to ion-exchange resins or other sorbents. This information will be used to recommend cleanup procedures.

Analytical methodology will include scintillation 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.

The effect of the above organic and inorganic species on Cs extraction behavior will also be measured. Emphasis will be placed on those minor components that partition strongly to the solvent. These are likely to include, for example, TBP and n-butanol, together with certain lipophilic anions. Standard ESS tests will be conducted with Cs-137 tracer. Selected wash solutions will also be employed in selected cases to explore the effectiveness of washing.

Lab-scale batch-equilibrium tests must also be conducted with waste simulant at variable temperatures (including 25°C) to perform flowsheet design and to predict performance under realistic temperature conditions. These tests should also include a range of feed compositions to allow the prediction of Cs distribution with real-waste compositions that do not exactly match that of the prescribed SRS waste simulant. The tests should also include a range of concentrations of the solvent components (TOA, modifier, and BOBCalixC6) to enable process performance to be understood as solvent components are gradually lost to degradation or to the aqueous streams in the process. The tests will employ the ESS batch equilibrium method with Cs-137 tracer.

7.3.5.3.2 Equilibrium Modeling of Distribution Behavior (CSSX SOWM 5.3)

An equilibrium model must be developed to improve the predictability of the solvent extraction process with regard to many process variables, including temperature, and to improve overall understanding of the process chemistry. This model should take into account variations in the major aqueous components (e.g., Na, K, Cs, nitrate, nitrite, hydroxide, aluminate) and the influence of matrix changes in the different sections of the flowsheet. It should not only predict Cs distribution behavior but should also include the distribution of the other major aqueous components of the system, especially Na and K. Ultimately, the model should allow expansion to include the distribution of minor components. The model should also include the variation of solvent-component concentrations.

This element will involve two activities: data collection and computer modeling. Although some information will be available from the above work, thermodynamic rigor would make it desirable to measure distribution ratios of Cs, K, and Na versus single aqueous electrolytes and simple mixtures. Simple tracer techniques (Cs-137 and Na-22) and ICP-AES will be employed to quickly generate data points over a range of component concentrations and temperatures. Computer modeling will be first carried out with the aid of SXFIT, which utilizes the Pitzer treatment and can handle unlimited electrolytes and solvent components. Within time constraints, other computer codes will be considered as judged worthwhile.

7.3.5.3.3 Solvent Stability and Cleanup Tests (CSSX SOWM 3.2.4, 4.1)

This work element combines several tasks all related to the issue of solvent radiation and thermal stability. In most cases, the work will involve close cooperation with other tasks at ORNL, ANL, and SRTC that are generating samples.

Samples of solvent subjected to radiation and heat treatment under various conditions relevant to the flowsheet will be received from tasks taking place at ORNL, ANL, and the SRTC.

Solvent from the ANL 5-day 32-stage contactor test on waste simulant will be analyzed and evaluated at ORNL for degradation and for trace-component buildup. Based on this information and available data on cleanup, a clean-up procedure will be recommended by ORNL to be carried out at ANL prior to the second 5-day test. The same recommendations will be provided to the SRTC for possible use in real-waste tests.

Samples from radiation and stability tests continued from FY00 must be analyzed to determine the fate of solvent components, appearance of breakdown products, and deterioration of performance. Samples will be from internal batch and loop irradiation tests conducted at ORNL and from the thermal stability tests conducted at ORNL. Analyses of samples of externally irradiated solvent received from SRTC will be completed. Cleanup studies will be carried out on any solvent samples that exhibit evidence of degradation. Cleanup will consist of contacts with potential aqueous wash solutions (e.g., NaOH) or possibly ion-exchange resins.

7.3.5.3.4 Analytical Methods Development (CSSX SOWM 4.2, 4.4.2)

Methods to evaluate solvent quality will continue to be studied in order to specify the baseline pristine solvent quality assay, in-process monitoring requirements, and post-process monitoring. Such methodology would likely include, for example, HPLC-MS, EM-MS, NMR, distribution behavior, etc. Organic-phase analytes of interest include the major solvent components, as well as minor organic and inorganic species shown above to be likely to build up in the solvent. Other analytes will be considered based on information from the distribution studies and other analytical work that indicates the particular importance of a given species. Methods need to be identified for monitoring the concentrations of solvent components so that solvent composition can be maintained within limits.

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

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

7.3.6 Solvent Decomposition and Contactor Hydraulic Performance (CSSX SOWM 4.1.3)

Solvent stability (chemical and radiological) is not completely understood. Degradation products could not only impact the extraction capabilities of the solvent matrix but also impact the hydraulic performance of the centrifugal contactors. These effects need to be investigated and means to mitigate their impact must be developed.

7.3.6.1 Previous Results

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

7.3.6.1.1 Precipitate and Rag Layer Formation

Researchers at ANL performed a bench-scale solvent extraction test using 2-cm centrifugal contactors.[69] This test consisted of two segments. The first segment involved a single pass of the solvent through the process. This test lasted 90 minutes. At the conclusion of this segment, ANL personnel drained the stages and inspected the fluids for either precipitates or a rag layer. No significant precipitation or rag layer formation occurred.

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

7.3.6.1.2 Phase Separation

The ANL researchers performed three measures of phase separation.[69] The first of these measures determined the dispersion number for the solvent/aqueous systems of interest. These tests show that, except for low O/A ratios in the strip section, very good to excellent performance (i.e., dispersion numbers greater than 8 x 10^{-4}) were obtained. Note that the baseline process design does not include operation at low O/A ratios in the strip section.

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

The proposed solvent extraction process has been demonstrated on miniature (2-cm nominal diameter) centrifugal contactors.[69] In that work, testing was first performed with a single stage contactor and then in a multi-stage array similar to the proposed CSSX flowsheet. The modifier is different from that currently proposed used in these tests (Cs-3). In the strip tests, cold Cs nitrate was added to facilitate Cs removal from the solvent. With the currently proposed modifier, addition of cold Cs is unnecessary.

7.3.6.1.3 Single-stage Testing

The flowsheet for the 2-cm centrifugal contactor tests were designed for 80% stage efficiency. To evaluate the actual efficiency, tests were run in a single-stage 2-cm contactor using the proposed solvent with various aqueous phases, including simulated SRS waste as feed. For extraction with the simulated waste, the measured efficiency averaged 97.1%. The scrub and strip tests averaged 80.9% and 99.7%, respectively. When flow rates were much lower than normal, or when O/A ratios were significantly different from one, the efficiency dropped as low as 79%.

7.3.6.1.4 Multi-stage Testing

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

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

7.3.6.2 FY00 - Results

7.3.6.2.1 Contactor Tests using SRS Simulant Waste and Internal Cs-137 Irradiation (CSSX SOWM 3.1.1.3, 4.1.3, 4.1.5)

Studies of the "second generation" CSSX solvent with 2-cm contactors were initiated in FY00 at ANL. Work with large contactors is being performed at ORNL to increase the reliability of engineering design extrapolations. Prior to FY00, no studies with the CSSX solvent and contactors larger than 2-cm had been performed. Commercially available 5-cm contactors were procured for these studies.

Throughput and phase separation. Initial hydraulic testing was performed using a single centrifugal contactor stage.[70] Relative organic and aqueous volumetric flowrates (O/A ratios) were established at values consistent with CSSX flowsheet conditions. At each combination of organic and aqueous flow rates, the contactor speed was varied until cross-phase contamination was observed in either or both phases. The onset of cross-phase contamination established a point defining the contactor-operating envelope for the specific test condition. Testing was performed at a sufficient number of flow conditions to establish operating envelopes applicable to the extraction, scrubbing, and stripping sections of the CSSX flowsheet. For the extraction segment of the flowsheet (O/A = 0.3, process baseline) the throughput varied from 1100 to 580 mL/min as the rotor speed varied from 6000 to 2800 rpm, respectively. No solvent carryover to the aqueous raffinate stream was observed. For the scrub and strip segments of the flowsheet (O/A = 5.0, process baseline) the throughput varied from 920 to 660 mL/min as the rotor speed varied from 6000 to 3000 rpm, respectively. A slight sheen was observed on the aqueous strip effluent. If the sheen corresponds to 20 ppm (v/v) solvent carryover, assuming the baseline flowsheet conditions, the solvent loss due to carryover would be ~14 gallons per year. Results from the analytical laboratory were unavailable when this document was prepared.

Single-stage mass transfer. Testing also involved contacting a solute-containing phase with an opposing phase in a single, 5-cm centrifugal contactor.[71] Solution compositions and flow conditions representative of those expected in the extraction, scrubbing, and stripping sections of the flowsheet were applied. Flowrates and contactor speeds used in testing were based on the results of the throughput/phase separation test. Both flowrates and contactor speeds were varied to investigate possible effects of residence time on mass transfer performance. Prior to testing, samples of both feed solutions were collected and equilibrated under controlled conditions. Solute concentrations in the equilibrated phases were used to determine equilibrium distribution coefficients. These values were compared against results from contactor testing to determine stage efficiency values. Results from the analytical laboratory were unavailable when this document was prepared.

Four-stage mass transfer. The configuration for the four-stage mass transfer testing was identical to that used in the single-stage mass transfer test, except that the single-stage contactor was replaced with an assembly of four contactor stages.[71] Testing was performed at conditions approximating those present in the extraction, scrubbing, and stripping sections of the CSSX baseline flowsheet. Samples of aqueous and organic effluents were collected from the inlets and outlets of each stage. Organic and aqueous inlet samples from each stage were equilibrated in the correct volume ratios. Samples of equilibrated and separated aqueous and organic phases were collected and analyzed for Cs and HNO_3 (when applicable). Comparison of equilibration sample results with outlet samples was used to determine individual stage efficiencies and the overall efficiency of the four-stage unit. Results from the analytical laboratory were unavailable when this document was prepared.

The throughput and mass transfer efficiency testing identified the need to select a centrifugal contactor design that emphasizes mixing characteristics versus solution pumping ability to reduce air entrainment, which may lead to foam generation.

Hydraulic performance. A test apparatus was designed, fabricated, and assembled for experiments designed to ascertain the impacts that solvent decomposition products from internal irradiation of the CSSX solvent may have on the hydraulic performance of the centrifugal contactors.[72] Leak testing, verification of the data acquisition software, and cold operational testing was completed. The apparatus will be installed in the hot cell early in FY01.

7.3.6.3 FY01 - Current Work (CSSX SOWM 4.1.3, 5.4)

FY01 tests involve operating a single centrifugal contactor with total recycle of the effluent streams to simulate the operation of a stage from the CSSX reference flowsheet. Simulated process solutions with added Cs-137 and three different sets of flowsheet conditions are being used to simulate one stage from each of the three major sections of the CSSX flowsheet (extraction, scrub and strip). The test apparatus is installed in a ORNL hot cell. The primary goal is to determine the effect of radiation-induced decomposition products on the hydraulic performance of a centrifugal contactor. In addition, information on the effects of Cs-137 irradiation on solvent performance (D_{Cs} and solvent degradation product formation) will also be collected.

Simulant solutions[60] represent an average of the SRS HLW waste composition, and the concentration is essentially invariant. Preparation of the simulant results in the formation of small amounts of insoluble material, which is removed by filtration prior to use. However, solids formation in filtered and stored simulant continues to occur slowly with time. The overall salt-treatment process involves a filtration step prior to the CSSX process. Because the product of the filtration will be collected in an interprocess tank, the continued slow precipitation of salts is likely to occur with the real waste. In addition, solids may precipitate as a result of the process chemistry itself, possibly as a result of alkaline compounds being exposed to acidic conditions as the solvent moves from the extraction section to the scrub section. The process robustness of the centrifugal contactors to variations in feed solution composition and to the presence of suspended solids must be investigated; however, their use at SRS since 1964 with varying feed solutions indicate that they have adequate robustness.

Contactor tests to determine the impact of solution composition (solvent component, scrub and strip acid concentrations, and simulant feed composition variations) will be conducted. The test matrix will include studies of the extraction, scrub, and strip segments of the proposed process. The goal of the work is to obtain the information necessary to define the hydraulic robustness of the process with respect to solution composition. Results from FY00 throughput studies will form the baseline of the proposed FY01 work.

A second set of experiments will be conducted in FY01 to define the impact that suspended solids in the waste feed will have on the hydraulic performance of the contactors (Work Scope Element 5.4.1.3). Suspended solids are likely to have at least two sources: (a) colloidal solids that survive filtration of the feed solution; and (b) precipitation processes owing to changes in pH at the extraction-scrub and scrub-strip process transitions. Experiments will be performed with solids generated from simulant solutions.

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

7.3.7 Waste Simulant and Real Waste 2-cm Contactor Flowsheet Tests (CSSX SOWM 3.1, 3.2, 4.3)

7.3.7.1 Previous Results

The proposed solvent extraction process has been demonstrated on miniature (2-cm nominal diameter) centrifugal contactors.[69] In that work, testing was first performed with a single stage contactor and then in a multi-stage array similar to the proposed CSSX flowsheet. The modifier (Cs-3) used in these tests was different from that currently defined in the baseline CSSX solvent. In the strip tests, cold Cs nitrate was added to facilitate Cs stripping from the solvent. With the current baseline solvent, which contains TOA, the addition of cold Cs is not necessary.

Prior work performed at ANL in FY98 showed that Cs can be extracted from caustic aqueous solutions representative of the HLW at the SRS using solvent extraction processes carried out in centrifugal contactors. The tests showed that, while the process worked, the solvent needed improvement and the stage efficiency in the 2-cm centrifugal contactor was less than desired. The solvent was subsequently improved at ORNL in FY99.

7.3.7.2 FY00 – Results (CSSX SOWM 3.1.1.1, 3.1.1.2)

During FY00, the stage efficiency of the 2-cm contactors was improved from 60% to >80%. Stages were added to yield a 32-stage cascade inside a glovebox, providing a facility for fully testing the CSSX flowsheet. With the improved solvent, the process flowsheet required for removing Cs from HLW at SRS was demonstrated using a waste simulant. The goal was to demonstrate the entire process while achieving a DF of at least 40,000 and CF of 12. It should be noted that the CSSX process interface to DWPF requires a minimum CF of 12; the process target for CSSX is 15. The test used simulant with Cs-137 spike as feed.

In September 2000, the "proof-of-concept" flowsheet test was completed. This test did not recycle the solvent. The DF achieved during the test was greater than 80,000, exceeding the test goal by a factor of two. The Cs concentration factor achieved was 16.5 versus the test goal of 15. The organic solvent output stream was stripped of Cs to a level equivalent to the Cs level in the aqueous raffinate stream.

7.3.7.3 FY01 - Current Work (CSSX SOWM 3.2.4)

At the start of FY01, analysis of the results from the flowsheet test conducted in FY00 will be completed and an ANL report covering that work will be published.

Two centrifugal contactor tests will be conducted with a 32-stage bank of 2-cm contactors housed in a glovebox at ANL. Tests will be conducted using solvent and waste simulant. The goal is to show that a DF of 40,000 and a CF of 15 can be simultaneously achieved. The waste simulant will be spiked with enough Cs-137 so that a DF of 40,000 can be measured accurately. The first test will limit the solvent recycle to a total of four times. The second test will involve 4 to 5 days of continuous operation of the system. The primary goal of the second test is to demonstrate that the DF and CF can be maintained over extended periods of operation. The secondary goal is to expose the solvent to as many process cycles as reasonably possible and observe whether degradation products form or whether feed impurities build up in the solvent.

Additional tests will be carried out in a multistage 4-cm centrifugal contactor to demonstrate solvent recovery from the aqueous raffinate. The solvent will be recovered from the aqueous raffinate by contacting it in a contactor stage with the solvent diluent Isopar$^{®}$ L as the organic phase. The 4-cm contactor will be used because it accommodates higher throughputs that give continuous interstage flows, as will be the case in plant-scale units. The tests will determine the conditions required for good operation and the rate of solvent recovery. To determine a process for separating the diluent from the recovered solvent, other tests (i.e., vacuum distillation) may be carried out. Based on the results of these tests, the economics of solvent recovery will be determined. This work will demonstrate that solvent can be recovered and will evaluate the cost of this recovery. From this work, the feasibility, need, and importance of a solvent recovery system can be determined.

A real waste test using 2-cm contactors will be conducted in the second quarter of FY01 at SRTC. The objectives of the real waste test are similar to that noted for the ANL tests, but with the added objective of ascertaining the impact of components, particularly trace components, contained in the real waste that are not contained in the average SRS simulant. The duration of the real waste test will allow the solvent to be recycled 28 times, which is 1% of the number of annual recycles that will occur in the proposed process plant. The number of solvent recycles is based on the waste feed volume needs (~130 L) and the desire for this test to represent a reasonable pre-pilot scale test.[73]

7.3.8 Solvent Commercialization (CSSX SOWM 6.1 – 6.3)

7.3.8.1 Previous Results

The extractant BOBCalixC6 has been provided in small batches (<50 kg) of high-quality material by IBC Advanced Technologies, a small specialty chemicals company, since 1998. The Cs-7SB modifier has only been produced at ORNL and is not commercially available. The Commercialization Plan or Technology Transfer Plan includes protecting intellectual property by way of patents and non-disclosure agreements 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.

7.3.8.2 FY00 – Results

In FY00, the BOBCalixC6 modifier was successfully prepared at ORNL at the 3.0- and 3.6-kg scale. The DOE is in the process of completing a patent application for these modifiers, most likely as a continuation-in-part of the previously filed patent application covering the CSSX process.[74]

In FY00, IBC Advanced Technologies, Inc., located in American Fork, UT, 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.[75]

Personnel at ORNL contacted candidate chemical producers and custom synthesis companies, and identified potential candidate firms to supply the chemicals on the scale required by the proposed process plant. The results of this effort were summarized in a series of letter reports submitted to SRS.[76,77,78]

7.3.8.3 FY01 – Current Work

The synthesis of the extractant, BOBCalixC6, and the modifier, Cs-7SB, is not complicated, and the important starting materials are available commercially. Companies involved in the toll manufacture of speciality chemicals will be able to meet the needs of the CSSX process plant. Activities in FY01 will be directed toward the identification of multiple producers.

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

The ability to prepare the BOBCalixC6 in commercial quantities has been demonstrated. However, at least one additional manufacturer should be contacted for producing the BOBCalixC6 for competitive procurement purposes. The potentially improved method for preparing the BOBCalixC6 will be transferred to the candidate companies under the guidance of legal and intellectual property personnel at ORNL. To demonstrate that a company other than IBC is capable of making the BOBCalixC6 at the required purity level, one candidate company will be selected to manufacture a 50-g quantity of the material.

The patent application covering the synthesis of the Cs-7SB modifier will be filed early in FY01. Interaction between DOE patent counsel and ORNL personnel will involve finalizing the application prior to submission to the U.S. Patent & Trademark Office. The synthetic procedure developed for the 3.6-kg scale will be written up and transferred to candidate companies. The first step in the commercial manufacture of Cs-7SB will be to contact several companies and assess their synthetic capabilities regarding the modifier manufacture. Quotes will then be obtained on the manufacture of 1-2 kg quantities of the modifier. Two candidate manufacturers will be selected to prepare these 1-2 kg amounts. It would be desirable to time this so that if these commercially prepared modifier batches meet specifications, solvent could be prepared using the material. Following that, candidate companies will bid for the opportunity to prepare a 10-kg quantity (sufficient to prepare 59 L of solvent). In selecting candidate companies, the ability to manufacture 100-kg quantities will be an important qualification factor. Many companies who can custom manufacture 10-kg quantities of materials do not have the equipment to manufacture 100+ kg quantities. It should be noted that every 10 L of solvent requires about 1.7 kg of Cs-7SB modifier.

7.4 Small Tank TPB Precipitation

In the STTP process, Sr and alpha are sorbed and Cs precipitated in two continuous stirred tank reactors arranged in series. The solids produced, with the radioactive species, are separated from the DSS by cross-flow filtration. The solids accumulate continuously in a concentrator tank, and are then sent in batches to a wash tank. The concentrated slurry is washed to reduce the salt content and the spent wash is used as dilution water in the first reactor.

The washed slurry is sent in two batches to the precipitate reactor feed tank. The precipitate is hydrolyzed with acid, and the organic product, largely benzene, is stored and incinerated. The aqueous product is sent to DWPF to be vitrified along with sludge waste.

7.4.1 R&D Roadmap Summary – Small Tank TPB Precipitation

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

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

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

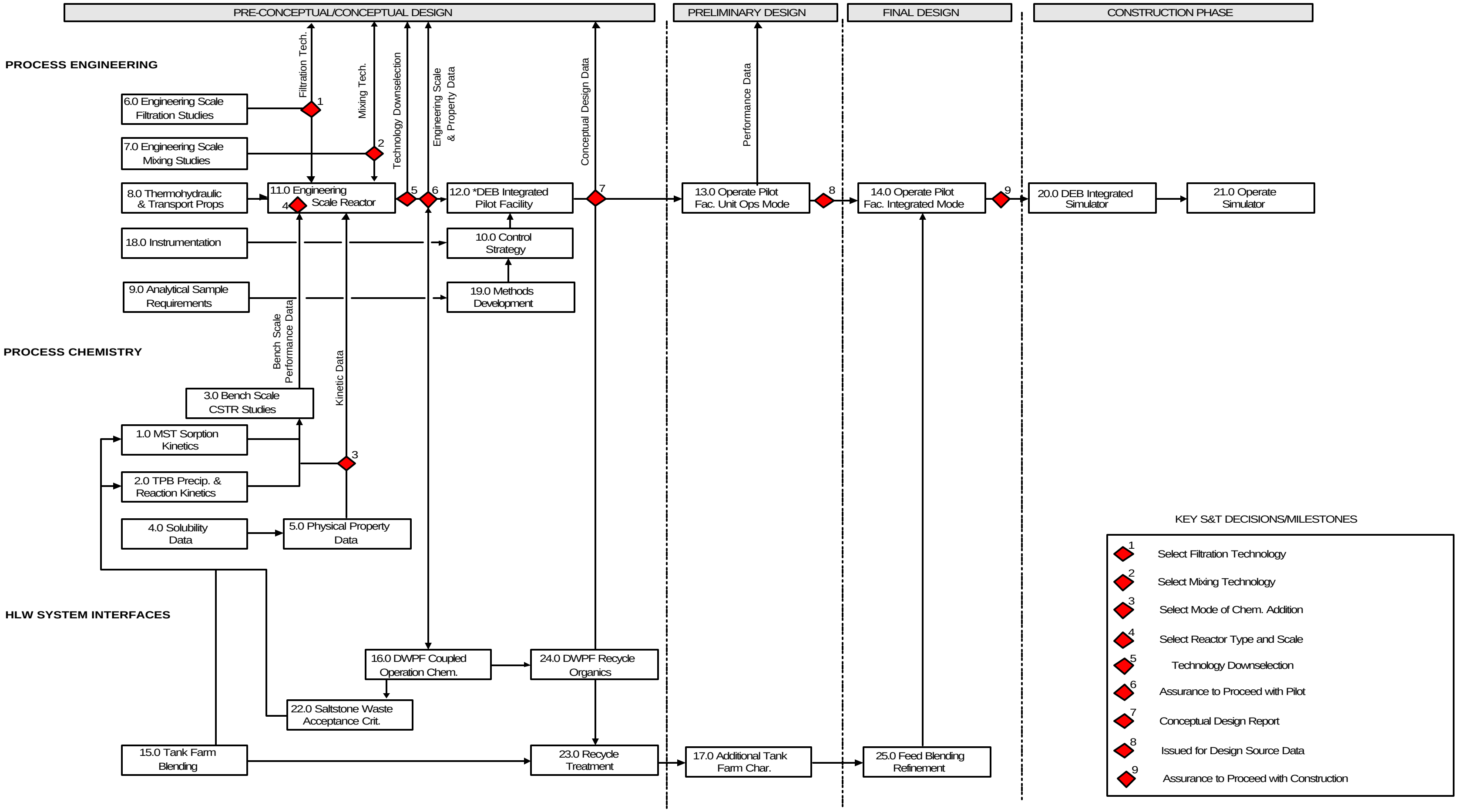
Process chemistry includes data on the thermal and hydraulic transport properties, reaction kinetics, and mass transfer properties that are needed to finalize the conceptual design. These data are used to establish the physical and engineering property basis for the project and detailed design. Examples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

Physical property and process engineering data from engineering scale tests will be developed during conceptual design. Confirmatory 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. This will establish the limits of operation and recovery, the limits of feed composition variability, and will confirm design assumptions. This testing directly supports development of operating procedures, simulator development, and operator training.

Additional development and testing during conceptual design will help assure proper feed and product interfaces of the Cs removal process with the HLW Tank Farm, DWPF and Saltstone. The issues of concern include assurance of glass, waste feed blending and characterization, and waste acceptance.

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



*DEB = Design, Engineer, and Build

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

For STTP, the key issues include understanding TPB precipitation kinetics, TRU sorption kinetics, reactor mixing, and excess TPB to support washing and to allow proper precipitation reactor sizing. While engineered features will address the key benzene safety concerns, catalytic decomposition of TPB at lower temperatures remains an issue relative to operability. Similarly, operation at a smaller scale than used in the original precipitation prompts questions related to potential foam formation and the need to mitigate the impact of system hydraulics.

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

7.4.2 Tetraphenylborate Decomposition Studies (STTP SOWM 2.1 - 2.4, 3.0)

In the late 1970s and the 1980s, the SRS developed a process for removing cesium from salt solutions by using NaTPB to precipitate the Cs. Since the precipitation process was carried out within the SRS HLW tanks, the process was known as the "In-Tank Precipitation (ITP)" process. SRS successfully completed a plant-scale demonstration of Cs removal from the salt solution; however, flammable benzene was also produced as a by-product of the precipitation reaction. This benzene generation at the time was attributed to TPB decomposition due to exposure of the TPB to the high radiation level in the waste. In 1995, SRS initiated the ITP process in HLW Tank 48, which contained ~450,000 gallons of radioactive salt solution; however, the process had to be halted after ~3 months of operation due to benzene generation rates which were much higher than expected. Subsequent studies led to the possibility that metals in the salt solution were acting as a catalyst for the decomposition of TPB to benzene. As a result, SRS concluded that safety and production requirements could not be met and ITP operations were terminated.

Catalytic decomposition of TPB is a high risk area which must be resolved if STTP is to be selected as the process for removal of Cs from the SRS HLW tanks.

7.4.2.1 Previous Results

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

The first area of emphasis was to establish conditions under which the decomposition reaction could be effectively inhibited. The first set of tests used inhibiting agents to reduce the reaction rate.[79] These tests were based on previous tests that identified potential inhibiting agents. The primary focus of these tests was to investigate the impact of elevated temperature and exposure to radiation on the performance of inhibiting agents. These tests indicated that the use of a proprietary oxidizing agent at higher temperatures was less effective than at reduced temperatures. Another inhibiting agent (Na sulfide) showed only modest ability to mitigate reaction rates at elevated temperatures while a third (dimethylglyoxime) provided good performance as an inhibitor. However, the impact of radiation on inhibitor performance is inconclusive at this time.

The second set of tests examined the use of low temperature to slow reaction rates.[80] Previous testing indicated that very little decomposition occurred at 25°C. Thus, testing was initiated to determine the impact of temperature on catalyst activity. These data indicated that the decomposition reaction for TPB exhibited an activation energy of ~47 kJ/mole. However, these tests did indicate that the presence of oxygen at low temperatures can prevent the activation of the catalyst. However, increased temperature can significantly decrease the incubation period for this reaction. These tests also indicated that the total quantity of soluble Pd(II) added to the system had very little impact on the final decomposition rate. Also, the addition of Pt(IV) resulted in significantly lower catalytic activity relative to Pd(II).

The final step in testing the proposed methods for inhibiting the decomposition reaction was measuring their efficacy with HLW from the SRS tank farm.[81] A series of tests were performed to determine the performance of these inhibitor methods with a composite of material from Tank 43H and 38H. These tests also evaluated simple removal of entrained solids as a potential inhibitor method. These tests indicated that reduction in temperature was the most effective method of reducing catalytic activity. However, even under conditions in which no inhibitor was added, the observed reaction rates were relatively low. This low activity was attributed to the absence of suspected catalyst species; in particular the absence of Pd. As such, the observed lack of efficacy of the selected inhibiting agents is expected.

While the above testing did not indicate a significant decrease in catalytic activity following filtration of the salt solution prior to introduction of the TPB, additional testing indicated that filtration following precipitation (and significant decomposition reaction), significantly decreased the catalytic activity of the filtrate.[82] These results suggest that the catalytically active species may well enter the system as a soluble species but may be converted to an insoluble species upon exposure to TPB (in a reactive system).

Additional testing explored the catalytic mechanism for the activation of Pd.[83] As indicated above, significant speculation on the role of oxygen in the activation of Pd catalyst had been strongly suggested. These tests indicated that the presence of oxygen at low temperatures (25°C) prevented the decomposition of NaTPB. However, at elevated temperatures (45°C) the presence of oxygen proved insufficient to eliminate catalytic activity.

Additional tests indicated that Pd on $BaSO_4$ was a more effective catalyst for the decomposition of TPB than Pd(0) on activated carbon or Pt(IV) on activated carbon. (Note that Pd(II) reduced in TPB slurries was more reactive than Pd on $Ba\ S0_4$). An additional study searched for spectrophotometric evidence of phenylborate – palladium complexes.[84] These UV-visible measurements were unable to detect the presence of any such complexes.

Work prior to FY00 concentrated on studies to determine what component(s) were catalyzing the decomposition of the TPB and what conditions were necessary for the decomposition reaction to occur. The major findings were: (1) Pd(0) supported on TPB solids was believed to be the active catalytic species, (2) dimethylglyoximine inhibited the reaction, (3) the reduction of temperature was the most effective method of reducing catalytic activity, and (4) the catalytically active species may enter the system as a soluble species and be converted to an insoluble species upon exposure to TPB in an active system.

7.4.2.2 FY00 – Results

One of the most significant issues associated with the small tank precipitation process involves closure of the open DNFSB 96-1 issues. The workscope to address these issues contains three primary elements: (1) developing an increased understanding of the catalyst system, (2) evaluating the catalytic activity in HLW samples, and (3) demonstrating the performance of the CSTR system in the presence of a significant decomposition.

To develop an increased understanding of the catalyst system, experts in the field of catalysis (Dr. James Boncella from the University of Florida and Dr. Bruce King from the University of Georgia) were contracted to review past work on the catalytic degradation of TPB and to guide future work in this area. As part of this effort, the consultants conducted literature studies documenting potential mechanisms for TPB degradation. The Suzuki Coupling Reaction, in which TPB hydrolysis by Pd and/or Hg has been demonstrated, was proposed as the possible mechanism for the TPB decomposition. Studies were conducted to determine if the proposed mechanism was correct; additional tests will be conducted in FY01.

Work in FY00 included studies to examine both potential catalysts and compounds which could have a synergistic effect on the catalytic decomposition. In looking at potential catalysts, work focused on Pd because previous studies showed that Pd was an active catalyst in alkaline waste conditions. These tests were designed to explore the fundamental form of the Pd responsible for the catalytic process; in particular, the oxidation state, state of the catalyst (homogeneous or heterogeneous), and type of support material. Varying forms of Pd were employed (supported, organometallic, reduced) and TPB surrogates were used. Pd(0) on alumina showed the highest activity for TPB decomposition and the reaction rate was shown to be dependent on the Pd concentration. It was also shown that Pd(II) reduced in simulated waste to form nanoclusters; some of which incorporated Hg. The nanoclusters had a large surface area and were very reactive. Also, reduced Pt on alumina was shown to have reactivity similar to Pd on alumina; however, the Pt concentration in the HLW tanks at SRS was minor relative to Pd. Ru and Rh on alumina was shown to be ~25% less reactive than Pd(0) on alumina. While Rh and Ru are more plentiful than Pd in the SRS HLW tanks, it is less likely that these have been reduced to the active metal form. Studies are currently underway to determine conditions that may reduce these components. These tests are also examining the potential mechanism for Pd catalysis, as suggested by a panel of experts.[85]

$$Pd^0 + TPB^- \longleftrightarrow Pd^- \cdot TPB$$
$$Pd^- \cdot TPB \longleftrightarrow PdH \cdot TPB + OH^-$$
$$PdH \cdot TPB \longleftrightarrow Ph_3 \cdot B + PhH + Pd^0$$

Testing was conducted to examine elements, which might have synergistic effects on the decomposition reaction. Hg was shown to be an important part of the decomposition reaction and was active whether added as a soluble salt or as diphenyl Hg (although some tests showed that the catalytic decomposition was greater if diphenyl Hg was used). Testing was also conducted to determine if Cd and Ag behave similar to Hg and could be used to enhance the catalytic decomposition in the absence of Hg. These tests indicated that Ag and Cd do not provide reactivity similar to Hg and that very little TPB decomposition occurred when Ag or Cd was used to replace Hg.

Additional tests were conducted to explore the potential synergism between the catalytic activity of various metals and Pd. In these tests, equimolar concentrations of Cu, Fe, Rh, and Ru were each added to a standard salt solution containing 2.6 mg/L of Pd(0) on alumina and reacted at 70°C. The Rh and Ru were added in reduced form on alumina powder and the Cu and Fe were added in +2 and +3 oxidation states, respectively. The data indicated that no significant synergistic interactions occurred with any of these metals. Pd(0) with either C(II) or Ru(0) was marginally more reactive than Pd(0) alone, and Rh(0) with Pd(0) was slightly less reactive than Pd(0) alone.

Testing was performed to investigate the role of degradation products in the activation of the Pd catalyst. Previous testing indicated that the presence of one or more of the degradation products must be present for TPB degradation to occur, and these degradation products play a significant role in the activation of the catalytic species. The data indicate that diphenylborinic acid may be the intermediate of importance in the decomposition reaction; however, additional studies are necessary to confirm this.

Another aspect of testing employed a variety of both solid state and liquid phase characterization techniques. NMR studies were performed to potentially provide a simpler technique for measurement of reaction kinetics. In addition, NMR offers the potential to identify organometallic Pd species. NMR testing on TPB degradation kinetics was completed during FY00. The tests indicted that good separation of the intermediates could not be obtained by NMR unless sample preparation, similar to the preparation necessary for HPLC, was conducted. Therefore, it was unlikely that any additional information, above what has been learned from HPLC tests, could be generated by further NMR tests. As a result, the TPB degradation kinetics NMR tests were terminated, and NMR work was initiated to study the role of different Hg species in the degradation reaction. Key findings included the following:

(1) Pd is capable of catalyzing the degradation in the absence of Hg;

(2) When Hg was added to the Pd system in the form of mercuric nitrate or phenylmercuric nitrate basic, the rate of TPB degradation was roughly the same as the rate without Hg present;

(3) When Hg was added to the system in the form of diphenylmercury, the rate of TPB degradation was greatly accelerated;

(4) No TPB degradation was observed for a system which contained phenylmercuric nitrate basic alone with no Pd present;

(5) The distribution of lower phenylborates (1PB, 2PB, and 3PB) varied as a function of the catalyst system;

(6) Sample analysis during the first 17 hours of reaction showed no presence of lower phenylborates, indicating that an "induction period" may be necessary; and

(7) The appearance of the metal precipitates in the reaction mixture varied with the catalyst system, possibly indicating that the formation of the active catalyst may vary with the chemical form of Hg added.

The results from the Hg NMR studies are being evaluated to resolve differences with information from previous bench-scale testing. The catalyst consultants, Dr. Boncella and Dr. King, are reviewing these results to determine if some of the NMR tests should be repeated or if additional tests need to be conducted in FY01 to resolve these differences.

Another method of exploring Pd speciation involved the use of electrochemical and spectroscopic techniques to evaluate the state of the aqueous phase Pd species. Tests will determine the oxidation states and behavior of potential catalytic metals in alkaline waste. These studies will employ available analytical tools such as cyclic voltammetry and FTIR in simplified salt solutions. In addition to Pd, a number of other potentially catalytic metals are being explored, including Ru and Rh. Potentially useful characterization techniques, such as x-ray photoelectron spectrometry, and electron microprobe and x-ray absorption, are being tested to determine the state of the solid phase catalyst.

The second aspect of this work continued to examine the catalytic activity of real waste. These tests will not only provide insight into the potential reaction rates that would be observed with real waste, but would also provide insight into the catalytic mechanism based on extensive analysis of the waste composition. In FY00, six SRS waste tanks were sampled for characterization and testing. Based on historical knowledge, these tanks were selected to be representative of the SRS storage tank waste and to bound the catalytic decomposition rates. Tests with these tank wastes were initiated in late FY00 and will continue into FY01.

The third aspect of the testing involved a 20-L CSTR (1/4000 scale) demonstration of the precipitation process in the presence of a significant decomposition reaction. The intent of this testing was to demonstrate that the proposed precipitation process would continue to provide DSS even in the presence of a significant decomposition reaction. The 1/4000-scale 20-L CSTR system used in FY99 testing was upgraded in FY00 to correct deficiencies and enhance automation and data acquisition.

Work at the SRTC was completed in FY00 to define a simulated catalyst system using reduced Pd supported on alumina, which would decompose soluble NaTPB in a continuous precipitation system. The test system used a single 1-L CSTR and a 1-L concentration tank fitted with a Mott sintered metal filter tube. The CSTR had a residence time of 8 hours. Testing occurred over a temperature range of 25^{o}C to 45^{o}C and the catalyst system included reduced Pd on alumina powder, Hg(II) nitrate, benzene, phenylboronic acid, and B52 antifoam. The SRS average waste salt solution was used during these tests. The objective of the test, based on benzene generation data from studies of HLW Tank 48, was to achieve a benzene generation rate of 10 mg/(L.h) at 10 wt% solids in the concentration tank. At 25^{o}C and 7.5 wt% solids in the concentrate tank, a benzene generation rate of 15 mg/(L.h) was achieved. As a result, the following catalyst system was recommended for the 20-L test system at ORNL: 7.8 mg/L Pd(0) on alumina powder, 80 mg/L Hg(II) nitrate, 720 mg/L benzene, 500 mg/L phenylboronic acid, and 1000 mg/L B52 antifoam.

In summarizing work completed during FY00, substantial progress was made in characterizing and understanding the catalytic decomposition mechanism. Major progress included: (1) contracting Dr. Boncella and Dr. King to assist with the catalyst characterization and development, (2) identification of the Suzuki Coupling Reaction as the potential mechanism for the decomposition, (3) verifying that Pd(0), Pt(0), Rh(0), and Ru(0) on alumina are catalytically active, (4) showing Pd is capable of catalyzing the degradation in the absence of Hg but that when Hg is added as diphenylmercury the rate is greatly increased, (5) showing that Hg promoted catalytic decomposition while Ag and Cd did not, (6) demonstrating that bi-metalic complexes between Pd and Cu, Fe, Rh, or Ru showed no significant synergistic effects, and (7) showing that Pd(II) reduced in simulated waste to form nanoclusters, some of which incorporated Hg.

7.4.2.3 FY01 – Current Work

FY01 work on TPB decomposition focuses on using additional HLW tank waste samples collected in FY00 to verify the relationship between waste composition and TPB decomposition during treatment. The rate of TPB decomposition will be determined for the six HLW waste samples identified with different catalyst systems. Additional testing to further define and validate the decomposition mechanism will be conducted. Consultants will continue to support catalyst development through review of the on-going catalyst studies, providing test recommendations, supporting external reviews, and providing information from literature reviews. Additional testing, based on the results of synergistic tests conducted in FY00, will be performed. Also, testing of nanoparticle Pd clusters is planned for FY01.

A contract has been placed with Dr. Martine Duff and Dr. Douglas Hunter from the University of Georgia’s Savannah River Ecology Laboratory to provide Extended X-ray Absorption Fine-Structure (EXAFS) spectroscopy analysis of potential catalyst materials. Work in FY01 will address the analysis of actual HLW sludge material encapsulated in phenolic resin. These analyses seek to identify the nature of the Pd in the HLW sludge. Analyses of Rh, Ru, and Pd-doped tetraphenylborate solids will also be conducted.

Demonstration testing is continuing in FY01 using the 1/4000-scale CSTR system. The CSTR system will operate to demonstrate the improved understanding of the catalyst system. This improved understanding occurred as a result of on-going bench-scale tests with surrogates and real waste. Both open loop and closed loop tests will be conducted. In the open loop test, the system will be operated using two CSTRs and the concentrate tank in series. The close loop tests will operate in a fully integrated mode, which includes operation with the two CSTRs and the concentrate tank in series, as well as washing, recovery, and recycle of NaTPB, while TPB is actively decomposing.

Operational parameters for these 1/4000-scale tests will be developed based on the results from on-going bench-scale tests with surrogate and real wastes.

7.4.3 Cs Precipitation Kinetics (STTP SOWM 2.5, 4.1)

The ITP process was designed to operate as a batch process. Prior work established the required kinetics and solubility information for the batch precipitation process.[86,87,88,89] The fundamental steps of interest for the precipitation reaction follow.

$$Na^{+} + TPB^{-} \longrightarrow NaTPB$$

$$K^{+} + TPB^{-} \longrightarrow KTPB$$

$$Cs^{+} + TPB^{-} \longrightarrow CsTPB$$

It should be noted that the above are equilibria equations and that the reverse rates are also important. Prior tests were unfortunately not designed to provide the data required for predicting the performance of a continuous process. Since the STTP process will utilize CSTRs, a significant research effort is necessary to investigate precipitation chemistry under more representative conditions.

7.4.3.1 Previous Results

The first segment of this work extended existing basic batch data under conditions approaching those of the continuous process. Kinetic precipitation data was obtained exploring a number of potential process variables.[90] These variables included the quantity of excess reagent employed, the ratio of K and Cs in the waste stream, the Na molarity of the solution and the degree of agitation employed. The most significant impact was associated with the degree of mixing employed. Both the quantity of excess reagent employed and the Na molarity moderately impacted the precipitation kinetics.

Earlier results indicated that a significant portion of the excess reagent was immediately precipitated as NaTPB and was not readily available for precipitation of K and Cs. The next segment of testing evaluated the extent of this phenomenon.[91] These tests indicated that NaTPB precipitation occurs by co-precipitation and also occurs by exceeding the local solubility limit during the mixing of the feed stream with the bulk reactor material. The amount of co-precipitation that occurs is a strong function of the Na molarity of the salt solution. These results further indicated that the precipitation of Cs^{+} and K^{+} effectively forms an isomorphic substituted crystal consisting of KTPB with CsTPB and NaTPB mixed throughout the crystalline lattice. Based on these results, a simplified model of the mixing that occurs during the precipitation reaction was developed.[92]

Based on the previous batch precipitation work, tests were performed to examine the performance of the precipitation process using the proposed CSTR configuration.[93] The primary goal of these tests was to demonstrate the ability to achieve the desired DF in the desired reactor configuration. Testing explored the impact of a number of variables on the achieved DF. These variables included the agitator type, the quantity of excess reagent employed, residence time in the reactors, concentration of NaTPB added, and the bulk solution Na molarity. These tests indicated that using of longer residence time and adding dilute NaTPB feedstocks resulted in the highest DFs. Conversely, use of different agitator types did not significantly alter the system performance.

The next stage of work was to demonstrate the continuous precipitation process using larger scale equipment.[94] A 1/4000-scale continuous precipitation system was fabricated, including concentration and washing stages. Two demonstrations were performed with this equipment. The first demonstration involved only the concentration step. The second demonstration also employed the washing step and recycled the wash water to the reactors (as required by the proposed design). The required Cs removal was demonstrated during both tests. The required Sr and U removal were demonstrated in the first test, feed solution preparation prohibited determination in the second test. However, only a limited quantity of the excess NaTPB was recovered during the washing.

The final element of the precipitation demonstration involved the continuous precipitation process using HLW from the SRS tank farm.[95] These tests used actual HLW from the SRS tanks and no components were added to or removed from the real waste samples used in the tests. The test system contained two CSTRs, each with an operating volume of ~500 mL, operating in series. Samples from the effluent of the second CSTR indicated that Cs decontamination factors (DF) >40,000 were achieved and the concentration of Sr was reduced to below 1 nCi/mL. However, the formation of foam posed a significant problem during the performance of this test element. One test was prematurely terminated due to the formation of foam and a second test was interrupted due to foam formation.

In summary, basic batch kinetics were extended to those approaching a continuous process and it was shown that the quantity of excess reagent, the Na molarity, and the degree of agitation impacted precipitation kinetics. The precipitation process was successfully demonstrated using surrogate wastes at a 1/4000 scale, with design DFs being met for Cs, Sr, and U. In a real waste CSTR tests the design DFs or Cs and Sr were obtained but could not be maintained because of operational problems associated with hydraulics and foaming.

7.4.3.2 FY00 – Results

A 20-L CSTR test to evaluate the decontamination efficiency of the STTP process was completed during FY00. Additional runs with this system will be conducted in FY01. The system used in the test for FY00 included two CSTRs operating in series and was a single-pass, 72-hour test with an 8-hour residence time in the CSTRs. The slurries in each vessel were mixed at 1200 to 1250 rpm while maintaining the temperature at 25^{o}C. No sludge or catalyst was added to the salt feed. Antifoam concentrations of IIT B52 were maintained at 50 ppm/v (parts per million by volume) in each CSTR and 100 ppm/v in the Slurry Concentration Tank. The concentration of Cs-137 in the salt feed (average SRS simulant) was ~9 mCi/L and ~6.2 mCi/L in the CSTR slurry. The concentrations of Sr-85 and U (93 wt% U-235) in the salt feed were 0.066 mCi/L and 0.9 mg/L, respectively.

The DFs for Cs, Sr, and U obtained for the filtrate from the Slurry Concentration Tank were >40,000, ~50, and ~5, respectively. The DF for Cs reached 10,000 in about 36 hours and 40,000 in about 70 hours. DFs of 40,000 were obtained in CSTR1 in about 12 hours and 26 hours in CSTR2. After obtaining a DF of 30 for Sr in the Slurry Concentration Tank in 36 hours, the DF slowly increased to about 50 at the end of the test. It took about 12, 18, and 22 hours, respectively, to obtain a DF of 2 for U in CSTR1, CSTR2, and the Slurry Concentrating Tank. A DF of about 5 for U was obtained at the end of the test in the concentrate filtrate. The DF values for Cs, Sr, and U exceeded the WAC standards needed for filtrate disposal in saltstone. HPLC analyses showed that no measurable NaTPB decomposition occurred during the test.

A feasibility study was conducted to evaluate the technical value and to estimate the cost and time required for performing an additional bench-scale CSTR experiment with actual waste. Bench-scale 1-liter CSTR tests conducted in FY99 were terminated due to foaming and hydraulic problems. Though sufficient Cs removal was achieved, the tests fell short of demonstrating sustained, steady state performance in maintaining sufficient Cs removal in a catalytically active system. The feasibility study for the second real waste CSTR test, which is to be conducted in FY01, addressed the objectives necessary to demonstrate a sustained, steady state test with real waste.

7.4.3.3 FY01 – Current Work

A real waste CSTR test will be conducted in FY01 utilizing two 1-L CSTRs in series. During initial operation at 25°C, it will be determined if the system can meet the design decontamination factors for Cs, Sr, and alpha emitters. The Cs decontamination factor must be maintained at >10,000 for at least two system turnovers. The antifoam developed and selected based on previous testing will be utilized in this real waste CSTR test and stable operation will be demonstrated. After operation at 25°C, the temperature will be raised to 45°C to determine the reactivity of catalysts present in the real waste sample and to evaluate the robustness of the process. This task will be conducted following the completion of 1/4000-scale CSTR testing at ORNL.

7.4.4 Washing And Filtration Studies (STTP SOWM 4.2, 4.3)

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

7.4.4.1 Previous Results

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

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

7.4.4.2 FY00 – Results

Bench scale tests were conducted during FY00 to determine the effect of the various antifoams on the recovery of NaTPB during the washing phase of the process. Recovery of TPB with no antifoam typically averaged ~60%. With the IIT B52 antifoam, which gave the best results as an antifoaming and defoaming agent, the NaTPB recovery dropped to 13%. Washing tests were also used on the sludge from the third 20-L CSTR run at ORNL, which also used the IIT B52 antifoam agent. These washing tests indicated that ~10% of the excess TPB was recovered.

The NaTPB recovery is primarily an economic issue; however, lower recoveries of TPB will result in the generation of larger quantities of benzene during the hydrolysis reaction. Preliminary analysis by WSRC Engineering indicated that the low recovery of NaTPB was not a major impact on the economics of the STTP process. Additional work on the NaTPB will be conducted after the down-selection process has been completed.

7.4.4.3 FY01 – Current Work

Additional work in evaluation of slurry washing and TPB recovery was deferred until the down-selection process for the SRS HLW salt disposition program has been completed.

7.4.5 Antifoam Development (STTP SOWM 5.1 - 5.7)

One of the prime needs for the STTP process is the development of a new antifoam. The severity of foaming problems during FY99 testing at SRS led to the recommendation to develop an improved antifoam as one of high risk technology areas for the STTP. This was supported by several outside review panels, including the NAS committee. The formation of foam proved to be a significant operational issue during the demonstration of CSTR performance with HLW.

7.4.5.1 Previous Results

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

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

- **Precipitation tank** - NaTPB is added to a 5-8 molar Na salt solution. Many antifoam agents are ineffective in this high salt solution. Agitation of the slurry is necessary for the mixing needed for a rapid precipitation rate in a CSTR. The slurry is a high ionic strength caustic slurry but has a low concentration of K TPB solids (0.5 - 1 wt% insoluble solids).

- **Concentration tank** - The dilute TPB solution is filtered to concentrate the slurry to approximately 10 wt% insoluble solids. A crossflow filter is used for this concentration step. The slurry is now both high ionic strength and has a high concentration of potassium TPB solids.

- **Wash tank** - The concentrated slurry is washed to remove as many of the non-radioactive salts as practical. Washing reduces the soluble salt concentrations by a factor of 16. The endpoint for the washing is 0.01 molar nitrite as required for hydrolysis processing. The slurry becomes a low ionic strength caustic slurry with a high concentration of K TPB solids.

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

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

7.4.5.2 FY00 – Results

The primary objective of this work was to identify a more effective antifoam agent to mitigate foaming during precipitation, concentration, and washing in the CSTRs. A research contract was established with the Illinois Institute of Technology (IIT) and Dr. Darsh Wasan, a known expert in the field of foam formation. IIT studied the foaming problem in a 10% KTPB slurry and determined that KTPB particles acted to effectively stabilize the foam. IIT identified three potential antifoam agents and all three antifoam agents were tested using simulated wastes. The IIT B52 antifoam agent performed better than the other antifoams at preventing foaming and was also found to be an effective defoamer. The IIT mechanism involves disintegration of the KTPB particle structure at the gas/liquid interface. After the IIT B52 was identified as the best performer in tests by IIT and SRTC, it was recommended for demonstration in the 20-L CSTR test system at ORNL. The ORNL 20-L antifoam test demonstrated that the IIT B52 antifoam was effective at controlling the foam in both CSTRs and in the concentrate tank.

While the IIT B52 was effective as an antifoaming and a defoaming agent, it did significantly limit the recovery of the NaTPB in downstream washing operations (see Section 7.4.4.2). The impact of the reduced NaTPB recovery was determined to be minimal in terms of costs and effects on down stream processes.

7.4.5.3 FY01 – Current Work

Data in early FY01 indicated that the effectiveness of the B52 antifoam was significantly affected by either aging or by batch variability. Samples from different batches of the B52 antifoam will be tested to evaluate the effects of aging and batch variability on the samples. If the issue of decreased effectiveness of the B52 antifoam with aging or batch variability can not be satisfactorily resolved, development and testing of other antifoams may be considered.

Antifoam development is being conducted in several additional areas during FY01. The impact of irradiation on the chosen antifoam will be determined by conducting a series of foam column experiments with irradiated and unirradiated antifoam samples. Analytical methods will also be developed for the chosen antifoam; these analytical methods will be used to conduct process simulation studies to determine the fate of the antifoam across the precipitation, concentrate, washing, and hydrolysis cycles. If the antifoam collects on the precipitate, future tests will be conducted to determine if the antifoam effects the melter feed or the glass forming properties. If the antifoam is removed with the filtrate, future tests will be conducted to determine if the antifoam effects the grout forming properties for saltstone. In addition, the analytical method will be used to evaluate the degradation of the antifoam agent due to chemical attack.

In addition to the above antifoam tests with surrogate wastes, the affects of antifoam with real wastes will be conducted in FY01. Antifoam was used in batch tests with the waste samples taken in FY00 from the six SRS HLW tanks to determine the effects of antifoam on the reactivity of the different wastes. The selected antifoam agent will also be utilized in a real waste CSTR test to demonstrate that the antifoam contributes to successful stable operation with acceptable DFs for Cs and alpha components while operating with real wastes.

7.4.6 Saltstone Facility (STTP SOWM 22.0)

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

7.4.6.1 Previous Results

Testing was performed to determine the impact of higher than previously tested concentration of TPB degradation products on the benzene evolution rates from saltstone,[96] the benzene TCLP results from saltstone,[97] and benzene generation rates from saltstone.[98] The results of these tests indicate that between 18% and 27% of the theoretical conversion of phenylborates occurs during the curing of saltstone. The maximum release rate increased as a function of curing temperature. Also, the presence of 3PB in the feed is the dominant source of benzene in the saltstone. The benzene concentration in the TCLP extract is nearly two orders of magnitude below the regulatory limits for saltstone cured at ambient temperatures and is an order of magnitude below the limit for saltstone cured at 85°C.

7.4.6.2 FY00 – Results

No work was conducted in FY00 on the impact of phenylborate decomposition products on saltstone.

7.4.6.3 FY01 – Current Work

Additional work in evaluating the impact of the DSS from the small tank precipitation process on the Saltstone Facility will be delayed until the down-selection process for the SRS HLW salt disposition program has been completed.

7.4.7 Hydrolysis Testing (STTP SOWM 5.8, 16.1 – 16.5)

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

7.4.7.1 Previous Results

Testing was performed to determine precipitate exposed to either no dose or to 65.6 Mrad could be processed.[99] These tests indicated that acceptable product was produced under both conditions. Furthermore, potential areas for further work were illuminated including optimizing reaction conditions and the extent of nitrite growth at lower proposed dose rates.

7.4.7.2 FY00 – Results

No additional work in evaluating the hydrolysis process was conducted in FY00.

7.4.7.3 FY01 – Current Work

Work will be conducted in FY01 on the effects of the antifoam selected for the STTP. This work will determine the fate of the antifoam across DWPF processes through the hydrolysis step, as well as the impact of the antifoam on the kinetics of the hydrolysis.

7.4.8 Glass Formulation Studies (STTP SOWM 16.0)

7.4.8.1 Previous Results

As indicated above, previous testing indicated that higher levels of MST would be required to achieve the necessary Sr and actinide removal. As a result, the impact of this higher MST loading on glass properties was investigated.[100] In addition, these tests also explored varying levels of PHA on the glass properties. Three different glasses were formulated for these studies.[101,102,103] All of the glasses formulated during these tests were very durable as measured by the PCT. In addition, performing 24-hour isothermal holds for the glass melts bound the liquidus temperature. This testing did indicate, however, that for Purex sludge, 30 wt% loading of Purex in glass may be near or at the edge of acceptability for liquidus. The viscosities of approximately half of the glasses formulated were measured. Again, when 30 wt% loading of Purex was tested, the viscosities were very near the lower viscosity limit.

However, crystal formation kinetics work was not explored during this work. The majority of glasses tested were predicted by the discriminator property model to be "phase separated" (multiple glass phases), but there was no experimental indication of phase separation.

7.4.8.2 FY00 – Results

No additional work in evaluation of crystal formation kinetics for vitrification operations was conducted in FY00.

7.4.8.3 FY01 – Current Work

During the first phase of the variability study on higher loading of PHA and MST, the PCCS models predicted 17 of the 23 glasses may be amorphously phase separated (i.e., the glasses may fail to meet the homogeneity constraint). While none of these glasses, all of which were rapidly quenched, exhibited poor PCT leaching characteristics; however, no kinetic studies were performed. FY01 work will complete these studies by cooling a limited number of glasses, using the canister centerline cooling profile, and then measuring PCT. These results will provide evidence on whether deleterious phase separation has occurred in glasses containing higher levels of PHA.

8.0 Pre-Down Selection 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 was $13.1 million and total projected funding for FY01 is $13.4 million. Total funding and funding source for each process is shown in Table 8.1.1. Alpha and strontium removal shows a significant increase in funding from FY00 to FY01, which can be attributed primarily to the exploration of alternatives to the current sorption and filtration baselines. It should be noted that CST shows a sizeable decrease in funding from FY00 to FY01, almost entirely in Gas Generation, due to the completion of the HFIR CST Column Test in FY00 and upcoming Tall Column Gas Disengagement Test which will be completed using FY00 carryover funds. Also, it is worth pointing out that the CSSX program did not begin until mid-FY00, so its FY00 funding level was actually greater than STTP and CST if annualized. In FY01, CSSX funding level continues to exceed funding levels for STTP and CST with the intent of accelerating the development of the technical maturity of CSSX relative to the other processes.

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

Table 8.1.1 Research and Development Program Funding

	FY00			**FY01**		
	EM-40	EM-50	Total	EM-40	EM-50	Total
Alpha and Sr Removal	600	930	1,530	1,620	960	2,580
CST Non-Elutable Ion Exchange	1,735	2,770	4,505	1,530	890	2,464
Caustic Side Solvent Extraction	3,325	0	3,325	2,350	2,620	4,970
Small Tank TPB Precipitation	515	3,260	3,775	1,992	1,350	3,342
Grand Total	**6,175**	**6,960**	**13,135**	**7,539**	**5,820**	**13,356**

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

	FY00						**FY01**					
	ORNL	**SRS**	**ANL**	**SNL**	**PNNL**	**Total**	**ORNL**	**SRS**	**ANL**	**SNL**	**PNNL**	**Total**
Alpha and Strontium Removal												
Monosodium Titanate (MST) Kinetics and Equilibrium		140				140		620				620
Alternative Alpha and Strontium Removal Technologies		270				270		540				540
MST Filtration and Settling		840				840		740				740
Alternatives to Solid/Liquid Separation						0		420				420
On-Line Effluent Monitor					280	280		260				260
	0	1250	0	0	280	1530	0	2580	0	0	0	2580
CST Non-Elutable Ion Exchange												
CST Column Performance												
Refinement of the Model		270				270		300				300
Alternative Column Configuration						0		270				270
CST Adsorbent Stability												
Alternative Pretreatment of IE-911				75		75				250		250
CST Chemical and Thermal Stability	380	350		200	100	1030	400	240		90	150	880
Waste/CST Precipitation Studies	110	80				190		130				130
Revised Manufacturing Process		400				400		480				480
Gas Generation												
Gas Disengagement	800					800						0
Cesium Loading Under Irradiation	1070	70				1140						0
CST Hydraulic Transfer												
Develop And Test Size-Reduction Method		250				250						
Develop Representative Sampling of CST/Sludge/Frit Slurry		350				350						0

	FY00						**FY01**					
	ORNL	**SRS**	**ANL**	**SNL**	**PNNL**	**Total**	**ORNL**	**SRS**	**ANL**	**SNL**	**PNNL**	**Total**
CST Non-Elutable Ion Exchange (continued)												
Coupled DWPF Operation						0						
DWPF Melter Operation						0		154				154
	2360	1770	0	275	100	4505	400	1574	0	340	150	2464
Caustic Side Solvent Extraction												
Solvent Preparation	520					520	140					140
Batch Equilibrium With Internal Irradiation Of Solvent	460	410				870	140	190				330
Batch Equilibrium With External Irradiation Of Solvent		200				200	140	50				190
Solvent Physical And Chemical Properties	370					370	550					550
Solvent Decomposition And Contactor Hydraulic Performance	580					580	370					370
Simulant and Real Waste 2-cm Contactor Flowsheet Tests		45	680			725		1590	1570			3160
Solvent Commercialization	60					60	230					230
	1990	655	680			3325	1570	1990	1570			4970
Small Tank TPB Precipitation												
Tetraphenylborate Decomposition Studies	1740	1425				3165	1350	1550				2900
Cesium Precipitation Kinetics						0						0
Washing And Filtration Studies						0						0
Antifoam Development		610				610		330				330
Saltstone Facility						0						0
Hydrolysis Testing						0		45				45
Glass Formulation Studies						0		67				67
	1740	2035				3775	1350	1992				3342
Grand Total	**6090**	**5710**	**680**	**275**	**380**	**13135**	**3320**	**8075**	**1570**	**340**	**150**	**13356**

8.2 Overview of the Salt Processing Program Schedule

The Level 0 Schedule for the SPP is presented in Figure 8.2.1. Science and technology development will proceed in parallel with preconceptual data package development, and science and technology reports for each Cs removal process will be prepared by March 31, 2001. The alpha and Sr removal approach that optimizes each flowsheet will be addressed in these reports. A science and technology summary report will be provided to DOE in support of the technology down selection. The down selection decision will feed into preparation of the SEIS and a Record of Decision by September 30, 2001.

8.3 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 8.3.1. The complete detailed schedule is shown in Appendix C. The detailed schedule in Appendix C is used by all program participants to manage their work. Schedule status is presented at a Technology Development Plan-of-the-Week Meeting and an SPP Plan-of-the-Week Meeting. Schedules are updated weekly. All changes that impact an EM-50 or EM-40 task approved schedule, scope, or budget must be approved by the SPP Change Control Board (see Section 10.0, R&D Program Controls). The SPP summary (Level 0) schedule (Figure 8.2.1) shows that several R&D activities proceed well into FY01. STTP bench-scale CST studies, CSSX real waste tests, CST manufacturing revisions with UOP, and MST kinetics/Pu oxidation state are examples of long-term activities. The program's goal is to resolve all high-risk technology issues in time to support the down select decision in June 2001 as shown in Figure 8.3.1. It is fully anticipated that technology development activities will continue for the selected alternative(s) well into the design phase.

Figure 8.2.1 Salt Waste Processing Project Level 0 Schedule

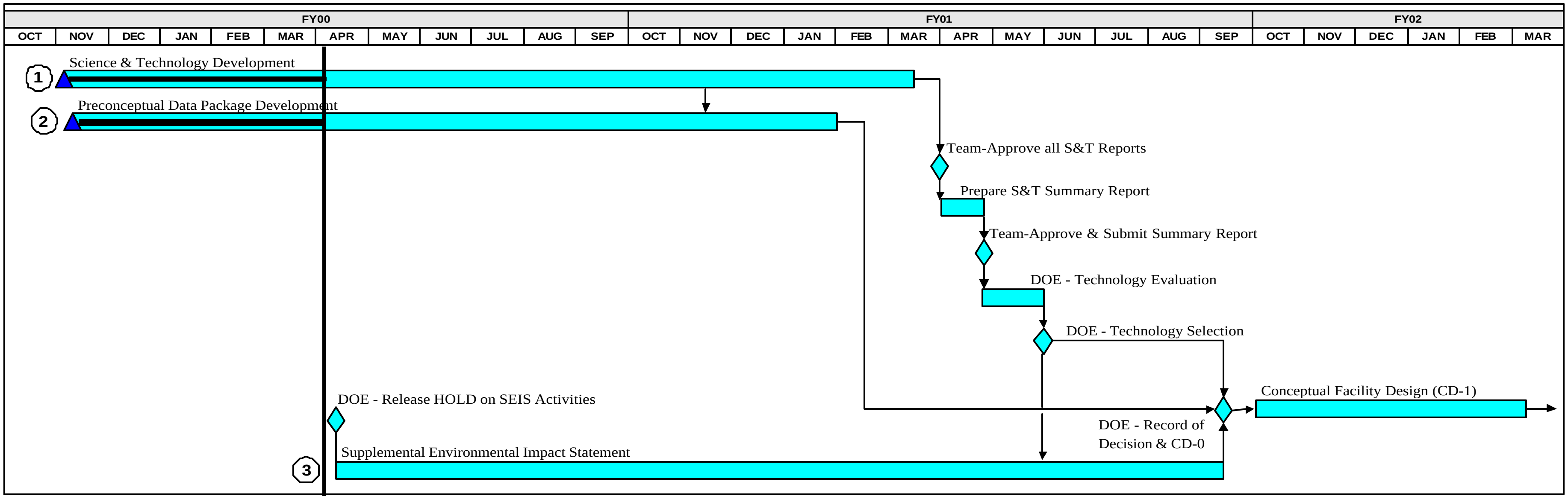
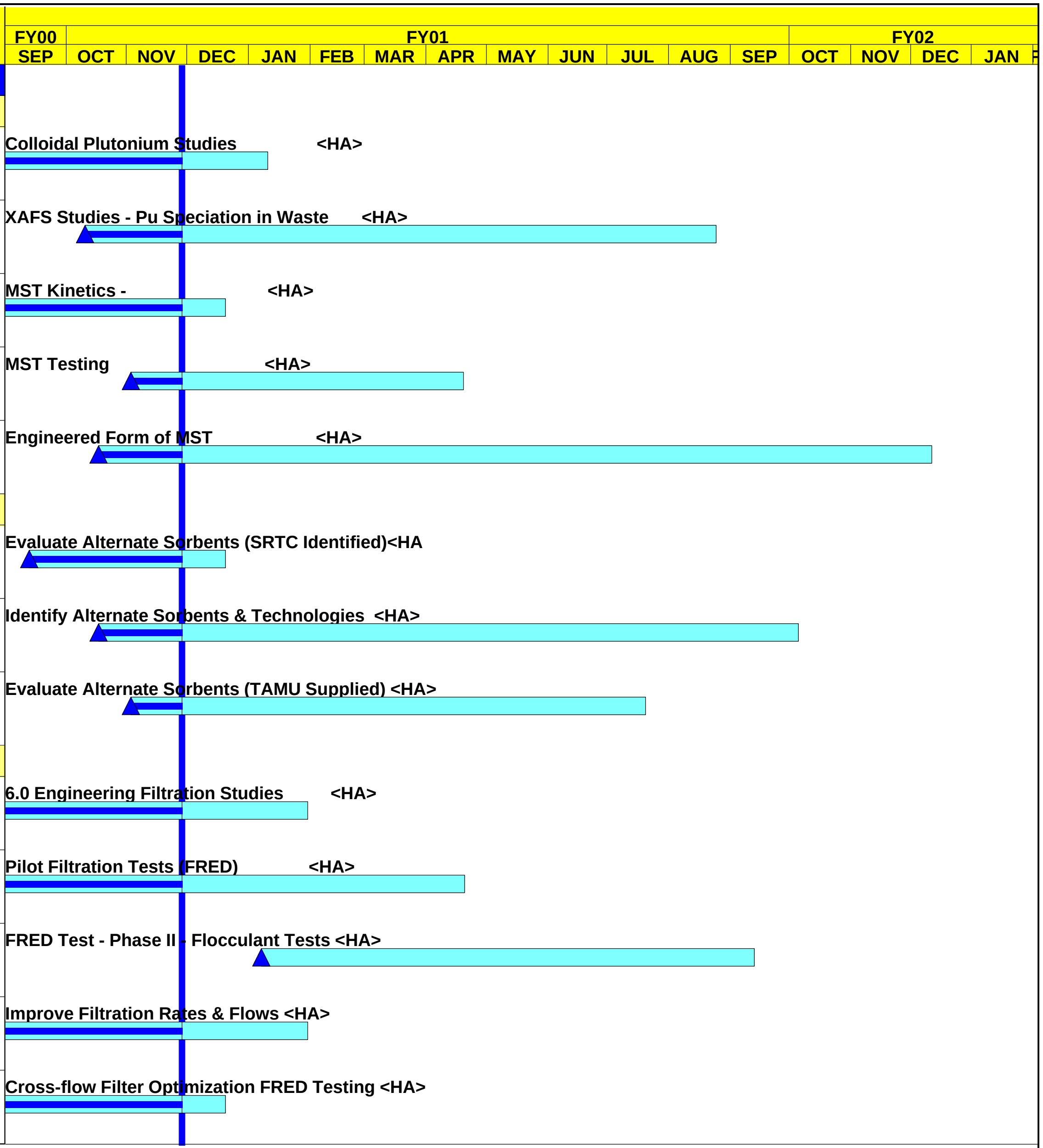


Figure 8.3.1 Summary R&D Program Schedule

Note: To be provided.

