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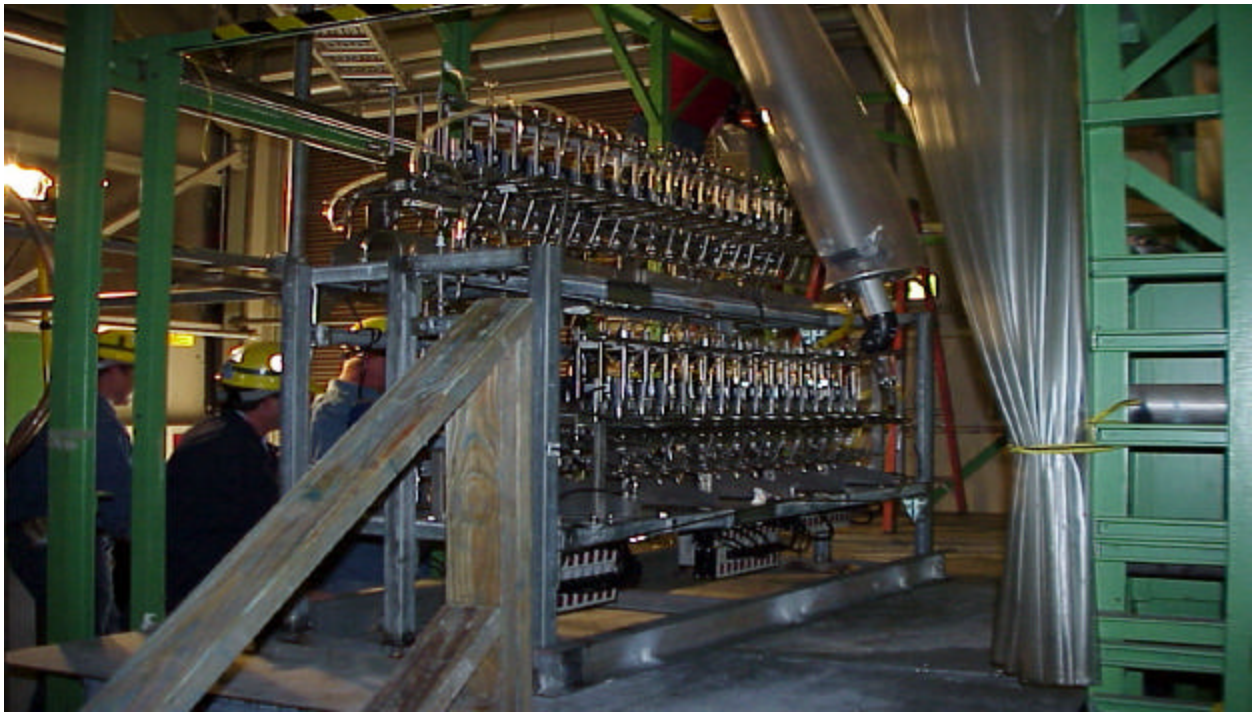
Tanks Focus Area

SAVANNAH RIVER SITE SALT PROCESSING PROJECT

RESEARCH AND DEVELOPMENT SUMMARY REPORT



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Pacific Northwest National Laboratory
Richland, Washington 99352

Tanks Focus Area

Savannah River Site Salt Processing Project

Research and Development Summary Report

Harry Harmon, Steve Schlahta, and Dennis Wester
Pacific Northwest National Laboratory

Joe Walker
Oak Ridge National Laboratory

Samuel Fink and Major Thompson
Westinghouse Savannah River Company

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Executive Summary

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 waste (water soluble) treatment portion of the SRS HLW effort. The overall SPP encompasses the selection, design, construction and operation of technologies to prepare the salt-waste feed material for immobilization at the site's Saltstone Production Facility (SPF) and vitrification facility (Defense Waste Processing Facility [DWPF]). Major constituents that must be removed from the salt waste and sent as feed to DWPF include actinides, strontium, and cesium.

Background

SRS successfully demonstrated the In-Tank Precipitation (ITP) process for salt waste treatment both on a moderate and full-scale bases with SRS salt waste in the 1980s. The ITP process separates the cesium isotopes from the non-radioactive salts by tetraphenylborate (TPB) 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 Facilities 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 to ensure safe operation at the needed production rate. On February 20, 1998, DOE-Savannah River (DOE-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.

Research And Development Program

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 (CST), Caustic Side Solvent Extraction (CSSX), Small Tank Tetraphenylborate Precipitation (STTP), and Direct Grouting (with no cesium removal).

Further review eliminated Direct Grouting as an option. 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,[1,2] 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, as necessary, the technology development roadmaps, develop down-selection criteria, and prepare a comprehensive Research and Development Program Plan[3] for the three candidate cesium removal technologies, as well as the alpha and strontium removal technologies that are part of the overall SPP.

The SPP Research and Development Program has been 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 fiscal year (FY) 2000 was $13.1 million. Total funding for FY 2001 is $13.4 million.

The Research and Development program was focused on resolving high-risk areas for Alpha/Sr removal and each alternative cesium removal process by mid-FY 2001 to support a DOE down-selection decision by June 2001. This Research and Development Summary Report describes the technology development results for each process (See Section 5.0 for a description of the processes.). Previous results are summarized and recently completed FY 2001 work is described.

Risk Assessment Process

Based on all available results from research and development efforts through April 2001, TFA has reassessed the risks of the eleven technology areas that were originally identified as "high risk" in early FY00. Our current, independent risk assessment was conducted by the TFA SPP Technology Development Manager, the Deputy Manager, and the System Leads for each of the four technology areas. The six individuals assigned probabilities and consequences (using the definitions below) to each area and compared results. Only minor differences in ratings were found and discussion of the results and basis for the evaluations led to clear consensus evaluation. No numerical scores or weighting was used in our assessment of the risks.

The original eleven "high risk" technology areas are shown below:

Alpha/Strontium Removal
- Monosodium Titanate (MST) Plutonium (Pu) Removal Performance
- MST/Filtration

Crystalline Silicotitanate Non-Elutable Ion Exchange
- Sorbent Stability
- Sorbent Handling and Sampling
- Gas Generation

Caustic Side Solvent Extraction
- Flowsheet Solvent System Proof-of-Concept
- Radiolytic Stability
- Chemical and Thermal Stability
- Real Waste Performance

Small Tank Tetraphenylborate Precipitation
- Catalytic Product Decomposition
- Reactor/Vessel Foaming

In our current assessment of these technology areas, we used the conventional definition of risk (risk = probability x consequences). For the probability term, we addressed the question, "What is the probability or estimated likelihood that the process will fail (not perform as intended) due to the previously identified "high risk" technology areas?" In our assessment, we used three levels of probability as defined below:

Probability	**Description**
Low	Unlikely to occur during facility life cycle
Moderate	May occur infrequently during facility life cycle
High	Will likely occur frequently during facility life cycle

We also used three levels of consequences and defined them as follows:

Consequences	**Description**	**Magnitude of Cost**
Low	Requires optimization for facility operation or delays mission completion by <0.5 year	<$50 Million
Moderate	Enlarges footprint of shielded facility or delays mission completion by 0.5 to 2 years	$50 - $350 Million
High	Threatens viability of implementation or delays mission completion by unacceptable duration	>$350 Million

Additional explanation of the risk assessment process is presented in Section 6.6.

Current Risk Assessments

The current risk assessment for each technology area is presented in the discussion below. The research and development results that provide the rationale for our risk assessment are summarized here and are presented in greater detail in Section 7.0.

Alpha/Sr Risks

A previous risk assessment[4] identified two high-risk areas for the Alpha/Strontium removal process: MST Plutonium Removal Performance and MST/Filtration.

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

The current research program also provides added confidence that the project will realize continued improvements in this technology. Basic structural studies will provide insight into the surface chemistry of the actinides on MST. The data will provide the needed information to either improve the synthesis of MST to enhance removal efficiency for plutonium or to replace that sorbent with a superior material.

The confidence in deployment of this process technology will increase as the site continues efforts to expand the available analytical data for the contents of the waste tanks. Demonstration of the use of centrifugal filters to test for colloids of plutonium stands as an example of efforts to improve the understanding of the fundamental waste chemistry. Likewise, research during the remainder of the current fiscal year will investigate the chemistry required for removal of plutonium present in different oxidation states.

With continued research efforts of comparable stature during the design, piloting, and construction of the facility, the likelihood of this technology failing appears limited. Furthermore, the most probable recovery from any such failure will simply require addition of more MST and will only result in a brief interruption of operations. **As a result of the existing studies, we perceive a lower probability for failure of this process chemistry. Also,**

recovery from a failure in performance simply requires addition of more monosodium titanate. Thus, we judge the overall risk as reduced to a low rating.

Initial feasibility tests show that addition of permanganate with a reducing agent (e.g., peroxide or formate) also removes these radionuclides from solution under the conditions studied. Similarly, personnel continue to explore the use of selected inorganic materials designed to decontaminate the waste. Although none currently equal or surpass MST in performance, the gained insight will help personnel improve the process efficiency as the project matures.

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

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

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

CST Risks

The previous risk assessment identified three areas of high risk with the use of CST Non-Elutable Ion Exchange: Sorbent Stability, Sorbent Sampling and Handling, and Gas Generation.

Sorbent Stability: Both thermal and chemical factors can affect the stability of the ion exchange sorbent IE-911 (CST and binder) and both were taken into consideration in assessing the risk associated with using IE-911. The thermal stability of IE-911 has been well defined. At relatively high temperatures (e.g., >80ºC which are not typically encountered under normal operating conditions), a significant fraction of absorbed cesium is desorbed. However, operating temperatures below 35ºC are acceptable and present a low risk to this technique. Chemical factors include the leaching of components from IE-911, formation of precipitates in the solutions, and coating of IE-911 particles with precipitates, all of which can ultimately lead to column plugging or particle agglomeration.

Initial batches of IE-911 produced by UOP, LLC, contained extraneous phases that reacted with highly alkaline solutions to release niobium (Nb) and, to a lesser extent, silicon (Si). Research performed during the past year has defined the treatment conditions necessary to remove >95% of the leachable Nb from the IE-911, substantially reducing the risk of column plugging due to this factor. Related research demonstrated minimal leaching of Si from IE-911 and therefore was deemed not likely to contribute significantly to sodium aluminosilicate formation. Factors that are connected indirectly with the use of IE-911, but generally associated with the use of ion-exchange, are formation of aluminum hydroxide ($Al(OH)_3$) (owing to inadvertent admission of water to a column containing highly alkaline aluminum-bearing waste) and coating of the particles with sodium aluminosilicate precipitates. These have been suggested as possible column-plugging mechanisms. Also, agglomeration of CST particles caused by sodium aluminosilicate deposition could impair removal of loaded CST from ion exchange columns. Experiments are under way to define further the potential impacts of such scenarios. **However, formation of precipitates in solution and coating of particles are unresolved issues and are considered to be a high risk for this process**.

Sorbent Handling and Sampling: Sluicing of as-received IE-911 (500 ± 200 µm diameter), size-reduction of IE-911, and representative sampling of (size-reduced) IE-911/sludge/frit slurry were considered in this risk area. Results of studies on sluicing of the relatively large IE-911 particles indicate that suspensions could be formed under the appropriate stirring conditions. Size-reduction of IE-911 particles was demonstrated in two brief vendor tests. The results indicated that particle-size distributions in the desired range could, with a high degree of confidence, be produced by either of two methods. Tests of size-reduction, as required on a larger scale, are expected to be successful.

Sampling of the three-component (size-reduced) IE-911/sludge/frit slurry was tested using a full-scale Hydragard® sampler in a test loop. The results indicated that the presence of IE-911 did not affect the performance of the Hydragard® sampler although it was discovered that the Hydragard® sampler itself exhibited a bias toward low frit with or without IE-911

present. Adjustment of the Hydragard® sampler to correct the bias toward low frit is not expected to be affected by the presence of size-reduced IE-911. **The assessment of these three aspects of sorbent handling and sampling indicates that the combined risk is low.**

Gas Generation: When IE-911 is loaded with Cs-137, gas will be generated in the waste solution due to water radiolysis. Two possible effects of this gas on the performance of the ion-exchange column were investigated. Disengagement of gas bubbles entrained in the liquid between ion-exchange columns was tested so that issues related to sorbent blinding and formation of gaseous voids at the top of downstream columns could be resolved. In addition, the gases formed consisted of oxygen, hydrogen and nitrogen oxides, a potentially flammable mixture. Gas disengagement was demonstrated under a variety of conditions that included sparging, reduced pressure, and ultrasonic cavitation. The results clearly indicated that gas-disengagement equipment (GDE) would be required between columns if ion exchange were selected and that the GDE will most likely be effective.

The effect of radiolytically generated gas on the absorption of cesium by IE-911 was also investigated. A test was performed within a spent fuel element of the High Flux Isotope Reactor at Oak Ridge National Laboratory in such a manner that gas would be generated radiolytically during the time that an IE-911 column was being loaded with cesium. Measurements of the cesium-breakthrough curves for the test column and the same column without the radiation field indicated that the cesium-breakthrough curves were identical within experimental uncertainty and followed the curve expected on the basis of VERSE modeling. **Thus, gas generation was judged to present a low technology risk for CST Non-Elutable Ion Exchange**.

Other CST R&D: Properties of the melter-feed simulants that were used in the 1999 and 2000 Hydragard® sample-loop tests were measured. The 1999 melter-feed simulants with or without size-reduced IE-911 had nearly identical rheological characteristics, yield stresses that were within the DWPF design basis range, and consistencies at or below the lower DWPF design basis limit. In contrast, with the 2000 simulants, adding size-reduced IE-911 to sludge/frit melter feed caused the yield stress to increase nearly three times and exceed the DWPF upper design basis limit. All of the consistency data were within the DWPF design basis limits. In another study, rheograms of Tank 8/40 fresh melter-feed simulants showed the expected pattern of increasing yield stress and consistency with increasing solids content for various melter feeds, all of which exceeded the DWPF design basis yield stress. In general, the behavior of the three slurries at low wt% solids is the same rheologically whereas differences are seen at higher wt% solids, with the Tank 8/40 blends containing IE-911 being more viscous than those that do not. These results suggest that the solids content of the slurry might have to be reduced (by ~4 wt%) if size-reduced IE-911 is used.

A CST-glass study was conducted to determine the effect, if any, on the Product Consistency Test (PCT) responses of CST glasses cooled at different rates. The glasses contained IE-911 and MST and three different simulated sludges. Two bounding cooling profiles, rapidly quenched and canister-centerline, were used in this study. Glasses were selected mainly to challenge the regions where amorphous phase separation is expected. There was essentially

no difference between the PCT responses for glasses subjected to the two cooling profiles. The results reveal that no deleterious amorphous phase separation occurred under either cooling regime. The very good durability of the IE-911-containing glasses implies that durability may not be the limiting factor for waste loading in this option.

CSSX Risks

The previous risk assessment identified four high risks for CSSX: Flowsheet Solvent System Proof-of-Principle, Chemical and Thermal Stability, Radiation Stability, and Real Waste Performance.

Flowsheet Solvent System Proof-of-Concept: The flowsheet solvent system was demonstrated in three tests using 2-cm centrifugal contactors at ANL with SRS average simulant solutions spiked with radioactive cesium-137 (Cs-137). Results from testing show that the requirements for waste and solvent decontamination (40,000) and the concentration factor (CF) for cesium from feed to cesium product (15) were met or exceeded. In addition, the first test demonstrated the need for control of the temperature in the extraction section of the centrifugal contactor cascade to ensure the highest waste decontamination. The solvent was recycled four times during the second test with no adverse effects on the process. Further demonstration of the flowsheet solvent system was provided in a 71-hour test. This test processed 180 liters of SRS simulant with 1.4 L of solvent, which was recycled through the system a total of 42 times during the test. During this test the solvent was washed in a single centrifugal contactor stage with dilute sodium hydroxide (NaOH) to remove dibutylphosphoric acid that was extracted from the waste as well as the 4-*sec*-butylphenol that is formed by degradation of the solvent. The average decontamination factor (DF) for this test was 159,000 for cesium from waste raffinate, and the average CF was 14.9. The process had to be shutdown twice during testing: the first time to replace a feed pump; and the second time to unplug a rotor that became plugged with solids suspended in the SRS simulant. In both cases, recovery was achieved, allowing the test to continue with minimal effect on the DFs or CFs. **These very successful demonstrations of the flowsheet solvent system makes the probability of failure of the flowsheet low and results in the risk being reduced to low**.

Chemical and Thermal Stability: The solvent system for the CSSX process consists of four chemicals: the extractant, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6), a modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy) -2-propanol (Cs-7SB), trioctylamine to aid stripping, and the diluent, Isopar® L. The extractant and modifier are new chemicals. The chemical and thermal stability of this four-component solvent had not been tested previously to determine the products of reaction or their effects on processing, which led to a high risk. Laboratory studies during FY 2000 and FY 2001 were aimed at understanding the chemistry of the solvent and any effects on the process as a result of chemical reactions or thermal degradation. Thermal stability studies showed that even after 235 days at an operating temperature of 35°C, performance remained good and did not necessitate solvent washing. Relative to the goal of a 1-year solvent lifetime, the solvent matrix and its performance did not unacceptably degrade due to thermal effects.

At 60°C, the extractant showed no measurable chemical changes. However, trioctylamine was degraded to dioctyl- and mono-octylamines. Only a trace (<2 mg/L) of 4-*sec*-butylphenol from degradation of the modifier could be detected. Nitration studies of the solvent showed no measurable nitration of either the solvent components or the degradation product, 4-*sec*-butylphenol, under extraction, scrub or strip conditions. The 4-*sec*-butylphenol did not affect extraction or scrubbing, but showed reduced stripping if allowed to build up in the solvent. Tests demonstrated that 4-*sec*-butylphenol was readily scrubbed from the solvent by 0.01-1 M NaOH solutions. Degradation of trioctylamine also affected stripping behavior, but addition of fresh trioctylamine to restore the concentration to 0.001 M restored stripping behavior. The overall conclusion of the studies was that chemical and thermal processes slowly degrade solvent, but effects on the solvent were easily corrected by caustic washing and periodic additions of trioctylamine. **Thus, the probability that chemical and thermal effects on the solvent will affect plant operation is low and the risk is also low.**

Radiation Stability: The risk for radiation stability was judged to be high in the earlier assessment because the solvent had not been tested to determine the products of reaction or their effects on processing. Dose calculations showed that the solvent will receive an annual dose of only 0.092 Mrad per year, assuming: 100% plant utilization; the baseline solvent inventory of 1000 gallons; and the application of the MST process prior to the CSSX process. The relatively low dose is the result of: the short residence time of the solvent in the centrifugal contactor cascade, the large inventory of solvent in the plant, and the nuclides contributing to the solvent dose (Cs-137 and barium-137m). Both external and internal radiation studies showed essentially the same results: production of 4-*sec*-butylphenol from modifier degradation and dioctylamine from degradation of trioctylamine (TOA). External radiation tests involved irradiation of solvent and simulant with Co-60 gamma source to doses exceeding the life of the plant by 10 fold. No significant degradation of the primary solvent components was observed for doses typical of the proposed facility lifetime. Less than 10% extractant loss occurred and no statistically significant loss of Cs-7SB modifier occurred at the maximum dose, although the 4-*sec*-butylphenol was ~0.4% of the initial modifier concentration. Less than 10% of the trioctylamine degraded at a dose of 6 Mrad.

Internal radiation studies were performed with both real waste solutions and simulant spiked to SRS-average waste Cs-137 concentration with total radiation doses from 1 to 13.5 years of plant operation. Internal radiation tests using spiked simulant (at the baseline process flowsheet organic-to-aqueous phase ratios for the extraction, scrub and strip sections) did not identify any dose-related impacts on dispersed-phase break times, third-phase formation, or interfacial crud formation. Neither the real-waste nor the spiked-simulant tests showed any effect of radiation on extraction or scrubbing, but stripping effectiveness was reduced due to high distribution coefficients. Washing the solvent with 0.01 M NaOH and replenishing the TOA concentration restored good stripping performance.

The radiation studies show the solvent to be quite stable to radiation with TOA being most sensitive to radiation-induced degradation. **As a result of these studies, the probability**

and consequently the risk that radiation effects will cause problems during plant operation is considered to be low.

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

During the flowsheet test, 105 liters of waste from tanks 37H and 44F were treated using 1.5 liters of solvent. The solvent was recycled continuously (~25 times) to the process after passing through a single centrifugal-contactor stage of NaOH wash solution. Decontamination Factors (DF) for the waste raffinate as high as 2 million were observed during the first 24 hours of the test. A composite of samples taken throughout the test (includes samples during upset conditions) gave a DF of 40,000 versus a requirement of 13,000 to meet the saltstone Waste Acceptance Criteria and a target of 40,000. The overall average DF for the spent solvent was 1.2 million versus a target of 40,000. Problems were encountered in measuring the flow rate of the waste feed stream resulting in low feed flow rate in the first 24 hours of the test. Consequently, the CFs averaged only 12.8 during that part of the test, which is lower than the target value of 15. Flow rate adjustments to the feed and strip streams resulted in varied, but higher, CFs during the remainder of the test. The CF exceeded 15 for several hours during the test, but averaged 14.4 during the last 10.5 hours of operation. Operational problems were encountered three times when the hydraulic capacity of the contactors was exceeded during efforts to achieve higher CFs. Recovery from the upsets was demonstrated proving the robustness of the process. The real waste test proved flowsheet viability, allowing the consequence to be lowered to moderate (potentially enlarging the footprint of the shielded facility). **However, our evaluation of the technology risk is lowered only to moderate because only one contactor test has been conducted and limited batch equilibration test results with real waste are available.** Confirmation of the batch equilibrium test results from the remaining tank waste samples will be available prior to down selection, which could further reduce this risk.

Other CSSX R&D: The extractant and modifier are not made commercially at present. Efforts are underway to improve the processes for manufacture and to find vendors willing to make these chemicals. The improved modifier (CS-7SB) was synthesized at a 3.6 kg scale in the laboratory to demonstrate scale-up and provide solvent for studies at ANL, ORNL, and SRTC. The larger batch size yielded high purity product with a product yield higher (95%) than 100 g batches. IBC Advanced Technologies, Inc. demonstrated scale-up of BOBCalixC6 synthesis by preparing a 1 kg batch of good purity. The patent which covers

the original CSSX process chemicals and conditions was issued January 16, 2001. A patent application covering the second generation modifiers was filed with the US Patent & Trademark Office.

ORNL identified potential candidate firms to supply the chemicals on the scale required by the proposed process plant (46 kg BOBCalixC6 and 677 kg of Cs-7SB modifier). The results of this effort were summarized in a series of letter reports submitted to SRS. An Expressions of Interest solicitation for the manufacture of 2 kg of modifier and 50 g of BOBCalixC6 was sent by SRS to 29 companies with seven positive responses received. Actual procurement of the material was placed on hold until the SPP technology selection decision is completed by DOE.

STTP Risks

The previous risk assessment identified two high risk areas in the STTP process: Catalytic Product Decomposition and Reactor/Vessel Foaming. In addition, R&D activities were performed in two additional areas: precipitate hydrolysis testing and glass formulation.

Catalytic Product Decomposition: The risk of catalytic decomposition of TPB, like that experienced in ITP Tank 48 in 1995, has been addressed through increasing the understanding of catalytic decomposition and through additional demonstrations of process performance.

SPP research efforts showed that decomposition was catalyzed by supported, noble metal ions which had been reduced to metals. In particular, reduced palladium and platinum were shown to be the most catalytically active species. Reduced rhodium and ruthenium, which are present in the HLW tanks, were shown to be ~25% as reactive as Pd(0). Tests indicated that phenylborate intermediates and mercury participate in the catalytic decomposition reaction, rather than acting as just reducing agents for the noble metals. Present data indicate that diphenylborinic acid (2PB) may be the intermediate of primary importance and that decomposition can take place in the presence of 2PB and supported Pd(0) alone. However, the presence of diphenylmercury (or mercury(II) salt), along with the other two components, yields a much more reactive system. Catalyst consultants have incorporated information from the ongoing research and development activities into proposed reaction and catalytic mechanisms which are consistent with those identified in literature studies.