Activity ID	Total Float	Activity Description	To Go Wk Days	Early Start	Early Finish	Lead
Alpha & Strontium Removal						
Monosodium Titanate (MST) Kinetics & Equilibrium						
WAMST1200	**60**	Colloidal Plutonium Studies <HA>	29*	14AUG00A	10JAN01	TBP
WAMST12100	**1,083**	XAFS Studies - Pu Speciation in Waste <HA>	187*	11OCT00A	24AUG01	LNO
WAMST13	**74**	MST Kinetics - <HA>	15*	12JAN00A	19DEC00	DTH
WAMST15000	**1,173**	MST Testing <HA>	97*	03NOV00A	18APR01	DTH
WAMST18000	**1,009**	Engineered Form of MST <HA>	261*	18OCT00A	11DEC01	DTH
Alternative Alpha And Strontium Removal						
WAMST13E	**1,255**	Evaluate Alternate Sorbents (SRTC Identified)<HA	15*	13SEP00A	19DEC00	DTH
WAMST16000	**1,055**	Identify Alternate Sorbents & Technologies <HA>	215*	18OCT00A	04OCT01	DTH
WAMST17000	**1,109**	Evaluate Alternate Sorbents (TAMU Supplied) <HA>	161*	03NOV00A	19JUL01	DTH
MST Filtration and Settling						
WACST600	**46**	6.0 Engineering Filtration Studies <HA>	43*	19NOV99A	30JAN01	MRP
WAMST23000	**1,172**	Pilot Filtration Tests (FRED) <HA>	98*	01AUG00A	19APR01	MRP
WAMST23500	**1,071**	FRED Test - Phase II - Flocculant Tests <HA>	173*	08JAN01	12SEP01	MRP
WAMST62	**46**	Improve Filtration Rates & Flows <HA>	43*	24JAN00A	30JAN01	MRP
WAMST623	**1,255**	Cross-flow Filter Optimization FRED Testing <HA>	15*	24JAN00A	19DEC00	MRP



Start Date	01OCT98
Finish Date	09MAY05
Data Date	29NOV00
Run Date	04DEC00 10:21

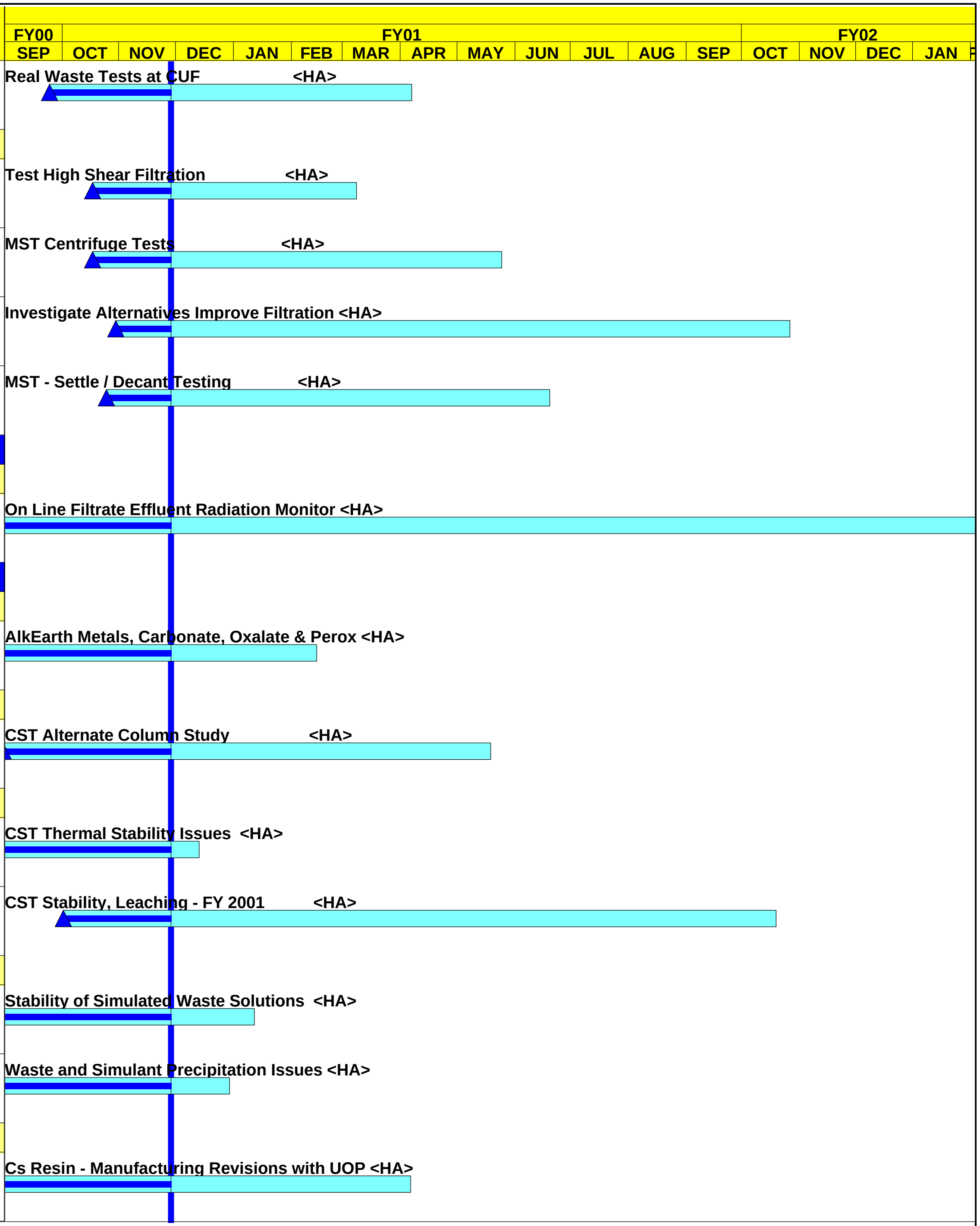
🟩 Early Bar
▬ Progress Bar
Critical Activity

SALT

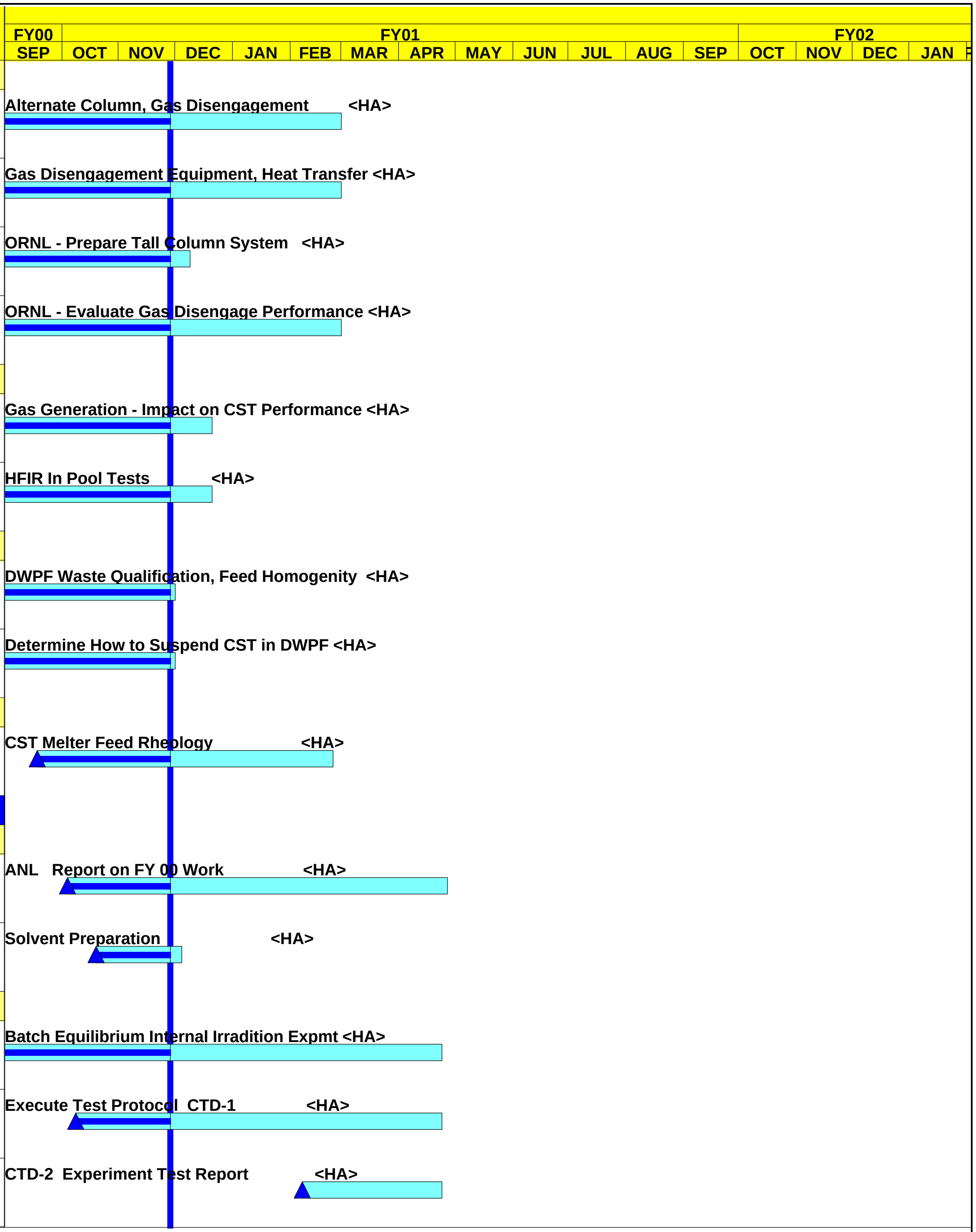
Westinghouse Savannah River
Salt Processing Program
Mid Level Summary

Information Only

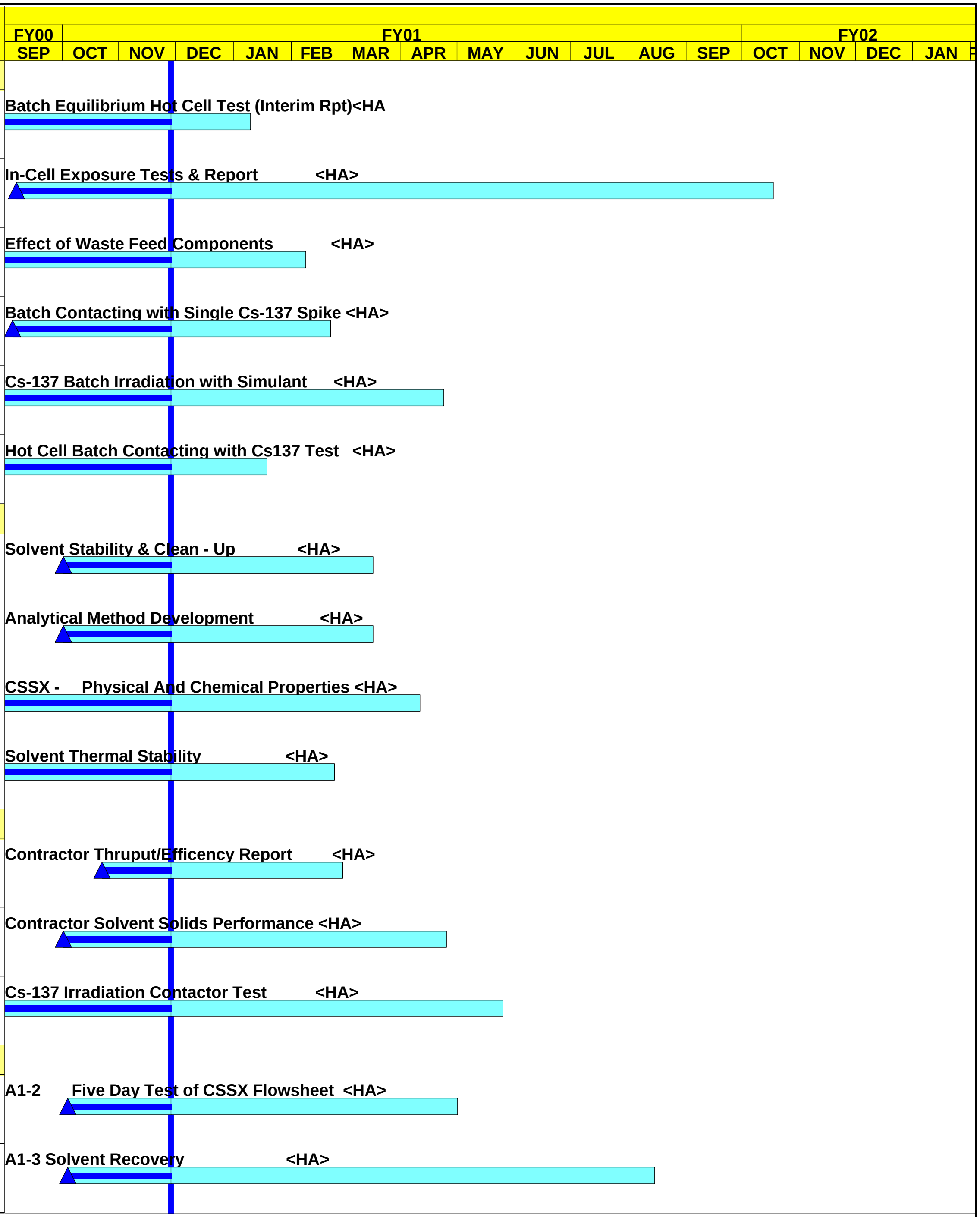
Activity ID	Total Float	Activity Description	To Go Wk Days	Early Start	Early Finish	Lead
WAMST6400	**-1**	Real Waste Tests at CUF <HA>	90*	25SEP00A	06APR01	MRP
Alternatives to Solid/Liquid Separation Testing						
WAMST19000	**1,202**	Test High Shear Filtration <HA>	68*	18OCT00A	07MAR01	MRP
WAMST20000	**1,147**	MST Centrifuge Tests <HA>	123*	18OCT00A	24MAY01	MRP
WAMST21000	**1,039**	Investigate Alternatives Improve Filtration <HA>	231*	30OCT00A	26OCT01	MRP
WAMST22000	**1,130**	MST - Settle / Decant Testing <HA>	140*	25OCT00A	19JUN01	MRP
On Line Monitor						
--						
WASDM0000	**417**	On Line Filtrate Effluent Radiation Monitor <HA>	287*	04OCT99A	09MAY02	KJR
CST Non-Elutable Ion Exchange						
CST - Refinement of the Model						
WACST52	**35**	AlkEarth Metals, Carbonate, Oxalate & Perox <HA>	54*	03JAN00A	14FEB01	FF
CST - Alternative Column Design						
WACOL0000	**1,151**	CST Alternate Column Study <HA>	119*	30AUG00A	18MAY01	LC
CST - Stability						
WACST23	**78**	CST Thermal Stability Issues <HA>	11*	03JAN00A	13DEC00	DDW
WAORN2301	**1,052**	CST Stability, Leaching - FY 2001 <HA>	232*	02OCT00A	18OCT01	TK
CST - Precipitation Kinetics						
WACST51	**1,240**	Stability of Simulated Waste Solutions <HA>	30*	03JAN00A	11JAN01	DDW
WAORN4001	**69**	Waste and Simulant Precipitation Issues <HA>	23*	03NOV99A	29DEC00	TK
CST - Revised Manufacturing Process						
WACST21	**0**	Cs Resin - Manufacturing Revisions with UOP <HA>	89*	21FEB00A	05APR01	WRW



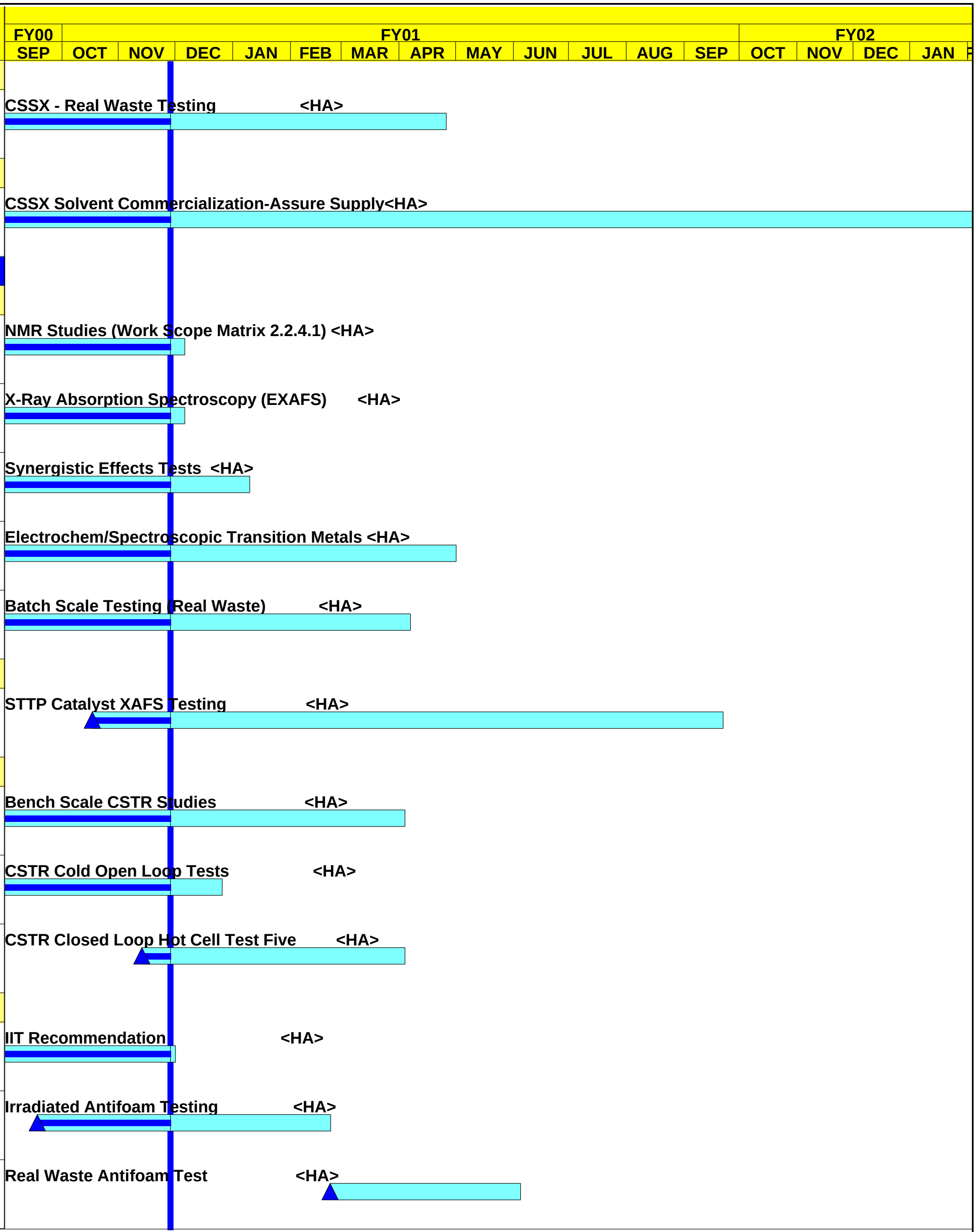
Activity ID	Total Float	Activity Description	To Go Wk Days	Early Start	Early Finish	Lead
CST - Gas Disengagement						
WACST8000	**1,159**	Alternate Column, Gas Disengagement <HA>	63*	08NOV99A	28FEB01	WVP
WAORN5001	**1,169**	Gas Disengagement Equipment, Heat Transfer <HA>	66*	03NOV99A	28FEB01	TK
WAORN5019	**1,169**	ORNL - Prepare Tall Column System <HA>	8*	04JAN00A	08DEC00	TK
WAORN5048	**1,169**	ORNL - Evaluate Gas Disengage Performance <HA>	66*	17JUL00A	28FEB01	TK
CST - Gas Generation						
WAORN6001	**76**	Gas Generation - Impact on CST Performance <HA>	16*	10NOV99A	20DEC00	TK
WAORN6066	**76**	HFIR In Pool Tests <HA>	16*	25AUG00A	20DEC00	TK
CST - Develop and Test Size Reduced Method						
WACST1900	**87**	DWPF Waste Qualification, Feed Homogenity <HA>	2*	19NOV99A	30NOV00	FGS
WACST194	**87**	Determine How to Suspend CST in DWPF <HA>	2*	17JAN00A	30NOV00	FGS
DWPF Melter Operation						
WACST195A	**29**	CST Melter Feed Rheology <HA>	60*	18SEP00A	23FEB01	JRH
Caustic Side Solvent Extraction						
CSSX - Solvent Preparation						
WAANL7100	**1,167**	ANL Report on FY 00 Work <HA>	103*	04OCT00A	26APR01	LNK
WACX41500	**1,280**	Solvent Preparation <HA>	4*	20OCT00A	04DEC00	LNK
Batch Equilibrium - Internal Solvent Irradiation						
WAORN7137	**-12**	Batch Equilibrium Internal Irradition Expmt <HA>	104*	07JUN00A	23APR01	LNK
WAORN7141	**-12**	Execute Test Protocol CTD-1 <HA>	104*	09OCT00A	23APR01	LNK
WAORN7154	**-12**	CTD-2 Experiment Test Report <HA>	53*	08FEB01	23APR01	LNK



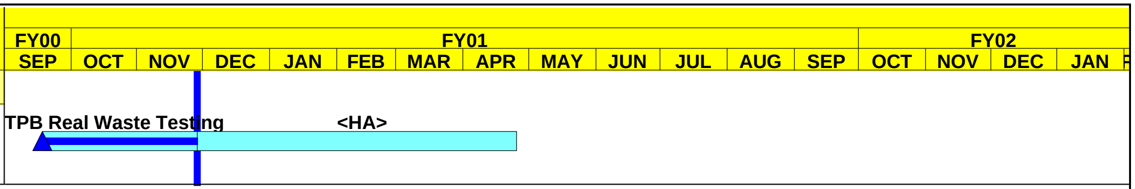
Activity ID	Total Float	Activity Description	To Go Wk Days	Early Start	Early Finish	Lead
Batch Equilibrium-External Solvent Irradiation						
WACX412	**61**	Batch Equilibrium Hot Cell Test (Interim Rpt)<HA	28*	03JUL00A	09JAN01	RAP
WACX412M00	**1,046**	In-Cell Exposure Tests & Report <HA>	224*	07SEP00A	17OCT01	RAP
WAORN7075	**-2**	Effect of Waste Feed Components <HA>	52*	18MAY00A	08FEB01	LNK
WAORN7081	**1,223**	Batch Contacting with Single Cs-137 Spike <HA>	61*	05SEP00A	21FEB01	LNK
WAORN7108	**-12**	Cs-137 Batch Irradiation with Simulant <HA>	104*	03APR00A	23APR01	LNK
WAORN7117	**33**	Hot Cell Batch Contacting with Cs137 Test <HA>	37*	03APR00A	18JAN01	LNK
CSSX - Physical & Chemical Properties						
WACX417000	**1,206**	Solvent Stability & Clean - Up <HA>	78*	02OCT00A	16MAR01	LNK
WACX417500	**1,206**	Analytical Method Development <HA>	78*	02OCT00A	16MAR01	LNK
WAORN7058	**-3**	CSSX - Physical And Chemical Properties <HA>	95*	03APR00A	10APR01	LNK
WAORN7066	**29**	Solvent Thermal Stability <HA>	63*	10MAY00A	23FEB01	LNK
Solvent Decomposition & Contactor Hydraulic Perf						
WACX41300	**1,218**	Contractor Thruput/Efficency Report <HA>	66*	23OCT00A	28FEB01	LNK
WACX41400	**1,179**	Contractor Solvent Solids Performance <HA>	105*	02OCT00A	24APR01	LNK
WAORN7161	**1,156**	Cs-137 Irradiation Contactor Test <HA>	128*	03APR00A	25MAY01	LNK
Waste Simulant & 2 cm Contactor Flowsheet						
WAANL7200	**1,165**	A1-2 Five Day Test of CSSX Flowsheet <HA>	105*	04OCT00A	30APR01	RL
WAANL7300	**1,091**	A1-3 Solvent Recovery <HA>	179*	04OCT00A	14AUG01	RL



Activity ID	Total Float	Activity Description	To Go Wk Days	Early Start	Early Finish	Lead
CSSX - Real Waste Contactor Testing						
WACX1000	**-10**	CSSX - Real Waste Testing <HA>	80*	10MAY00A	25APR01	RWB
CSSX - Solvent Commercialization & Supply						
WACX33000	**621**	CSSX Solvent Commercialization-Assure Supply<HA>	390*	10MAY00A	12NOV02	RWB
Small Tank TPB Precipitation						
Tetraphenyborate Decomposition Studies						
WAORNL2001	**87**	NMR Studies (Work Scope Matrix 2.2.4.1) <HA>	5*	08DEC99A	05DEC00	TK
WATPB2201	**1,265**	X-Ray Absorption Spectroscopy (EXAFS) <HA>	5*	30MAR00A	05DEC00	RAP
WATPB223	**61**	Synergistic Effects Tests <HA>	28*	28JAN00A	09JAN01	MJB
WATPB225	**106**	Electrochem/Spectroscopic Transition Metals <HA>	105*	24JAN00A	30APR01	TBP
WATPB23	**-1**	Batch Scale Testing (Real Waste) <HA>	90*	30MAY00A	06APR01	MJB
XAFS Studies for Catalyst Identification						
WATPB21300	**1,064**	STTP Catalyst XAFS Testing <HA>	206*	18OCT00A	21SEP01	MJB
TPB - Solubility Data						
WAORN3001	**2**	Bench Scale CSTR Studies <HA>	90*	01OCT99A	03APR01	JW
WAORN3070	**12**	CSTR Cold Open Loop Tests <HA>	19*	20JUN00A	25DEC00	JW
WAORN3216	**2**	CSTR Closed Loop Hot Cell Test Five <HA>	90*	13NOV00A	03APR01	JW
TPB - Antifoam Physical Properties						
WATPB51000	**1,268**	IIT Recommendation <HA>	2*	03APR00A	30NOV00	DPL
WATPB53000	**1,116**	Irradiated Antifoam Testing <HA>	59*	18SEP00A	22FEB01	JRH
WATPB56	**1,141**	Real Waste Antifoam Test <HA>	70*	23FEB01	04JUN01	RAP



Activity ID	Total Float	Activity Description	To Go Wk Days	Early Start	Early Finish	Lead
TPB Real Waste Testing						
WATPB4400	**-12**	TPB Real Waste Testing <HA>	101*	18SEP00A	24APR01	JTC



9.0 Post-Down Selection R&D Program

The Department of Energy (DOE) is scheduled to select the preferred Cs removal process in June 2001. It is anticipated that a backup technology will also be identified. After this down-selection decision, the nature of the R&D work on the selected process will transition from technology development to providing input for pilot plant design and to generating data needed for conceptual and preliminary design of the Salt Waste Processing Facility. This will include laboratory studies, bench scale tests, and prototype equipment development. R&D activities are expected to continue on the backup technology, and additional direction will be provided by DOE regarding scope of the desired R&D activities for the technology.

Future work areas for each technology have been identified that will be pursued as appropriate following the down-selection. The work described below is not intended to be comprehensive of all future R&D that will be required, but rather to indicate key areas that are needed extensions of the pre-down-selection R&D described in Section 7. These activities would be conducted in late FY01 and beyond.

9.1 Alpha and Sr Removal

9.1.1 Monosodium Titanate (MST) Kinetics and Equilibrium

Work in future years will continue to examine sorption kinetics with a variety of real waste samples as these samples become available through routine waste characterization efforts. The increasing database of characterization information will permit development of a highly reliable model to predict process performance.

Improved understanding of binding mechanisms may suggest lines of inquiry directed at improving the formulation of the MST. Similarly, past experience in storing the chemical suggests that modifications in the synthesis process may decrease the material’s tendency to settle and harden over time. Finally, the program needs to assess the influence of storage conditions on the sorbent’s shelf life.

9.1.2 Alternative Alpha and Strontium Removal Technologies

The extent of future work on alternate sorbents depends strongly on the findings of currently defined research on MST and the alternate materials or approaches. Any promising new sorbent would require a series of tasks to examine scale-up of synthesis and commercialization of the material. Integrated testing of the new sorbents within the entire waste processing system will occur. In particular, testing will need to verify the efficacy of the current chemical cleaning methods for the cross-flow filters or develop alternate cleaning strategies.

9.1.3 MST Filtration and Settling

Future work will largely focus on pilot-scale testing to the extent necessary. The studies will assess operational aspects of the equipment. Rheology properties of MST/sludge slurries will be measured to aid in sizing and development work on the filter feed pumps. Similarly, more extensive testing with radioactive samples would need to occur if the program elects to pursue the use of chemical additives to improve separation efficiency.

9.1.4 Feed Clarification Alternatives

If the program selects an approach other than cross-flow filtration, future work will need to test the technology with actual waste samples. Also, testing will need to examine performance of the technology at the pilot-scale.

9.1.5 On-Line Effluent Monitor

Future work will deploy the prototype unit within a technical demonstration facility, or pilot-scale facility. If, however, the independent consultant judges the technical maturity of the analyzer as insufficient for deployment at this scale, the program will reassess the research program appropriately.

9.2 CST Non-Elutable Ion Exchange

9.2.1 Alternative Column Design Prototype

The design basis columns for CST non-elutable ion exchange are relatively large. This raises a concern that a fully loaded column will contain approximately 5 MCi of Cs-137 and create an exceedingly intense radiation field. In addition, incidents of column plugging and clumping of CST particles suggest that fixed-bed columns may not be the most suitable for the Salt Processing Project. Therefore, alternative column designs are being evaluated. One of the most interesting designs consists of a pulsed moving bed or “Higgins” loop. The perceived advantages of such a design are that the CST particles are fed into the bottom of a column and move up whereas the feed solution enters the top of the column and moves down. This produces a column that contains fully loaded sorbent only in the upper portion of the column. Periodic agitation of the bed also minimizes the chances of clumping. Although in principle the design is more suitable to processing of the of SRS salt waste, UOP has raised a concern about attrition of particles due to the agitation and SRS personnel have raised a concern about the fate of fines in such a design. Therefore, before an alternative design can be selected, a prototype column must be built and tested.

9.2.2 Size-Reduction Scaled-up Vendor Demonstration

Representative sampling of the CST/sludge/frit slurry is required for reliable operation of DWPF. The particle size of spent CST is too large to enable representative sampling by the Hydragard® sampler. Therefore, CST must be reduced in size before it is mixed with the sludge/frit slurry and delivered to DWPF. Two vendors performed brief small-scale demonstrations of size-reduction equipment during FY00. Although the results are encouraging, issues related to prolonged operation, maintenance, and wear of the equipment were not addressed. Therefore, additional tests scaled up to larger quantities of CST are needed in order to assess the ruggedness of the equipment and the complexity involved with servicing the equipment. The complete integration of size-reduction into DWPF must be developed. The integrated DWPF interface development would include receiving loaded CST, storing, grinding, particle size analysis, and quantitative transfers.

9.2.3 On-line Particle-Size Analyzer

After size-reduction, the particle-size distribution of the CST must be determined to ensure that the slurry will be homogeneous and sampled representatively. The current design requires the removal of grab samples to measure these values. However, this method is somewhat unreliable because the particle size distribution could depend on the level from which the sample is taken, especially if some settling has occurred. Therefore, a more desirable method would be measuring the particle-size distribution in-line while the slurry is flowing and homogeneously mixed.

9.2.4 Calculation of Equilibrium State of Tank Waste

Experiments in which CST particles were treated with SRS simulants demonstrated that aluminosilicate tends to crystallize out and eventually produces a coating on the particles that may be responsible for slower kinetics and reduced capacity for Cs absorption. In addition, several SRS simulants were observed to develop precipitates with time. The precipitation of the aluminosilicate is hypothesized to result when a simulant that is supersaturated with respect to aluminum and possibly silicon makes contact with a surface upon which the precipitate can nucleate and propagate. The various wastes that will be processed by either CST non-elutable ion exchange or caustic-side solvent extraction should be evaluated by thermodynamic calculations to determine if the same state of supersaturation with respect to aluminum or silicon exists in them. If so, a strategy for dilution of these wastes must be developed to ensure that precipitation of aluminosilicates will not interfere with the Cs-removal processes. Initial testing will begin in FY01, but the need for additional studies are anticipated.

9.2.5 Effect of Temperature on Cs Loading and Gas Generation

The effect of gas generation on Cs loading of CST (IE-911) was measured by placing a column with CST in the radiation field created by a spent fuel assembly from HFIR. For this experiment, the temperature was tightly controlled within the 25-35°C range. The gas generation expected at these temperatures was calculated so that the results could be incorporated into the experimental design. It is also necessary to take into account that Cs-sorption decreases with increasing temperature. For this reason, additional calculations are needed to determine how radiolytic heating affects the CST capacity for Cs sorption. Increasing the temperature in the column would lower the amount of Cs loaded and thereby lead to the production of less gas.

9.2.6 Clumping of CST

Treatment of CST (IE-911) with various solutions has caused the CST to clump together. Statements by UOP indicate that this clumping is to be expected and will not interfere with column operation. ORNL researchers have observed that the clumps are easily broken up and do not form clumps again after being broken up. However, the clumping incidents have involved CST that was in contact with fresh simulant for only a short time (see Section 7.2.3.3.1). The data collected thus far in this area give no indication of how the CST will behave if it is located near the top of the lead column and interacts with fresh waste for a period of months. Precipitation of aluminosilicates in the first few inches of the lead column could lead to firmly solidified clumps that are not easily broken up or even to pluggage due to excessive build up of an aluminosilicate precipitate.

9.2.7 Test Re-engineered CST

Improved manufacturing by UOP of the engineered form of CST (IE-911) will produce a “reference” batch and two pre-production batches of IE-911 that are designed to contain lower amounts of leachable Nb. Variations in the manufacturing of large lots of production samples could possibly alter the properties of the product with respect to Cs absorption or aluminosilicate precipitation, among others. Therefore, the production batches of IE-911 from UOP will undergo various tests at SRTC, ORNL, SNL and PNNL. Tests at SRTC will focus on K_d measurements, Cs-loading curves, column tests, leaching tests, and physical properties. These tests will be supplemented at ORNL with long-term column tests using average simulant at room temperature and long-term batch leaching tests using average and high-OH simulants at five temperatures. Tests at SNL will examine the leached materials with SEM and TEM. Tests at PNNL will determine the Cs-absorption capacity of the new materials.

9.2.8 Further Evaluation of Revised CST Pretreatment Process

The development of a significantly different pretreatment process will necessitate further R&D to demonstrate the process, obtain preliminary design bases, and prove that the pretreatment does not impact CST performance. The improved pretreatment processes currently under development are designed to remove leachable Nb from the sorbent. Preliminary results suggest that pH adjustment (acid—base) is an important factor in converting excess Nb into a form that is easily leached from fresh IE-911. Fresh sorbent that has been pretreated will be tested to show that the Cs loading capacity and absorption kinetics are comparable to the baseline values.

9.2.9 DWPF Glass Composition and Property Correlations

Waste qualification for DWPF included an extensive statistically-based test that proved the slurry receipt adjustment tank (SRAT), slurry mix evaporator (SME) and melter feed tank were homogeneously mixed and that the Hydragard® results matched the tank composition. This was performed in the DPWF during cold runs (simulants) and involved manual grab samples from the (full-scale) vessels. It may be necessary to repeat the waste qualification tests using a full-scale SRAT/SME and full-scale duplicate of a DWPF Hydragard® system to prove that CST/sludge/frit slurries meet the same compositional requirements.

The fundamental philosophy behind the DWPF glass quality control program is "if you know the composition of the melter feed, then you can predict the glass properties". Homogeneity, with sampling and analysis, is the "know the composition" part while the property correlations (liquidus, viscosity, and durability) are the "predict the properties" part. These are then put into a statistically based program called the Product Composition Control System (PCCS) that uses the analytical results, along with all the sampling, analytical, and correlation uncertainties, to predict whether a particular SME batch will be processable (liquidus and viscosity) and acceptable for the repository (durability). New glass fit compositions could be required to achieve the desired properties. It will be necessary to perform extensive experiments to expand the correlations to include new melter feed composition containing CST. New uncertainties will then have to be established and the PCCS modified to include the new information.

9.2.10 Foam Control in the SRAT/SME

Prior testing indicated that CST caused increased foaming. SRTC has been working to improve foam control in the SRAT/SME. Experiments would be needed to evaluate whether the improved foam control program satisfactorily controls foaming caused by CST. If not, additional development would be required.

9.2.11 DWPF Melter Feed Homogeneity

The DWPF melter feed loop system (located in the SRTC Thermofluids Laboratory) will be tested using a combined, simulated HLW sludge, CST, and frit feed. This test will include a statistical comparison of the chemical composition of the contents of the MFT tank with the composition of the material that is diverted to the melter through the feed delivery system. The goal is to demonstrate that CST does not preferentially divert to the melter, preferentially remain with the MFT slurry, or cause segregation of the sludge and frit. Simulated feed will be produced as part of this task using the Glass Feed Preparation System (GFPS).

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

9.3 Caustic Side Solvent Extraction

9.3.1 Solvent Preparation

Solvent preparation related to experimental activities required for conceptual design must be completed and the solvent performance verified with appropriate quality assurance tests. Activities related to transferring to SRS the knowledge and techniques for solvent preparation must be undertaken.

Assistance will be required by SRS related to scale-up of the extractant and modifier synthesis. Issues related to appropriate synthetic steps for large-scale preparations will be addressed.

9.3.2 Solvent Optimization

Final decisions on the solvent composition must be made, as R&D information obtained in FY00 and thus far in FY01 point to possible improvements in solvent performance. Optimal concentrations of solvent components could be employed, including a higher modifier concentration, lower extractant concentration, and a higher TOA concentration. Higher modifier concentration confers 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 suggests that increasing the TOA concentration will improve the stripping in the presence of organic components in the waste feed.

The impact on the performance of the flowsheet due to possible changes in the current baseline solvent composition will need to be evaluated with small-scale contactor studies.

9.3.3 Solvent Stability and Cleanup Tests

Solvent cleanup and reconstitution are important issues. Current efforts focusing on NaOH washing of the solvent appears to be effective; however, the number of solvent recycles has been limited. Large numbers of solvent cycles may require a more optimal washing and/or solvent treatment. Data are needed from the standpoint of extensive solvent recycle regarding the identity of minor components that build up in the solvent, the partitioning of these components, and the effectiveness of various solvent cleanup and reconstitution techniques. Experiments involving extensive solvent recycle will be needed, together with efforts to identify the impurities that become concentrated in the solvent. Tests may also be needed to determine distribution and other properties of the impurities, such as coalescence, third-phase formation, and the effects on Cs distribution.

Current data show the baseline solvent is chemically, thermally and radiolytically stable. However, data on certain degradation products, such as nitration products, will still be needed to properly address safety issues. Hence, experiments will be needed for the identification and analysis of nitrated degradation products relevant to process and plant safety.

9.3.4 Flowsheet Optimization

A detailed model of the complete flowsheet will be needed to predict performance as the feed composition changes with waste sources and blending operations. Some work will be completed in FY01, mainly regarding the major variables of temperature and concentrations of the major ions in the feed. This model will need to be expanded to include the effect of other ions and known impurities, as well as the effect of changes in solvent-component concentrations. The solvent-component concentrations will vary with usage and with the normal precision of solvent makeup expected in a production plant environment. The modeling activity will need to be supported by the determination of distribution ratios of all the important species in the waste feed. A large data set for the current baseline solvent will be available from FY00 and FY01 activities.

For the design of a temperature management system in the process plant, studies to gain an understanding of the heat sources within the flowsheet will be required. Some of the possible heat sources include Joule heating of the solutions within the mixing and separating zones of the contactor, chemical reactions, and heats of dilutions.

Results obtained in FY00 with the 5-cm contactors during the throughput and mass transfer efficiency tests suggest the need to design the contactors so that solution-mixing processes dominate any rotor pumping action. The commercially procured contactors used in the FY00 tests were designed primary for oil-water separation with the rotors having considerable pumping action. With the CSSX flowsheet O/A ratios, particularly in the scrub and stripping segments, this results in a potential foaming problem caused by the large amount of air pulled into the separating zone of the contactor. Design and experimental verification studies will be required to meet the contactor design needs.

Results from the “proof-of-concept” flowsheet test performed by ANL in late FY00 show that the mass transfer of the contactors stops when the cesium concentration in the extraction and strip segments achieve ~ 2×10^{-9} M. The end of test stage drain samples yielded data, which represents phase equilibrium conditions, that indicates the distribution of cesium between the organic and aqueous phases is the correct ratio. These observations suggest that mass transfer in the contactor may have reached a limited value. Slow reaction kinetics at very low concentrations, which would decrease contactor stage efficiency, could be one possible explanation for the observations. A second explanation could be very low level contamination, such as surface adsorption, of the contactor stages. Studies involving contactor mass transfer efficiency at low concentrations are required to understand the observations. The information from the proposed studies will provide technically important input to any proposed changes in the size of the baseline contactor cascade.

Although the CSSX baseline flowsheet includes a step for removal of alpha radionuclides and Sr, the required DF is relatively low. Currently, no data exists on how these radionuclides distribute in CSSX. To gain the necessary data, experiments should be designed and conducted as appropriate to understand how the distribution of these species depend on aqueous and solvent compositional variables. The benefit of these data would be not only knowledge of the distribution of such species in the flowsheet, but it may also provide an indication of whether the potential exists to effect removal within CSSX. In addition it may also be of benefit to extend such studies to include the removal of Sr and alpha radionuclides by other solvent systems that could be used in tandem with CSSX. A number of potential extractants are known from available literature. Thus, tests should be designed to investigate the possibility of either removing Sr and alpha radionuclides within CSSX or in an alternate process in tandem with CSSX.

9.3.5 Solvent Rheology

Some studies of CSSX solvent rheology have been completed; however, these data are limited. Additional studies need to be completed that define the rheology of the solvent with respect to temperature, composition, etc. These studies would also include density variations as a function of temperature.

9.4 Small Tank Tetraphenylborate Precipitation

9.4.1 Cs Precipitation Kinetics

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

Testing will be performed to further evaluate the phenomenon of co-precipitation of NaTPB. These tests will focus on the impact of a number of parameters effecting the extent of NaTPB precipitation, including the agitation energy employed, the bulk Na molarity, the concentration of the TPB ion in the feed stock, and the K concentration in the waste feed. In addition, these tests will use available analytical tools, such as XRD, to illuminate the fundamental nature of the crystals formed. Additional studies will investigate the mixing achieved during the precipitation reaction through the use of radiotracers, such as Na^{22}. Further testing will attempt to produce mixed crystals of known stoichometry and to determine the nature of these crystals, both by XRD and by determining the solubility of these crystals. These tests will likely provide insight into the optimal conditions for operations of the precipitation process. It is anticipated that results from these tests will be incorporated into a 1/4000-scale demonstration of the precipitation process. A fundamental understanding of residence time distribution in the CSTRs will improve understanding of Cs, Sr, and actinide removal from the waste. Testing will include analysis of precipitation rates as a function of residence time, as well as analysis of precipitate particle sizes.

9.4.2 Precipitation Process Optimization

Several opportunities exist to improve performance and control of the STTP process. Those that will be considered include adding TPB to both reactors (“dual strike”) method of TPB addition and improved mixing.

9.4.3 Washing and Filtration Studies

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

9.4.4 Hydrolysis Testing

Additional work will explore ways to minimize the Cu catalyst concentration and determine the corresponding maximum acceptable range of formic acid addition. Testing will also develop a relationship between nitrite and nitrate concentration in the product stream and the absorbed dose. The identified optimum process parameters will be validated with a complete bench-scale hydrolysis process. Work in future years will likely explore variations of the proposed hydrolysis process, including exploring the use of other catalysts, other forms of the Cu catalyst (such as supported Cu) or recovery of the Cu from the product stream (to minimize the impact of Cu on glass quality). The technical feasibility of recycling the catalyst will also be assessed.

9.4.5 Saltstone Facility

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

9.5 Salt Waste Processing Pilot Plant

Construction of a pilot plant is planned to demonstrate unit and integrated operations of the selected radionuclide removal processes.[104] The pilot plant will fulfill the following objectives:

- Collect process data (feedback to plant design as appropriate) on:
  - Unit operations,
  - Integrated process,
  - Process extremes and upset conditions,
  - Process validation, and
  - Equipment evaluations.
- Provide training for engineers and operators.
- Provide facility troubleshooting support.
- Qualify feeds for integrated operation.
- Provide tours and public education of the selected process.

Sizing of the pilot plant will consider pilot facilities in the chemical industry, which are typically on a scale of 1/100 to 1/10. The use of simulated waste with radionuclide tracers for some tests may be employed, and the use of real radioactive waste during testing may also be required.

The pilot plant will be located in an existing process area that is well away from the site boundary and where operations with radiological materials have already occurred. Current plans call for the pilot plant to be located either at the Late Wash Facility, near DWPF, or in another area that is similar or comparable to the location of the full facility.

The pilot plant will be located in a fully functional facility. Modularized design will be used, as appropriate, to facilitate remote modifications. The pilot plant will be provided with support services and balance of plant processes, including utilities, process support, structural systems, and infrastructure/habitability services to support operations and to ensure safety of personnel, equipment, and the environment. It will be equipped with the necessary scaled down hardware, instrumentation and controls.

The pilot plant lifetime will span from development until construction of the Salt Waste Processing Facility is complete. Provisions will be made for periodic decontamination, possible reuse, and ultimate decontamination and decommissioning.

10.0 R&D Program Controls

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

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

The SPP/R&D Project is using existing procedures as described in this R&D Project Controls description, rather than developing separate project management procedures.

10.1 Work Authorization

Scope, cost, and schedule of SPP/R&D work for the SRS Salt Processing alternatives are documented in performer-developed documents – either an EM-50 Technical Task Plan (TTP) or EM-40 WSRC Annual Operating Plan (AOP). In both cases, existing procedures and guidance define planning requirements. In addition, Technical Task Requests (TTR) are prepared and issued for all SPP tasks, regardless of funding source, by WSRC HLW Processing Engineering in accordance with WSRC Engineering procedures. TTRs link SPP work scope (as defined in the Scope of Work Matrices in Appendix A) to specific performers, and pass on task acceptance criteria, analytical methods, calibration, and quality assurance requirements so that task data are reliable for use in WSRC Engineering pre-conceptual design activities. TTRs require the development of a Technical Task Plan, which is not to be confused with an EM-50 TTP, and will be referred to as a TTR-TTP. The TTR-TTP establishes the task scope and describes how the performer plans to implement requirements identified in the subject TTR.

Work on the part of a project performer is authorized to begin once WSRC HLW Process Engineering approves a TTR-TTP and funds are authorized. Funds are authorized via an approved EM-40 AOP or an approved EM-50 TTP.

10.2 Change Control

The technical baseline established in the R&D Program Plan provides the basis on which any change will be evaluated.

The EM-40 AOP and EM-50 TTP, in conjunction with TTR-TTPs, define the specific technical activities necessary to meet the objectives established in the R&D Program Plan. Once a task is approved, all changes that impact an approved scope, schedule, or budget are subject to review and approval by the SPP Change Control Board (CCB) prior to formal submission for subsequent approvals as described in the respective EM-40 AOP or EM-50 procedures. The SPP CCB is comprised of the TFA SPP/R&D Technology Development Manager, WSRC SPP Program Manager, WSRC SPP Pre-Conceptual Design Engineering Manager, WSRC HLW Process Engineering Manager, and WSRC SPP Operations Manager.

Changes that impact the EM-50 financial plan or affect a TFA HQ level milestone are approved by the TFA Program Manager and documented by means of a Technical Change Request (TCR). TCRs may be initiated by any of the individuals who have concurred on or approved the EM-50 TTP. All TCRs are initially sent to the TFA SPP/R&D Deputy/Project Controls Manager for review to ensure that the TCR contains adequate justification. Once approved, the TCR is submitted to the appropriate contract and budget authority for processing.

The TFA Program Manager (EM-50) and the DOE-SR SPP Manager (EM-40) are responsible for approving and submitting formal budget/contract changes identified according to the requirements of the particular task funding type (i.e., financial plan, Inter-Office Work Order [IWO], AOP). In addition, the SPP CCB and the TFA Program Manager evaluate all changes for their impact to the technical baseline and ensure proper coordination and approval of the DOE Technical Working Group (TWG). Changes expected to require TWG approval include: TWG directed changes, changes in technology options, changes with a budget impact of greater than $1M, or changes which impact a TWG identified milestone.

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Appendix A

Salt Processing Technology Development Scope of Work Matrices, Roadmaps, and Logic Diagrams

Appendix A

Salt Processing Technology Development Scope of Work Matrices, Roadmaps, and Logic Diagrams

The guiding documents for this Research and Development Program Plan are the Science and Technology Roadmaps for Alpha and Strontium (Sr) Removal, Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange, Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP). The Science and Technology Roadmaps provide the technology development paths forward towards successful deployment of the three options. The Tanks Focus Area has conducted a review of the existing roadmaps and has recommended additions to the current workscope, including evaluation of alternative processes for alpha and Sr removal. The recommended changes were approved by the Technical Working Group and have been incorporated in the roadmaps presented here.

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

HLW-SDT-2000-00047
Revision: 3

SAVANNAH RIVER SITE

HIGH LEVEL WASTE SALT DISPOSITION SYSTEMS ENGINEERING TEAM

APPLIED TECHNOLOGY INTEGRATION SCOPE OF WORK MATRIX FOR ALPHA REMOVAL

(Demonstration Phase)

APPROVED:_________________________ **DATE:**________________
K. J. Rueter, SPP Engineering Director

APPROVED:_________________________ **DATE:**________________
T. P. Pietrok, TFA Program Manager

APPROVED:_________________________ **DATE:**________________
K. T. Lang, EM-40 SPP Program Manager

Change Control Record

Document Name Applied Technology Integration Scope of Work Matrix for Alpha Removal (Demonstration Phase)	*Unique Identifier* HLW-SDT-2000-00047

Summary of Changes

Revision Date	*Matrix Revision*	*BCF Number(s)*	*Reasons for change*	*Items Affected by the change*
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.

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 Demonstration Phase. The guiding documents for this Workscope Matrix are the HLW Salt Disposition SE Team Science and Technology Roadmaps for Small Tank TPB Precipitation, CST Non-Elutable Ion Exchange and Caustic Side Solvent Extraction. The S&T Roadmaps provide the technology development paths forward towards successful deployment of the three options. 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 Demonstration 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 downselection decision. Some work also is included in these SOWMs that has been identified as appropriate post-downselection R&D. However, no attempt has been made to compile a comprehensive list of all post-downselection R&D in these documents. Additional R&D planning will be required to support future stages of the project, e.g. conceptual design, pilot plant design and operation, final design, and startup support.

ATTACHMENT 1 – Alpha Removal Work Scope Matrix

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Chemistry							
1.0	MST Sorption Kinetics	*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 hrs 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.* 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.			HLW-SDT-TTR-99-30.0[1] WSRC-RP-99-01080[2] WSRC-TR-2000-00290[3] WSRC-RP-2000-00361[3] HLW-SDT-TTR-99-33.0[1] WSRC-RP-99-01080[2] WSRC-TR-2000-00229[3] WSRC-TR-2000-00290[3] WSRC-RP-2000-00361[3] WSRC-TR-2000-00142[3]	WSRC-TR-99-00134[3] WSRC-TR-99-00219[3] WSRC-TR-99-00286[3]	CST: 10 TPB: 4 CSSX: 6
		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+.	Lab	SRTC			
		1.2 Develop an understanding of the sorption mechanism for the radionuclides on MST.	Lab	SRTC			
		1.2.1 Examine real waste samples for evidence that the radionuclides (and especially the actinides) exist as colloids.					
		1.2.2 Measure the kinetics of sorption and capacity for single radionuclides					
		1.2.3 Perform 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-downselect)					
		1.2.4 Examine the influence of oxidation state of the sorption of Pu onto MST.					
		1.3 Study Allied Signal NaT as a replacement for MST	Lab	SRTC			
		1.4 Study alternative alpha removal technologies	Lab	SRTC			
		1.4.1 Literature review of alternative alpha removal technologies, including magnetic precipitation					
		1.4.2 Perform scoping studies based on literature evaluation					
		1.5 Evaluate alternative filter cleaning methods if new sorbents are chosen (Preliminary Design) (post-downselect)					

Note: See Matrix Legend for definition of column content

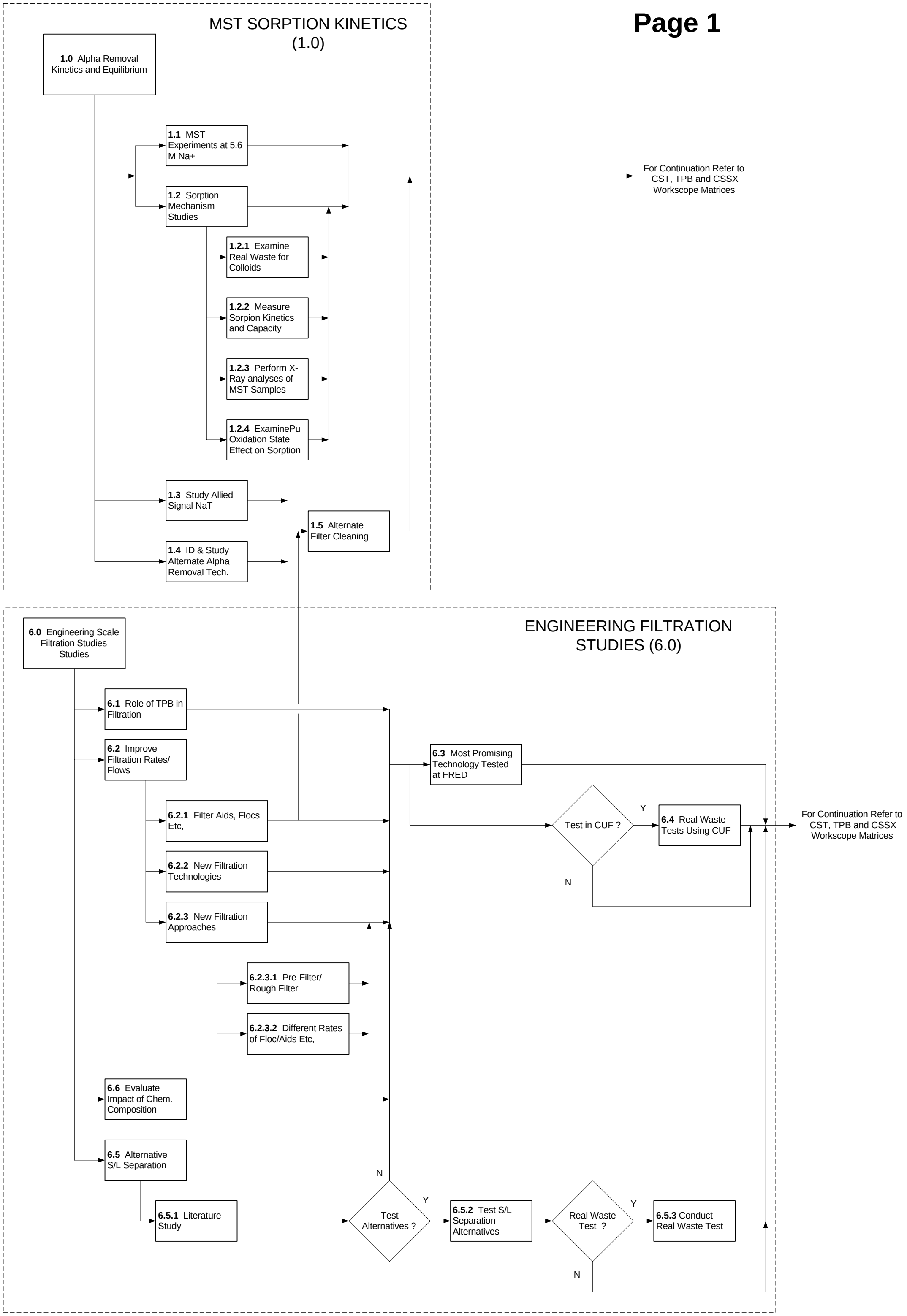
Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Engineering							
6.0	Engineering Scale Filtration Studies	*Filtration of MST and sludge is required to prevent plugging of the ion exchange column. Initial data indicates low flux rates for the filtration 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.* 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] WSRC-TR-99-00483[2] WSRC-TR-2000-00288[3] WSRC-TR-2000-00270[3] WSRC-TR-2000-00287[3] WSRC-RP-2000-00685[3] HLW-SDT-TTR-2000-00013[1]	WSRC-TR-99-00343[3]	CST: 9, 15 TPB: Design Input CSSX: 5
		6.1 Elucidate role of TPB in filtration	NA	SRTC			
		6.2 Investigate/test ways to improve filtration rates/fluxes	Lab	SRTC			
		6.2.1 Filter aids, flocs, etc					
		6.2.2 Different filtration technologies					
		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			
		6.4 Perform real waste tests using CUF	Bench	SRTC			
		6.5 Evaluate alternative solid/liquid separation technologies	Lab	SRTC			
		6.5.1 Literature study					
		6.5.2 Test promising alternative solid/liquid separation technologies, if warranted by literature study					
		6.5.3 Conduct Real Waste Test					
		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			
9.0	Analytical Sample Requirements	*The analytical sample requirements including on-line analysis must be developed to support control strategy development.* Develop at-line (or on-line) analyzer for ^{137}Cs, ^{90}Sr, and total alpha.	Full	PNNL/ Analytical Meas.Lab		G-TC-H-00030	CST: 5 TPB: 7 CSSX: 7
		9.1 Issue request for interest package for vendor solicitation					
		9.1.1 Conduct independent assessment of vendor bids and technical maturity of analyzer technology					
		9.2 Procure and test analyzer (post-downselect)					
		Activities to resolve these issues are common to CST, TPB and CSSX					

Note: See Matrix Legend for definition of column content

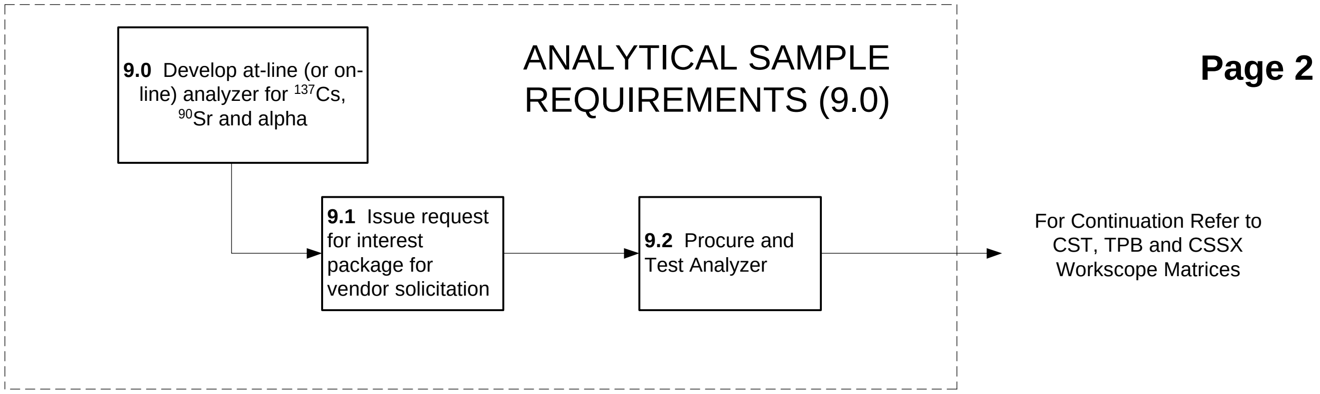
Matrix Legend

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



ATTACHMENT 2 – Alpha Removal S&T Logic Diagrams



HLW-SDT-99-0354
Revision: 5

SAVANNAH RIVER SITE

HIGH LEVEL WASTE SALT DISPOSITION SYSTEMS ENGINEERING TEAM

APPLIED TECHNOLOGY INTEGRATION SCOPE OF WORK MATRIX FOR CST NON-ELUTABLE ION EXCHANGE

(Demonstration Phase)

APPROVED:____________________________ **DATE:**_________________
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Change Control Record

Document Name	*Unique Identifier*
Applied Technology Integration Scope of Work Matrix for CST Non-Elutable Ion Exchange (Demonstration Phase)	HLW-SDT-99-0354

Summary of Changes

Revision Date	*Matrix Revision*	*BCF Number(s)*	*Reasons for change*	*Items Affected by the change*
December 2, 1999	0	NA	Initial Issue	NA
December 27, 1999	1	NA	Incorporates ECF # HLW-SDT-99-0387 which added TTR/TTP/TR references, ties to uncertainty IDs, updates to reflect feedback from TTR/TTP development and incorporated minor editorial comments	All changes identified with revision bars
January 10, 2000	2	NA	Incorporates ECF# HLW-SDT-2000-00010 which aligned workscope matrix with finalized FY00 approved workscope and incorporated DOE review comments by removing holds and identifying work to be initiated in FY01 and incorporated minor editorial comments.	All changes identified with revision bars
February 15, 2000	3	NA	Incorporates ECF# HLW-SDT-2000-00050 which removed information from items common to all three technologies that are now being controlled through Alpha Removal workscope matrix HLW-SDT-2000-00047 and changed Section 9.0 to show WSRC overview of UOP R&D.	All changes identified with revision bars

Change Control Record (Continued)

Revision Date	*Matrix Revision*	*BCF Number(s)*	*Reasons for change*	*Items Affected by the change*
July 10, 2000	4	NA	Incorporates ECF # HLW-SDT-2000-00267 which dispositions comments from the TFA team.	All changes identified with revision bars.
November 21, 2000	5	N/A	Incorporates ECF # HLW-SDT-2000-00464 which dispositions comments from TFA team and updates document with FY00 science and technology results	All changes identified with revision bars.

Use of Workscope Matrix

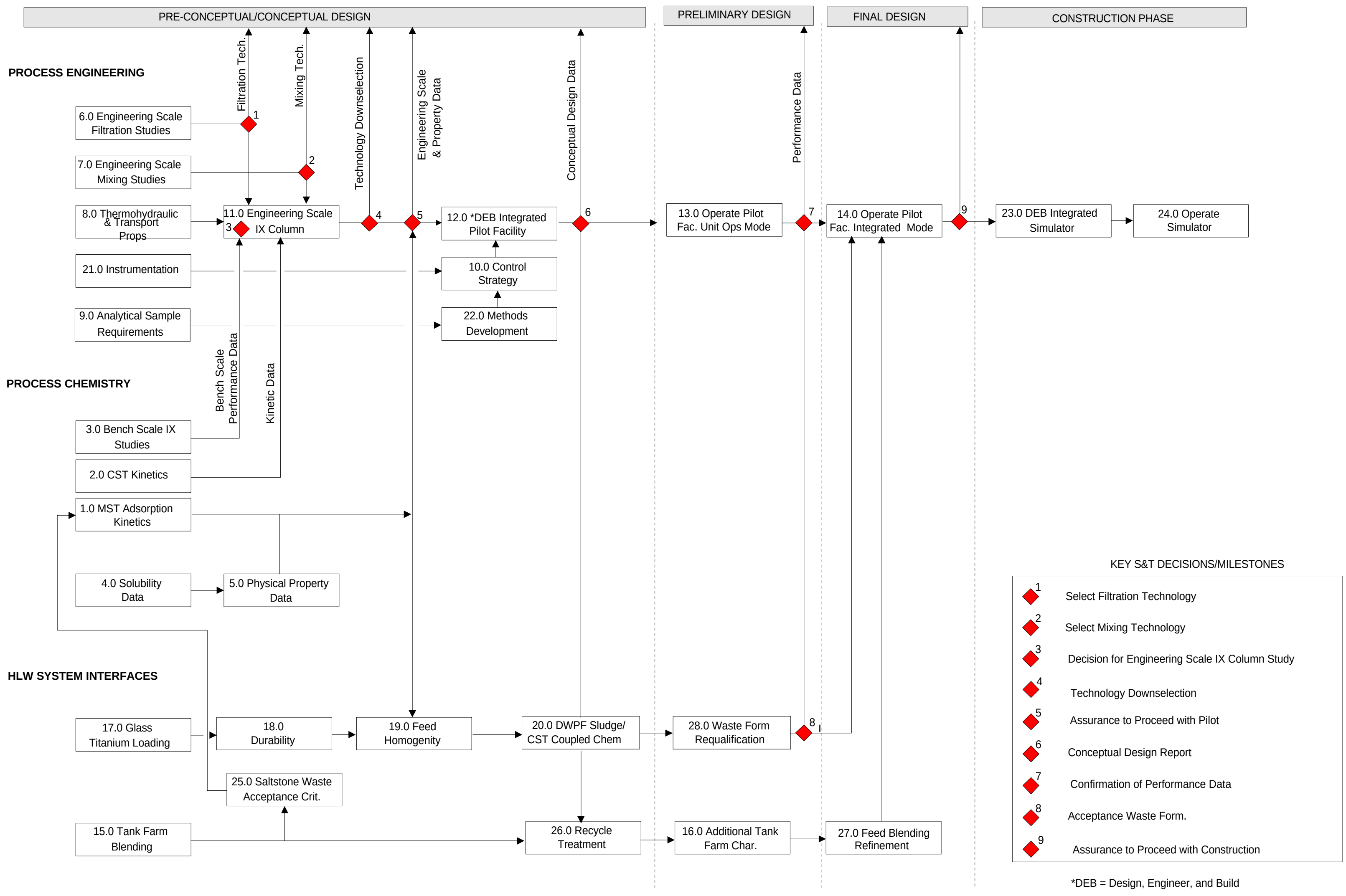
This Workscope Matrix has been developed to define the Science and Technology (S&T) development activities to be performed during the Demonstration Phase. The guiding document for this Workscope Matrix is the HLW Salt Disposition SE Team Science and Technology Roadmap (Attachment 1). The S&T Roadmap provides the technology development path forward towards successful deployment of the CST Non-Elutable Ion Exchange 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 Demonstration 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 downselection decision. Some work also is included in these SOWMs that has been identified as appropriate post-downselection R&D. However, no attempt has been made to compile a comprehensive list of all post-downselection R&D in these documents. Additional R&D planning will be required to support future stages of the project, e.g. conceptual design, pilot plant design and operation, final design, and startup support.

ATTACHMENT 1 – Science and Technology Roadmap

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



ATTACHMENT 2 - CST Non-Elutable Ion Exchange Work Scope Matrix

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Chemistry							
1.0	MST Sorption Kinetics	*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 hrs 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.* 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+. 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.					
		1.3.1 Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
2.0	CST Kinetics	*The ability of CST to remove Cs from aqueous waste solutions needs to be investigated as a function of temperature and waste composition. Potassium, strontium, nitrate, and hydroxide are known to impact the equilibrium loading of Cs on the CST. Mass transfer coefficients as a function of column geometry and velocity vs. diffucivity must also be determined to ensure proper ion exchange column sizing. The ability of CST to sorb Sr, Pu and U must be determined to avoid potential criticality issues. De-sorption of the Cs due to normal and abnormal operations such as temperature swings must be determined. Thermal stability of CST must be determined.* During Phase IV experiments, observations led to questions regarding the presence and fate of excess materials, "dry back" fines, lot-to-lot variability, chemical and thermal stability, and predictability of resin performance in SRS waste. Significant additional effort is required to understand the implications and to assure applicability to SRS processing requirements. In fact, the resin may have to be "reengineered" to meet SRS needs. During FY00, it was recognized that MTZ length is approximately proportional to $1/C_o$ (C_o = initial concentration) and that a substantial amount of the projected waste feeds would have [Cs] significantly lower than was used to size the columns. Also, model results for projected waste compositions should be compared against the standard simulants.			HLW-SDT-TTR-99-34.0^1 WSRC-RP-99-01079^2 HLW-SDT-TTR-99-36.1^1 Subcontract AC18850N^2 WSRC-RP-2000-00812^2 HLW-SDT-TTR-99-36.2^1 Subcontract AC18850N^2 WSRC-RP-99-01079^2 WSRC-RP-2000-00812^2 HLW-SDT-TTR-99-38.1^1 WSRC-RP-99-01079^2 AL2WT21/A.1^2 AL2WT21/A.2^2 RL3WT21/A.2^2 RL3WT21/B.1^2 RL3WT21/B.2^2 HLW-SDT-TTR-99-38.2^1 ORNL/CF-99/67^2 AL2WT21/A.1^2 AL2WT21/A.2^2 RL3WT21/A.2^2	HLW-SDT-99-0238^3 WSRC-TR-99-00313^3 HLW-SDT-99-0273^3 WSRC-TR-99-00312^3 WSRC-TR-99-00374^3	11, 13, 15, 29, 31
		2.1 Work with UOP to:	Lab	UOP			
		2.1.1 Eliminate or remove excess materials					
		2.1.2 Eliminate or reduce chloride or change to nitrate form					

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		2.1.3 Eliminate or reduce attrition			RL3WT21/B.1[2] RL3WT21/B.2[2]		
		2.1.4 Reduce lot-to-lot variability (Develop rapid, reliable tests(s) to detect lot-to-lot variability - short term kinetics/pore diffusion test)					
		2.1.5 Pretreatment of reengineered resin					
		2.1.6 Improve the particle size distribution of IE-9xx as it is produced					
		2.1.7 Consultation from Sandia National Laboratory					
		2.1.8 Finalize re-engineered form					
		2.2 Resolve/understand CST chemical stability issues					
		2.2.1 Long term exposure					
		2.2.1.1 Expose CST to waste at normal operating temperatures for 8 – 9 months and then perform standard column run	Lab	ORNL			
		2.2.1.2 Stability/precipitation during NaOH pretreatment and exposure to 5.6 M waste – proprietary constituents • Static and dynamic exposure with frequent solution replenishment • Varying salt composition and temperature • Solid (CST and precipitate) characterization • Effect on pore size (macro and micro) • K_d measurement and column run at end of exposure	Lab	SRTC			
		2.2.1.3 Evaluate alternative CST pre-treatment process	Lab	SNL			
		2.2.1.4 Laboratory confirmation	Lab	SNL			
		2.3 Resolve/understand CST thermal stability issues	Lab	SRTC			
		2.3.1 Thermal/equilibrium desorption/leaching • Understand mechanism by which Cs was leached in ORNL tests • Leaching? CST phase change? shift in equilibrium?					
		2.3.2 Determine why Cs did not reload after temperature dropped					
		2.3.2.1 Using actual simulants to determine the rate of Cs-137 desorption from loaded CST (IE-910, IE-911, and binder if available) as a function of temperature – tests would include cycling temperature from 25 to 50-80 °C	Lab	SRTC			
		2.3.2.2 Contract with Sandia National Laboratory and Pacific Northwest National Laboratory to provide consulting and characterization services	NA	SNL/ PNNL			
		2.4 Expand the understanding of cesium removal kinetics and CST capacity for other actual tank wastes by examining Cs removal efficiency for various radioactive waste matrices in inventory at SRS					
		2.4.1 Obtain small dip samples (approx. 100 mL) from different SRS waste tank supernates and perform Kd measurements and waste characterization for elemental composition	Lab	SRTC			

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		2.4.2 Using the IX column model, perform case studies to evaluate the effect of projected waste composition (both salt composition and [Cs]) on the MTZ length and CST loading: compare to model results for the SRS simulants. Waste compositions shall be as developed by the salt removal plan. (post-downselect)	NA	SRTC			
		2.5 Second generation CST - Determine if CST can be re-engineered to sorb alpha (i.e., Pu) : e.g., add a Pu sorbant with the IE-911 to form a combined, engineered resin that would remove Cs, Sr, and Pu? (post-downselect)	Lab	UOP			
3.0	Bench Scale IX Studies	*Radioactive bench scale column tests must be conducted to determine the radiolytic generation rate of hydrogen and other gases. These gases represent potential safety and column operational issues.* Due to various constraints, we were unable to run the small column flowing test in a radiation field during Phase IV. These tests would investigate the impact of gas formation (both radiolytic and non-radiolytic) on the CST performance of a flowing column.			HLW-SDT-TTR-99-31.1[1] WSRC-RP-99-01079[2] WSRC-TR-2000-00177[3] HLW-SDT-TTR-99-31.2[1] ORNL/CF-99/66[2]	WSRC-TR-99-00308[3] WSRC-TR-99-00285[3] HLW-SDT-99-0248[3] HLW-SDT-99-0257[3]	11, 33
		3.1 Provide better understanding of large column behavior to guide design interpretation of small column tests 3.1.1 Improve calculations of gas generation in large columns 3.1.2 Define rate and location of bubble formation as Cs loading progresses 3.1.3 Estimate diffusion rates of gases out of CST particles, compare to generation rate and confirm with experiments	NA	SRTC			
		3.2 Demonstrate and measure the effect of internal and external bubbles on Cs sorption 3.2.1 Determine method for generating gas bubbles in macro channels (including method to verify pressure and volume) 3.2.2 Measure rate of sorption of Cs in CST w/ and w/o bubbles (use Kd or flowing column tests at 1 Mrad/hr	Lab	SRTC/ ORNL			
4.0	Solubility Data	*Solubility of various salts must be determined to define the lower bounds of operating temperature and minimum tank farm dilution requirements.*			HLW-SDT-TTR-99-31.1[1] WSRC-RP-99-01079[2]		Design Input
		4.1 Determine H_2 and O_2 solubility as a function of temperature, Na+ concentration, and salt composition.	Lab	SRTC			
5.0	Physical Property Data	*General physical property data such as density, viscosity, yield stress and consistency of slurries, as a function of state variables such as temperature is required to support the design effort. Settling velocity and re-suspension requirements must be determined.* At least one case of column plugging was observed and attributed to post-precipitation of aluminates from simulant. Also, others (UOP and ORNL) have stated that dilution of real wastes must be performed with NaOH to avoid gibbsite and alumino-silicate precipitation. It is necessary to develop an understanding of simulant preparation and waste dilution that prevents post-precipitation that could cause column plugging. Work performed during FY00 demonstrated the ease with which salt solutions			HLW-SDT-TTR-99-37.1[1] WSRC-RP-99-01079[2] WSRC-TR-2000-00167[3] HLW-SDT-TTR-99-37.2[1] ORNL/CF-99/65[2] HLW-SDT-TTR-99-38.2[1] WSRC-RP-99-01079[2] AL2WT21/A.2[2] RL3WT21/A.2[2] RL3WT21/B.2[2] RL3WT21/B.3[2]	WSRC-RP-99-00597[3] WSRC-TR-99-00219[3] WSRC-RP-99-00836[3]	11, 35

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		supersaturated with aluminates could be formed. Additionally, these solutions reached equilibrium very slowly. It is possible that real SRS wastes could be supersaturated with subsequent precipitation of silicoaluminates within the CST columns. Using a combination of bench-top experiments and high-ionic strength solution modeling to:					
		5.1 Develop an understanding of and prevention of post-precipitation in waste simulants and modify simulants if required					
		5.1.1 Determine how to dilute waste solutions to prevent precipitation and post-precipitation of aluminates, alumino-silicates, and any other insoluble salts that may form due to dilution	Lab	SRTC			
		5.1.2 Perform scoping tests to examine the chemistry of leached Si and proprietary chemical, silica contained in the salt solution and the associated soluble Al.	Lab	SRTC			
		5.1.3 Measure the effects of the chemistries on the K_d for CST (IE-911) desorption/resorption at two temperatures	Lab	SRTC			
		5.1.4 Characterize leached CST samples (surfaces, crystal structures etc.,) with solid characterization techniques (XRD, BET, SEM, IR, and Raman)	Lab	SNL/ PNNL			
		5.1.5 Waste/simulant equilibrium studies					
		5.1.5.1 Evaluate the accuracy of the ORNL computer model	NA	ORNL			
		5.1.5.2 Determine equilibrium state of waste in SRS tanks with respect to crystallization of solids	Bench	SRTC			
		5.1.5.3 Measure impact of diluting radioactive waste with NaOH	Bench	ORNL			
		5.1.5.4 Compare SRS simulant compositions with radioactive wastes in tanks (post-downselect)	Bench	SRTC			
		5.1.5.5 Develop waste composition limits for feed to CST IX process (post-downselect)	NA	HLW-PE			
		5.2 Determine the effect of carbonate, oxalate and peroxide on the capacity and Cs removal kinetics	Lab	SRTC/ Texas A&M			
		5.2.1 Measure sorption isotherms for a range of cesium starting concentrations					
		5.2.2 Develop new coefficients for ZAM model (Texas A&M) for Cs sorption. (post-downselect)					
		5.2.3 Perform K_d measurements with different anion concentrations to determine magnitude of fouling of CST – utilize WPT γ-counter, SEM, IR, Raman					
		5.3 CST Capacity	Lab	SRTC			
		5.3.1 Extend data on IE-911 (includes binder) capacity as function of temperature in various salt solutions					
		5.3.2 Include comparisons of nitrate form and IE-910					

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Engineering							
6.0	Engineering Scale Filtration Studies	*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 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.* 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. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
7.0	Engineering Scale Mixing Studies	*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.* Identified activities will be conducted during Conceptual Design	NA	NA	NA		34
8.0	Thermo-hydraulic and Transport Properties	*Thermal and hydraulic properties must be determined to allow for determination of heat removal loads and technologies (jacketed vessels, cooling coils, heat exchanger, etc.). The crush strength of the CST is especially important. Determination of the CST minimum transportation and fluidization velocity is required.* Many questions/concerns about the CST process are related to equipment design and operation. These have not been previously addressed and have been carried as uncertainties and risks. A number of these questions/concerns will be addressed.			HLW-SDT-TTR-99-32.1[1] WSRC-RP-99-01117[2] ORNL/CF-99/68[2] HLW-SDT-TTR-99-32.2[1] ORNL/CF-99/68[2] HLW-SDT-TTR-2000-12[1] WSRC-RP-2000-00887[2]	HLW-SDT-99-0133[3] HLW-SDT-99-0141[3] WSRC-TR-99-00116[3] WSRC-TR-99-00313[3] WSRC-TR-99-00285[3] WSRC-SDT-99-0257[3] WSRC-TR-99-00374[3]	2, 3, 4, 6, 7
		8.1 Investigate pre-conceptual designs for moving packed beds and fluidized beds 8.1.1 Hire a consultant for preliminary evaluation of alternative configurations and other fixed bed configurations 8.1.2 Evaluate industrial designs for moving bed columns	NA	HLW-DE			
		8.2 Investigate improvements in current fixed packed bed design 8.2.1 Simplify valving 8.2.2 Reduce complexity of column changeout activities 8.2.3 Alternative column size and configurations	NA	HLW-DE			
		8.3 Investigate pre-conceptual designs' gas disengagement equipment 8.3.1 Test selected designs	Large Column	ORNL			
		8.4 Measure heat transfer characteristics of CST column with gas bubbles	Lab	ORNL			

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
9.0	Analytical Sample Requirements	*The analytical sample requirements including at-line analysis must be developed to support control strategy development.* Develop an at line analyzer for Cs, Sr, and total alpha. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details					
10.0	Control Strategy	*Control Strategy must be developed to support the designing, engineering, and building of the pilot facility.* Pre-Conceptual Design of the Pilot Facility has started	NA	NA	NA		4
11.0	Engineering Scale IX Column	*The bench scale kinetic data, and remoteability requirements may indicate the need for intermediate scale ion exchange column testing prior to designing, engineering, and building of the pilot facility. Demonstration of the ability to remotely load and unload the columns is essential. Impact of column operation due to size reduction of the CST during operation is required.* Pre-Conceptual Design of the Pilot Facility has started	NA	NA	NA		Design Input
12.0	Design, Engineer, and Build (DEB) Integrated Pilot Facility	*A pilot scale (to be determined) facility will be built to support the confirmation of design data and development of operator training.* 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
13.0	Operation of the Pilot Facility in a Unit Operations Mode	*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.* 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
14.0	Operation of the Pilot Facility in an Integrated Operations Mode	*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.* Activities will be conducted during Preliminary Design.	NA	NA	NA		Design Input
21.0	Instrumentation	Activities will be conducted during Conceptual Design.	NA	NA	NA		Design Input
22.0	Methods Development	Activities will be conducted during Conceptual Design.	NA	NA	NA		Design Input
23.0	Design, Engineer and Build (DEB) Integrated	Activities will be conducted during Construction.	NA	NA	NA		Design Input

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
	Simulator						
24.0	Operate Simulator	Activities will be conducted during Construction.	NA	NA	NA		Design Input
High Level Waste System Interface							
15.0	Tank Farm Blending	*The production sequences of emptying the tank farm has been studied in the past and have indicated potential tank blending issues regarding Np, U, Pu, and Sr. The current blend strategy must be reviewed to determine if alternate blending strategies can reduce the 5 to 8x concentration spikes in these components or if the alpha removal requirements must be modified to meet the Saltstone waste acceptance limits.* Additional blending studies will be conducted during Conceptual Design.	NA	NA	NA		Design Input
16.0	Additional Tank Farm Characterization	*While the tank farm waste has been characterized, additional characterization may be required to define the range of expected compositions during facility operation.* Additional activities will be conducted during Preliminary Design.	NA	NA	NA		Design Input
17.0	Glass Titanium Loading	*The current waste qualification envelope is limited to 1 wt % TiO_2. The use of MST and CST increases the Ti loading to as much as 5 wt %. Re-qualification is therefore required.* Additional glass property model development will begin during Conceptual Design.	NA	NA	NA	WSRC-TR-99-00245[3] WSRC-TR-99-00289[3] WSRC-TR-99-00291[3] WSRC-TR-99-00293[3] WSRC-TR-99-00384[3] WSRC-TR-99-00323[3]	12
18.0	Durability	*Initial data regarding the glass composition vs. durability correlation indicated that modification of this essential correlation is required. The initial parametric study indicated that all the CST containing glasses produced resulted in leach rates exceeding the 95% upper confidence interval of the existing correlation. Liquids and viscosity correlations may required updating.* Durability and liquidus measurements made in FY99 were on rapidly quenched glasses. The durabilities were very good and there was no sign of unacceptably high liquidus temperatures. Glass cooled more slowly at the center of a canister may form secondary phases (the DWPF durability correlation is only valid for homogeneous glass.)				WSRC-TR-99-00384[3]	Design Input
		18.1 Perform canister centerline cooling tests for selected CST/sludge/frit glasses	Bench	SRTC			
19.0	Feed Homogeneity	*The DWPF waste qualification envelope is based on maintaining the proper ratio of solids to water throughout the process. Testing must be conducted to ensure the current agitation and sampling equipment in the DWPF is adequate.* Phase IV tests showed (1) as-received CST could be easily resuspended but did not form a uniform slurry in a DWPF-scaled tank, (2) as-received CST with sludge and frit plugged the Hydragard sampler, (3) size-reduced CST settled and compacted so that it was extremely difficult to break up and resuspend, and (4) size-reduced CST with sludge and frit was not representatively sampled (~12 % low in frit) by the Hydragard.			HLW-SDT-TTR-99-35.0[1] WSRC-RP-99-01115[2]	WSRC-TR-99-00244[3] WSRC-TR-99-00309[3]	14, 28

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		19.1 Develop representative SRAT/SME sampling of CST/sludge/frit slurry 19.1.1 Determine cause for non-representative Hydragard sample of CST/sludge/frit slurry 19.1.2 Determine if uniformly size-reduced CST can be representatively sampled by the Hydragard	Bench	SRTC			
		19.2 Develop and test size reduction method 19.2.1 Consult with West Valley, Hanford K-Basin, UOP 19.2.2 Identify acceptable equipment and characteristics 19.2.3 Obtain equipment and perform testing 19.2.4 Determine if CST needs to be pretreated and loaded	NA	SRTC/ Vendor			
		19.3 Evaluate on-line CST particle size analyzer (post-downselect)	Bench	SRTC			
		19.4 Determine how to suspend CST in the DWPF 19.4.1 Determine CST loading of discarded IX slurry 19.4.2 Develop relationship between wt% CST in slurry and SG of slurry (bench-scale experiment) 19.4.3 Mockup CST storage tank using TFL 1/240th scale SME 19.4.4 Suspend/resuspend size-reduced CST so as to assure uniform transfers 19.4.5 Resuspend and homogenize size-reduced and as-received CST; considerations include: • Glass-compatible additive to prevent compaction or aid dispersion • Agitator speed • Fluidic mixer • Sonics	Bench	SRTC			
		19.5 Demonstrate ability to feed CST/sludge/frit slurry to melter (post-downselect) 19.5.1 Reconstruct the melter feed loop at the Thermal Fluids lab 19.5.2 Run tests sampling output of feed loop to demonstrate melter feed is representative of feed tank contents	Bench	SRTC			
		19.6 Determine the rheology of freshly prepared CST/sludge/frit slurries 19.6.1 Prepare CST/sludge/frit slurries using CST size-reduced to $< 177\ \mu$ and CST size-reduced to $< 25\ \mu$ with a sludge/frit slurry as a control 19.6.2 Measure yield stress and consistency as a function of total wt % solids	Bench	SRTC			
20.0	DWPF Sludge/CST Coupled Chemistry	*Initial data indicated some foam formation during the DWPF feed preparation processes. Investigation into alternative antifoams is required. The impact on DWPF and tank farm operations must be assessed.* Activities to be conducted during Conceptual Design.	NA	NA	NA	WSRC-TR-99-00277[3] WSRC-TR-99-00302[3]	32, 28

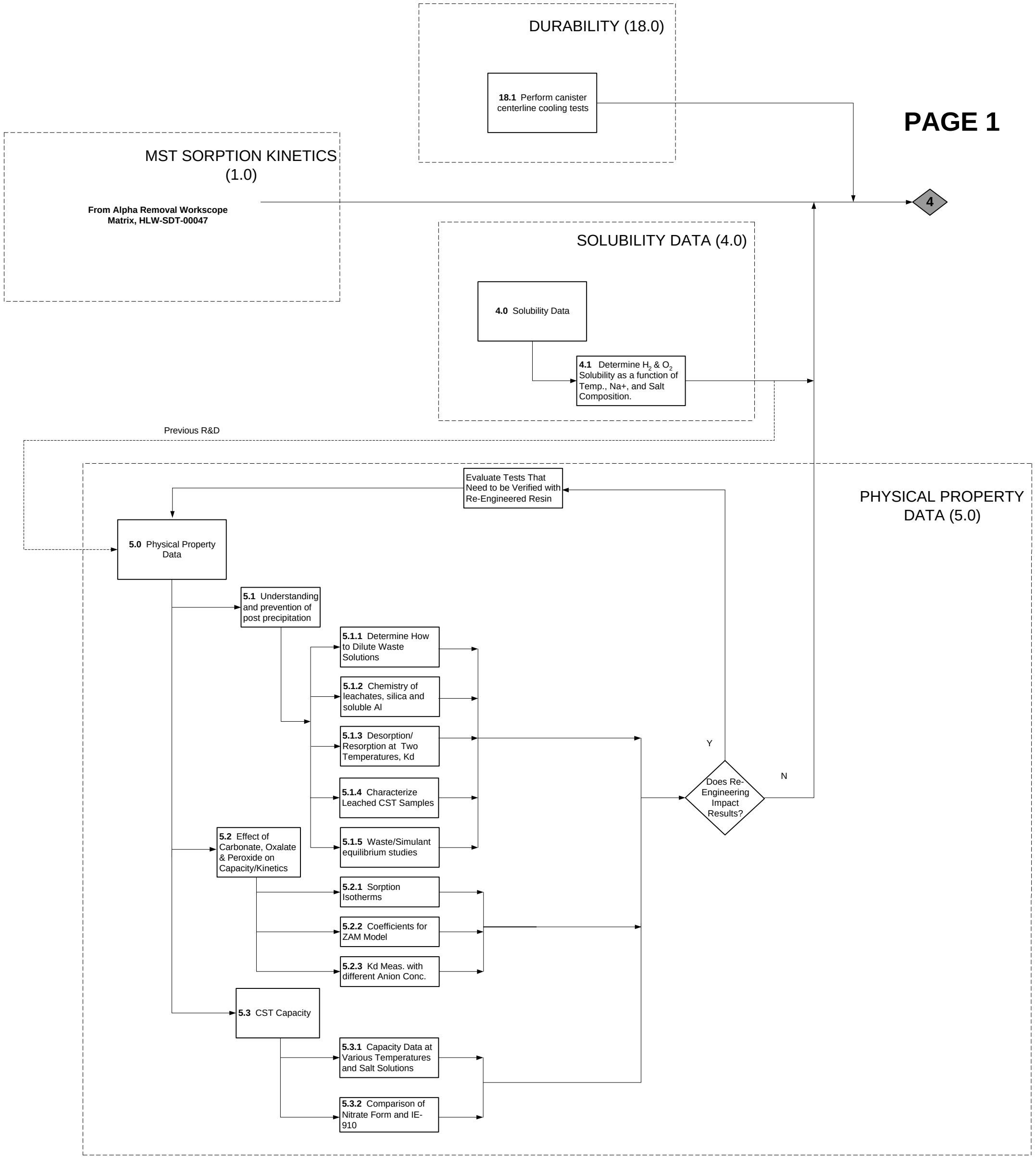
Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
25.0	Saltstone Waste Acceptance Criteria	No identified scope.	NA	NA	NA		Design Input
26.0	Recycle Treatment	No identified scope.	NA	NA	NA		Design Input
27.0	Feed Blending Refinement	Activities to be conducted during Final Design.	NA	NA	NA		Design Input
28.0	Waste Form Requalification	Activities to be started during Conceptual Design.	NA	NA	NA		Design Input

Matrix Legend

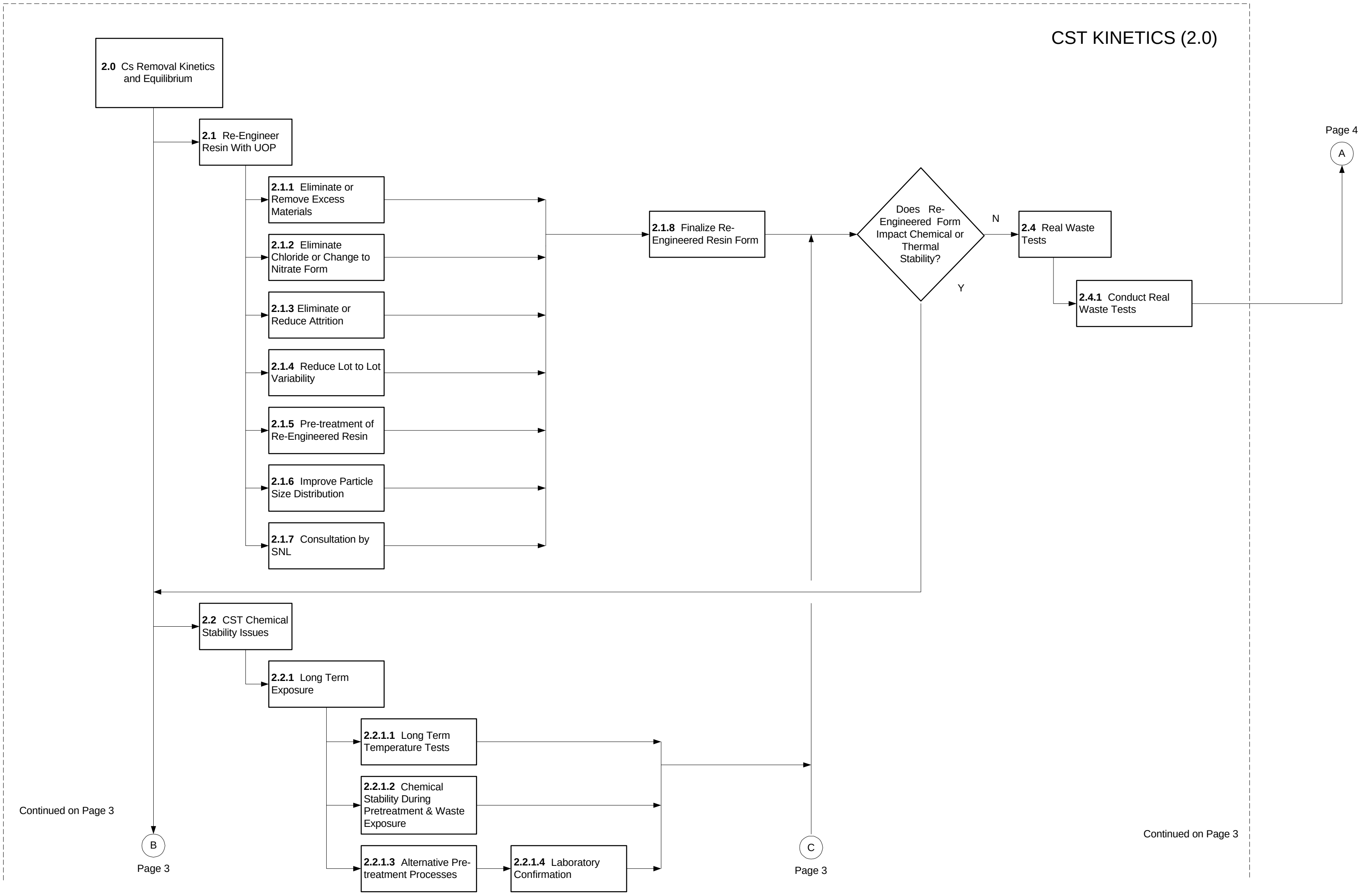
Item No.	Corresponds to the block number on the Science and Technology Roadmap and Logic Diagrams; provides a tie between documents.
Item	General title of the S&T block; corresponds to block title on the Science and Technology Roadmap and Logic Diagrams.
Considerations	Discusses the considerations pertinent 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). Italicized text is extracted from previous CST roadmap HLW-SDT-980165 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 3 - CST Non-Elutable Ion Exchange S&T Logic Diagrams (1 of 5)

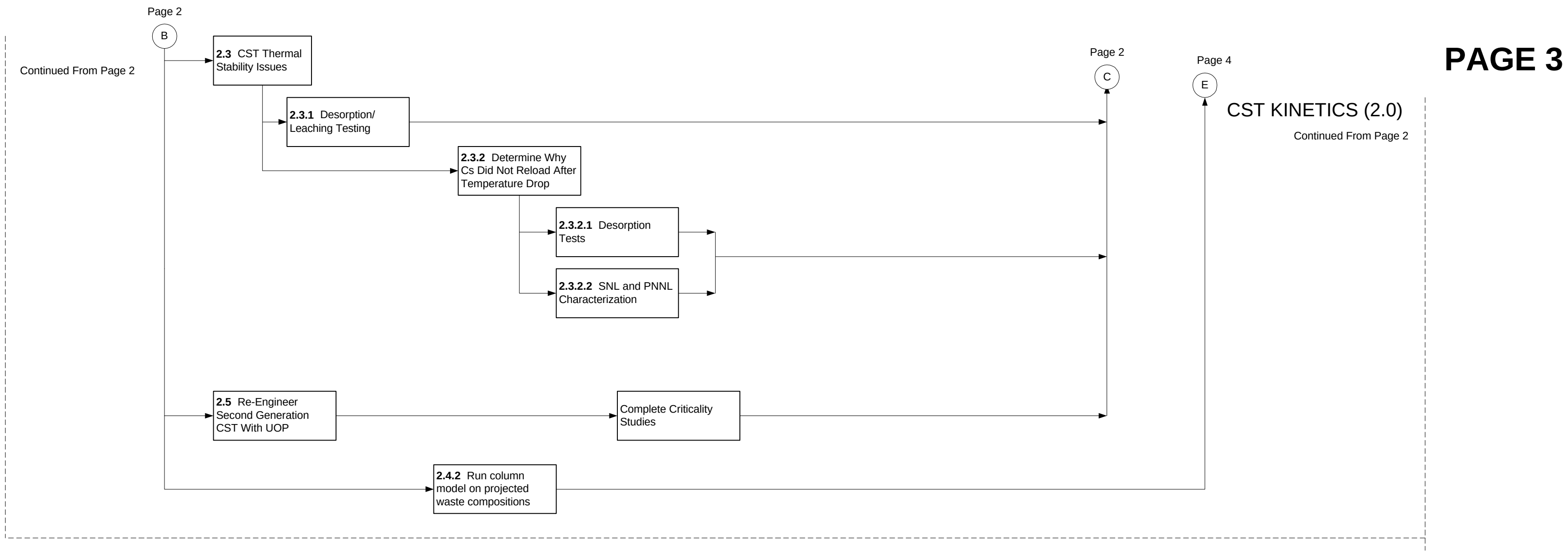


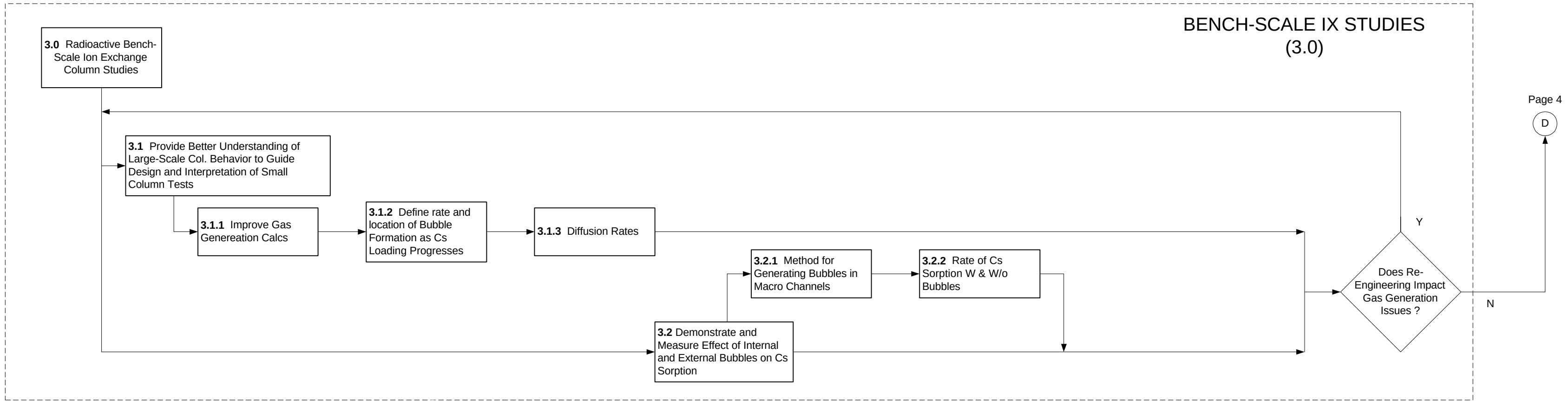
ATTACHMENT 3 - CST Non-Elutable Ion Exchange S&T Logic Diagrams (2 of 3)

PAGE 2

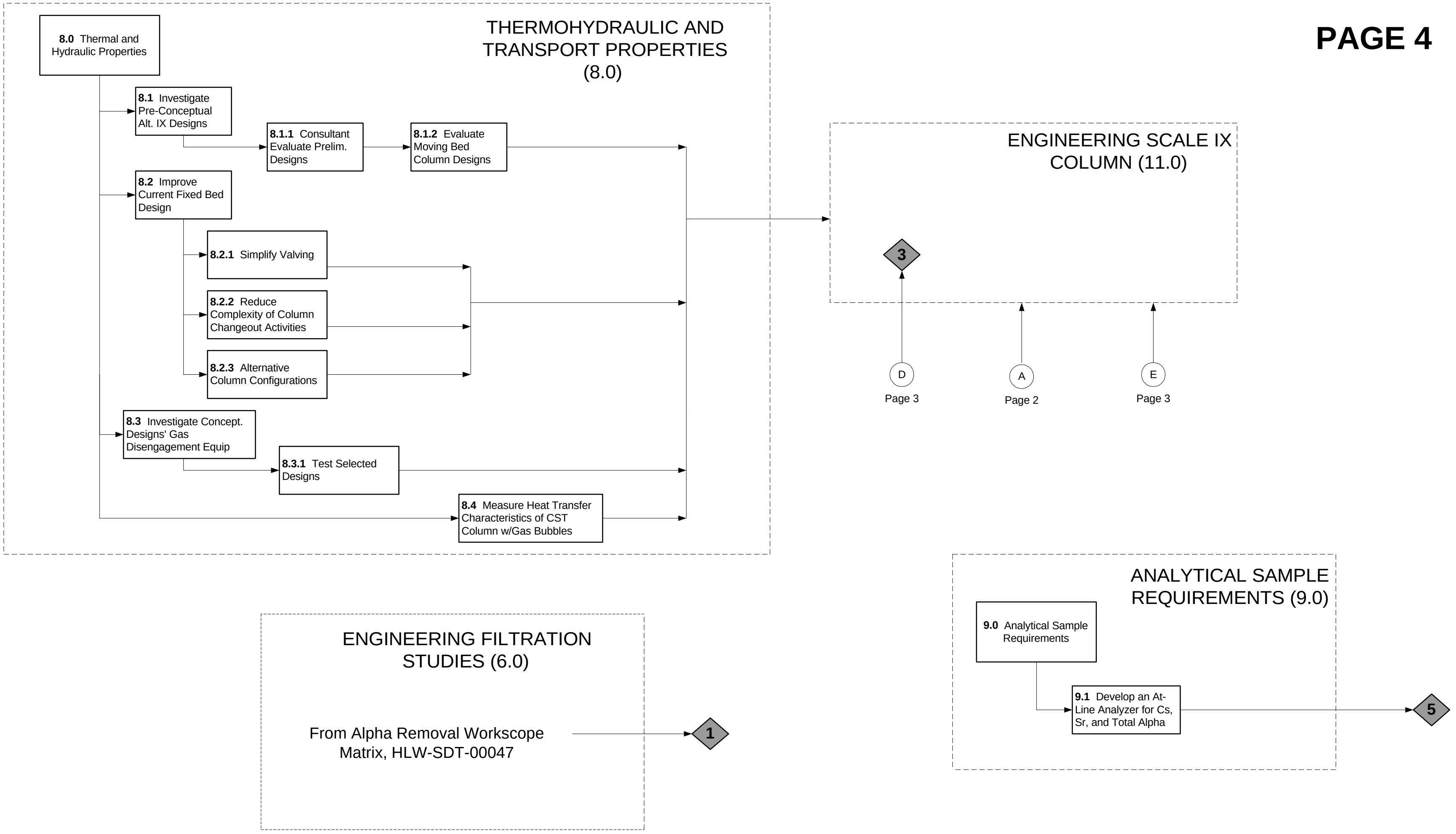


ATTACHMENT 3 - CST Non-Elutable Ion Exchange S&T Logic Diagrams (3 of 5)



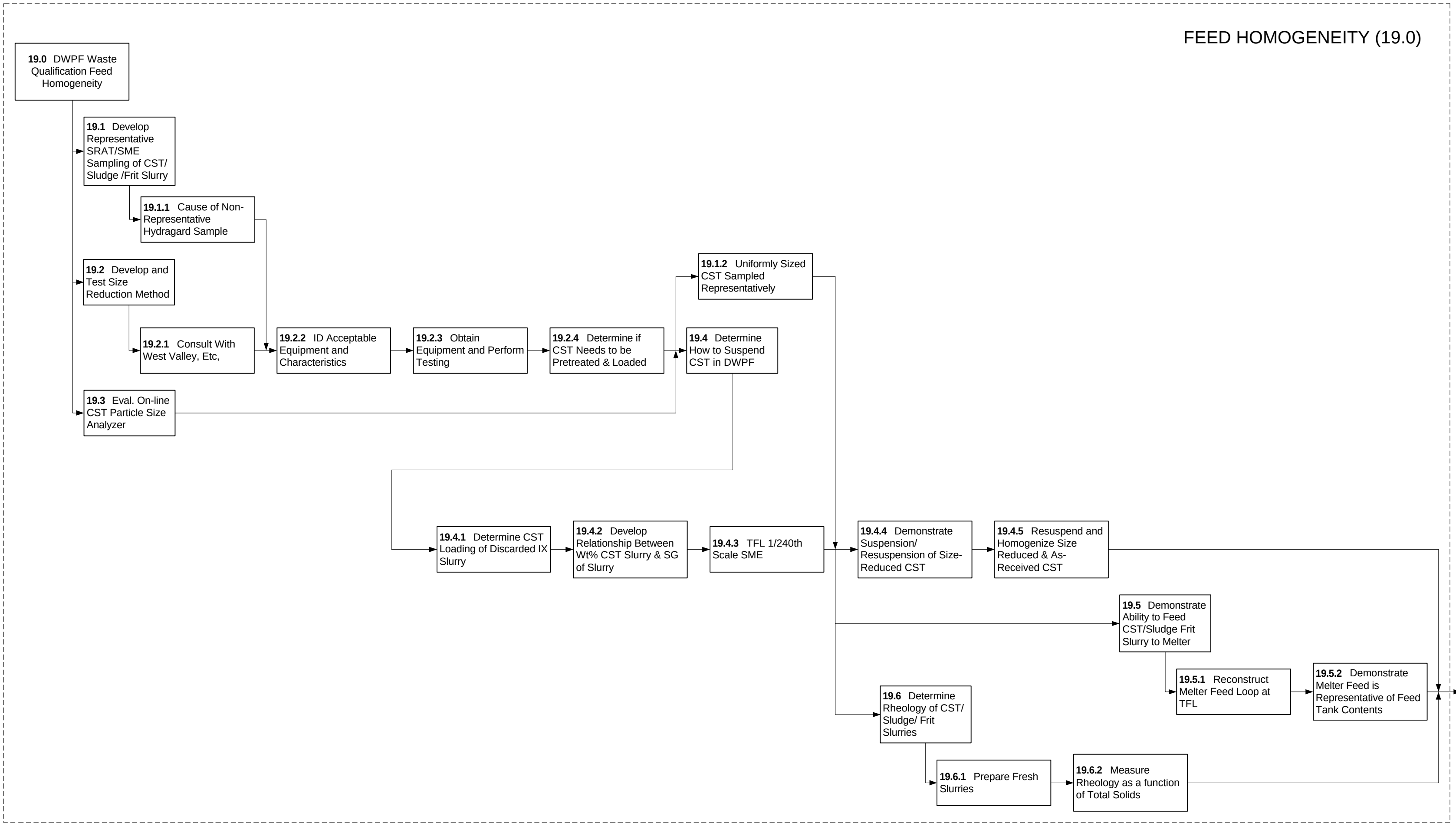


ATTACHMENT 3 - CST Non-Elutable Ion Exchange S&T Logic Diagrams (4 of 5)



ATTACHMENT 3 - CST Non-Elutable Ion Exchange S&T Logic Diagrams (5 of 5)

PAGE 5



HLW-SDT-2000-00051
Revision: 4

SAVANNAH RIVER SITE

HIGH LEVEL WASTE SALT DISPOSITION SYSTEMS ENGINEERING TEAM

APPLIED TECHNOLOGY INTEGRATION SCOPE OF WORK MATRIX FOR CAUSTIC-SIDE SOLVENT EXTRACTION

(Demonstration Phase)

APPROVED:_____________________________ **DATE:**_________________
K. J. Rueter, SPP Engineering Director

APPROVED:_____________________________ **DATE:**_________________
T. P. Pietrok, TFA Program Manager

APPROVED:_____________________________ **DATE:**_________________
K. T. Lang, EM-40 SPP Program Manager

Change Control Record

Document Name Applied Technology Integration Scope of Work Matrix for Caustic-Side Solvent Extraction (Demonstration Phase)	*Unique Identifier* HLW-SDT-2000-00051

Summary of Changes

Revision Date	*Matrix Revision*	*BCF Number(s)*	*Reasons for change*	*Items Affected by the change*
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.

Use of Workscope Matrix

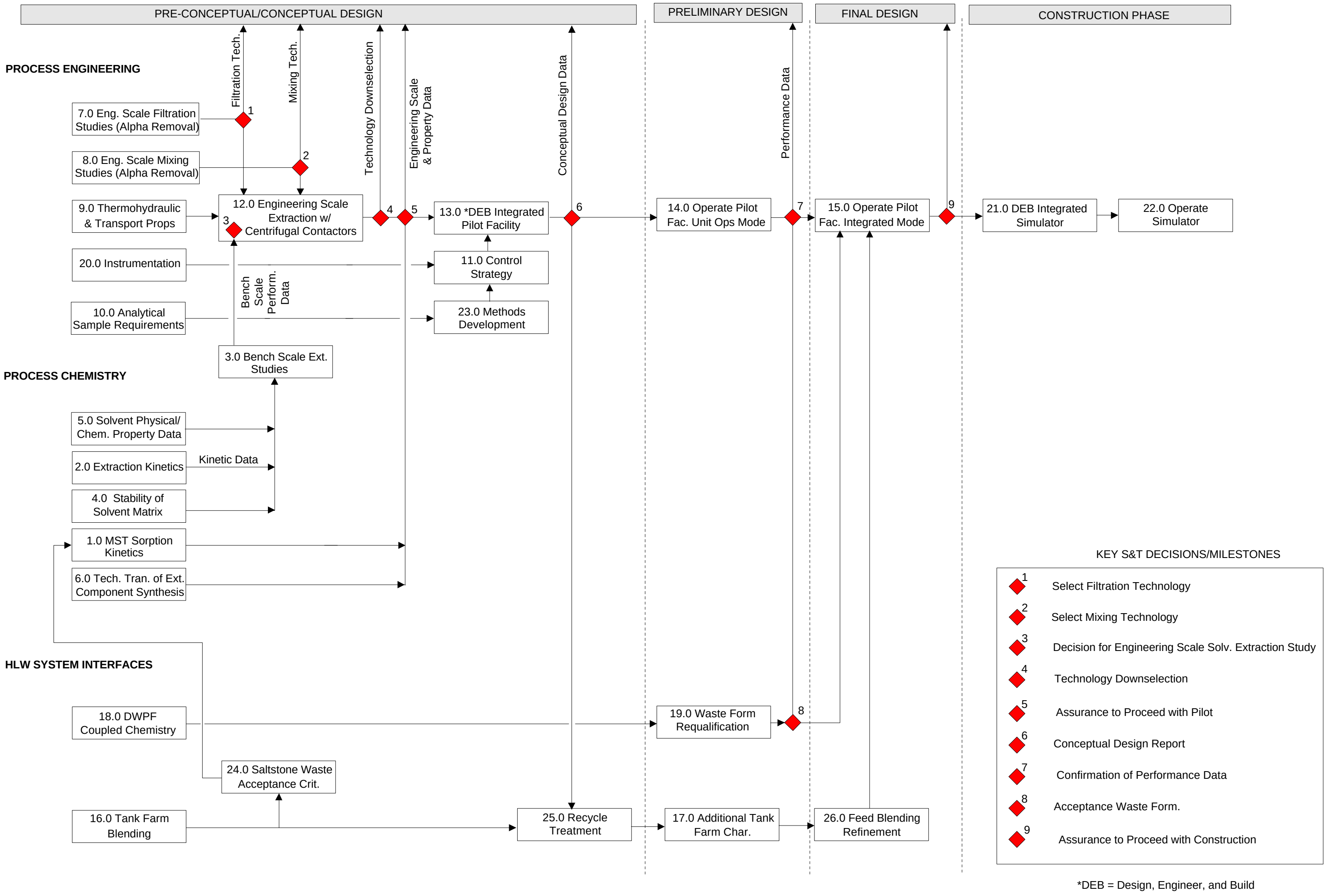
This Workscope Matrix has been developed to define the Science and Technology (S&T) development activities to be performed during the Demonstration Phase. The guiding document for this Workscope Matrix is the HLW Salt Disposition SE Team Science and Technology Roadmap (Attachment 1). This S&T Roadmap 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 Demonstration 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 downselection decision. Some work also is included in these SOWMs that has been identified as appropriate post-downselection R&D. However, no attempt has been made to compile a comprehensive list of all post-downselection R&D in these documents. Additional R&D planning will be required to support future stages of the project, e.g. conceptual design, pilot plant design and operation, 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 Work Scope Matrix

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		Process Chemistry					
1.0	MST Sorption Kinetics	*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 hrs 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.* 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+. 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 waste. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
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	WSRC-TR-98-000368^3 ANL Report # 1, 10/98^3 ORNL FY98 Report^3	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).			HLW-SDT-TTR-2000-01^1 ORNL-CASD-2^2 ANL-1^2 HLW-SDT-TTR-2000-02^1 WSRC-RP-2000-285^2 WSRC-RP-2000-286^2 HLW-SDT-TTR-2000-03^1 ORNL-CTD-2^2 HLW-SDT-TTR-2000-06^1 ANL-1^2 ORNL-CASD-2^2 ORNL-CTD-1^2 HLW-SDT-TTR-2000-07^1 ORNL-CASD-1^2 HLW-SDT-TTR-2000-10^1	WSRC-TR-98-000368^3 ANL Report # 1, 10/98^3 ORNL FY98 Report^3	1, 4, 26
		3.1 Test flowsheet on waste simulant in 2 cm centrifugal contactors					
		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			

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		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 ºC					
		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					
		3.2.4 Test flowsheet on waste simulant in 2cm centrifugal contactors (see 3.1)	Bench	ANL			
		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					
		3.2.4.2 Perform contactor test with 5 day recycle					
		3.2.4.2.1 Confirm performance of solvent; monitor decontamination factors (DFs) and concentration factors (CFs); monitor hydraulic performance					
		3.2.4.2.2 Analyze recycled solvent taken from strip effluent; look for degradation products and polymer formation					
		3.2.4.2.3 Look for trace component buildup					
		3.2.4.3 Solvent Cleanup					
		3.2.4.3.1 Evaluate clean-up procedures					
		3.2.4.3.2 Clean-up solvent as necessary					
		3.2.4.4 Perform second 5-day recycle test (post-downselect)					
		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)	Bench	ANL			
		3.2.6.1 At constant 25 ºC					
		3.2.6.2 At variable temperature					

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		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 distribution behavior of actinides and determine if they could build-up 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 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-downselect) 3.2.8.2.5 Confirm hydrodynamic stability 3.2.8.3 Solvent Cleanup (if required)	Bench	SRTC			
		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-downselect)	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.			HLW-SDT-TTR-2000-02[1] WSRC-RP-2000-285[2] HLW-SDT-TTR-2000-03[1] ORNL-CTD-2[2] ORNL-CASD-2[2] HLW-SDT-TTR-2000-04[1] ORNL-CASD-2[2] HLW-SDT-TTR-2000-08[1] ORNL-CTD-1[2]	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]	1, 3, 23
		4.1 Evaluate radiolytic and chemical stability of solvent 4.1.1 External radiation (Co-60) with the following variables: * Modifier alkyl group structure * Diluent structure * Aqueous phase composition * Temperature and mixing 4.1.1.1 Identify solvent degradation products (at each aqueous	Lab	ORNL/ SRS			

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		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)					
		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					
		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: * Modifier alkyl group structure * Diluent structure * Temperature and mixing	Hot Cell	ORNL/ SRS			
		4.1.2.1 Identify solvent degradation products, crud formation, emulsions					
		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: * high activity Cs-137 waste simulant * scrub solution	Bench	ORNL			
		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-downselect)					
		4.1.4.2 Effect of noble metals					
		4.1.5 Conduct four stage 5 cm contactor test to determine stage efficiencies	Bench	ORNL			
			Lab	ORNL			

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		4.2 Evaluate methods (e.g., HPLC-MS, ES-MS, NMR, distribution behavior, etc.) to ascertain solvent quality					
		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	Bench	ANL			
		4.3.1 Conduct 4-cm contactor test at ANL (cold) with diluent and aqueous effluent recycle	Lab	ORNL			
		4.3.1.1 Develop methods to isolate useful solvent components (vac distill diluent; chromatography to recover calix)	Bench	ANL			
		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-downselect)	Lab	ORNL			
		4.4 Establish limits for solvent component balance and degradation					
		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					
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.			HLW-SDT-TTR-2000-02[1] WSRC-RP-2000-285[2] HLW-SDT-TTR-2000-04[1] ORNL-CASD-2[2] ORNL-CTD-1[2]	ANL Report #1, 10/98[3] HLW-SDT-99-0283[3] ORNL FY98 Report[3] ORNL/TM-1999/209[3]	1
		5.1 Solubility and partitioning behavior as a function of temperature and aqueous phase composition	Lab	ORNL			
		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 build-					

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		up in solvent 5.1.6 Determine partitioning behavior of components using real waste 5.1.7 Batch contact with Cs-137 spike 5.2 Evaluate the effect of major and minor components that are expected to be present in actual waste 5.2.1 Partitioning behavior of organics (e.g., surfactants, TBP degradation products) in waste 5.2.2 Partitioning behavior of other inorganics (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 5.3.1 Investigate extraction equilibria throughout the sections (ex, 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) 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: 5.4.1.1 Temperature 5.4.1.2 Solvent component concentration 5.4.1.3 Suspended solids in feed	Lab NA Lab	ORNL ORNL ORNL/ SRS			
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 tech transfer to suitable companies for production. The technology transfer scope will be initiated in FY00 and be completed in FY01. 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	NA	ORNL	HLW-SDT-TTR-2000-05[1] ORNL-CASD-1[2] ORNL-CASD-3[2]	ORNL FY98 Report[3]	9, 22

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		in US; foreign?) 6.1.3 Technology transfer of Synthesis Procedure for Calix 6.1.3.1 Identify potential calixarene producers 6.1.3.2 Legal issues/Obtain non-disclosure agreements as necessary 6.1.3.3 Develop QA requirements and production specification 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 2nd Generation Modifier Synthesis and Scale-up 6.2.1 Optimize synthesis procedure for scale-up for 2nd Gen modifier family 6.2.1.1 Improve purification procedure and economics 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 applic. on 2nd Gen family 6.2.2.2 Determine if foreign filing is appropriate 6.2.3 Technology transfer of Synthesis Procedure for 2nd Generation Modifiers 6.2.3.1 Identify potential modifier producers 6.2.3.2 Legal issues/Obtain non-disclosure agreements as necessary 6.2.3.3 Develop QA requirements and production specification 6.2.3.4 Obtain quotations on bulk manufacture; select producer(s) (post-downselect) 6.2.3.5 Place order for multi-kg quantity from selected producer(s) (post-downselect) 6.2.3.6 Check purity; estimate large-scale production cost (post-downselect) 6.3 Solvent Formulation 6.3.1 Identify Trioctylamine (TOA) suppliers 6.3.2 Identify scope of acceptable diluents (are there suitable substitutes for ExxonMobil's Isopar® L?)					

Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		6.3.3 Identify solvent compositional requirements/tolerances/QA 6.3.4 Finalize solvent formulation and specifications					
		Process Engineering					
7.0	Engineering scale filtration studies (Alpha Removal)	*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.* 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. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
8.0	Engineering Scale Mixing Studies (Alpha Removal)	*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.* (Preliminary Design Scope)	NA	NA	NA		27
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 Reqs	*The analytical sample requirements including on-line analysis must be developed to support control strategy development.* Develop an at line analyzer for Cs, Sr, and total alpha. Activities to resolve these issues are common to CST, TPB and CSEX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
11.0	Control Strategy	*Control Strategy must be developed to support the designing, engineering, and building of the pilot facility.* Pilot Plant Conceptual Design will be conducted post downselect	NA	NA	NA		Design Input
12.0	Engineering Scale Extraction with	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**.**	NA	NA	NA	ANL Report # 2, 10/98[3] ANL Report # 1, 10/98[3] ORNL FY98 Report[3]	26

Note: See Matrix Legend for definition of column content

Item No.	**Item**	**Considerations**	**Scale**	**Location**	**Path Forward Doc.**	**Reference Doc.**	**Uncertainty**
	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, with real SRS HLW. 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 contactor test and the sensitivity of the process flowsheet to "process upsets."					
13.0	Design, Engineer, and Build (DEB) the Pilot Facility	*A pilot scale (to be determined) facility will be built to support the confirmation of design data and development of operator training.* 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
14.0	Operation of the Pilot Facility in a Unit Operations Mode	*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.* 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
15.0	Operation of the Pilot Facility in an Integrated Operations Mode	*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.*	NA	NA	NA		Design Input
20.0	Instrumentation	See 13.0	NA	NA	NA		Design Input
21.0	Design, Engineer and Build (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				ORNL FY98 Report[3]	1

Note: See Matrix Legend for definition of column content

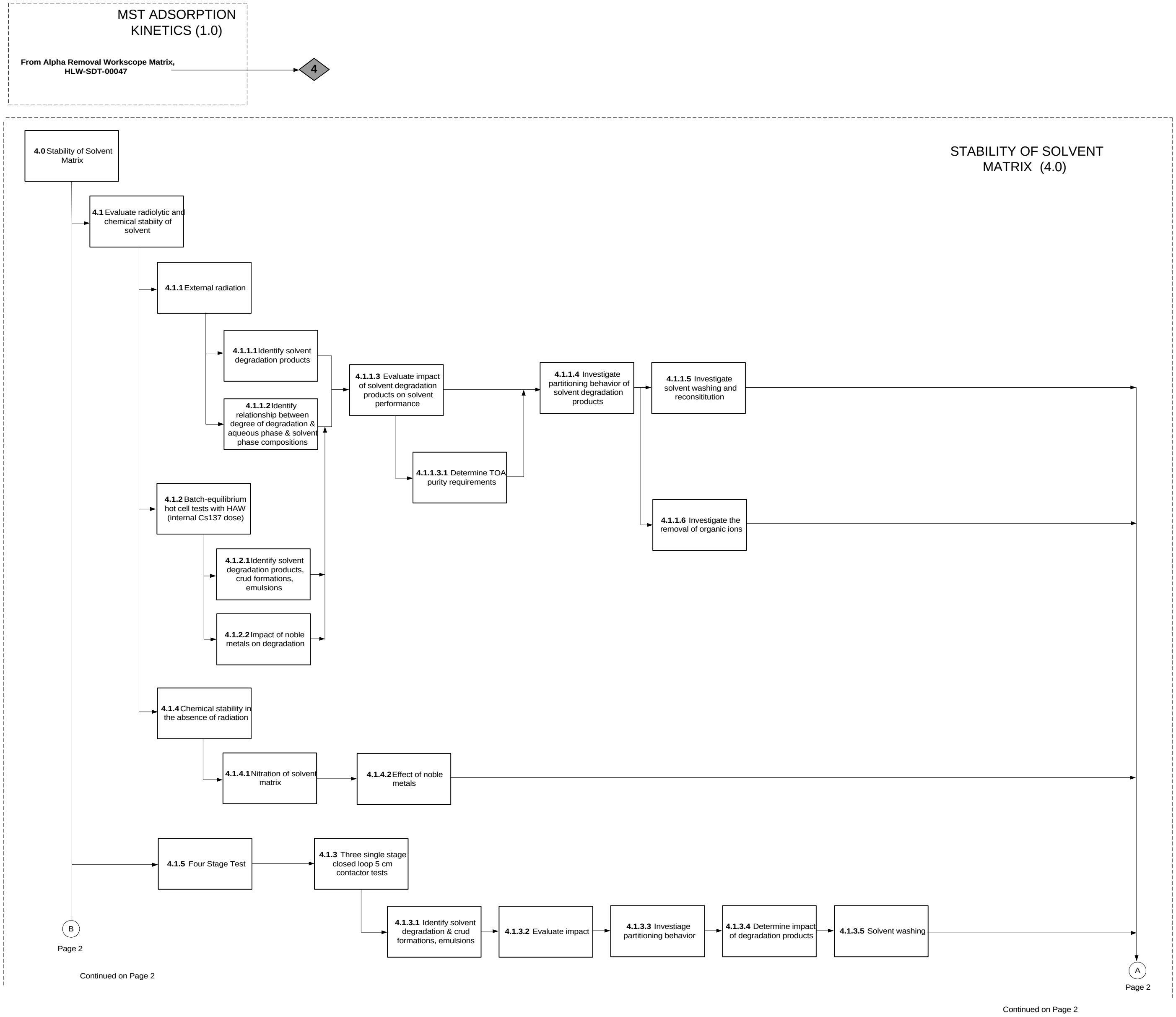
Item No.	Item	Considerations	Scale	Location	Path Forward Doc.	Reference Doc.	Uncertainty
		meets the CIF Waste Acceptance Criteria. 16.1 Determine whether strip effluent meets DWPF feed requirements (This work performed under Section 3.1) 16.1.1 Cs concentration factor adequate? 16.1.2 Concentration of other species in strip effluent acceptable? 16.2 Determine whether raffinate meets Saltstone Facility WAC 16.2.1 Solvent components in raffinate 16.2.2 Solvent degradation products in raffinate 16.3 Determine whether spent solvent meets CIF WAC (post-downselect)	NA	SRS SRS ORNL SRS			
17.0	Additional Tank Farm Characterization	*While the tank farm waste has been characterized, additional characterization may be required to define the range of expected compositions during facility operation.* Waste characterization 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 Requal-ification	No needs identified at this time	NA	NA	NA		Design Input
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 PreliminaryDesign.	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)

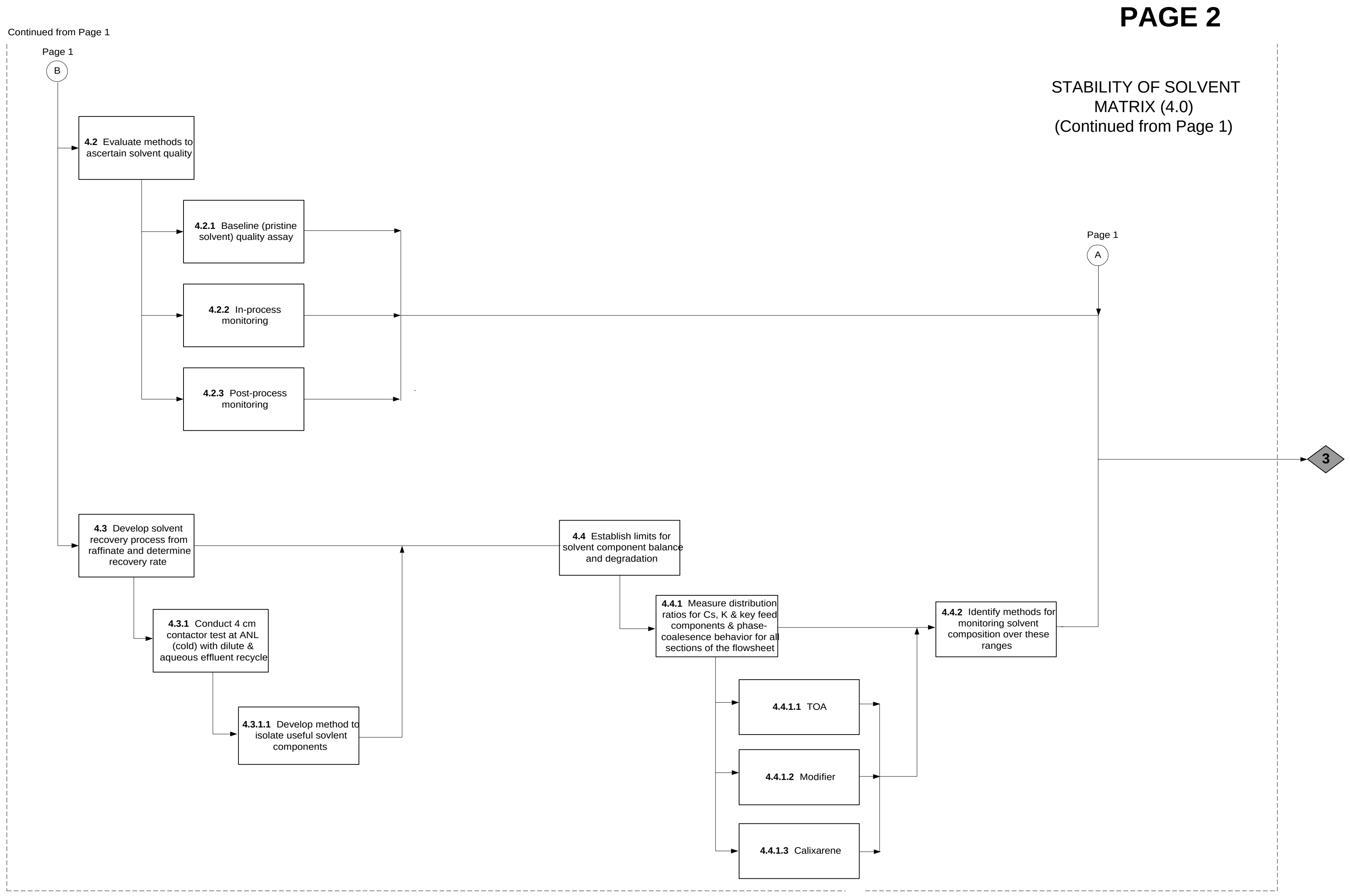
PAGE 1



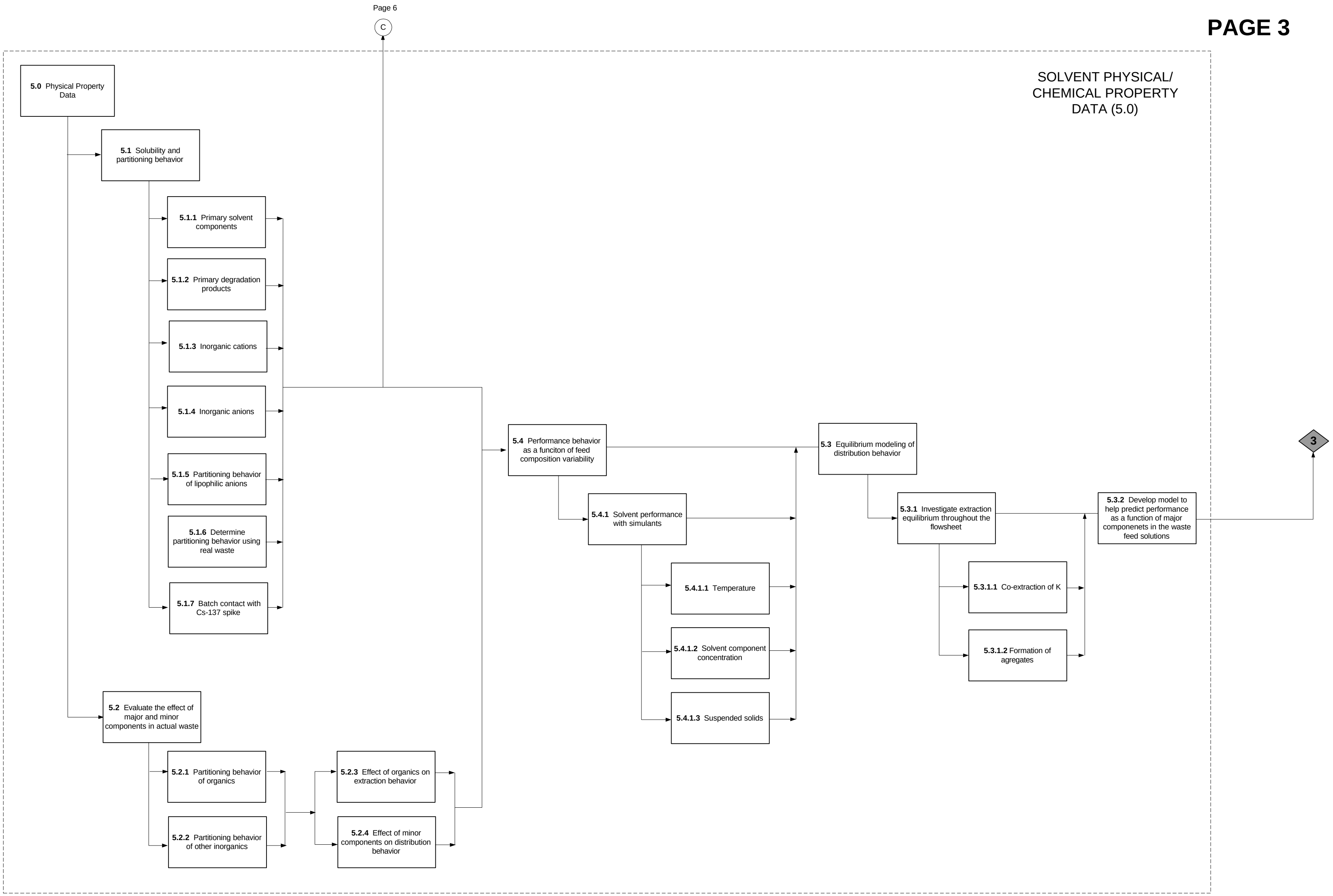
Continued on Page 2

Continued on Page 2

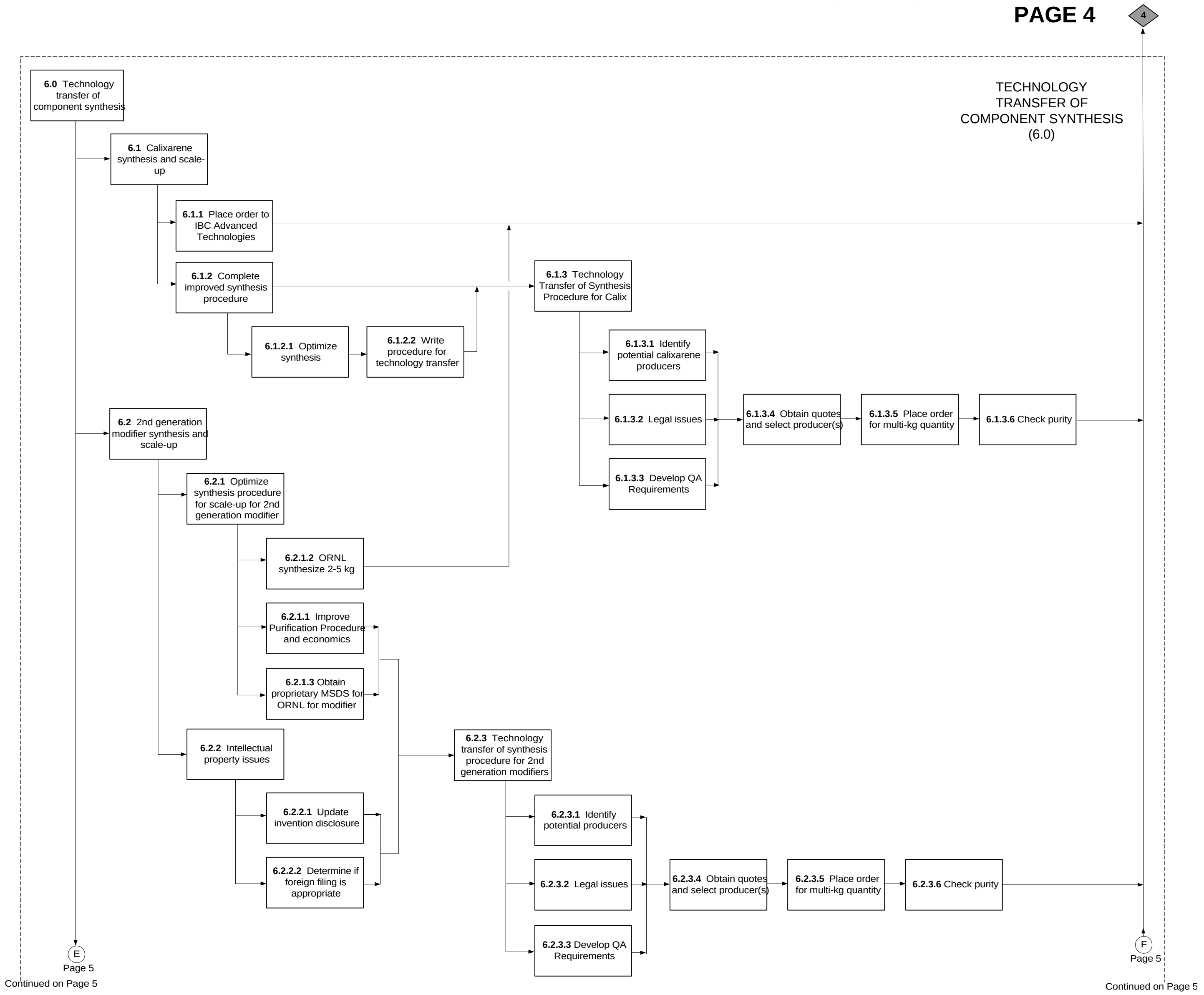
ATTACHMENT 2 - Caustic-Side Solvent Extraction S&T Logic Diagrams (2 of 7)



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

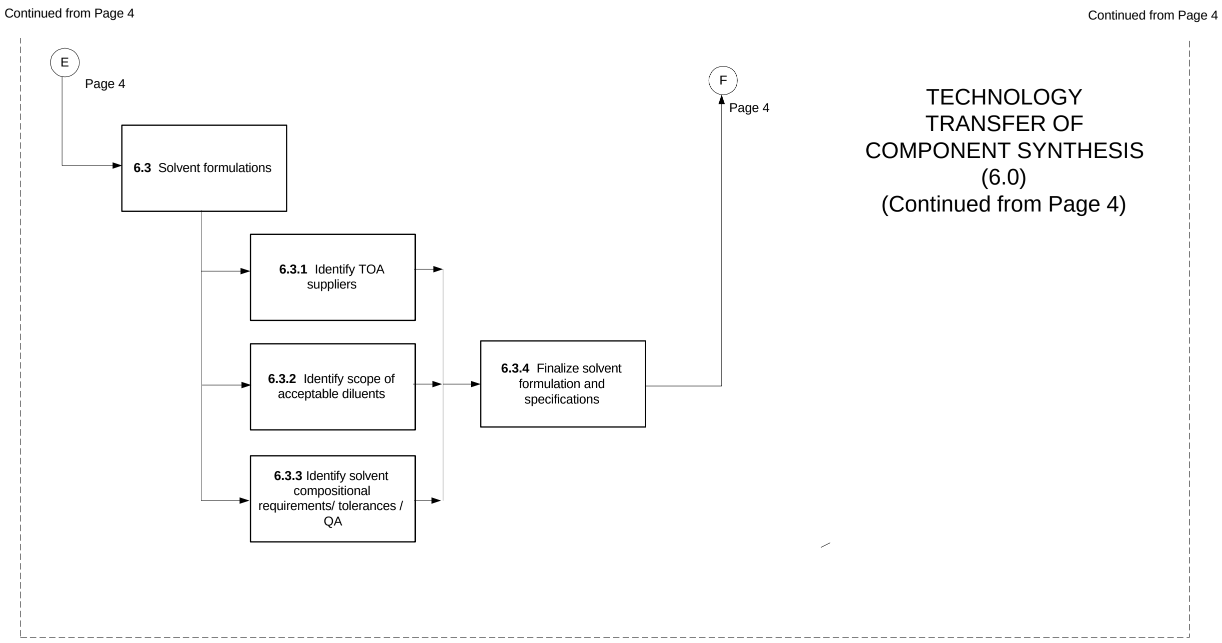


ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (4 of 7)



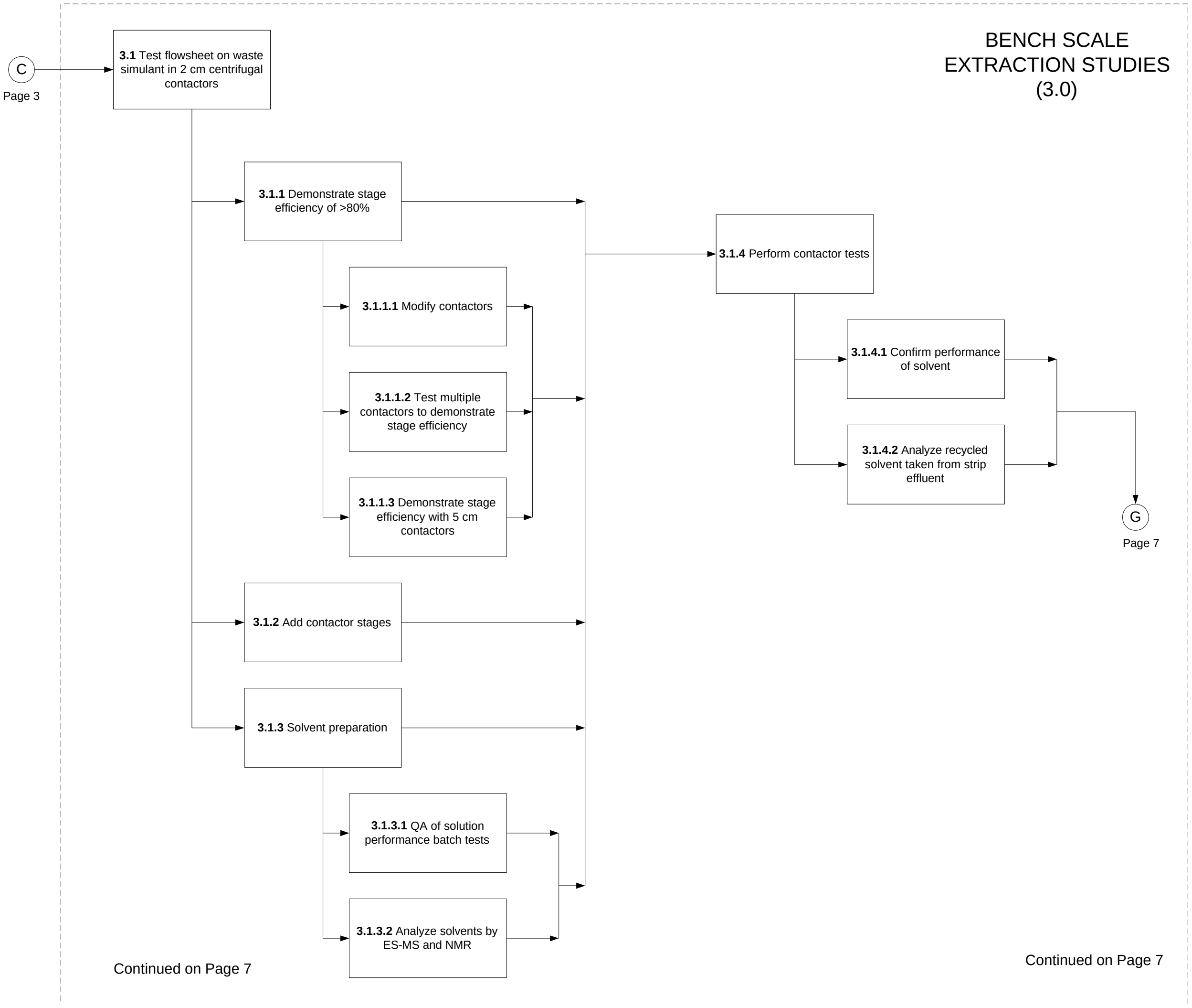
ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (5 of 7)

PAGE 5

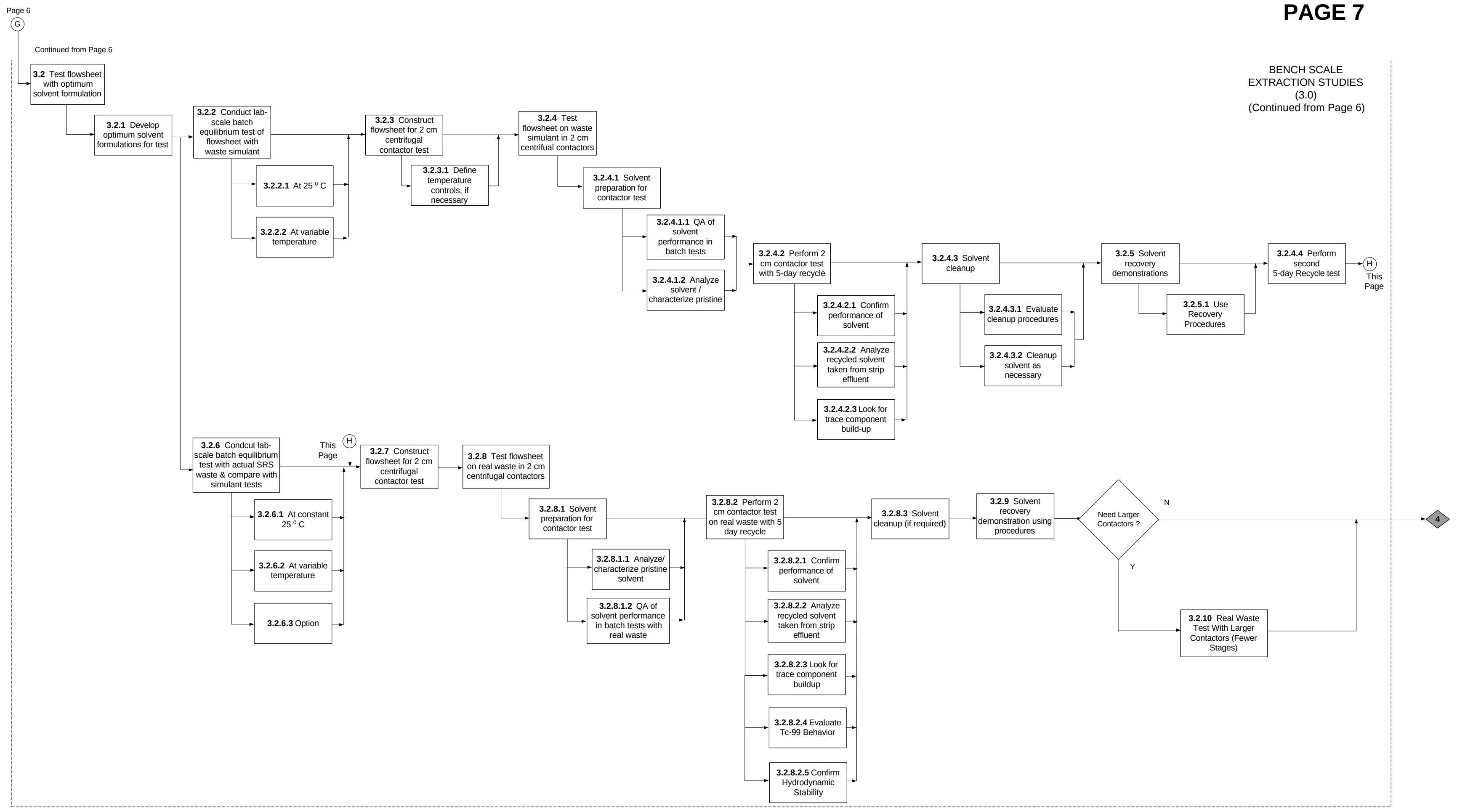


ATTACHMENT 3 - Caustic-Side Solvent Extraction S&T Logic Diagrams (6 of 7)

PAGE 6



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



HLW-SDT-99-0353
Revision: 5

SAVANNAH RIVER SITE

HIGH LEVEL WASTE SALT DISPOSITION SYSTEMS ENGINEERING TEAM

APPLIED TECHNOLOGY INTEGRATION SCOPE OF WORK MATRIX FOR SMALL TANK TPB PRECIPITATION

(Demonstration Phase)

APPROVED:___________________________ **DATE:**_________________
K. J. Rueter, HLW Program Manager

APPROVED:___________________________ **DATE:**_________________
T. P. Pietrok, TFA Program Manager

APPROVED:___________________________ **DATE:**_________________
K. T. Lang, EM-40 SPP Program Manager

Change Control Record

Document Name Applied Technology Integration Scope of Work Matrix for Small Tank TPB Precipitation (Demonstration Phase)	*Unique Identifier* HLW-SDT-99-0353

Summary of Changes

Revision Date	*Matrix Revision*	*BCF Number(s)*	*Reasons for change*	*Items Affected by the change*
December 2, 1999	0	NA	Initial Issue	NA
December 27, 1999	1	NA	Incorporates ECF # HLW-SDT-99-0388 which added TTR/TTP/TR references, ties to uncertainty IDs, updates to reflect feedback from TTR/TTP development and incorporated minor editorial comments	All changes identified with revision bars
January 10, 2000	2	NA	Incorporates ECF# HLW-SDT-2000-00011 which aligned workscope matrix with finalized FY00 approved workscope and incorporated DOE review comments by removing holds and identifying work to be initiated in FY01 and incorporated minor editorial comments.	All changes identified with revision bars
February 15, 2000	3	NA	Incorporates ECF# HLW-SDT-2000-00050 which removed information from items common to all three technologies that are now being controlled through Alpha Removal workscope matrix HLW-SDT-2000-00047.	All changes identified with revision bars
July 10, 2000	4	NA	Incorporates ECF # HLW-SDT-2000-00266 which dispositions comments from the TFA team.	All changes identified with revision bars.

Change Control Record (Continued)

Revision Date	*Matrix Revision*	*BCF Number(s)*	Reasons for change	*Items Affected by the change*
November 27, 2000	5	N/A	Incorporates ECF # HLW-SDT-2000-00463 which dispositions comments from TFA team and updates document with FY00 science and technology results	All changes identified with revision bars.

Use of Workscope Matrix

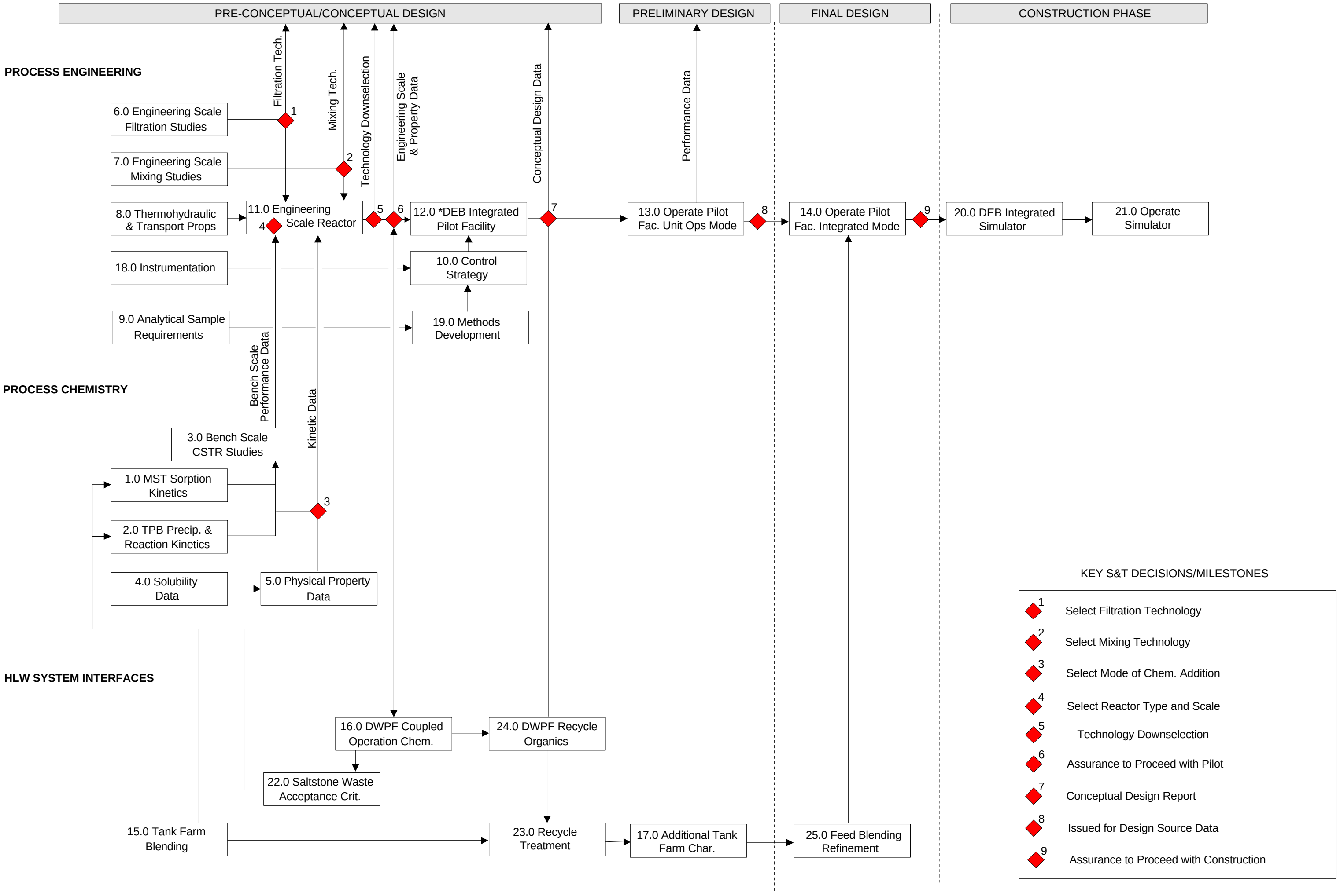
This Workscope Matrix has been developed to define the Science and Technology (S&T) development activities to be performed during the Demonstration Phase. The guiding document for this Workscope Matrix is the HLW Salt Disposition SE Team Science and Technology Roadmap (Attachment 1). The S&T Roadmap provides the technology development path forward towards successful deployment of the Small Tank TPB Precipitation 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 Demonstration 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 downselection decision. Some work also is included in these SOWMs that has been identified as appropriate post-downselection R&D. <u>However, no attempt has been made to compile a comprehensive list of all post-downselection R&D in these documents</u>. Additional R&D planning will be required to support future stages of the project, e.g. conceptual design, pilot plant design and operation, final design, and startup support.