Batch catalytic decomposition tests were conducted on six different SRS HLW tank samples at both ~25°C and at 45°C (for a total of twelve tests). Cesium precipitation reached the Saltstone limit of 45 nCi/g in ten of the twelve tests; however, the time required for the samples to meet this limit varied from <500 hours to >3500 hours. The most probable cause for the differences in the rate of decontamination was the extremely low solubility of NaTPB in high ionic strength salt solutions. Once added, the majority of the NaTPB precipitated out of solution and its dissolution was very slow under the mild degree of agitation. Attempts to increase the rate of agitation were unsuccessful. Of the twelve tests, only two showed evidence of TPB degradation, and both of these tests came from Tank 35H, which had higher

levels of soluble mercury than the other waste samples. The TPB degradation rates in Tank 35H were much less than the maximum seen in previous real waste and surrogate waste tests in terms of calculated benzene production (i.e., 0.2 mg/(L-h) for Tank 35H vs. 10 mg/(L-h) maximum in other tests).

A test system using 20-L Continuous Stirred Tank Reactors (CSTR) with Cs-137 spiked simulants demonstrated that adequate decontamination could be maintained while the STTP was undergoing active catalytic decomposition at both 25°C and 45°C. Also, the CSTR test using real SRS HLW successfully demonstrated that stable operation with acceptable DFs for Cs-137 and Sr-90 could be obtained at both 25°C and 45°C.

In summary, an increased understanding of the catalytic decomposition has certainly been achieved. However, catalytic decomposition tests were conducted on samples from several different SRS HLW tanks and evidence of catalytic decomposition was detected in only one HLW sample. In spite of what has been learned to date, exactly what activates the catalytic decomposition in real waste is not fully known. Nevertheless, should decomposition occur, research and development tests indicate that required DFs will be met. As a result, there is only a moderate probability that catalytic decomposition will affect the STTP process. If catalytic decomposition does occur to an extent that DFs were not met, moderate consequences, which could require enlarging the footprint of the shielded facility, could result. **Therefore, the risk of catalytic product decomposition to the STTP process is moderate.**

Foaming: Foaming could occur in the precipitate tank, the concentration tank, and the wash tank for the STTP process. The candidate antifoam must not only be effective in controlling foam in these three tanks, but must also not negatively impact downstream processes or waste forms. An antifoam known as IIT B52 has been developed by Illinois Institute of Technology and extensively tested in foam column tests. These foam column tests were very aggressive; actual foaming conditions during STTP processing would be much less severe. The IIT B52 antifoam was very effective in the foam column tests with precipitated and concentrated slurries, and somewhat less effective with washed slurries. In long-term tests with synthetic wastes in CSTRs, which are more representative of the actual STTP conditions, the IIT B52 was very effective in controlling foaming in all three environments. The IIT B52 was also demonstrated to be effective in 1-L CSTRs using actual SRS HLW.

The active ingredient in the IIT B52 antifoam is a surfactant, sodium bis(2-ethylhexyl) sulfosuccinate. Testing showed that the IIT B52 was consumed during the precipitation, concentration, and washing cycles. No active antifoam agent was detected in the dilute precipitate, the concentrated precipitate, the washed precipitate, or the permeate from the concentration and washing. Additional studies found that irradiation of the antifoam or precipitate did not significantly reduce the effectiveness of the antifoam.

IIT B52 was shown to be an effective antifoam for the STTP process. The probability is low that reactor/vessel foaming will occur to such an extent that processing is negatively impacted. If foaming should occur, the consequences are low and would only require

optimization for operation of the facility. **Therefore, the risk to the STTP process of reactor/vessel foaming is considered to be low.**

Other STTP R&D: Studies were done to determine the impact of IIT B52 antifoam on hydrolysis kinetics. The antifoam agent IIT B52 was found to have no detectable effect upon acid hydrolysis of a tetraphenylborate (TPB) simulant slurry containing 2000 ppm of the antifoam agent. Analysis of reactor contents at the completion of feeding revealed no detectable quantity of the antifoam agent. Analysis of all process streams at the completion of the hydrolysis cycle also revealed no detectable quantity of the antifoam agent. It was concluded that IIT B52 rapidly decomposes in the feed slurry and/or during acid hydrolysis.

A glass formulation study was conducted to determine the effect of cooling rate on glasses made from sludge and precipitate hydrolysis aqueous (PHA) product from the STTP process. Two bounding cooling profiles were used in this study: rapidly quenched and a canister centerline cooling curve. The results showed that there was no practical difference between the PCT responses for glasses subjected to the two cooling profiles. These results reveal that no deleterious (amorphous) phase separation occurred under either cooling regime. All of the glasses readily satisfied the requirement that the PCT responses be at least two standard deviations below the PCT response of the standard environmental analysis glass. Furthermore, the PCT responses were almost entirely within the prediction intervals of the DWPF Durability Model.

Summary

The assigned probabilities, consequences, and resulting risks (described above) are summarized for each cesium-removal process in Table ES.1. The appropriate alpha and strontium risks are included with each of the three cesium removal processes since alpha and strontium removal are required for all. The alpha and strontium risks are the same for CST and CSSX because the same processing approach is assumed for both. However, filtration (equipment size) is a low risk issue for the STTP process because MST and sludge filtration performance is much better when filtered simultaneously with TPB precipitates. It is also important to recognize that in early FY 2000 two of these technology areas (CSSX real waste performance and STTP catalytic product decomposition) were felt to have high consequences, i.e., "threatened viability of implementation." TFA believes that the successful tests in FY 2001 support reducing the maximum consequences of these areas to moderate (potentially enlarging the footprint of the shielded facility).

These technology risk assessments will be used as part of DOE's selection of the preferred cesium-removal process. The DOE Technical Working Group is responsible for evaluating all input, making the final risk assessments, applying the down-selection criteria, and recommending the preferred alternative to DOE-HQ management.

Table ES.1. Current Assessment of Previous "High Risk" Technology Areas for Alternative Cesium Removal Processes

Cs Removal Process	Technical Risk	Probability*	Consequence (Potential Impact)	Risk
CST	MST Pu Removal Performance	Moderate	Low (Optimization)	Low
	MST/Filtration	Moderate	Moderate (Footprint)	Moderate
	Sorbent Stability	High	Moderate (Footprint)	High
	Sorbent Handling and Sampling	Low	Moderate (Footprint)	Low
	Gas Generation	Low	Moderate (Footprint)	Low
CSSX	MST Pu Removal Performance	Moderate	Low (Optimization)	Low
	MST/Filtration	Moderate	Moderate (Footprint)	Moderate
	Flowsheet Solvent System Proof-of-Concept	Low	Moderate (Footprint)	Low
	Radiolytic Stability	Low	Moderate (Footprint)	Low
	Chemical and Thermal Stability	Low	Moderate (Footprint)	Low
	Real Waste Performance	Moderate	Moderate (Footprint)	Moderate
STTP	MST Pu Removal Performance	Moderate	Low (Optimization)	Low
	MST/Filtration	Low	Low (Optimization)	Low
	Reactor/Vessel Foaming	Low	Moderate (Footprint)	Low
	Catalytic Product Decomposition	Moderate	Moderate (Footprint)	Moderate

* The probability or estimated likelihood that the process will fail (not perform as intended).

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Steve Schlahta, Deputy Manager
TFA Salt Processing Project Technology Development

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Acronyms and Abbreviations

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

ANL	Argonne National Laboratory
AOP	Annual Operating Plan
AST	Alpha Sorption Tank
CCIX(TM)	Countercurrent Ion Exchange Technology
CF	Contamination Factor
CIF	Consolidated Incineration Facility
CSSX	Caustic Side Solvent Extraction
CST	crystalline silicotitanate
CST	CST Non-Elutable Ion Exchange
CSTR	Continuously Stirred Tank Reactor
DF	Decontamination Factor
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE-HQ	U.S. Department of Energy-Headquarters
DSS	decontaminated salt solution
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
ESP	Extended Sludge Processing Facility
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
HLW	high level waste
HM	H modified (SRS enriched uranium solvent extraction process)
HPLC	high pressure liquid chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LLC	Limited Liability Corporation
LLW	low level waste
ITP	In-Tank Precipitation
IWO	Internal Work Order
MST	monosodium titanate
MTZ	Mass Transfer Zone
NAS	National Academy of Sciences
NMR	nuclear magnetic resonance
NRC	National Research Council
ORNL	Oak Ridge National Laboratory
PCCS	Product Composition Control System
PEG	Program Execution Guidance
PHA	precipitate hydrolysis aqueous
PNNL	Pacific Northwest National Laboratory
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
SNL	Sandia National Laboratories

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
TNX	Service works or pilot plant facility at Savannah River Site
TPB	tetraphenylborate
TTP	Technical Task Plan
TRU	transuranic
TWG	Technical Working Group
UFMB	Up-Flow Moving Bed
UOP	UOP LLC, Mt. Laurel, NJ
USC	University of South Carolina
VERSE	VErsatile Reaction SEparation (simulator for liquid chromatography)
VSEP	Vibratory Shear Enhanced Processing
WAC	Waste Acceptance Criteria
WSRC	Westinghouse Savannah River Company
XAFS	X-ray Absorption Fine-Structure
ZAM	Zheng-Anthony-Miller (CST equilibrium model)

1.0 Introduction

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

In March 2000, DOE-Headquarters (DOE-HQ) requested the Tanks Focus Area (TFA) to assume management responsibility for the SPP technology development program at SRS. The TFA was requested to conduct several activities, including review and revision of the technology development roadmaps, development of down-selection criteria, and preparation of a comprehensive research and development (R&D) program plan for three candidate Cs removal technologies, as well as the alpha and Sr removal technologies that are part of the overall SPP. The TFA issued a revised R&D program plan[3] in November 2000. 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 summary report describes the technology development results for each process. Previous and FY00 results are summarized and recent FY01 results are described in Section 7.0.

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 low-level waste (LLW) disposal.

To achieve this goal, the previous SRS contractor, E.I. duPont De Nemours and Company successfully demonstrated the In-Tank Precipitation (ITP) process both on a moderate and full-scale bases 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 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 Facilities 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 ensure safe operations at the production rate needed to support the STP and FFA. On January 22, 1998, WSRC informed DOE that 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 the Office of 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 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; thus 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[1] in October 1999 and their final report[2] 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 R&D on each alternative was required to reduce technical uncertainty prior to a down-selection decision. Accordingly, DOE postponed plans to issue a draft Request for Proposal to the private sector seeking input on design and construction of the needed treatment facilities. DOE-SR also delayed the issuance of the Draft Supplemental Environmental Impact Statement (SEIS) on SRS HLW treatment alternatives pending further development of salt processing technology alternatives.

In 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. The TFA issued the R&D program plan[3] in November 2000. To support the down-selection, TFA was requested to provide this R&D Summary Report which provides a summarized version of the recent results of the alpha/Sr removal process, as well as the three alternative Cs removal technologies.

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

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

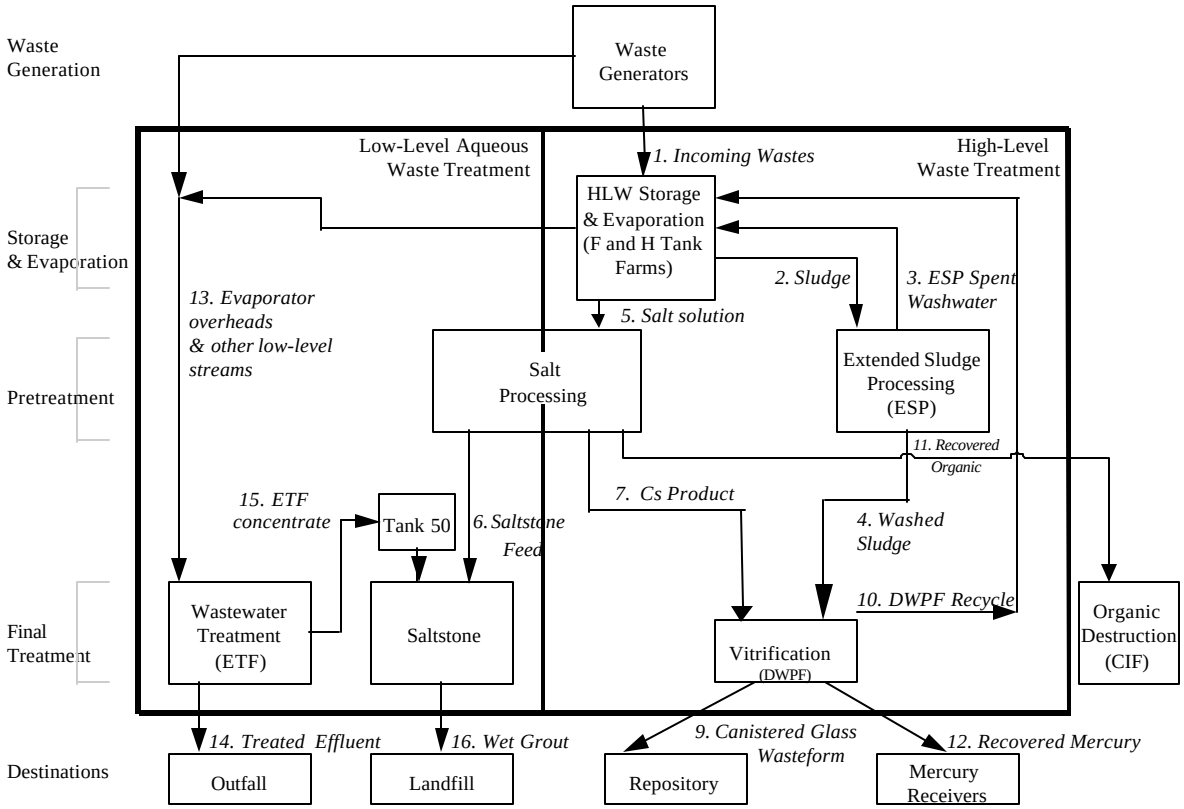

Figure 3.1. High-Level Waste Major Interfaces

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 by acid hydrolysis 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 and in the Final Supplemental Environmental Impact Statement Defense Waste Processing Facility,[5] the existing SRS HLW System consists of seven inter-connected 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 radio-nuclides in the salt for final disposition in support of environmental protection, safety, and current and planned missions. In 1994, the plan 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 that any alternative must fulfill to recover HLW storage space and meet the FFA/STP.

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. 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).
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

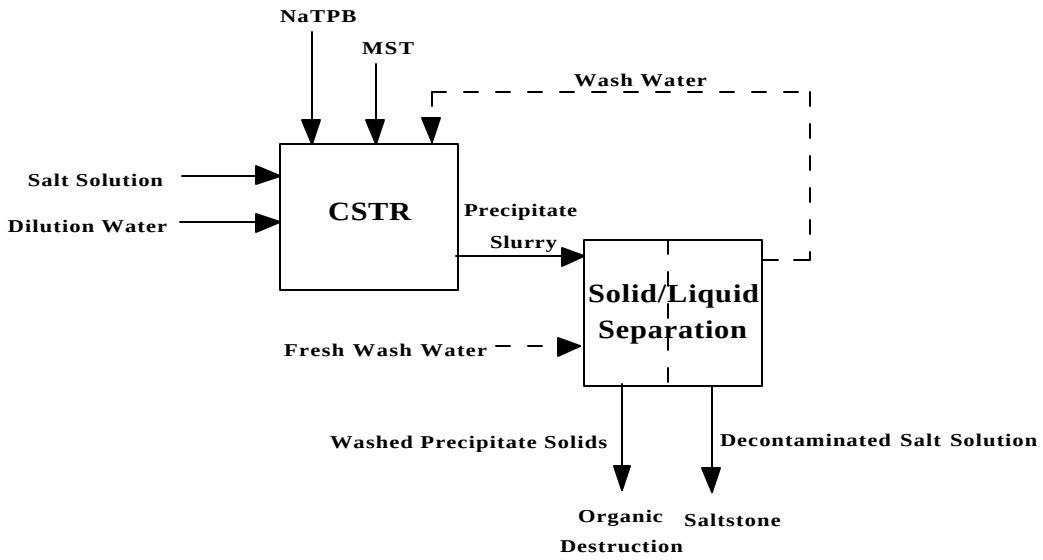

Figure 5.1. Alpha and Sr Removal Flow Diagram for Small Tank Tetraphenylborate Precipitation

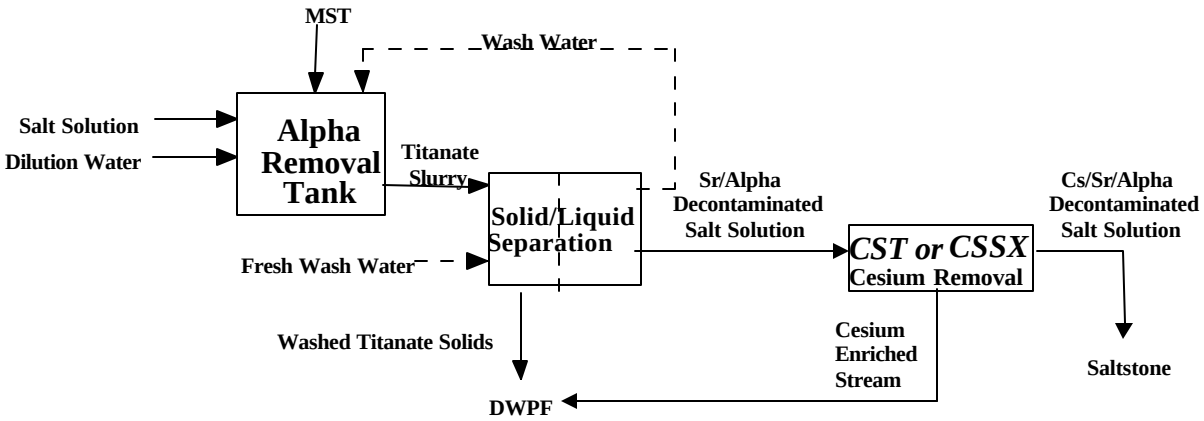

Figure 5.2. Alpha and Sr Removal Flow Diagram for CST Non-Elutable Ion Exchange and Caustic Side Solvent Extraction

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.[6,7,8] 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.

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 sorbent loading and unloading operations in the Alpha Sorption Tank (AST) within the shielded facility. Soluble alpha contaminants and Sr-90 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.

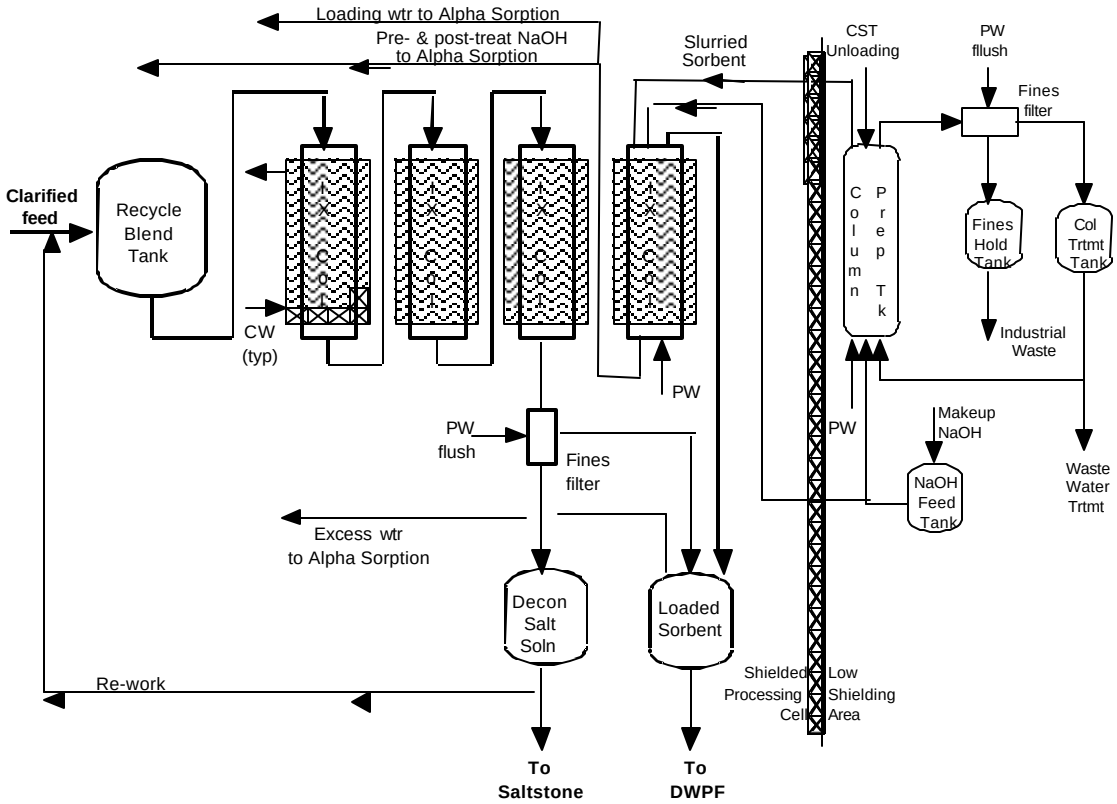

Figure 5.3. CST Non-Elutable Ion Exchange Flow Diagram

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 Sorbent Hold Tanks where it is combined with the solids from the fines filter. Excess sluicing water is removed to produce a 10 wt% CST slurry in water. The excess water is sent to the Alpha Sorption Tank. The particle size of the CST will be reduced by grinding to facilitate slurry transfer and to ensure representative sampling in DWPF. The CST slurry is stored in the Loaded Sorbent Hold Tank until it can be transferred to the DWPF for incorporation into HLW waste glass.

Before being loaded into a column, the CST sorbent 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 sorbent 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 sorbent 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 step 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

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

Prior to treatment by solvent extraction, actinides and Sr are removed from the waste by sorption with MST as shown in Figure 5.2. The resulting slurry is then filtered to remove the MST and sludge solids.

The CSSX process uses a novel solvent system made up of four components: calix[4]arene-bis-(*tert*-octylbenzo-crown-6) known as BOBCalixC6, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-secbutylphenoxy)-2-propanol, known as modifier Cs-7SB, trioctylamine known as TOA, and Isopar® L, the diluent. The solvent is contacted with the alkaline waste stream in a series of countercurrent centrifugal contactors (the extraction stages) where Cs and nitrate are extracted into the solvent phase. The resulting clean aqueous raffinate is transferred to the SPF for conversion to saltstone. Following Cs extraction, the solvent is scrubbed with dilute acid to remove other soluble salts particularly Na and K from the solvent stream (the scrub stages). The scrubbed solvent then passes into the strip stages where it is contacted with a very dilute acid stream to transfer the Cs to the aqueous phase. The aqueous strip effluent containing pure Cs nitrate, which is 15 times more concentrated than in the waste, is transferred to the DWPF for vitrification. Figure 5.4 contains a schematic representation of the proposed solvent extraction flowsheet.

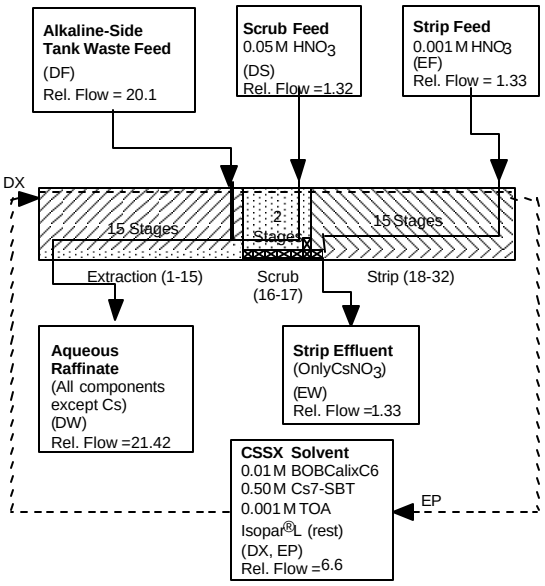

Figure 5.4. Caustic Side Solvent Extraction Flow Diagram

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.[9]

Over long periods of time, either the modifier, the TOA, or the calixarene may degrade either chemically or radiolytically. The most likely degradation is that of the modifier to form a phenolic compound that is soluble in the organic phase in contact with acid solutions. However, the modifier was designed 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 first an acidic wash of the solvent followed by a caustic wash of the solvent to maintain solvent performance. These two wash stages are intended to remove any acidic or caustic impurities that may accumulate in the solvent system over time. In particular, the caustic wash is known to remove the modifier degradation products. In addition, the 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 may contain either soluble solvent components and/or entrained organic phase. This potential loss may represent an economic concern due to the expensive solvent components or a problem in downstream operations. The proposed process contains solvent recovery processes for the aqueous effluent streams. Additional contactor stages are provided to remove soluble organics and in particular to remove solvent from the exiting streams with a small amount of Isopar® L. The aqueous phase from these stages is then sent to a settling tank where any remaining entrained organic (mostly the Isopar® L) is allowed to float and is decanted. The Isopar® L containing solvent is distilled to recover the extractant and modifier. The Isopar® L added in the two solvent recovery processes is sent to the CIF.

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

5.4 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, sodium tetraphenylborate (NaTPB) solution, MST slurry, spent wash water and dilution water are continuously added to the first of two Continuous Stirred Tank Reactors (CSTR) 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 tetraphenylborate (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.

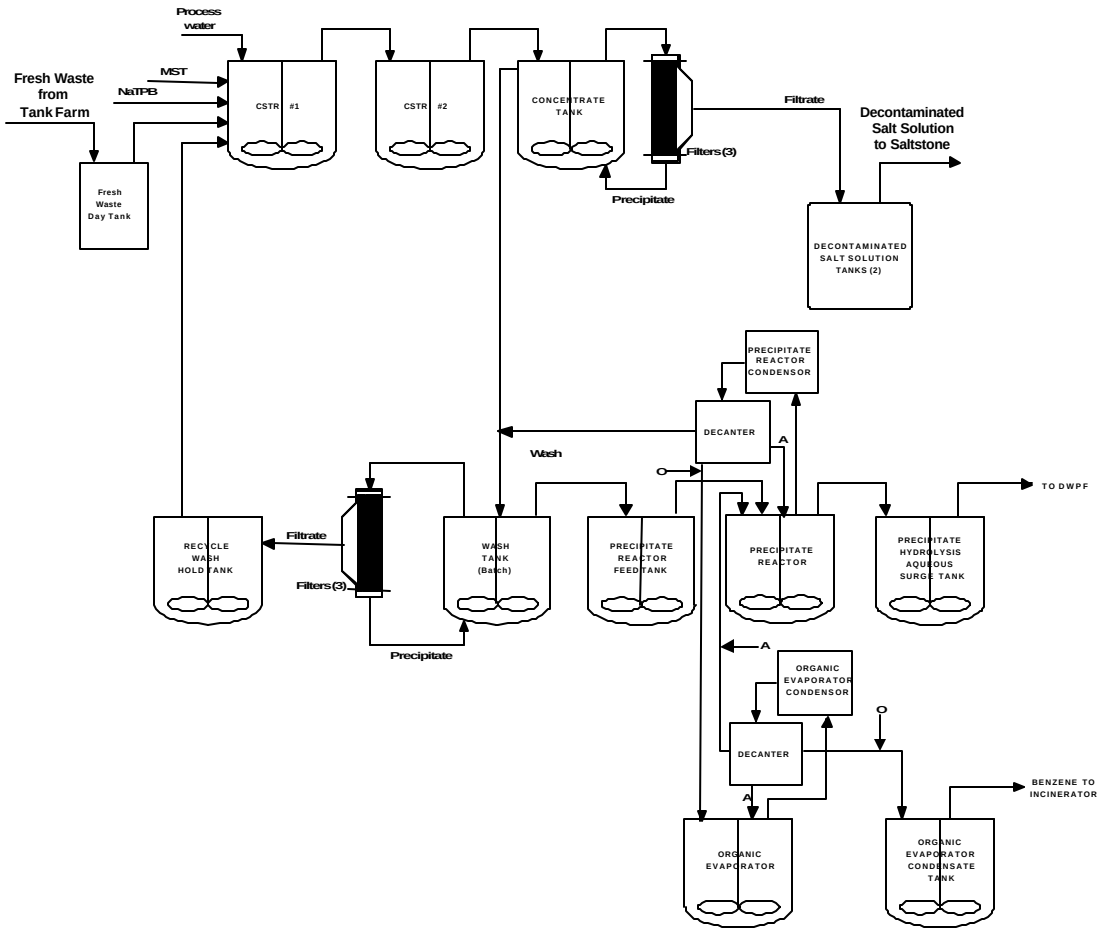

Figure 5.5. Small Tank Tetraphenylborate Precipitation Flow Diagram

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. NaTPB 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 Reactor Feed 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 precipitate hydrolysis is combined with sludge feed in the DWPF and incorporated into HLW waste glass.

In the initial proposal for the STTP 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 and Assessment of Risks

Initially, a large number of technical issues and concerns were identified with each of the four processes described in Section 5.0 of this R&D Summary Report. Further evaluation of these issues and concerns resulted in the identification of a smaller number of high technical risks to implementation of each of the four processes. A goal of the R&D program has been to specifically address the high technical risks with each process, thus reducing the consequences associated with making a down-selection decision.

The key technology needs for each process are summarized below.

6.1 Alpha and Sr Removal

The Savannah River Site Salt Processing Project plans to use 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 indicated 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, required 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 based on kinetics data at 5.6M sodium.[10] Strontium removal occurred rapidly under alkaline conditions with no apparent influence from the presence of competing sorbates such as actinides. Of the actinides, Pu removal proved most important to satisfying the requirements for total alpha activity in the DSS. In general, MST exhibited slower removal rates for Pu and other actinides than observed for Sr. Testing indicated that the actinides compete for sites on the MST. Both U and Np exhibit much higher solubility in alkaline solutions than Pu. Consequently, the extent and rate of Pu removal depended strongly on the total actinide concentration. Hence, while the current pre-conceptual designs achieved the requirements for radionuclides, the use of MST limited 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 required solid-liquid separation of a stream containing the MST combined with entrained sludge solids (metal oxides and hydroxides). The cross-flow filtration proved notably slower for those designs.

While MST adequately meet 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 also investigated 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 alternatives

Of these, the "high risk" areas were identified as MST Pu removal performance and filtration (equipment size).

Finally, the conceptual designs would benefit from 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 sorbent and column pluggage events have been observed in previous testing. This has led to a desire to re-engineer the sorbent 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. When CST is fully loaded with Cs-137, gas will be generated 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 had become 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 were:

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

The ability of CST to remove Cs from aqueous solutions as a function of temperature and waste composition was 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 were 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 were 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) were also 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 were needed 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 were driven by four high risk areas of technical uncertainty:

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

Technology development needs were also driven by the need to demonstrate the commercial availability of the CSSX solvent components. This need would 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, NaTPB, 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 were 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 safety risks to personnel and potential environmental releases. Therefore, the high risk technology areas were:

- Catalytic product decomposition, and
- Foaming in vessels.

Initial data from batch reactor experiments indicated that MST kinetics would control the size of the reactor. Knowledge of the rate and equilibrium (solubility) of alkali metal tetraphenylborate compounds 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 were required.

6.5 Other Technology Development Needs

Other specific technology development needs had been identified based on technical issues and concerns that were identified in earlier phases of the program. These needs are listed in Appendix B of the "Savannah River Site Processing Project Research and Development Program Plan."[3] The technology development activities described in Section 7.0 focus primarily on resolving the high risk issues described above.

6.6 Risk Assessment Process

Based on all research efforts through the available FY01 results, TFA has reassessed the risks of the eleven technology areas that were identified as "high risk" in early FY00 (see above descriptions in Sections 6.1-6.4). Our current, independent risk assessment was conducted by the TFA SPP Technology Development Manager, the Deputy Manager, and the System Leads for each of the four technology areas. The six individuals assigned probabilities and consequences (using the definitions below) to each area and compared results. Only minor

differences in ratings were found and discussion of the results and basis for the evaluations led to clear consensus evaluation. No numerical scores or weighting was used in our assessment of the risks.

In our current assessment of these areas, we used the conventional definition of risk (risk = probability x consequences). For the probability term, we addressed the question, "What is the probability or estimated likelihood that the process will fail (not perform as intended) due to the previously identified "high risk" technology areas?" In our assessment, we used three levels of probability as defined below:

Probability	**Description**
Low	Unlikely to occur during facility life cycle
Moderate	May occur infrequently during facility life cycle
High	Will likely occur frequently during facility life cycle

We also used three levels of consequences and defined them as follows:

Consequences	**Description**	**Magnitude of Cost**
Low	Requires optimization for facility operation or delays mission completion by <0.5 year	<$50 Million
Moderate	Enlarges footprint of shielded facility or delays mission completion by 0.5 to 2 years	$50 - $350 Million
High	Threatens viability of implementation or delays mission completion by unacceptable duration	>$350 Million

The risk matrix, showing the product of these probability and consequence terms, is shown in Table 6.1.

6.7 Current Risk Assessments

The current risk assessment for each technology area is presented in the discussion below. The research and development results that provide the rationale for our risk assessment are summarized here and are presented in greater detail in Section 7.0.

6.7.1 Alpha/Sr Risks

A previous risk assessment[4] identified two high-risk areas for the Alpha/Strontium removal process: MST Plutonium Removal Performance and MST/Filtration.

MST Pu Removal Performance: During the past several years, SPP personnel examined the sorption of plutonium – and other radionuclides – by MST under prototypical conditions for the three process options. These studies included numerous experiments with actual

Table 6.1. Risk Matrix

Probability	Low	Moderate	High
High	M	H	H
Moderate	L	M	H
Low	L	L	M

Consequences

HLW, tests with simulated waste containing added actinides and strontium, and plutonium and strontium removal as part of flowsheet demonstrations with each of the cesium removal process options using both simulated and actual wastes. The accumulated data demonstrated successful operation across a variety of waste compositions while meeting process requirements defined for the proposed facility. While the rate of plutonium sorption limits the nominal processing capacity for the process options, there is little doubt that MST adequately removes plutonium with an acceptable efficiency. Recent studies demonstrate that relative to plutonium removal, MST performs better than the principal competing inorganic sorbents either currently available at commercial scale or in final stages of development. However, feasibility tests with permanganate additions show equal or superior removal of the radionuclides as compared to sorption on MST. As research of that chemistry continues, the baseline design could readily incorporate that chemistry option.

The current research program also provides added confidence that the project will realize continued improvements in this technology. Basic structural studies will provide insight into the surface chemistry of the actinides on MST. The data will provide the needed information to either improve the synthesis of MST to enhance removal efficiency for plutonium or to replace that sorbent with a superior material.

The confidence in deployment of this process technology will increase as the site continues efforts to expand the available analytical data for the contents of the waste tanks. Demonstration of the use of centrifugal filters to test for colloids of plutonium stands as an example of efforts to improve the understanding of the fundamental waste chemistry.

Likewise, research during the remainder of the current fiscal year will investigate the chemistry required for removal of plutonium present in different oxidation states.

With continued research efforts of comparable stature during the design, piloting, and construction of the facility, the likelihood of this technology failing appears limited. Furthermore, the most probable recovery from any such failure will simply require addition of more MST and will only result in a brief interruption of operations. **As a result of the existing studies, we perceive a lower probability for failure of this process chemistry. Also, recovery from a failure in performance simply requires addition of more monosodium titanate. Thus, we judge the overall risk as reduced to a low rating**.

Initial feasibility tests show that addition of permanganate with a reducing agent (e.g., peroxide or formate) also removes these radionuclides from solution under the conditions studied. Similarly, personnel continue to explore the use of selected inorganic materials designed to decontaminate the waste. Although none currently equal or surpass MST in performance, the gained insight will help personnel improve the process efficiency as the project matures.

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

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

To reduce the risk, the project continues to pursue alternate means of solid-liquid separation. The options under investigation include use of a centrifuge or of a high-shear, rotary cross-flow filter. Initial vendor testing of the latter equipment using simulated waste shows

significant promise of improved performance. Similarly, personnel continue to investigate alternate process configurations that, for instance, use chemical additives to achieve enhanced sedimentation in advance of the process facility. Such approaches may reduce the burden for the cross-flow filter thereby substantially reducing the implementation risk.

6.7.2 CST Risks

The previous risk assessment identified three areas of high risk with the use of CST Non-Elutable Ion Exchange: Sorbent Stability, Sorbent Sampling and Handling, and Gas Generation.

Sorbent Stability: Both thermal and chemical factors can affect the stability of the ion exchange sorbent IE-911 (CST and binder) and both were taken into consideration in assessing the risk associated with using IE-911. The thermal stability of IE-911 has been well defined. At relatively high temperatures (e.g., >80ºC which are not typically encountered under normal operating conditions), a significant fraction of absorbed cesium is desorbed. However, operating temperatures below 35ºC are acceptable and present a low risk to this technique. Chemical factors include the leaching of components from IE-911, formation of precipitates in the solutions, and coating of IE-911 particles with precipitates, all of which can ultimately lead to column plugging or particle agglomeration.

Initial batches of IE-911 produced by UOP, LLC, contained extraneous phases that reacted with highly alkaline solutions to release niobium (Nb) and, to a lesser extent, silicon (Si). Research performed during the past year has defined the treatment conditions necessary to remove >95% of the leachable Nb from the IE-911, substantially reducing the risk of column plugging due to this factor. Related research demonstrated minimal leaching of Si from IE-911 and therefore was deemed not likely to contribute significantly to sodium aluminosilicate formation. Factors that are connected indirectly with the use of IE-911, but generally associated with the use of ion-exchange, are formation of aluminum hydroxide ($Al(OH)_3$) (owing to inadvertent admission of water to a column containing highly alkaline aluminum-bearing waste) and coating of the particles with sodium aluminosilicate precipitates. These factors have been suggested as possible column-plugging mechanisms. Also, agglomeration of CST particles caused by sodium aluminosilicate deposition could impair removal of loaded CST from ion exchange columns. Experiments are under way to define further the potential impacts of such scenarios. **However, formation of precipitates in solution and coating of particles are unresolved issues and are considered to be a high risk for this process**.

Sorbent Handling and Sampling: Sluicing of as-received IE-911 (500 ± 200 µm diameter), size-reduction of IE-911, and representative sampling of (size-reduced) IE-911/sludge/frit slurry were considered in this risk area. Results of studies on sluicing of the relatively large IE-911 particles indicate that suspensions could be formed under the appropriate stirring conditions. Size-reduction of IE-911 particles was demonstrated in two brief vendor tests. The results indicated that particle-size distributions in the desired range could, with a high

degree of confidence, be produced by either of two methods. Tests of size-reduction, as required on a larger scale, are expected to be successful.

Sampling of the three-component (size-reduced) IE-911/sludge/frit slurry was tested using a full-scale Hydragard® sampler in a test loop. The results indicated that the presence of IE-911 did not affect the performance of the Hydragard® sampler although it was discovered that the Hydragard® sampler itself exhibited a bias toward low frit with or without IE-911 present. Adjustment of the Hydragard® sampler to correct the bias toward low frit is not expected to be affected by the presence of size-reduced IE-911. **The assessment of these three aspects of sorbent handling and sampling indicates that the combined risk is low.**

Gas Generation: When IE-911 is loaded with Cs-137, gas will be generated in the waste solution due to water radiolysis. Two possible effects of this gas on the performance of the ion-exchange column were investigated. Disengagement of gas bubbles entrained in the liquid between ion-exchange columns was tested so that issues related to sorbent blinding and formation of gaseous voids at the top of downstream columns could be resolved. In addition, the gases formed consisted of oxygen, hydrogen and nitrogen oxides, a potentially flammable mixture. Gas disengagement was demonstrated under a variety of conditions that included sparging, reduced pressure, and ultrasonic cavitation. The results clearly indicated that gas-disengagement equipment (GDE) would be required between columns if ion exchange were selected and that the GDE will most likely be effective.

The effect of radiolytically generated gas on the absorption of cesium by IE-911 was also investigated. A test was performed within a spent fuel element of the High Flux Isotope Reactor at Oak Ridge National Laboratory in such a manner that gas would be generated radiolytically during the time that an IE-911 column was being loaded with cesium. Measurements of the cesium-breakthrough curves for the test column and the same column without the radiation field indicated that the cesium-breakthrough curves were identical within experimental uncertainty and followed the curve expected on the basis of VERSE modeling. **Thus, gas generation was judged to present a low technology risk for CST Non-Elutable Ion Exchange**.

Other CST R&D: Properties of the melter-feed simulants that were used in the 1999 and 2000 Hydragard® sample-loop tests were measured. The 1999 melter-feed simulants with or without size-reduced IE-911 had nearly identical rheological characteristics, yield stresses that were within the DWPF design basis range, and consistencies at or below the lower DWPF design basis limit. In contrast, with the 2000 simulants, adding size-reduced IE-911 to sludge/frit melter feed caused the yield stress to increase nearly three times and exceed the DWPF upper design basis limit. All of the consistency data were within the DWPF design basis limits. In another study, rheograms of Tank 8/40 fresh melter-feed simulants showed the expected pattern of increasing yield stress and consistency with increasing solids content for various melter feeds, all of which exceeded the DWPF design basis yield stress. In general, the behavior of the three slurries at low wt% solids is the same rheologically whereas differences are seen at higher wt% solids, with the Tank 8/40 blends containing

IE-911 being more viscous than those that do not. These results suggest that the solids content of the slurry might have to be reduced (by ~4 wt%) if size-reduced IE-911 is used.

A CST-glass study was conducted to determine the effect, if any, on the Product Consistency Test (PCT) responses of CST glasses cooled at different rates. The glasses contained IE-911 and MST and three different simulated sludges. Two bounding cooling profiles, rapidly quenched and canister-centerline, were used in this study. Glasses were selected mainly to challenge the regions where amorphous phase separation is expected. There was essentially no difference between the PCT responses for glasses subjected to the two cooling profiles. The results reveal that no deleterious amorphous phase separation occurred under either cooling regime. The very good durability of the IE-911-containing glasses implies that durability may not be the limiting factor for waste loading in this option.

6.7.3 CSSX Risks

The previous risk assessment identified four high risks for CSSX: Flowsheet Solvent System Proof-of-Principle, Chemical and Thermal Stability, Radiation Stability, and Real Waste Performance.

Flowsheet Solvent System Proof-of-Concept: The flowsheet solvent system was demonstrated in three tests using 2-cm centrifugal contactors at ANL with SRS average simulant solutions spiked with radioactive cesium-137 (Cs-137). Results from testing show that the requirements for waste and solvent decontamination (40,000) and the concentration factor (CF) for cesium from feed to cesium product (15) were met or exceeded. In addition, the first test demonstrated the need for control of the temperature in the extraction section of the centrifugal contactor cascade to ensure the highest waste decontamination. The solvent was recycled four times during the second test with no adverse effects on the process. Further demonstration of the flowsheet solvent system was provided in a 71-hour test. This test processed 180 liters of SRS simulant with 1.4 L of solvent, which was recycled through the system a total of 42 times during the test. During this test the solvent was washed in a single centrifugal contactor stage with dilute sodium hydroxide (NaOH) to remove dibutylphosphoric acid that was extracted from the waste as well as the 4-*sec*-butylphenol that is formed by degradation of the solvent. The average decontamination factor (DF) for this test was 159,000 for cesium from waste raffinate, and the average CF was 14.9. The process had to be shutdown twice during testing: the first time to replace a feed pump; and the second time to unplug a rotor that became plugged with solids suspended in the SRS simulant. In both cases, recovery was achieved, allowing the test to continue with minimal effect on the DFs or CFs. **These very successful demonstrations of the flowsheet solvent system makes the probability of failure of the flowsheet low and results in the risk being reduced to low**.

Chemical and Thermal Stability: The solvent system for the CSSX process consists of four chemicals: the extractant, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6), a modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy) -2-propanol (Cs-7SB), trioctylamine to aid stripping, and the diluent, Isopar® L. The extractant and modifier are

new chemicals. The chemical and thermal stability of this four-component solvent had not been tested previously to determine the products of reaction or their effects on processing, which led to a high risk. Laboratory studies during FY 2000 and FY 2001 were aimed at understanding the chemistry of the solvent and any effects on the process as a result of chemical reactions or thermal degradation. Thermal stability studies showed that even after 235 days at an operating temperature of 35°C, performance remained good and did not necessitate solvent washing. Relative to the goal of a 1-year solvent lifetime, the solvent matrix and its performance did not unacceptably degrade due to thermal effects.

At 60°C, the extractant showed no measurable chemical changes. However, trioctylamine was degraded to dioctyl- and mono-octylamines. Only a trace (<2 mg/L) of 4-*sec*-butylphenol from degradation of the modifier could be detected. Nitration studies of the solvent showed no measurable nitration of either the solvent components or the degradation product, 4-*sec*-butylphenol, under extraction, scrub or strip conditions. The 4-*sec*-butylphenol did not affect extraction or scrubbing, but showed reduced stripping if allowed to build up in the solvent. Tests demonstrated that 4-*sec*-butylphenol was readily scrubbed from the solvent by 0.01-1 M NaOH solutions. Degradation of trioctylamine also affected stripping behavior, but addition of fresh trioctylamine to restore the concentration to 0.001 M restored stripping behavior. The overall conclusion of the studies was that chemical and thermal processes slowly degrade solvent, but effects on the solvent were easily corrected by caustic washing and periodic additions of trioctylamine. **Thus, the probability that chemical and thermal effects on the solvent will affect plant operation is low and the risk is also low.**

Radiation Stability: The risk for radiation stability was judged to be high in the earlier assessment because the solvent had not been tested to determine the products of reaction or their effects on processing. Dose calculations showed that the solvent will receive an annual dose of only 0.092 Mrad per year, assuming: 100% plant utilization; the baseline solvent inventory of 1000 gallons; and the application of the MST process prior to the CSSX process. The relatively low dose is the result of: the short residence time of the solvent in the centrifugal contactor cascade, the large inventory of solvent in the plant, and the nuclides contributing to the solvent dose (Cs-137 and barium-137m). Both external and internal radiation studies showed essentially the same results: production of 4-*sec*-butylphenol from modifier degradation and dioctylamine from degradation of trioctylamine (TOA). External radiation tests involved irradiation of solvent and simulant with Co-60 gamma source to doses exceeding the life of the plant by 10 fold. No significant degradation of the primary solvent components was observed for doses typical of the proposed facility lifetime. Less than 10% extractant loss occurred and no statistically significant loss of Cs-7SB modifier occurred at the maximum dose, although the 4-*sec*-butylphenol was ~0.4% of the initial modifier concentration. Less than 10% of the trioctylamine degraded at a dose of 6 Mrad.

Internal radiation studies were performed with both real waste solutions and simulant spiked to SRS-average waste Cs-137 concentration with total radiation doses from 1 to 13.5 years of plant operation. Internal radiation tests using spiked simulant (at the baseline process flowsheet organic-to-aqueous phase ratios for the extraction, scrub and strip sections) did not

identify any dose-related impacts on dispersed-phase break times, third-phase formation, or interfacial crud formation. Neither the real-waste nor the spiked-simulant tests showed any effect of radiation on extraction or scrubbing, but stripping effectiveness was reduced due to high distribution coefficients. Washing the solvent with 0.01 M NaOH and replenishing the TOA concentration restored good stripping performance.