ATTACHMENT 1 – Small Tank TPB Precipitation Science and Technology Roadmap

SCIENCE AND TECHNOLOGY ROADMAP FOR SMALL TANK TPB PRECIPITATION CESIUM REMOVAL PROCESS



*DEB = Design, Engineer, and Build

ATTACHMENT 2 – Small Tank TPB Precipitation Work Scope Matrix

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
Process Chemistry							
1.0	MST Sorption Kinetics	*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 reactor design. The effect of TPB on MST kinetics must be known. Initial data from batch reactor data indicates the MST kinetics are controlling the size of the reactor. The impact of the higher MST loading and varying levels of PHA on glass properties must also be evaluated.* 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. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
2.0	TPB Precipitation and Reaction Kinetics	*The addition of TPB will be used to precipitate the Cs-137 and other metals. The rate and equilibrium (solubility) of MTPB precipitation as a function of temperature, ionic strength and mixing is required to support the reactor design. Additional studies on TPB decomposition under the expected process conditions are required.* During the experimental work conducted by SRTC for the closure of DNFSB 96-1, discrepancies in the decomposition rates for TPB for real waste and simulants were observed. Also, a possibility exists for some catalyst or catalyst system to produce decomposition rates which overwhelm the precipitation and filtration rates. The understanding of catalyst activation and catalytic synergistic effects must be improved to explain the real waste/simulant discrepancy. For process design, an upper bound for decomposition rates should be determined.			HLW-SDT-TTR-99-20[1] WSRC-RP-99-01114[2] SRT-LWP-2000-00117[3] HLW-SDT-TTR-99-21[1] WSRC-RP-99-01114[2] ORNL/CF-99/71[2] WSRC-TR-2000-00230[3] WSRC-TR-2000-00276[3] HLW-SDT-TTR-99-27[1] WSRC-RP-99-01114[2] ORNL/CF-99/64[2] ORNL/TM-2000/300[3]	WSRC-TR-99-00216[3] ORNL/TM-1999/234[3] WSRC-TR-99-00345[3] WSRC-TR-99-00325[3] WSRC-TR-99-00375[3]	4, 5, 2
		2.1 Contract consultants to assist in	NA	SRTC			
		2.1.1 Developing list of potential catalysts					
		2.1.2 Developing potential catalytic synergistic effects					
		2.1.3 Outline methods for conducting experiments					
		2.1.4 Review of existing data for experimental adequacy.					
		2.1.5 Develop catalyst working mechanism					
		2.2 Define catalyst/synergistic effects	Lab	SRTC			
		2.2.1 Perform literature searches					
		2.2.2 Conduct additional catalyst identification tests to delineate the role					

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		of intermediates 2.2.3 Conduct synergistic effects tests with the various catalysts identified and combinations recommended by experts 2.2.4 Conduct experiments to determine the form of Pd that is most reactive in the decomposition of TPB 2.2.4.1 NMR tests 2.2.4.2 Mechanistic Pd testing 2.2.5 Perform electrochemical and spectroscopic studies of transition metals 2.2.6 Perform Ru/Rh activation tests 2.2.7 Perform expanded metals testing (8 additional cycle 1 demo metals) 2.2.8 Develop and test new simulant					
		2.3 Conduct real waste versus simulant tests 2.3.1 Select Waste Tanks 2.3.2 Obtain real waste samples 2.3.3 Characterize real waste for potential catalysts and/or catalyst combinations	Lab	SRTC			
		2.4 Conduct CSTR Test with a simulated waste/TPB system that clearly decomposes in batch tests 2.4.1 Conduct demo-scale (20L Open Loop Activated Catalyst) unit operations tests at ORNL 2.4.2 Conduct demo-scale (20L Closed Loop Activated Catalyst) integrated operations tests at ORNL	Bench (20 L)	ORNL			
		2.5 Conduct additional CSTR real waste test using recommended antifoam to demonstrate sustained DF, balanced hydraulics, and reduced foaming 2.5.1 Evaluate feasibility and need for additional CSTR real waste test 2.5.2 Conduct real waste CSTR test 2.5.3 Determine effect of temperature on ramp up once steady state has been attained	Bench (20 L)	SRTC			
		2.6 Evaluate enhancements to precipitation process and equipment such as dual strike (adding TPB to both reactors), different TPB addition methods, and mixing techniques. (post-downselect)	Bench (20 L)	ORNL/ SRTC			
3.0	Bench Scale CSTR Studies	*To date TPB experimentation has not been conducted in a reactor. Batch reactor data has been used to size the reactor in the pre-conceptual stages.* FY00 scope includes 0.5 L and 20 L CSTR testing to support TPB decomposition catalyst activation, NaTPB distribution, precipitate washing and antifoam development. Open loop tests will be conducted at ORNL as a part of the scope for 2.0, 4.0, and 5.0. Two closed loop tests will be conducted as a part of the bench scale reactor studies that	Bench	ORNL	HLW-SDT-TTR-99-27[1] ORNL/CF-99/64[2] ORNL/TM-2000/300[3]	ORNL/TM-1999/234[3] WSRC-TR-99-00345[3] WSRC-TR-99-00116[3] WSRC-TR-99-00325[3]	23, 24

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		incorporate knowledge obtained from the other portions of the program.					
4.0	Solubility Data Work to be initiated in FY01	*NaTPB solubility data and rate of re-dissolution data is needed to support the reactor design. Under certain conditions the rate of dissolution of TPB can be the rate determining step for the precipitation of cesium. Solubility of CsTPB and KTPB has been studied in the past but may require confirmation due to changes in the operating conditions. Solubility of other salts must be determined to define the lower bounds of operating temperature and minimum tank farm dilution requirements. Benzene stripping from filtrate requires investigation.* The distribution of NaTPB between the phases needs to be understood in greater detail. During ITP operations and subsequent experimental work, the solubility of NaTPB has been questioned. Recent studies have indicated that an isomorphic crystal is formed when Cs and K are precipitated using NaTPB. The understanding of this crystal and its formation must be increased. (see 4.1) The washing experiments conducted at SRTC resulted in an approximately 70% recovery of the excess NaTPB added to the process. The 20L pilot scale facility was much less successful in recovering the excess NaTPB (~30%). The amount of excess recovered directly impacts the amount of glass made in the DWPF. Also, since the excess is planned for recycle back to the CSTRs, the % recovery directly impacts the cost of the raw material for operating the plant. The recovery of NaTPB should be improved and the recovery understood in light of the plant operating conditions. (see 4.2)				WSRC-TR-99-00243[3] WSRC-TR-99-00154[3] WSRC-TR-99-00155[3] WSRC-TR-99-00156[3] WSRC-TR-99-00216[3]	5, 23
		4.1 TPB Precipitation Testing (post-downselect) 4.1.1 Develop technology resources in the field of crystallization 4.1.1.1 Establish a consulting contract with an expert in the field of crystallization 4.1.1.2 Continue membership in the Association for Crystallization Technology	NA	SRTC			
		4.1.2 Conduct DSC testing 4.1.2.1 Measure precipitation rates directly through the use of DSC 4.1.2.2 Measure heat of crystallization 4.1.2.3 Confirm viability of measurements using dilute aqueous solutions 4.1.2.4 Perform subsequent tests to explore mixed crystal formation from complex salt solutions	Lab	SRTC/ ORNL			
		4.1.3 Perform Na tracer studies 4.1.3.1 Perform batch precipitation tests with radiotracer Na	Lab	SRTC			
		4.1.4 Perform spectroscopic measurement of crystals 4.1.4.1 Prepare mixed crystals of Na, K and Cs TPB 4.1.4.1.1 Perform analysis by x-ray diffraction and by electron-microprobe	Lab	SRTC			

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		4.1.5 Perform residence time scan					
		4.1.5.1 Analyze precipitation rates Vs residence time	Lab	SRTC			
		4.1.5.2 Perform particle size analysis					
		4.1.6 Perform small-scale mixing tests to explore the following variables:	Lab	SRTC			
		4.1.6.1 Feed K concentration testing					
		4.1.6.2 Mixing energy					
		4.1.6.3 Bulk sodium molarity					
		4.1.6.4 Resultant crystal composition (by digestion, XRD and dissolution)					
		4.1.7 Perform 20 L scale optimum utility demonstration based on conditions derived from previous testing	Bench	ORNL			
		4.1.7.1 Use test results to assist model development					
		4.1.7.2 Use test results to develop future programs including equipment modification					
		4.2 Perform Dissolution Tests (post-downselect)					
		4.2.1 Perform K+ dissolution tests with the following variables: • Multiple TPB/K ratios • Concentrations between 10- and 12 wt% • Sodium molarity • Anti-foam concentrations • Agitator type and speed	Lab	SRTC			
		4.2.2 Perform TPB dissolution tests with the following variables: • Multiple TPB/K ratios • Concentrations between 10- and 12 wt% • Sodium molarity • Anti-foam concentrations • Agitator type and speed					
		4.2.3 Perform Pellet studies					
		4.2.3.1 Prepare pellets of NaTPB and measure dissolution rates with and without K+ present					
		4.2.4 Determine if larger scale equipment is required					
		4.2.5 Develop scale equipment design					
		4.2.6 Perform calculations to modify 20 L ORNL test equipment					
		4.2.7 Modify 20 L ORNL test equipment					
		4.3 Perform washing studies					
		4.3.1 Perform bench-scale (PREF) washing studies to confirm washing behavior based on dissolution tests	Bench	SRTC			

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
		4.3.2 Perform 20 L open loop test to confirm impact of scale washing on performance (material from 4.1.7)	Bench	ORNL			
		4.3.3 If batch tests (4.3.1 and 4.3.2) indicate viability, perform semi-batch washing tests (post-downselect)	Bench	ORNL			
5.0	Physical Property Data	*General physical property data such as density, viscosity, yield stress and consistency of slurries, as a function of state variables such as temperature is required to support the design effort.* Foaming in tetraphenylborate mixtures during agitation was identified early in the development of the original ITP process. ITP used tributylphosphate to reduce foaming in the stripper columns, while the Late Wash and DWPF facilities used Surfynol 420^{tm} to reduce precipitate foaming. Surfynol 420^{tm} was selected for use in the Small Tank Phase IV work because the impact on downstream processes has already been evaluated. Foaming was observed in the experimental work at SRTC and ORNL. An antifoaming agent that is effective in suppressing foaming in TPB solutions must be identified. The causes of any differences in foaming characteristics between real waste and simulants understood and the effectiveness of the selected antifoam agents tested.			HLW-SDT-TTR-99-25[1] WSRC-RP-99-1089[2] WSRC-TR-2000-00297[3]	WSRC-TR-99-00345[3]	5, 23
		5.1 Consult with academic expert to identify potentially effective antifoam agents to be tested using a bench-scale prototype of the precipitation/ washing equipment.	NA	SRTC/IIT			
		5.1.1 Evaluate filtration (or other purification methods) of fresh TPB solutions to reduce foaming					
		5.2 Test effectiveness of each identified anti-foam agent at bench scale	Lab	SRTC			
		5.2.1 Test effect of anti-foam on washing					
		5.3 Test the most effective anti-foam agent under irradiated conditions to identify reduced effectiveness caused by irradiation	NA	NA			
		5.4 Determine an analytical technique to enable determination of the fate of anti-foam agent across the precipitation, concentration, washing and hydrolysis cycles	NA	NA			
		5.5 Test the most effective anti-foam agent using a CSTR test cycle, using surrogate feed (perform anti-foam agent material balance)	Bench	SRTC			
		5.6 Test the most effective anti-foam agent using a lab-scale test cycle, using actual waste (perform anti-foam agent material balance)	NA	NA			
		5.7 Perform 20 L open loop demo	Bench	ORNL			
		5.8 Evaluate downstream HLW system impacts of chosen antifoam agent	TBD	TBD			
Process Engineering							
6.0	Engineering Scale Filtration	*Filtration of TPB slurries containing MST has been studied extensively in the past. The change to a continuous process requires a re-evaluation of cleaning techniques, and control strategy. Should the MST and TPB chemical strikes be separated. Filtration of*					

Note: See Matrix Legend for definition of column content

Item No.	Item	Considerations	Scale	Lead Org.	Path Forward Doc.	Reference Doc.	Uncertainty
	Studies	*MST alone must be studied to ensure proper filter sizing. Filtration cleaning studies including the impact of spent cleaning solution will be studied. The effect of antifoam requires investigation.* The role of TPB in the filtration process needs to be determined. This work will also aid the search and development of a filter aid for the CST process. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
7.0	Engineering Scale Mixing Studies	*As noted in the kinetic sections above, good reactor mixing is essential to proper reactor sizing. Simple mixing by agitation or recirculation may not be adequate. Alternate mixing technologies will be studied, and a selection made.* Identified activities will be conducted during Conceptual Design	NA	NA	NA		Design Input
8.0	Thermo-hydraulic and transport Properties	*Thermal and hydraulic properties must be measured to allow for determination of heat removal loads and technologies (jacketed vessels, cooling coils, heat exchanger, etc.).* Identified activities will be conducted during Conceptual Design	NA	NA	NA		Design Input
18.0	Instrumentation	Activities will be conducted during Conceptual Design	NA	NA	NA		Design Input
19.0	Methods Development	Activities will be conducted during Conceptual Design	NA	NA	NA		Design Input
9.0	Analytical Sample Reqs.	*The analytical sample requirements including on-line analysis must be developed to support control strategy development.* Develop an at line analyzer for Cs, Sr, and total alpha. Activities to resolve these issues are common to CST, TPB and CSSX, Refer to Alpha Removal Workscope Matrix (HLW-SDT-2000-00047) for further details.					
10.0	Control Strategy	*Control Strategy must be developed to support the designing, engineering, and building of the pilot facility.* Pre-Conceptual Design of the Pilot Facility has started	NA	NA	NA		7
11.0	Engineering Scale Reactor	*The bench scale kinetic data, engineering scale filtration and mixing studies and bench scale reactor studies may indicate the need for intermediate scale reactor testing prior to designing, engineering, and building of the pilot facility.* Pre-Conceptual Design of the Pilot Facility has started	NA	NA	NA		Design Input
12.0	Design, Engineer, and Build (DEB) the intetgrated	*A pilot scale (to be determined) facility will be built to support the confirmation of design data and development of operator training.* Pilot Facility Conceptual Design will be conducted in parallel with a final technology	NA	NA	NA		Design Input

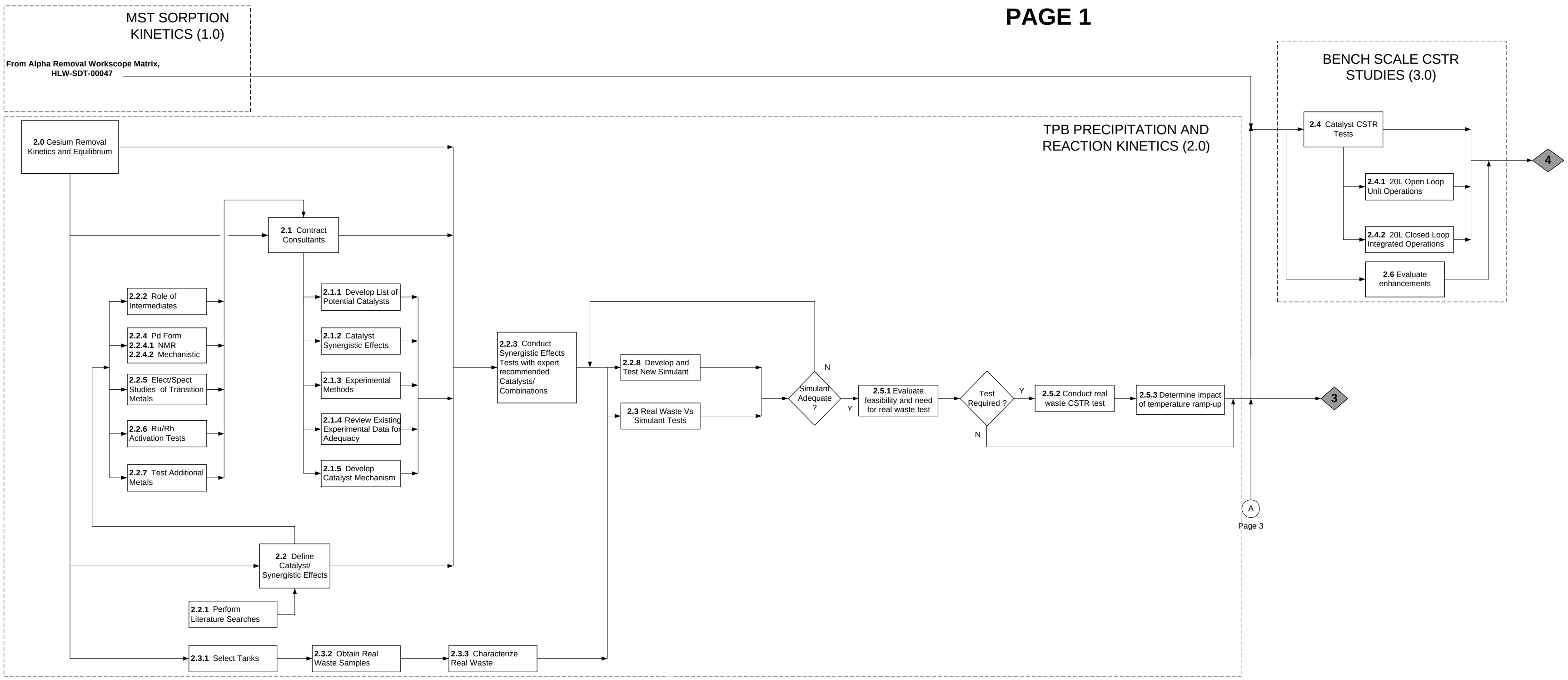
Item No.	**Item**	**Considerations**	**Scale**	**Lead Org.**	**Path Forward Doc.**	**Reference Doc.**	**Uncertainty**
	Pilot Facility	selection. Pilot Facility design will be conducted on the selected technology.					
13.0	Operate the Pilot Facility in a Unit Operations Mode	*The pilot facility testing will include a phase of single unit operations to confirm bench scale property data, operational parameters and proof of concept component testing.* 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
14.0	Operate the Pilot Facility in an Integrated Mode	*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. This testing will aide in operator training and simulator development which in accordance with the overall project roadmap is completed during the construction phase of the project.* Activities will be conducted during Conceptual Design	NA	NA	NA		Design Input
20.0	Design, Engineer, and Build (DEB) Integrated Simulator	Activities will be conducted during construction	NA	NA	NA		Design Input
21.0	Operate Simulator	Activities will be conducted during construction	NA	NA	NA		Design Input
High Level Waste System Interface							
15.0	Tank Farm Blending	*The production sequences of emptying the tank farm has been studied in the past and have indicated potential tank blending issues regarding Np, U, Pu, and Sr. The current blend strategy must be reviewed to determine if alternate blending strategies can reduce the 5 to 8x concentration spikes in these components or if the alpha removal requirements must be modified to meet the Saltstone waste acceptance limits.* Additional blending studies will be conducted during Conceptual Design	NA	NA	NA		
16.0	DWPF Coupled Operation Chemistry Work to be initiated in FY01	*The use of TPB as a precipitating agent requires an additional processing step in the DWPF (Salt Processing Cell) to remove the organics prior to vitrification of the waste. This process has been operated full scale during DWPF cold chemical operations, but limited radioactive testing has been conducted. Technical issues requiring investigation includes organic byproduct accumulation in the off-gas systems and trace organic being returned to the tank farm via the recycle condensate. The Small Tank TPB process exceeds the ratio of salt to sludge tested during DWPF cold chemical operations, extension of the glass property correlations may be required. Development of vessel vent cleaning and recycle organic removal technology may be required.* The hydrolysis process in the DWPF was the limiting process for the original Small Tank TPB Precipitation Process. The latest Salt Disposition Facility flowsheet has incorporated the hydrolysis process and removed it from the DWPF flowsheet. The process needs to be				WSRC-TR-99-00262[3] WSRC-TR-99-00290[3] WSRC-TR-99-00292[3] WSRC-TR-99-00294[3] WSRC-TR-99-00272[3] WSRC-TR-99-00332[3] WSRC-TR-99-00293[3] WSRC-TR-99-00279[3]	1, 3

Item No.	**Item**	**Considerations**	**Scale**	**Lead Org.**	**Path Forward Doc.**	**Reference Doc.**	**Uncertainty**
		properly sized in the new flowsheet. Additionally, some alternatives to the current hydrolysis process need to be investigated in order to reduce the amount of Cu used and the Tank Farm recycle.					
		16.1 Develop relationship of nitrate and nitrite concentration in CSTR product TPB as a function of absorbed dose (post-downselect)	Lab	SRTC			
		16.2 Conduct experiments to develop the optimum Cu/formic acid ratio as a function of time	Lab	SRTC			
		16.3 Confirm these experiments at the bench scale	1/240th	SRTC			
		16.4 Assess alternate catalyst forms to copper nitrate (post-downselect)	Lab	SRTC			
		16.5 Assess technical feasibility of recycling catalyst (post-downselect)	Lab	SRTC			
		16.6 Determine the effects of kinetics on phase separation by using canister centerline cooling profile	Lab	SRTC			
17.0	Additional Tank Farm Characterization	*While the tank farm waste has been characterized, additional characterization may be required to define the range of expected compositions during facility operation.* See 5.6 and 2.3	NA	NA	NA		Design Input
22.0	Saltstone Waste Acceptance Criteria	No identified scope	NA	NA	NA		Design Input
23.0	Recycle Treatment	No identified scope	NA	NA	NA		Design Input
24.0	DWPF Recycle Organics	No identified scope	NA	NA	NA		Design Input
25.0	Feed Blending Refinement	Activities will be conducted during Final Design	NA	NA	NA		Design Input

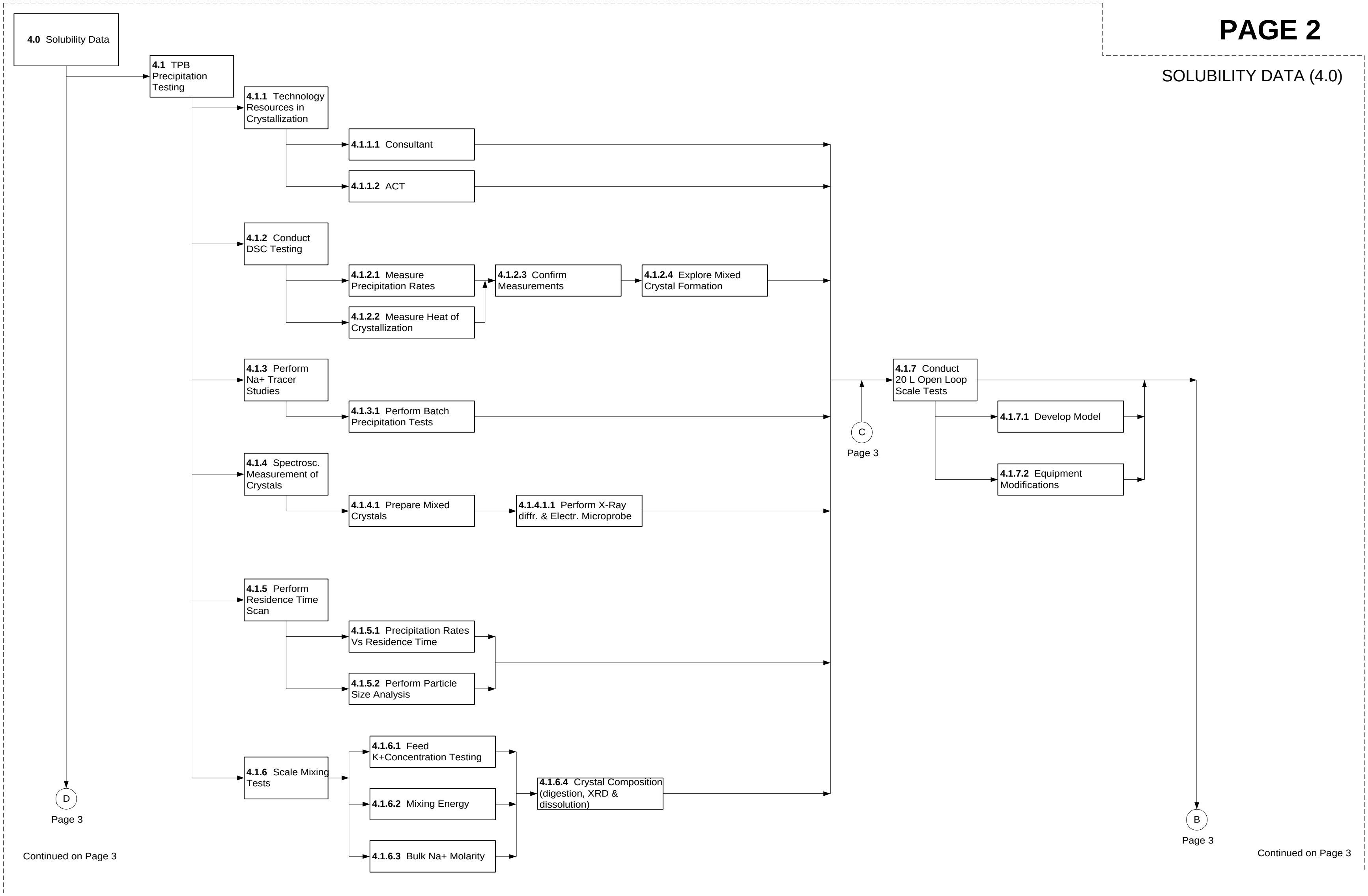
Matrix Legend

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). Italicized text is extracted from previous TPB roadmap HLW-SDT-980164 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

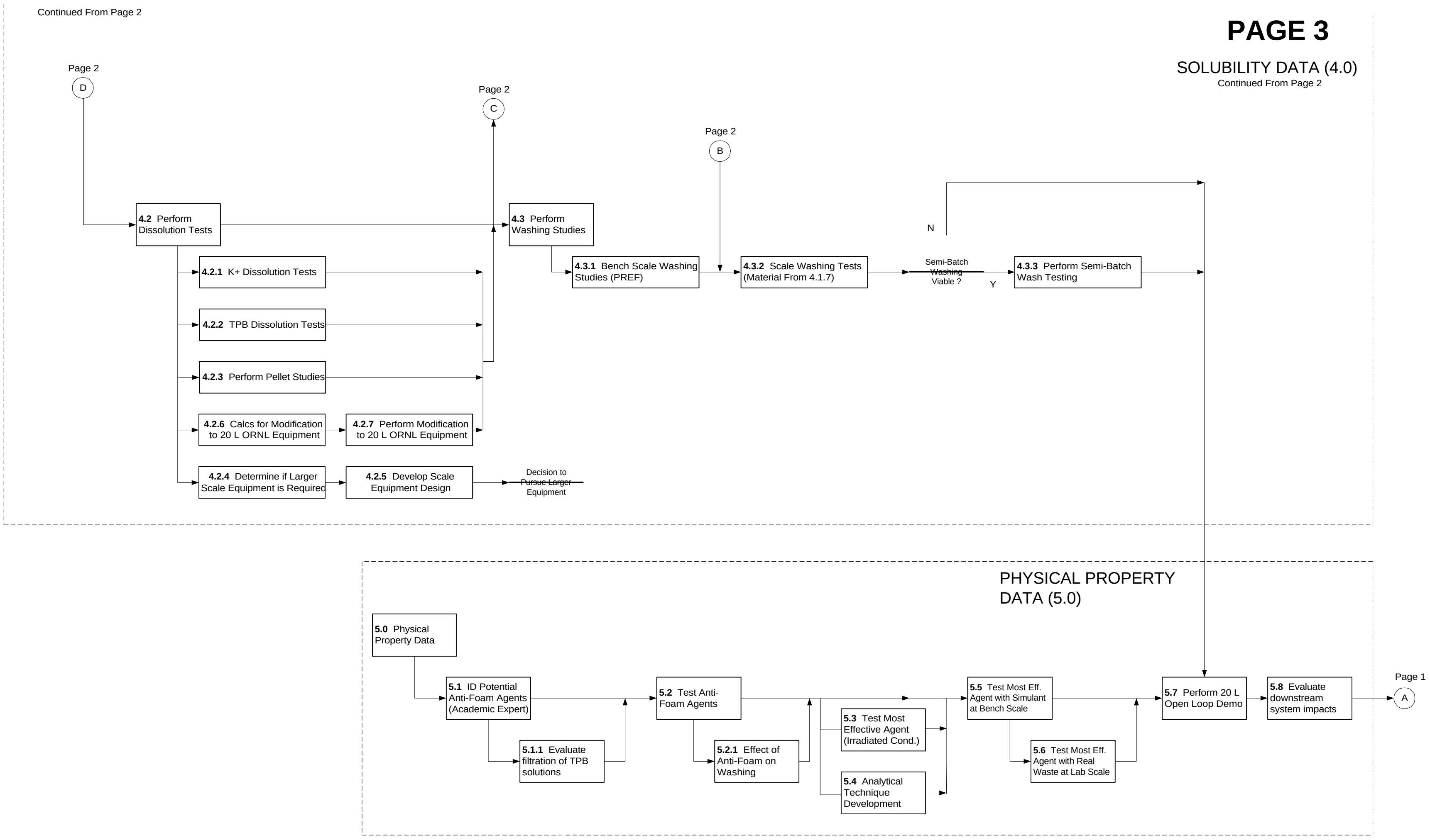
ATTACHMENT 3 – Small Tank TPB Precipitation S&T Logic Diagrams (1 of 4)



ATTACHMENT 3 – Small Tank TPB Precipitation S&T Logic Diagrams (2 of 4)

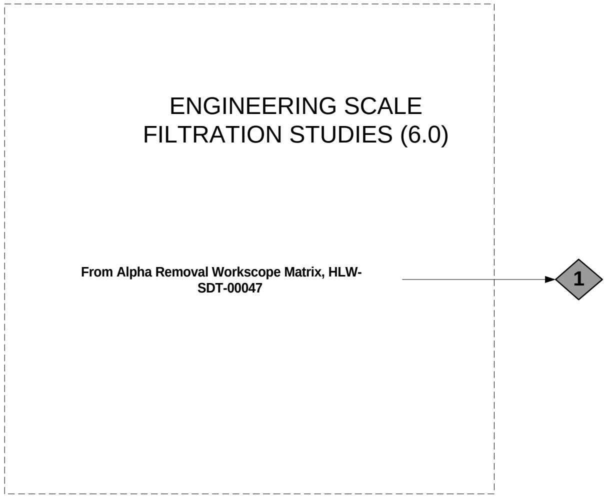


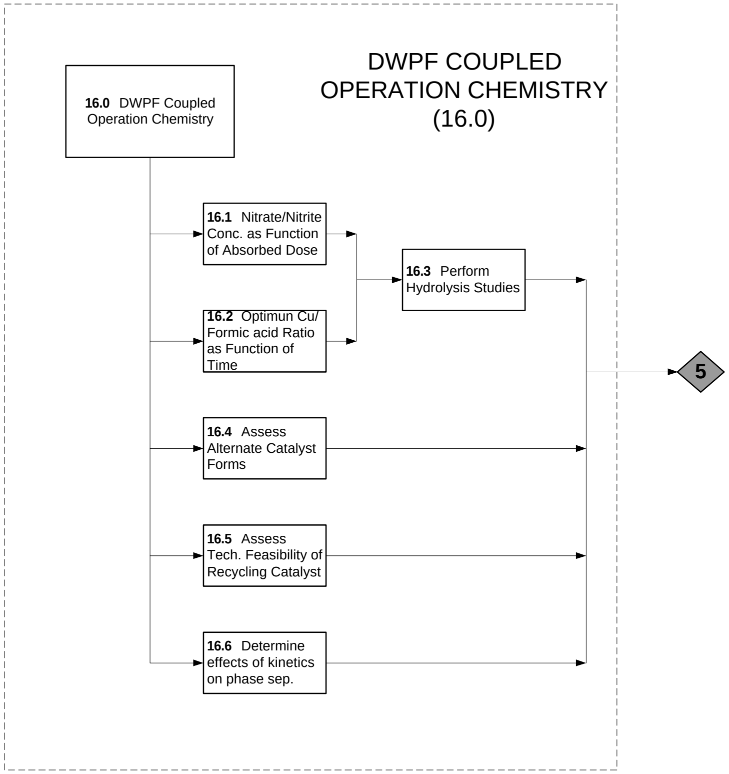
ATTACHMENT 3 – Small Tank TPB Precipitation S&T Logic Diagrams (3 of 4)



ATTACHMENT 3 – Small Tank TPB Precipitation S&T Logic Diagrams (4 of 4)

PAGE 4





Appendix B

Technology Development Needs

Appendix B

Technology Development Needs

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

Alpha and Strontium Removal

Actinide and Strontium Removal Performance

- Define measures to improve actinide decontamination with monosodium titanate (MST) - including slow kinetics for plutonium bonding - to reduce equipment size
- Demonstrate that the designed amounts of MST will provide sufficient decontamination of transuranic elements
- Define the reactions that may be caused by temperature or chemistry changes resulting from the MST strike; define impacts to the process. (Data suggest heating and cooling of the slurry prior to filtration may improve the processing rate.)
- Develop alternative sorbents for alpha and strontium removal
- Define the effect of neptunium content spikes in some tanks to the Performance Assessment and Waste Acceptance Criteria. Define necessary mitigating measures.
- Define the effect that the MST strike has on americium disposition
- Identify and confirm the feasibility of required feed blend
- Develop new analytical techniques to reduce the delay (1 week) in measuring the decontamination factor for strontium in the MST process
- Define the mechanisms for hydrogen generation in the MST strike process; identify, design and develop methods for hydrogen control
- Define the effect of neptunium content spikes in some tanks

Solid-Liquid Separation Performance

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

Crystalline Silicotitanate (CST) Non-Elutable Ion Exchange

Resin Stability

- Define potential for MST and/or sludge solids to breakthrough and transfer to columns.
- Define how the proprietary constituents that have been demonstrated to precipitate and leach from resin will impact the integrated flow sheet
- Define the potential for aluminum precipitation in various operating modes. Develop and demonstrate mitigation measures as needed
- Define the fate of resin and cesium on a loaded column under accident scenario
- Perform a pilot-scale treatment study to demonstrate that the CST process can meet performance requirements

Resin Handling and Sampling

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

Gas Generation

- Define measures to mitigate deflagration of resin column due to radiolysis of water (H_2 generation)
- Develop and demonstrate a method to degas the resin to prevent resin blinding with H_2, and O_2
- Develop methods to mitigate potential for deflagrations/detonations due to hydrogen accumulation in the vapor spaces
- Define a strategy for managing hydrogen in the spent resin vessel
- Document and validate research and development results that indicate steam pressurization of a resin column results in less H_2 generation than current Authorization Basis (AB) assumptions

High-Level Waste System Interface Issues

- Determine if the CST process can produce glass that meets compositional Environmental Assessment standards and processing limit
- Determine if the waste stream can be maintained homogeneous enough (slurry, particle size and sampling) to define specifications for modifying the Defense Waste Processing Facility (DWPF) Hydragard® Sampler and assure that it will perform reliably
- Determine if adequate testing can be done to demonstrate the glass composition standards within the limited physical access available to DWPF
- Determine limiting process support requirements, such as tank blending strategies for cesium, which may preclude use of the technology.
- Determine if MST/CST will have a deleterious effect on glass form due to increased concentration of TiO_2 in glass
- Perform testing to requalify glass form to allow use of CST process
- Develop and demonstrate a method to analyze the composition of CST in conjunction with other DWPF feed components
- Develop/demonstrate means to analyze CST in DWPF
- Complete and validate research results that catalytic H_2 production rate from formic acid is less than the authorization basis for DWPF feed pretreatment processes

General Issues

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

Caustic Side Solvent Extraction (CSSX)

Sovlent System Proof-Of-Concept

- Demonstrate ability to recover and reuse solvent while maintaining the required DF and CF
- Provide a sound technical basis for contactor efficiency to separate the organic stream from the aqueous stream (current basis assumes 95%)
- Determine if increasing temperature or adding nitrate improves the DF
- Determine if cold cesium will be used in the stripping stage of the process, and if so, will it occupy active sites
- Define optimal solvent formulation and temperature dependency
- Develop a method to determine the composition of the 4-compound solvent system
- Prevent/minimize CRUD formation at the organic to aqueous interface, thereby increasing stage efficiency and minimizing/reducing number of stages or flow sheet changes
- Define the disposal routes for spent solvent and the feasibility of implementing the preferred alternative
- Define the CSSX operating window with respect to solvent components and impurities

- Develop understanding to determine if addition of organic removal for raffinate must be added to the process

Radiolytic Stability

- Perform testing process that accurately simulates radiolysis of solvent by Cs-137
- Determine the potential for radiolysis to nitrate the solvent
- Define appropriate solvent cleanup method to remove deleterious degradation products (all 4 solvent components)

Chemical Stability

- Evaluate the potential for nitration of organics in the strip stream; as required, identify and design mitigation measures
- Develop measures to mitigate flammability of organic solvent (process and sumps)
- Identify and mitigate potential for fire in the extraction process
- Mitigate the corrosive effects of fluoride from degradation of aromatic modifier

Real Waste Performance

- Confirm solvent performance on real waste (achieve DF of 40,000 at CF of 12)
- Demonstrate the hydraulic performance of CSSX using a real waste mixture
- Determine by analysis of recycled solvent if degradation or polymer products are forming; if so, assess impact
- Determine if trace components are concentrating in recycled solvent; if so, assess impact

High-level Waste System Interface Issues

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

Small Tank Tetraphenylborate Precipitation (STTP)

Catalytic Product Decomposition

- Develop and document an understanding of the process chemistry and meet requirements of DFNSB Recommendation 96-1
- Determine if additional (currently unknown) catalytic effects of catalyst buildup through plate-out will increase benzene levels and exceed permit levels and or cause activation greater than the bounding levels (DF decrease)

- Define the procedure for recovering from a batch that decomposes (catalyst activation greater than bounding case resulting in loss of DF)
- Perform radioactive waste tests to provide essential data for equipment design and confirm analytical results from cold tests
- Determine the effects of materials of construction on catalytic effect
- Determine if the slow kinetics of MST and TPB will preclude reaching the required DF; if so, identify mitigation measures

Foaming

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

High-level Waste System Interface Issues

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

General Issues

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

Appendix C

Research and Development Program Schedule

Appendix C

Research and Development Program Schedule

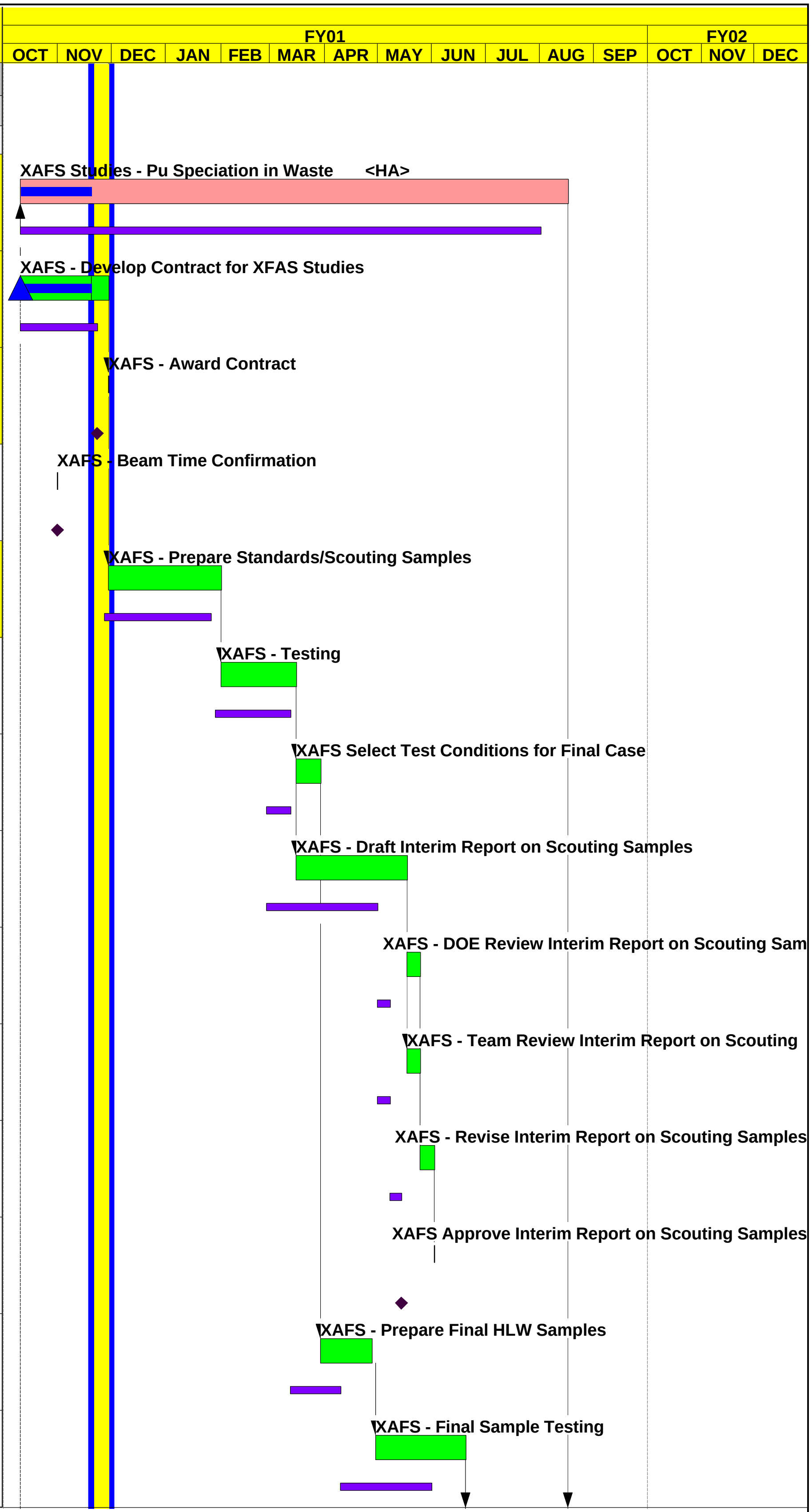
The following pages are the updated (as of November 2000) Salt Processing Program Research and Development schedule on the planned work for each alternative (Alpha and Strontium Removal, Crystalline Silicotitanate Non-Elutable Ion Exchange, Caustic Side Solvent Extraction, and Small Tank Tetraphenylborate Precipitation).

Alpha & Strontium Removal

Monosodium Titanate (MST) Kinetics & Equilibrium

Pu Speciation in Waste - XAFS Study

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST12100	185*	**590**	11OCT00A	16AUG01	LNO
WAMST12102	6	**590**	11OCT00A	29NOV00	LNO
WAMST12104	0	**590**		29NOV00	LNO
WAMST12106	0			31OCT00A	LNO
WAMST12112	42	**590**	30NOV00	31JAN01	LNO
WAMST12114	30	**590**	01FEB01	15MAR01	LNO
WAMST12116	10	**590**	16MAR01	29MAR01	LNO
WAMST12122	44	**643**	16MAR01	17MAY01	LNO
WAMST12124	5	**643**	18MAY01	24MAY01	JWM
WAMST12126	5	**643**	18MAY01	24MAY01	KJR
WAMST12128	5	**643**	25MAY01	01JUN01	LNO
WAMST12130	0	**643**		01JUN01	KJR
WAMST12142	20	**590**	30MAR01	27APR01	LNO
WAMST12144	36	**590**	30APR01	19JUN01	LNO

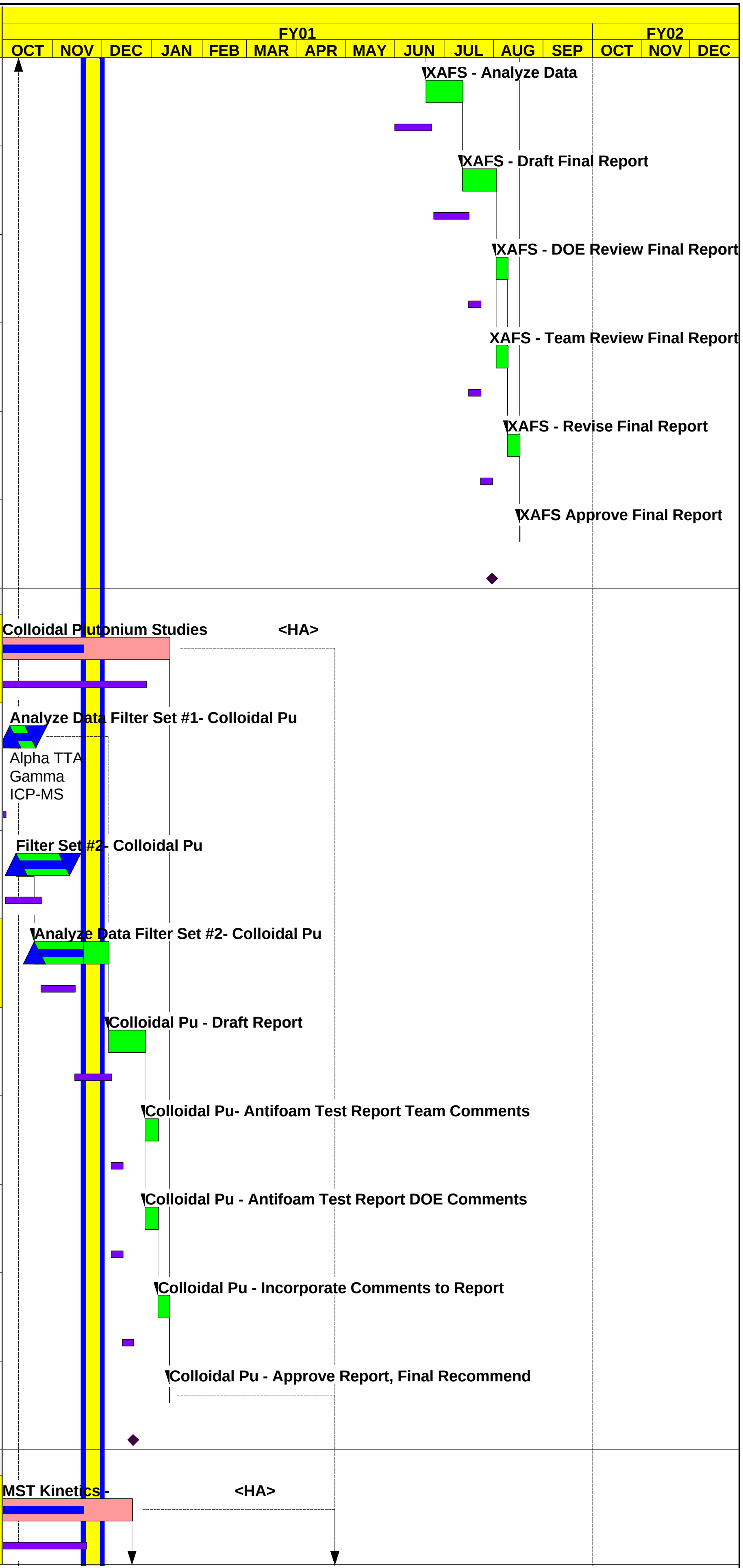


Start Date	01OCT98
Finish Date	26SEP02
Data Date	20NOV00
Run Date	21NOV00 12:34

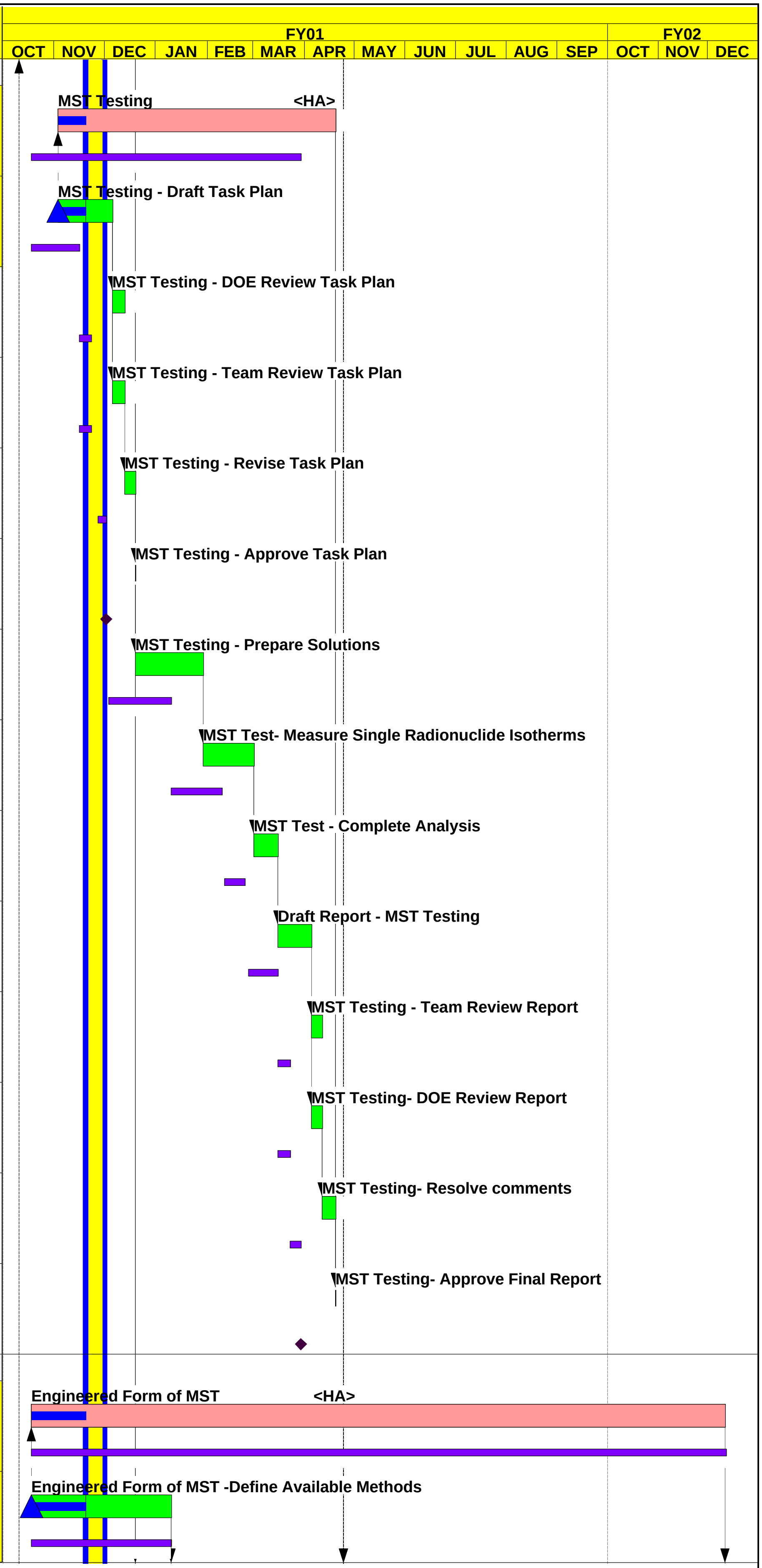
Westinghouse Savannah River Co
Salt Processing Program
Plan of the Month
(All to go & in progress activities)

🟩 Early Bar
🟪 Target (Early Start)
🟦 Progress Bar
🟥 Critical Activity

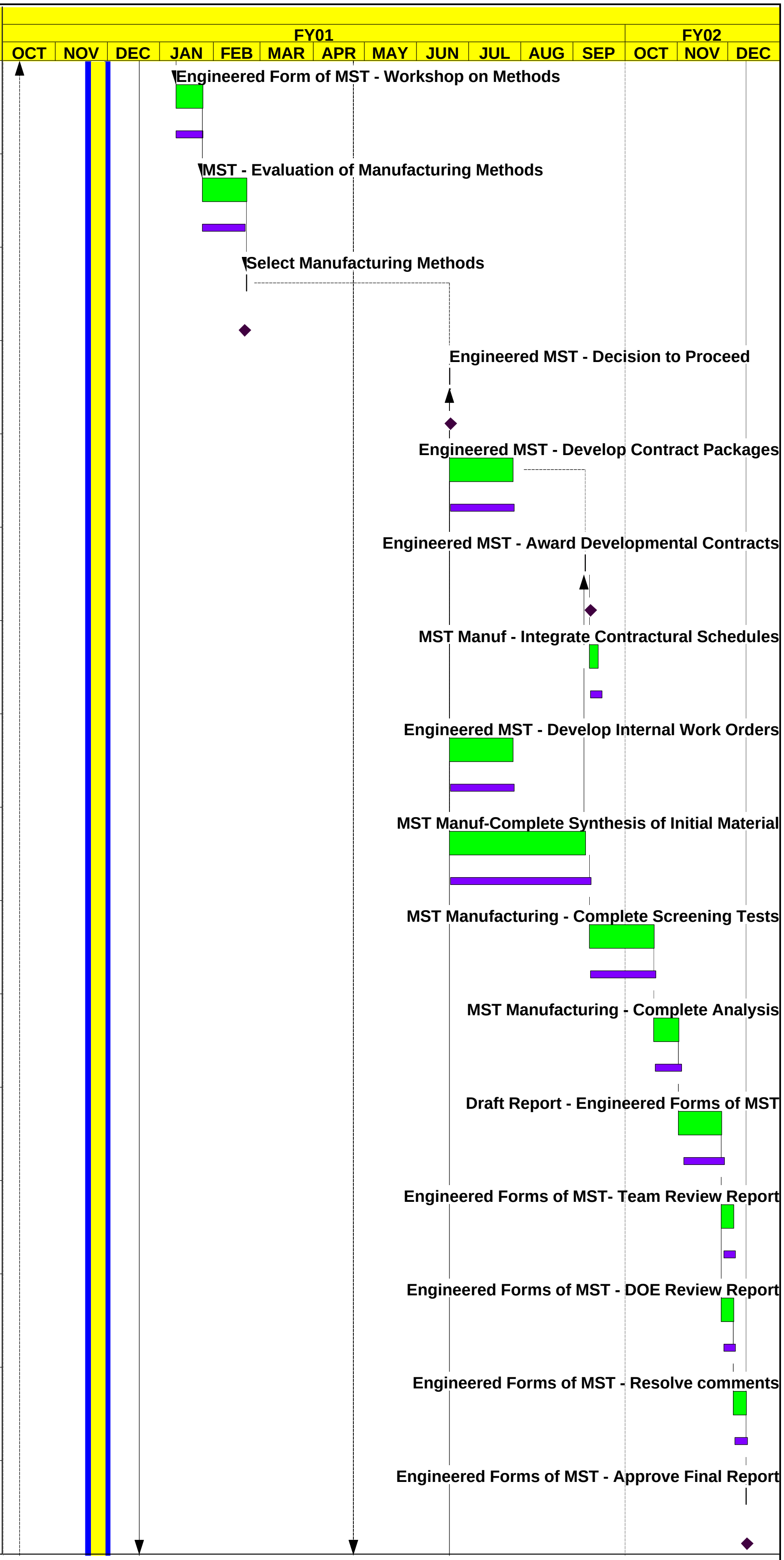
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST12146	16	**590**	20JUN01	12JUL01	LNO
WAMST12152	15	**590**	13JUL01	02AUG01	LNO
WAMST12154	5	**590**	03AUG01	09AUG01	JWM
WAMST12156	5	**590**	03AUG01	09AUG01	KJR
WAMST12158	5	**590**	10AUG01	16AUG01	LNO
WAMST12160	0	**590**		16AUG01	KJR
Collodial Pu					
WAMST1200	34*	**59**	14AUG00A	11JAN01	TBP
WAMST1215	0*		05OCT00A	20OCT00A	TBP
WAMST1225	0		09OCT00A	10NOV00A	TBP
WAMST1230	9*	**59**	20OCT00A	04DEC00	TBP
WAMST1235	15	**59**	05DEC00	27DEC00	TBP
WAMST1240	5	**59**	28DEC00	04JAN01	TBP
WAMST1245	5	**59**	28DEC00	04JAN01	TBP
WAMST1250	5	**59**	05JAN01	11JAN01	TBP
WAMST1255	0	**59**		11JAN01	KJR
Honeywell Sodium Titanate					
WAMST13	20*	**73**	12JAN00A	19DEC00	DTH



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
Monosodium Titanate Testing					
WAMST15000	102*	**673**	03NOV00A	19APR01	DTH
WAMST15010	10*	**673**	03NOV00A	05DEC00	DTH
WAMST15020	5	**760**	06DEC00	12DEC00	DTH
WAMST15030	5	**673**	06DEC00	12DEC00	DTH
WAMST15032	5	**673**	13DEC00	19DEC00	DTH
WAMST15040	0	**673**		19DEC00	DTH
WAMST15050	26	**673**	20DEC00	29JAN01	DTH
WAMST15060	22	**673**	30JAN01*	01MAR01	DTH
WAMST15070	10	**673**	02MAR01	15MAR01	DTH
WAMST15110	14	**673**	16MAR01	04APR01	DTH
WAMST15120	5	**673**	05APR01	11APR01	DTH
WAMST15130	5	**673**	05APR01	11APR01	DTH
WAMST15140	5	**673**	12APR01	19APR01	DTH
WAMST15160	0	**673**		19APR01	DTH
Engineered Form of MST					
WAMST18000	264*	**511**	18OCT00A	10DEC01	DTH
WAMST18010	33*	**594**	18OCT00A	10JAN01	DTH



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST18020	11	**594**	11JAN01	25JAN01	DTH
WAMST18030	17	**594**	26JAN01	20FEB01	DTH
WAMST18040	0	**594**		20FEB01	DTH
WAMST18050	0	**511**	20JUN01		DTH
WAMST18060	26	**511**	20JUN01	26JUL01	DTH
WAMST18070	0	**570**		07SEP01	DTH
WAMST18080	5	**570**	10SEP01	14SEP01	DTH
WAMST18090	26	**605**	20JUN01	26JUL01	DTH
WAMST18210	56	**511**	20JUN01	07SEP01	DTH
WAMST18220	28	**511**	10SEP01*	17OCT01	DTH
WAMST18230	11	**511**	18OCT01	01NOV01	DTH
WAMST18540	15	**511**	02NOV01	26NOV01	DTH
WAMST18560	5	**511**	27NOV01	03DEC01	DTH
WAMST18570	5	**511**	27NOV01	03DEC01	DTH
WAMST18580	5	**511**	04DEC01	10DEC01	DTH
WAMST18590	0	**511**		10DEC01	DTH



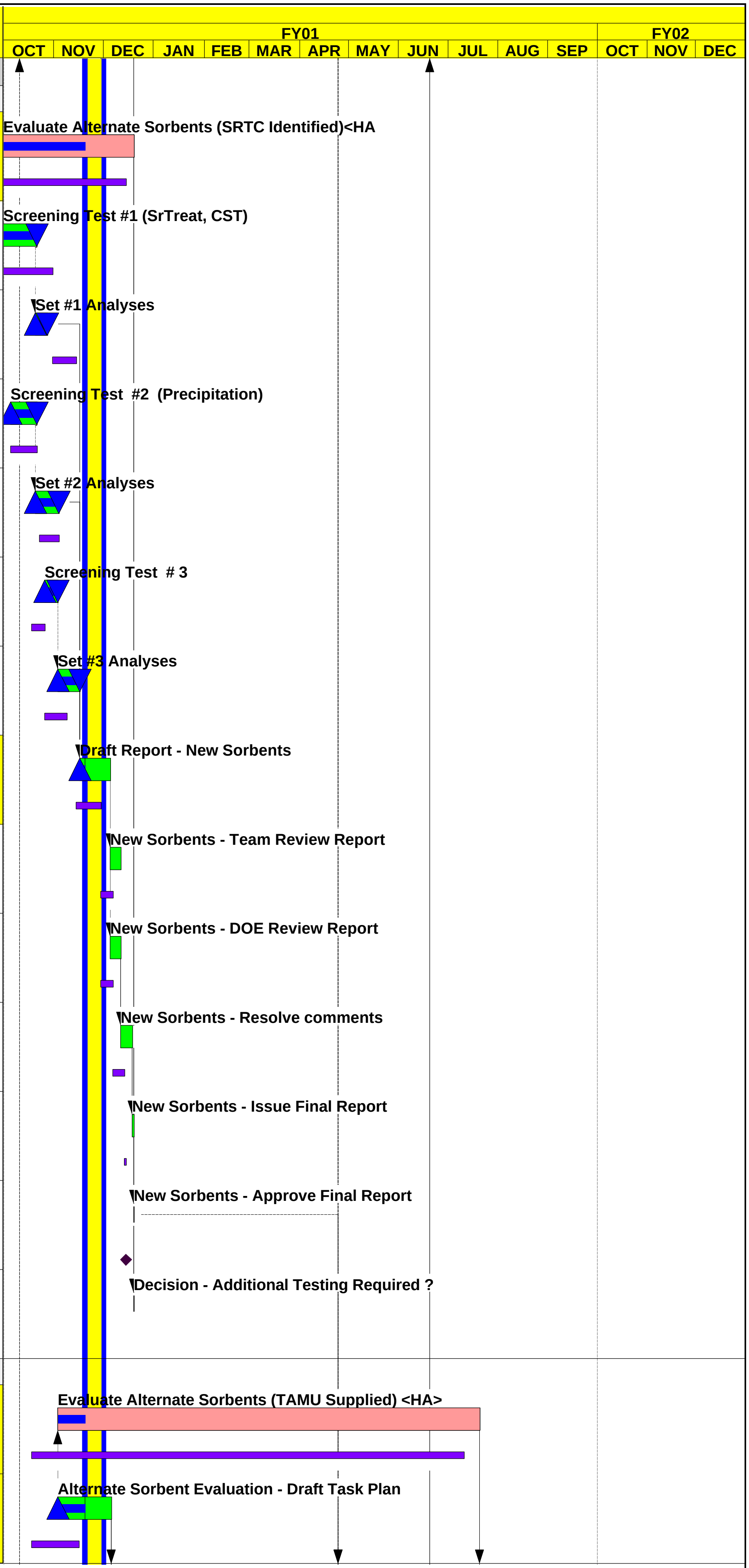
Alternative Alpha And Strontium Removal

Evaluate Alternate Sorbents (SRTC Identified)

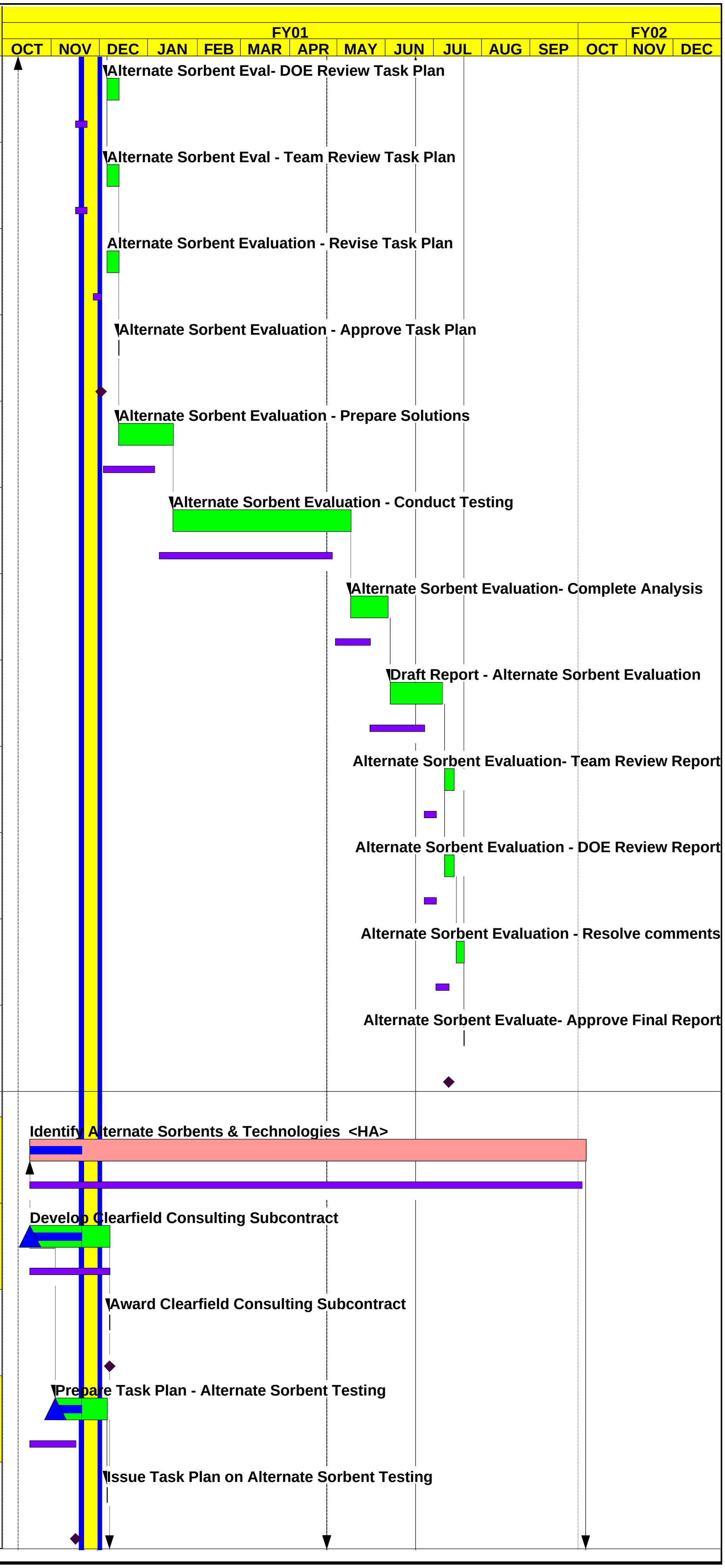
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST13E	20*	**755**	13SEP00A	19DEC00	DTH
WAMST13F	0		13SEP00A	20OCT00A	DTH
WAMST13F1	0		20OCT00A	27OCT00A	DTH
WAMST13F3	0		05OCT00A	20OCT00A	DTH
WAMST13F4	0*		20OCT00A	03NOV00A	DTH
WAMST13F5	0*		26OCT00A	02NOV00A	DTH
WAMST13F6	0		03NOV00A	16NOV00A	DTH
WAMST13H	9*	**73**	17NOV00A	04DEC00	DTH
WAMST13K	5	**73**	05DEC00	11DEC00	DTH
WAMST13M	5	**73**	05DEC00	11DEC00	DTH
WAMST13O	5	**73**	12DEC00	18DEC00	DTH
WAMST13P	1	**73**	19DEC00	19DEC00	DTH
WAMST13Q	0	**73**		19DEC00	DTH
WAMST13Q1	0	**755**		19DEC00	DTH

Evaluation of Alternate Sorbents (TAMU Supplied)

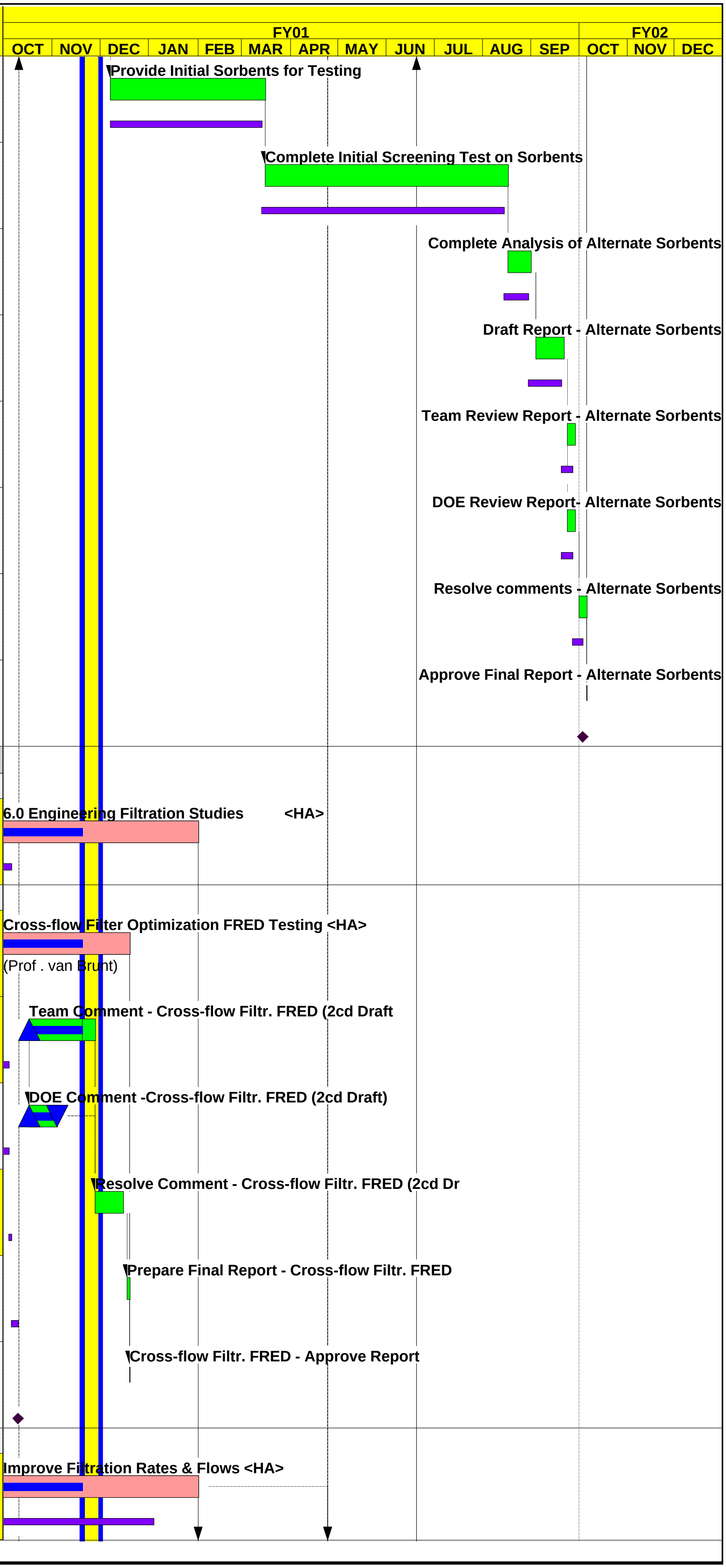
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST17000	166*	**609**	03NOV00A	20JUL01	DTH
WAMST17010	10*	**609**	03NOV00A	05DEC00	DTH



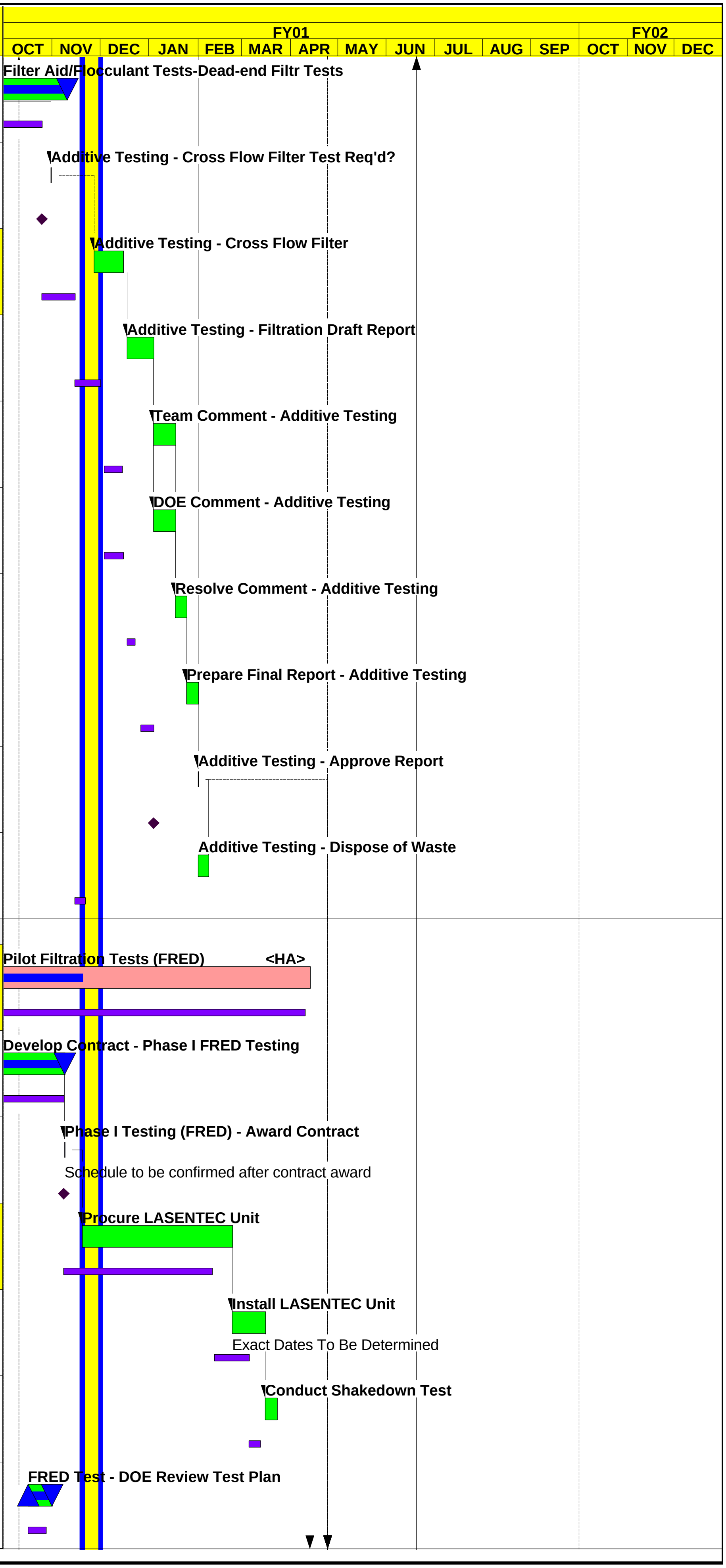
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST17020	5	**760**	06DEC00	12DEC00	DTH
WAMST17030	5	**609**	06DEC00	12DEC00	DTH
WAMST17040	5	**609**	06DEC00	12DEC00	DTH
WAMST17050	0	**609**		12DEC00	DTH
WAMST17060	22	**609**	13DEC00	16JAN01	DTH
WAMST17070	79	**609**	17JAN01*	09MAY01	DTH
WAMST17080	16	**609**	10MAY01	01JUN01	DTH
WAMST17090	24	**609**	04JUN01	06JUL01	DTH
WAMST17100	5	**609**	09JUL01	13JUL01	DTH
WAMST17110	5	**609**	09JUL01	13JUL01	DTH
WAMST17120	5	**609**	16JUL01	20JUL01	DTH
WAMST17130	0	**609**		20JUL01	DTH
Evaluate Alternate Sorbents & Technologies					
WAMST16000	220*	**555**	18OCT00A	05OCT01	DTH
WAMST16010	12*	**555**	18OCT00A	07DEC00	DTH
WAMST16050	0	**555**		07DEC00	DTH
WAMST16052	10*	**765**	03NOV00A	05DEC00	DTH
WAMST16054	0	**765**		05DEC00	DTH



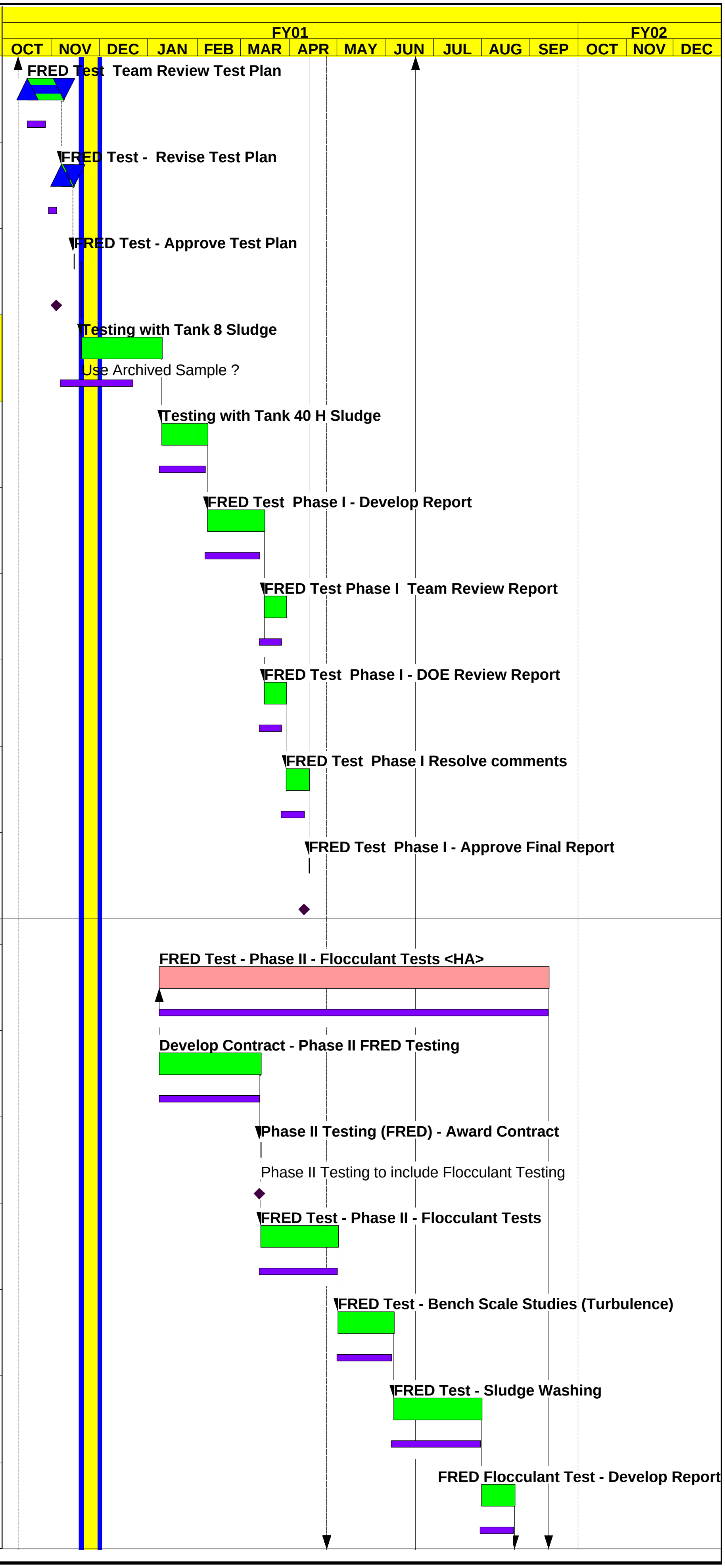
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST16060	66	**555**	08DEC00	15MAR01	DTH
WAMST16070	107	**555**	16MAR01	16AUG01	DTH
WAMST16080	11	**555**	17AUG01	31AUG01	DTH
WAMST16090	14	**555**	04SEP01	21SEP01	DTH
WAMST16110	5	**555**	24SEP01	28SEP01	DTH
WAMST16120	5	**555**	24SEP01	28SEP01	DTH
WAMST16130	5	**555**	01OCT01	05OCT01	DTH
WAMST16140	0	**555**		05OCT01	DTH
MST Filtration and Settling					
Filteration Studies - General Planning					
WACST600	48*	**45**	19NOV99A	31JAN01	MRP
FRED Testing (FY 2000)					
WAMST623	20*	**755**	24JAN00A	19DEC00	MRP
WAMST623G5	4	**755**	17OCT00A	27NOV00	MRP
WAMST623G6	0*		17OCT00A	03NOV00A	JWM
WAMST623G7	14	**755**	28NOV00	15DEC00	MRP
WAMST623G8	2	**755**	18DEC00	19DEC00	MRP
WAMST623H	0	**755**		19DEC00	KJR
Means to Improve Filter Flux					
WAMST62	48*	**45**	24JAN00A	31JAN01	MRP



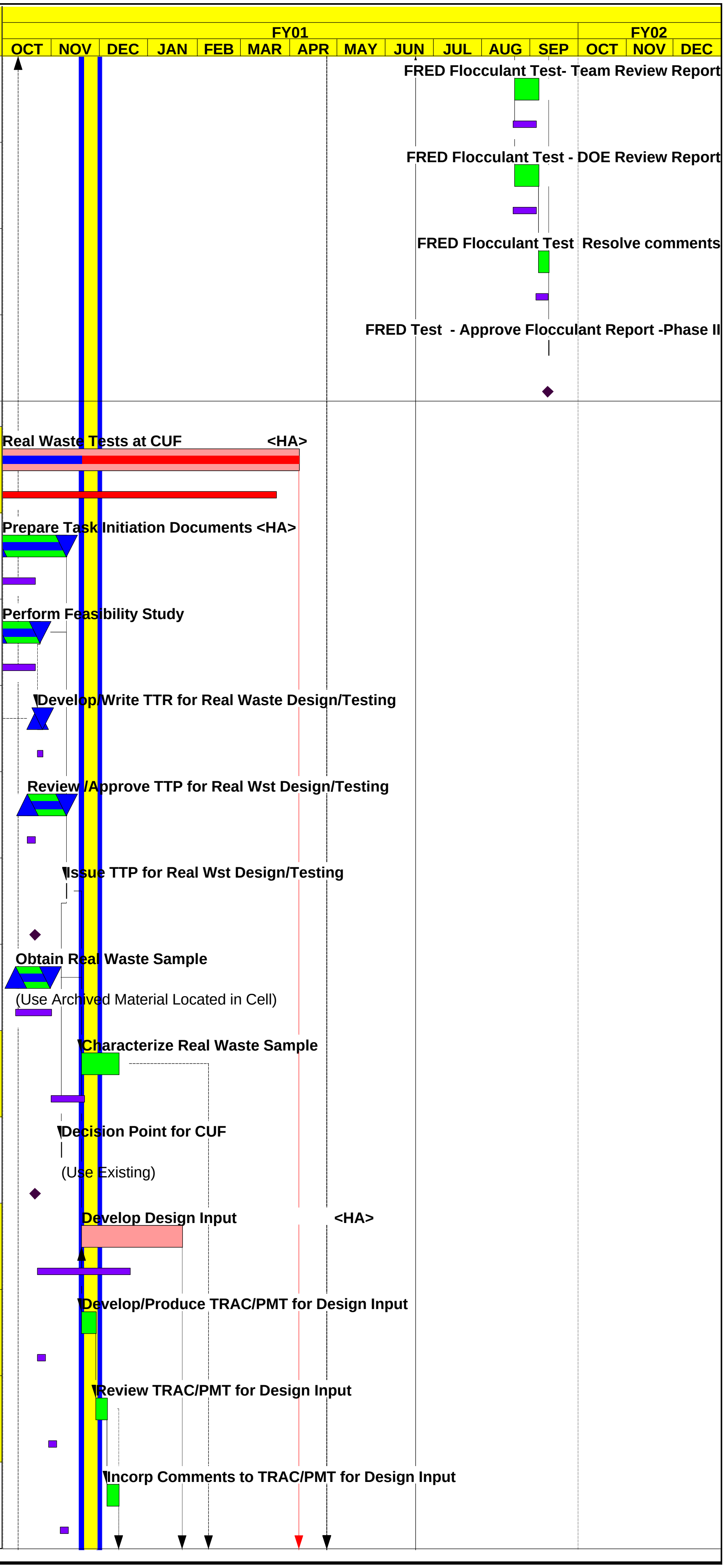
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST621E	0		06SEP00A	09NOV00A	MRP
WAMST621G	0		31OCT00A		MRP
WAMST621J	15	**44**	27NOV00*	15DEC00	MRP
WAMST621L	10	**44**	18DEC00	03JAN01	MRP
WAMST621N2	8	**35**	04JAN01	17JAN01	KJR
WAMST621N3	10	**45**	04JAN01	17JAN01	JWM
WAMST621N4	5	**45**	18JAN01	24JAN01	MJB
WAMST621N5	5	**45**	25JAN01	31JAN01	WRW
WAMST621P	0	**45**		31JAN01	KJR
WAMST621R	5	**722**	01FEB01	07FEB01	MRP
FRED Test Phase I - Pilot Filtration					
WAMST23000	98*	**677**	01AUG00A	12APR01	MRP
WAMST23010	0		01AUG00A	08NOV00A	MRP
WAMST23030	0			08NOV00A	MRP
WAMST23040	63	**692**	20NOV00	22FEB01	MRP
WAMST23042	15	**692**	23FEB01	15MAR01	MRP
WAMST23044	5	**692**	16MAR01	22MAR01	MRP
WAMST23060	0*		16OCT00A	31OCT00A	JWM



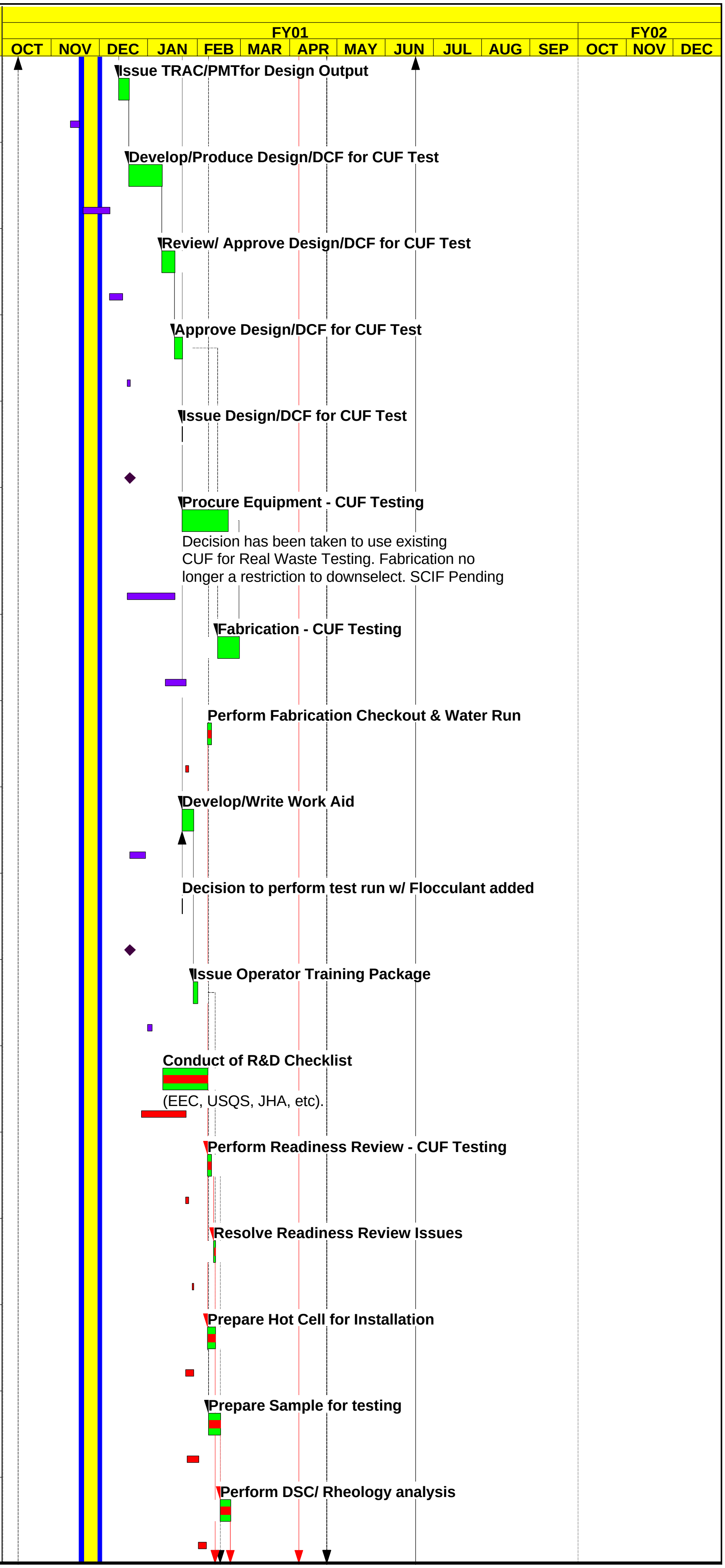
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST23070	0		16OCT00A	08NOV00A	KJR
WAMST23080	0		07NOV00A	14NOV00A	MRP
WAMST23090	0			14NOV00A	KJR
WAMST23100	32	**677**	20NOV00	09JAN01	MRP
WAMST23110	21	**677**	10JAN01*	07FEB01	MRP
WAMST23120	25	**677**	08FEB01	15MAR01	MRP
WAMST23130	10	**677**	16MAR01	29MAR01	KJR
WAMST23140	10	**677**	16MAR01	29MAR01	JWM
WAMST23150	10	**677**	30MAR01	12APR01	MRP
WAMST23160	0	**677**		12APR01	KJR
FRED Test Phase II - Flocculent					
WAMST23500	173*	**572**	08JAN01	12SEP01	MRP
WAMST23510	46	**572**	08JAN01*	13MAR01	MRP
WAMST23520	0	**572**		13MAR01	MRP
WAMST23530	34	**572**	14MAR01	01MAY01	MRP
WAMST23532	24	**572**	02MAY01	05JUN01	MRP
WAMST23534	39	**572**	06JUN01	31JUL01	MRP
WAMST23540	15	**572**	01AUG01	21AUG01	MRP