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

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

During the flowsheet test, 105 liters of waste from tanks 37H and 44F were treated using 1.5 liters of solvent. The solvent was recycled continuously (~25 times) to the process after passing through a single centrifugal-contactor stage of NaOH wash solution. Decontamination Factors (DF) for the waste raffinate as high as 2 million were observed during the first 24 hours of the test. A composite of samples taken throughout the test (includes samples during upset conditions) gave a DF of 40,000 versus a requirement of 13,000 to meet the saltstone Waste Acceptance Criteria and a target of 40,000. The overall average DF for the spent solvent was 1.2 million versus a target of 40,000. Problems were encountered in measuring the flow rate of the waste feed stream resulting in low feed flow rate in the first 24 hours of the test. Consequently, the CFs averaged only 12.8 during that part of the test, which is lower than the target value of 15. Flow rate adjustments to the feed and strip streams resulted in varied, but higher, CFs during the remainder of the test. The CF exceeded 15 for several hours during the test, but averaged 14.4 during the last 10.5 hours of operation. Operational problems were encountered three times when the hydraulic capacity of the contactors was exceeded during efforts to achieve higher CFs. Recovery from the upsets was demonstrated proving the robustness of the process. The real waste test proved flowsheet viability, allowing the consequence to be lowered to moderate (potentially enlarging the footprint of the shielded facility). **However, our evaluation of the technology risk is lowered only to moderate because only one contactor test has been conducted and limited batch equilibration test results with real waste are available.** Confirmation of the batch equilibrium test results from the remaining tank waste samples will be available prior to down selection, which could further reduce this risk.

Other CSSX R&D: The extractant and modifier are not made commercially at present. Efforts are underway to improve the processes for manufacture and to find vendors willing to make these chemicals. The improved modifier (CS-7SB) was synthesized at a 3.6 kg scale in the laboratory to demonstrate scale-up and provide solvent for studies at ANL, ORNL, and SRTC. The larger batch size yielded high purity product with a product yield higher (95%) than 100 g batches. IBC Advanced Technologies, Inc. demonstrated scale-up of BOBCalixC6 synthesis by preparing a 1 kg batch of good purity. The patent which covers the original CSSX process chemicals and conditions was issued January 16, 2001. A patent application covering the second generation modifiers was filed with the US Patent & Trademark Office.

ORNL identified potential candidate firms to supply the chemicals on the scale required by the proposed process plant (46 kg BOBCalixC6 and 677 kg of Cs-7SB modifier). The results of this effort were summarized in a series of letter reports submitted to SRS. An Expressions of Interest solicitation for the manufacture of 2 kg of modifier and 50 g of BOBCalixC6 was sent by SRS to 29 companies with seven positive responses received. Actual procurement of the material was placed on hold until the SPP technology selection decision is completed by DOE.

6.7.4 STTP Risks

The previous risk assessment identified two high risk areas in the STTP process: Catalytic Product Decomposition and Reactor/Vessel Foaming. In addition, R&D activities were performed in two additional areas: precipitate hydrolysis testing and glass formulation.

Catalytic Product Decomposition: The risk of catalytic decomposition of TPB, like that experienced in ITP Tank 48 in 1995, has been addressed through increasing the understanding of catalytic decomposition and through additional demonstrations of process performance.

SPP research efforts showed that decomposition was catalyzed by supported, noble metal ions which had been reduced to metals. In particular, reduced palladium and platinum were shown to be the most catalytically active species. Reduced rhodium and ruthenium, which are present in the HLW tanks, were shown to be ~25% as reactive as Pd(0). Tests indicated that phenylborate intermediates and mercury participate in the catalytic decomposition reaction, rather than acting as just reducing agents for the noble metals. Present data indicate that diphenylborinic acid (2PB) may be the intermediate of primary importance and that decomposition can take place in the presence of 2PB and supported Pd(0) alone. However, the presence of diphenylmercury (or mercury(II) salt), along with the other two components, yields a much more reactive system. Catalyst consultants have incorporated information from the ongoing research and development activities into proposed reaction and catalytic mechanisms which are consistent with those identified in literature studies.

Batch catalytic decomposition tests were conducted on six different SRS HLW tank samples at both ~25°C and at 45°C (for a total of twelve tests). Cesium precipitation reached the

Saltstone limit of 45 nCi/g in ten of the twelve tests; however, the time required for the samples to meet this limit varied from <500 hours to >3500 hours. The most probable cause for the differences in the rate of decontamination was the extremely low solubility of NaTPB in high ionic strength salt solutions. Once added, the majority of the NaTPB precipitated out of solution and its dissolution was very slow under the mild degree of agitation. Attempts to increase the rate of agitation were unsuccessful. Of the twelve tests, only two showed evidence of TPB degradation, and both of these tests came from Tank 35H, which had higher levels of soluble mercury than the other waste samples. The TPB degradation rates in Tank 35H were much less than the maximum seen in previous real waste and surrogate waste tests in terms of calculated benzene production (i.e., 0.2 mg/(L-h) for Tank 35H vs. 10 mg/(L-h) maximum in other tests).

A test system using 20-L Continuous Stirred Tank Reactors (CSTR) with Cs-137 spiked simulants demonstrated that adequate decontamination could be maintained while the STTP was undergoing active catalytic decomposition at both 25°C and 45°C. Also, the CSTR test using real SRS HLW successfully demonstrated that stable operation with acceptable DFs for Cs-137 and Sr-90 could be obtained at both 25°C and 45°C.

In summary, an increased understanding of the catalytic decomposition has certainly been achieved. However, catalytic decomposition tests were conducted on samples from several different SRS HLW tanks and evidence of catalytic decomposition was detected in only one HLW sample. In spite of what has been learned to date, exactly what activates the catalytic decomposition in real waste is not fully known. Nevertheless, should decomposition occur, research and development tests indicate that required DFs will be met. As a result, there is only a moderate probability that catalytic decomposition will affect the STTP process. If catalytic decomposition does occur to an extent that DFs were not met, moderate consequences, which could require enlarging the footprint of the shielded facility, could result. **Therefore, the risk of catalytic product decomposition to the STTP process is moderate.**

Foaming: Foaming could occur in the precipitate tank, the concentration tank, and the wash tank for the STTP process. The candidate antifoam must not only be effective in controlling foam in these three tanks, but must also not negatively impact downstream processes or waste forms. An antifoam known as IIT B52 has been developed by Illinois Institute of Technology and extensively tested in foam column tests. These foam column tests were very aggressive; actual foaming conditions during STTP processing would be much less severe. The IIT B52 antifoam was very effective in the foam column tests with precipitated and concentrated slurries, and somewhat less effective with washed slurries. In long-term tests with synthetic wastes in CSTRs, which are more representative of the actual STTP conditions, the IIT B52 was very effective in controlling foaming in all three environments. The IIT B52 was also demonstrated to be effective in 1-L CSTRs using actual SRS HLW.

The active ingredient in the IIT B52 antifoam is a surfactant, sodium bis(2-ethylhexyl) sulfosuccinate. Testing showed that the IIT B52 was consumed during the precipitation, concentration, and washing cycles. No active antifoam agent was detected in the dilute

precipitate, the concentrated precipitate, the washed precipitate, or the permeate from the concentration and washing. Additional studies found that irradiation of the antifoam or precipitate did not significantly reduce the effectiveness of the antifoam.

IIT B52 was shown to be an effective antifoam for the STTP process. The probability is low that reactor/vessel foaming will occur to such an extent that processing is negatively impacted. If foaming should occur, the consequences are low and would only require optimization for operation of the facility. **Therefore, the risk to the STTP process of reactor/vessel foaming is considered to be low.**

Other STTP R&D: Studies were done to determine the impact of IIT B52 antifoam on hydrolysis kinetics. The antifoam agent IIT B52 was found to have no detectable effect upon acid hydrolysis of a tetraphenylborate (TPB) simulant slurry containing 2000 ppm of the antifoam agent. Analysis of reactor contents at the completion of feeding revealed no detectable quantity of the antifoam agent. Analysis of all process streams at the completion of the hydrolysis cycle also revealed no detectable quantity of the antifoam agent. It was concluded that IIT B52 rapidly decomposes in the feed slurry and/or during acid hydrolysis.

A glass formulation study was conducted to determine the effect of cooling rate on glasses made from sludge and precipitate hydrolysis aqueous (PHA) product from the STTP process. Two bounding cooling profiles were used in this study: rapidly quenched and a canister centerline cooling curve. The results showed that there was no practical difference between the PCT responses for glasses subjected to the two cooling profiles. These results reveal that no deleterious (amorphous) phase separation occurred under either cooling regime. All of the glasses readily satisfied the requirement that the PCT responses be at least two standard deviations below the PCT response of the standard environmental analysis glass. Furthermore, the PCT responses were almost entirely within the prediction intervals of the DWPF Durability Model.

6.8 Summary of Risks

In Table 6.2, the assigned probabilities, consequences, and resulting risks (described above) are summarized for each cesium-removal process. Note that the alpha and Sr risks are repeated for each of the three processes since alpha and Sr removal are required for all. The alpha and Sr risks are the same for CST and CSSX because the same processing approach is assumed for both. However, filtration (equipment size) is a low risk issue for the STTP process because MST and sludge filtration performance is much better when filtered simultaneously with TPB precipitates. It is also important to recognize that in early FY 2000 two of these technology areas (CSSX real waste performance and STTP catalytic product decomposition) were felt to have high consequences, i.e., “threatened viability of implementation.” TFA believes that the successful tests in FY 2001 support reducing the maximum consequences of these areas to moderate (potentially enlarging the footprint of the shielded facility).

Table 6.2. Current Assessment of Previous "High Risk" Technology Areas for Alternative Cesium Removal Processes

Cs Removal Process	Technical Risk	Probability*	Consequence (Potential Impact)	Risk
CST	MST Pu Removal Performance	Moderate	Low (Optimization)	Low
	MST/Filtration	Moderate	Moderate (Footprint)	Moderate
	Sorbent Stability	High	Moderate (Footprint)	High
	Sorbent Handling and Sampling	Low	Moderate (Footprint)	Low
	Gas Generation	Low	Moderate (Footprint)	Low
CSSX	MST Pu Removal Performance	Moderate	Low (Optimization)	Low
	MST/Filtration	Moderate	Moderate (Footprint)	Moderate
	Flowsheet Solvent System Proof-of-Concept	Low	Moderate (Footprint)	Low
	Radiolytic Stability	Low	Moderate (Footprint)	Low
	Chemical and Thermal Stability	Low	Moderate (Footprint)	Low
	Real Waste Performance	Moderate	Moderate (Footprint)	Moderate
STTP	MST Pu Removal Performance	Moderate	Low (Optimization)	Low
	MST/Filtration	Low	Low (Optimization)	Low
	Reactor/Vessel Foaming	Low	Moderate (Footprint)	Low
	Catalytic Product Decomposition	Moderate	Moderate (Footprint)	Moderate

* The probability or estimated likelihood that the process will fail (not perform as intended).

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 solid-liquid separation for a waste stream with substantially different physical properties. 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 additional storage tanks to maintain the desired waste-processing rate.

7.1.1 R&D Roadmap Summary – Alpha and Sr Removal

This science and technology roadmap for alpha and Sr removal (Figure 7.1) is a subset of the overall SPP roadmaps (see Appendix A of the R&D Program Plan[3] or the SPP website at http://www.srs.gov/general/srtech/spp/progplan.htm). The alpha and strontium removal roadmap 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 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 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. These pilot-scale operations will establish the limits of operation and

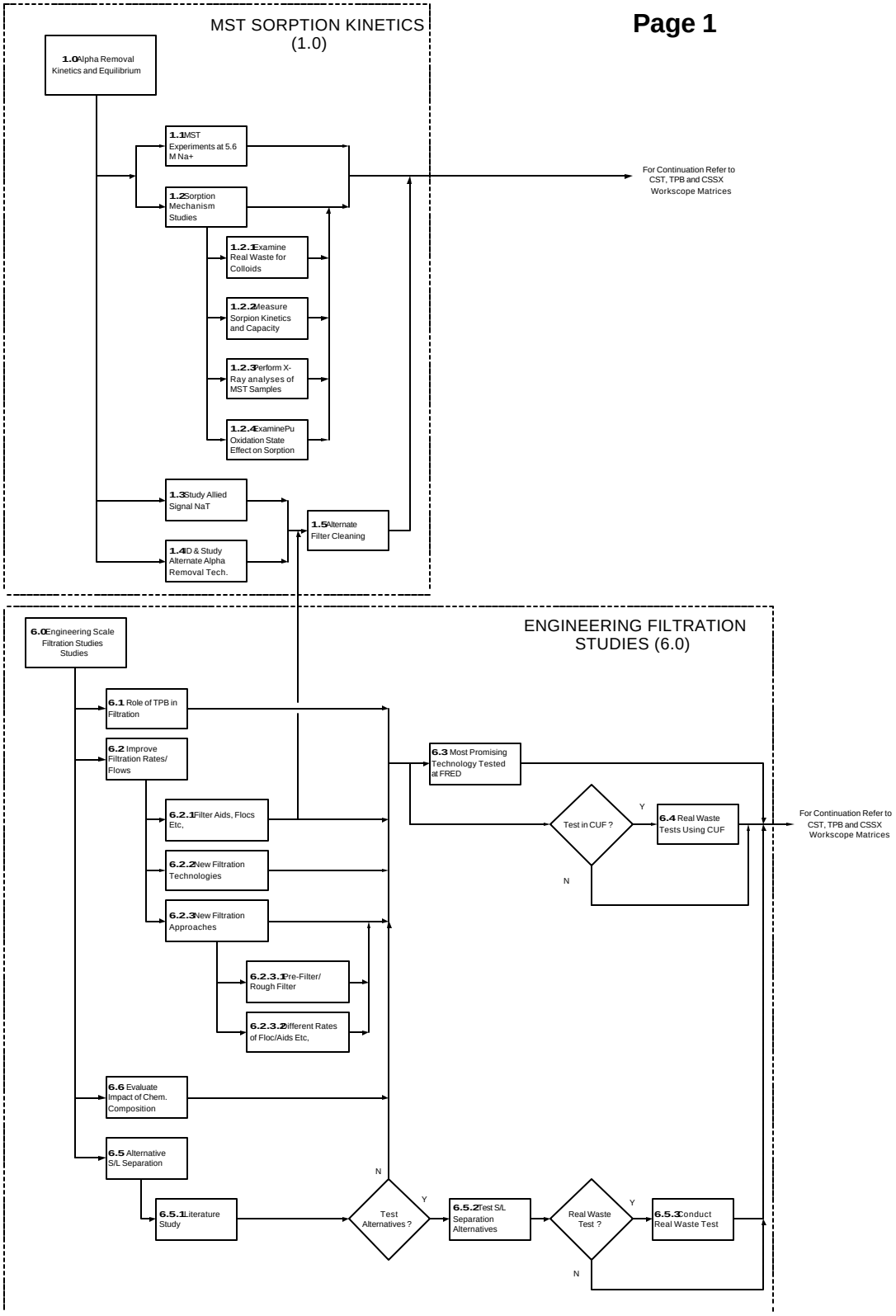

Figure 7.1. Science and Technology Roadmap for Alpha and Sr Removal Process

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.

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.[11,12] 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 prior studies[13] 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 the actinides and strontium, 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.

Laboratory tests[14] 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 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.[15]

* SOWM refers to the Scope of Work Matrix provided in Appendix A of the Savannah River Site Salt Processing Project Research and Development Program Plan, Revision 1, November 2000. The numbers link to that document and provide the reader with additional reference materials.

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 U removal proved lower from the 5.6 M Na solution than the 7.5 M Na solutions. The author suspected – but did not confirm – that uranium removal might have occurred via precipitation as sodium diuranate in the test using 7.5 M waste, adding a confounding mechanism. Similarly, the Np kinetics proved slower in the test using 5.6 M solution for an unidentified reason. 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 – Results

Researchers[16] recently examined samples from different waste tanks (7F, 13H, 26F, and 35H) for evidence of colloidal plutonium by filtration through increasingly smaller pore-size membranes. The work used centrifugal filters with pore-size rating from 10,000 molecular weight (MW), or 1.5 nm, to 0.45 micron typical of the filters proposed for the facility. The data from the filtration indicates either the absence of colloidal plutonium or that any colloids present remain sufficiently small to pass through the finest filter tested (10,000 MW, or ~1.5 nm). While workers recommend additional testing to fully develop the characterization protocols, the study does advance the understanding of existing data for the tanks. Implementing the method for routine samples in the future will provide the data necessary to determine the exact amounts of MST – or alternate sorbent – needed for treatment of waste.

Various tests in FY 2001 continued to demonstrate the robustness and success of MST in treating both simulated and actual high-level waste. Tests demonstrated that MST proved effective in removing strontium, plutonium, and uranium at nominal conditions in a demonstration of the STTP process using simulated waste and in the presence of catalytic decomposition of the tetraphenylborate due to palladium catalysis.[17] MST performance was demonstrated for both strontium and plutonium using actual waste during a demonstration of the STTP process.[18] In that case, both strontium and plutonium removal efficiency proved equal to or superior to the defined performance requirements. Also, acceptable strontium removal was demonstrated for the pretreatment step in the CSSX process.[19] In that demonstration, the researchers used MST that failed to meet the particle size requirements and provided only minimal mixing during treatment. Nevertheless, the removal proved sufficient to meet process requirements.

The accumulated experimental data confirms the current cost estimates for the proposed options. The limited ability to remove Np by addition of MST requires blending of wastes from selected tanks prior to treatment. This blending provides an acceptable level of confidence for successfully processing the wastes. SRTC defined the planned additional testing for FY 2001.[20] Collection of additional data on MST sorption for individual radionuclides will increase confidence in predicting the behavior of the sorbent. Also, characterization data on actual waste will provide a better understanding of the speciation of Pu and Np in the waste.[21,22]

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.[14] 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, the project conducted a review of available literature for data related to a number of actinide and Sr removal technologies.[23] 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 Dr. 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. Researchers evaluated the performance of three samples of the material relative to Sr and actinide removal.[24] Also, the same samples were evaluated to determine the influence on cross-flow filter performance.[25]

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 Dr. 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 SRTC recommended additional testing to measure removal kinetics during the first eight hours of contact between the solution and

sorbent. It was 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 – Results

SRTC[26] conducted screening tests of strontium and actinides removal with crystalline silicotitanate (CST), SrTreat® and sodium nonatitanate (ST) samples and by precipitation upon addition of nonradioactive strontium, calcium and sodium permanganate. Several of the alternate sorbents and the precipitation method exhibited strontium and actinide removal characteristics as good as or better than the reference MST material. They recommended continued evaluation of the ST and SrTreat® materials and the precipitation method as alternatives to MST for a batch process to remove strontium and actinides. Such efforts need to focus on improving plutonium and neptunium removal characteristics to ensure that the Saltstone limits can be met at bounding waste conditions.

By late 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.[27] 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.

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

7.1.4.1 Previous Results

Each cesium removal 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. A recent publication[28] 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.[29] 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.[30,31,32,33,34,35] 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 Oak Ridge National Laboratory (ORNL) staff examined the rheology, settling, and resuspension characteristics of MST/sludge slurries in both laboratory and pilot-scale experiments.[36] 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 cooling 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.[37] 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.[6,7] 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.[38] 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, SRTC started additional experiments to examine the use of flocculating agents or filter aids to improve separation efficiency.[39] 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[40] 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.

SRTC personnel completed two evaluations[41,42] to examine how sodium tetraphenylborate enhances the rates of cross-flow filtration for slurries of MST and metal hydroxide sludge. The improved filterability of tetraphenylborate (TPB) slurry was attributed to the hydrophobic nature of the crystalline organic that forms a firm but porous filter cake, allowing salt solution to pass through without duly compressing the cake.[41] Addition of inorganic sludge or MST has an adverse effect on filtration, but the overall filtration rate with tetraphenylborate proves satisfactory. The absence of the organic results in poor filtration performance due primarily to the difficulty in filtering the residual inorganic sludge rich in iron and aluminum precipitates. Ferric hydrolysis products and colloids from a bulky and sticky filter cake significantly reducing filtration rate. An independent evaluation by consultant, Dr. Mark Clark (University of Illinois), reached similar conclusions during an independent evaluation.[42] That evaluation offered a number of suggestions for future investigation methods to further investigate the solid-liquid separation efficiency.

7.1.4.3 FY01 – Results

Pilot-scale experiments examined the filtration of simulated sludge resembling the contents of Tank 8F.[43] The measurements contrast with those of an earlier study[38] using MST in

combination with a simulated sludge resembling the combined contents of Tanks 8F and 40H. In general, the measured flux in the absence of MST proved lower, particularly as the total concentration of solids approached the highest expected in the facility. Furthermore, the data suggested a more frequent need for chemical cleaning to restore flux to the target value.

All existing filtration data for MST and sludge slurries (absent TPB) come from tests with simulated wastes. To address this limitation, SRTC[44] conducted filtration tests using several actual sludge samples from Tanks 51H, 11H, and 8F, combined with monosodium titanate and supernatant from Tanks 37F and 44H. The tests varied the axial velocity and transmembrane pressure in a statistically designed matrix to mimic conditions in previous filtration tests performed using the larger scale Parallel Rheology Experimental Filter and the Filtration Research Engineering Demonstration (i.e., pilot scale equipment). The tests with actual waste demonstrated fluxes equal to or greater than observed with the simulated wastes in the larger equipment. Flux did vary depending upon the process history of the samples. Previously dried sludge samples, although suspended in similar supernatant, filtered faster than sludge without previous drying. Nevertheless, the complete data do show that early data with simulated waste agree reasonably with the measurements for actual waste providing conservative design information for the facility.

These tests also measured the rheology of the slurries and performed thermal analyses to understand the behavior of solids as a result of radiolytic heating during extended storage. The rheology measurements for the concentrated sludge and for the slurry containing both sludge and MST (for a total concentration of 6.0 wt% insoluble solids) demonstrated yield stresses less than 3.5 Pa. This data will help in selecting the pumps for the process facility. An FY99 study by ORNL[36] demonstrated that under such conditions the viscosity and yield stress of simulated slurries increased. The thermal analyses showed an endothermic reaction at approximately 80°C in solutions containing sludge and MST. This reaction likely caused the shift in yield stress identified in the tests using simulated waste.

Ongoing testing will continue at USC during FY01. The tests will examine the filter flux for two sludge simulants with varying amounts of MST. The two slurries will simulate the two primary types of waste stored at SRS. Also, the contract with USC 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.

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.[37] 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.[14]

7.1.5.2 FY00 – Results

During FY00, SRTC conducted an evaluation of alternate methods for achieving the required separation of solids from liquid.[45] 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, a workshop was held with representatives from SRTC, SRS HLW and SRS Solid Waste Divisions, and the academic community on the specific application of interest. Based on the findings, SRTC 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 the addition of flocculating additives. If flocculation with cross-flow filtration proves ineffective, SRTC should investigate high shear filtration [using a centrifugal filter or Vibratory Shear Enhanced Processing (VSEP) filter] as well as flocculation in combination with centrifugation.

During FY00, WSRC personnel performed a systems evaluation study of alternate equipment configurations for the Alpha and Sr removal portion of the ion exchange and solvent extraction processes.[46] 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.

Dr. Baki Yarar (Colorado School of Mines) provided an independent assessment of potential alternate means to achieve the required solid-liquid separation for the facility.[47] His recommendations chiefly centered on using sedimentation prior to cross-flow filtration. He also endorsed examination of chemical additives to enhance both the sedimentation and the filtration efficiency. The project contracted Dr. Yarar to conduct additional studies aimed at defining the behavior of such additives and defining a research program that would lead to synthesis of additives that provide better performance than those currently under testing.