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST23550	10	**572**	22AUG01	05SEP01	KJR
WAMST23560	10	**572**	22AUG01	05SEP01	JWM
WAMST23570	5	**572**	06SEP01	12SEP01	MRP
WAMST23580	0	**572**		12SEP01	KJR
Real Waste Filter Testing					
WAMST6400	94*	**-1**	25SEP00A	06APR01	MRP
WAMST6401	0*		25SEP00A	09NOV00A	JTC
WAMST6403	0		25SEP00A	23OCT00A	JTC
WAMST6405	0		23OCT00A	25OCT00A	JTC
WAMST6409	0		16OCT00A	09NOV00A	MRP
WAMST6411	0			09NOV00A	MRP
WAMST6415	0*		09OCT00A	30OCT00A	MRP
WAMST6417	15	**38**	20NOV00	12DEC00	MRP
WAMST6419	0			06NOV00A	KJR
WAMST6421	41*	**7**	20NOV00	22JAN01	LC
WAMST6423	5	**8**	20NOV00	28NOV00	JTC
WAMST6425	5	**8**	29NOV00	05DEC00	JTC
WAMST6427	5	**8**	06DEC00	12DEC00	JTC



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST6429	5	**8**	13DEC00	19DEC00	JTC
WAMST6431	9	**6**	20DEC00	09JAN01	LC
WAMST6433	5	**6**	10JAN01	17JAN01	LC
WAMST6435	2	**6**	18JAN01	22JAN01	LC
WAMST6437	0	**6**		22JAN01	LC
WAMST6439	20	**709**	23JAN01	20FEB01	MRP
WAMST6441	9	**709**	14FEB01	27FEB01	MRP
WAMST6443	2	**-1**	08FEB01*	09FEB01	MRP
WAMST6445	5	**7**	23JAN01	29JAN01	MRP
WAMST6446	0	**7**		22JAN01	MRP
WAMST6447	2	**7**	30JAN01	31JAN01	MRP
WAMST6449	20	**-1**	11JAN01	07FEB01	MRP
WAMST6451	2	**-1**	08FEB01	09FEB01	MRP
WAMST6453	1	**-1**	12FEB01	12FEB01	MRP
WAMST6455	3	**-1**	08FEB01	12FEB01	MRP
WAMST6457	5	**-1**	09FEB01	15FEB01	MRP
WAMST6459	3	**-1**	16FEB01	21FEB01	MRP

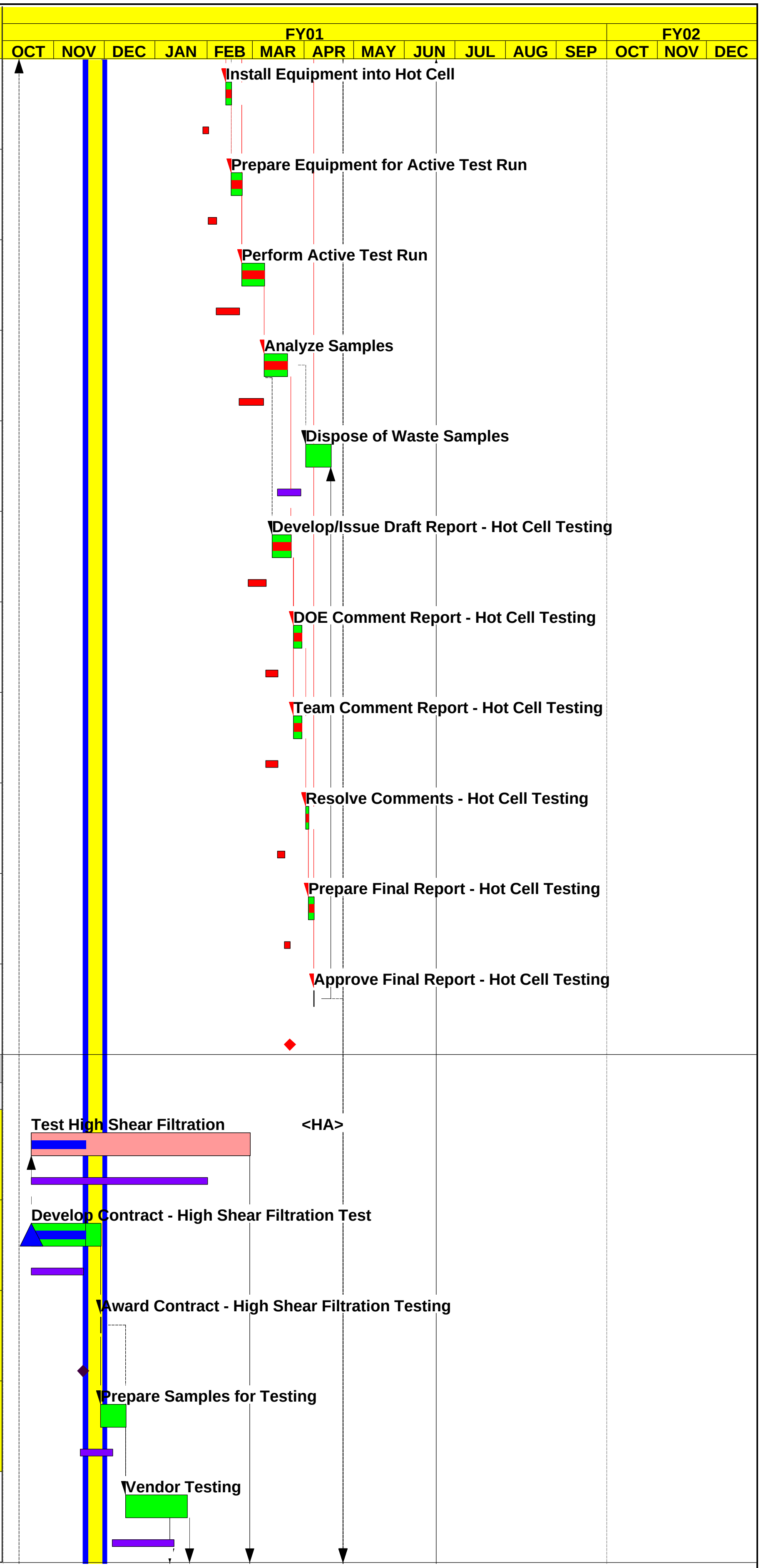


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST6461	3	**-1**	13FEB01	15FEB01	MRP
WAMST6463	3	**-1**	16FEB01	21FEB01	MRP
WAMST6465	14	**-1**	22FEB01	07MAR01	MRP
WAMST6467	10	**-1**	08MAR01	21MAR01	MRP
WAMST6469	10	**676**	02APR01	16APR01	MRP
WAMST6471	9	**-1**	13MAR01	23MAR01	MRP
WAMST6473	5	**-1**	26MAR01	30MAR01	JWM
WAMST6474	5	**-1**	26MAR01	30MAR01	JTC
WAMST6475	2	**-1**	02APR01	03APR01	MRP
WAMST6477	3	**-1**	04APR01	06APR01	MRP
WAMST6479	0	**-1**		06APR01	KJR

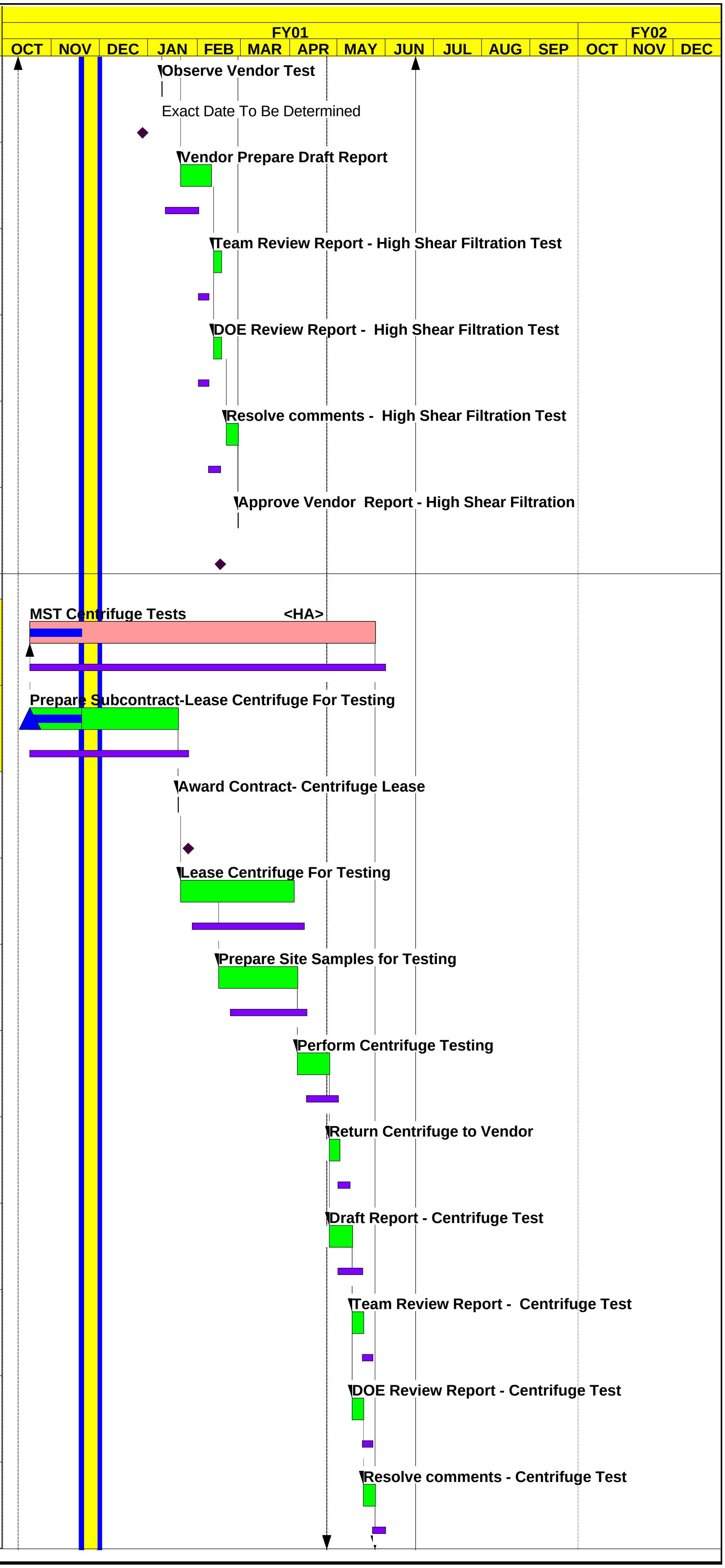
Alternatives to Solid/Liquid Separation Testing

Test High Shear Filtration

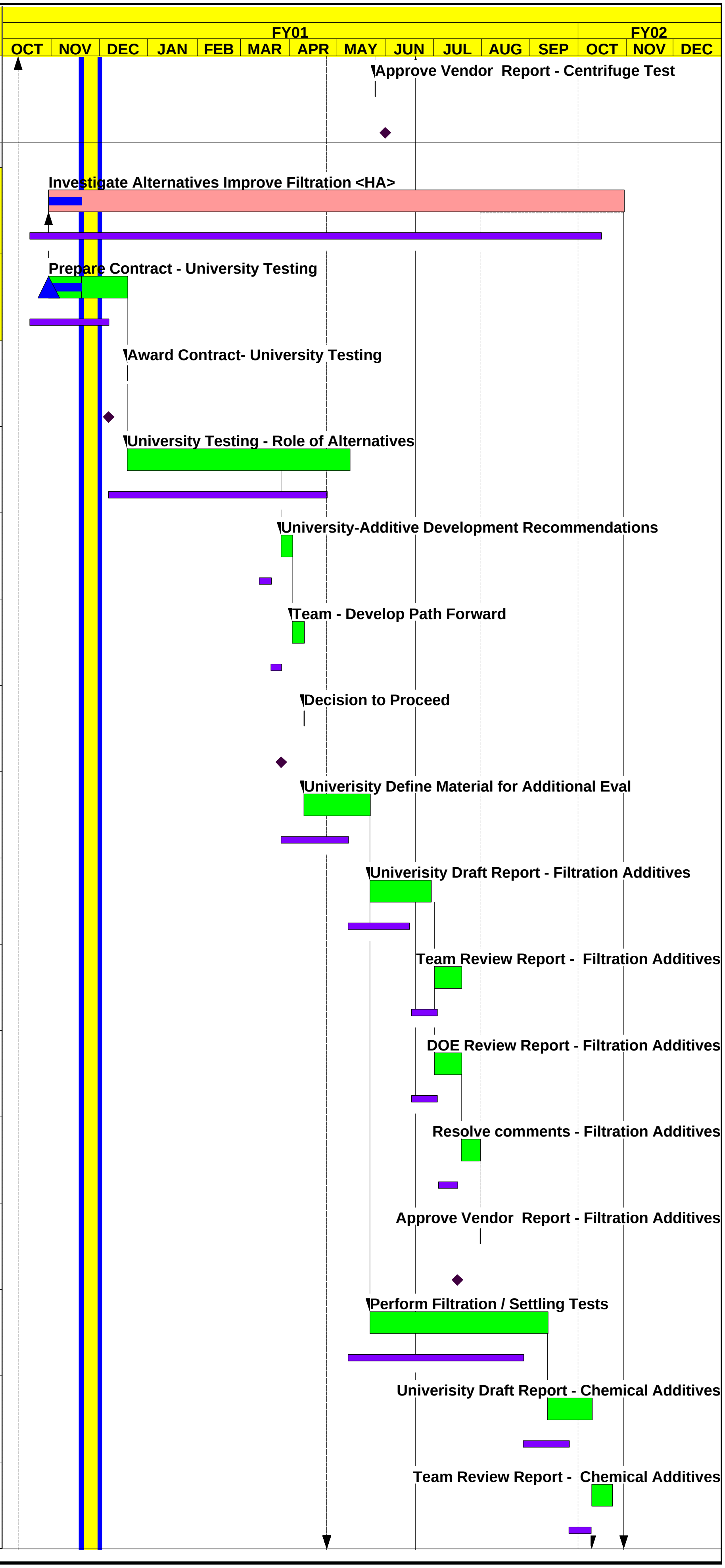
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST19000	65*	**710**	18OCT00A	26FEB01	MRP
WAMST19010	5*	**710**	18OCT00A	28NOV00	MRP
WAMST19020	0	**710**		28NOV00	MRP
WAMST19030	11	**710**	29NOV00	13DEC00	MRP
WAMST19040	24	**710**	14DEC00	19JAN01	MRP



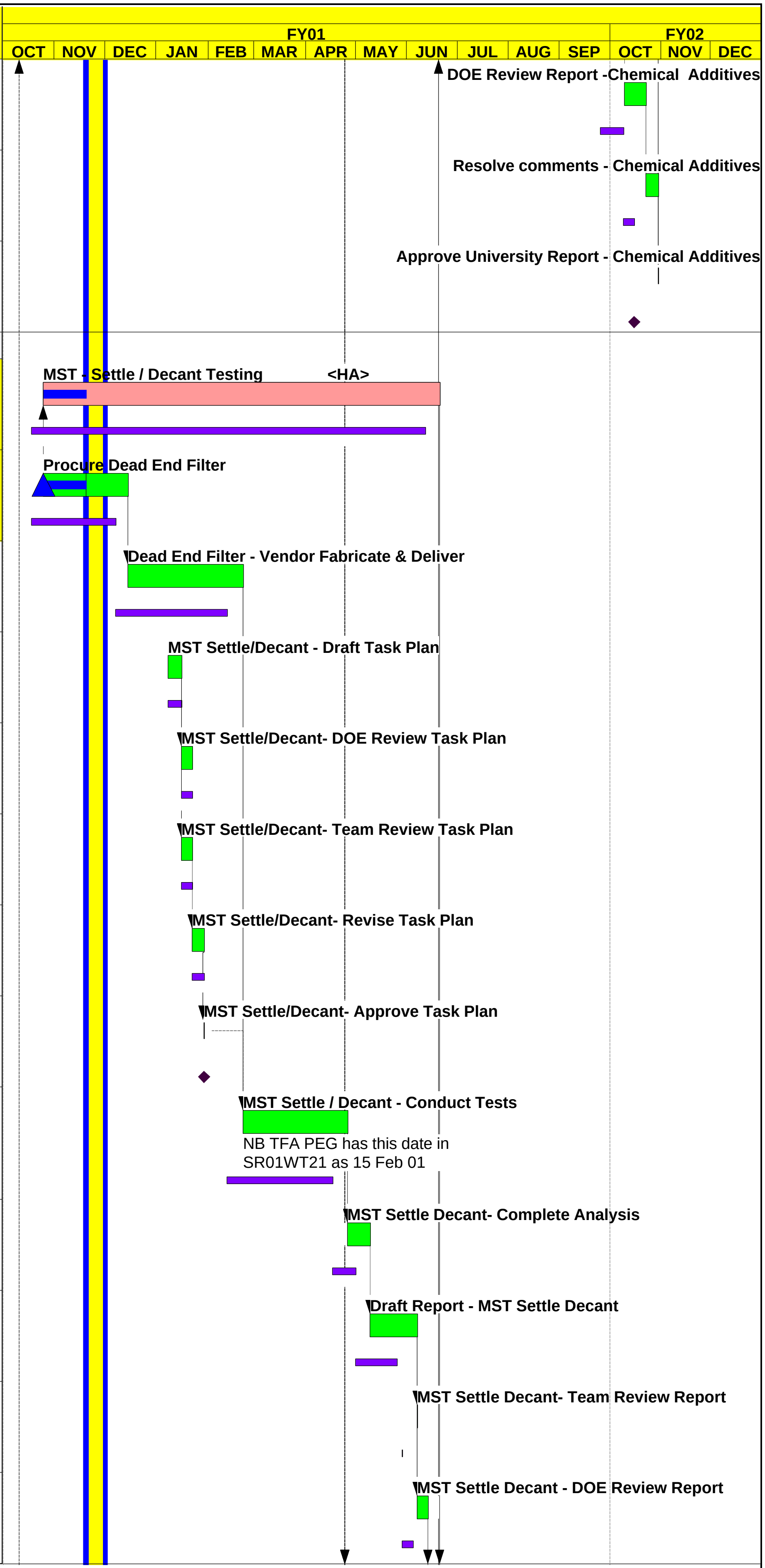
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST19050	0	**743**	10JAN01		MRP
WAMST19090	15	**710**	22JAN01	09FEB01	MRP
WAMST19100	5	**710**	12FEB01	16FEB01	KJR
WAMST19110	5	**710**	12FEB01	16FEB01	JWM
WAMST19120	5	**710**	20FEB01	26FEB01	MRP
WAMST19130	0	**710**		26FEB01	MRP
Test Alternate Separation Tech - Centrifuge					
WAMST20000	127*	**648**	18OCT00A	24MAY01	MRP
WAMST20010	40*	**648**	18OCT00A	19JAN01	MRP
WAMST20020	0	**648**		19JAN01	MRP
WAMST20023	51	**648**	22JAN01	03APR01	MRP
WAMST20030	35	**648**	15FEB01	05APR01	MRP
WAMST20040	13	**648**	06APR01	25APR01	MRP
WAMST20050	5	**664**	26APR01	02MAY01	MRP
WAMST20060	11	**648**	26APR01	10MAY01	MRP
WAMST20070	5	**648**	11MAY01	17MAY01	KJR
WAMST20080	5	**648**	11MAY01	17MAY01	JWM
WAMST20090	5	**648**	18MAY01	24MAY01	MRP



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST20100	0	**648**		24MAY01	MRP
Alternate Separation Tech - Improve Filtration					
WAMST21000	236*	**539**	30OCT00A	29OCT01	MRP
WAMST21010	19*	**539**	30OCT00A	18DEC00	MRP
WAMST21020	0	**539**		18DEC00	MRP
WAMST21030	96	**539**	19DEC00	08MAY01	MRP
WAMST21040	5	**539**	27MAR01	02APR01	MRP
WAMST21050	5	**539**	03APR01	09APR01	MRP
WAMST21060	0	**539**		09APR01	MRP
WAMST21065	29	**539**	10APR01	21MAY01	MRP
WAMST21070	28	**539**	22MAY01	29JUN01	MRP
WAMST21080	12	**603**	02JUL01	18JUL01	KJR
WAMST21090	12	**603**	02JUL01	18JUL01	JWM
WAMST21100	8	**603**	19JUL01	30JUL01	MRP
WAMST21110	0	**603**		30JUL01	MRP
WAMST21210	78	**539**	22MAY01	11SEP01	MRP
WAMST21220	20	**539**	12SEP01	09OCT01	MRP
WAMST21230	9	**539**	10OCT01	22OCT01	MRP



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST21240	9	**539**	10OCT01	22OCT01	MRP
WAMST21250	5	**539**	23OCT01	29OCT01	MRP
WAMST21260	0	**539**		29OCT01	MRP
MST Settle Decant Testing					
WAMST22000	145*	**630**	25OCT00A	20JUN01	MRP
WAMST22010	17*	**630**	25OCT00A	14DEC00	MRP
WAMST22040	45	**630**	15DEC00	21FEB01	MRP
WAMST22110	6	**646**	08JAN01*	15JAN01	MRP
WAMST22120	5	**734**	16JAN01	22JAN01	JWM
WAMST22130	5	**646**	16JAN01	22JAN01	KJR
WAMST22140	5	**646**	23JAN01	29JAN01	MRP
WAMST22150	0	**646**		29JAN01	KJR
WAMST22210	44	**630**	22FEB01	25APR01	MRP
WAMST22220	10	**630**	26APR01	09MAY01	MRP
WAMST22410	19	**630**	10MAY01	06JUN01	MRP
WAMST22420	0	**630**	07JUN01	06JUN01	KJR
WAMST22430	5	**630**	07JUN01	13JUN01	JWM



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAMST22440	5	**630**	14JUN01	20JUN01	MRP
WAMST22490	0	**630**		20JUN01	MRP
On Line Monitor					
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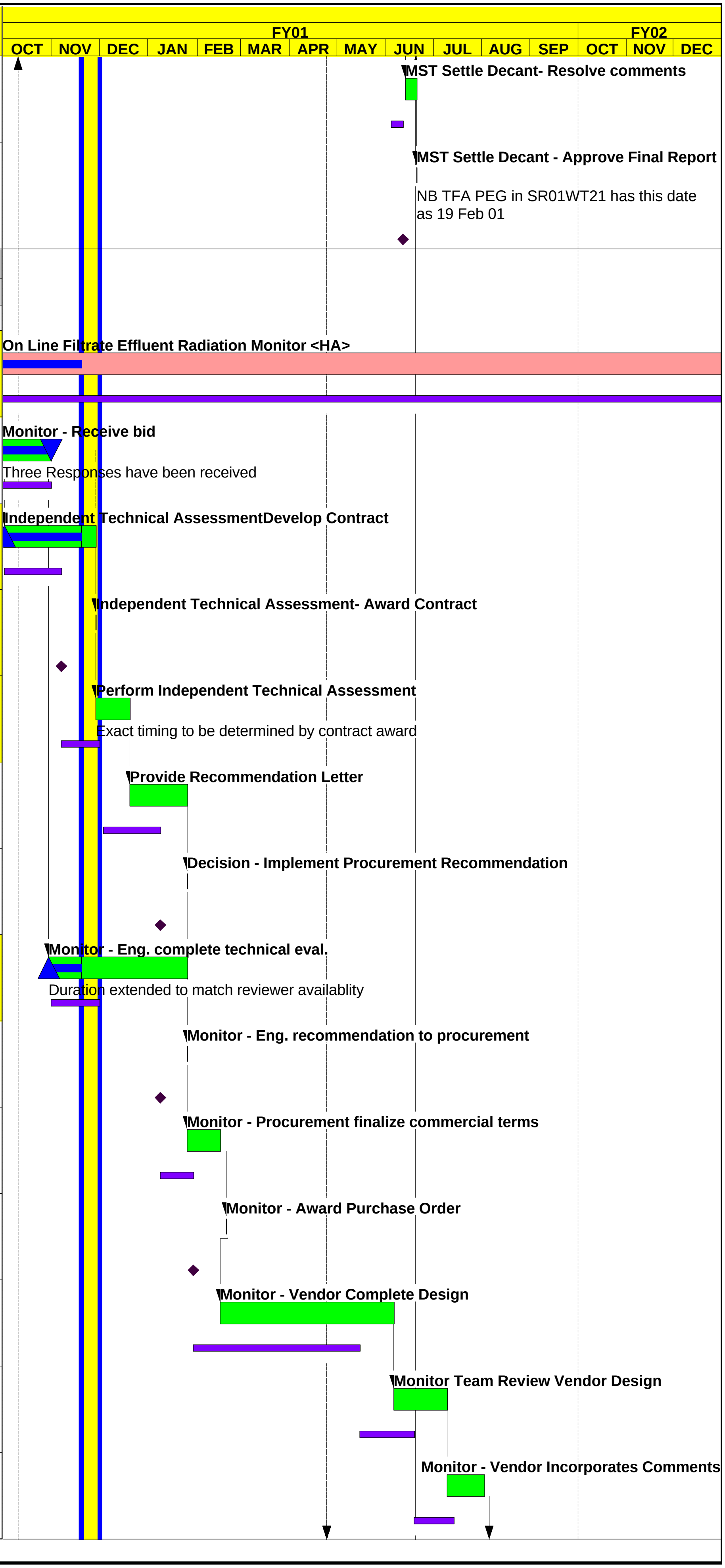
'					
WASDM0000	291*	**326**	04OCT99A	09MAY02	KJR
WASDM00320	0*		18SEP00A	31OCT00A	LC
WASDM00322	4*	**323**	02OCT00A	28NOV00	LC
WASDM00324	0	**323**		28NOV00	LC
WASDM00326	13	**323**	29NOV00	20DEC00	LC
WASDM00327	18	**323**	21DEC00	25JAN01	LC
WASDM00328	0	**323**		25JAN01	LC
WASDM00330	35*	**323**	30OCT00A	25JAN01	LC
WASDM00340	0	**323**		25JAN01	LC
WASDM00350	15	**408**	26JAN01	15FEB01	LC
WASDM00360	0	**323**	20FEB01		LC
WASDM00370	75	**408**	16FEB01	05JUN01	LC
WASDM00380	18	**324**	06JUN01	09JUL01	LC
WASDM00390	18	**408**	10JUL01	02AUG01	LC



NB TFA PEG in SR01WT21 has this date as 19 Feb 01

Three Responses have been received

Exact timing to be determined by contract award

Duration extended to match reviewer availablity

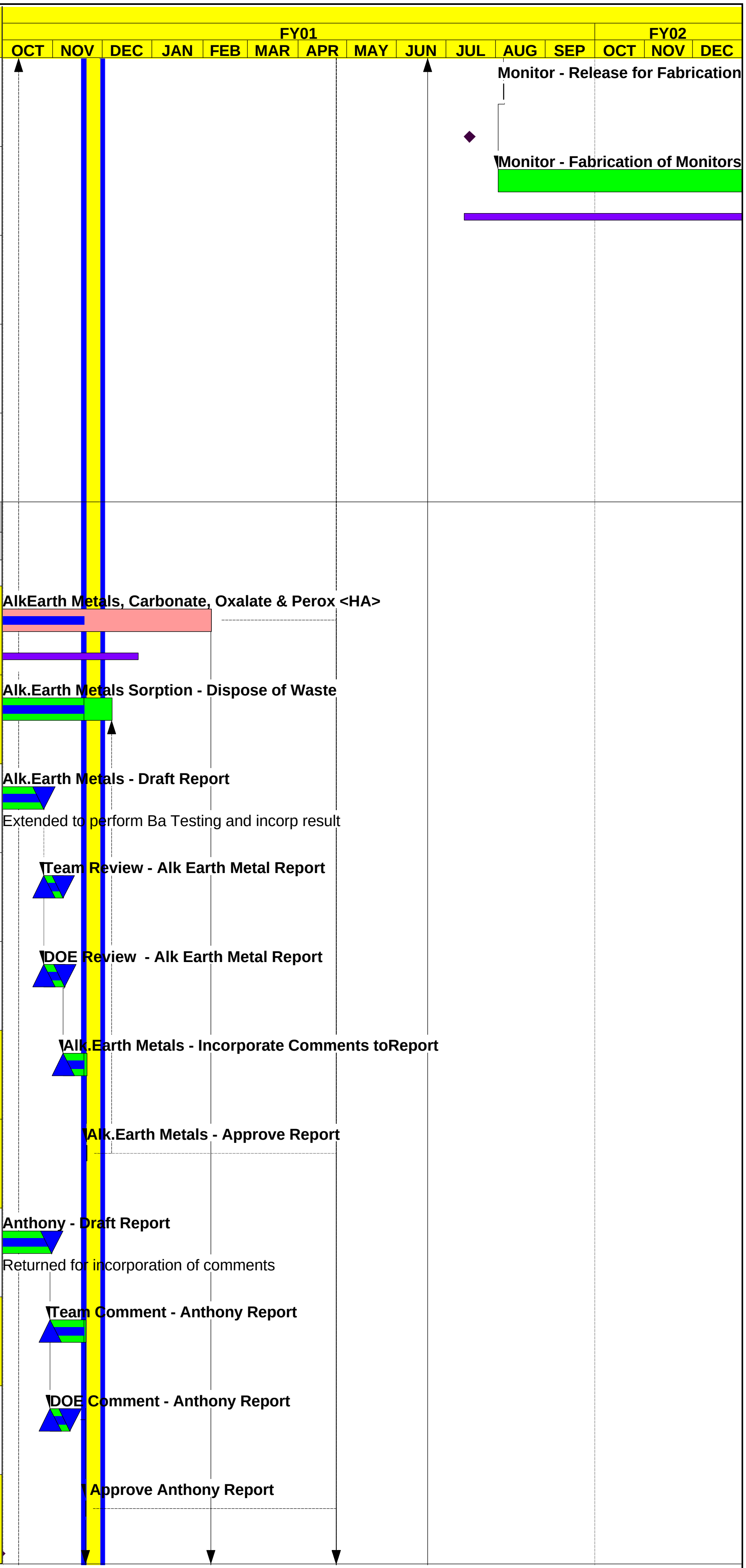
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WASDM00400	0	**323**	06AUG01		LC
WASDM00410	162	**408**	03AUG01	27MAR02	LC
WASDM00420	24	**408**	28MAR02	01MAY02	LC
WASDM00430	0	**408**	02MAY02		LC
WASDM00440	6	**408**	02MAY02	09MAY02	LC

CST Non-Elutable Ion Exchange

CST - Refinement of the Model

CST Influence on Carbonate, Oxalate, & Peroxide

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST52	51*	**42**	03JAN00A	05FEB01	FF
WACST5201P	11	**764**	31JUL00A	06DEC00	FF
WACST5201R	0		11SEP00A	25OCT00A	FF
WACST5201S	0*		26OCT00A	06NOV00A	FF
WACST5201T	0		26OCT00A	07NOV00A	FF
WACST5201U	2	**91**	07NOV00A	21NOV00	FF
WACST5201W	0	**91**		21NOV00	KJR
WACST5202E	0		12SEP00A	30OCT00A	FF
WACST5202F	1*	**33**	30OCT00A	20NOV00	FF
WACST5202G	0		30OCT00A	10NOV00A	FF
WACST5202K	0	**42**		20NOV00	KJR

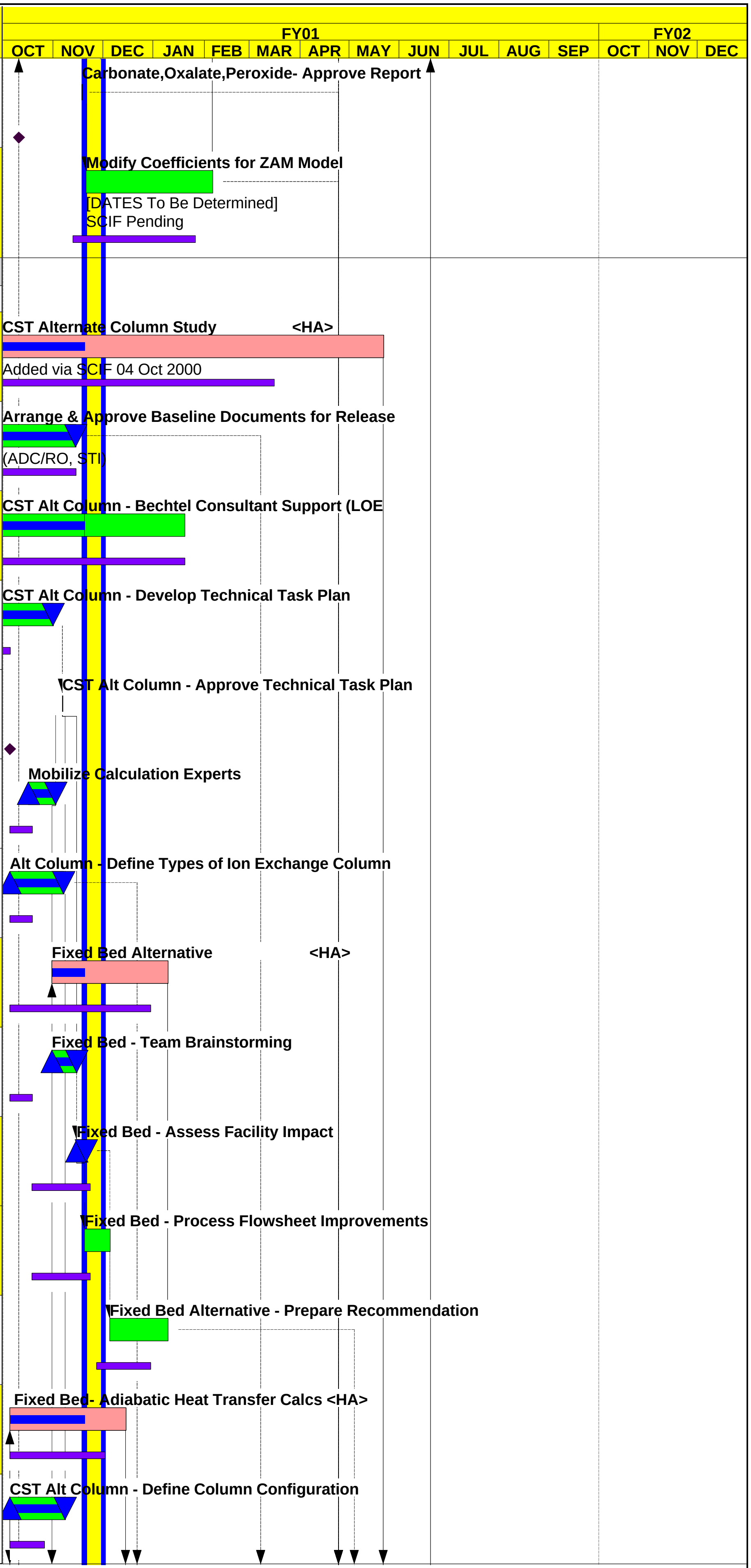


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST5203G	0	**43**		17NOV00	KJR
WACST522	50	**42**	21NOV00	05FEB01	FF

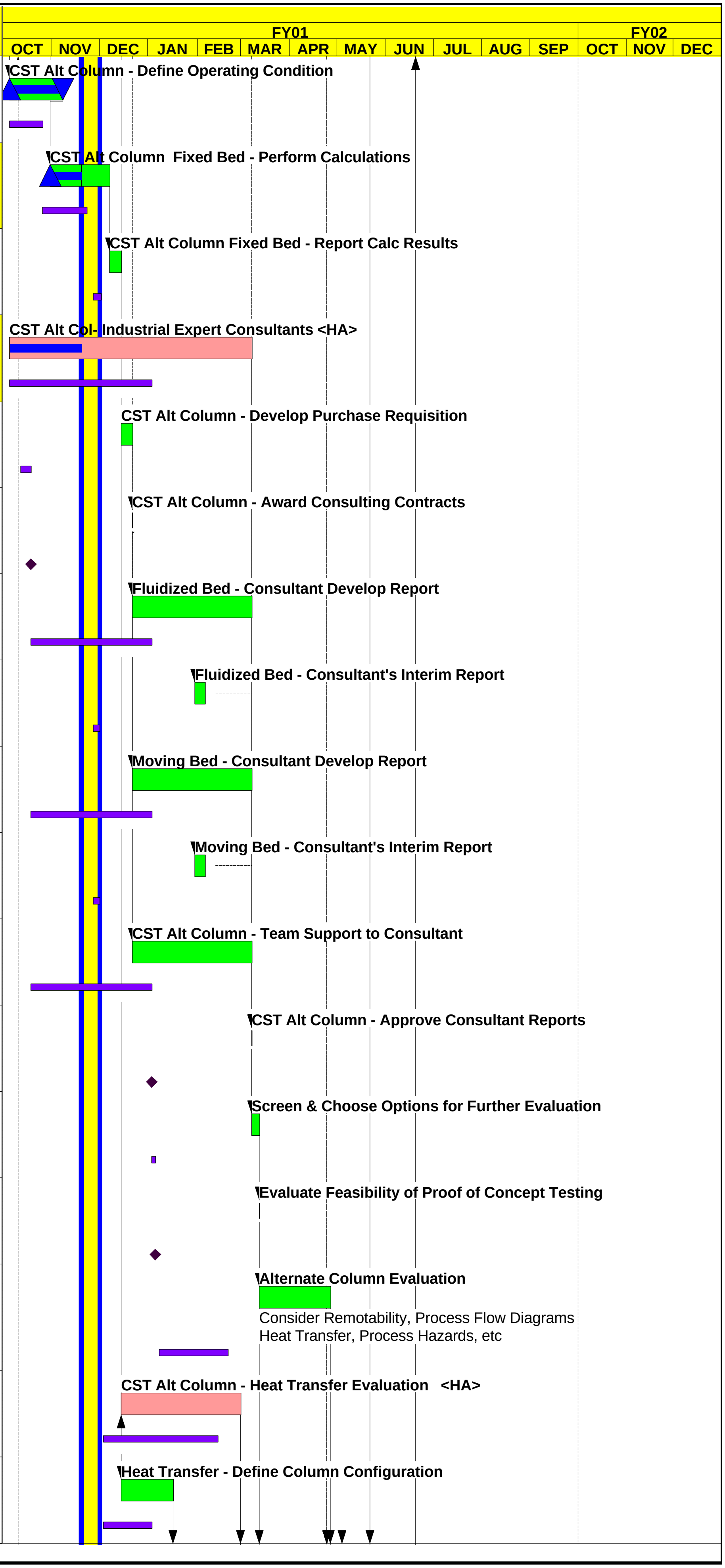
CST - Alternative Column Design

Alternative CST Column Design Studies

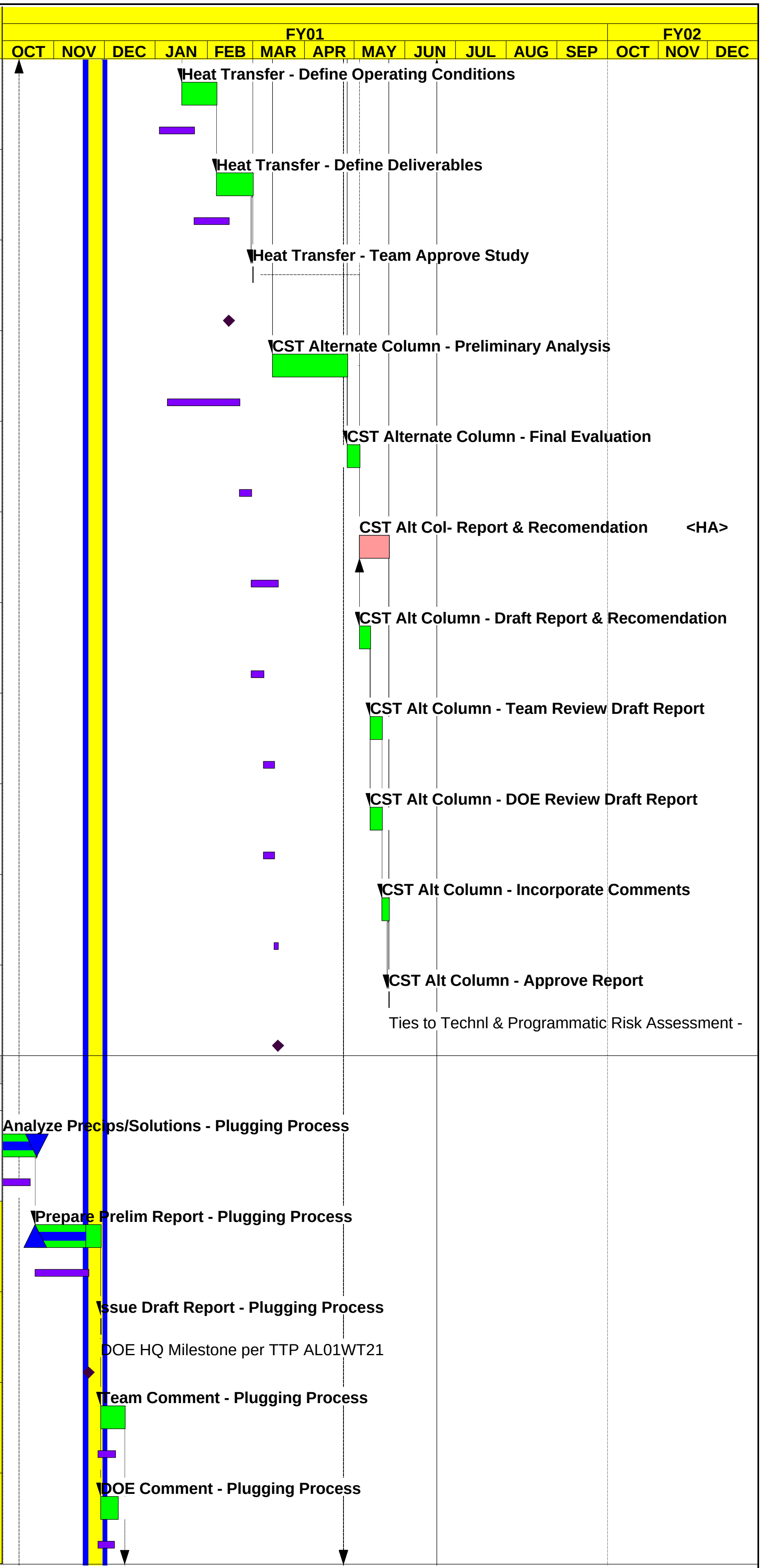
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACOL0000	124*	**651**	30AUG00A	21MAY01	LC
WACOL1020	0		30AUG00A	13NOV00A	RTJ
WACOL1100	40*	**668**	21SEP00A	19JAN01	LC
WACOL1230	0		21SEP00A	31OCT00A	LC
WACOL1240	0		06NOV00A		LC
WACOL1250	0*		16OCT00A	01NOV00A	LC
WACOL1260	0*		05OCT00A	06NOV00A	MRP
WACOL1300	32*	**731**	31OCT00A	09JAN01	MRP
WACOL1310	0		31OCT00A	14NOV00A	KJR
WACOL1320	0		15NOV00A	20NOV00A	LC
WACOL1330	9	**731**	20NOV00	04DEC00	JTC
WACOL1340	23	**731**	05DEC00	09JAN01	JTC
WACOL1350	17*	**696**	05OCT00A	14DEC00	MRP
WACOL1360	0		05OCT00A	07NOV00A	JTC



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACOL1370	0		05OCT00A	07NOV00A	JTC
WACOL1380	12*	**696**	31OCT00A	07DEC00	SYL
WACOL1390	5	**696**	08DEC00	14DEC00	MRP
WACOL1400	72*	**651**	05OCT00A	07MAR01	MRP
WACOL1430	5	**651**	15DEC00*	21DEC00	MRP
WACOL1440	0	**651**	22DEC00		MRP
WACOL1450	50	**651**	22DEC00	07MAR01	MRP
WACOL1452	4	**672**	31JAN01	05FEB01	MRP
WACOL1460	50	**651**	22DEC00	07MAR01	MRP
WACOL1462	4	**672**	31JAN01	05FEB01	MRP
WACOL1470	50	**651**	22DEC00	07MAR01	MRP
WACOL1490	0	**651**		07MAR01	KJR
WACOL1510	3	**651**	08MAR01	12MAR01	LC
WACOL1520	0	**651**		12MAR01	KJR
WACOL1530	32	**651**	13MAR01	26APR01	JTC
WACOL1600	50*	**696**	15DEC00	28FEB01	MRP
WACOL1610	20	**696**	15DEC00	16JAN01	MRP



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACOL1620	15	**696**	17JAN01	06FEB01	MRP
WACOL1630	15	**696**	07FEB01	28FEB01	MRP
WACOL1640	0	**696**		28FEB01	KJR
WACOL1700	32	**651**	13MAR01	26APR01	KJR
WACOL1710	5	**651**	27APR01	03MAY01	MRP
WACOL1800	12*	**651**	04MAY01	21MAY01	MRP
WACOL1810	5	**651**	04MAY01	10MAY01	MRP
WACOL1820	5	**651**	11MAY01	17MAY01	KJR
WACOL1830	5	**651**	11MAY01	17MAY01	JWM
WACOL1840	2	**651**	18MAY01	21MAY01	MRP
WACOL1890	0	**651**		21MAY01	KJR
CST - Alternative PreTreatment of IE-911					
SRS & ORNL - Results on Leaching					
WACST2345	0		05SEP00A	20OCT00A	DW
WACST2350	5	**69**	20OCT00A	28NOV00	DW
WACST2350A	0	**69**		28NOV00	DW
WACST2350B	8	**54**	29NOV00	12DEC00	KJR
WACST2350C	8	**70**	29NOV00	08DEC00	JWM

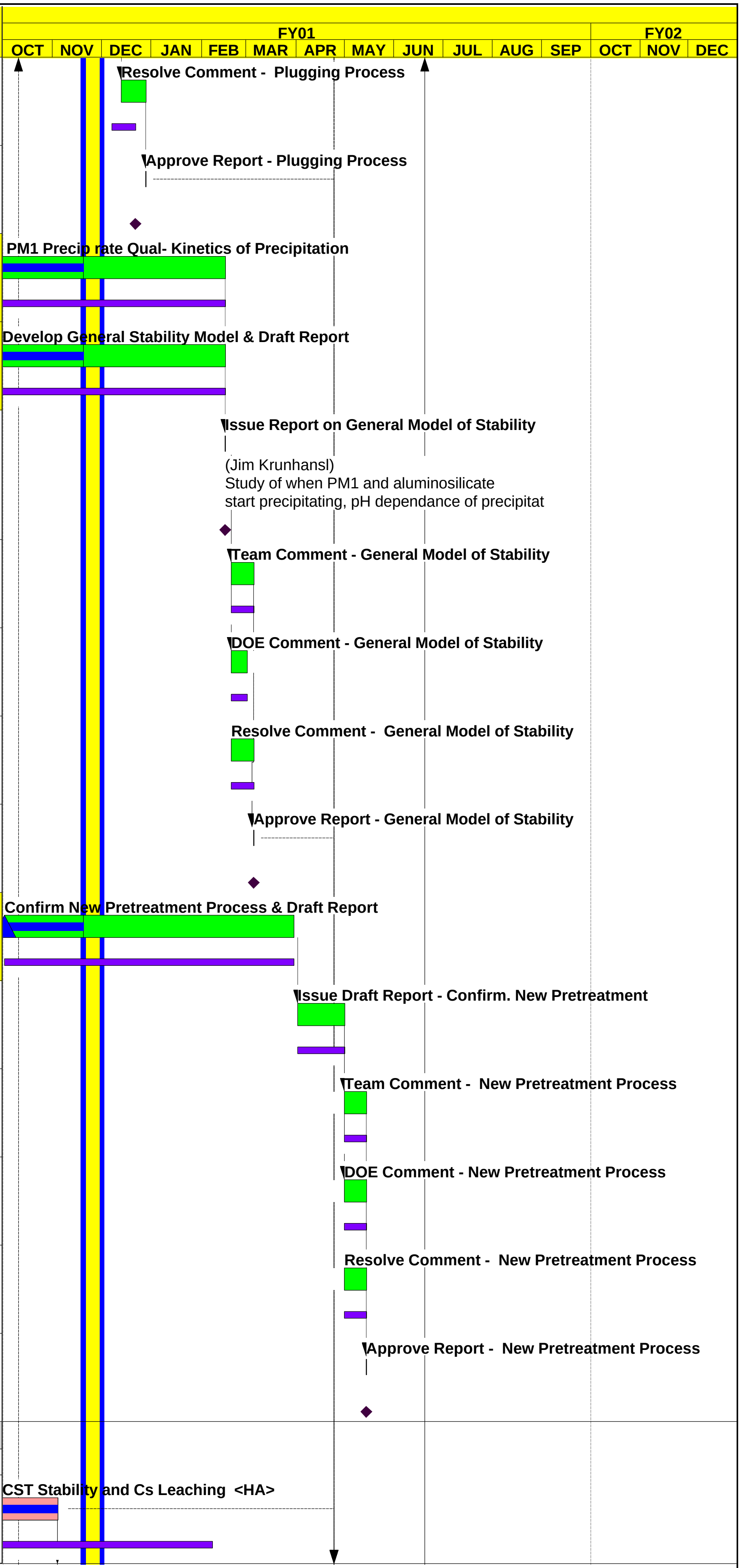


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST2350D	10	**68**	13DEC00	28DEC00	DW
WACST2350F	0	**68**		28DEC00	KJR
WACST2355	59*	**25**	09AUG00A	15FEB01	DW
WACST2356	59*	**25**	16AUG00A	15FEB01	DW
WACST2358	0	**25**		15FEB01	DW
WACST2358A	8	**19**	20FEB01	05MAR01	KJR
WACST2358B	8	**25**	20FEB01	01MAR01	JWM
WACST2358C	10	**23**	20FEB01	05MAR01	DW
WACST2358D	0	**23**		05MAR01	KJR
WACST2390B	89*	**656**	02OCT00A	30MAR01	DW
WACST2390C	20	**656**	02APR01	30APR01	DW
WACST2390D	8	**522**	01MAY01	14MAY01	KJR
WACST2390E	10	**656**	01MAY01	14MAY01	JWM
WACST2390F	10	**656**	01MAY01	14MAY01	DW
WACST2390G	0	**656**		14MAY01	KJR

CST - Stability

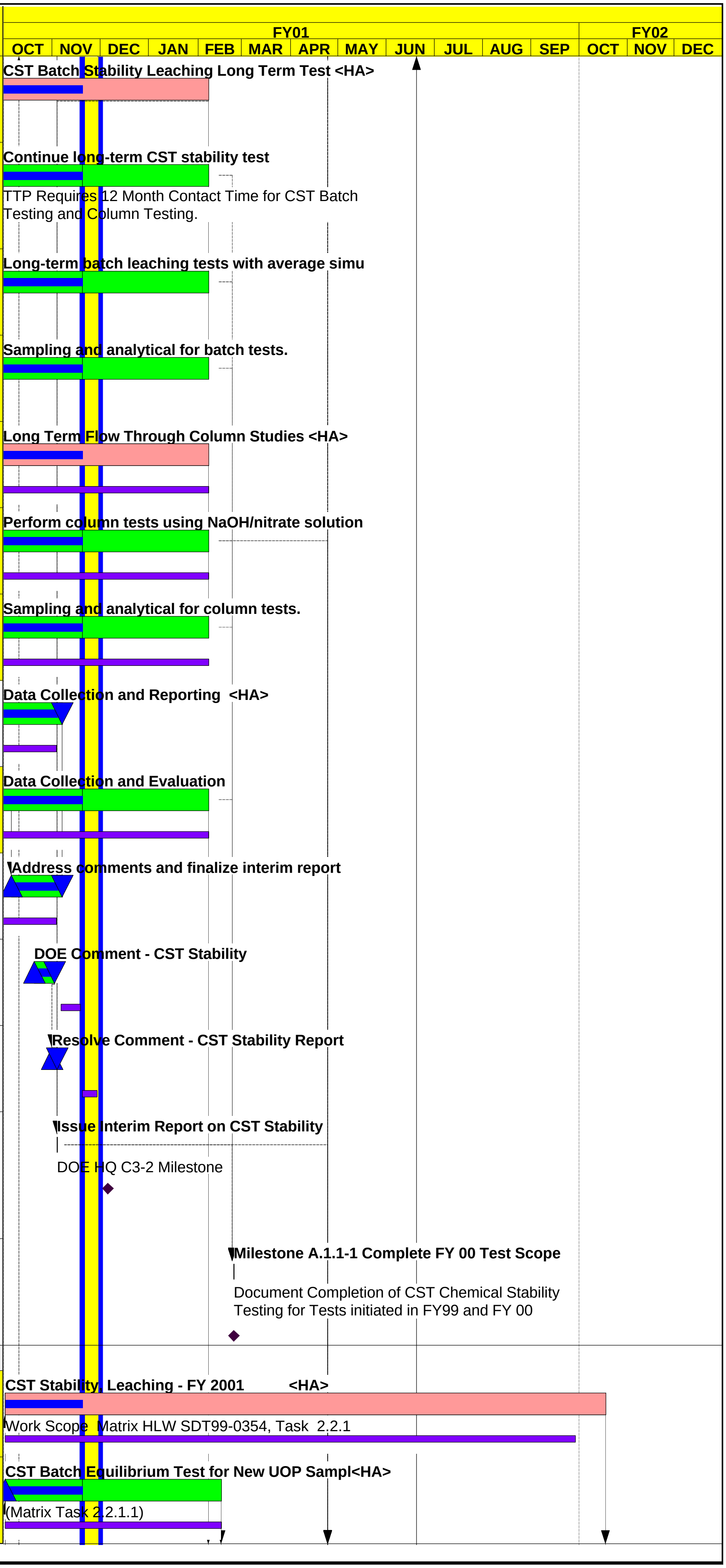
CST Stability - Long Term Exposure

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORNL2201	0*		01OCT99A	03NOV00A	TK

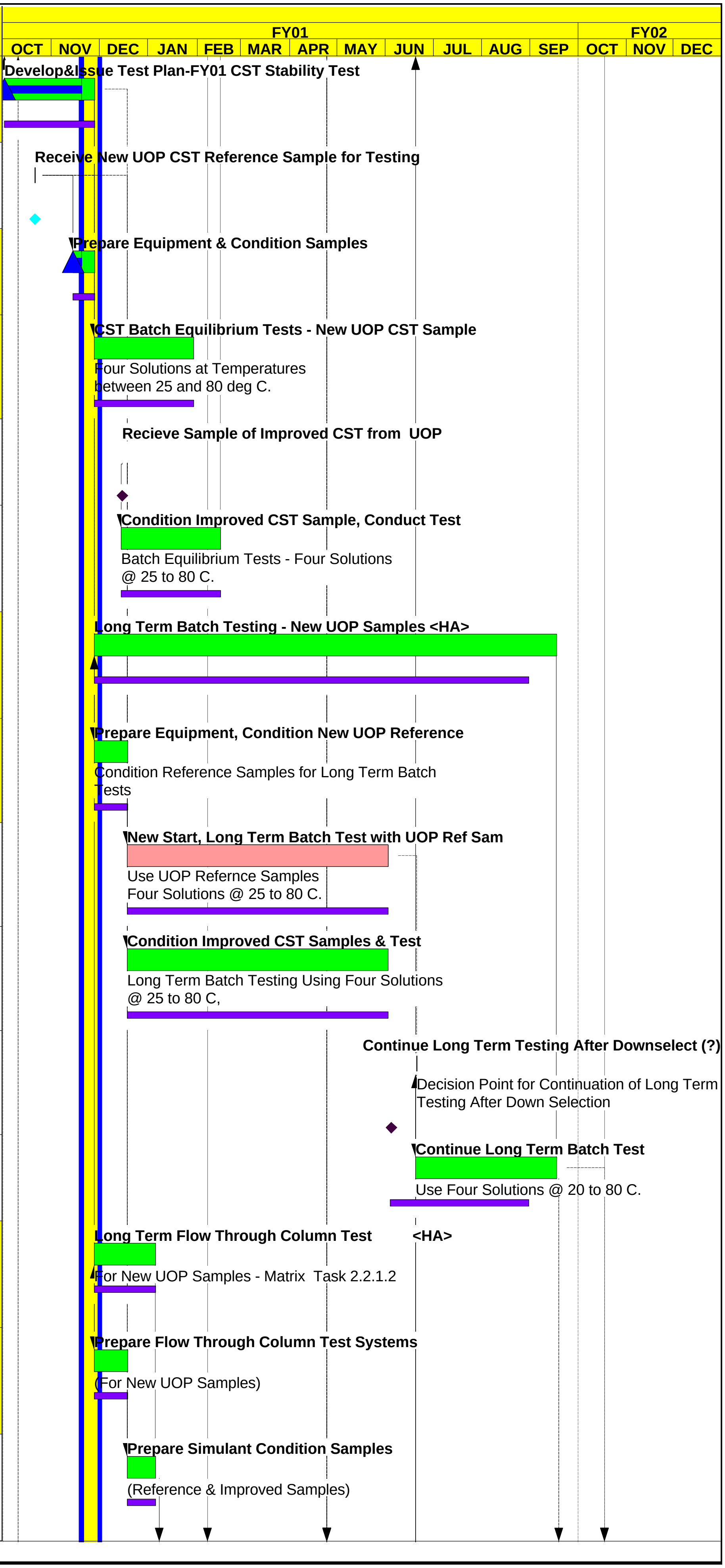


(Jim Krunhansl)
Study of when PM1 and aluminosilicate
start precipitating, pH dependance of precipitat

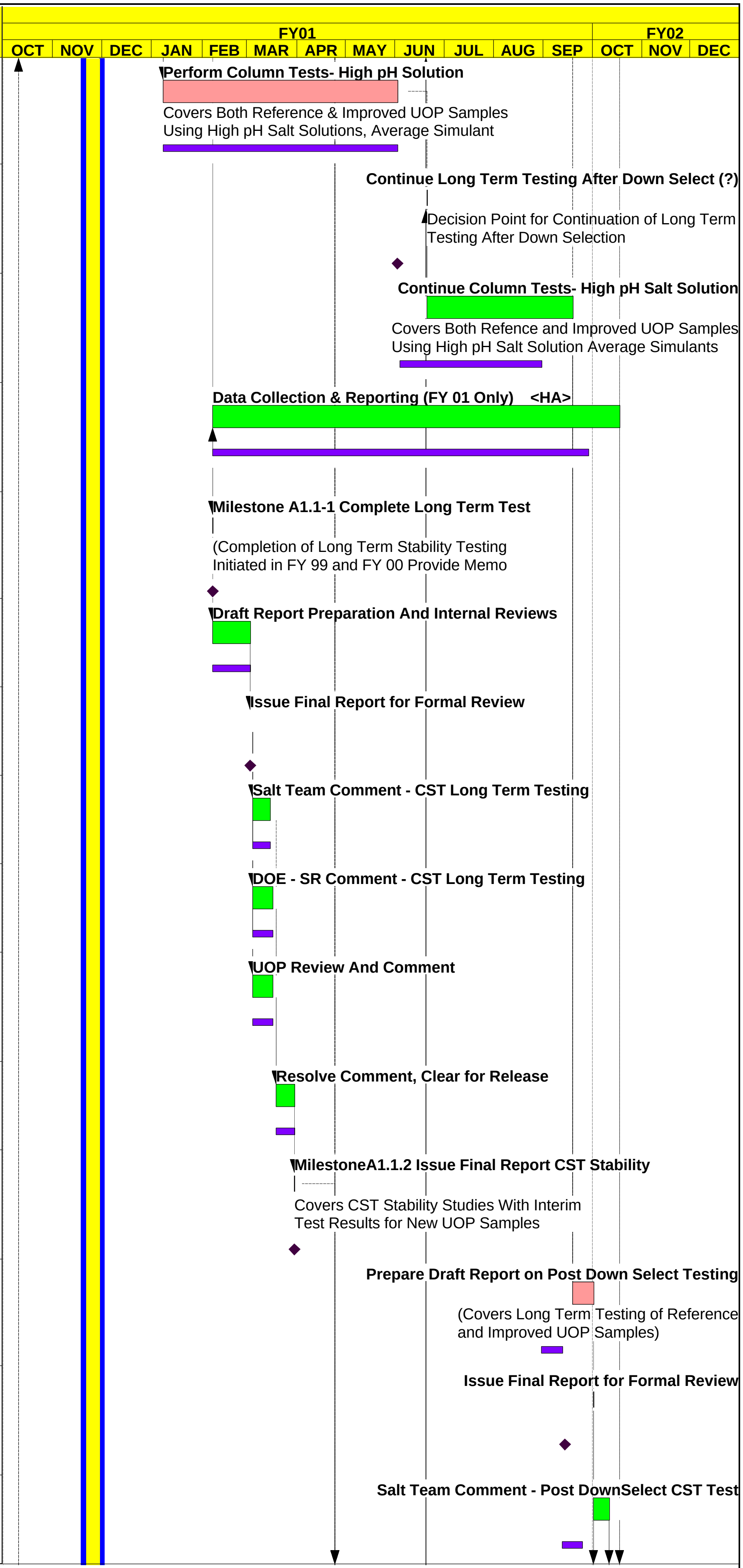
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORNL2211	57*	**732**	01OCT99A	07FEB01	TK
WAORNL2212	57*	**732**	01OCT99A	07FEB01	TK
WAORNL2216	57*	**732**	09FEB00A	07FEB01	TK
WAORNL2218	57*	**732**	01OCT99A	07FEB01	TK
WAORNL2219	57*	**732**	12JAN00A	07FEB01	TK
WAORNL2222	57*	**41**	09FEB00A	07FEB01	TK
WAORNL2223	57*	**732**	14FEB00A	07FEB01	TK
WAORNL2225	0*		01OCT99A	06NOV00A	TK
WAORNL2226	57*	**4**	01OCT99A	07FEB01	TK
WAORNL2231	0*		06OCT00A	06NOV00A	TK
WAORNL2233	0*		20OCT00A	01NOV00A	JWM
WAORNL2234	0		01NOV00A	03NOV00A	TK
WAORNL2236	0			03NOV00A	TK
WAORNL2237	0	**720**		23FEB01*	TK
CST Thermal Stability Issues (ORNL)					
WAORN2301	237*	**552**	02OCT00A	17OCT01	TK
WAORN2302	63*	**726**	02OCT00A	15FEB01	TK



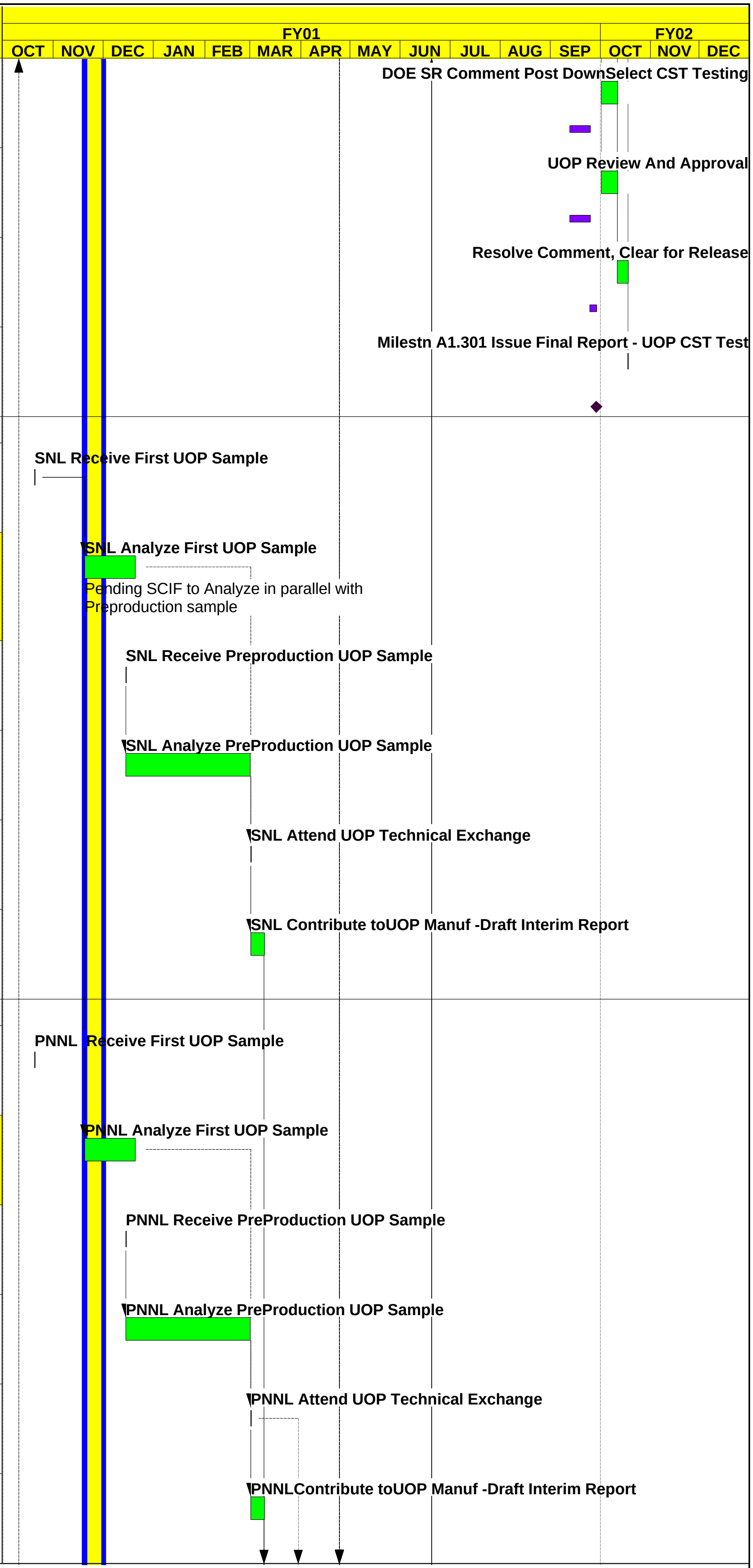
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN2303	5*	**565**	02OCT00A	27NOV00	TK
WAORN2304	0			20OCT00A	TK
WAORN2305	5*	**739**	14NOV00A	27NOV00	TK
WAORN2306	45	**739**	28NOV00	29JAN01	TK
WAORN2307	0	**567**		15DEC00*	TK
WAORN2308	45	**726**	15DEC00	15FEB01	TK
WAORN2309	210*	**553**	28NOV00	17SEP01	TK
WAORN2310	15	**566**	28NOV00	18DEC00	TK
WAORN2311	119	**566**	19DEC00	01JUN01	TK
WAORN2312	119	**650**	19DEC00	01JUN01	TK
WAORN2313	0	**553**		20JUN01	TK
WAORN2314	64	**553**	20JUN01	17SEP01	TK
WAORN2315	29*	**565**	28NOV00	05JAN01	TK
WAORN2316	15	**565**	28NOV00	18DEC00	TK
WAORN2317	14	**565**	19DEC00	05JAN01	TK



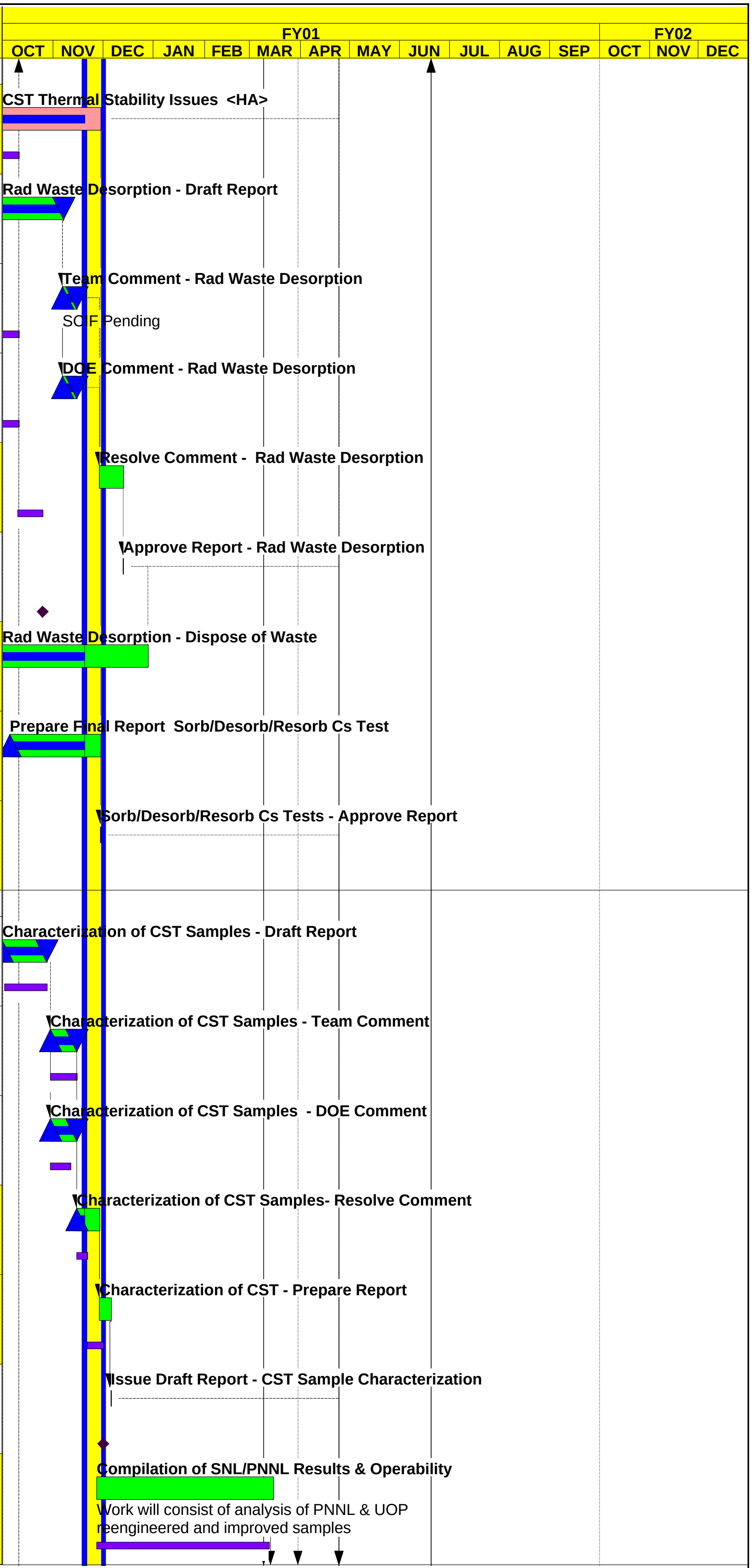
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN2318	105	**565**	08JAN01	01JUN01	TK
WAORN2319	0	**552**		20JUN01	TK
WAORN2320	64	**552**	21JUN01	18SEP01	TK
WAORN2321	180*	**552**	08FEB01	17OCT01	TK
WAORN2322	0	**4**	08FEB01		TK
WAORN2323	17	**4**	08FEB01	02MAR01	TK
WAORN2324	0	**4**		02MAR01	TK
WAORN2325	7	**5**	05MAR01	14MAR01	KJR
WAORN2326	10	**4**	05MAR01	16MAR01	TK
WAORN2327	10	**4**	05MAR01	16MAR01	TK
WAORN2328	10	**4**	19MAR01	30MAR01	TK
WAORN2329	0	**4**		30MAR01	TK
WAORN2330	9	**552**	19SEP01	01OCT01	TK
WAORN2331	0	**552**		01OCT01	TK
WAORN2332	8	**552**	02OCT01	11OCT01	TK



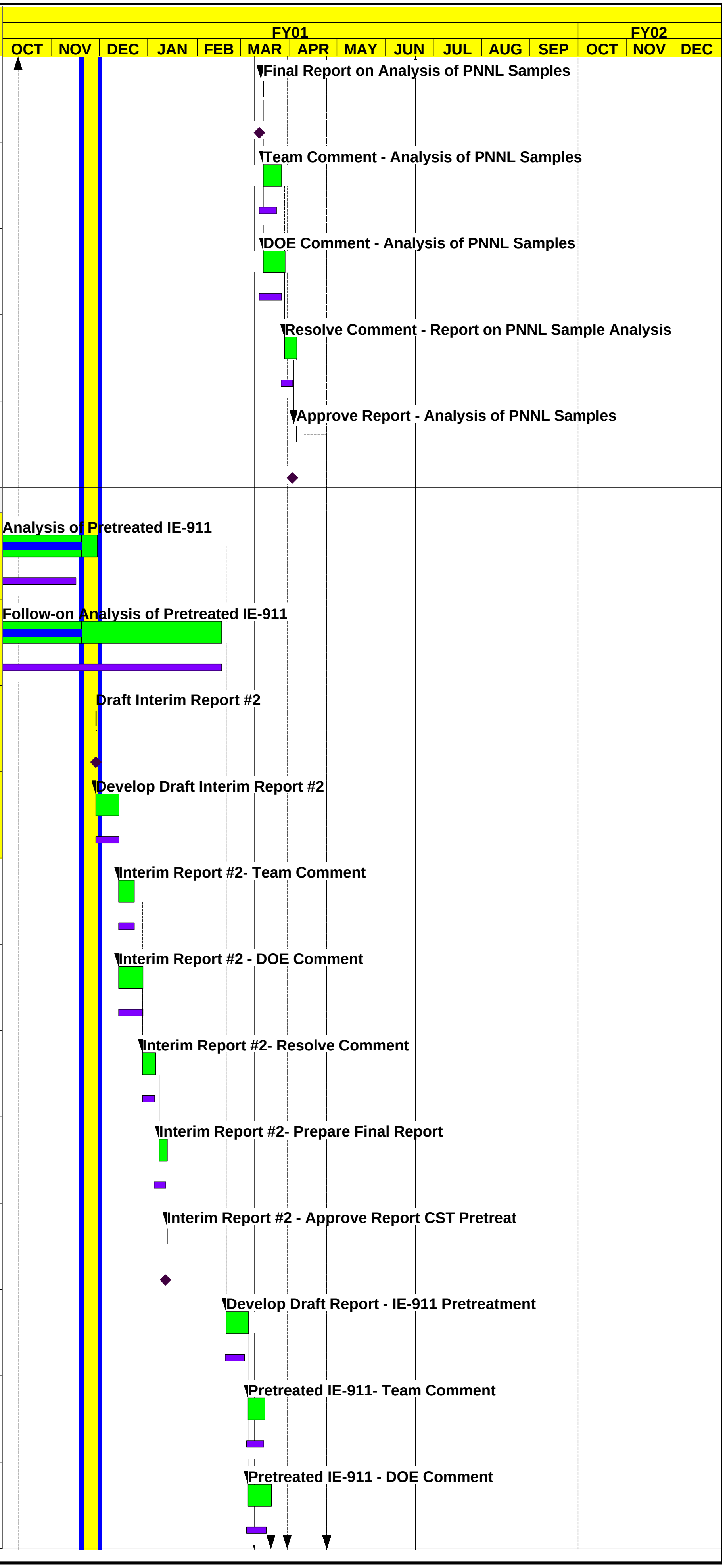
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN2333	8	**552**	02OCT01	11OCT01	TK
WAORN2334	8	**552**	02OCT01	11OCT01	TK
WAORN2335	4	**552**	12OCT01	17OCT01	TK
WAORN2336	0	**552**		17OCT01	TK
Sandia National Labs - CST Testing					
WACST2410A	0		20OCT00A		DW
WACST2410B	21	**47**	20NOV00	20DEC00	DW
WACST2410C	0	**1**	15DEC00*		DW
WACST2410D	50	**1**	15DEC00	28FEB01	DW
WACST2410E	0	**0**		01MAR01*	DW
WACST2410F	6	**0**	02MAR01	09MAR01	DW
PNNL - CST Testing					
WACST2408A	0		20OCT00A		DW
WACST2408B	21	**47**	20NOV00	20DEC00	DW
WACST2408C	0	**1**	15DEC00*		DW
WACST2408D	50	**1**	15DEC00	28FEB01	DW
WACST2408E	0	**0**		01MAR01*	DW
WACST2408F	6	**0**	02MAR01	09MAR01	DW