7.1.5.3 FY-01 - Results

SRTC conducted measurements of the influence of various chemical additives on solid-liquid separation using simulated waste.[48] The experiments demonstrated rapid aggregation of solids in the simulated waste with relatively quick sedimentation using either hydroxamated amines or any of a series of Alclar® additives. A number of other additives proved less effective. The hydroxamated amines and Alclar® flocculants also notably increased filter flux significantly in dead-end filter tests. However, the additives yielded only marginal improvement in flux when using a cross-flow filter. It was speculated that the reduced performance results due to shearing of the aggregates at the hydraulic conditions of the filtration. Based on these findings, the project deferred future testing at pilot-scale and with actual waste until completion of studies examining the use of the additives in a process configuration that incorporates sedimentation and decanting prior to filtration.

In related work, Dr. Yarar reviewed this information and performed tests with the simulated sludge, MST, and flocculants.[40] Following this review, he provided a report that included a general description of flocculation mechanisms, properties of particles in liquids, water-soluble polymer flocculants, optimal conditions for flocculation, the effect of agitation on flocculation, and the effects of system parameters on flocculation. He also provided recommendations for future flocculant tests. WSRC personnel judged the recommended work as either duplicative of existing program work elements or unlikely to successfully develop new chemical additives. The recommended process variations represent notable changes in process equipment or require completion of the remainder of the FY01 work scope prior to reaching a decision to pursue. Hence, no additional work will occur along these lines during FY01.

SRTC coordinated a set of vendor tests examining a centrifugal, high-shear implementation of cross-flow filtration for simulated waste containing metal hydroxide sludge and MST.[49] The filtrate throughput proved higher than the facility design target and reached as much as ~4X observed in comparable testing using the pilot-scale equipment for conventional cross-flow filtration. The majority of the testing used a composite filter media of ceramic and stainless steel rated as 0.1 micron in pore size. Additional testing, albeit more limited in scope, showed nearly identical performance using a 0.5 stainless steel filter.

The project also solicited testing by vendors of other non-conventional filtration equipment.[50] Several of these vendors deemed their equipment as unlikely to meet the stringent requirements of the project and therefore declined to participate in testing.

Previous 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.[51]

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 extraction operation.

Table 7.1. Predicted Radionuclide Concentrations

Radionuclide	Soluble Feed (Ci/gal)	Clarified Salt Solution (Ci/gal)	Decontaminated Salt Solution nCi/g (SPF WAC Limits)
Sr-90	3.28E-02	5.60E-04	4.00E+01
Cs-137	1.34E+00	1.12E+00	4.50E+01
U-232	3.79E-8	1.76E-08	N/A
U-234	2.44E-08	1.14E-08	N/A
U-235	1.96E-09	9.12E-10	N/A
U-236	3.34E-09	1.55E-09	N/A
U-238	1.26E-07	5.86E-08	N/A
Np-237	6.50E-08	5.44E-08	3.00E-02
Pu-238	8.439E-04	3.50E-05	N/A
Pu-239	7.40E-05	3.07E-06	N/A
Pu-240	1.82E-05	7.54E-07	N/A
Pu-241	3.73E-04	1.55E-05	2.00E+02
Pu-242	9.68E-09	4.01E-10	N/A
Am-241	1.48E-04	1.24E-04	N/A
Am-242m	1.84E-07	1.54E-07	N/A
Cm-244	3.16E-05	2.65E-05	N/A
Cm-245	2.107E-9	1.76E-09	N/A
Total Soluble Alpha	7.55E-03	6.32E-03	1.80E+01
Co-60	2.27E-05	2.27E-05	6.00E+00
Ru-106	4.84E-04	4.84E-04	1.28E+02
Sb-125	2.88E-04	2.88E-04	7.60E+01
Sn-126	5.30E-05	5.30E-05	1.40E+01
Eu-154	6.50E-05	6.50E-05	1.60E+01

Notes: Ba-137m and Y-90 exist at equilibrium concentrations in the feed, but may exist at other relative concentrations in the other process streams presenting different challenges for the analytical monitor depending on point of installation in the design.

Note that the alpha and Sr removal process inherently sorbs various elements at different efficiencies and will change the relative distribution of radioactive elements. 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. For MST, previous findings at Sandia National Laboratories on related compounds show some affinity for Cs and Y. Future research and testing will eventually determine how these process steps affect these contaminants and thereby influence the waste prior to analysis. The variance in relative concentration of the radionuclides between the feed waste and the waste after each process step will increase the complexity for the analyses.

Previous work at PNNL developed the technology for the at-line/on-line 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.[52,53] The specification documents provided the requirements for the design of a prototype monitor to meet the requirements of any one of the three Cs-removal process alternatives. The plan was for the prototypical monitor to be tested during process demonstration of the selected Cs-removal technology.

7.1.6.3 FY01 – Results

In early FY01, WSRC personnel solicited vendor bids to design and fabricate a prototype analyzer for testing. Two separate groups, both a contractor-led (i.e., WSRC) team and Dr. Emile Schweikert (Texas A&M University), an independent consultant, evaluated the bids in parallel. In addition to reviewing the vendor proposals, the consultant evaluated the design concept and proposed deployment approach for the analyzers. As part of that review, the consultant also assessed similar efforts in progress for the River Protection Project at Hanford. The combined reviews indicated the proposed approaches from the three vendors appeared unlikely to successfully meet the needs defined for the facility. As a result, the project will defer procurement efforts pending additional research and development efforts for the monitor technology.

7.2 CST Non-Elutable Ion Exchange

The proposed ion-exchange process employs IE-911 sorbent, which consists of CST and a zirconium hydroxide binder, to remove Cs from the salt solution. In this process, a 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 IE-911 columns to remove the Cs. Because Cs cannot be easily recovered by elution, Cs-loaded IE-911 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

This science and technology roadmap for CST Non-Elutable Ion Exchange (Figure 7.2) is a subset of the overall SPP roadmaps (see Appendix A of the R&D Program Plan[3] or the SPP website at http://www.srs.gov/general/srtech/spp/progplan.htm). The CST 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 IE-911 particles are transferred from the ion-exchange columns to DWPF, sampled in the IE-911/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 and of feed composition variability and will confirm design assumptions. This testing directly supports development of operating procedures, simulator development and operator training.

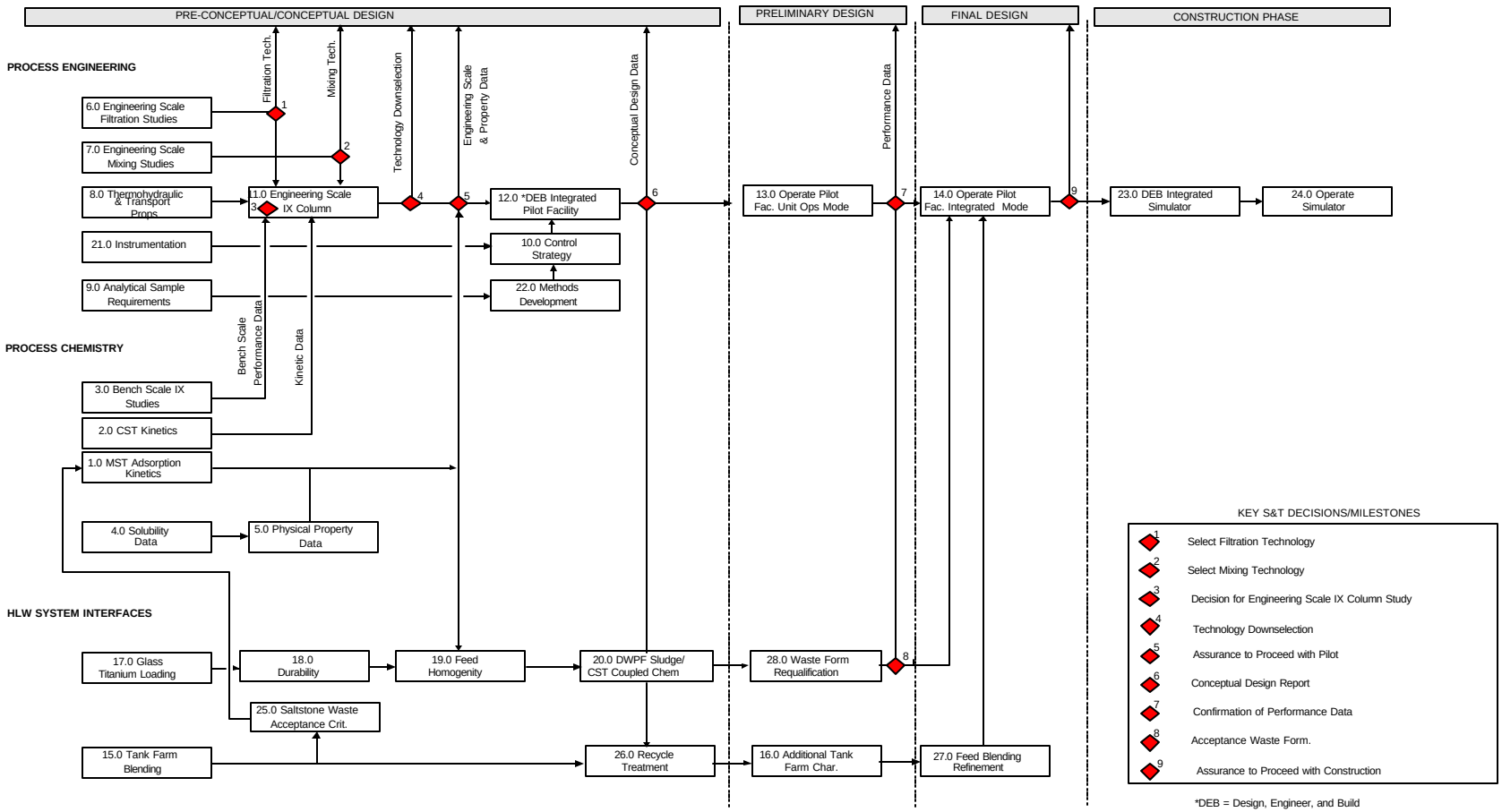

Figure 7.2. Science and Technology Roadmap for CST Non-Elutable Ion Exchange Cs Removal Process

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.

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, column design parameters, sorbent sampling and handling, and glass requalification. The chemical and thermal stabilities of the IE-911 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. The need for representative sampling and for maintaining feed homogeneity requires that the IE-911 be reduced in size before addition to the slurry. Immobilization of the loaded IE-911 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.

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 mathematical models that can be used to predict the performance of a plant-scale column of IE-911 sorbent. The models 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

Previous studies measured Cs distribution on samples of the CST powder form[54] and the IE-911 engineered form.[55] Results of column tests[56] indicated that Cs removal matched that predicted by the ZAM computer model[57] to within 30%. The numerical solutions of the governing equations and boundary conditions in the mathematical model of the column are performed by the VErsatile Reaction SEparation (VERSE) simulation package.[58] This model has been validated in many previous studies.[59]

SRTC[60] checked the constructed model by performing ion-exchange experiments at three different superficial velocities in small (1.5 cm × 10 cm) columns. Experimental data agreed with the predicted column performance from the VERSE computer model with the exception of the column run at a superficial velocity of 4.1 cm/min, where Cs breakthrough was much faster than predicted. A number of the possible sources of the discrepancy between model predictions and experimental results were evaluated, and lot-to-lot variability was suggested as the leading cause of the deviation. IE-911 Lot #96-4 shows a dynamic capacity

approximately 30% below other lots of IE-911, which explains why the best computer fit to these data was obtained by reducing the capacity of the IE-911 by 30%. Lastly, the presence of organic constituents (e.g., dibutylphosphate and tributylphosphate) exhibited little or no effect on column performance over the limited duration tested.[61] SRTC verified column capacity and kinetic data obtained using simulated waste with those obtained using radioactive waste and confirmed model predictions for a full-length column.[62] All of the treated waste met Saltstone process requirements for Cs-137 (<45 nCi/g). Cs-137 loading on IE-911 in this test reached 376 Ci/L. Comparison of test data to ZAM model predictions suggests intra-particle diffusivity may exceed previous estimates.

These results suggested the need for additional studies of the pore diffusivity for IE-911 because 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 column experiments in FY00, alkaline-earth metals, carbonate, oxalate, and peroxide ions were passed through columns loaded with IE-911 to obtain equilibrium measurement data for various ionic constituents.[54] Results of these studies showed that Cs loading on IE-911 increased by several percent with typical carbonate concentrations in the simulated salt solution (compared to simulant without carbonate). Next, the researcher used the ZAM model[57] 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 increasing carbonate content, consistent with the observation. Removing oxalate from SRS-average simulant solution had no effect on Cs loading of IE-911 and IE-910. Likewise, results from ZAM modeling indicated little effect on Cs loading up to 0.1 M oxalate. Finally, two sets of experiments conducted simultaneously showed that peroxide decreased Cs loading on IE-911 by several percent. The peroxide concentration in batch experiments equaled 0.13 M immediately after injection and decreased to 0.0034 M five hours later. 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. The results of this work indicate that carbonate, oxalate, and peroxide should have little effect on the performance of the IE-911 columns.[63]

7.2.2.1.3 FY01 – Results

Studies at SRTC indicated that IE-911 granules contain components that leach into the nuclear-waste simulants during processing. Texas A&M University conducted several series of ion-exchange experiments with eight simulants and samples from four batches of CST consisting of powder from UOP (IE-910) and CST samples DG141, TAM5-4, and TAM5-5.[64] The simulants were analyzed after the ion-exchange experiments for Ti, Si, and Nb that might have leached from the CST. Each simulant was prepared based on standard simulant and contained other ingredients such as oxalic acid, sodium carbonate, and hydrogen peroxide. Oxalic acid had no significant effect on the performance of CST. The

observed carbonate effect is much smaller than what is predicted using our models. It was observed that CST was dissolved by simulants with 1 and 0.1 M H_2O_2, respectively. Hydrogen peroxide can attack and break up the CST as indicated by a high level of Ti leached in ion-exchange experiments using simulants with 1 M and 0.1 M H_2O_2. A low level of H_2O_2 (0.0025 M) in the simulants does not have any effect on leaching of Si, Ti and Nb or on the K_d values for Cs loading.

Another study investigated the effect of variations in alkaline-earth metal concentrations on cesium loading.[65] The study focused on SRS-average simulant with varying amounts of calcium, barium and magnesium. Calcium exhibited the highest solubility of the alkaline-earth metals in SRS simulants, 5×10^{-4} M, exceeding the value predicted by the OLI® Software (1.85×10^{-5} M). Calcium at this concentration decreased the cesium loading on IE-910 by 12%. No decrease in the cesium loading on IE-911 was observed. Langmuir isotherm parameters were determined and used to predict dynamic loading of a column. The calculations suggest a negligible influence of calcium on cesium removal. Barium solubility in SRS-average simulant was measured as 9.9×10^{-6} M. Barium did not influence cesium loading on IE-910. Measurements ($<1.55 \times 10^{-10}$ M) and predictions indicate magnesium solubility is too low in SRS waste for magnesium to compete effectively with cesium for sorption on IE-911.

Finally, cesium sorption from high-level radioactive-waste solutions onto IE-911 at ambient temperature has been investigated.[66] Researchers characterized six radioactive waste samples from five high-level waste tanks in the SRS tank farm, diluted the wastes to 5.6 M Na^+, and made equilibrium and kinetic measurements of cesium sorption. The equilibrium measurements were compared to ZAM model predictions. The kinetic measurements were compared to simulant solutions whose column performance has been measured. The test results indicated the following. The ZAM model predicts within 33% the loading of cesium from a variety of SRS wastes. Wastes from both F and H Areas and with high and low K/Cs ratios showed good agreement with predictions. The kinetics of sorption were nearly identical in all tests with SRS radioactive waste and simulants, suggesting current modeling parameters are adequate for predicting radioactive waste performance. These data support the continued use of the ZAM model for predictions of process performance.

Although these results greatly extend the performance database for IE-911 in SRS wastes, additional measurements are recommended if this technology is selected. The waste samples tested to date are all high-hydroxide supernate solutions. Samples of dissolved salt cake, which will have higher nitrate ion concentrations and lower hydroxide concentrations, have not been tested for any of the three Salt Alternative processes. Future tests with radioactive waste should also emphasize accurate measurements of the distribution at low cesium concentrations. The kinetics test procedure used in this study did not reveal significant differences in sorption kinetics between different waste samples. However, the test protocol did not allow derivation of the apparent diffusivity used in column-modeling calculations. It is recommend that a protocol be developed for evaluating this aspect of sorption kinetics.

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 Non-Elutable Ion-Exchange process are related to equipment design and operation. Among these concerns are issues associated with a large IE-911 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 IE-911 process stipulates an array of three operating columns with a fourth column held in reserve. This design strategy (lead column to 90% break-through, middle column becomes lead column, guard column becomes middle column, reserve column becomes guard column) minimizes the amount of IE-911 incorporated in the borosilicate glass, thereby minimizing the number of canisters produced. The length and the diameter of the column are dependent upon the removal characteristics of the IE-911 mass transfer zone (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 – Results

The large inventory of radionuclides and attendant shielding requirements; heat transfer and heat management; prolonged contact of IE-911 with the process solution; preparation and downstream processing of large batches of IE-911; ease of recovery from process upsets; and radiolytic gas generation, accumulation and removal are major concerns with CST Non-Elutable Ion Exchange. A study of alternative column designs was initiated in FY01 to explore ion-exchange column-design concepts outside of the baseline case that may resolve some of these concerns.[67] The study has identified two promising commercially proven ion-exchange-column designs. Both of these are moving-bed ion-exchange columns that process the radioactive salt solution in such a way that small portions of Cs-loaded IE-911 are periodically removed from the columns. Therefore, most of the above concerns can be minimized. The study recommended that the moving-bed ion-exchange concept be further investigated to develop and demonstrate its suitability, including proof-of-principle tests for Counter-Current Ion Exchange (CCIX) and Up-Flow Moving Bed (UFMB), as soon as practical. If ion exchange is selected, post-down-select activities for IE-911 would include development of a fast-track R&D program to produce the data required specifically for moving-bed alternatives, to select either CCIX or UFMB, and to develop a pre-conceptual design to support pilot-facility design.

In addition, various aspects of the process design, footprint, nozzles and jumpers, service utilities, and building cranes were examined for two fixed-bed alternatives, i.e., shorter columns and two parallel trains.[68] Neither of the design alternatives produces significant heat-loading or heat-management improvements over the baseline case. Although the total curies per column can be halved with half the sorbent bed in either of the alternate designs,

the time to heat the process solution to boiling inside the column does not change. Shorter columns do reduce the exposure time of IE-911 to process solution to a minimum of six to eight months. However, this reduced exposure time does not effectively change the risks associated with exposure because some interparticle adhesion is observed within six months.

In support of studies on column performance, the thermal conductivities of IE-911—air and IE-911—average simulant mixtures were measured over temperature ranges of 20ºC - 130ºC and 23ºC - 65ºC, respectively.[69] The void fraction of granulated IE-911 was also measured because this parameter is important in predicting the thermal conductivity of two-phase mixtures from the thermal conductivities of the component parts. Methods available in the literature to estimate the thermal conductivity of two-phase mixtures from the conductivities of the components were used to back-calculate the thermal conductivity of the solid phase. The conductivity of the solid phase varied nearly linearly with temperature. Measurements of the thermal conductivity of IE-911—simulant mixtures were made at a limited number of temperatures owing to the tendency of water to evaporate rapidly from the mixture, resulting in crystallization of salts. The conductivities of IE-911—average simulant mixtures were estimated and compared reasonably well with the calculations. Latent heat effects associated with adsorbed water or waters of hydration were observed. The information made it clear that measurements of thermal conductivity of wet IE-911 (i.e., immersed and then drained of the bulk liquid) would be compromised.

In another study,[70] temperature distributions across an IE-911 column as a function of transit time after the initiation of accidents when there is loss of the salt-solution flow in the CST column under abnormal conditions of the process operations were computed. The calculations were conservative so that the model results showed the maximum centerline temperatures achievable by the CST design configurations. It was assumed that the IE-911 column was cooled by natural convection. Results of a sensitivity analysis indicated that the cooling mechanism at the column wall has no impact on the transient maximum temperature of the column, which can reach ~1900°F for the IE-911/air case.

7.2.3 IE-911 Sorbent Stability (CST SOWM 2.0)

Chemical and thermal stability of IE-911, one of the high-risk areas for CST Non-Elutable Ion Exchange, is the focus of several major R&D efforts. The research on sorbent stability can be arbitrarily divided into four topics: alternative pretreatment of IE-911, IE-911 chemical and thermal stability, waste/simulant precipitation studies, and revised manufacturing process.

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

7.2.3.1.1 FY00 – Results

An effective pretreatment regime would remove from IE-911 those leachable components that could possibly precipitate or mineralize during column operation and cause downstream problems. Previous work in this area indicated that at least one 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 IE-911 pretreatment with NaOH.[71] 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 simulant showed solid deposits with similar elevated concentrations of Nb.

Results of stability tests indicate that Nb and Si are leached from the IE-911 along with minor amounts of Ti and Zr. UOP staff indicated that IE-910 (CST) contains excesses of Nb (4 wt%) and Si (1 wt%). The quantities of Nb and Si leached from the samples of IE-911 do not exceed the excesses in the IE-910 precursor, suggesting negligible leaching of elements from the microstructure of the IE-910.

Small-scale leaching tests in which NaOH (3 M) was recirculated through a column packed with IE-911 (chloride form) demonstrated that a plug could form owing to formation of a solid. Thus, a column of IE-911 (nitrate form) was prepared at SNL and pretreated with NaOH. Within one day of starting the pretreatment, solids formed in the system and plugged the column. Analysis of the solids indicated a preponderance of Nb, although other IE-911 components were detected in the solids as well. Exposing the plug to a fresh 3M NaOH solution caused the plug to dissolve slowly.

Results published in an SRTC technical report[72] 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.

7.2.3.1.2 FY01 – Results

Part of the work in FY01 was aimed at quantifying the degree of supersaturation needed to initiate precipitation of hydrous Nb oxide and monitoring the precipitation kinetics. It was expected that the precipitation rate would 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 was an important part of developing an overall predictive model for the formation of the plugging material. SNL performed leaching and column testing with simulants to confirm the effectiveness of the recommended pretreatment process.[73]

Four column experiments were carried out to test a variety of pretreatment protocols. These studies showed that with the correct procedure it is possible to pretreat IE-911 in a column mode without plugging the column. They also demonstrated that when problems occurred the cause was always just a small accumulation of material at the input end of the column. No instances of mass fouling of the column pore spaces were observed.

Mechanisms that may lead to decreased performance are now understood. In general, niobium solubility was found to increase as the pH climbs. This result explains why flushing a column with fresh NaOH solutions can occasionally redissolve a plug that has formed due to the slow liberation of acid, which is an inherent property of IE-911. It appears several days exposure to a basic solution is needed during pretreatment to be sure that no acidic sites

on the CST are left that might interact with wastes solutions. The pretreatment must achieve a stable pH in excess of 13. However, further research revealed that Nb remains problematical if it is not removed from the system. The Nb species that leaches initially from the IE-911 is most likely a monomer, the solubility of which increases with increasing pH. Over the course of several days, this monomeric species forms an oligomeric species, most probably a hexamer, the solubility of which decreases with increasing pH. This decrease in solubility results in the precipitation of the hexamer, which has the ability to plug columns.

The results of this work produced an alternative pretreatment regime that reduces 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 was 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 greatly reduces the risk of using IE-911 in plant-scale operations.