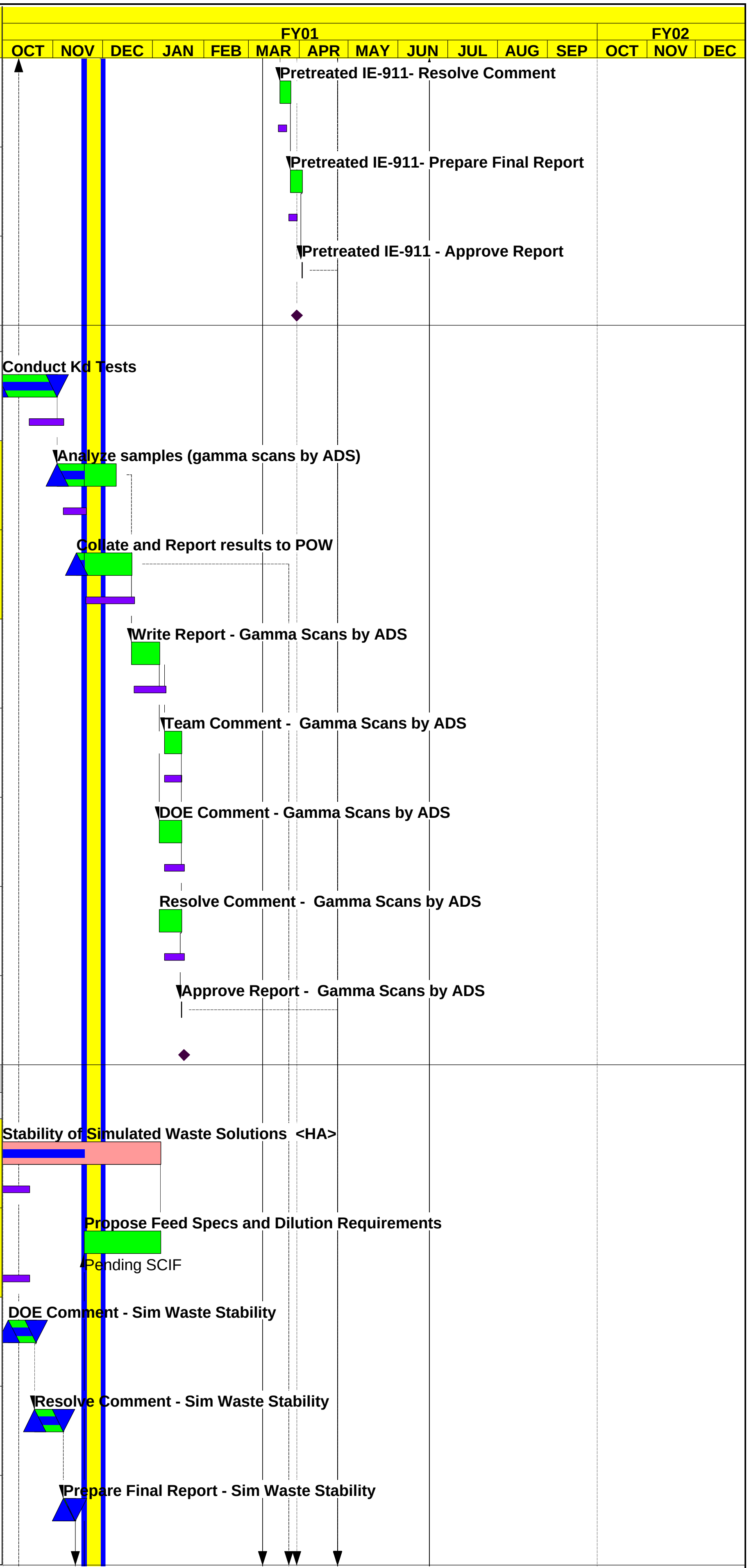
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
CST Thermal Stability Issues (SRTC)					
WACST23	6*	**87**	03JAN00A	29NOV00	DDW
WACST2311G	0		15SEP00A	06NOV00A	DDW
WACST2311H	0		06NOV00A	14NOV00A	KJR
WACST2311L	0		06NOV00A	14NOV00A	JWM
WACST2311M	10	**78**	29NOV00*	12DEC00	DW
WACST2311N	0	**78**		12DEC00	KJR
WACST2311P	25	**750**	15SEP00A	28DEC00	DDW
WACST231G5	6*	**87**	05OCT00A	29NOV00	WRW
WACST231K	0	**87**		29NOV00	KJR
CST Sample Characterization					
WACST2310	0*		29SEP00A	27OCT00A	DW
WACST2315	0		30OCT00A	14NOV00A	DW
WACST2320	0		30OCT00A	14NOV00A	DW
WACST2325	5	**83**	15NOV00A	28NOV00	DW
WACST2330	5	**83**	29NOV00	05DEC00	DW
WACST2335	0	**83**		05DEC00	KJR
WACST2410	74	**1**	27NOV00*	14MAR01	DW



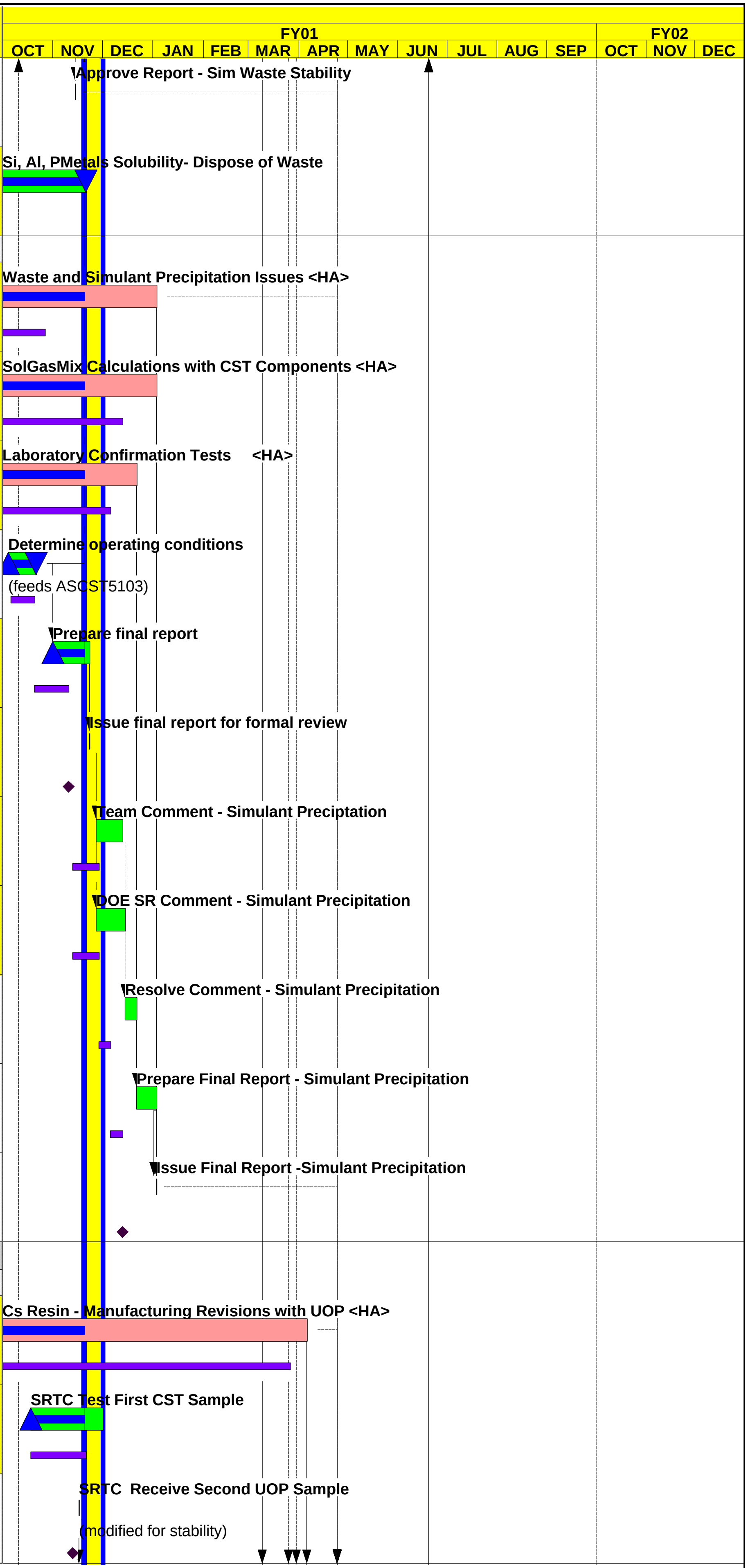
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST2411	0	**1**		14MAR01	KJR
WACST2411A	8	**1**	15MAR01	26MAR01	KJR
WACST2411B	10	**1**	15MAR01	28MAR01	JWM
WACST2411C	5	**1**	29MAR01	04APR01	DW
WACST2411E	0	**1**		04APR01	KJR
Examination of Temperature Effects on CST					
WACST2387	6	**57**	09AUG00A	29NOV00	DW
WACST2389	60*	**3**	14AUG00A	16FEB01	DW
WACST2393	0	**28**	29NOV00*		DW
WACST2395	10	**28**	29NOV00	12DEC00	DW
WACST2397	8	**28**	13DEC00	22DEC00	KJR
WACST2399	10	**28**	13DEC00	28DEC00	JWM
WACST2401	5	**28**	29DEC00	05JAN01	DW
WACST2403	5	**28**	08JAN01	12JAN01	DW
WACST2405	0	**28**		12JAN01	KJR
WACST2407	10	**3**	20FEB01	05MAR01	DW
WACST2407A	8	**3**	06MAR01	15MAR01	KJR
WACST2407B	10	**3**	06MAR01	19MAR01	JWM



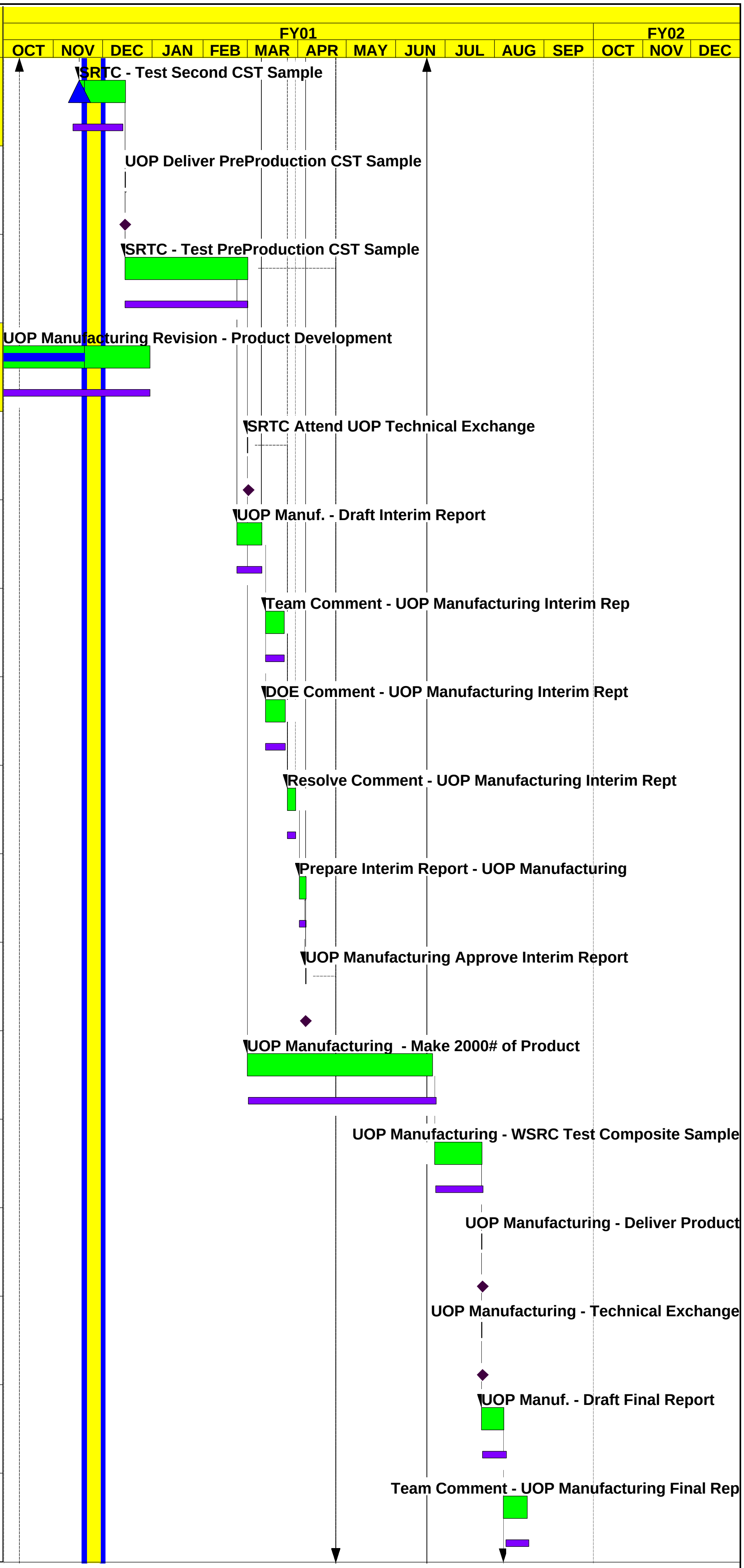
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST2407C	5	**3**	20MAR01	26MAR01	DW
WACST2407D	5	**3**	27MAR01	02APR01	DW
WACST2407E	0	**3**		02APR01	KJR
CST - Real Waste Testing					
WACST241D1	0*		26SEP00A	02NOV00A	DDW
WACST241E	13*	**60**	03NOV00A	08DEC00	DDW
WACST241F	19*	**54**	15NOV00A	18DEC00	DDW
WACST241G	10	**54**	19DEC00	04JAN01	DDW
WACST241J	8	**43**	08JAN01	18JAN01	JTC
WACST241K	10	**54**	05JAN01	18JAN01	JWM
WACST241L	10	**54**	05JAN01	18JAN01	DDW
WACST241M	0	**54**		18JAN01	KJR
CST - Precipitation Kinetics					
CST Post Precipitation					
WACST51	30*	**745**	03JAN00A	05JAN01	DDW
WACST5103	30	**745**	20NOV00	05JAN01	DDW
WACST512L	0		04OCT00A	20OCT00A	JWM
WACST512M	0		20OCT00A	06NOV00A	DDW
WACST512N	0		07NOV00A	13NOV00A	DDW



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST512O	0			13NOV00A	KJR
WACST512P	0		31JUL00A	20NOV00A	DDW
Waste & Simulant Precipitation					
WAORN4001	31*	**67**	03NOV99A	02JAN01	TK
WAORN4020	31*	**67**	01MAY00A	02JAN01	TK
WAORN4023	23*	**70**	18JUL00A	21DEC00	TK
WAORN4030	0		04OCT00A	20OCT00A	TK
WAORN4031	3*	**71**	01NOV00A	22NOV00	TK
WAORN4032	0	**71**		22NOV00	TK
WAORN4032A	10	**54**	27NOV00*	12DEC00	KJR
WAORN4032B	14	**66**	27NOV00*	14DEC00	JWM
WAORN4032C	5	**66**	15DEC00	21DEC00	TK
WAORN4032D	5	**66**	22DEC00	02JAN01	TK
WAORN4032E	0	**67**		02JAN01	TK
CST - Revised Manufacturing Process					
UOP Manufacturing Revisions					
WACST21	93*	**0**	21FEB00A	05APR01	WRW
WACST211B	7*	**768**	18OCT00A	30NOV00	WRW
WACST211C	0		17NOV00A		WRW



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST211D	17*	**0**	17NOV00A	14DEC00	WRW
WACST211E	0	**0**	15DEC00*		WRW
WACST211F	50	**0**	15DEC00	28FEB01	WRW
WACST21E	26*	**93**	19SEP00A	29DEC00	WRW
WACST21H	0	**17**		28FEB01	WRW
WACST21H1	12	**0**	22FEB01	09MAR01	WRW
WACST21H2	8	**0**	12MAR01	22MAR01	KJR
WACST21H3	10	**0**	12MAR01	23MAR01	JWM
WACST21H4	5	**0**	26MAR01	30MAR01	WRW
WACST21H5	4	**0**	02APR01	05APR01	WRW
WACST21H6	0	**0**		05APR01	KJR
WACST21I	80	**578**	01MAR01	22JUN01	WRW
WACST21J	20	**578**	25JUN01	23JUL01	WRW
WACST21K	0	**608**		23JUL01	WRW
WACST21L0	0	**608**		23JUL01	WRW
WACST21L1	10	**578**	24JUL01	06AUG01	WRW
WACST21L2	8	**460**	07AUG01	20AUG01	KJR



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST21L3	10	**578**	07AUG01	20AUG01	JWM
WACST21L4	5	**578**	21AUG01	27AUG01	WRW
WACST21L5	5	**578**	28AUG01	04SEP01	WRW
WACST21M	0	**578**		04SEP01	KJR

CST - Gas Disengagement

CST - Alternate Column - Planning

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST8000	67*	**660**	08NOV99A	28FEB01	WVP

ORNL CST Testing - Summary

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN5001	72*	**669**	03NOV99A	28FEB01	TK

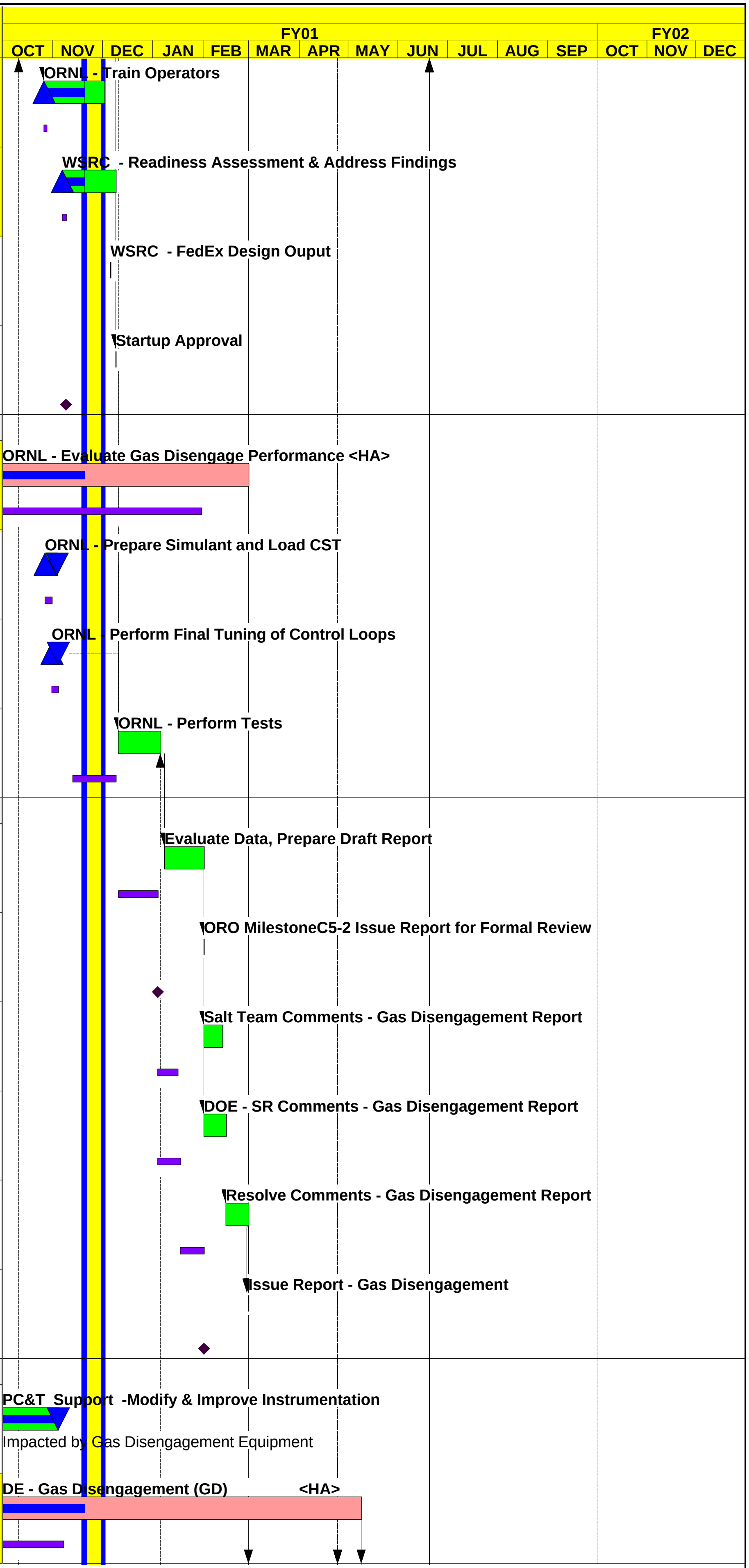
Thermal Conductivity Studies

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN5006	3*	**786**	17JAN00A	22NOV00	TK
WAORN5018	3	**786**	20OCT00A	22NOV00	TK

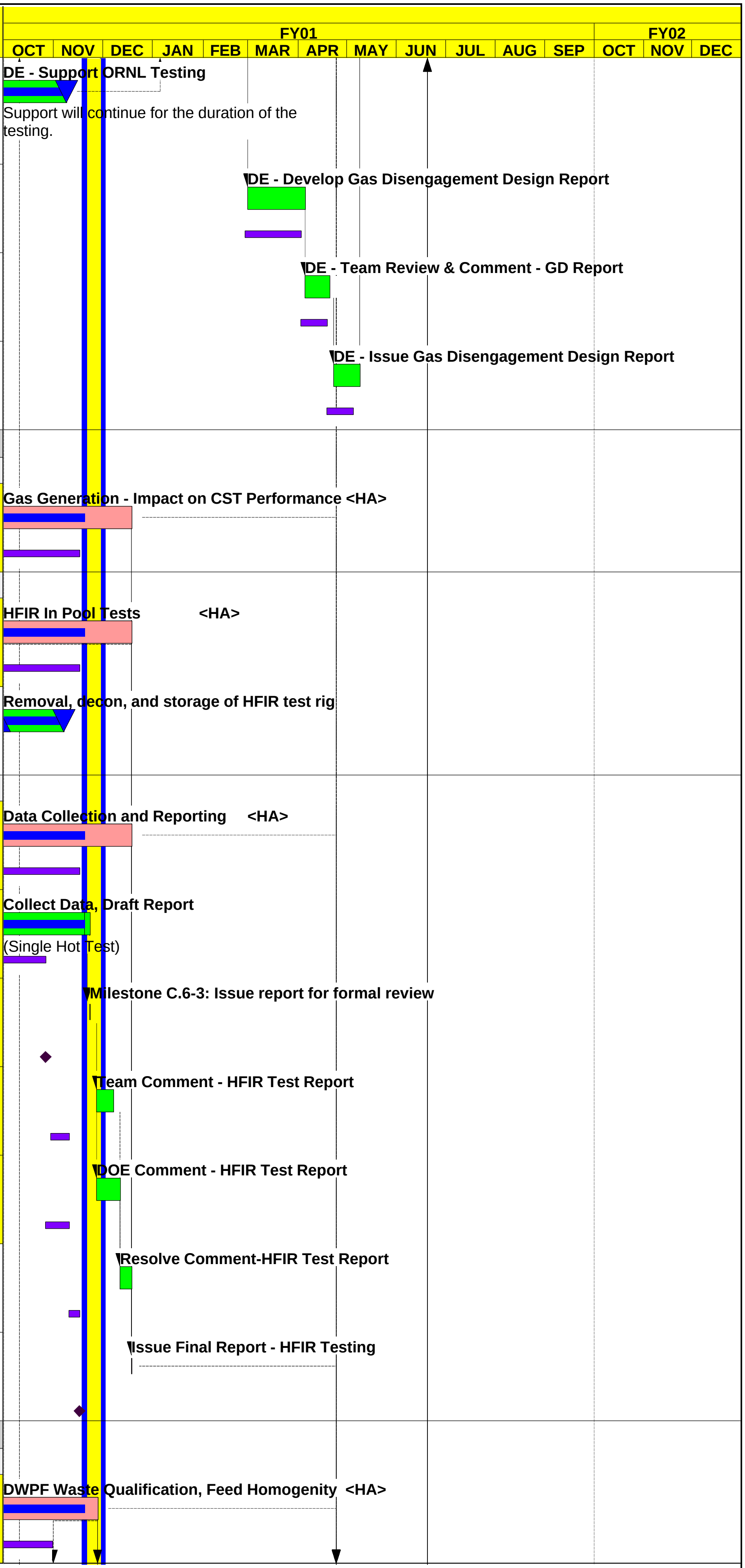
Tall Column Test Preparations

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN5019	14*	**668**	04JAN00A	08DEC00	TK
WAORN5027	14*	**668**	16FEB00A	08DEC00	TK
WAORN5037A	0		09OCT00A	20OCT00A	TK
WAORN5038	0		12JUL00A	20OCT00A	TK
WAORN5039	0		23OCT00A	31OCT00A	TK
WAORN5040	0*		18OCT00A	25OCT00A	TK
WAORN5044	0		23OCT00A	03NOV00A	TK

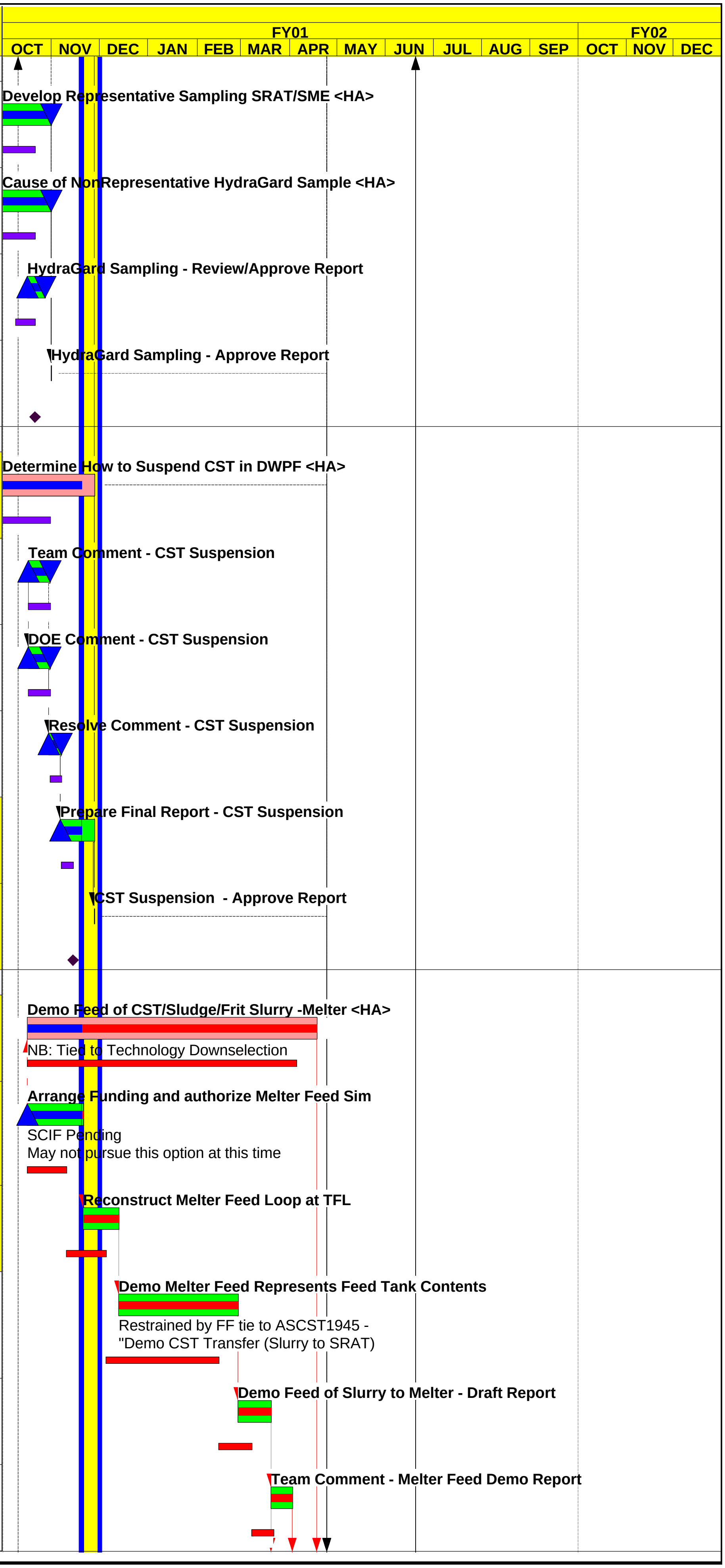
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN5045	9*	**673**	26OCT00A	01DEC00	TK
WAORN5046	14*	**668**	06NOV00A	08DEC00	TK
WAORN5046A	0	**778**	06DEC00*		TK
WAORN5047	0	**668**		08DEC00	TK
Evaluate Gas Disengagement Performance					
WAORN5048	72*	**669**	17JUL00A	28FEB01	TK
WAORN5051	0		27OCT00A	02NOV00A	TK
WAORN5052	0		31OCT00A	03NOV00A	TK
WAORN5053	20	**668**	11DEC00	05JAN01	TK
Tall Column - Prepare Final Report					
WAORN5054	18	**668**	08JAN01	31JAN01	TK
WAORN5055	0	**668**		31JAN01	TK
WAORN5056	6	**523**	01FEB01	12FEB01	KJR
WAORN5057	10	**669**	01FEB01	14FEB01	JWM
WAORN5058	10	**669**	15FEB01	28FEB01	TK
WAORN5059	0	**669**		28FEB01	TK
SRS Support to ORNL - DE, PC&T					
WAPCT5027	0		08MAY00A	03NOV00A	TRT
WAZZDE5041	115*	**660**	17JAN00A	08MAY01	LC



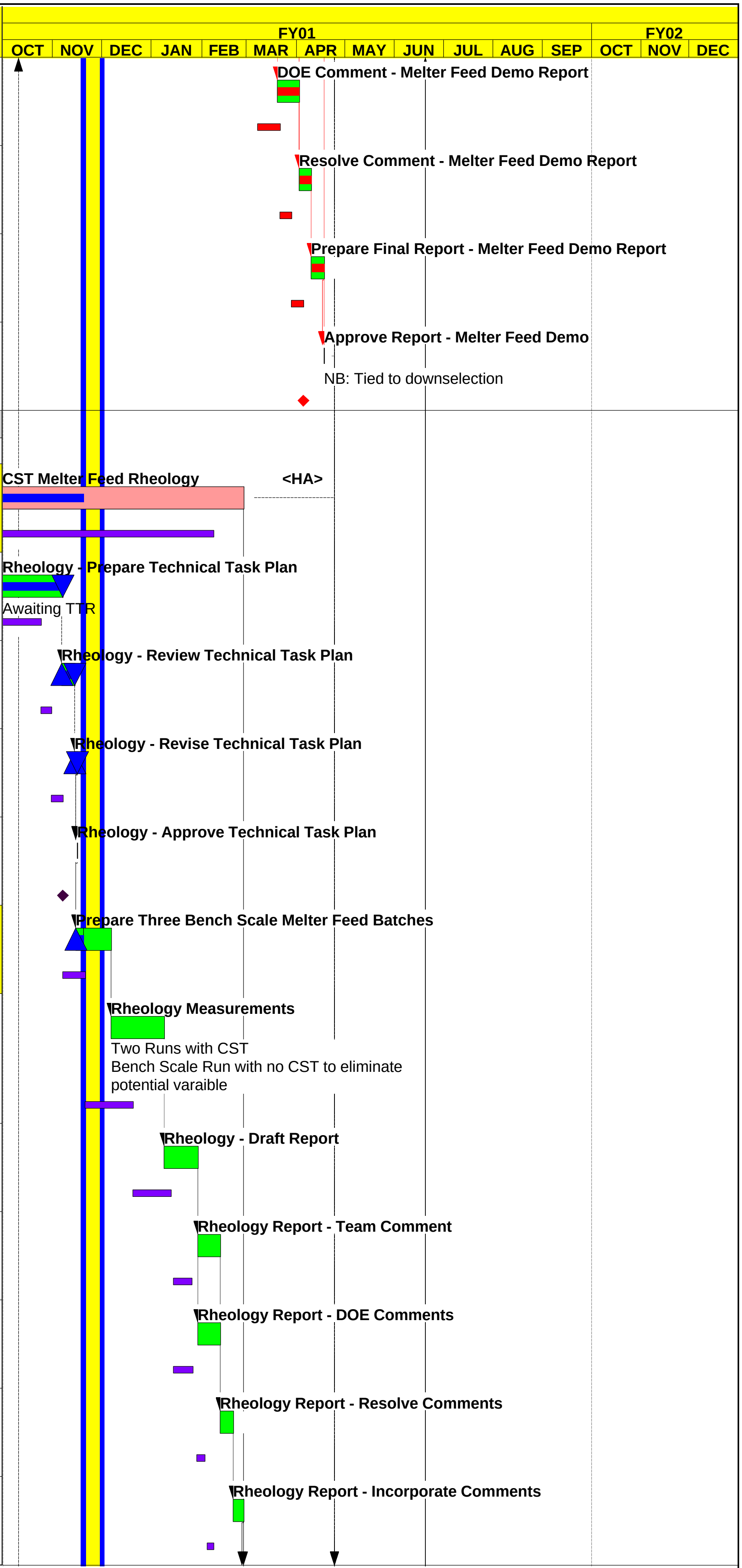
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAZZDE5046	0		31MAR00A	08NOV00A	LC
WAZZDE5047	25	**660**	01MAR01	04APR01	LC
WAZZDE5048	11	**660**	05APR01	20APR01	LC
WAZZDE5049	12	**660**	23APR01	08MAY01	LC
CST - Gas Generation					
Gas Generation - Impact on CST Loading					
WAORN6001	20*	**78**	10NOV99A	18DEC00	TK
HFIR In Pool Testing					
WAORN6066	20*	**78**	25AUG00A	18DEC00	TK
WAORNL6070	0		27SEP00A	06NOV00A	TK
HFIR Test Report					
WAORN6079	20*	**78**	22SEP00A	18DEC00	TK
WAORN6080	3*	**79**	22SEP00A	22NOV00	TK
WAORN6081	0	**79**		22NOV00	TK
WAORN6082	8	**60**	27NOV00*	07DEC00	KJR
WAORN6083	11	**74**	27NOV00	11DEC00	JWM
WAORN6084	5	**74**	12DEC00	18DEC00	TK
WAORN6085	0	**74**		18DEC00	TK
CST - Develop and Test Size Reduced Method					
DWPF Waste Qualification - Homogenity					
WACST1900	4*	**89**	19NOV99A	27NOV00	FGS



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
DWPF Waste Qual - SRAT / SME Sampling					
WACST191	0*		17JAN00A	31OCT00A	FGS
WACST1911	0*		17JAN00A	31OCT00A	FGS
WACST1911J	0*		16OCT00A	27OCT00A	FGS
WACST1911K	0			31OCT00A	KJR
CST Suspension at DWPF					
WACST194	4*	**89**	17JAN00A	27NOV00	FGS
WACST1944H	0*		17OCT00A	30OCT00A	FGS
WACST1944I	0		17OCT00A	30OCT00A	FGS
WACST1944L	0		30OCT00A	06NOV00A	FGS
WACST1944M	4*	**89**	06NOV00A	27NOV00	FGS
WACST1944N	0	**89**		27NOV00	KJR
Demonstrate CST Sludge Frit Slurry Feed to Melte					
WACST195	100*	**-7**	16OCT00A	17APR01	FGS
WACST1952	1	**-8**	16OCT00A	20NOV00	FGS
WACST1952A	14	**-8**	21NOV00	12DEC00	FGS
WACST1952D	50	**-8**	13DEC00	26FEB01	FGS
WACST1952E	15	**-8**	27FEB01	19MAR01	FGS
WACST1952F	8	**-6**	20MAR01	02APR01	FGS



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST1952G	10	**-7**	20MAR01	02APR01	FGS
WACST1952H	5	**-7**	03APR01	09APR01	FGS
WACST1952I	5	**-7**	10APR01	17APR01	FGS
WACST1952J	0	**-7**		17APR01	KJR
DWPF Melter Operation					
CST Melter Feed Rheology					
WACST195A	65*	**28**	18SEP00A	26FEB01	JRH
WACST195B	0*		18SEP00A	06NOV00A	JRH
WACST195C	0		06NOV00A	13NOV00A	JRH
WACST195D	0		14NOV00A	15NOV00A	JRH
WACST195E	0			15NOV00A	JRH
WACST195H	11*	**28**	15NOV00A	06DEC00	JRH
WACST195I	20	**28**	07DEC00	08JAN01	JRH
WACST195J	15	**28**	09JAN01	29JAN01	JRH
WACST195K	8	**22**	30JAN01	12FEB01	JRH
WACST195L	10	**28**	30JAN01	12FEB01	JRH
WACST195M	5	**28**	13FEB01	20FEB01	JRH
WACST195N	4	**28**	21FEB01	26FEB01	JRH



NB: Tied to downselection

Awaiting TTR

Two Runs with CST
Bench Scale Run with no CST to eliminate
potential varaible

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACST195O	0	**28**		26FEB01	JRH

Caustic Side Solvent Extraction

CSSX - Solvent Preparation

Solvent Preparation

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX41500	10*	**779**	20OCT00A	04DEC00	LNK
WACX415010	0		20OCT00A	03NOV00A	LNK
WACX415020	9*	**779**	15NOV00A	01DEC00	LNK
WACX415030	10*	**779**	15NOV00A	04DEC00	LNK
WACX415040	10*	**779**	15NOV00A	04DEC00	LNK

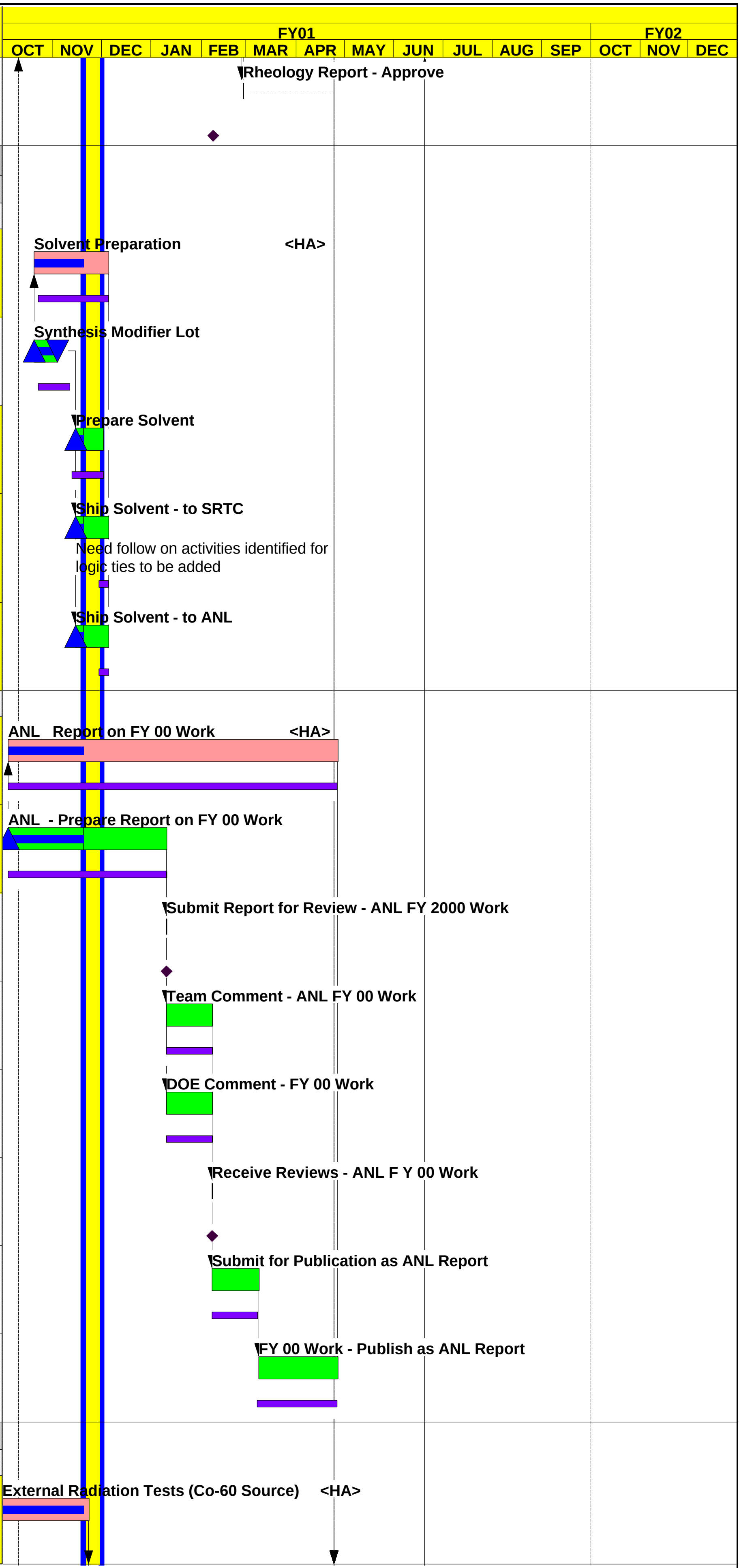
ANL Report Preparation

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAANL7100	107*	**668**	04OCT00A	26APR01	LNK
WAANL7110	33*	**668**	04OCT00A	10JAN01	LNK
WAANL7120	0	**668**		10JAN01	LNK
WAANL7130	16	**531**	11JAN01	07FEB01	KJR
WAANL7140	20	**668**	11JAN01	07FEB01	JWM
WAANL7150	0	**668**		07FEB01	LNK
WAANL7160	20	**668**	08FEB01	08MAR01	LNK
WAANL7190	34	**668**	09MAR01	26APR01	LNK

Batch Equilibrium - Internal Solvent Irradiation

Solvent - External Radiation - Co-60 Source

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX411	3*	**65**	12APR00A	22NOV00	RAP



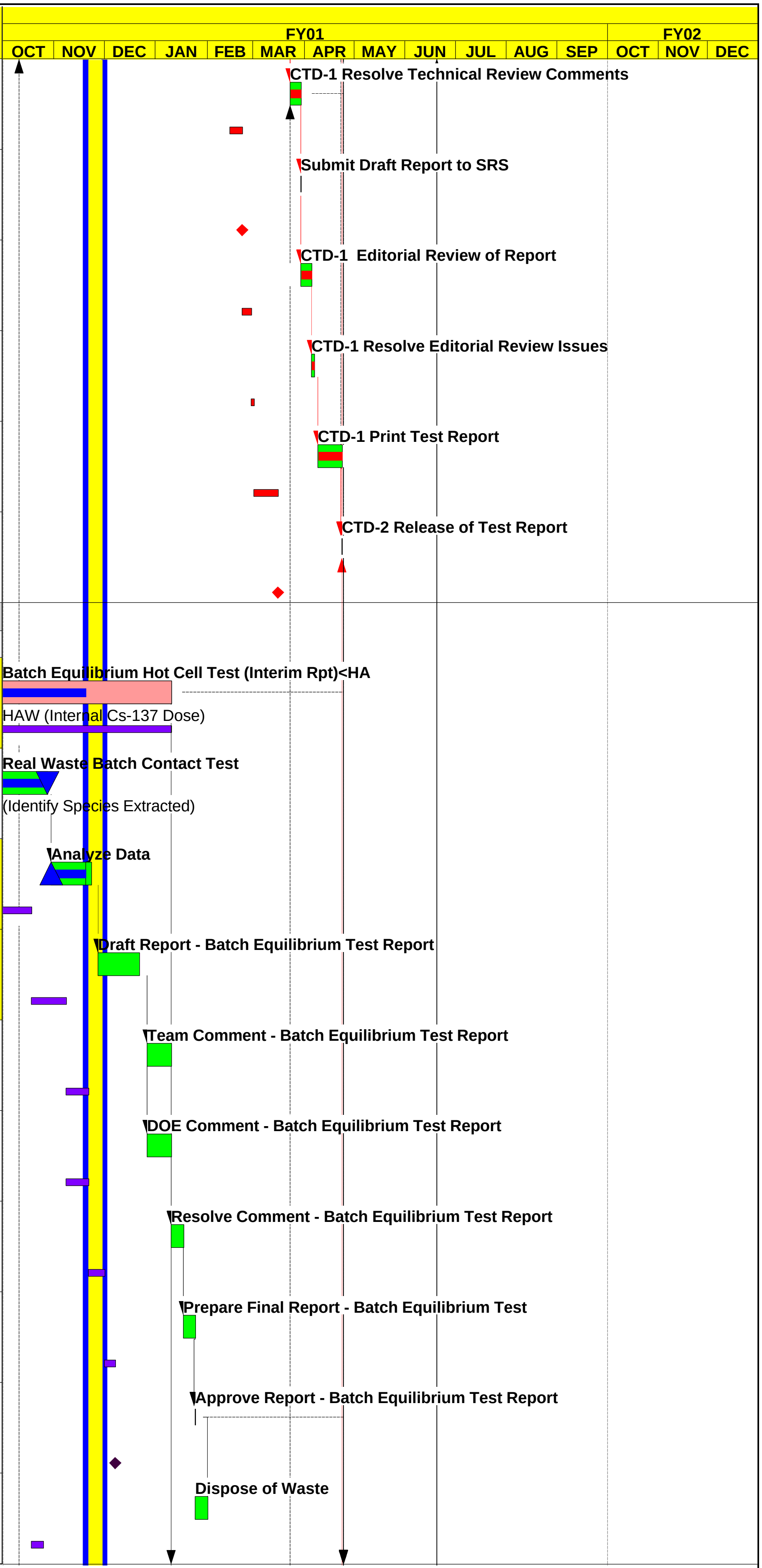
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX41105B	0		11OCT00A	23OCT00A	KJR
WACX41105C	0		11OCT00A	02NOV00A	JWM
WACX41105D	0		31OCT00A	13NOV00A	RAP
WACX41105E	3*	**65**	14NOV00A	22NOV00	RAP
WACX41105F	0	**65**		22NOV00	KJR
WACX41106	12*	**763**	25AUG00A	07DEC00	RAP
WACX4115	25	**65**	27NOV00	03JAN01	
Batch Equilibrium Internal Irradiation Experimt.					
WAORN7137	110*	**-12**	07JUN00A	23APR01	LNK
WAORN7141	110*	**-12**	09OCT00A	23APR01	LNK
WAORN7151	78*	**20**	02OCT00A	08MAR01	LNK
WAORN7152	57*	**-12**	02OCT00A	07FEB01	LNK
WAORN7153A	11	**20**	08FEB01	22FEB01	LNK
WAORN7153B	10	**20**	23FEB01	08MAR01	LNK
WAORN7154	53*	**-12**	08FEB01	23APR01	LNK
WAORN7155	21	**-12**	08FEB01	08MAR01	LNK
WAORN7155A	10	**-12**	09MAR01	22MAR01	LNK
WAORN7155B	10	**-12**	09MAR01	22MAR01	HDH

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN7156	5	**-12**	23MAR01	29MAR01	LNK
WAORN7156A	0	**-12**		29MAR01	LNK
WAORN7157	4	**-12**	30MAR01	04APR01	LNK
WAORN7158	2	**-12**	05APR01	06APR01	LNK
WAORN7159	11	**-12**	09APR01	23APR01	LNK
WAORN7160	0	**-12**		23APR01	LNK

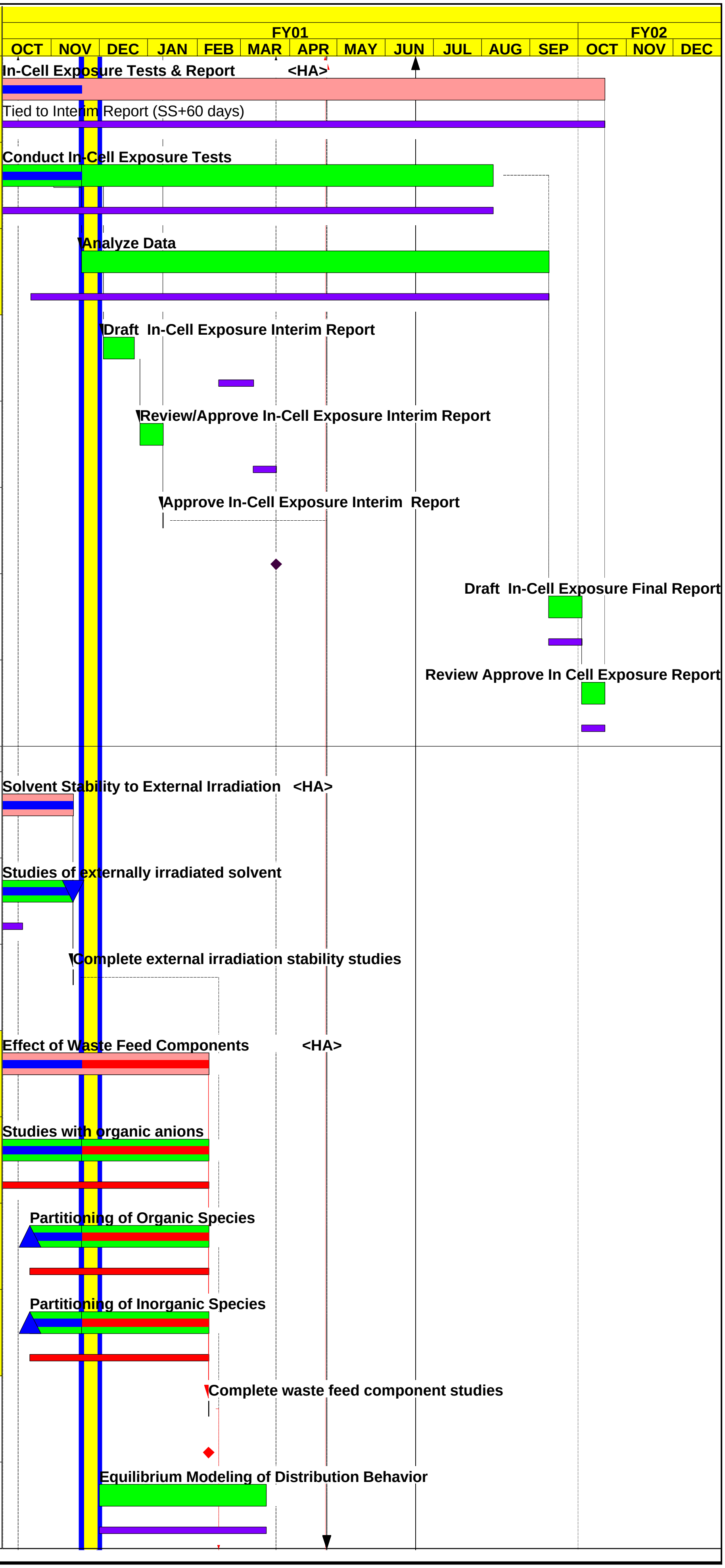
Batch Equilibrium-External Solvent Irradiation

Solvent - Batch Equilibrium Hot Cell Test

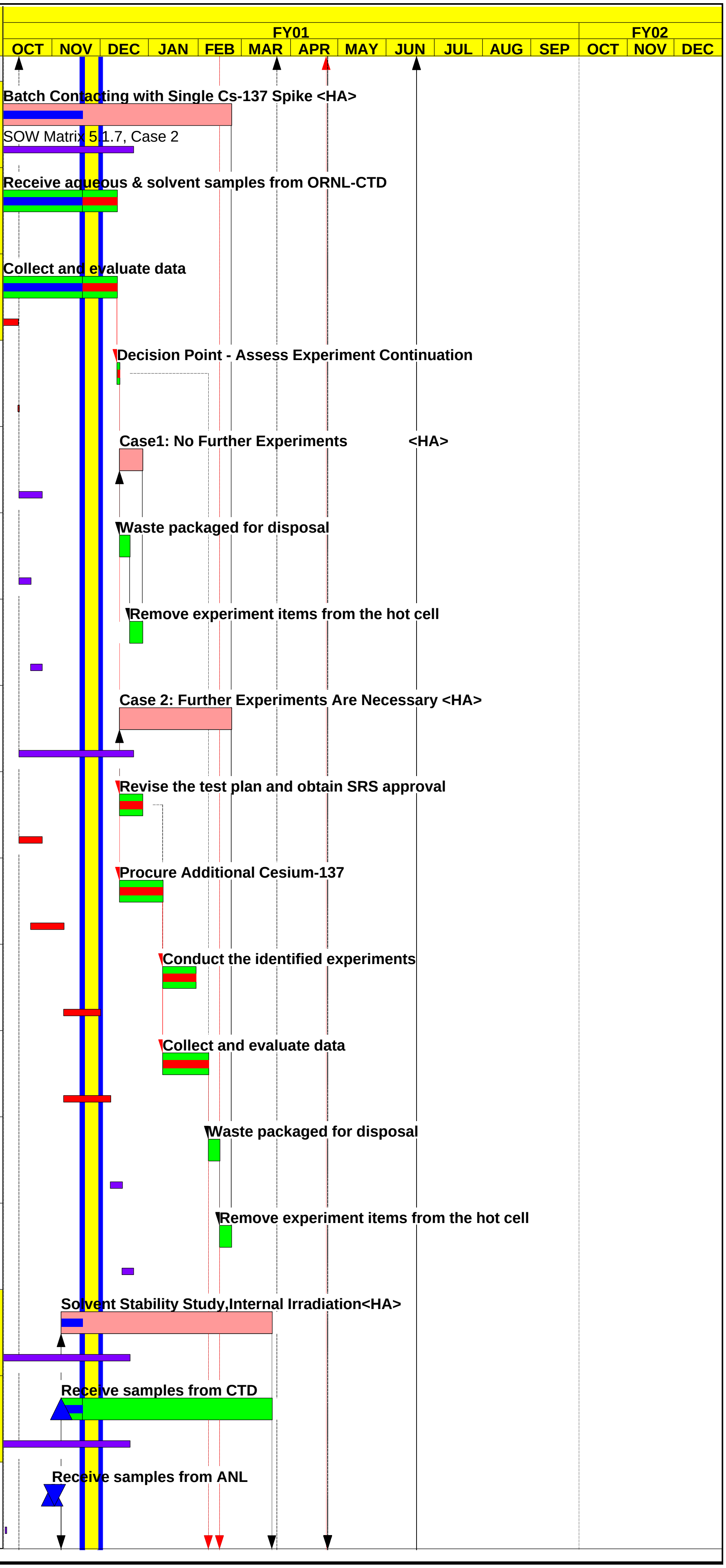
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX412	33*	**60**	03JUL00A	10JAN01	RAP
WACX412C	0*		07SEP00A	27OCT00A	RAP
WACX412E	3	**50**	30OCT00A	22NOV00	RAP
WACX412E1	19	**50**	27NOV00	21DEC00	RAP
WACX412E2	8	**39**	27DEC00	10JAN01	KJR
WACX412E3	10	**50**	27DEC00	10JAN01	JWM
WACX412E4	5	**50**	11JAN01	17JAN01	RAP
WACX412E5	5	**50**	18JAN01	24JAN01	RAP
WACX412E6	0	**50**		24JAN01	KJR
WACX412M	5	**727**	25JAN01	31JAN01	RAP



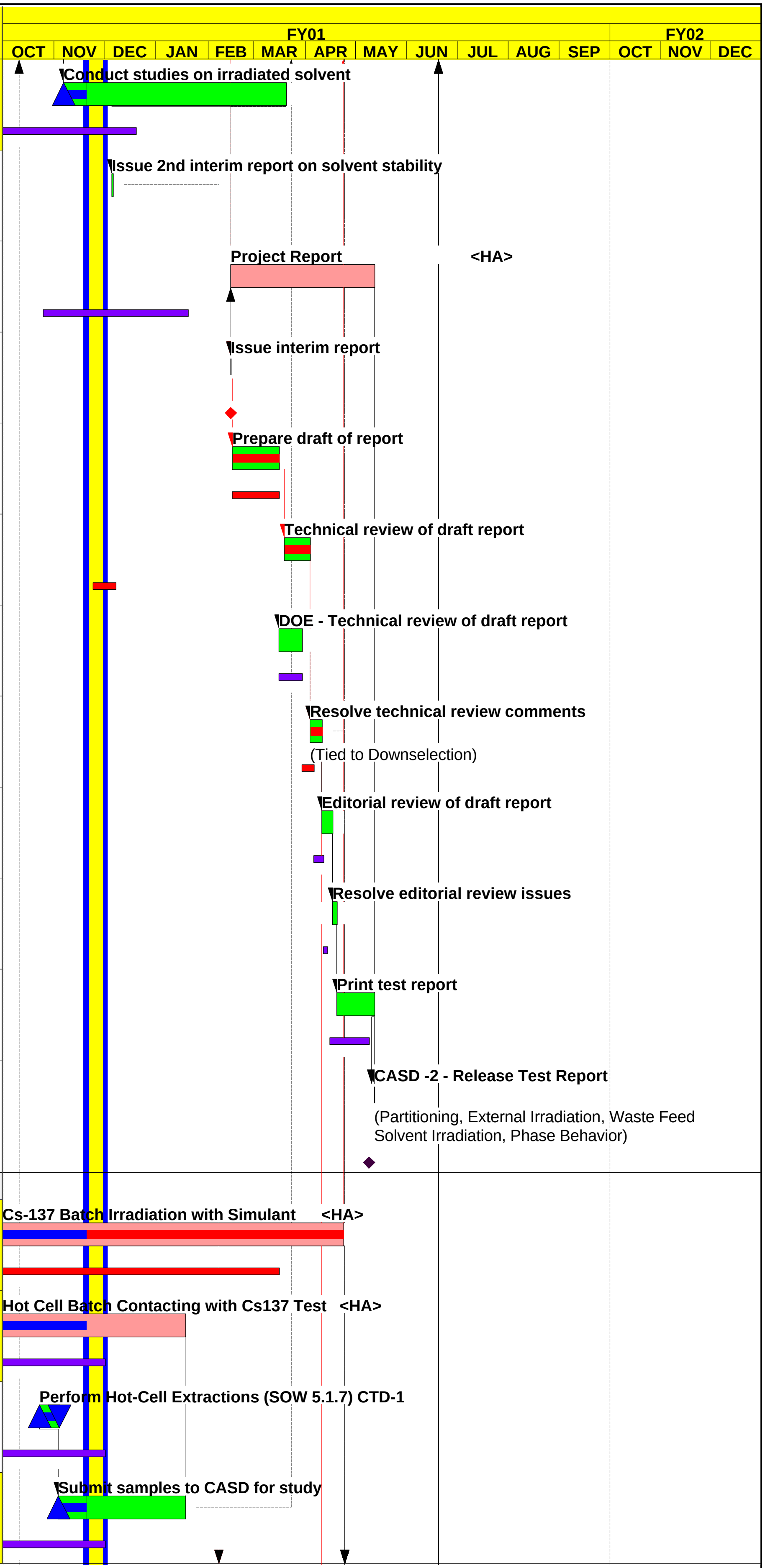
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX412M00	228*	**547**	07SEP00A	17OCT01	RAP
WACX412N	178*	**60**	07SEP00A	07AUG01	RAP
WACX412P	203*	**547**	20NOV00	12SEP01	RAP
WACX412R	15	**60**	04DEC00	22DEC00	RAP
WACX412T	10	**60**	27DEC00	10JAN01	KJR
WACX412V	0	**60**		10JAN01	KJR
WACX412W	15	**547**	13SEP01	03OCT01	RAP
WACX412X	10	**547**	04OCT01	17OCT01	RAP
Solvent Stability to External Irradiation					
WAORN7070	0*		01JUN00A	13NOV00A	LNK
WAORN7072	0		01JUN00A	13NOV00A	LNK
WAORN7074	0			13NOV00A	LNK
WAORN7075	58*	**-2**	18MAY00A	08FEB01	LNK
WAORN7076	58*	**-2**	18MAY00A	08FEB01	LNK
WAORN7076A	58*	**-2**	18OCT00A	08FEB01	LNK
WAORN7076B	58*	**-2**	18OCT00A	08FEB01	LNK
WAORN7077	0	**-2**		08FEB01	LNK
WAORN7077A	76	**705**	01DEC00*	16MAR01	LNK



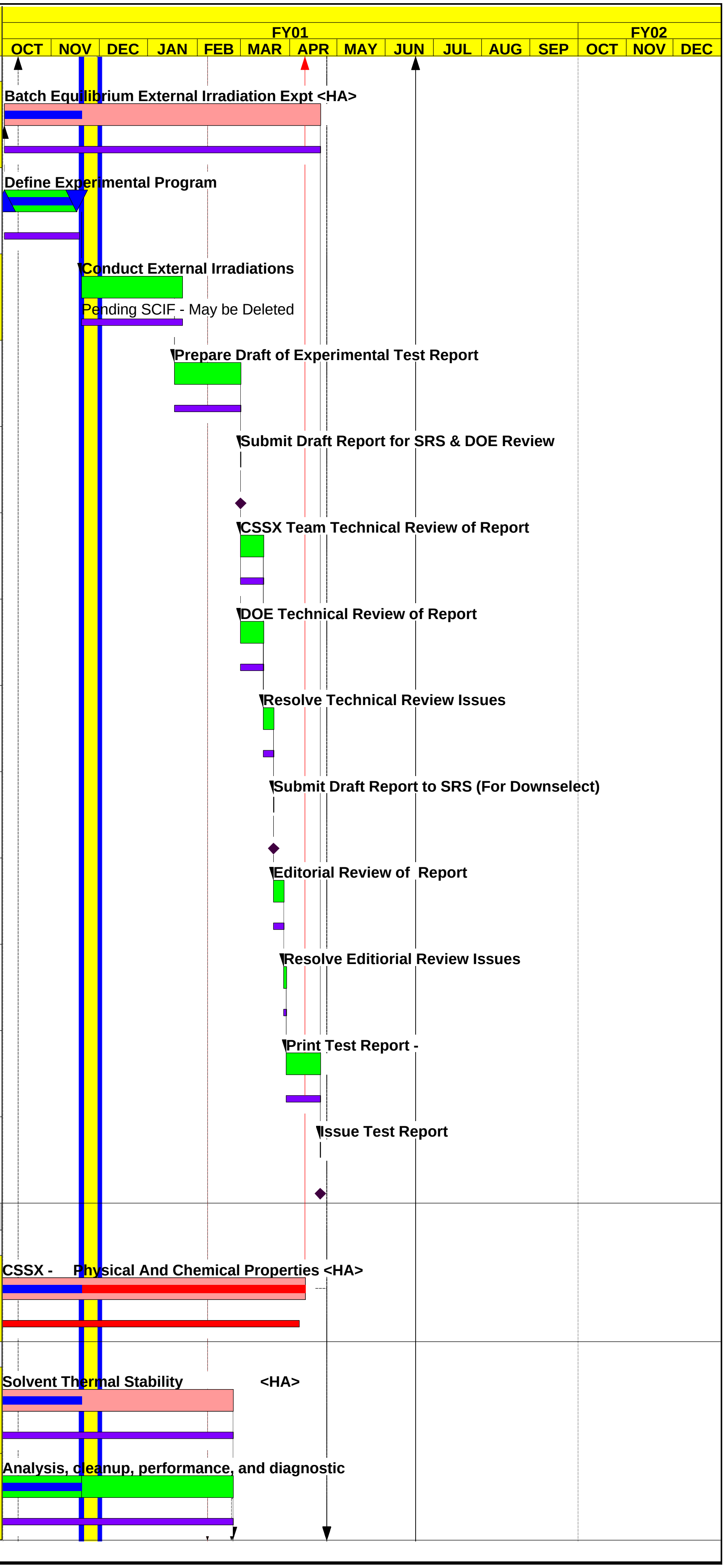
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
Batch Contacting with Single Cs-137 Spike					
WAORN7081	67*	**722**	05SEP00A	21FEB01	LNK
WAORN7082	15*	**-13**	05SEP00A	11DEC00	LNK
WAORN7083	15*	**-13**	05SEP00A	11DEC00	LNK
WAORN7084	1	**-13**	12DEC00	12DEC00	HDH
WAORN7085	11*	**762**	13DEC00	27DEC00	LNK
WAORN7086	7	**1,058**	13DEC00	19DEC00	LNK
WAORN7087	6	**762**	20DEC00	27DEC00	LNK
WAORN7088	51*	**722**	13DEC00	21FEB01	LNK
WAORN7089	11	**-13**	13DEC00	27DEC00	LNK
WAORN7089A	20	**-13**	13DEC00	09JAN01	LNK
WAORN7090	21	**-16**	10JAN01	30JAN01	LNK
WAORN7091	21	**-13**	10JAN01	07FEB01	LNK
WAORN7092	5	**722**	08FEB01	14FEB01	LNK
WAORN7093	5	**722**	15FEB01	21FEB01	LNK
WAORN7094	85*	**21**	06NOV00A	19MAR01	LNK
WAORN7095	85*	**21**	06NOV00A	19MAR01	LNK
WAORN7096	0		01NOV00A	01NOV00A	LNK



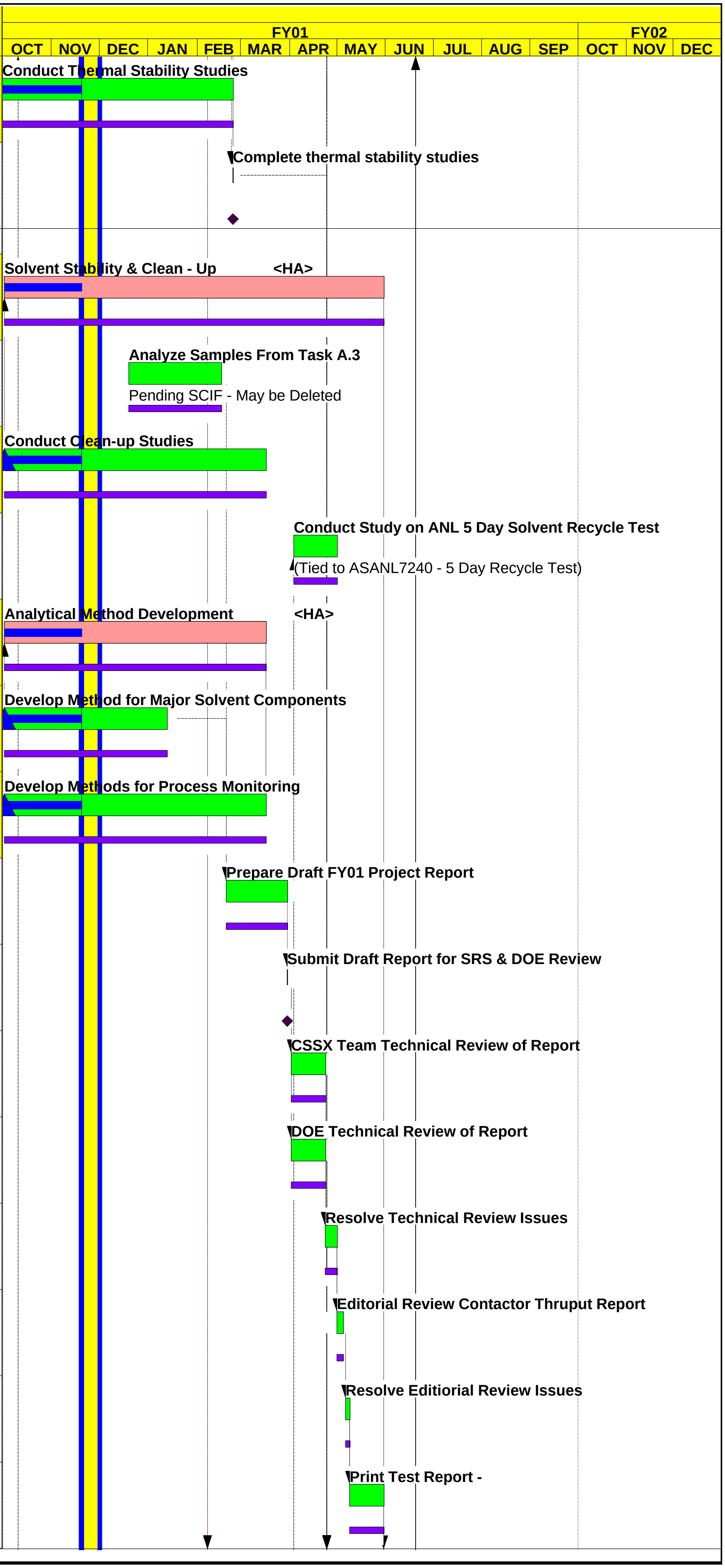
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN7097	85*	21	06NOV00A	19MAR01	LNK
WAORN7098	1	33	05DEC00	05DEC00	LNK
WAORN7099	62*	665	15FEB01	11MAY01	LNK
WAORN7100	0	-2	15FEB01		LNK
WAORN7101	20	-2	16FEB01	15MAR01	LNK
WAORN7102	10	-2	19MAR01	03APR01	LNK
WAORN7102A	10	0	16MAR01	29MAR01	HDH
WAORN7103	5	-3	04APR01	10APR01	LNK
WAORN7104	4	665	11APR01	16APR01	LNK
WAORN7105	3	665	17APR01	19APR01	LNK
WAORN7106	16	665	20APR01	11MAY01	LNK
WAORN7107	0	665		11MAY01	LNK
Batch Irradiation with Simulant					
WAORN7108	110*	-12	03APR00A	23APR01	LNK
WAORN7117	43*	33	03APR00A	18JAN01	LNK
WAORN7124	0		23OCT00A	03NOV00A	LNK
WAORN7125	43*	33	03NOV00A	18JAN01	LNK



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
Batch Equilibrium External Irradiation Experi'mt					
WACX418000	109*	**680**	02OCT00A	20APR01	LNK
WACX418010	0		02OCT00A	16NOV00A	LNK
WACX418100	45	**680**	20NOV00	22JAN01	LNK
WACX418810	30	**680**	18JAN01	28FEB01	LNK
WACX418820	0	**680**		28FEB01	LNK
WACX418830	10	**680**	01MAR01	14MAR01	KJR
WACX418840	10	**680**	01MAR01	14MAR01	JWM
WACX418850	5	**680**	15MAR01	21MAR01	LNK
WACX418860	0	**680**		21MAR01	LNK
WACX418910	4	**680**	22MAR01	27MAR01	LNK
WACX418920	2	**680**	28MAR01	29MAR01	LNK
WACX418930	16	**680**	30MAR01	20APR01	LNK
WACX418990	0	**680**		20APR01	LNK
CSSX - Physical & Chemical Properties					
CSSX - Physical & Chemical Properties					
WAORN7058	101*	**-3**	03APR00A	10APR01	LNK
Solvent Thermal Stability					
WAORN7066	69*	**29**	10MAY00A	23FEB01	LNK
WAORN7067	69*	**30**	10MAY00A	23FEB01	LNK



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN7068A	69*	**29**	23JUN00A	23FEB01	LNK
WAORN7069	0	**29**		23FEB01	LNK
Solvent Stability & Clean-up					
WACX417000	137*	**652**	02OCT00A	30MAY01	LNK
WACX417010	43	**653**	20DEC00*	16FEB01	LNK
WACX417100	84*	**705**	02OCT00A	16MAR01	LNK
WACX417200	19	**674**	04APR01*	30APR01	LNK
WACX417500	84*	**705**	02OCT00A	16MAR01	LNK
WACX417510	39*	**678**	02OCT00A	12JAN01	LNK
WACX417520	84*	**705**	02OCT00A	16MAR01	LNK
WACX417810	29	**652**	20FEB01*	30MAR01	LNK
WACX417820	0	**652**		30MAR01	LNK
WACX417830	16	**652**	02APR01	23APR01	KJR
WACX417840	16	**652**	02APR01	23APR01	JWM
WACX417850	5	**652**	24APR01	30APR01	LNK
WACX417910	4	**652**	01MAY01	04MAY01	LNK
WACX417920	2	**652**	07MAY01	08MAY01	LNK
WACX417930	16	**652**	09MAY01	30MAY01	LNK

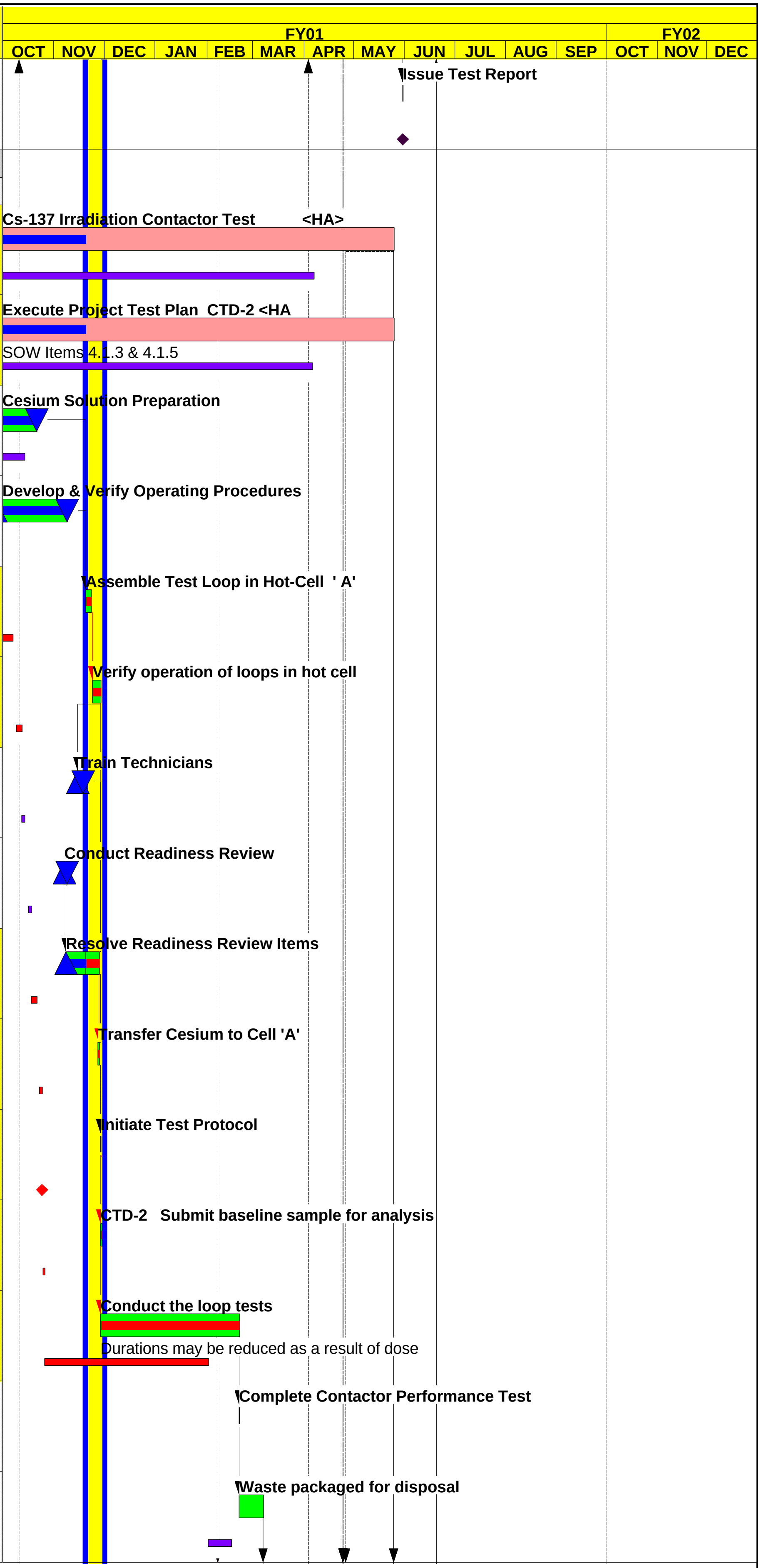


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX417990	0	**652**		30MAY01	LNK