In another study,[74] the chemical mechanisms responsible for the precipitation of $Al(OH)_3$, sodium hydrous niobium oxide, and sodium aluminum silicate (cancrinite) were investigated. Pretreatment with Al-free NaOH solutions eliminates problems associated with $Al(OH)_3$ precipitation. However, this is likely to precipitate hydrous sodium niobium oxide that can also plug columns. Sodium-aluminosilicate precipitates will only occur during in-service exposure to actual wastes (or waste simulants). A thermodynamic analysis is being developed to define a performance envelope where waste solutions can safely be brought in contact with the IE-911 (see Section 7.2.3.3). Several conclusions were made based on the results of this study. Causes of column plugging by Al and Nb-rich materials are considered understood. Manufacturing and pretreatment techniques to avoid these problems have been developed. In-service precipitation of sodium aluminosilicate is still a concern.

At this point the situation with IE-911 pretreatment was re-evaluated. A consensus was reached that the pretreatment should be performed before the IE-911 is supplied to the end user. Therefore, factors that would lead to efficient removal of extraneous Nb phases at the site of manufacture were investigated. The manufacturer has assumed the responsibility for removal of Nb from IE-911 so that minimal pretreatment will be necessary at SRS. The results of these studies are reported below (Section 7.2.3.4).

7.2.3.2 IE-911 Chemical and Thermal Stability (CST SOWM 2.2, 2.3)

7.2.3.2.1 FY00 – Results

Long-term exposure. The long-term stability of IE-911 in simulant solutions at various temperatures was determined because any loss of flow or cooling to columns of the baseline design could result in high temperatures from radiolytic heating. One aim of this work was to examine the possible role of long-term exposure to salt solution on IE-911 degradation because the third (or guard) column would be exposed to salt solution for 6 to 12 months before it is actually placed in service as the primary Cs-removal column. Final results of these tests are reported under FY01. Another aim was to determine the underlying

mechanism(s) responsible for the apparent non-absorption of Cs after heat treatment. Two candidate mechanisms were phase changes of the CST and pore blockage by precipitation. Thus, staff members treated samples of IE-911 in batch and flow-through column tests with simulants at temperatures of 25ºC - 80ºC. Experiments were conducted to examine the effects of soluble Si and Al. The leaching and precipitation of Nb and Zr during NaOH pretreatment and exposure to SRS waste simulants were also examined.

Batch tests. Long-term (12-month) batch leaching tests using the average, high-OH, and high-nitrate simulants and high-pH salt solution were initiated to determine the effect of temperature and solution composition on the behavior of the IE-911 [chloride (Lot 88-5) and nitrate (Lot 99-7) forms] and IE-910. After storage for two months, samples stored at all temperatures (25ºC - 80°C) in the average, high-OH and high-nitrate simulants were cemented together. However, the cemented IE-911 was easily broken up and did not reform into clumps. The IE-911 stored in the high-pH salt solution did not form any clumps at any storage temperature during the testing period. Nodules that appeared on the IE-911 particles were found to be an aluminosilicate. The results indicated an initial (sometime during the first month) degradation in the Cs-sorption properties of IE-911 as it contacted simulants at higher temperatures, but no further change after that. The IE-911 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 30ºC and 35°C, respectively). However, these apparent reductions in Cs sorption can be traced to the effect of the added mass of aluminosilicate on the IE-911 particles, which effectively "dilutes" the amount of active sorbent present. Several research groups addressed the deposition of aluminosilicates on the IE-911 particles (see Section 7.2.3.2.2).

Column tests. SRS-average simulant and high-pH salt solution were recirculated separately through two small PVC columns containing pretreated IE-911 (Lot 98-5) at room temperature and were analyzed periodically for dissolved metals to measure IE-911 leaching and precipitation of simulant components. Samples of the IE-911 were removed periodically and tested for Cs sorption and other properties. The IE-911 in the top of the average-simulant column was clumped together when the first sample was taken after one month. The IE-911 throughout the column was lightly cemented together although backwashing while lightly tapping on the column helped breakup the clumps of IE-911 and resettle the bed. Photomicrographs showed that smaller IE-911 particles and fragments tended to collect in the upper part of the columns, which probably occurred during the initial backwashing of the column. The Cs-loading capacity of the IE-911 from the column leaching tests indicated no change in the Cs capacity of the IE-911 along the length of the columns. The distribution coefficient of samples from the average-simulant column was 23% lower and the Cs loading on the IE-911 was 12% lower after 6 months exposure. The ICP results for Al, Si and Nb in the column feed solutions are consistent with the precipitation of sodium aluminosilicate. For both solutions, Nb rapidly leached from the IE-911, up to an apparent solubility limit, each time new feed solution was introduced. These results are consistent with those from the batch experiments. The apparently reduced Cs-loading capacity resulted from the deposition of aluminosilicates on the IE-911 particles, which effectively increased their mass and

diluted the active material. The results indicate that IE-911 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.

Heat treatment of IE-911 in the range 25ºC - 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 35ºC and 55°C provide a number of conclusions. Pretreating the IE-911 with NaOH lowers the equilibrium K_d to values that compare well with the ZAM model in the three SRS simulants. There was no loss in K_d at 35°C for the test conducted in average simulant that did not contain Si or Al. These data support the theory that the loss in K_d is related to aluminosilicate formation. Leached and heat-treated samples were examined at SRTC and SNL by a variety of analytical methods. IE-911 particles were coated with a layer of aluminosilicate ~1 micron thick when stored in SRS simulants at elevated temperatures.

SRTC developed a small-column test program to evaluate IE-911 stability by measuring the effluent profile for Al, Si, Nb, and Zr as a function of feed composition. Concentrations of Al and Si were related in a manner consistent with the precipitation of an aluminosilicate. The mechanism for Cs binding of IE-910 and TAM-5 was examined for SRS 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 (XRD) patterns of the two materials also revealed no detectable difference. The synthesis used by UOP to prepare IE-910 was identical to that used at Texas A&M University to prepare TAM-5.

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 IE-911 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 IE-911 performance.

7.2.3.2.2 FY01 – Results

Determinations of the long-term chemical stability of IE-911 were completed at ORNL in FY01.[75] Both batch and column leaching tests were conducted for a full 12 months. These tests involved contacting samples of CST with four simulant solutions at various temperatures and analyzing the IE-911 once each month to determine any changes.

Short-term batch tests were conducted initially to determine the impact of the equilibrium shift that occurs when the temperature is elevated. The cesium capacity of the IE-911 drops significantly (76%) as the temperature of the simulant and IE-911 during loading increases from 23ºC to 80°C. This change in cesium loading capacity is well predicted by the ZAM model, and is reversible when the temperature is returned to 23°C if the contact time at elevated temperature is short in duration.

Long-term batch testing has shown no change in cesium capacity for IE-911 samples stored at 23°C in average, high-OH or high-nitrate simulants for up to 12 months. IE-911 samples

stored for up to 12 months at storage temperatures of 30ºC, 35ºC, and 50°C showed drops in cesium capacity (measured at room temperature) of 9%, 11%, and 15%, respectively. Samples of IE-911 stored in the simulants at 80°C showed a drop in cesium capacity of about 23% after one month of storage with no further change in the cesium capacity for storage times up to 12 months.

Column tests were performed to evaluate the stability of IE-911 with long-term exposure to recirculating SRS-average simulant solution at room temperature. The cesium-loading capacity decreased slowly over 12 months, with a drop of 30% for IE-911 from the top of the bed and 13% for IE-911 from the bottom of the bed. A similar column test using a high-pH salt solution has not shown any change in the cesium capacity of the IE-911.

IE-911 in both the batch and column tests has shown a tendency to become agglomerated by cancrinite. IE-911 clumps were visible in batch samples stored at 30°C, 35°C, 50°C and 80°C after one month and in room temperature samples after two months. The cancrinite forms bridges between the particles that cause clumps to form, but these clumps can be broken up fairly easily. The ratio of cancrinite to IE-911 in the samples can be calculated from measured concentrations of Al and Ti. This ratio can be used to eliminate the cancrinite weight in the calculation of the Cs-loading capacity for the IE-911 samples from the leaching tests and calculate an adjusted cesium capacity for just the IE-911 in the samples. These calculations show that the cancrinite accounts for the apparent drop in cesium capacity for most of the IE-911 samples from the batch and column leaching tests. Two sets of samples show more loss in cesium capacity than can be accounted for by the cancrinite precipitate, IE-911 samples from the top of the column-leaching test using average simulant after 8 to 12 months, and IE-910 from the batch test in average simulant at 80°C. For both of these tests, an additional unknown mechanism is involved in the reduced cesium capacity of the IE-911. These batch and column tests using the older production batches of IE-911 show that no major changes occur in the utility of CST during long-term exposure to simulant solutions at various temperatures.

New batch and column leaching tests are in progress using samples of baseline (9090-76) and pre-production (MH-9098-9) IE-911 from UOP (see Section 7.2.3.4). The baseline IE-911 was pretreated with 3 M NaOH prior to being used. The pre-production IE-911 was used as received. Both samples have shown less of a tendency to clump than the earlier IE-911. Both of the new IE-911 samples formed clumps after storage in simulant for one month at 80°C. The pre-production sample formed clumps after two months at 50°C. All of the remaining batch samples are free-flowing after three months. The column test using baseline IE-911 contained clumps of IE-911 after two months exposure to recirculating simulant. The cesium capacity of the new samples from the batch and column tests at room temperature is similar to that of the comparable samples from the original tests that used older IE-911 (Lot 98-5). There has been a slower decease in cesium capacity for the new samples stored at higher temperatures in the batch leaching tests. The samples stored at 50°C and 80°C showed drops of 4% and 14%, respectively, after two months. The samples stored at lower temperatures have shown no decrease in cesium capacity to date. These results indicate that most of the apparent drop in cesium capacity is caused by the added mass of cancrinite that

precipitates on the IE-911 from the simulant solutions. The long-term stability of the pre-production batch of IE-911 is similar to that of the older production batches except that the rate of cancrinite precipitation appears to be slower. The reduced amount of cancrinite results in a slower loss in apparent cesium capacity and slower formation of IE-911 clumps.

Studies of IE-911 investigated the effect of time on the Cs-loading at elevated temperature. Work at ORNL[76] showed that cesium that was desorbed from IE-911 at elevated temperature was not completely resorbed when the temperature was lowered to ambient. In these tests, Cs-loaded IE-911 was heated for extended periods of time (60 days) in average simulant. Measurements taken after the material was brought to ambient temperature (~25°C) showed the cesium did not completely resorb. Therefore, the SRTC examined this apparent irreversibility in greater detail.

The results from tests conducted at SRTC at temperatures of 35°C and 55°C indicated the following. Pretreating the IE-911 with NaOH lowers the equilibrium distribution coefficient by an amount that is accounted for by the difference in formula weights of the hydrogen and sodium forms of the CST. Elevating the temperature to 55°C for a short duration (1 day) lowered the K_d value measured at 25°C by 7%. Raising the temperature to 35°C showed no effect on the K_d. The loss in cesium capacity is magnified when represented as K_d. For example, after a 55°C temperature excursion, only 0.4% of the initially sorbed cesium did not resorb.

Data from tests conducted with a temperature excursion (55°C) of 14 days indicate a detrimental effect (20% reduction) on K_d but only 1 to 2% change in the percentage of cesium initially removed. Again, raising the temperature to 35°C showed no effect. In this case, loss of K_d did occur in waste simulants devoid of added Al and Si. Solid-state characterization of the surfaces showed the formation of sodium aluminosilicate. The formation correlates with time at elevated temperature. However, the aluminosilicate deposition does not correlate to loss of cesium K_d. The results of these tests confirmed a high-temperature (55°C) "effect". The tests did not show any effect at lower temperature (35°C) even following exposures for 28 days. Moreover, the tests conducted with short duration at elevated temperature showed only minor effects (i.e., <10% loss in K_d).

Real waste from Tank 44F was used in another series of tests[77] in which cesium desorption from IE-911 was measured during storage at ambient temperature and following temperature increases to 35°C and 55ºC. The test results indicate the following. Cesium on IE-911 does not desorb significantly during storage. Approximately 0.03% of the cesium desorbed from loaded IE-911 during nine months of storage at ambient temperature in dilute NaOH (~0.2 M). These conditions should give results comparable to those from process operations. The amount of Cs desorbed when the temperature increases depends on the magnitude of the temperature increase. At 35ºC, 5 - 10% of the cesium desorbed; at 55ºC, 8 - 17%. When the temperature returned to ambient, the cesium largely resorbed. After heating to 35ºC, no irreversible desorption occurred. In most cases, more cesium sorbed after the heat treatment. After heating to 55ºC, irreversibly desorbed cesium was ≤2.1% of the total cesium. These

results with loaded sorbent in radioactive waste show less irreversible desorption than previous tests in simulated waste solutions. The difference may result from the differences in test conditions (i.e., temperature and duration of heating). The current tests more realistically represent probable process temperature upsets involving loaded sorbent, whereas previous tests are more representative of upsets with long heating durations[76] or partially loaded sorbent.[78]

A comprehensive series of pre-treatment, simulant treatment, and column and batch studies were investigated as a multi-laboratory effort in order to understand the cause and mechanism of factors that affect IE-911 performance, avoid future performance issues, and define the operability limits of IE-911. The treatment experiments were performed at SRS and ORNL. Samples were analyzed at SNL.[79]

A variety of as-received NaOH-treated and simulant-treated (from ORNL and SRS) samples of IE-911 were characterized by several techniques at SNL. As-received IE-911 (UOP batches 99-7 and 99-9) is composed mainly of well-crystallized acidified CST with ~3:1 Ti:Nb ratio, ~10 wt% zirconia binder, and three minor impurity phases: amorphous silica (~10 vol%), amorphous alumina (~5 vol%) and niobium titanate (~3 vol%). The surface morphology of the as-received pellets is smooth and featureless. The major Nb-containing impurity phase (IPX) was identified as the niobium titanate. Studies of its ion-exchange and solubility properties determined that this source of leachable Nb must be exposed to an acid wash (pH = 1) followed by NaOH treatment in order to remove it. The acid wash had already been implemented by UOP as a step in the binding process. Therefore, the addition by UOP of a caustic wash step in the batch mode resulted in successful removal of the impurity phase (see Section 7.2.3.4).

Samples treated in aluminum-containing simulant (SRS-average simulant) all have cancrinite precipitated on the pellet surfaces. Cancrinite deposition is limited to the pellet surface and does not penetrate the core of the pellets. Simulant exposure at 120°C resulted in extensive IE-911 destruction.

A major thrust of the SNL studies was to characterize the improved IE-911 (baseline-acid and pre-production-caustic-washed [see Section 7.2.3.4]) to determine if the leachable components had been minimized or removed. The amount of IPX in the pre-production IE-911 was reduced by a factor of 20 compared with the original IE-911 acid-form (UOP batches 98-5, 99-7, and 99-9). According to TEM inspection, IPX is almost completely removed from pre-production IE-911. Single crystals of Nb oxide (which is regarded to be largely insoluble in NaOH) several microns in diameter are found (<1 vol%) in both the baseline and pre-production IE-911. The leachable Si is determined to arise from trace impurities of silicate and aluminosilicate that are incorporated into the IE-910 and IE-911 during the manufacturing process. These Si-containing impurities are uncontrollable and vary in an unpredictable manner in composition, morphology, leachability and concentration between batches. The Nb-based impurities observed in the baseline IE-911 included IPX, crystalline Nb oxide, and a Ti-Nb-oxide phase whereas predominantly the crystalline Nb oxide is found in pre-production IE-911.

The revised manufacturing process did not have as drastic an effect on the composition, morphology or concentration of silica impurities. The leachable silica decreases by ~40% from the baseline to pre-production IE-911 batches. According to TEM, the silica impurities were similar in these batches and may be the source of leachable Si. However, there are compositional and morphological variations in these impurities from batch to batch and impurity to impurity.

The $Zr(OH)_4$ binder was also characterized, particularly its behavior in caustic solutions, in order to understand better the behavior and spectroscopic characterization of IE-911. These studies showed that the binder is very stable upon extended exposure to NaOH solution and that the binder is affected by treatment with NaOH solution. The changes in the binder may be responsible for the cracking and exfoliation that was observed when NaOH-treated IE-911 was prepared for SEM studies. The preparation involves heating IE-911 under vacuum, conditions that are certainly not realistic during plant operation.

Experimental results from PNNL[80] addressed the chemical and thermal stability of Cs-loaded IE-911. The purpose of the study was to determine the time and temperature profiles at which irreversible desorption of Cs from the IE-911 occurs and to determine the cause of the apparent reduced Cs capacity of the IE-911. Cs-loading/desorption/reloading tests were used. Variables in the test included the heat-treatment temperature and time, initial Cs concentration in simulant, IE-911-to-simulant volume ratio, as well as different IE-911 batches. The Cs uptake of IE-911 was measured in each phase. Changes in the concentrations of other cations in the simulant, such as Si, Ti, Zr, Nb, were also measured in some tests. The Cs-loaded ion exchangers were analyzed by several techniques following high-temperature and room-temperature exposure. Different batches of IE-911 showed similar Cs K_d values at room temperature. Compared to other batches, the pre-production batch has much lower leachable Nb and Ti. After exposure to 55ºC and 80ºC, some Cs desorbed from IE-911. The higher the heat-treatment temperature, the more Cs desorbed. After the temperature was lowered to ambient, Cs that desorbed at high temperature could be resorbed by IE-911 in some tests. However, the Cs desorption was irreversible in other tests. High Cs loading, high simulant/IE-911 ratio, and high-temperature heat treatment cause irreversible Cs desorption.

Separate experiments showed that the SRS-average simulant is not stable. A hexagonal nitrate cancrinite-type sodium aluminosilicate precipitated from simulant shortly after exposure to 55°C and 80°C. SEM analysis showed that a sodium aluminosilicate coating formed on the surface of IE-911 beads after exposure to simulant at 55°C and 80ºC. The morphology of the coating depends on the heat-treatment temperature, heat-treatment time, IE-911-to-simulant ratio, IE-911 batch number, and simulant composition. IE-911 is not the major Si source for the aluminosilicate precipitation. Most of the components in the precipitation come from the simulant. The coating should not be the major reason for the irreversible Cs desorption because it was found on the surface of almost all the heat-treated IE-911 samples (samples with reversible and irreversible Cs-desorption). Also, cancrinite-type aluminosilicate has large size openings in its structure so that Cs should be able to

diffuse through these pores to IE-911 when the temperature was lowered. Up to now, the mechanism for the irreversible Cs desorption is still under investigation.

7.2.3.3 Waste/Simulant Precipitation Studies (CST SOWM 5.1)

7.2.3.3.1 FY00 – Results

Researchers investigated the stability of SRS simulated waste solutions and the solubility of Nb and Zr in them.[81] 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. These instabilities may have caused or exacerbated most of the plugging incidents observed in testing of IE-911. Especially significant was the precipitation of sodium aluminosilicate after heating average and high-nitrate simulants.

Thermodynamic equilibrium calculations were performed using SOLGASMIX software[82] and a thermodynamic property database compiled at ORNL from available literature data. Initial calculations were performed to confirm a recent result[83] and the reliability of the ORNL thermodynamic property database. Next, the calculations were expanded to include the full range of those ions listed in the literature.[84] 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, Pitzer's activity coefficient method[85] 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.

Thermodynamic modeling[86] of SRS-average, high-nitrate, and high-OH simulant solutions showed the possibility of metastable solutions. Cancrinite was predicted to form in each of the simulants with little or no silicon remaining in solution at equilibrium. Gibbsite was predicted to precipitate in both average and high-nitrate simulants. Sodium fluoride-sulfate was predicted to precipitate in high-nitrate simulant. For all three simulants, the initial modeling calculations predicted the precipitation of sodium oxalate from solution as the temperature was increased from 25°C to 50ºC. Results of the laboratory solubility studies were in contrast to the calculations for oxalate at 25ºC, indicating the necessity of carrying out a reassessment of the solubility data on oxalates in the simulant solutions. Following the calculation of the ion concentrations, temperature, etc., necessary for precipitation, laboratory tests were performed to confirm the results of the thermodynamic analyses. Results obtained for the three simulants in this step were fed back into the model to refine it. Solids that

formed included sodium oxalate, nitrate, carbonate, and fluoride-sulfate, and aluminum hydroxide. 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. Recent measurements from the Ian Wark Research Institute, University of South Australia,[87] substantiate the finding of low solubility of cancrinite in NaOH solutions. 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 showed that only Sr, Ba, and Pb have solubilities greater than millimolar levels. The results from calculations on IE-911 (Ti and Nb) and binder (Zr) components agree with leaching studies carried out at ORNL and SRTC. These results are highly significant because they indicate that the simulants used in virtually all of the experiments with IE-911 are metastable with respect to precipitation of aluminosilicates.

Therefore, the deposition of the aluminosilicates on IE-911 particles observed in experiments on the chemical and thermal stability of IE-911 may or may not have any significance with respect to tank waste. The results indicate that 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.

7.2.3.3.2 FY01 – Results

Simulants. Studies with simulants are continuing in the direction of measuring the equilibrium saturation limits of Al and Si. Thus, a "seed" of gibbsite [$Al(OH)_3$] was placed in portions of the three simulants (SRS-average, high-nitrate, and high-OH). The systems were allowed to equilibrate for approximately 16 weeks, after which the Al concentration in average and high-nitrate simulants had decreased whereas that in high-OH simulant had increased. In experiments performed at PNNL to demonstrate that SRS-average simulant is unstable with respect to aluminosilicate precipitation, precipitates appeared in samples of the simulant that were stored at 50°C and 80ºC for several days. Finally, studies in progress at SNL are measuring the equilibrium concentration of Al and Si in high-nitrate simulant. These values will be supplied to ORNL for use in modeling studies.

Thermodynamic modeling is continuing at ORNL with incorporation of the values for Al and Si concentrations found experimentally at SRTC and PNNL into the calculations to provide a benchmark for further studies of real waste solutions. The model correctly indicated the precipitation of aluminosilicates in the average and high-nitrate simulants.

Real waste. Cesium sorption (equilibrium and kinetic) from high-level radioactive waste solutions onto IE-911 at ambient temperature has been measured. The equilibrium measurements were compared to ZAM[57,88] model predictions. The kinetic measurements were compared to simulant solutions whose column performance has been measured. The test results indicated the following. The ZAM model predicts within 33% the loading of cesium

from a variety of Savannah River Site wastes. Wastes from both F and H Areas and with high and low K/Cs ratios showed good agreement with predictions. The kinetics of sorption were nearly identical in all tests with SRS radioactive waste and simulated SRS waste, suggesting current modeling parameters are adequate for predicting radioactive waste performance.

Data for the concentrations of major ions (Na, Al, Si, NO_3^-, etc.) were obtained from either the WSRC database or more recent analytical results and were used to calculate the thermodynamic state of waste in several SRS tanks. The calculations indicate that waste in Tanks 46, 43, 38, 30, 29, and 23 is unstable with respect to precipitation of gibbsite and/or cancrinite. The model was also used to calculate the effect of dilution on stable waste compositions and those that are metastable. The effect of adding NaOH of various molarities to various wastes was calculated.

Should this option be selected, further work should include tests with waste obtained by dissolving salt cake and development of a more sensitive test for comparing sorption kinetics.

7.2.3.4 Revised Manufacturing Process (CST SOWM 2.1)

7.2.3.4.1 FY00 – Results

Results from experiments with the engineered form (IE-911) of CST (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 Section 7.2.3). In addition, lot-to-lot variability in the Cs-sorption capacity was noted. Therefore, a technical exchange with UOP, LLC, was 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. A series of IE-911 batches were prepared. These included the baseline (9090-76), laboratory-scale, and pre-production (caustic-washed, MH-9098-9) batches. All batches were prepared under carefully controlled conditions that were set using the baseline batch in order to reduce lot-to-lot variability. The laboratory-scale batch was prepared in order to confirm that reduced levels of leachable components were present prior to preparing the same formulation on a larger scale as the pre-production batch.

7.2.3.4.2 FY01 – Results

Collaboration with UOP to develop an engineered form of CST (IE-911) compatible with SRS waste concluded successfully in FY01. The production of test batches of reformulated materials and the occurrence of technical reviews followed the schedule. Product specifications (target definition) were defined and agreed to by WSRC. Updates on pretreatment work at SNL were provided to UOP in order to optimize their efforts.