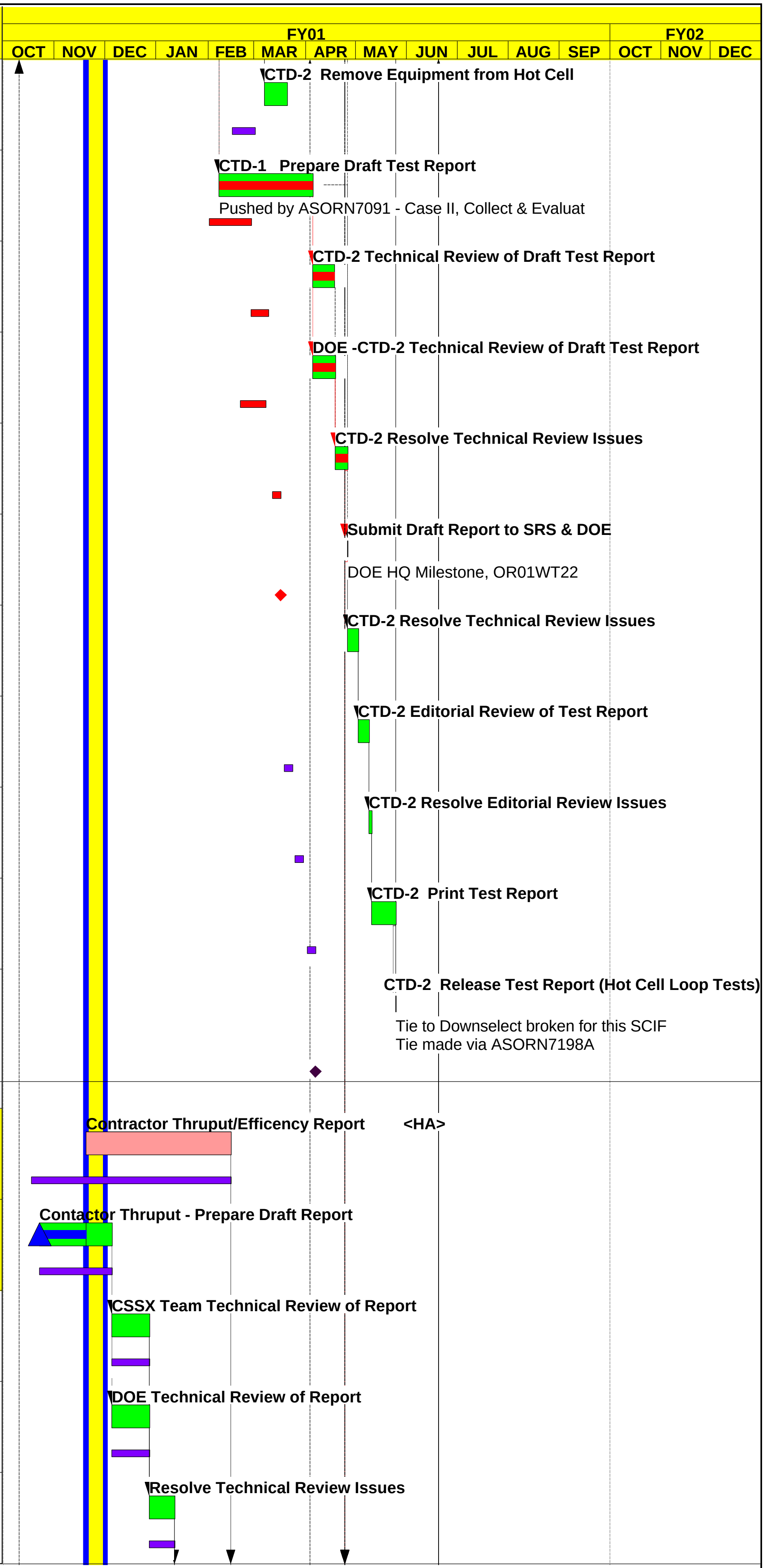
Solvent Decomposition & Contactor Hydraulic Perf

ORNL - CSSX - Contactor Radiation Stability Test

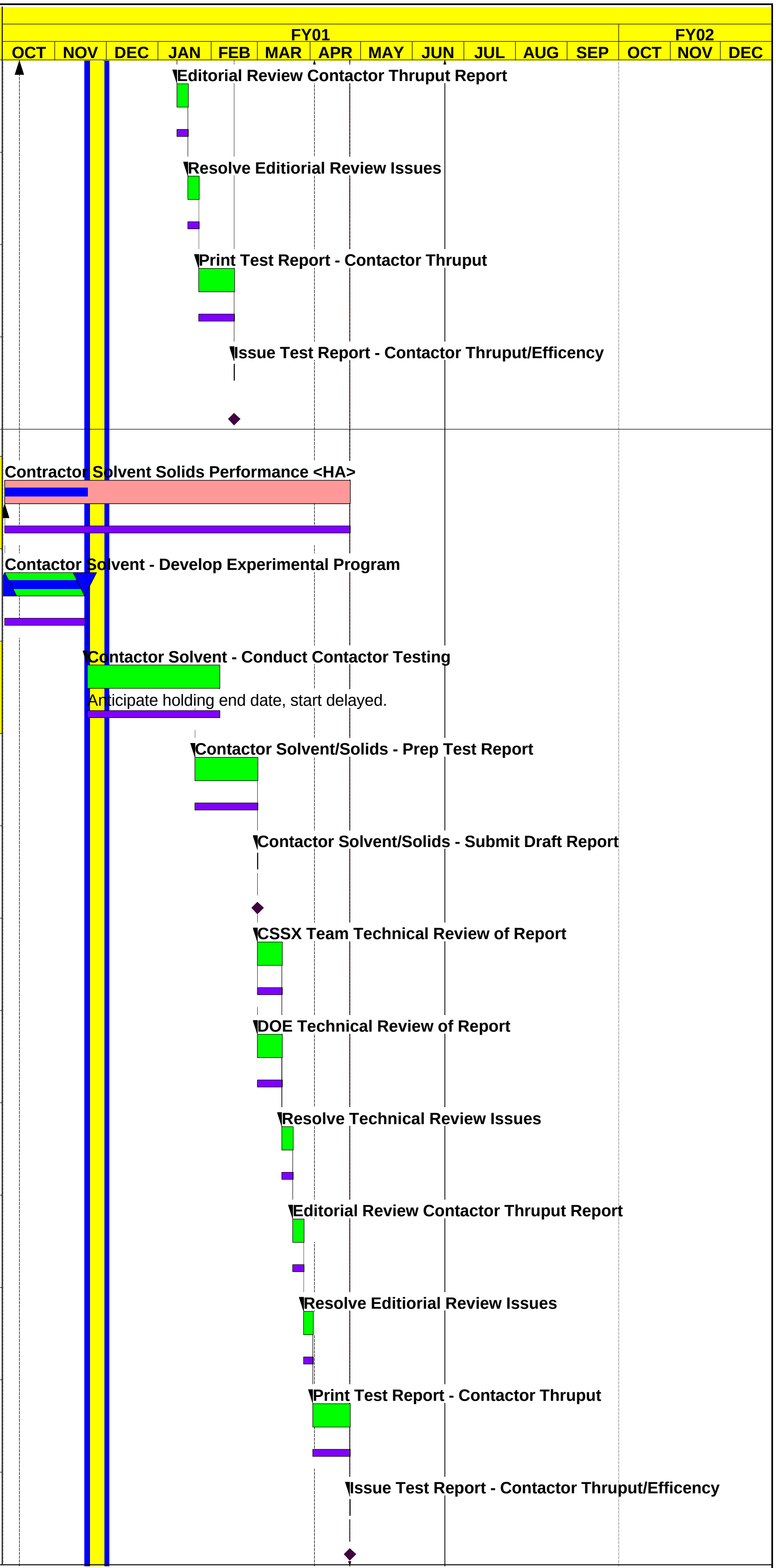
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN7161	133*	**656**	03APR00A	24MAY01	LNK
WAORN7171	133*	**656**	03APR00A	24MAY01	LNK
WAORN7173B	0		18SEP00A	20OCT00A	LNK
WAORN7179C	0		25SEP00A	08NOV00A	LNK
WAORN7180	3	**-12**	20NOV00	22NOV00	LNK
WAORN7182	3	**-12**	24NOV00	28NOV00	LNK
WAORN7182A	0		15NOV00A	17NOV00A	LNK
WAORN7182B	0		07NOV00A	08NOV00A	LNK
WAORN7182C	5	**-10**	08NOV00A	27NOV00	LNK
WAORN7182D	1	**-10**	27NOV00*	27NOV00	LNK
WAORN7183	0	**-12**	29NOV00		LNK
WAORN7184	1	**-12**	29NOV00	29NOV00	LNK
WAORN7192	60	**-12**	29NOV00	20FEB01	LNK
WAORN7192A	0	**723**		20FEB01	LNK
WAORN7194	10	**703**	21FEB01	06MAR01	LNK



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN7195	10	**703**	07MAR01	20MAR01	LNK
WAORN7196	40	**-13**	08FEB01	04APR01	LNK
WAORN7197	9	**-13**	05APR01*	17APR01	KJR
WAORN7197A	9	**-13**	05APR01*	18APR01	HDH
WAORN7198	5	**-14**	19APR01	25APR01	LNK
WAORN7198A	0	**-14**		25APR01	LNK
WAORN7198D	5	**656**	26APR01	02MAY01	LNK
WAORN7199	4	**656**	03MAY01	08MAY01	LNK
WAORN7200	2	**656**	09MAY01	10MAY01	LNK
WAORN7201	10	**656**	11MAY01	24MAY01	LNK
WAORN7202	0	**656**		24MAY01	LNK
Contactor Thruput Efficency Report					
WACX41300	62*	**727**	20NOV00	14FEB01	LNK
WACX41310	10*	**727**	23OCT00A	04DEC00	LNK
WACX41330	17	**727**	05DEC00	27DEC00	KJR
WACX41340	17	**727**	05DEC00	27DEC00	JWM
WACX41350	11	**727**	28DEC00	11JAN01	LNK

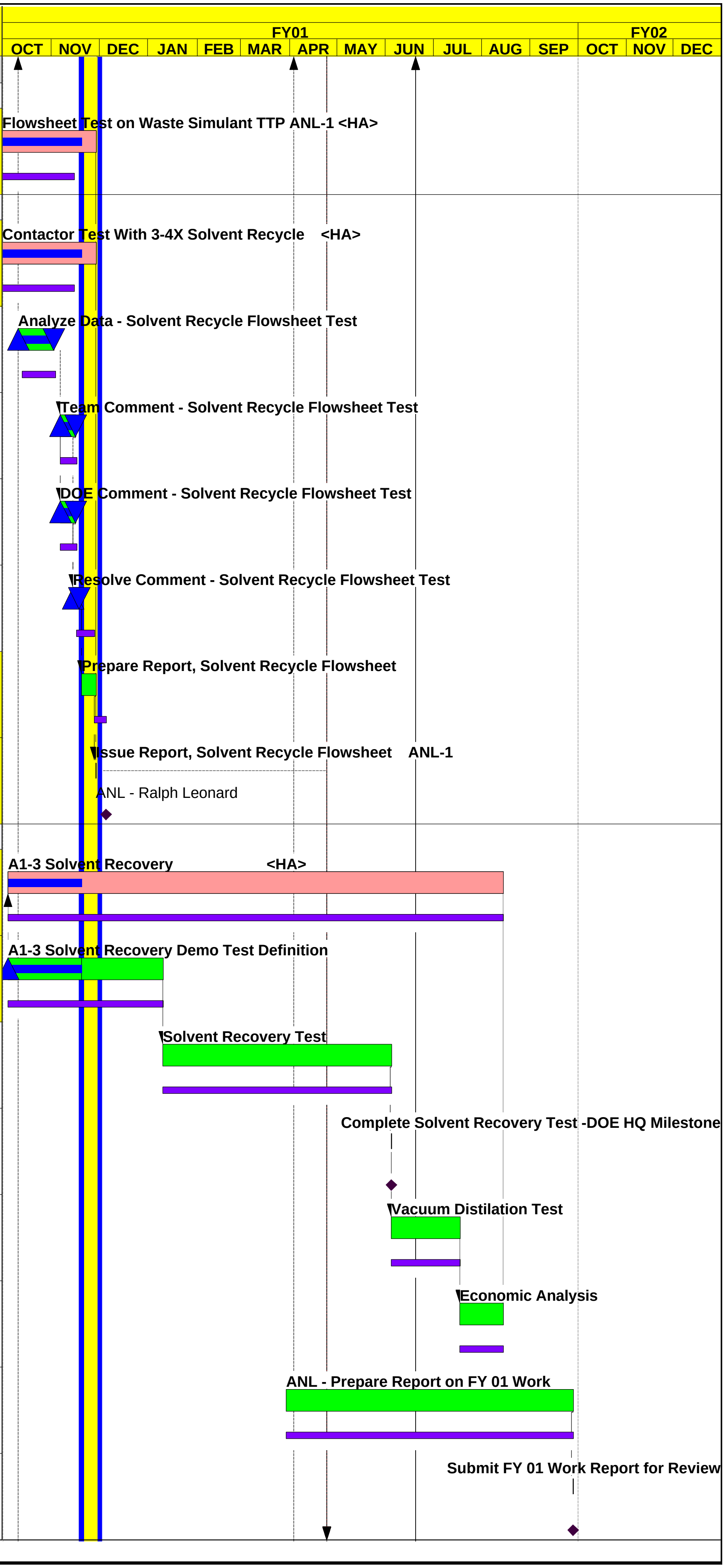


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX41360	5	**727**	12JAN01	18JAN01	LNK
WACX41365	4	**727**	19JAN01	24JAN01	LNK
WACX41370	15	**727**	25JAN01	14FEB01	KJR
WACX41380	0	**727**		14FEB01	JWM
Contactor Solvent Solids Performance					
WACX41400	111*	**678**	02OCT00A	24APR01	LNK
WACX414010	0		02OCT00A	17NOV00A	LNK
WACX414012	55*	**678**	20NOV00	05FEB01	LNK
WACX414016	27	**678**	23JAN01	28FEB01	LNK
WACX414018	0	**678**		28FEB01	LNK
WACX414020	10	**678**	01MAR01	14MAR01	KJR
WACX414030	10	**678**	01MAR01	14MAR01	JWM
WACX414040	5	**678**	15MAR01	21MAR01	LNK
WACX414050	4	**678**	22MAR01	27MAR01	LNK
WACX414060	4	**678**	28MAR01	02APR01	LNK
WACX414070	16	**678**	03APR01	24APR01	KJR
WACX414080	0	**678**		24APR01	JWM

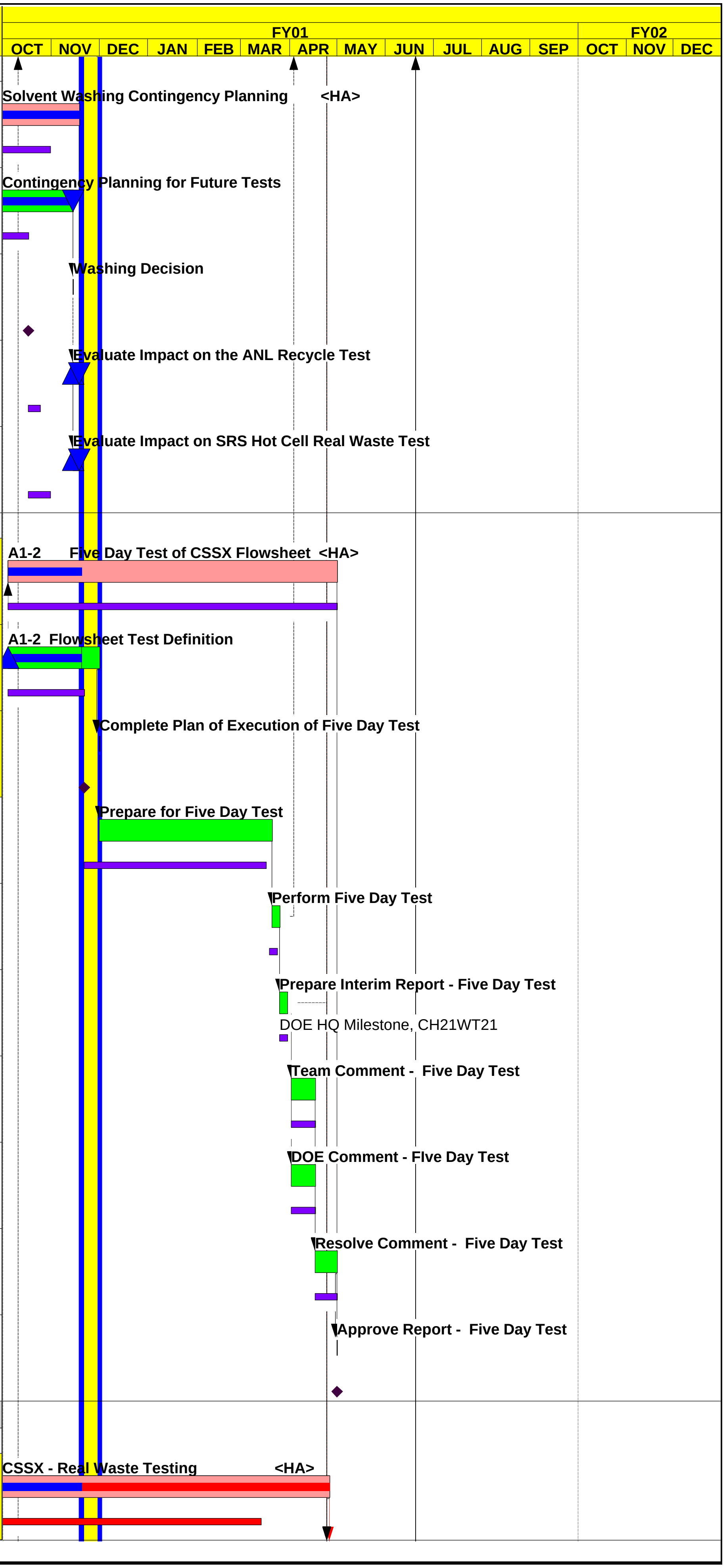


Anticipate holding end date, start delayed.

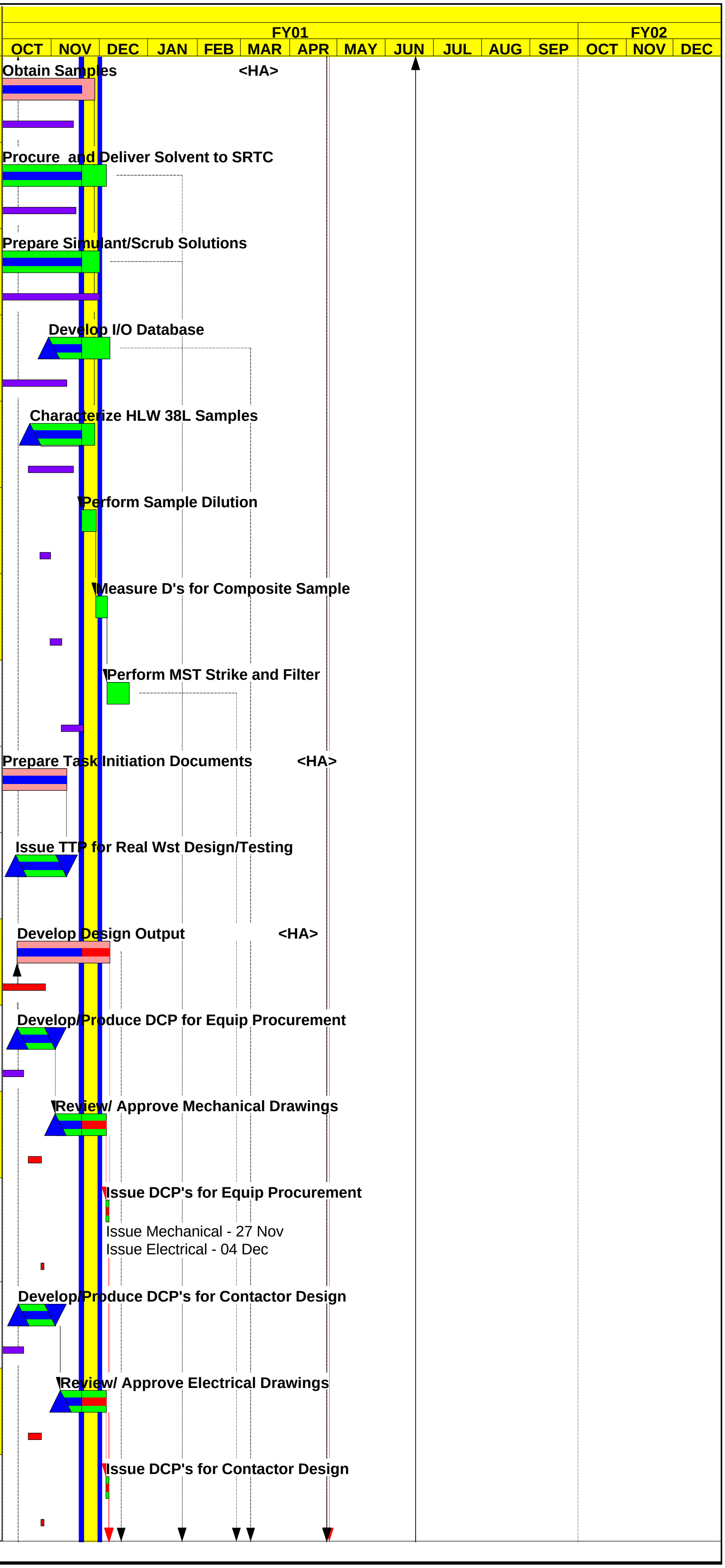
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
Waste Simulant & 2 cm Contactor Flowsheet					
ORNL - CSSX - Proof of Concept					
WAORN7036	6*	**92**	03APR00A	28NOV00	LNK
Contactor Test with 3 - 4 x Solvent Recycle					
WAORN7048	6*	**92**	03APR00A	28NOV00	LNK
WAORN7055A	0		11OCT00A	01NOV00A	LNK
WAORN7055B	0		06NOV00A	15NOV00A	KJR
WAORN7055C	0		06NOV00A	15NOV00A	JWM
WAORN7055D	0		14NOV00A	17NOV00A	LNK
WAORN7055E	5	**88**	20NOV00	28NOV00	LNK
WAORN7056	0	**88**		28NOV00	LNK
Solvent Recovery					
WAANL7300	183*	**592**	04OCT00A	14AUG01	RL
WAANL7310	33*	**592**	04OCT00A	10JAN01	RL
WAANL7320	145	**862**	11JAN01	04JUN01	RL
WAANL7322	0	**862**		04JUN01	RL
WAANL7330	24	**471**	05JUN01	17JUL01	RL
WAANL7350	20	**592**	18JUL01	14AUG01	RL
WAANL7410	126	**561**	30MAR01*	27SEP01	RL
WAANL7420	0	**561**		27SEP01	RL



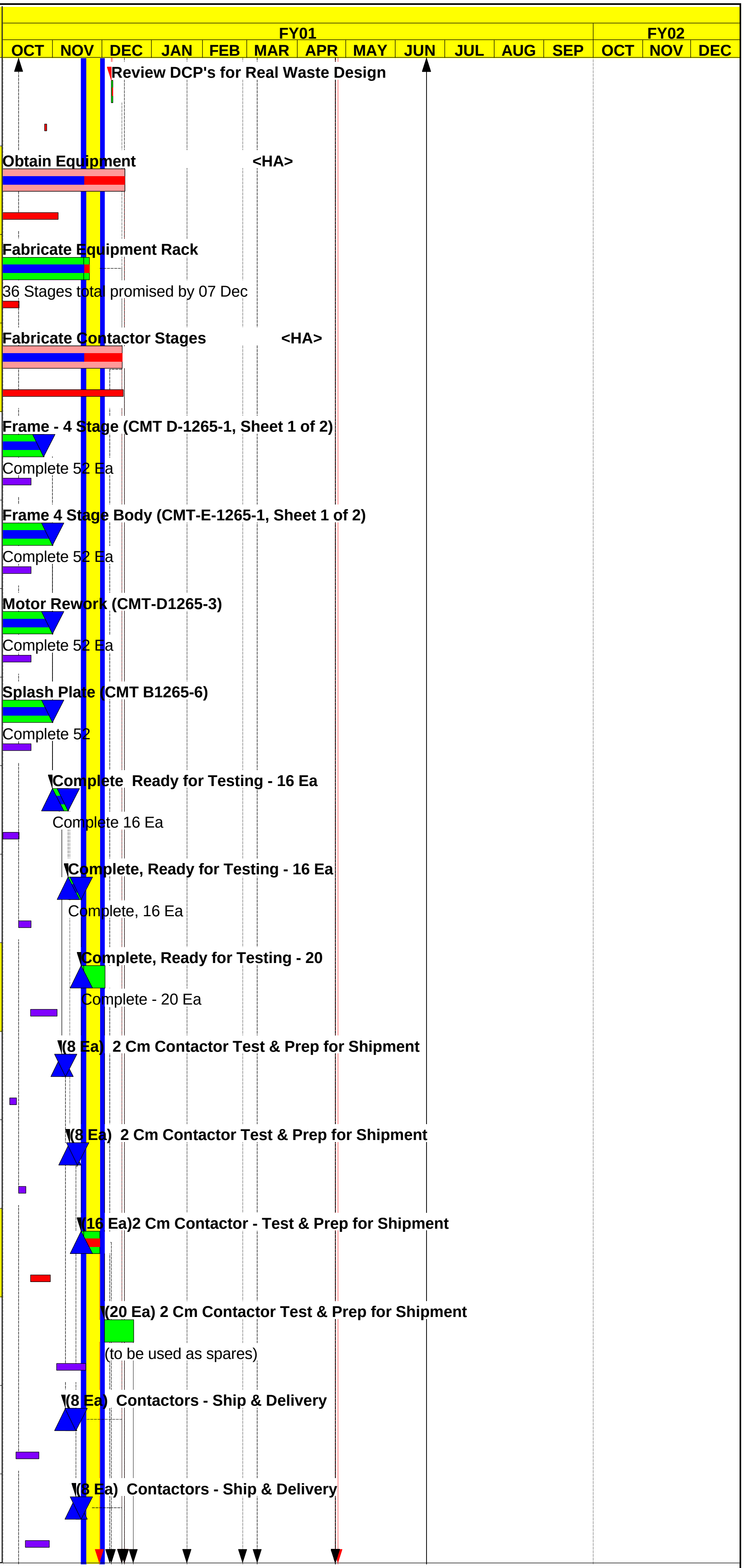
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
CSSX - Solvent Washing Plan & Evaluation					
WAORN70551	0*		18SEP00A	17NOV00A	LNK
WAORN70552	0		18SEP00A	13NOV00A	LNK
WAORN70553	0			13NOV00A	LNK
WAORN70555	0		14NOV00A	17NOV00A	LNK
WAORN70556	0*		14NOV00A	17NOV00A	LNK
Five Day Test of CSSX Flowsheet					
WAANL7200	109*	**666**	04OCT00A	30APR01	RL
WAANL7210	7*	**3**	04OCT00A	30NOV00	RL
WAANL7220	0	**3**		30NOV00	RL
WAANL7230	74	**3**	01DEC00*	20MAR01	RL
WAANL7240	5	**4**	21MAR01*	25MAR01	RL
WAANL7250	5	**4**	26MAR01	30MAR01	RL
WAANL7254	8	**530**	02APR01	16APR01	KJR
WAANL7256	10	**666**	02APR01	16APR01	JWM
WAANL7258	10	**666**	17APR01	30APR01	RL
WAANL7259	0	**666**		30APR01	KJR
CSSX - Real Waste Contactor Testing					
CSSX - Real Waste Contactor Testing					
WACX1000	84*	**-10**	10MAY00A	25APR01	RWB



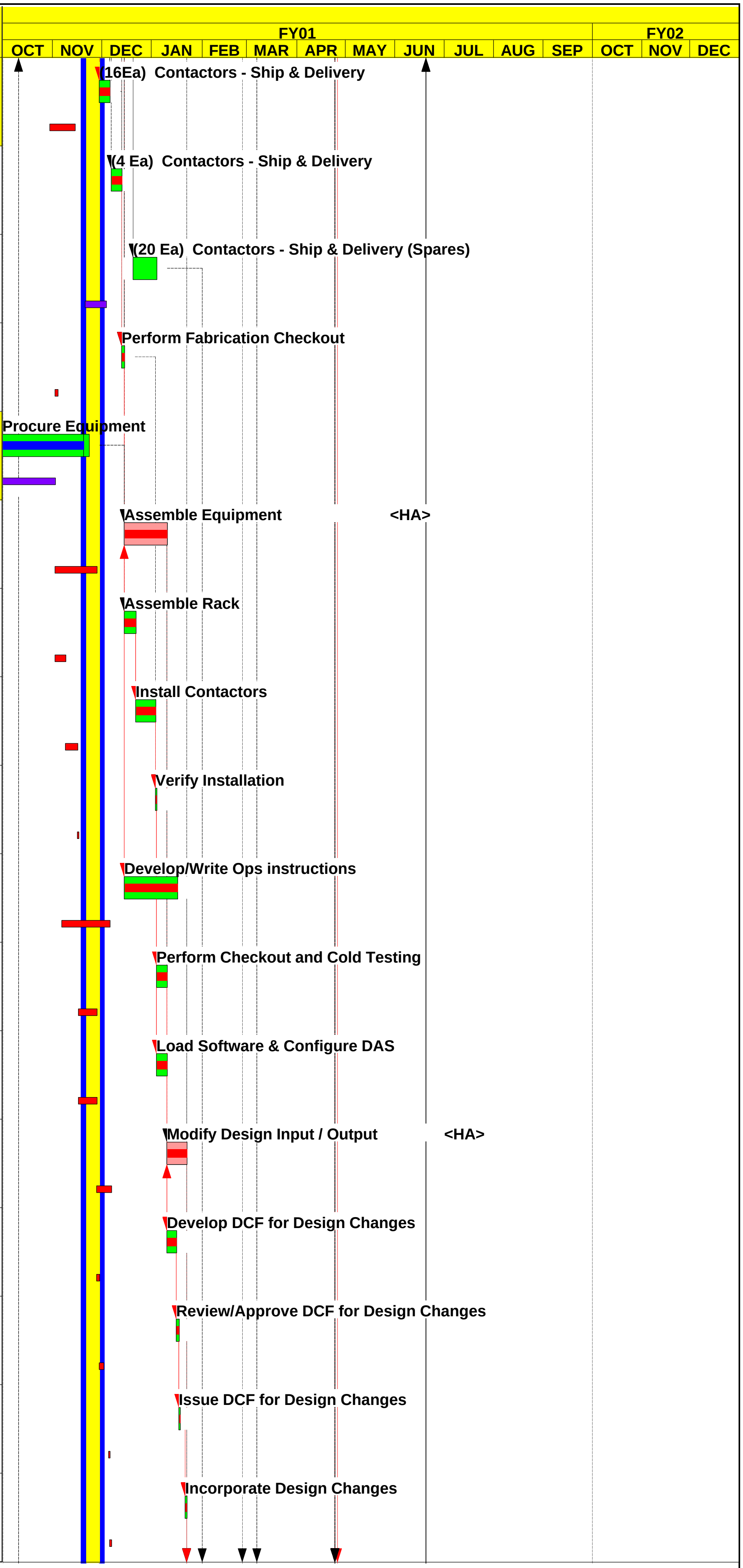
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX2300	4*	**31**	03AUG00A	27NOV00	RNH
WACX2300A	9*	**19**	02AUG00A	04DEC00	LNK
WACX2300B	7*	**21**	02AUG00A	30NOV00	RAP
WACX2300C	12*	**46**	30OCT00A	07DEC00	TRT
WACX2305	4	**31**	18OCT00A	27NOV00	RAP
WACX2306	5	**31**	20NOV00	28NOV00	RAP
WACX2307	5	**31**	29NOV00	05DEC00	RAP
WACX2308	10	**31**	06DEC00	19DEC00	RAP
WACX2320	0*		08AUG00A	09NOV00A	RAP
WACX2325	0		09OCT00A	09NOV00A	RAP
WACX2340	10*	**-8**	10OCT00A	07DEC00	LC
WACX2341	0		10OCT00A	02NOV00A	LC
WACX2342	9*	**-11**	03NOV00A	04DEC00	LC
WACX2343	2	**-8**	05DEC00	06DEC00	LC
WACX2344	0		11OCT00A	02NOV00A	LC
WACX2345	9*	**-11**	06NOV00A	04DEC00	LC
WACX2346	2	**-8**	05DEC00	06DEC00	LC



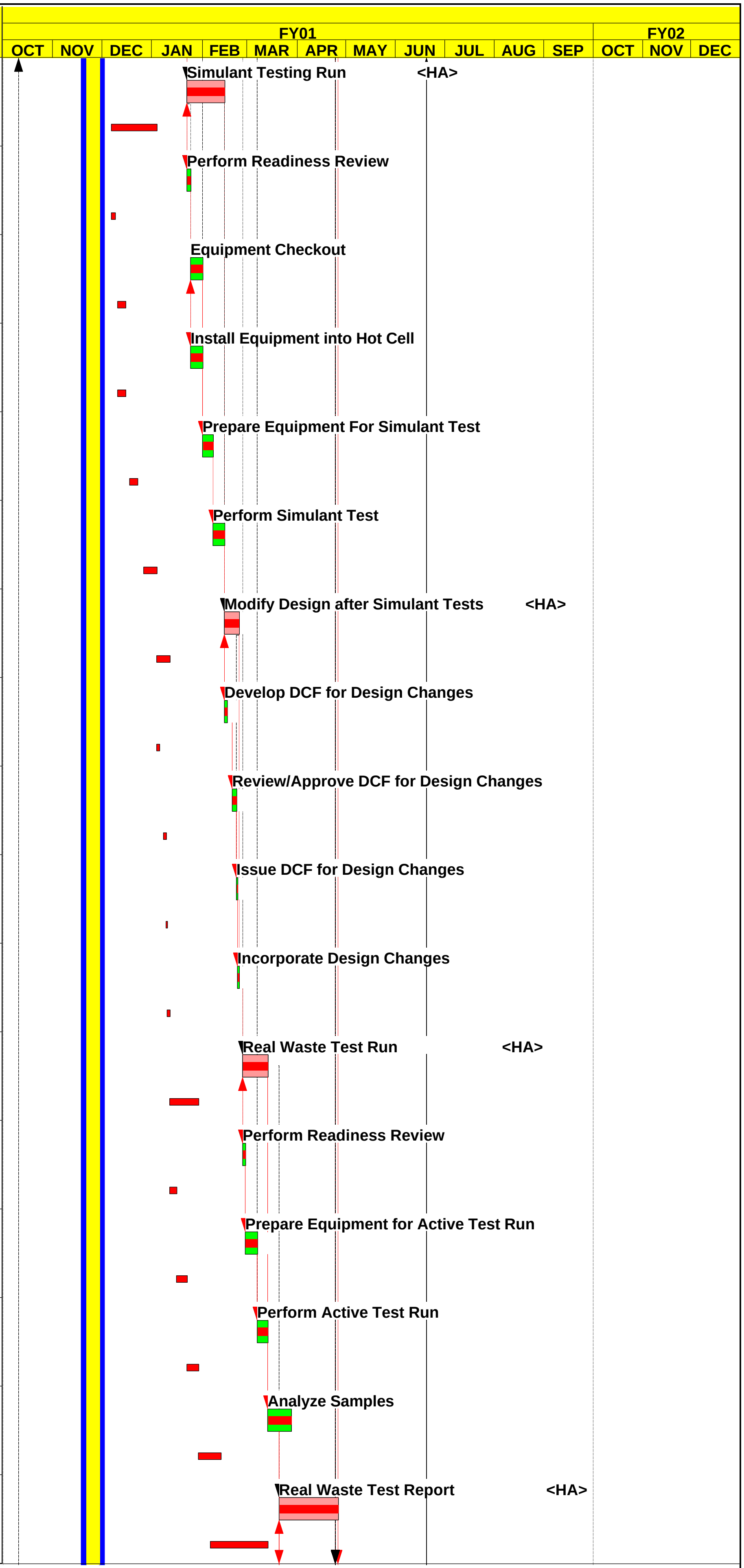
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX2347	1	**-8**	07DEC00	07DEC00	LC
WACX2360	17*	**-13**	02AUG00A	14DEC00	RAP
WACX2361	3*	**-1**	20SEP00A	22NOV00	RAP
WACX236200	15*	**-13**	20SEP00A	12DEC00	RAP
WACX236201	0		20SEP00A	25OCT00A	RAP
WACX236202	0		20SEP00A	31OCT00A	RAP
WACX236204	0		20SEP00A	31OCT00A	RAP
WACX236207	0		20SEP00A	31OCT00A	RAP
WACX236272	0*		01NOV00A	09NOV00A	RL
WACX236274	0		10NOV00A	17NOV00A	RL
WACX236276	13*	**9**	18NOV00A	02DEC00	RL
WACX236282	0		06NOV00A	08NOV00A	RL
WACX236284	0		11NOV00A	15NOV00A	RL
WACX236286	10*	**-14**	18NOV00A	29NOV00	RL
WACX236288	18	**9**	03DEC00	20DEC00	RL
WACX236292	0		09NOV00A	14NOV00A	RL
WACX236294	0		15NOV00A	17NOV00A	RL



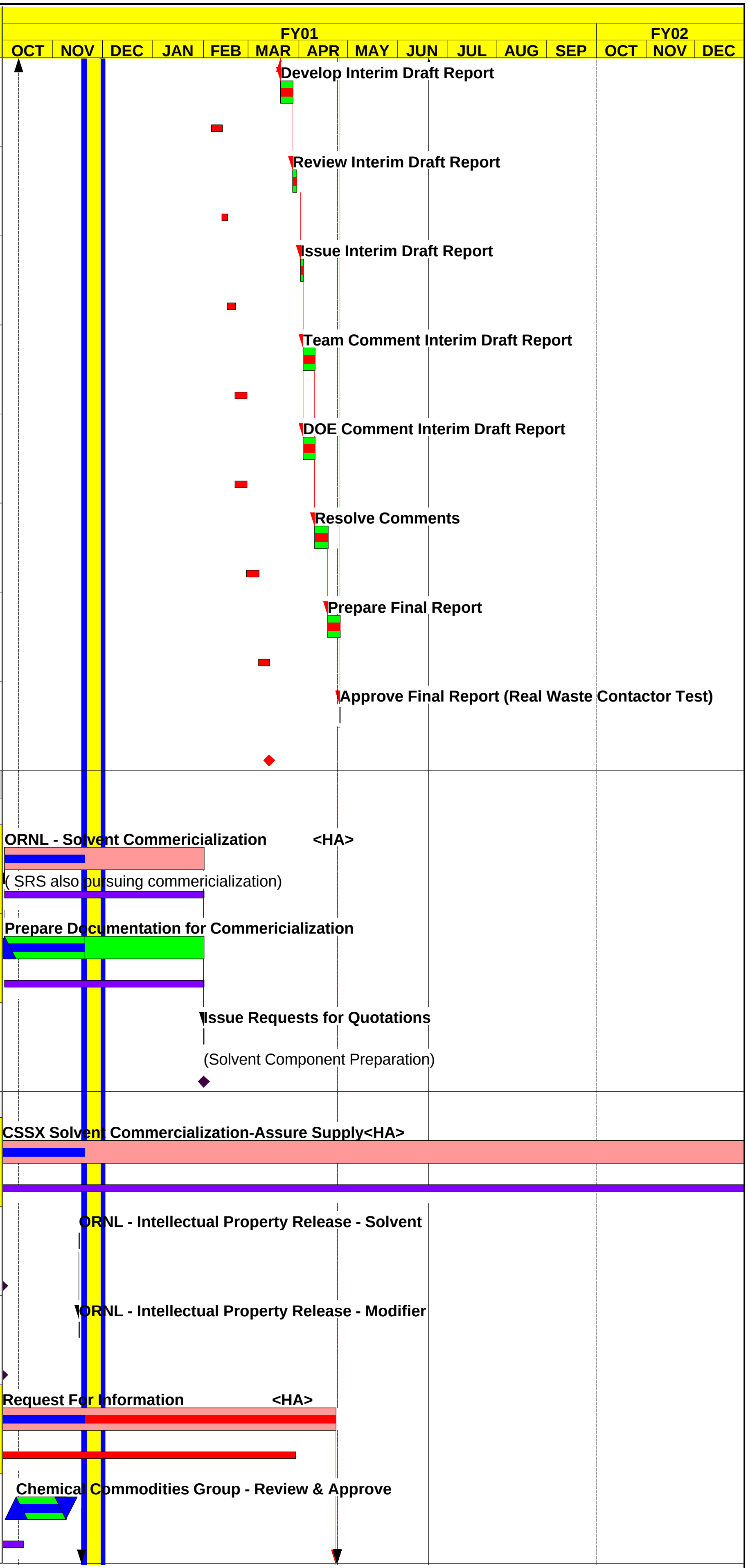
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX236296	6	**-14**	30NOV00	05DEC00	RL
WACX236297	6	**-21**	07DEC00*	12DEC00	RL
WACX236298	14	**9**	21DEC00	03JAN01	RL
WACX2363	2	**-13**	13DEC00	14DEC00	RAP
WACX2364	3*	**5**	02AUG00A	22NOV00	RAP
WACX2370	16*	**-13**	15DEC00	10JAN01	RAP
WACX2371	5	**-13**	15DEC00	21DEC00	RAP
WACX2372	5	**-13**	22DEC00	02JAN01	RAP
WACX2373	1	**-13**	03JAN01	03JAN01	RAP
WACX2374	20	**-9**	15DEC00	16JAN01	RAP
WACX2375	5	**-13**	04JAN01	10JAN01	RAP
WACX2376	5	**-13**	04JAN01	10JAN01	RAP
WACX2390	6*	**-10**	11JAN01	22JAN01	LC
WACX2391	2	**-10**	11JAN01	15JAN01	LC
WACX2392	2	**-10**	16JAN01	17JAN01	LC
WACX2393	1	**-10**	18JAN01	18JAN01	LC
WACX2394	1	**-10**	22JAN01	22JAN01	LC



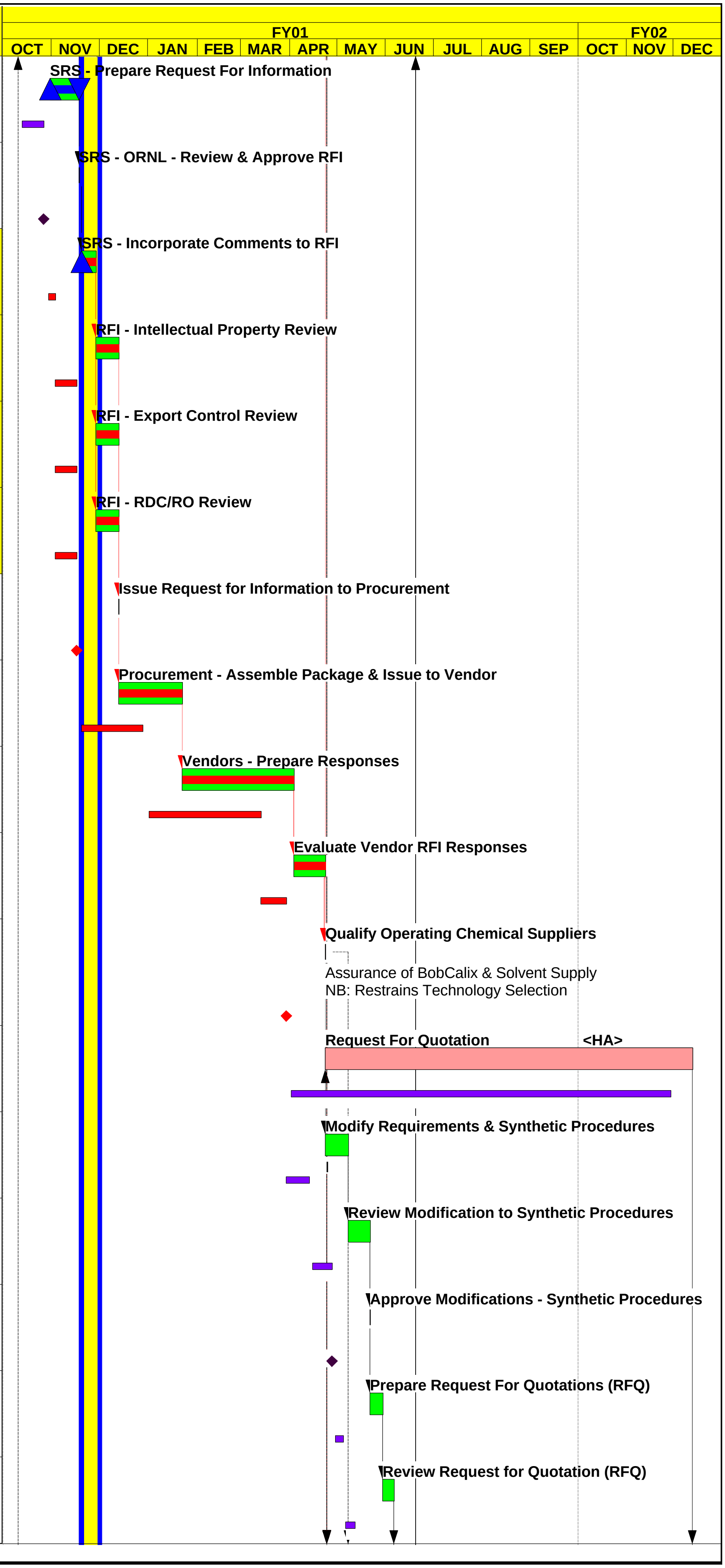
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX2400	17*	**-13**	23JAN01	14FEB01	RAP
WACX2401	2	**-13**	23JAN01	24JAN01	RAP
WACX2402	5	**-13**	25JAN01	31JAN01	RAP
WACX2403	5	**-13**	25JAN01	31JAN01	RAP
WACX2404	5	**-13**	01FEB01	07FEB01	RAP
WACX2405	5	**-13**	08FEB01	14FEB01	RAP
WACX2410	6*	**-13**	15FEB01	23FEB01	LC
WACX2411	2	**-13**	15FEB01	16FEB01	LC
WACX2412	2	**-13**	20FEB01	21FEB01	LC
WACX2413	1	**-13**	22FEB01	22FEB01	LC
WACX2414	1	**-13**	23FEB01	23FEB01	LC
WACX2420	12*	**-13**	26FEB01	13MAR01	RAP
WACX2421	2	**-13**	26FEB01	27FEB01	RAP
WACX2422	5	**-13**	28FEB01	06MAR01	RAP
WACX2423	5	**-13**	07MAR01	13MAR01	RAP
WACX2424	10	**-13**	14MAR01	27MAR01	RAP
WACX2430	25*	**-13**	21MAR01	25APR01	RAP



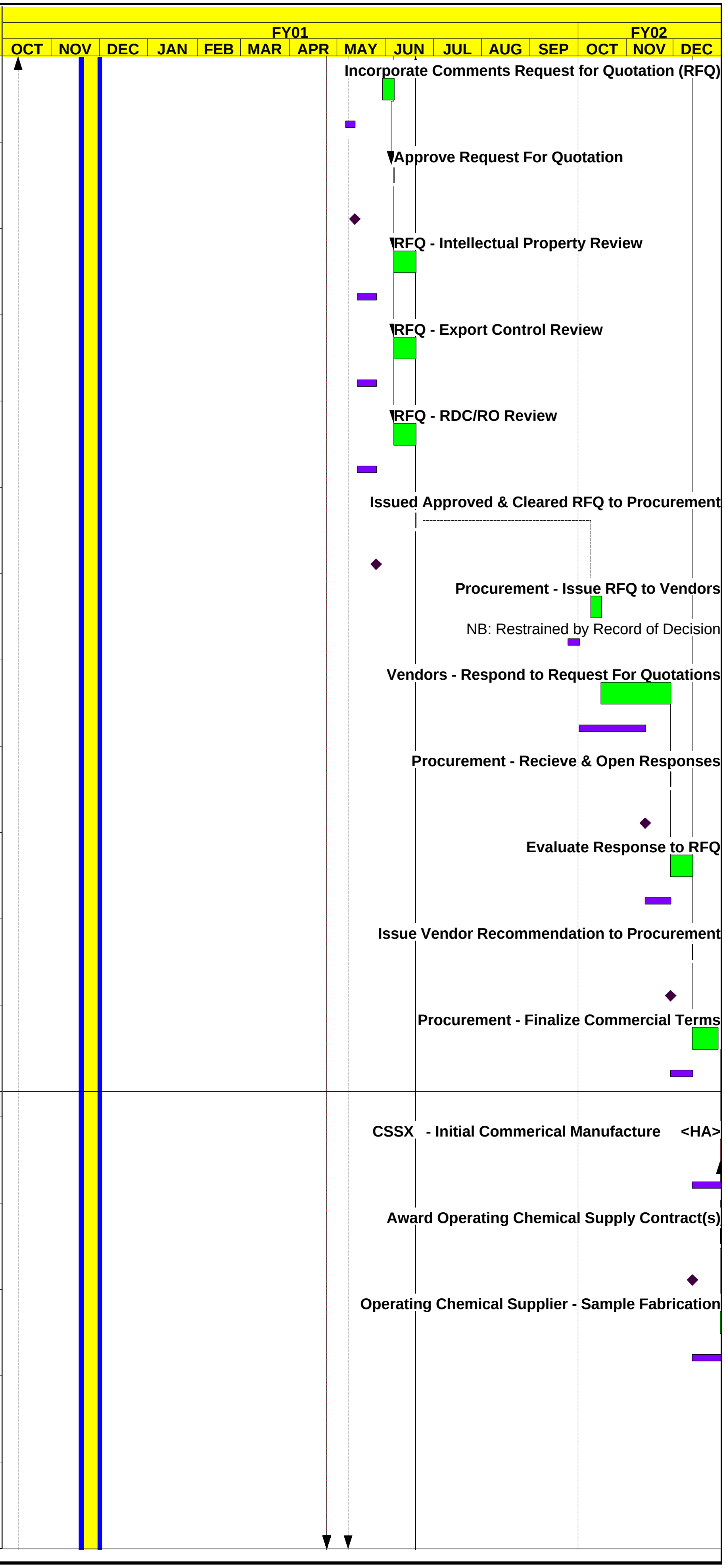
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX2431	5	**-13**	21MAR01	27MAR01	RAP
WACX2432	3	**-13**	28MAR01	30MAR01	RAP
WACX2433	2	**-13**	02APR01	03APR01	RAP
WACX2434	5	**-13**	04APR01	10APR01	KJR
WACX2435	5	**-13**	04APR01	10APR01	JWM
WACX2436	5	**-13**	11APR01	18APR01	RAP
WACX2437	5	**-13**	19APR01	25APR01	RAP
WACX2438	0	**-13**		25APR01	KJR
CSSX - Solvent Commercialization & Supply					
Solvent Commericialization					
WACX416000	52*	**737**	02OCT00A	31JAN01	LNK
WACX416100	52*	**737**	02OCT00A	31JAN01	LNK
WACX416200	0	**737**		31JAN01	LNK
CSSX - Commercialization & Supply Assurance					
WACX33000	368*	**249**	10MAY00A	26SEP02	RWB
WACX33110	0	**617**		16NOV00	RWB
WACX33120	0	**617**		16NOV00	RWB
WACX33300	82*	**-2**	10MAY00A	23APR01	RWB
WACX33340	0		09OCT00A	08NOV00A	RWB



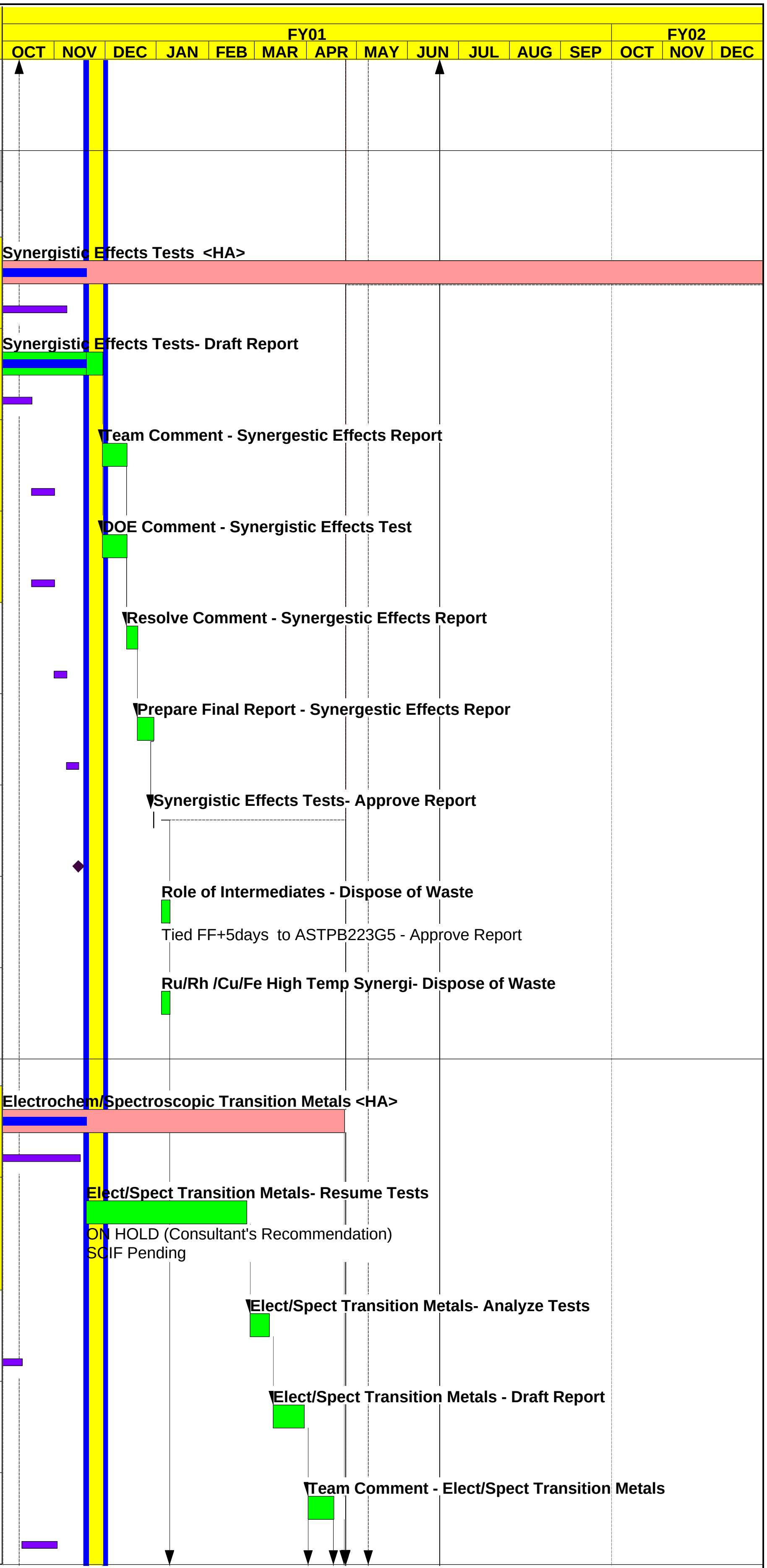
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX33410	0		31OCT00A	17NOV00A	RWB
WACX33420	0			17NOV00A	RWB
WACX33430	4*	**-2**	20NOV00A	28NOV00	RWB
WACX33440	10	**-3**	29NOV00	12DEC00	RWB
WACX33450	10	**-3**	29NOV00	12DEC00	RWB
WACX33460	10	**-3**	29NOV00	12DEC00	RWB
WACX33470	0	**-2**		12DEC00	RWB
WACX33480	20	**-2**	13DEC00	22JAN01	RWB
WACX33520	40	**-2**	23JAN01	03APR01	RWB
WACX33530	10	**-2**	04APR01	23APR01	RWB
WACX33540	0	**-2**		23APR01	RWB
WACX33600	129*	**248**	24APR01	12DEC01	RWB
WACX33610	10	**390**	24APR01	07MAY01	RWB
WACX33620	10	**390**	08MAY01	21MAY01	RWB
WACX33630	0	**390**		21MAY01	RWB
WACX33640	5	**390**	22MAY01	29MAY01	RWB
WACX33650	5	**390**	30MAY01	05JUN01	RWB



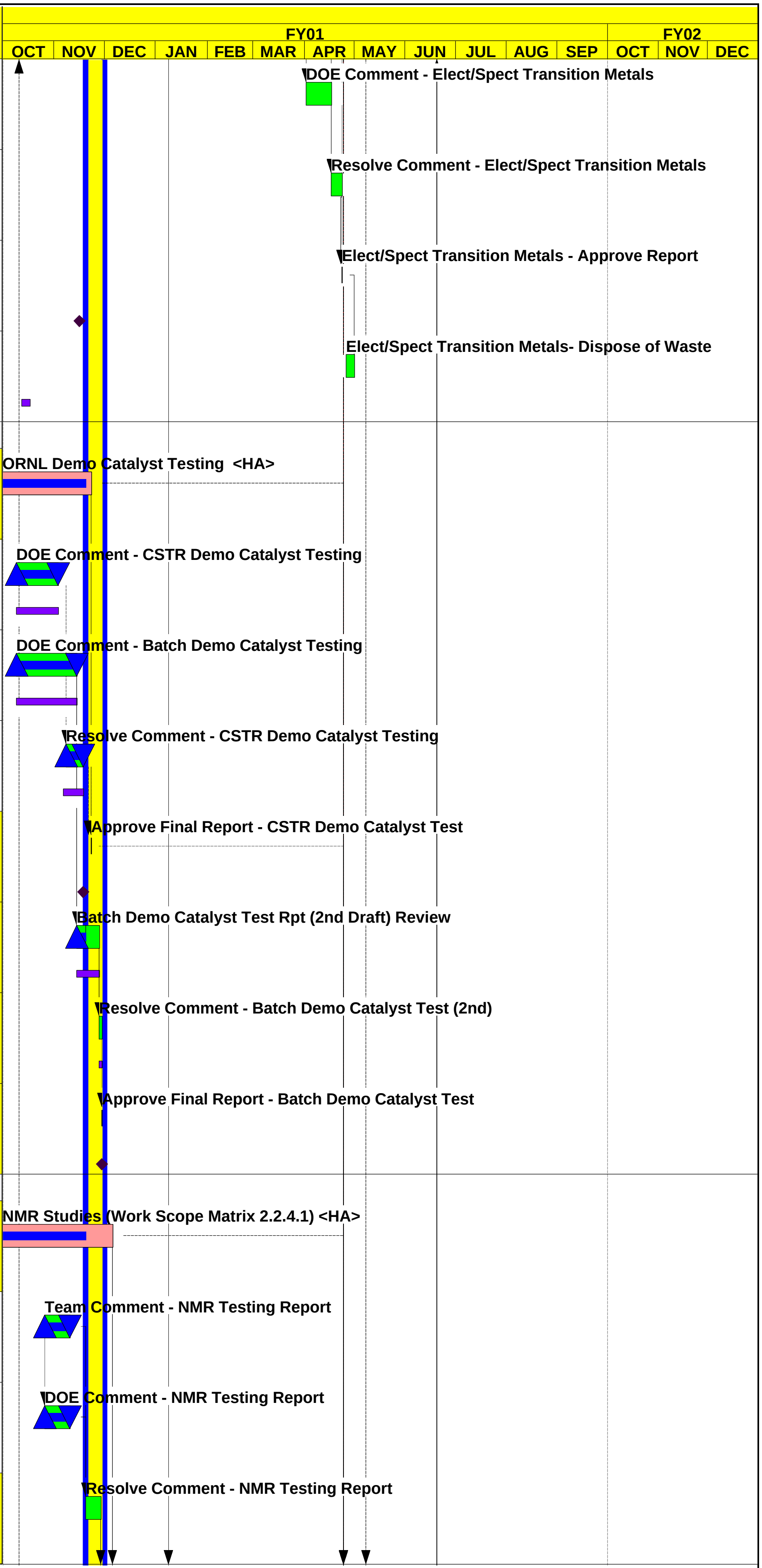
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX33660	5	**390**	30MAY01	05JUN01	RWB
WACX33670	0	**390**		05JUN01	RWB
WACX33680	10	**390**	06JUN01	19JUN01	RWB
WACX33700	10	**390**	06JUN01	19JUN01	RWB
WACX33710	10	**390**	06JUN01	19JUN01	RWB
WACX33720	0	**390**		19JUN01	RWB
WACX33730	5	**313**	09OCT01	15OCT01	RWB
WACX33740	30	**313**	16OCT01	28NOV01	RWB
WACX33750	0	**313**		28NOV01	RWB
WACX33760	10	**313**	29NOV01	12DEC01	RWB
WACX33770	0	**313**		12DEC01	RWB
WACX33780	10	**313**	13DEC01	28DEC01	RWB
CSSX - Operating Chemical Supply & Fabrication					
WACX33900	150*	**249**	31DEC01	26SEP02	RWB
WACX33910	0	**249**	31DEC01		RWB
WACX33920	60	**249**	31DEC01	17APR02	RWB
WACX33930	20	**249**	18APR02	22MAY02	RWB
WACX33940	10	**249**	23MAY02	11JUN02	RWB



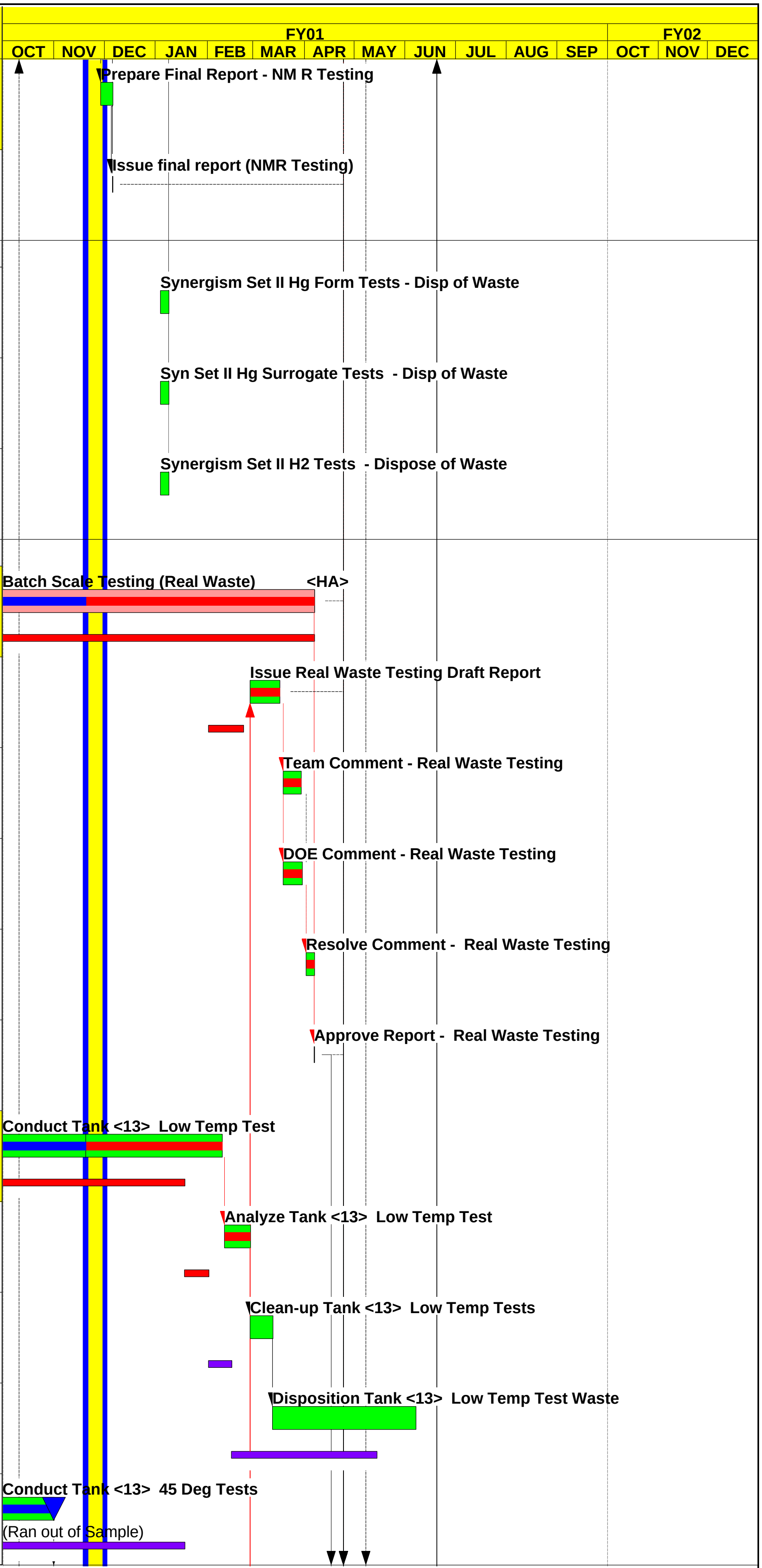
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACX33950	60	**249**	12JUN02	26SEP02	RWB
Small Tank TPB Precipitation					
Tetraphenyborate Decomposition Studies					
TPB - Examine Synergistic Effects					
WATPB223	464*	**311**	28JAN00A	26SEP02	MJB
WATPB223G	6*	**66**	19JUL00A	29NOV00	MJB
WATPB223G1	8	**52**	30NOV00	13DEC00	KJR
WATPB223G2	10	**67**	30NOV00	13DEC00	JWM
WATPB223G3	5	**67**	14DEC00	20DEC00	MJB
WATPB223G4	5	**67**	21DEC00	29DEC00	MJB
WATPB223G5	0	**67**		29DEC00	KJR
WATPB223G6	3	**744**	04JAN01	08JAN01	MJB
WATPB226P	3	**744**	04JAN01	08JAN01	MJB
Electrochem/Spectroscopic Transition Metal Test					
WATPB225	104*	**111**	24JAN00A	23APR01	TBP
WATPB225D	64	**111**	20NOV00	23FEB01	TBP
WATPB225E	10	**111**	26FEB01	09MAR01	TBP
WATPB225F	15	**111**	12MAR01	30MAR01	TBP
WATPB225G	8	**88**	02APR01	16APR01	KJR



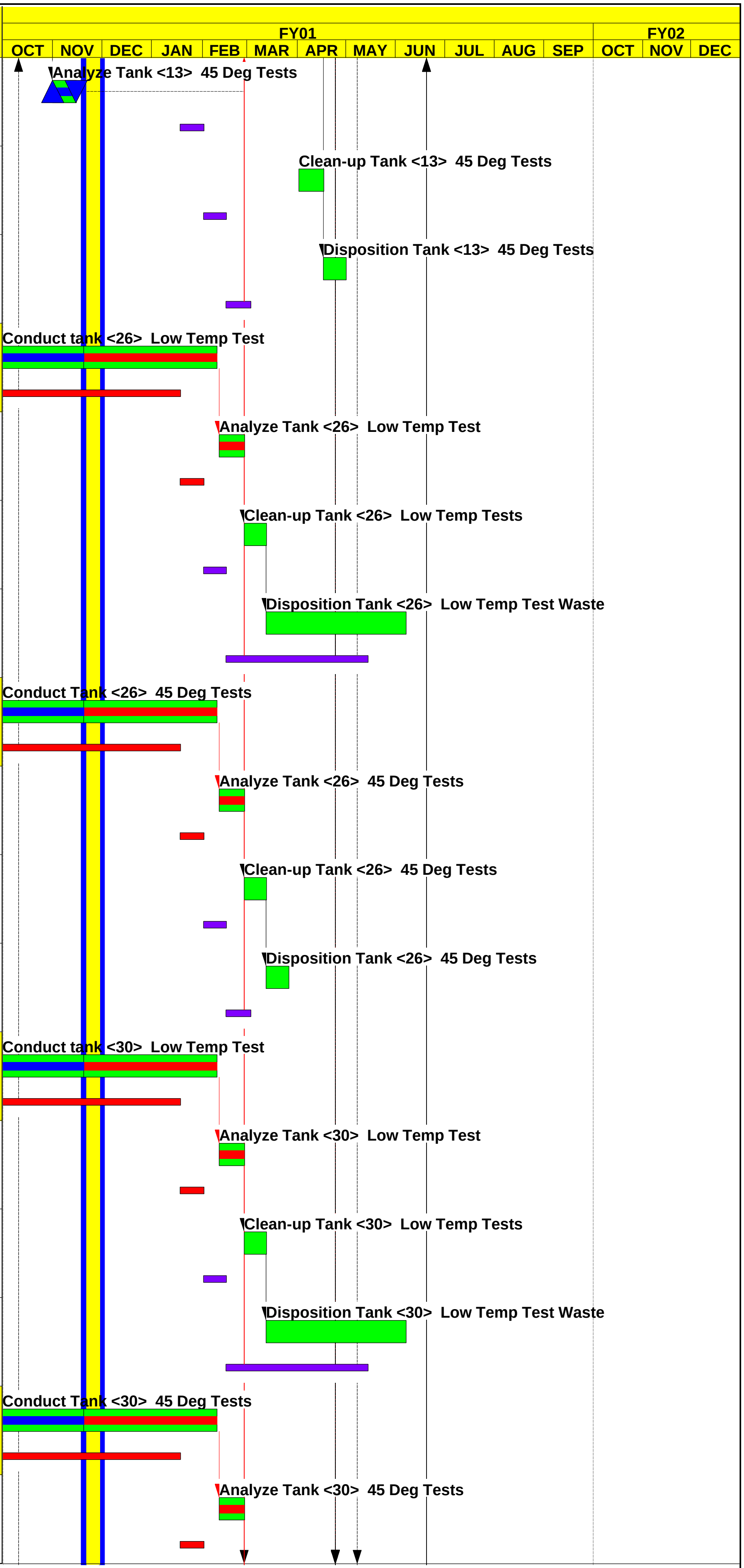
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB225H	10	**111**	02APR01	16APR01	JWM
WATPB225I	5	**111**	17APR01	23APR01	TBP
WATPB225K	0	**111**		23APR01	KJR
WATPB225P	3	**666**	26APR01	30APR01	TBP
Demo Catalyst Testing					
WATPB228	3*	**90**	21JUN00A	22NOV00	MJB
WATPB228S	0		09OCT00A	02NOV00A	JWM
WATPB228S2	0		09OCT00A	13NOV00A	JWM
WATPB228T	0		08NOV00A	17NOV00A	LNO
WATPB228U	0	**90**		22NOV00*	KJR
WATPB228V	4*	**769**	14NOV00A	27NOV00	LNO
WATPB228W	2	**769**	28NOV00	29NOV00	LNO
WATPB228X	0	**769**		29NOV00	KJR
NMR Testing					
WAORNL2001	11*	**87**	08DEC99A	05DEC00	TK
WAORNL2021	0		26OCT00A	09NOV00A	KJR
WAORNL2022	0		26OCT00A	09NOV00A	JWM
WAORNL2023	5	**83**	20NOV00	28NOV00	TK



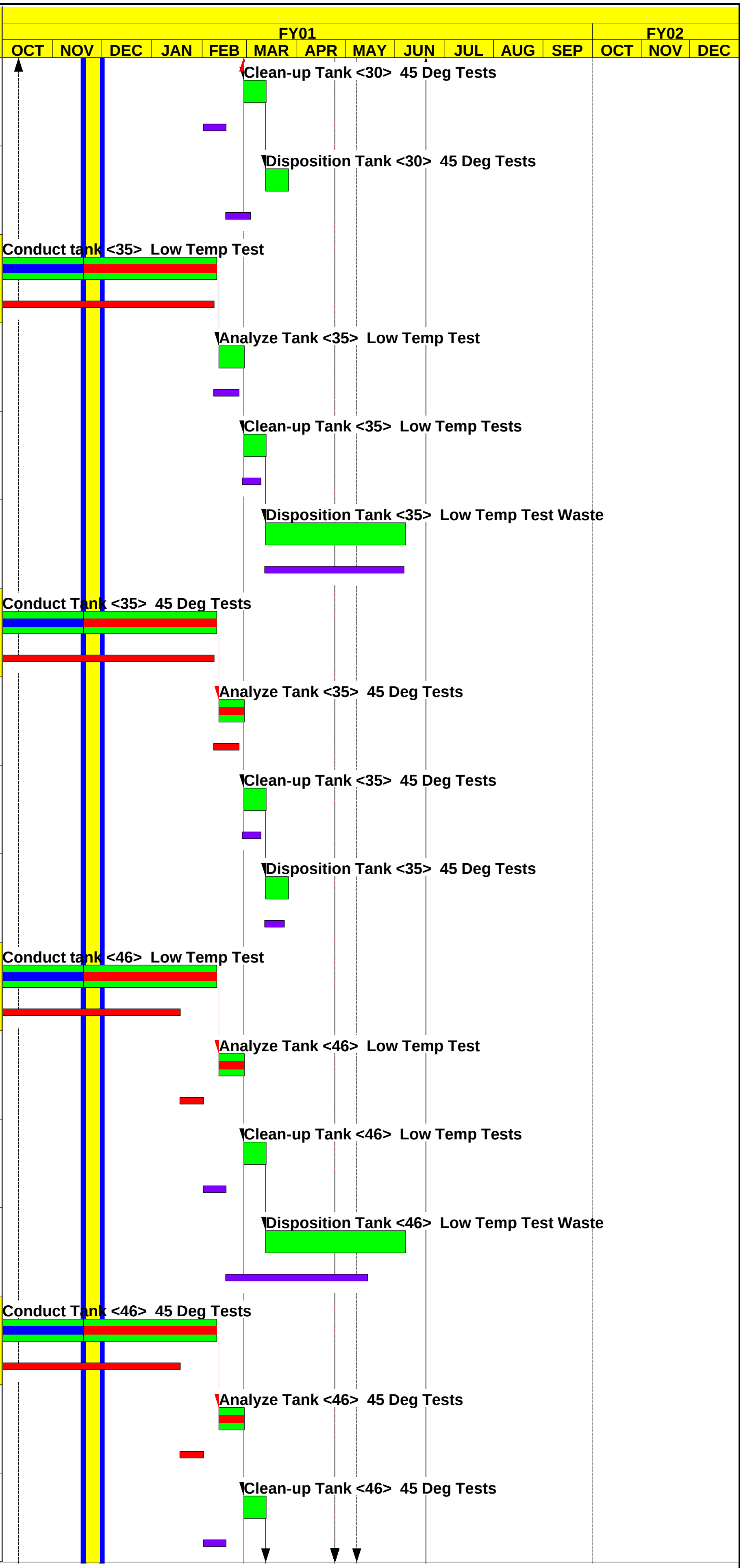
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORNL2024	5	**83**	29NOV00	05DEC00	TK
WAORNL2025	0	**87**		05DEC00	TK
TPB - Synergism Set II					
WATPB222U	3	**744**	04JAN01	08JAN01	MJB
WATPB222Z	3	**744**	04JAN01	08JAN01	MJB
WATPB226N	3	**744**	04JAN01	08JAN01	MJB
Batch Scale Test (Real Waste)					
WATPB23	94*	**-1**	30MAY00A	06APR01	MJB
WATPB230D	14	**-1**	27FEB01	16MAR01	MJB
WATPB230D2	8	**-1**	19MAR01	29MAR01	KJR
WATPB230D3	10	**-1**	19MAR01	30MAR01	JWM
WATPB230D4	5	**-1**	02APR01	06APR01	DW
WATPB230D5	0	**-1**		06APR01	KJR
WATPB2313D	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2313F	10	**-1**	12FEB01	26FEB01	MJB
WATPB2313G	10	**640**	27FEB01	12MAR01	MJB
WATPB2313H	60	**640**	13MAR01	06JUN01	MJB
WATPB2313I	0		08AUG00A	31OCT00A	MJB



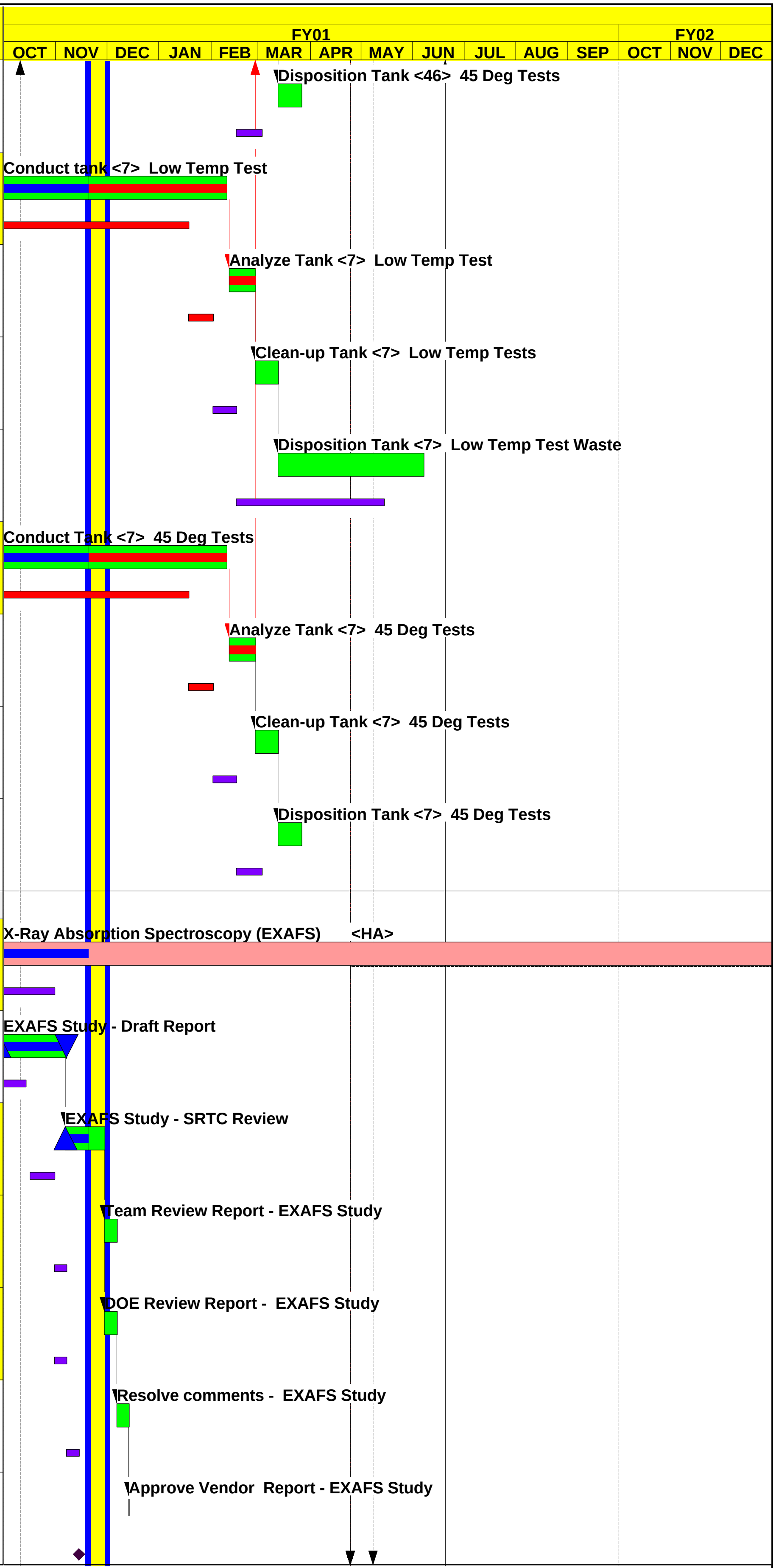
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB2313K	0		01NOV00A	14NOV00A	MJB
WATPB2313L	10	**666**	02APR01	16APR01	MJB
WATPB2313M	10	**666**	17APR01	30APR01	MJB
WATPB2326D	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2326F	10	**-1**	12FEB01	26FEB01	MJB
WATPB2326G	10	**640**	27FEB01	12MAR01	MJB
WATPB2326H	60	**640**	13MAR01	06JUN01	MJB
WATPB2326I	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2326K	10	**-1**	12FEB01	26FEB01	MJB
WATPB2326L	10	**690**	27FEB01	12MAR01	MJB
WATPB2326M	10	**690**	13MAR01	26MAR01	MJB
WATPB2330D	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2330F	10	**-1**	12FEB01	26FEB01	MJB
WATPB2330G	10	**640**	27FEB01	12MAR01	MJB
WATPB2330H	60	**640**	13MAR01	06JUN01	MJB
WATPB2330I	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2330K	10	**-1**	12FEB01	26FEB01	MJB



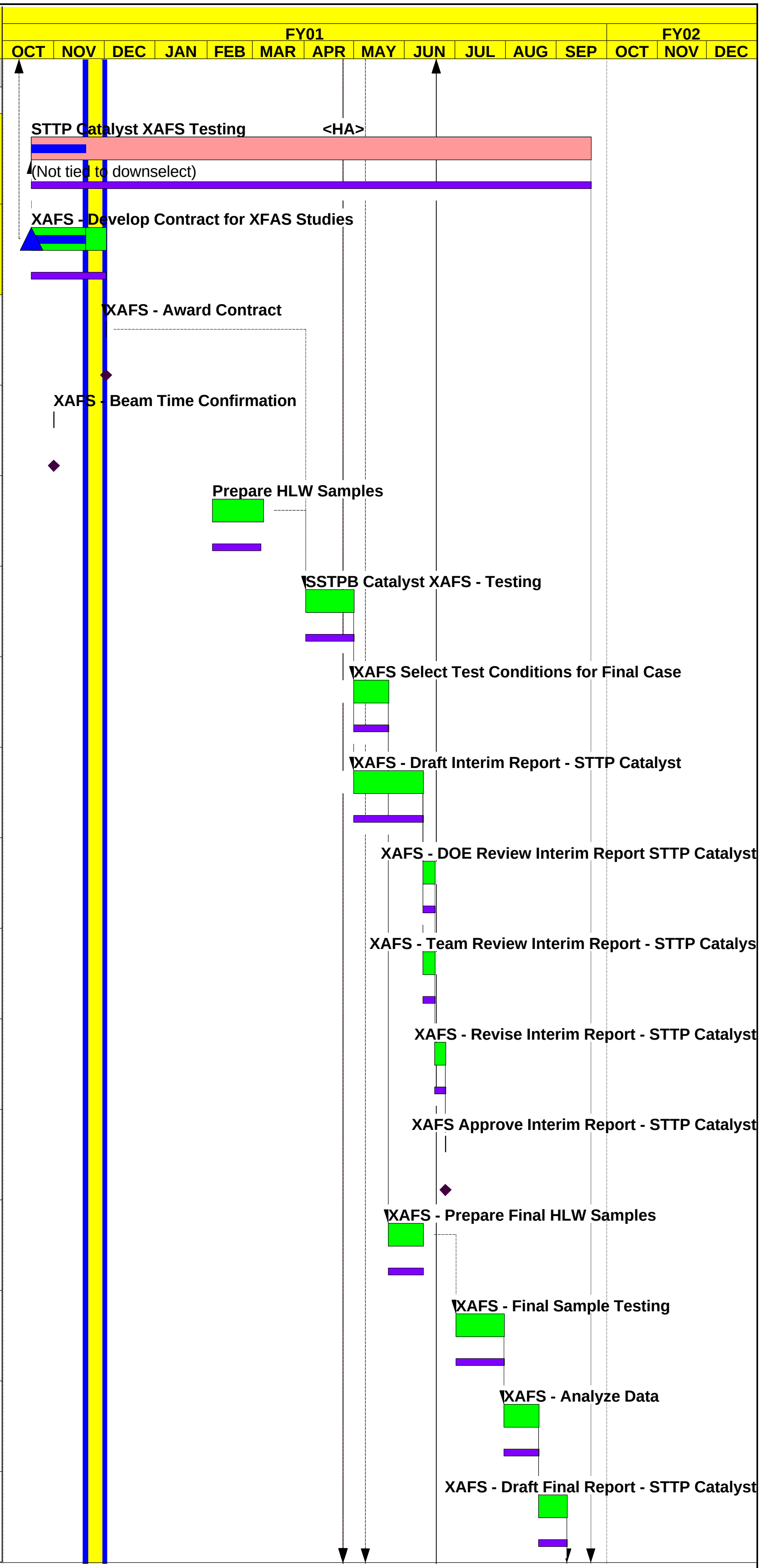
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB2330L	10	**690**	27FEB01	12MAR01	MJB
WATPB2330M	10	**690**	13MAR01	26MAR01	MJB
WATPB2335D	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2335F	10	**640**	12FEB01	26FEB01	MJB
WATPB2335G	10	**640**	27FEB01	12MAR01	MJB
WATPB2335H	60	**640**	13MAR01	06JUN01	MJB
WATPB2335I	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2335K	10	**-1**	12FEB01	26FEB01	MJB
WATPB2335L	10	**690**	27FEB01	12MAR01	MJB
WATPB2335M	10	**690**	13MAR01	26MAR01	MJB
WATPB2346D	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2346F	10	**-1**	12FEB01	26FEB01	MJB
WATPB2346G	10	**640**	27FEB01	12MAR01	MJB
WATPB2346H	60	**640**	13MAR01	06JUN01	MJB
WATPB2346I	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB2346K	10	**-1**	12FEB01	26FEB01	MJB
WATPB2346L	10	**690**	27FEB01	12MAR01	MJB



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB2346M	10	**690**	13MAR01	26MAR01	MJB
WATPB237D	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB237F	10	**-1**	12FEB01	26FEB01	MJB
WATPB237G	10	**640**	27FEB01	12MAR01	MJB
WATPB237H	60	**640**	13MAR01	06JUN01	MJB
WATPB237I	82*	**-1**	08AUG00A	09FEB01	MJB
WATPB237K	10	**-1**	12FEB01	26FEB01	MJB
WATPB237L	10	**690**	27FEB01	12MAR01	MJB
WATPB237M	10	**690**	13MAR01	26MAR01	MJB
X-Ray Absorption Spectroscopy					
WATPB2201	464*	**311**	30MAR00A	26SEP02	RAP
WATPB2201N	0*		27SEP00A	06NOV00A	RAP
WATPB2201P	6	**759**	06NOV00A	29NOV00	KJR
WATPB2201R	5	**759**	30NOV00	06DEC00	KJR
WATPB2201S	5	**759**	30NOV00	06DEC00	JWM
WATPB2201T	5	**759**	07DEC00	13DEC00	MJB
WATPB2201U	0	**759**		13DEC00	MJB



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
XAFS Studies for Catalyst Identification					
Experimental Methods - XAFS Studies					
WATPB21300	210*	**565**	18OCT00A	21SEP01	MJB
WATPB21302	8*	**660**	18OCT00A	01DEC00	MJB
WATPB21304	0	**660**		01DEC00	MJB
WATPB21306	0			31OCT00A	MJB
WATPB21314	21	**597**	05FEB01*	06MAR01	MJB
WATPB21316	20	**579**	02APR01*	30APR01	MJB
WATPB21318	15	**579**	01MAY01	21MAY01	MJB
WATPB21320	29	**627**	01MAY01	11JUN01	MJB
WATPB21322	5	**627**	12JUN01	18JUN01	JWM
WATPB21324	5	**627**	12JUN01	18JUN01	KJR
WATPB21326	5	**627**	19JUN01	25JUN01	MJB
WATPB21328	0	**627**		25JUN01	MJB
WATPB21330	14	**579**	22MAY01	11JUN01	MJB
WATPB21332	20	**565**	02JUL01*	30JUL01	MJB
WATPB21334	15	**565**	31JUL01	20AUG01	MJB
WATPB21336	12	**565**	21AUG01	06SEP01	MJB

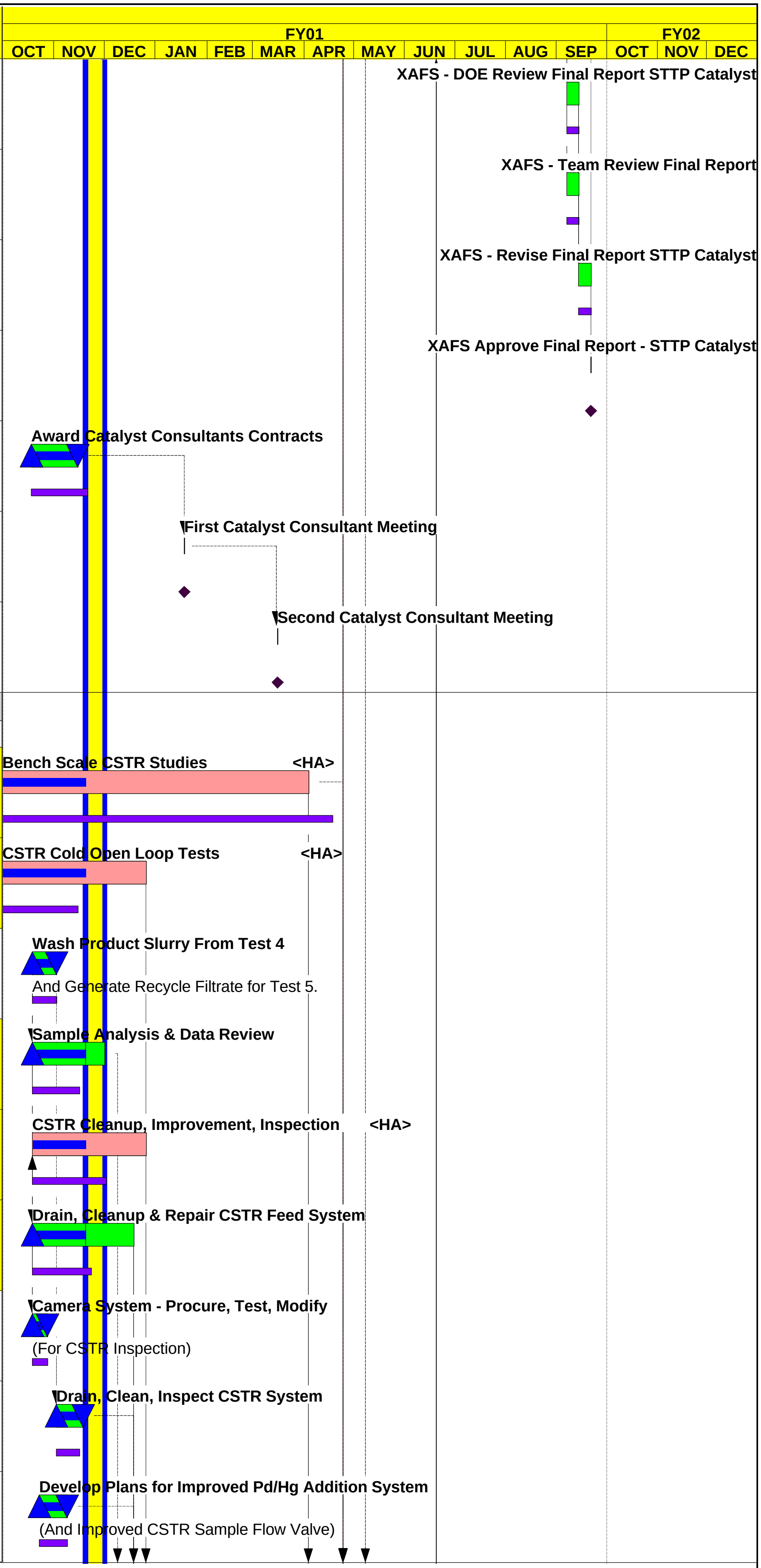


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB21338	5	**565**	07SEP01	13SEP01	JWM
WATPB21340	5	**565**	07SEP01	13SEP01	KJR
WATPB21342	6	**565**	14SEP01	21SEP01	MJB
WATPB21344	0	**565**		21SEP01	KJR
WATPB21352	0		18OCT00A	14NOV00A	LNO
WATPB21354	0	**736**		18JAN01*	LNO
WATPB21356	0	**697**		15MAR01*	LNO

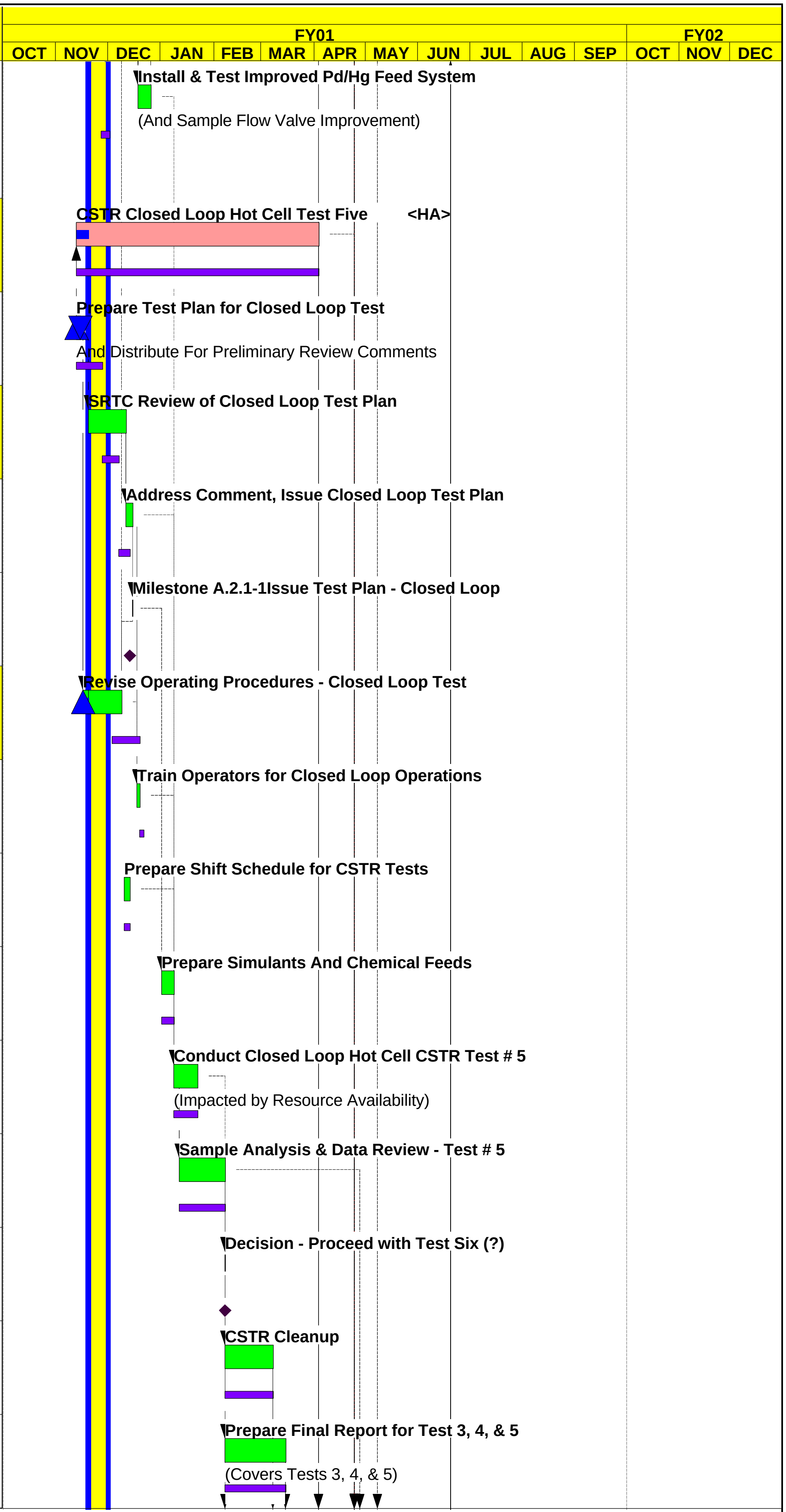
TPB - Solubility Data

Bench Scale CSTR Testing (20 L)

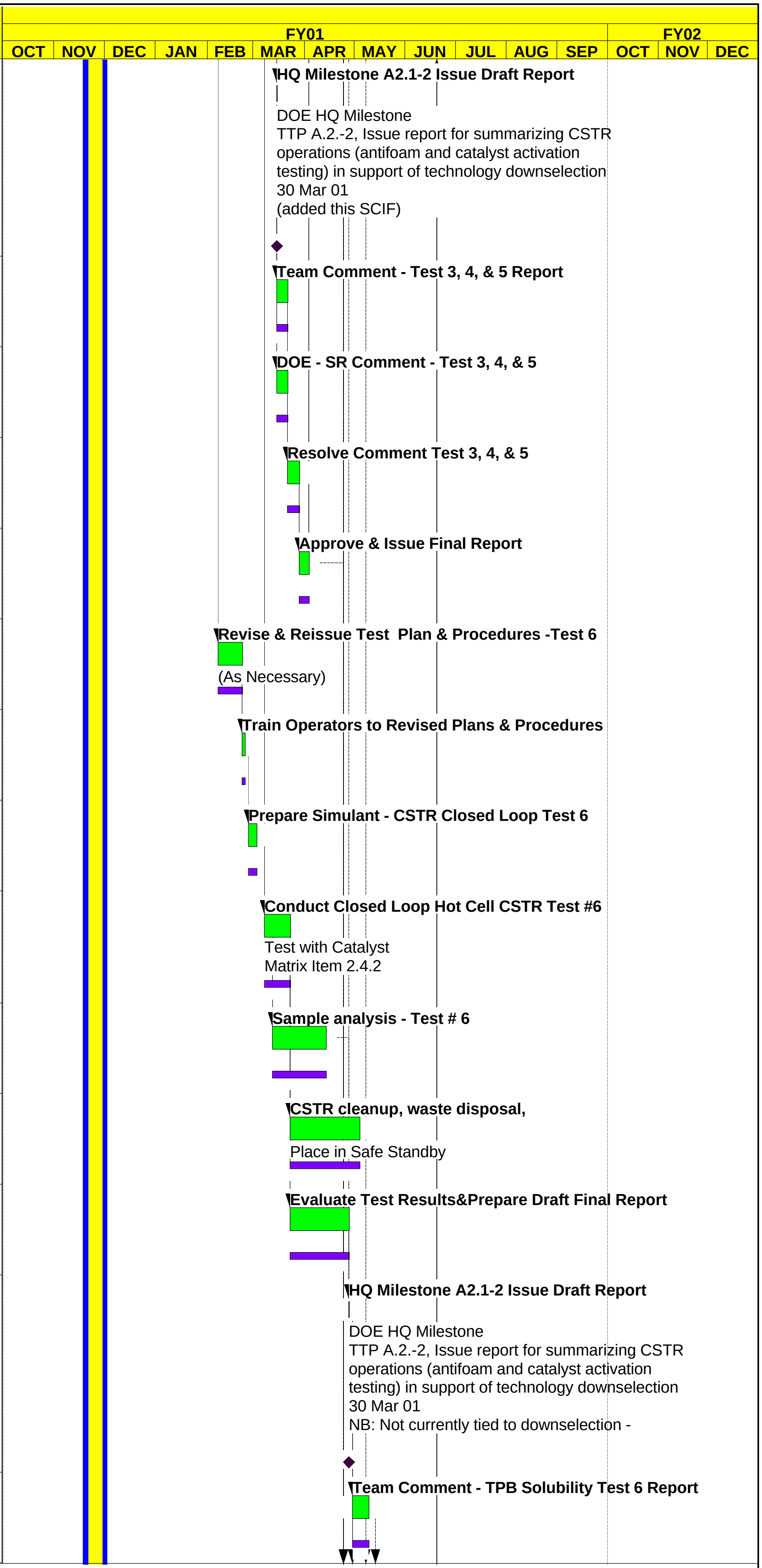
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN3001	96*	**2**	01OCT99A	03APR01	JW
WAORN3070	25*	**12**	20JUN00A	25DEC00	JW
WAORN3208	0		19OCT00A	01NOV00A	JW
WAORN3209	8*	**27**	19OCT00A	30NOV00	JW
WAORN3210	25*	**12**	19OCT00A	25DEC00	JW
WAORN3211	20*	**12**	19OCT00A	18DEC00	JW
WAORN3212	0		19OCT00A	27OCT00A	JW
WAORN3213	0		02NOV00A	17NOV00A	JW
WAORN3214	0		23OCT00A	08NOV00A	JW



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN3215	5	**12**	19DEC00*	25DEC00	JW
WAORN3216	96*	**2**	13NOV00A	03APR01	JW
WAORN3217	0		13NOV00A	14NOV00A	JW
WAORN3218	12*	**8**	20NOV00	11DEC00	KJR
WAORN3219	4	**12**	12DEC00	15DEC00	JW
WAORN3220	0	**12**		15DEC00	JW
WAORN3221	14*	**21**	17NOV00A	08DEC00	JW
WAORN3222	2	**16**	18DEC00	19DEC00	JW
WAORN3223	3	**20**	11DEC00*	13DEC00	JW
WAORN3224	5	**2**	02JAN01*	08JAN01	JW
WAORN3225	10	**2**	09JAN01	22JAN01	JW
WAORN3226	19	**2**	12JAN01	07FEB01	JW
WAORN3227	0	**653**		07FEB01	JW
WAORN3228	20	**650**	08FEB01	07MAR01	JW
WAORN3229	25	**2**	08FEB01	14MAR01	JW



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN3230	0	**2**		14MAR01	JW
WAORN3231	4	**1**	15MAR01	21MAR01	KJR
WAORN3232	5	**2**	15MAR01	21MAR01	JWM
WAORN3233	5	**2**	22MAR01	28MAR01	JW
WAORN3234	4	**2**	29MAR01	03APR01	JW
WAORN3235	10	**653**	08FEB01	21FEB01	JW
WAORN3236	2	**653**	22FEB01	23FEB01	JW
WAORN3237	5	**653**	26FEB01*	02MAR01	JW
WAORN3238	11	**650**	08MAR01	22MAR01	JW
WAORN3239	24	**660**	13MAR01	13APR01	JW
WAORN3240	30	**671**	23MAR01	03MAY01	JW
WAORN3241	26	**650**	23MAR01	27APR01	JW
WAORN3242	0	**650**		27APR01	JW
WAORN3243	7	**512**	30APR01	09MAY01	KJR



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAORN3244	10	**642**	30APR01	11MAY01	JWM
WAORN3245	10	**642**	14MAY01	25MAY01	JW
WAORN3246	5	**650**	28MAY01	01JUN01	JW
WAORN3247	72*	**565**	21JUN01	28SEP01	JW
WAORN3248	10	**560**	21JUN01*	05JUL01	JW
WAORN3249	30	**560**	06JUL01	16AUG01	JW
WAORN3250	20	**560**	17AUG01	14SEP01	JW
WAORN3251	10	**560**	17SEP01	28SEP01	JW
WAORN3252	5	**565**	17SEP01	21SEP01	JW

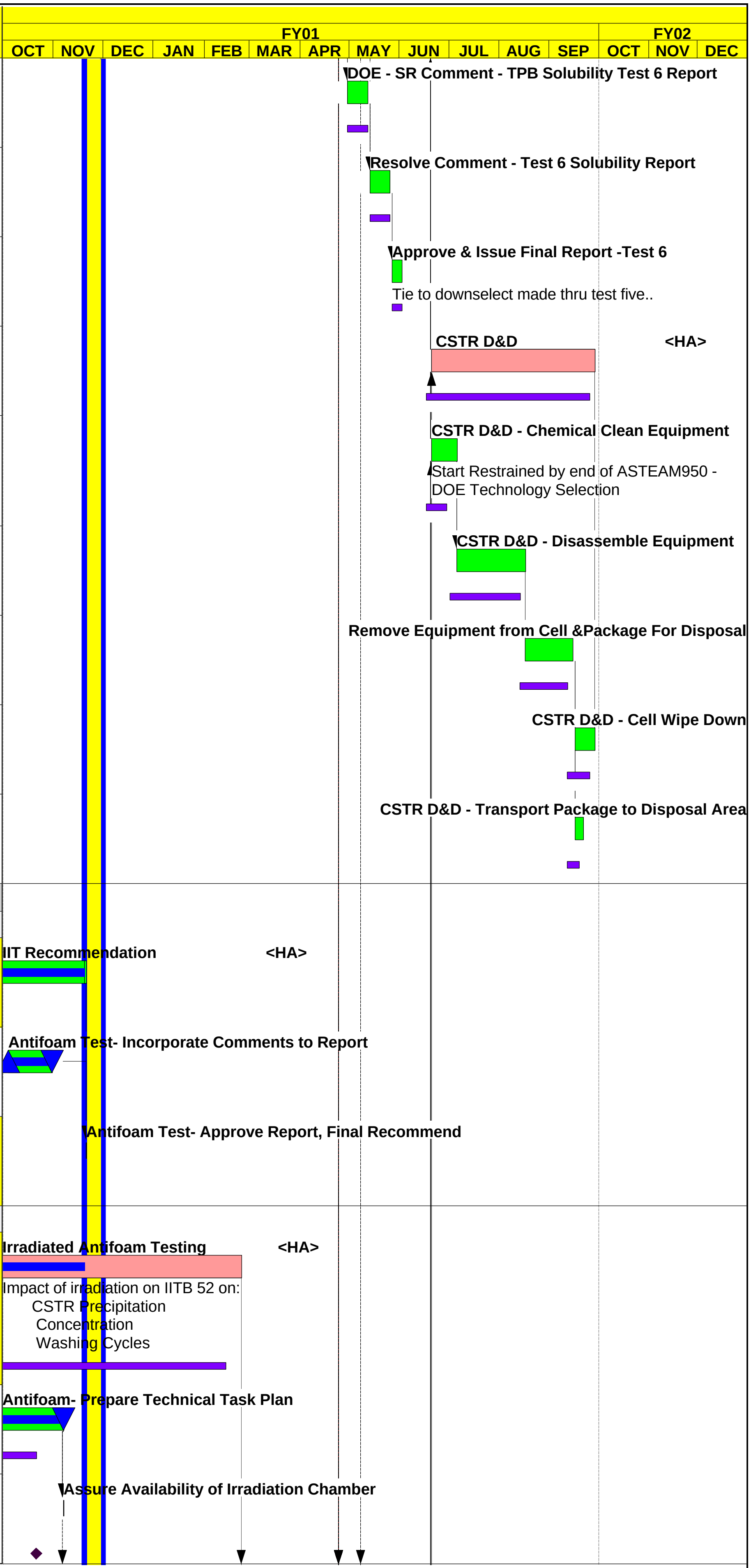
TPB - Antifoam Physical Properties

Antifoam Test - Simulant Waste - Bench Scale

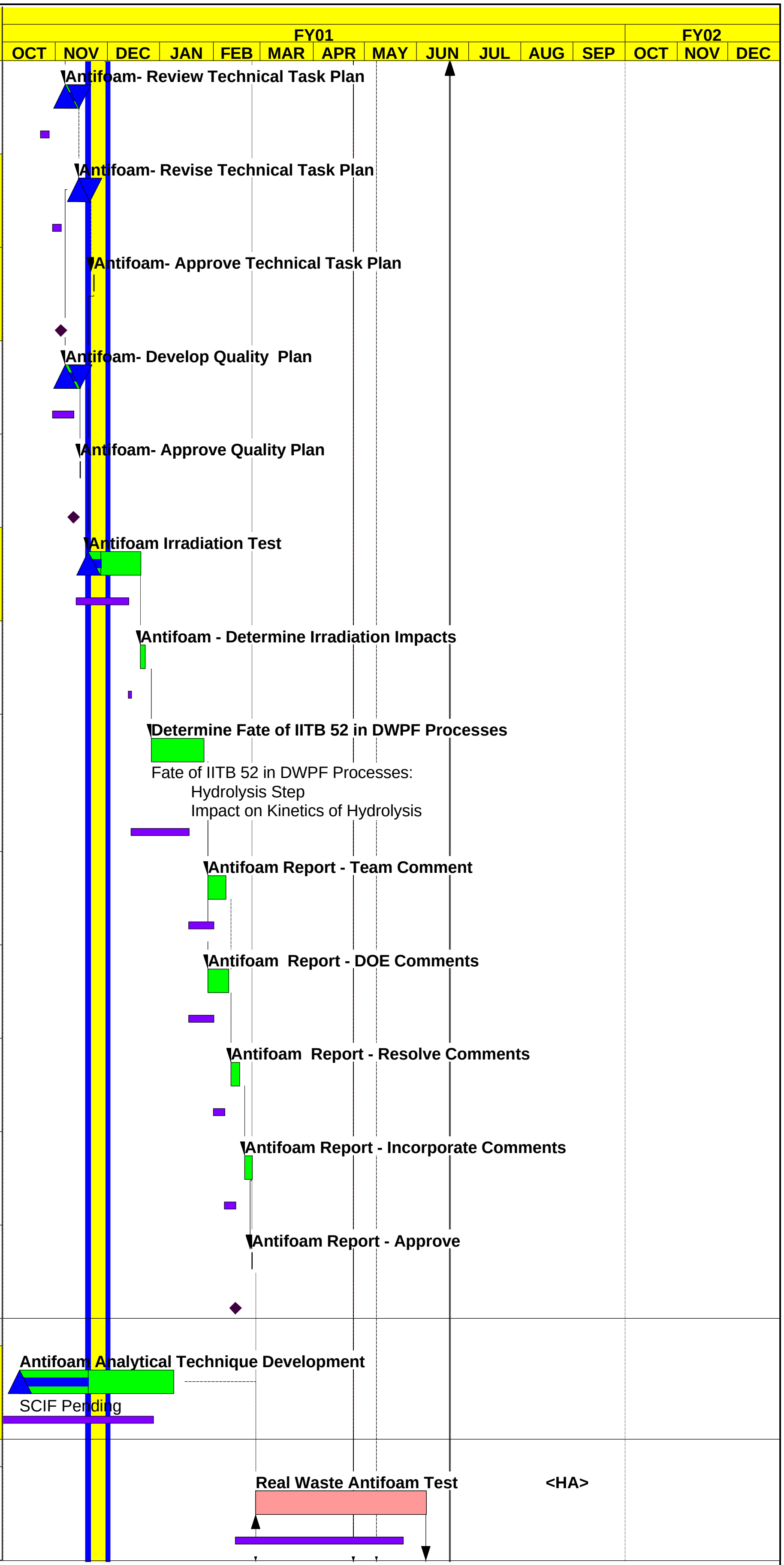
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB51000	1*	**774**	03APR00A	20NOV00	DPL
WATPB52940	0		04OCT00A	30OCT00A	DPL
WATPB52950	0	**774**		20NOV00	KJR

Antifoam - Irradiated Test

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB53000	64*	**616**	18SEP00A	23FEB01	JRH
WATPB53030	0		18SEP00A	06NOV00A	JRH
WATPB53040	0			06NOV00A	JRH



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB53050	0		06NOV00A	13NOV00A	JRH
WATPB53060	0		14NOV00A	20NOV00A	JRH
WATPB53070	0	**616**		22NOV00*	JRH
WATPB53080	0		06NOV00A	14NOV00A	JRH
WATPB53090	0			14NOV00A	JRH
WATPB53100	18*	**616**	20NOV00A	20DEC00	JRH
WATPB53200	2	**616**	21DEC00	22DEC00	JRH
WATPB53310	22	**616**	27DEC00	26JAN01	JRH
WATPB53320	8	**489**	29JAN01	08FEB01	KJR
WATPB53330	10	**616**	29JAN01	09FEB01	JWM
WATPB53340	5	**616**	12FEB01	16FEB01	JRH
WATPB53350	4	**616**	20FEB01	23FEB01	JRH
WATPB53390	0	**616**		23FEB01	KJR
Antifoam Analytical Technique					
WATPB54	31*	**649**	11OCT00A	08JAN01	DPL
Antifoam - Real Waste Test					
WATPB56	70*	**641**	26FEB01	05JUN01	RAP

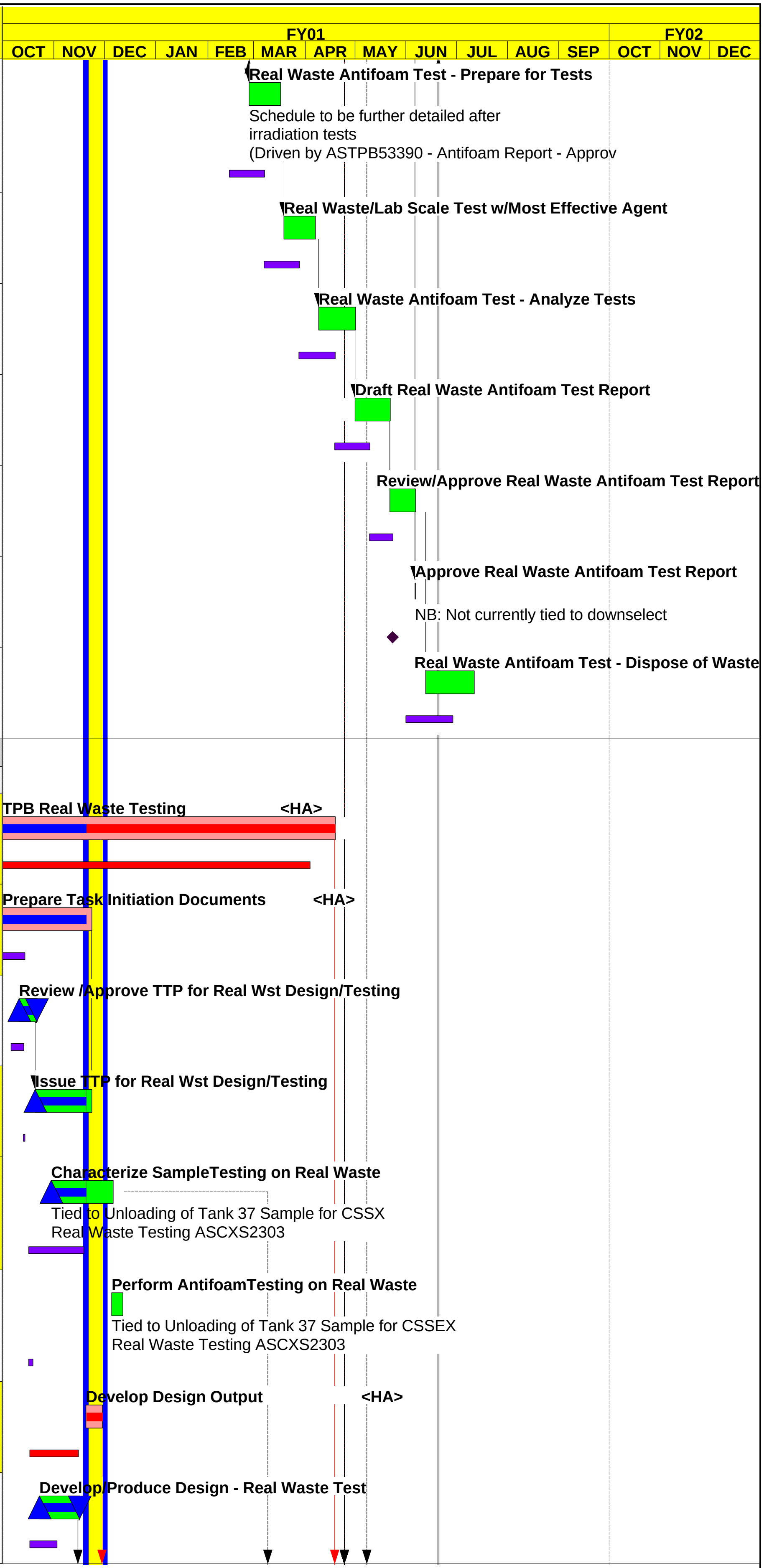


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB56A	15	**616**	26FEB01	16MAR01	RAP
WATPB56C	15	**616**	19MAR01	06APR01	RAP
WATPB56E	15	**616**	09APR01	30APR01	RAP
WATPB56G	15	**616**	01MAY01	21MAY01	RAP
WATPB56J	10	**616**	22MAY01	05JUN01	KJR
WATPB56K	0	**641**		05JUN01	KJR
WATPB56P	20	**616**	13JUN01	11JUL01	RAP

TPB Real Waste Testing

TPB Real Waste Testing

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB4400	101*	**-8**	18SEP00A	18APR01	JTC
WATPB4401	3*	**772**	18SEP00A	22NOV00	JTC
WATPB4409	0		11OCT00A	20OCT00A	TBP
WATPB4411	3*	**772**	20OCT00A	22NOV00	TBP
WATPB4414B	10*	**56**	30OCT00A	05DEC00	TBP
WATPB4414C	5	**761**	05DEC00*	11DEC00	TBP
WATPB4425	5*	**-5**	20NOV00	29NOV00	LC
WATPB4427	0		23OCT00A	15NOV00A	LC



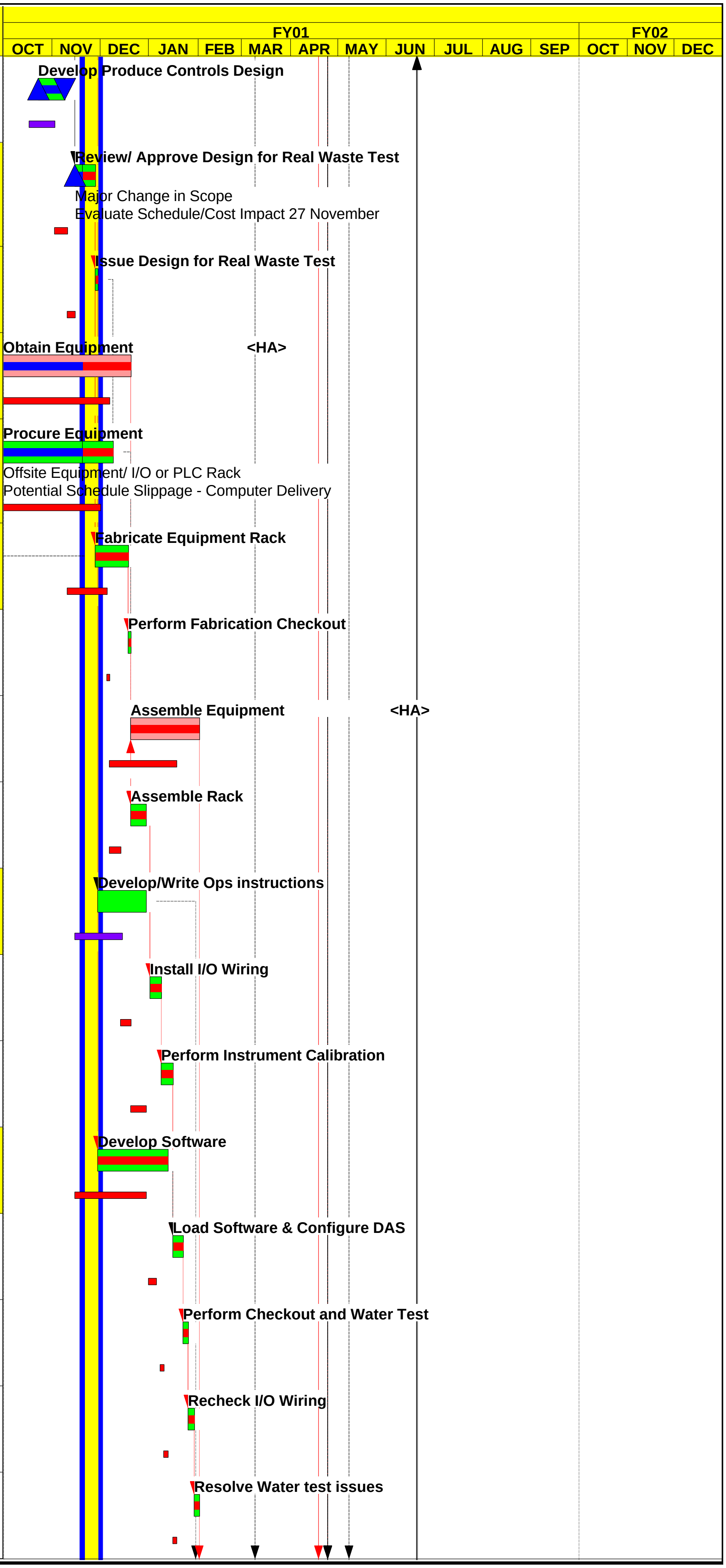
Schedule to be further detailed after irradiation tests
(Driven by ASTPB53390 - Antifoam Report - Approv

NB: Not currently tied to downselect

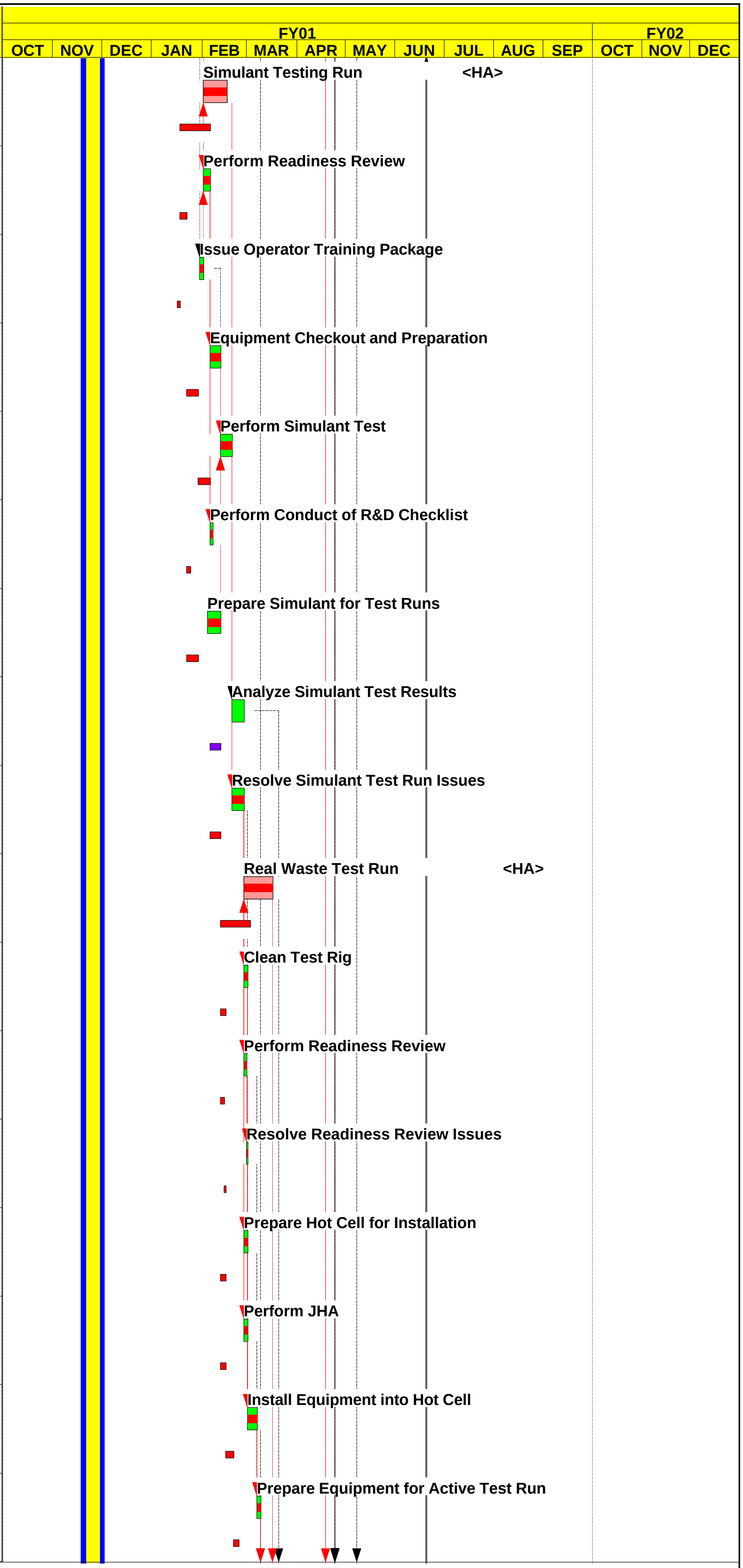
Tied to Unloading of Tank 37 Sample for CSSX Real Waste Testing ASCXS2303

Tied to Unloading of Tank 37 Sample for CSSEX Real Waste Testing ASCXS2303

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB4429	0*		23OCT00A	08NOV00A	LC
WATPB4431	3*	**-8**	15NOV00A	27NOV00	LC
WATPB4433	2	**-8**	28NOV00	29NOV00	LC
WATPB4435	21*	**-10**	18SEP00A	20DEC00	TBP
WATPB4436	13*	**-2**	18SEP00A	08DEC00	TBP
WATPB4437	15	**-10**	28NOV00	18DEC00	TBP
WATPB4441	2	**-10**	19DEC00	20DEC00	TBP
WATPB4445	28*	**-10**	21DEC00	01FEB01	TBP
WATPB4447	5	**-10**	21DEC00	29DEC00	TBP
WATPB4449	20	**12**	30NOV00	29DEC00	TBP
WATPB4451	5	**-10**	02JAN01	08JAN01	TBP
WATPB4453	5	**-10**	09JAN01	15JAN01	TBP
WATPB4454	29	**-9**	30NOV00	12JAN01	TBP
WATPB4455	5	**-10**	16JAN01	22JAN01	TBP
WATPB4457	3	**-10**	23JAN01	25JAN01	TBP
WATPB4459	2	**-10**	26JAN01	29JAN01	TBP
WATPB4461	3	**-8**	30JAN01	01FEB01	TBP



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB4465	11*	**-8**	02FEB01	16FEB01	TBP
WATPB4467	2	**-9**	02FEB01	05FEB01	TBP
WATPB4469	2	**-9**	31JAN01	01FEB01	TBP
WATPB4471	5	**-9**	06FEB01	12FEB01	TBP
WATPB4473	7	**-13**	13FEB01	19FEB01	TBP
WATPB4474	2	**-8**	06FEB01	07FEB01	TBP
WATPB4475	6	**-9**	05FEB01	12FEB01	TBP
WATPB4477	5	**8**	20FEB01	26FEB01	TBP
WATPB4479	5	**-8**	20FEB01	26FEB01	TBP
WATPB4481	14*	**-8**	27FEB01	16MAR01	TBP
WATPB4482	3	**-8**	27FEB01	01MAR01	TBP
WATPB4483	2	**-8**	27FEB01	28FEB01	TBP
WATPB4484	1	**-8**	01MAR01	01MAR01	TBP
WATPB4485	3	**-8**	27FEB01	01MAR01	TBP
WATPB4486	3	**-8**	27FEB01	01MAR01	TBP
WATPB4487	3	**-8**	02MAR01	06MAR01	TBP
WATPB4489	3	**-8**	07MAR01	09MAR01	TBP

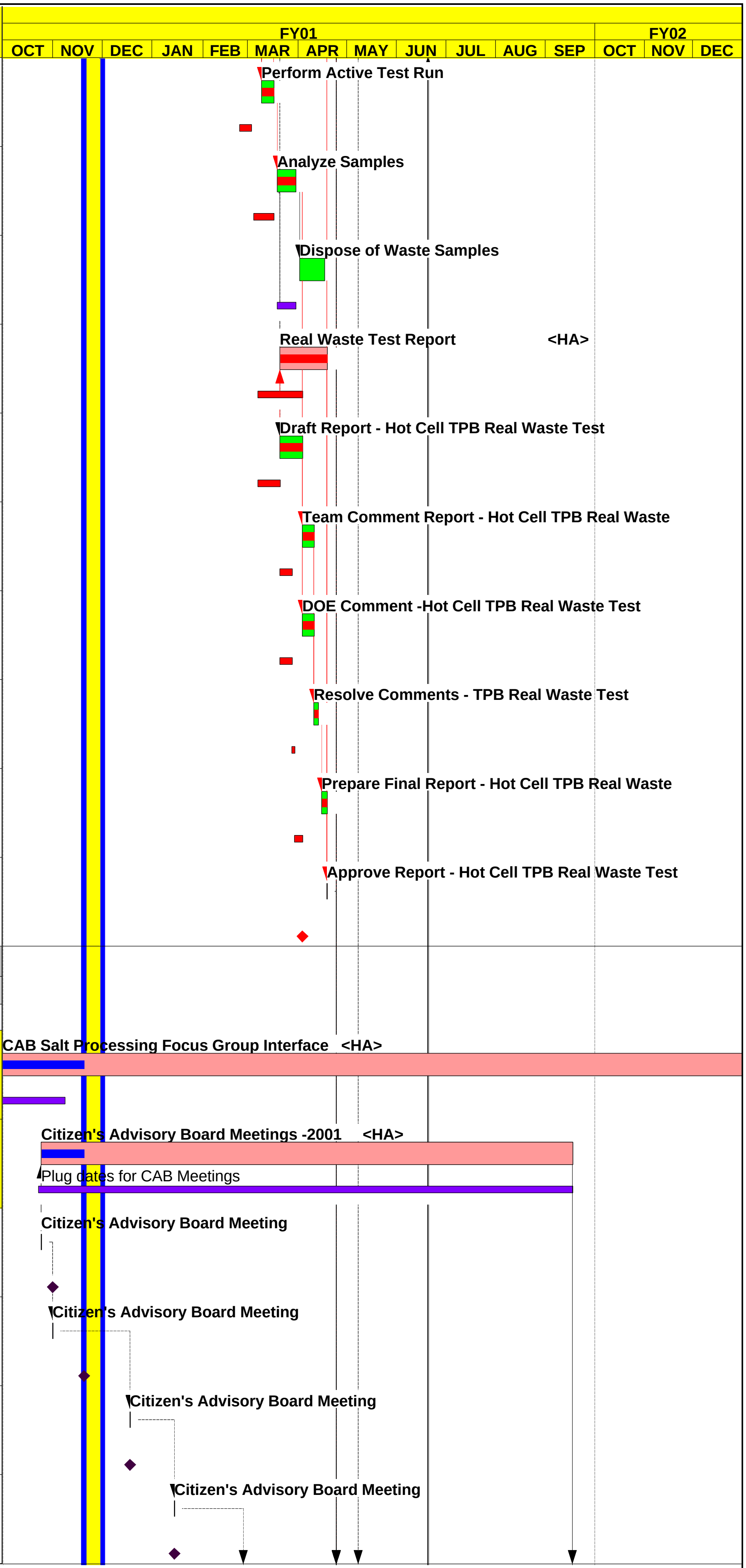


Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATPB4491	7	**-10**	10MAR01	16MAR01	TBP
WATPB4493	10	**-8**	19MAR01	30MAR01	TBP
WATPB4495	10	**676**	02APR01	16APR01	TBP
WATPB4499A	20*	**-8**	21MAR01	18APR01	TBP
WATPB4499B	10	**-8**	21MAR01	03APR01	TBP
WATPB4499E	5	**-8**	04APR01	10APR01	TBP
WATPB4499F	5	**-8**	04APR01	10APR01	JWM
WATPB4499G	2	**-8**	11APR01	12APR01	TBP
WATPB4499H	3	**-8**	16APR01	18APR01	TBP
WATPB4499I	0	**-8**		18APR01	KJR

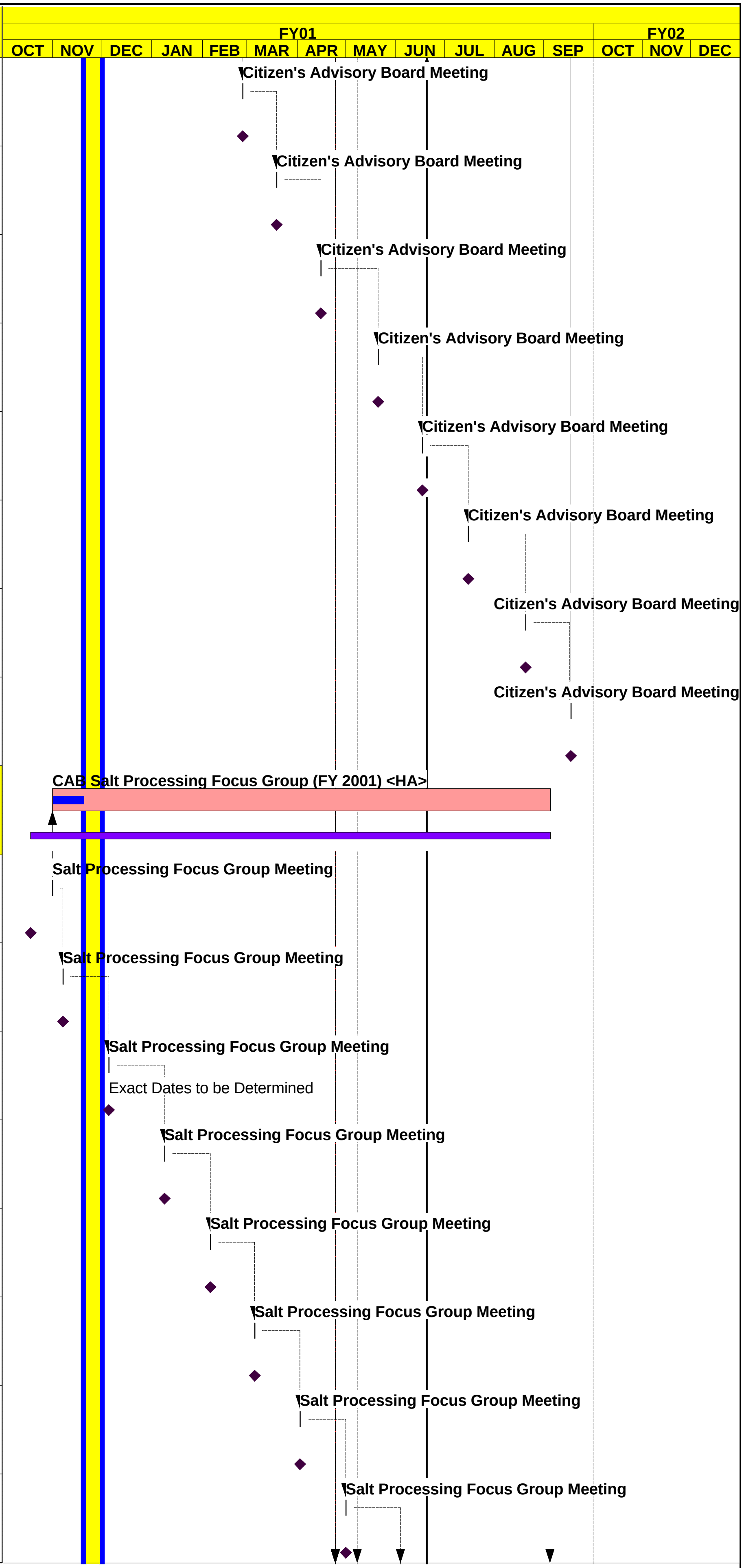
Selection Support & Engineering

SPP - Citizen's Advisory Group Meetings

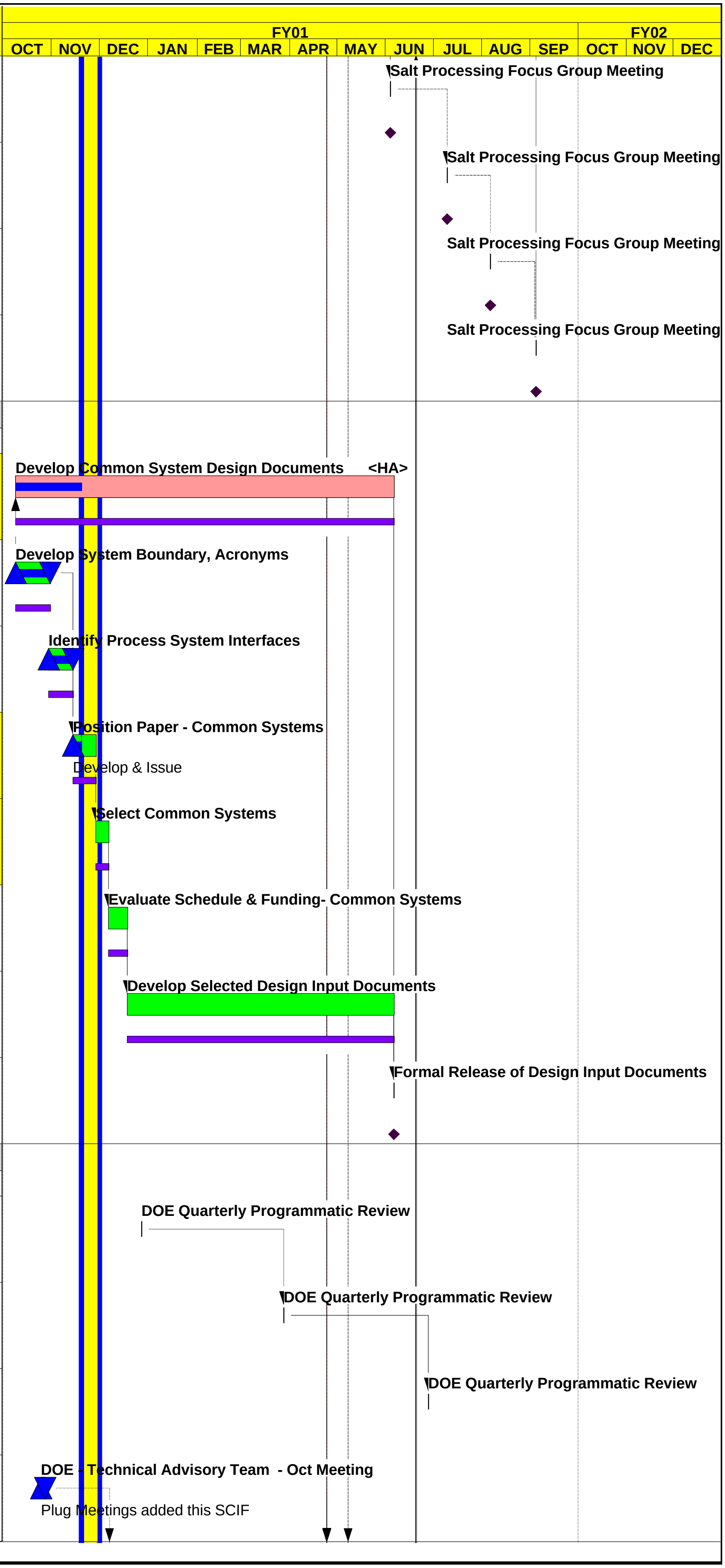
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACAB0000	368*	**249**	04NOV99A	26SEP02	KJR
WACAB2001	163*	**454**	24OCT00A	17SEP01	KJR
WACAB210	0		24OCT00A		KJR
WACAB212	0		01NOV00A		KJR
WACAB214	0	**603**	18DEC00*		KJR
WACAB216	0	**590**	15JAN01*		KJR



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WACAB218	0	**567**	26FEB01*		KJR
WACAB220	0	**555**	19MAR01*		KJR
WACAB222	0	**540**	16APR01*		KJR
WACAB224	0	**520**	21MAY01*		KJR
WACAB226	0	**505**	18JUN01*		KJR
WACAB228	0	**490**	16JUL01*		KJR
WACAB230	0	**470**	20AUG01*		KJR
WACAB232	0	**454**		17SEP01*	KJR
WAFGM2001	156*	**461**	01NOV00A	04SEP01	KJR
WAFGM310	0		01NOV00A		KJR
WAFGM320	0		07NOV00A		KJR
WAFGM330	0	**610**	05DEC00*		KJR
WAFGM340	0	**593**	09JAN01*		KJR
WAFGM350	0	**577**	06FEB01*		KJR
WAFGM360	0	**562**	06MAR01*		KJR
WAFGM370	0	**546**	03APR01*		KJR
WAFGM380	0	**531**	01MAY01*		KJR



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAFGM390	0	**513**	04JUN01*		KJR
WAFGM410	0	**493**	10JUL01*		KJR
WAFGM420	0	**477**	07AUG01*		KJR
WAFGM430	0	**461**		04SEP01*	KJR
Common System Design Documents					
WADOC1000	106*	**511**	09OCT00A	05JUN01	RWB
WADOC1010	0*		09OCT00A	30OCT00A	RWB
WADOC1020	0		30OCT00A	13NOV00A	RWB
WADOC1030	4*	**511**	14NOV00A	28NOV00	RWB
WADOC1050	5	**511**	29NOV00	06DEC00	RWB
WADOC1060	6	**511**	07DEC00	18DEC00	RWB
WADOC1070	91	**511**	19DEC00	05JUN01	RWB
WADOC1199	0	**511**		05JUN01	RWB
Liason Meetings					
WAMTG110	0	**625**	28DEC00		JWM
WAMTG120	0	**625**	28MAR01		JWM
WAMTG130	0	**625**	28JUN01		JWM
WATAG160	0		25OCT00A	27OCT00A	JWM



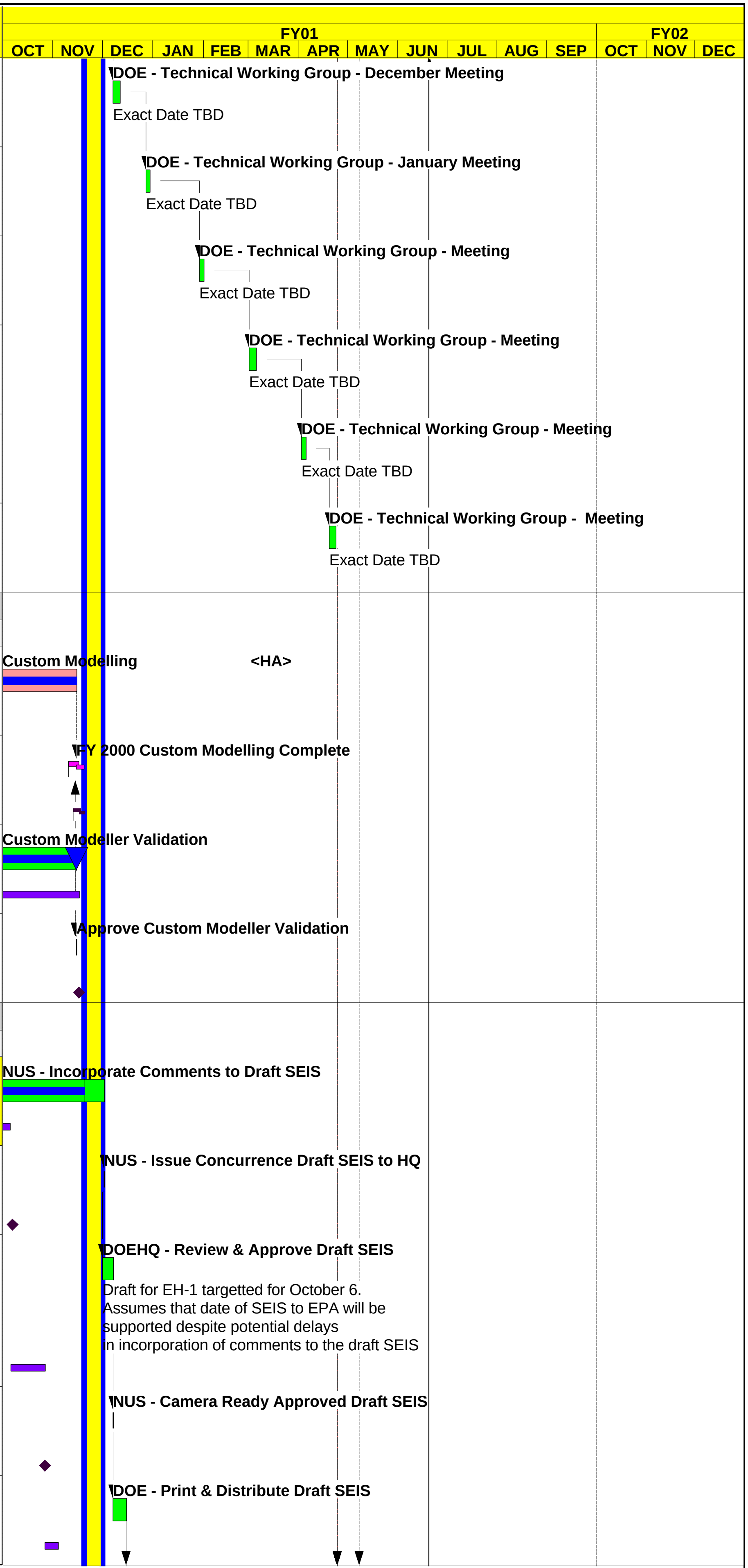
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATAG180	2	**671**	08DEC00*	11DEC00	JWM
WATAG190	2	**671**	28DEC00	29DEC00	JWM
WATAG200	2	**671**	30JAN01	31JAN01	JWM
WATAG210	2	**671**	02MAR01	05MAR01	JWM
WATAG220	2	**671**	03APR01	04APR01	JWM
WATAG230	2	**671**	20APR01	23APR01	JWM

Custom Model Conversion

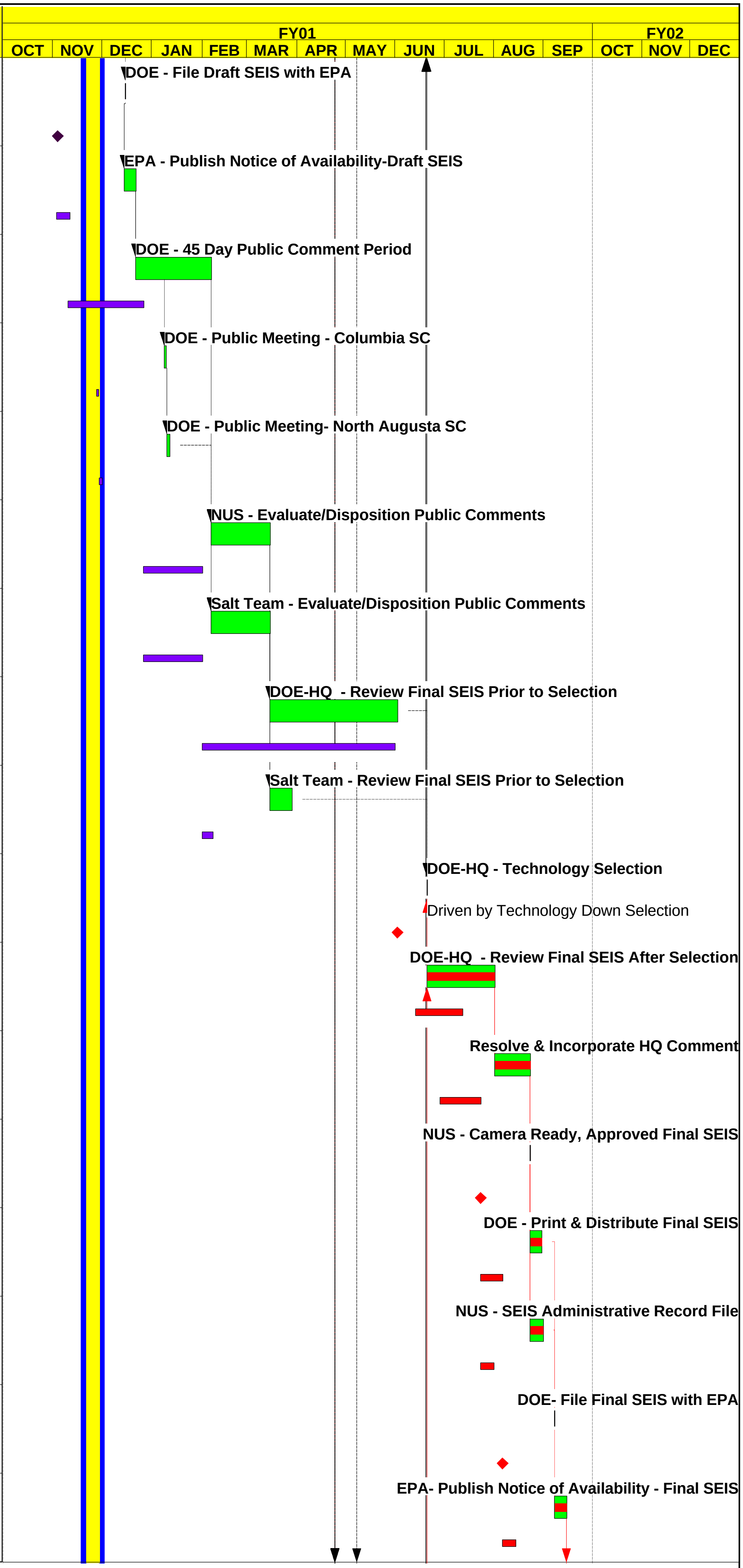
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WAPROC0402	0*		04OCT99A	14NOV00A	JTC
WAPROC0479	0			14NOV00A	JTC
WAPROC0492	0		08JUN00A	14NOV00A	JTC
WAPROC0498	0			14NOV00A	JTC

Supplemental Environmental Impact Statement

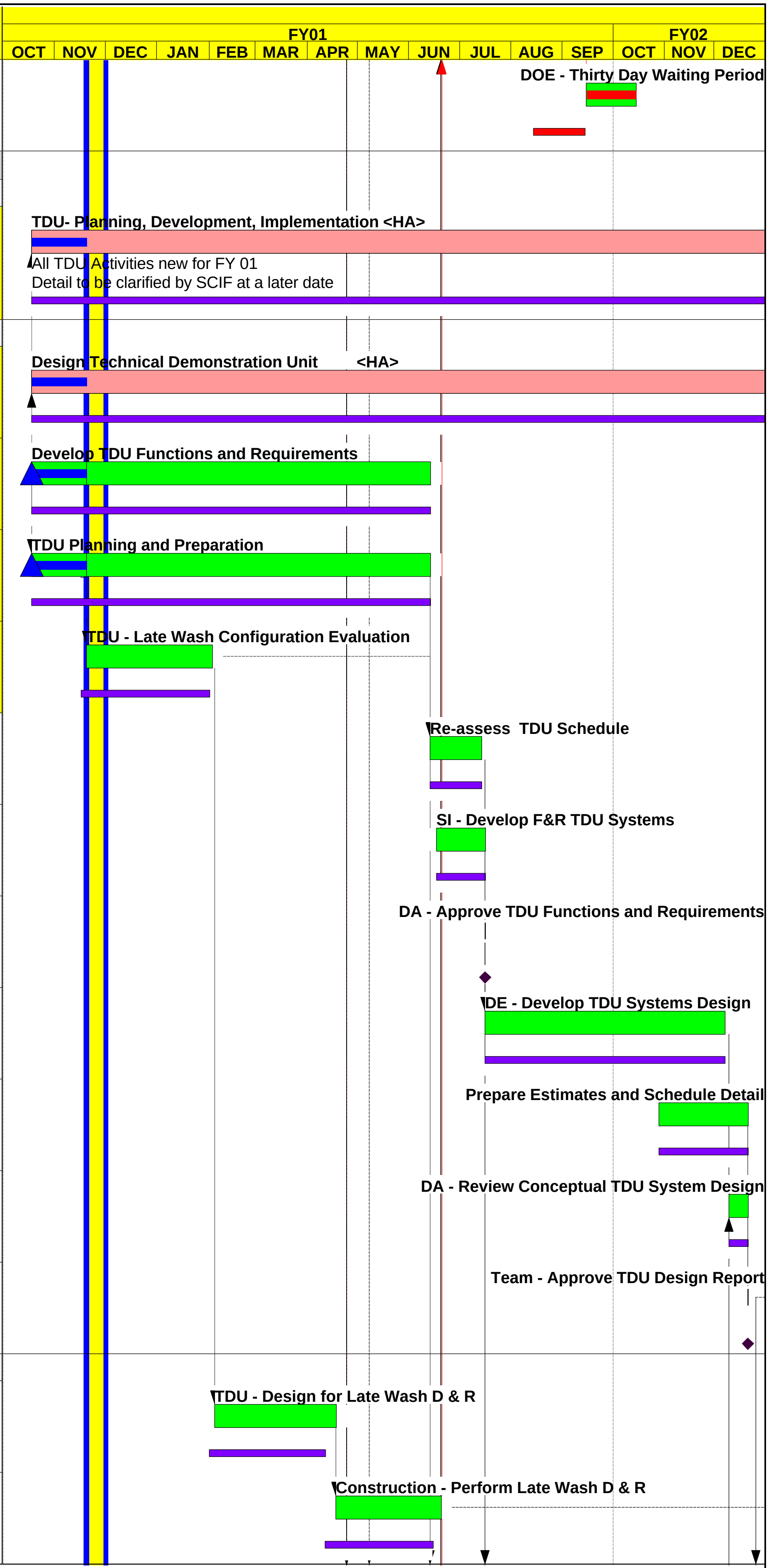
Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WASEIS1600	8*	**0**	15SEP00A	01DEC00	JWM
WASEIS1900	0	**0**		01DEC00	JWM
WASEIS2100	5	**0**	01DEC00	07DEC00	JWM
WASEIS2300	0	**0**		07DEC00	JWM
WASEIS2400	6	**0**	08DEC00	15DEC00	JWM



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WASEIS2900	0	**0**		15DEC00	JWM
WASEIS3100	7	**0**	15DEC00	21DEC00	JWM
WASEIS3200	47	**0**	22DEC00	06FEB01	JWM
WASEIS3300	1	**26**	09JAN01	09JAN01	JWM
WASEIS3410	1	**26**	11JAN01	11JAN01	JWM
WASEIS3420	25	**0**	07FEB01	14MAR01	JWM
WASEIS3440	20	**0**	07FEB01	14MAR01	KJR
WASEIS3510	55	**0**	15MAR01	01JUN01	JWM
WASEIS3512	14	**65**	15MAR01	28MAR01	KJR
WASEIS3520	0	**-13**		20JUN01	JWM
WASEIS3530	29	**-5**	21JUN01	01AUG01	JWM
WASEIS3600	16	**-5**	02AUG01	23AUG01	JWM
WASEIS3710	0	**-5**		23AUG01	JWM
WASEIS3720	7	**-6**	24AUG01	30AUG01	JWM
WASEIS3730	6	**-5**	24AUG01	31AUG01	JWM
WASEIS3900	0	**-1**		07SEP01	JWM
WASEIS4100	7	**-14**	08SEP01	14SEP01	JWM



Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WASEIS4200	30	**-14**	15SEP01	14OCT01	JWM
Pilot Plant (Technical Demonstration Unit)					
Technical Demonstration Unit - Summary					
WATDU0000	427*	**348**	18OCT00A	05AUG02	RWB
TDU - Conceptual Engineering					
WATDU1000	283*	**392**	18OCT00A	09JAN02	RWB
WATDU1050	140*	**394**	18OCT00A	13JUN01	RWB
WATDU1100	140*	**394**	18OCT00A	13JUN01	RWB
WATDU1210	50	**484**	20NOV00	02FEB01	RWB
WATDU1400	21	**394**	14JUN01	13JUL01	LC
WATDU1700	16	**312**	18JUN01	16JUL01	LC
WATDU1710	0	**312**		16JUL01	KJR
WATDU1720	80	**312**	17JUL01	06DEC01	LC
WATDU1740	30	**312**	29OCT01	20DEC01	LC
WATDU1800	8	**312**	10DEC01	20DEC01	KJR
WATDU1810	0	**312**		20DEC01	KJR
TDU - Design for Late Wash D & R					
WATDU1220	50	**501**	05FEB01	17APR01	RWB
WATDU1240	44	**501**	18APR01	19JUN01	LC



All TDU Activities new for FY 01
Detail to be clarified by SCIF at a later date

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
TDU - Case Specific Design & Engineering					
WATDU1300	143*	**392**	14JUN01	09JAN02	LC
WATDU1730	80	**312**	17JUL01	06DEC01	LC
WATDU1910	8	**312**	26DEC01	09JAN02	LC
WATDU1920	0	**392**		09JAN02	LC
WATDU1930	100	**392**	10JAN02	03JUN02	LC
TD04					
WATDU3000	297*	**348**	01NOV00A	29JAN02	
WATDU3300	0	**509**		29JAN02	
TD05					
WATDU4000	130	**348**	30JAN02	05AUG02	LC
WATDU610	0	**348**		05AUG02	RWB

Technology Down Selection Process

Technology Down Selection Process

Activity ID	Work Days	Float Wk Days	Early Start	Early Finish	Lead
WATEAM910	0	**-13**		25APR01	KJR
WATEAM920	8	**-13**	26APR01	07MAY01	KJR
WATEAM930	0	**-13**		07MAY01	KJR
WATEAM940	31	**-13**	08MAY01	20JUN01	JWM
WATEAM950	0	**-13**		20JUN01	JWM