UOP produced baseline batches of IE-911 and IE-910 for which the manufacturing parameters were tightly controlled during the preparation. These materials were delivered to SRTC, ORNL, SNL, and PNNL in the fall of 2000. Tighter control of the manufacturing parameters have resulted in less lot-to-lot variability in the two batches of IE-911 that have subsequently been produced.

Efforts to reduce leaching focused on caustic washing before IE-911 is shipped. Data obtained at SNL about the pH at which the CST and binder must be combined so that the leach removes the overwhelming majority of the Nb were extremely useful in developing a superior product. The laboratory-scale batch of 100 g was sent to the DOE laboratories in December 2000. After evaluation of the laboratory-scale batch, the pre-production batch of IE-911 was produced by mid-January 2001. Samples were sent to SRTC, ORNL, SNL, and PNNL for characterization of the material using the methods described in other parts of this section. The status of the final deliverable in the contract, a 2,000-lb batch of the improved material, is currently under discussion.

Researchers from across the DOE complex worked with personnel from UOP to assess the impact of the manufacturing changes on the use of IE-911 for the removal of cesium from SRS high-level waste.[89] The results of the extensive examination of newly prepared laboratory-scale and pre-production samples of caustic-washed IE-911 were compared with those for commercially available and baseline samples. Conclusions from this work include the following. A significant fraction (~95%) of leachable Nb is removed and Si leaching is reduced (~58%) but not eliminated. UOP treatment removed the impurity phase of Nb, but not amorphous Si. The capacity (mg Cs/g IE-911) of the pre-production sample is comparable to that of the baseline sample and better than the laboratory sample. A column-breakthrough experiment indicates the manufacturing change did not affect the mass-transfer-zone length. The time dependency (kinetics) to reach equilibrium is not affected by the change in UOP manufacturing process. The temperature dependence is the same as for previously supplied materials. Pore analysis, particle size, thermal behavior, and packing density measurements indicate the process change does not affect the engineered material. The results of these tests indicate that UOP has produced a material that can be used in the ion-exchange columns with a minimum of pretreatment at SRS.

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

7.2.4.1 Previous Results

A previous study[90] measured the impact of IE-911 on the rate of formation and composition of radiolytically generated gases in simulated SRS liquid waste. The test results showed that radiolytically generated gas bubbles form rapidly at expected process dose rates. Irradiation of IE-911 slurries produced oxygen (in high-nitrate simulant), hydrogen (in high-OH simulant), and nitrous oxide (N_2O). 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[91] for a full-scale process column.

Additional work investigating the effect of gas generation was performed on a larger scale.[92] Radiolytic gas generation in the IE-911 column was simulated by the decomposition of hydrogen peroxide. In the course of the laboratory studies, it was determined that peroxide leaches metals from the IE-911. These findings have little implication in an actual system, since radiolytically generated hydrogen peroxide is present at extremely low levels (approximately 10^{-6} M, see Section 7.2.2.1). The gas-generation test provided information on bed retention and release of gas produced in 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.

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. The tall-column apparatus at ORNL was modified to test prototypical equipment to perform gas-disengagement experiments. The use of hydrogen peroxide for non-radioactive examination offered benefits over a radioactive test.

7.2.4.2.2 FY01 - Results

Gas-disengagement equipment (GDE) was installed on the existing CST tall-column unit at ORNL for the purpose of removing free gas generated during tall-column testing. The system was designed to operate under varying conditions to establish the operating-envelope and performance requirements for the CST process. The gas-disengagement chamber was operated in three modes that included simultaneous control of both the sweep/sparge air through the chamber vapor space and the liquid level in the chamber and bypassing of the gas-disengagement chamber altogether so that no control issues exist. The test results[93] showed that GDE can effectively remove gas to a level that prevents bulk accumulation in the bed of downstream columns when the GDE is operated at atmospheric (or lower) pressures. Foregoing gas separation or operating at high pressures can cause some accumulation of gas in downstream columns. Over a range of gas-generation rates up to 40 times the rate that could be expected from radiolysis, the gas measured in the effluent from the GDE was essentially unchanged. This indicates that the equipment is effective in separating entrained gas at atmospheric pressures. Recommendations include the following. The column design should include gas vents at tops of columns to permit the release of gas that will accumulate slowly over time. Gas separation between columns should be performed at lower pressures than will be encountered within the downstream column.

After the experiment was completed, sluicing of the IE-911 from the column proved difficult due to a crusty consistency that was particularly hard at the top of the tall-column where hydrogen peroxide was introduced. It was concluded that the deposition of aluminum from

the simulant and metals previously leached from the IE-911 acted as a binder. Some binding was also observed in the short column, but back-flushing with simulant and nitrogen gas broke up the IE-911 so it could be removed by sluicing.

In support of this evaluation, analysis of simulant samples indicated that some Nb and Ti were leached from the IE-911. The concentrations of these metals in the simulant appeared to increase in response to feed of concentrated hydrogen peroxide and then decrease, indicating that the metals had precipitated from solution. Scanning electron microscopic analysis of IE-911 samples showed deposition of globular nodules and cubic crystals on the particle surface. Energy dispersive x-ray spectroscopy identified these deposits as being rich in aluminum, silicon and titanium, confirming the above conclusion.

Should CST Non-Elutable Ion Exchange be selected, additional tests are recommended in two primary areas. First, equipment that supports a falling film to permit entrained gas to separate from the liquid could be very effective and reduce the inventory of simulant in the GDE. Second, tests of ultrasound-enhanced separation at various power levels seem prudent based on preliminary results. Equipment could be operated in pulsed mode if equipment capable of continuous operation cannot be identified. These tests would help define the most effective gas separation technique.

7.1.6.4 Cs Loading Under Irradiation (CST SOWM 3.2)

7.2.4.3.1 FY00 – Results

Another concern associated with deployment of IE-911 is the effect of gas generation from radiolysis of water on Cs removal by IE-911. The calculation of gas generation in large columns was improved. The rate and location of bubble formation during Cs loading was defined. The diffusion rate of gases out of IE-911 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.

A spent-fuel element in the HFIR pool was used in a test designed to measure Cs adsorption in the presence of gas generated in a high gamma-radiation field and the rate of gas generation. Cesium was successfully loaded onto IE-911-containing columns in a test capsule that was placed inside the center cavity of a HFIR fuel element. The capsule 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 IE-911 column in order to load the Cs onto the IE-911. The radiation dose received by the column of IE-911 was representative of that expected for treatment of SRS HLW supernate. Samples of the supernate were collected every 4 hours for Cs analysis. A Cs-loading curve was generated from the data.

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.[94,95]

7.2.4.3.2 FY01 – Results

Loading of the column under expected nominal full-scale field conditions in the HFIR pool showed that radiolytic gases were formed at a previously calculated generation rate of 0.4 mL per liter of feed solution at dose rates ranging from 12.4 to 10.4 Mrad/h over a 168-h period.[96] When the resulting cesium-breakthrough curve in the gamma field was compared with that of a control experiment in the absence of a gamma field, no discernable difference in the curves (within analytical error) was detected. Both curves were in good agreement with the VERSE computer-generated curve. The results clearly indicate that the production of radiolytic gases within a full-scale column in a radiation field expected to be nearly 16 times as intense as that encountered in an actual field-loaded column is not expected to result in reduced Cs-loading capacity during operation at the Savannah River Site.

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

7.2.5.1 Previous Results

Sluicing. Pumping tests conducted during prior research in a recirculating loop showed that a 24 wt% slurry of IE-911 in water can be transported at fluid velocities of 4.3 ft/s with no visible settling of the IE-911 particles. A 5 wt% slurry will stay suspended at a velocity of 3.8 ft/s. The IE-911 was easily mobilized after purposely plugging sections of pipe. The IE-911 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 IE-911 particles.

Additionally, slurries of IE-911 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, so the apparent abrasivity was the result of chemical corrosion by the water. Mixtures of as-received IE-911 and SRS sludge simulants showed minimal tendency to cause caking or hard layers.

IE-911 was easily sluiced into and from an ion-exchange column using water and air. Pressure drop through the column and across the Johnson screen and the effect of flow rate on pressure drop were measured. 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 the hydraulic tests. The pressure drop across the Johnson screen remained constant throughout six tests, indicating no accumulation on the screen. No channeling was detected. Prior to sluicing the IE-911 from the column, the simulant in the column was displaced with 2 M NaOH and then with deionized water. Water was used to sluice the IE-911 in order to facilitate handling of the spent IE-911. The two-step displacement process was used to avoid possible precipitation of $Al(OH)_3$ from the 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 IE-911 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.

The water interface moved slightly faster than the IE-911 interface, leaving about 17 cm of IE-911 in the bottom of the column after the first sluicing.

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

7.2.5.2.1 FY00 – Results

Literature was reviewed and other DOE sites were contacted about their experience with size-reduction processes in order to select the best method for accomplishing IE-911 particle-size reduction. 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 (WVDP) were contacted about their experience in grinding zeolite. Criteria selected for evaluating a method of particle-size reduction are: (1) The method must be capable of processing a wet slurry (10%) of IE-911 solids in water; (2) Size reduction should be accomplished 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.

The 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, which 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. A kinetic grinding system from Micro Grinding Systems, Inc., was one of the most promising technologies identified for reducing particle size of 105-K East Basin sludge on the Hanford site and was the technology chosen for processing contaminated zeolite stored in a waste tank at WVDP. The raw zeolite has a particle-size distribution very similar to that of the IE-911. Tests at WVDP showed that 800 to 900 micron-sized particles were ground 98 - 100% below 200 microns and about 90% below 100 microns.

Grinding tests were contracted to both IKA Works and Micro-Grinding Systems.[97] The IKA equipment best satisfied the process selection criteria. However, it was also highly desirable to evaluate the Micro-Grinding equipment for IE-911 particle-size reduction because WVDP has successfully ground zeolite with specifications very similar to those of the SRS CST application using this equipment. The equipment tests ground approximately 50 pounds of solids. With the IKA equipment, a nominal 10 wt% slurry was used as feed. About 5% of the IE-911 appeared to pass unchanged through the equipment. The experience of the vendor was used to estimate the desirable slurry concentration for the Micro-Grinding system because it is most efficient at higher slurry concentrations. The test was conducted successfully. Size-reduced IE-911 from both tests was returned to SRTC for evaluation of mixing, settling and resuspension characteristics.

The results of these preliminary experiments give a clear indication that size-reduction of IE-911 particles presents little risk to their use. According to the data, it should be possible to reduce the size of IE-911 particles so that homogeneous slurries can be produced and sampled representatively. Both vendors demonstrated the capability of size reducing IE-911

to a maximum particle size <177 µm. IE-911 is a relatively friable material that did not severely challenge the grinding capabilities of either device. However, neither vendor was entirely successful at reducing as-received IE-911 to a maximum particle size <20 microns.

7.2.5.2.2 FY01 – Results

Vendor tests completed in FY00 provided results demonstrating that IE-911 can be reduced to a size comparable with the frit or sludge particles. On this basis, no further work in this area was planned for FY01.

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

The Slurry Mix Evaporator (SME) represents the final control point in the glass-making process. Thus, the slurry in the tank must be homogeneously mixed and representatively sampled to determine the composition. The contents of the SME are sampled using a Hydragard® sampling valve. The Hydragard® valve draws a side stream from a recirculation loop and directs the stream through the sampling valve. After a preset time, usually 40 seconds, the Hydragard® valve is closed and a sample of the slurry is trapped in a vial. Chemical analyses of these samples form the basis for glass quality assurance.

The ability to mix homogeneously IE-911 into the sludge/frit slurry, to obtain representative samples of a melter feed slurry containing IE-911 from the Hydragard® valve,[98] to determine if the recirculation flow rate has an influence on the Hydragard® sample composition, and to observe if the time that the Hydragard® valve is left open affects the sample composition must be considered to evaluate the impact of adding IE-911 to the slurry.

7.2.5.3.1 FY00 – Results

Studies of the IE-911/frit/sludge slurry using the Hydragard® sampler did not show uniform results when compared with a grab sample taken from the feed tank.[7] The Hydragard® samples exhibited 12% frit depletion. As expected, the sludge/frit slurry with large as-received IE-911 particles repeatedly plugged the Hydragard® sampler because the Hydragard® sampling system was configured to sample sludge with frit particles that are nominally ~175 microns in diameter. Operation of the Hydragard® sampler with slurries of size-reduced IE-911 was compared to operation with sludge/frit slurries in order to determine minimal size distributions for adequate IE-911 slurry sampling. Samples taken by the Hydragard® sampler showed a bias toward low frit with or without size-reduced IE-911 present. Thus, the operation of the Hydragard sampler itself should be re-assessed. However, it was concluded that IE-911 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 10 wt% IE-911 it was observed that an unusually thick slurry containing 52 wt% total solids could not be adequately mixed in the 1/240th scale DWPF tank. 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 IE-911 cannot be similarly concentrated, DWPF glass production rates will be reduced.

7.2.5.3.2 FY01 - Results

Suspension. A testing facility was configured to define agitator configurations and mixing parameters capable of maintaining a homogeneous IE-911/water slurry containing 10 wt% as-received IE-911 (particle size range 30 to 60 mesh) or 10 wt% size-reduced IE-911 (maximum particle size 177 µm).[99] The blade and impeller sizes (5-inch) and agitator speeds (500 rpm or greater) required to maintain homogeneity were determined using a baffled mixing vessel that dimensionally approximated a 1/240th scale DWPF Chemical Process Cell process vessel and size-reduced IE-911. Resuspension of the size-reduced IE-911 solids into a homogeneous slurry after the size-reduced IE-911 had been allowed to settle for 6 days was readily achievable. Limited testing with a 10 wt% slurry composed of ~1 wt% IE-911 particles >177 µm defined the conditions under which it was not possible to achieve a homogeneous slurry (8-inch impellers, 700 rpm). A contract has been established with Philadelphia Mixers to define agitator configurations and mixing parameters capable of maintaining a homogeneous water slurry containing 10 wt% as-received IE-911. Therefore, our work primarily addresses test results with size-reduced IE-911.

Sampling. For a 26 wt% oxide sludge and 74 wt% oxide frit (defined as the baseline case), an ~9.5% enrichment of sludge and a 3.4% depletion of frit were seen in Hydragard® samples relative to grab samples.[100] Two campaigns were carried out with feed containing the same solids wt% in the slurry (~46%) as the baseline case and with reduced solids (42 wt%) (sludge, 26; IE-911, 10; and frit, 64 wt%). The results of this study indicate that introduction of size-reduced IE-911 into a melter feed slurry of frit and sludge does not enhance the enrichment of sludge or the depletion of frit observed in the baseline case of the Hydragard® vs. the grab samples. In order to make a valid comparison between the Hydragard® samples and the grab samples, it was also necessary to prove that the tank was homogeneously mixed, that the recirculation flow rate did not significantly influence the sample results from the Hydragard® sampler, and that the sampling time did not affect the Hydragard® results. This testing was done by taking grab samples at the top and bottom of the tank and varying the recirculation rate and sampling time. The slurries for all three phases showed a bias toward higher sludge and lower frit in the Hydragard® samples versus the grab samples. IE-911 components sampled the same as the sludge components. The bias toward frit loss in the Hydragard® showed some tendency to increase with increasing recirculation loop flow. Valve open times between 5 and 60 seconds had no (consistently) significant effect on Hydragard® sample composition. Rheological properties of the sludge/frit melter feed and the size-reduced IE-911/sludge/frit melter feed were measured. Adding IE-911 to the slurry significantly increased the yield stress. However, the consistencies of both types of slurry were comparable implying that once the slurries were flowing they behaved similarly. A 52 wt% total solids sludge/frit/IE-911 slurry could not be agitated because the yield stress was too high to obtain motion in significant portions of the slurry.

The data from these tests indicate no problem with sampling size-reduced IE-911 (<177 µm) with the Hydragard® system because the behavior of the IE-911 components within the Hydragard® system mimics that of the sludge components.

7.2.6 Coupled DWPF Operation (CST SOWM 20.0)

7.2.6.1 Previous Results

Little information existed on the ability of IE-911 to alter the amount of hydrogen formed radiolytically in the Slurry Receipt Adjustment Tank (SRAT), in which size-reduced IE-911 would be added to the sludge/frit slurry. Hence, personnel conducted process simulations at bench scale and at small pilot scale (1/240th DWPF) to examine this risk.[101,102] The maximum observed SRAT hydrogen generation rate was 0.0034 lb/hr (~0.5% of the current DWPF limit of 0.65 lb/hr) during the sludge-only run without IE-911 present and occurred at the end of the SRAT reflux cycle. The maximum Slurry Mix Evaporator (SME) hydrogen generation rate was 0.012 lb/hr (~5% of the current DWPF limit of 0.23 lb/hr) during the size-reduced IE-911 run and occurred at the beginning of the SME dewater cycle. The size-reduced IE-911 runs produced slightly more hydrogen than the as-received IE-911 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 down-selection.

7.2.7 DWPF Melter Operations

7.2.7.1 Glass Titanium Loading (CST SOWM 17.0)

7.2.7.1.1 Previous Results

Compositional changes in sludge and frit were examined with a statistically designed approach.[103] The sludge-, frit- and IE-911-loading were varied in order to assess the operating window for glass composition in DWPF. Existing models were used to predict the processing and product properties for each of the compositions. The results indicated that the viscosities and liquidus models for the IE-911/sludge glasses appeared adequate to cover the different compositional regions. Glasses at reasonable loadings of IE-911 and sludge had durabilities acceptable for DWPF. However, the durability model under-predicts the measured Product Consistency Test (PCT) values.

Twenty two glasses containing Purex sludge and three glasses containing H-Area Modified (HM) sludge were fabricated and tested.[104] The fabricated glasses were tested for durability and characterized by measuring the viscosity and determining an approximate bounding liquidus temperature. The goal of this work was to identify any major problems from a glass perspective that could potentially preclude the use of IE-911 at DWPF. The glasses produced were close to the targeted compositions. The analytical measurements were of high quality. The results indicated all 25 glasses were very durable as measured by the PCT. The 22 Purex-loaded glasses clustered tightly in one region, whereas the HM glasses clustered at an even lower value for boron release. The measured durabilities are not correlated to the

values of the DWPF homogeneity constraint for these glasses. 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 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. On the other hand, the HM sludge-containing glasses had, as predicted, viscosities (~160 poise) that were far above the limit. Thus, the HM sludge-containing glasses fabricated for this study are not acceptable for processing in the DWPF.

7.2.7.1.2 FY00 – Results

No work in this area was conducted in FY00.

7.2.7.1.3 FY01 - Results

A CST-glass study was conducted[105] to determine the effect, if any, on the PCT responses of CST glasses cooled at different rates. The glasses contained IE-911 and MST (plus a simulated sludge representing Purex, Blend, or HM) in amounts consistent with coupled operations using the CST option for salt disposition. Two bounding cooling profiles, rapidly quenched and canister-centerline, were used in this study. Glasses were selected mainly to challenge the regions where amorphous phase separation is expected. The current DWPF homogeneity constraint predicted that many of the CST glasses could be phase separated. (Only 2 of the 17 glasses were predicted to be homogeneous.) It was important to ensure that deleterious phase separation does not occur for either cooling profile because the constraint was not developed using the compositional region that includes these levels of IE-911 and MST. There was essentially no difference between the PCT responses for glasses subjected to the two cooling profiles. In fact, although small, the boron PCT responses for the centerline cooling glasses were more durable than the rapidly quenched glasses. These results reveal that no deleterious amorphous phase separation occurred under either cooling regime. XRD analysis revealed that trevorite and hematite were present in some of the glasses. SEM analyses of the crystals that formed on the surface of the glasses revealed titanium rods and spots, trevorite, trevorite enriched with titanium, and a phase rich in Mn and Fe. One glass contained a crystal high in uranium content. The durabilities of the CST glasses are significantly lower than the PCT values for glasses containing PHA[106] and for Environmental Assessment (EA) glasses. The PCT results are highly clustered, consistent with previous work. The measured PCT values fall above the upper 95% prediction interval of the DWPF model used to predict durability, again consistent with previous results. The very good durability of the IE-911-containing glasses implies that durability may not be the limiting factor for waste loading in this option.

7.2.8 Feed Homogeneity (CST SOWM 19.0)

7.2.8.1 Previous Results

The HLW aqueous slurry in the Melter Feed Tank (MFT) is pumped through a recirculation loop. 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.

7.2.8.2 FY01 – Results

An excessively high yield stress for size-reduced (<177 µm) IE-911/sludge/frit DWPF melter feed was observed in a previous study.[107] This may have been due to the fact that the slurry was more than a year old, that it contained size-reduced IE-911, that it contained different frit, and/or other factors. Thus, the Immobilization Technology Section measured properties of the melter feed simulants used in the 1999 and 2000 Hydragard® sample loop tests. The melter feeds were characterized for wt% total (TS) and insoluble solids (IS), pH, composition, particle-size distribution, and rheology. The two 1999 melter feeds, sludge/frit and size-reduced-IE-911/sludge/frit, had nearly identical rheological characteristics (at 39-51 wt% TS), yield stresses within the DWPF design basis range, and consistencies at or below the lower DWPF design basis limit. The compositions of the two 2000 melter feeds differed significantly from the 1999 melter feeds. The wt% frit oxides were constant in 1999; the wt% sludge oxides, in 2000. The size-reduced IE-911/sludge/frit melter feed had nearly three times the yield stress of the sludge/frit melter feed (at ~46 wt% TS). The 2000 tests with size-reduced-IE-911/sludge/frit (at 42.4 wt% and 45.9 wt% TS) both occurred with slurries whose yield stress exceeded the DWPF upper design basis limit. The 2000 sludge/frit melter feed yield stress and all of the consistency data were within the DWPF design basis limits. Problems mixing melter feed slurries in the Hydragard® sample loop tank were determined to be primarily due to an insufficient quantity of feed rather than rheological properties.

Another study was performed[108] to produce fresh melter feeds based on (1) Tank 8/40 blend (sludge/frit only), (2) fine-Tank 8/40 blend (<30 µm IE-911), and (3) coarse-Tank 8/40 blend (<177 µm IE-911). Melter feeds were prepared using a prototypical bench scale DWPF Chemical Process Cell (SRAT/SME) cycle. Processing conditions corresponded to the nominal Tank 8/40 sludge blend case developed in September 2000.[109] Rheograms were run shortly after the completion of the SRAT/SME cycles on six different solids concentrations for each melter feed. This permitted a comparison between the three melter feeds without the issues of variations in processing conditions, material age, and handling history. The rheograms showed the expected pattern of increasing yield stress and consistency with increasing solids content for the different melter feeds. All the melter feeds exceeded the DWPF design basis yield stress (at ~42 wt% TS), which was comparable to another study.[110] In general, at low wt% solids the behavior of the three slurries are the same rheologically. As the wt% solids increases, the <177 µm IE-911/sludge/frit was the most viscous, followed by the <30 µm IE-911/sludge/frit and then the sludge/frit-only slurry. The change is most

notable in the yield stress. However, the data were almost never within DWPF design basis region. The yield-stress data seem to show the same general behavior when comparing the blends using data from two rheometers. The <30 µm IE-911/sludge/frit yield stress was comparable to the blend-sludge/frit yield stress where the DWPF design limit was not exceeded. The DWPF yield stress upper design limit was exceeded at a very low wt% TS and IS values for all the blends. In general, the Tank 8/40 blends containing IE-911 are more viscous than those of the Tank 8/40 Blend. Above 43 wt% TS or 39 wt% IS solids, the yield stresses for the IE-911 slurries start to diverge and rapidly increase from that of Tank 8/40 blend as the wt% solids increases.

If CST Non-Elutable Ion Change is selected, additional tests in which the pH is varied could provide a slurry that can be processed using the existing DWPF slurry-design basis limit. The experiments were conducted with a base material that was outside of the DWPF design basis for yield stress (15 - 150 dynes/cm^2) starting at low wt% solids. A decision needs to be made as to whether or not DWPF actually processes within this range. If it does not, then findings using viscous fluids may have little relevance to the actual plant performance. A rheometer with comparable measuring capabilities to the one at TNX (SRTC development facility for 200 Areas) is located in the Shielded Cells. A sample of real DWPF melter feed should be submitted for rheological characterization. The rheology task team should be chartered to define a program that will enable development of a better set of experimental errors for TS and IS, yield stress, and consistency. This program would enable experimenters to produce statistically significant conclusions when comparing the properties of two different slurries.

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 to extract cesium in a series of countercurrent centrifugal contactors (the extraction stages). The resulting clean aqueous raffinate is transferred to Saltstone for disposal. Following cesium (Cs) extraction, the solvent is scrubbed with dilute acid (0.05 M) to remove other soluble salts from the solvent stream (the scrub stages). The scrubbed solvent then passes into the strip stages where it is contacted with a very dilute (0.001 M) acid stream to transfer the Cs to the aqueous phase. The aqueous strip effluent is transferred to the DWPF. The baseline process also includes washing the aqueous exit streams with diluent to recover solvent and washing the solvent with acid and base to remove extracted impurities and solvent degradation products.

The basis and composition of the waste simulant to be used in all CSSX testing are described in an SRS position paper.[111] 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

The science and technology roadmap for Caustic Side Solvent Extraction (Figure 7.3) is a subset of the overall SPP roadmaps (see Appendix A of the R&D Program Plan[3] or the SPP website at http://www.srs.gov/general/srtech/spp/progplan.htm). The CSSX roadmap defines needs in the following three basic categories:

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

Process chemistry includes data on the thermal and hydraulic transport properties and mass transfer properties that are needed to finalize the conceptual design. These data are used to establish the physical and engineering property basis for the project and detailed design.

Examples of key decisions resulting from these activities include 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.

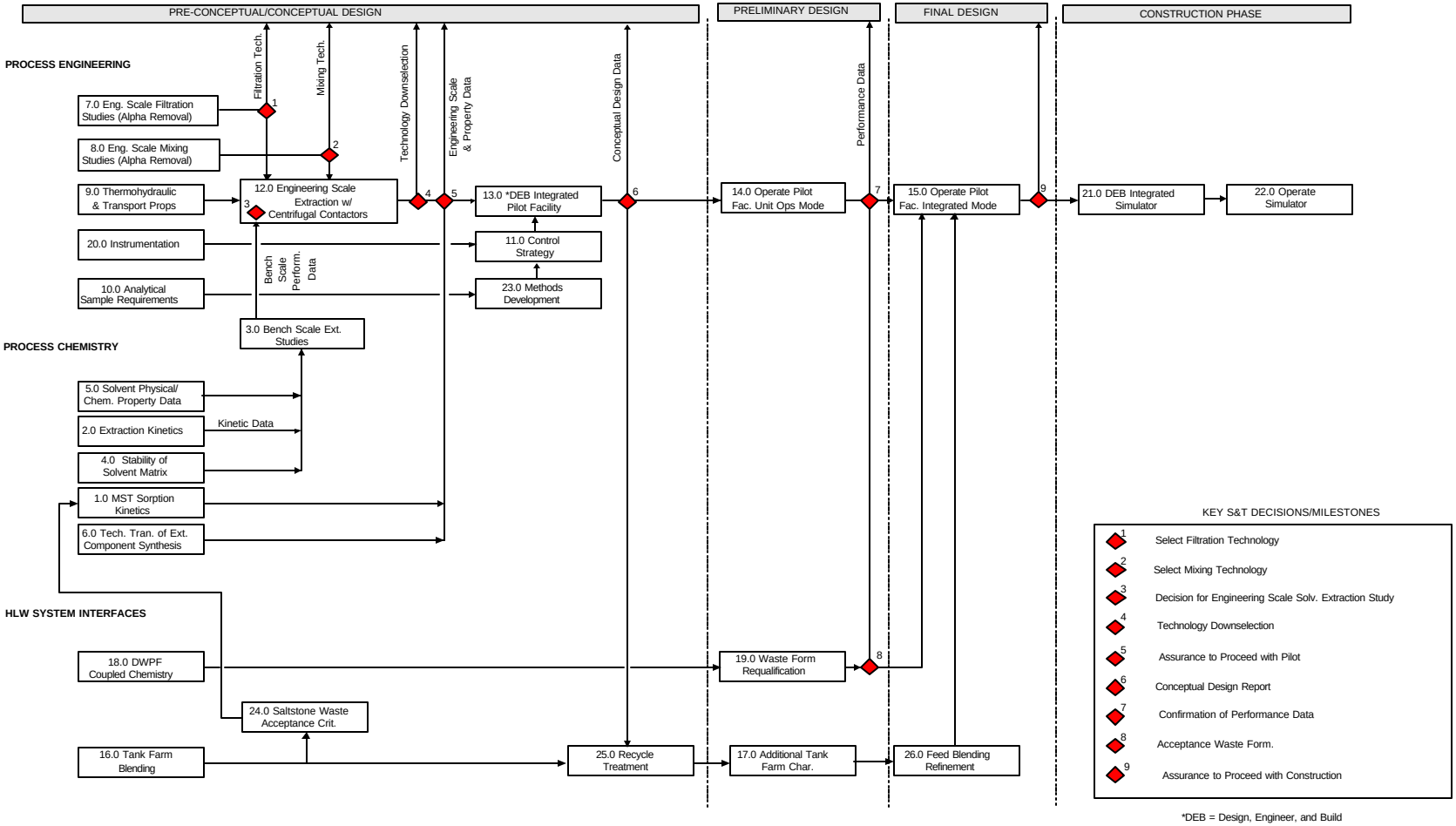

Figure 7.3. Science and Technology Roadmap for Caustic Side Solvent Extraction Cs Removal Process

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

7.3.2 Flowsheet Integrated Proof of Concept (CSSX SOWM 3.1, 3.1.1.1, 3.1.1.2, 3.1.2, 3.1.4, 3.1.4.1, 3.2.4.2)

The proposed process with the present solvent contains a different modifier and a different stripping aid than the previously tested solvent. Thus, proof-of –concept tests were needed to prove the new solvent.

7.3.2.1 Previous Results

The proposed solvent extraction process was demonstrated earlier in miniature (2-cm nominal diameter) centrifugal contactors.[112] In that work, testing was first performed with a single stage contactor and then in a multi-stage cascade similar to the proposed CSSX flowsheet. The modifier (Cs-3) used in the 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.

7.3.2.2 System Configuration

7.3.2.2.1 FY00/01 - Results

The solvent extraction equipment for the proof-of-concept flowsheet tests, was a 32-stage 2-cm centrifugal contactor cascade located in a glovebox at ANL.[113,114] The contactors, which are fabricated in banks of four stages, were built in accordance with ANL print number CMT-E1265, January 6, 1994. The contactors were configured into 15 extraction, 2 scrub, and 15 strip stages. The feed was chilled in an ice bath before entering the contactors in order to reduce the temperature in the extraction section of the cascade. The scrub and strip contactors were not cooled; typical temperatures in the strip section during the flowsheet tests were between 32°C and 35°C.

Prior to execution of the proof-of-concept flowsheet tests two modifications were made to the contactors with the goal of achieving stages efficiencies >80% and a higher total volumetric throughput capacity. First, the inlet diameter of the 2-cm rotor was enlarged from 0.312 inches to 0.422 inches to increase the liquid height in the annular mixing zone. Second, a stainless steel wire rope was put into each interstage line to wick solution from stage to stage and thereby eliminate slug flow phenomena observed in earlier tests. Measured stage efficiencies for the extraction, scrub, and strip segments of the cascade were 92%, 89%, and 88%, respectively. The third modification involved increasing the total throughput in the extraction section by 50% by increasing the size of the weir holes by 0.01 inch so as to achieve an aqueous strip flow rate above 2 mL/min.

Prior to the multi-day test, a chiller bar was attached to the contactor bodies of the extraction stages to maintain the temperature between 20°C and 23°C. Cooling fluid for the chiller bar was provided from a refrigerated water bath located outside the glovebox. During the multi-day flowsheet test that involved solvent recycle, a single wash contactor stage was added to the original 32-contactor cascade. The solvent output from the wash stage flowed directly to the first extraction stage.

The simulant waste feed and solvent recycle pumps were located inside the glovebox. The scrub, strip and solvent wash solution feed pumps were located outside the glovebox.

The CSSX waste simulant was spiked with Cs-137 to yield an activity of approximately 0.5 mCi/L. The solvent was prepared and tested for acceptable performance at ORNL prior to being shipped to ANL (See Section 7.3.6.1).

7.3.2.3 Waste Simulant 2-cm Contactor Flowsheet Tests

7.3.2.3.1 FY00 - Results

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 the CSSX waste simulant. The goal was to demonstrate the entire process while achieving a decontamination factor (DF) of at least 40,000 and concentration factor (CF) of 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 initial DF achieved during the test was greater than 80,000, exceeding the test goal by a factor of two. However, the DF decreased during the test as a result of high temperatures in the extraction section of the contactors. 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.

7.3.2.3.2 FY01 - Results

In FY01, two additional centrifugal contactor tests were conducted with temperature of the system lowered to 25 ^{o}C - 26°C in the extraction section. Tests were conducted using solvent and waste simulant spiked with enough Cs-137 so that a DF of 40,000 could be measured accurately. The first test did not recycle the solvent, but solvent was recycled to a total of four times in the second test. The results were excellent in both tests with waste and spent solvent DFs approaching 100,000 and Cs concentration factor averaging more than 15. These tests proved the flowsheet and showed that control of the temperature in the extraction section of the contactors was essential to good waste decontamination.

Another test was done to demonstrate continuous operation of the system over multiple days with solvent recycle and solvent washing. The flowsheet operated for a total of 71 hours (the nominal 5-day test) in a 33-stage minicontactor (2-cm centrifugal contactor) with controlled temperature in the extraction section. This first multi-day demonstration of CSSX flowsheet was done using an average SRS simulant for the waste feed. It showed that we were able to achieve and maintain the two key process goals: (1) the cesium was removed from the waste with decontamination factors greater than 40,000 and (2) the recovered cesium was concentrated by a factor of 15 in dilute nitric acid. In the multi-day test, 1.4 L of solvent was used to process 180 liters of SRS simulant, so that the solvent was recycled a total of 42 times. The average decontamination factor was 159,000 for cesium and the average concentration factor was 14.9. The process had to be shutdown twice. The first time was to replace a feed pump. The second time was to unplug a rotor that was partially plugged with solids suspended in the SRS simulant. In both cases, recovery was achieved allowing continuation of the test without a significant effect on DF or CF. This multi-day test showed the ability of the CSSX solvent to be used for at least 42 solvent recycles, the ability to recover from process upsets, and the need to keep solids out of the centrifugal contactor, especially for the small (2-cm) contactor.

7.3.3 Solvent Chemical and Thermal Stability (CSSX SOWM 4.1, 5.0, 5.2, 5.1.1, 5.1.2, 5.1.5, 5.4, 4.1.4, 5.1.3, 4.4.1, 5.2.1, 5.2.2, 5.3, 3.2.4, 4.2, 4.4.2)

The chemical and thermal stability of the solvent was not sufficiently understood. Degradation products could impact the extraction capabilities of the solvent matrix. These degradation products needed to be identified. The ability to remove degradation products from the solvent matrix may be required for this process to operate efficiently. Thus, the stability of the solvent, and the ability to prolong its useful lifetime, has been investigated. There is no separation of FY00 and FY01 results for this section due to the work being done in both fiscal years and reported in a single report.[115]

7.3.3.1 Previous Results

No degradation of the BOBCalixC6 was observed following continuous contact with alkaline high nitrate simulant for up to 570 hours at 53 $\pm$ 2ºC. However, the Cs-3 modifier was

degraded by 50%, causing a reduction in the cesium distribution ratio (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 $\pm$ 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 lower 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.

Researchers at ORNL[116] 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 dodecyl-sulfonate, 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.

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.

7.3.3.2 FY00 and FY01 Results

7.3.3.2.1 Solvent Chemical and Physical Properties

Physical and chemical property data for the solvent matrix had to be obtained. 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, had to be obtained. Experiments were conducted to determine this information.

Cesium distribution behavior under flowsheet conditions was characterized as a function of many variables and was shown to be reproducible by flexible batch methodology. Successful batch measurements require: (1) that the temperature be constant and known, (2) that the phases be contacted with sufficient time and agitation to reach equilibrium, (3) that the phases be completely separated before sampling, and (4) that sampling be performed without contamination by the other phase. The particular type of analytical methodology used was not important as long as it was precise, reliable, and free of interferences.

Within the expected operating temperature range 20ºC - 35°C, no issues were identified regarding cesium distribution or loading. However, a significant temperature dependence that causes the D_{Cs} to decrease 6% - 10% per degree with increasing temperature necessitates process-temperature management. Separate temperature control of extraction and stripping can be exploited to significantly increase process performance, either to reduce footprint (number of stages) or to enhance process robustness in meeting process requirements (i.e., a decontamination factor of 40,000, concentration factor of 15, and feed flow of 20.1 gal/min).

A large set of data was collected for the distribution of the alkali metal cations Na^+, K^+, and Cs^+ from the full simulant, simple simulants, and simple one- or two-component electrolyte solutions. The chief competing species, K^+ ion, was found to reduce Cs^+ ion extraction and stripping performance, but within SRS bounding conditions this competitive effect raises no issues regarding meeting process requirements. Experiments comparing the baseline solvent with and without BOBCalixC6, show that the calixarene has little ability to bind Na^+ ion, and the observed Na^+ extraction by the baseline solvent is largely due to ion exchange of the modifier's proton. Potassium and sodium report almost completely to the scrub solution. Measurements of the pH of the scrub and strip solutions under various conditions revealed acid-balance behavior of the system, which appears especially to be influenced by release to the strip solution of some of the acid that was extracted by TOA and modifier under scrub conditions. Ion chromatography showed that nitrate, nitrite, chloride, and dibutylphosphate are the primary anions extracted from the simulant by the baseline solvent. All the anions except for nitrate and dibutylphosphate report to the scrub solution, while the nitrate and dibutylphosphate are washed out by NaOH solutions.

Experiments with simple salt solutions showed that the process should be relatively tolerant to variations in the anion content among these three major anions, nitrate, nitrite, and hydroxide. Each of these anions contributes significantly to the driving force for cesium

extraction and thus they should be mutually compensating at constant sodium concentration. This desirable property was in fact observed in more complex simulant recipes tested.

An equilibrium model was developed to improve the predictability of the solvent extraction process with regard process variables, including temperature, and to improve overall understanding of the process chemistry. The model takes into account variations in the major aqueous components (e.g., Na, K, Cs, nitrate, nitrite, hydroxide, and aluminate) and the influence of matrix changes in the different sections of the flowsheet. The model predicts Cs distribution behavior as well as the distribution of the other major aqueous components of the system, Na and K.[117]

The model for the extraction of cesium from different mixtures of sodium hydroxide, sodium nitrate, sodium chloride, and sodium nitrite containing potassium at variable concentrations has been developed. The model was based on the cesium, potassium, and sodium distribution ratios obtained with simple systems containing single salts. These results were modeled with the program SXFIT that calculates formation constants of complexes formed in the organic phase based on initial concentrations of components in both organic and aqueous phases. The model was applied to five different SRS waste simulants and the corresponding cesium extraction results were predicted satisfactorily.

The model gives a reasonably good fit considering the large number of data points (almost 300) that were included in the fit. The overall agreement is adequate for such a large data set and the number of species assumed in the organic phase is very small. In addition, all the formation constants are consistent within themselves. They follow the values of the Gibbs energy of partitioning for the four anions. The ultimate test is to predict the cesium distribution ratios to be expected based on initial concentrations.

7.3.3.2.2 Chemical and Thermal Effects

Studies on solvent chemical and thermal stability were started in FY00 and completed in FY01. Results of the studies show the solvent has very good thermal stability. Batch extraction data show that acceptable extraction, scrubbing and stripping performance is sustained after 235 days of constant exposure of the solvent to the full simulant, scrub solution, or strip solution at 35°C. This exposure corresponds to approximately 15 years of operation at the maximum sustained operating temperature of 35°C without solvent washing. The only solvent component that displays any sign of chemical instability to prolonged contact to aqueous solutions of the flowsheet is the TOA, and the degradation manifests itself only under more severe conditions involving 110 days or longer of continuous contact with the scrub solution at 61°C. The resulting decrease in the TOA concentration was associated with an increase in the scrub and stripping cesium distribution ratios. Normal performance was re-established upon replenishing the TOA and solvent washing. For purposes of estimating the rate of replacement of solvent components, the TOA loss is estimated to be approximately 0.1 mM per year (10%). Comparison of solvent degradation in the presence or absence of noble metal catalysts showed that potential catalysts in the full simulant have no apparent effect.

Nitration of the solvent components has been studied. Nitration of 4-*sec*-butylphenol has been observed at acid concentrations of 0.3 M and higher. Nitration occurs by displacement of the *sec*-butyl group and has been detected by NMR. Analyses of the quantity produced at 35°C in 7 - 28 days vary with acid concentration and time as expected. The analytical method has been able to detect as little as 0.15 % in these tests. A yellow color has always been observed during batch and continuous contactor testing. The color is thought to be due to nitrated aromatics, but analyses have never been able to detect any nitrated organic products. The intensity of the yellow color is greatest at high radiation doses, but again nitration has been below detection.

7.3.3.2.3 Component Partitioning

Partitioning of the various components of the solvent is important to determining the need and frequency of adding additional solvent components to the system as well as the need for recovery of solvent components from the aqueous streams exiting solvent extraction. The baseline process includes such solvent recovery. Information is needed to decide whether solvent recovery is required on various streams and, if so, define the quantity that must be recovered.

The partitioning of solvent components to the aqueous phase was found to be negligible. Little if any solvent replacement in the absence of solvent recovery will likely be required owing to purely solubility loss. Distribution ratios (D) for BOBCalixC6, Cs-7SB, and TOA in the baseline solvent in contact with the process aqueous phases at 25°C are all essentially too high for accurate measurement. The partition ratios are highest for the full simulant: $D_{BOBCalixC6}$ >12,500, $D_{Cs\text{-}7SB}$ >50,000, and D_{TOA} >30,000. For scrub and strip solutions, the bounds are: $D_{BOBCalixC6}$ >12,500, $D_{Cs\text{-}7SB}$ >8000, and D_{TOA} >6000. Using $D_{BOBCalixC6}$ = 12,500 as the most conservative basis for extractant loss to the waste raffinate, 2800 solvent cycles at O:A = 0.33 implies a cumulative loss of 49% of the BOBCalixC6 annually. This replacement meets the original goal of one solvent replacement per year. However, estimates of the true lipophilicity of BOBCalixC6 imply a $D_{BOBCalixC6}$ value many orders of magnitude higher than the experimental lower bound of 12,500. Thus, any need for solvent recovery or replacement is expected to arise predominantly due to entrainment losses.

7.3.3.2.4 Effects of Major and Minor Components (CSSX SOWM 4.2, 4.4.2)

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 were addressed. 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.

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.

Three neutral organic components of the full simulant, trimethylamine (TMA), tributyl-phosphate (TBP), and 1-butanol (BuOH), were examined to estimate their fate in the flow-sheet. Among the three compounds, possible implications for process upset are greatest for TMA. It was found that TMA mildly partitions to the solvent during extraction ($P_{TMA} = 4.3$ for baseline solvent and full simulant at 25°C). Accordingly, the TMA will move with the solvent into the scrub stages in the flowsheet where it will be protonated, partition into the aqueous phase ($P_{TMA} = 1.9 \times 10^{-4}$ for baseline solvent and 50 mM HNO_3 at 25°C), and returned to the feed stage. With such a feedback loop, the TMA could in principle build up to high concentrations in the solvent. However, TMA is very volatile so it will probably leak out of the system primarily via the purge gas used in the contactors. Unlimited buildup of TMA could lead to complete consumption of the acid in the scrub stage when the TMA reaches 10 mM in the solvent. This condition would in effect limit the buildup to 10 mM TMA, whence the TMA would start to pass into the stripping section and be removed with the strip effluent. At the presumed maximum 0.17 mM level of TMA in the waste, the steady-state concentration of TMA in the solvent entering the strip section would then be 0.51 mM, equivalent to 2.5 mM of aqueous base, more than sufficient to neutralize the 1 mM acid in the strip solution. The consequences of this scenario are not clear and are in need of further investigation. Tests starting with 10 mM TMA in the solvent revealed no effect on extraction, scrub, and strip performance. Although the chemistry of the process could shift as described, whether the process would cease to function is not obvious, as acid balance is not part of the driving force in stripping. Rather, nitrate concentration is the driving force, and it should not be impacted. Straightforward options to deal with the problem include sparging the aqueous feed or reducing the solvent flow rate so that the O:A ratio in the extraction section gives an extraction factor less than unity.

TBP is present at very low concentrations in the waste (maximum 1.9×10^{-6} M) but parti-tions strongly to the solvent, where $D_{TBP} = 1880$ for the baseline solvent equilibrated at 25°C with the full simulant. This partition ratio indicates that TBP could only build up in the solvent to 3.5 mM at steady state, as the raffinate exiting stage #1 will start to wash out the TBP when it reaches this level in the solvent. This level is too low to have any effect on extraction, scrubbing, or stripping. 1-Butanol is present to at most 2.7×10^{-5} M in the waste and partitions mildly to the solvent, where $D_{BuOH} = 7.5$ for the baseline solvent equilibrated at 25°C with the full simulant. However, the partition ratio is not high enough to allow it to build up to more than 0.2 mM, again too low to have any effect on solvent performance.

A survey of the elements present in the simulant, including Cr, Cu, Fe, Mo, Hg, Ag, Pb, Pd, Rh, Ru, Sn, Zn, Cl, and F, could not detect any buildup in the solvent on limited cycles nor do they appear in the scrub or strip stages in significant concentrations.

7.3.3.2.5 Solubility and Third Phase Formation

Solubility phenomena were examined more extensively than planned, as some limiting features were encountered. Long-term observation of the baseline solvent under various conditions revealed no tendency to form solid phases at 25°C or at 4ºC - 6°C. Crystallization of a hydrate of the alternative modifier, Cs-6, was observed, eliminating this modifier from future consideration. However, the same crystallization phenomena were found not to apply to the case of Cs-7SB, which is believed to be related its two asymmetric carbon atoms and concomitant existence of four stereoisomers. Although no issues were therefore identified for the modifier solubility, close inspection of the solubility of BOBCalixC6 revealed that the baseline solvent is somewhat supersaturated at 25°C. Crystallization of BOBCalixC6 was induced by making highly supersaturated solutions, whereupon crystallization at 25°C yielded solutions having approximately 8 mM of the extractant. When the modifier concentration is raised to 0.75 M; however, the extractant solubility so obtained is 12.7 mM, and thus there is motivation to employ higher modifier concentrations in future solvent-optimization tasks. This change also offers advantages in raising D_{Cs} values, allowing the BOBCalixC6 concentration to be decreased (affords cost savings), as well in decreasing the operating temperature of the solvent to 15°C (see below). Further investigation is needed, both to arrive at a more acceptable solvent composition and to understand the factors controlling extractant solubility.

Third-phase formation was found to occur as a result of either Cs^+ or K^+ ion loading and is associated with the generally recognized limited solubility of ion-pair complexes in non-polar organic solvents. It was found that high Cs^+ ion loading can be tolerated, however, and conditions leading to high loading will not be found in the flowsheet. On the other hand, K^+ ion loading is significant, and the solubility limit of its complexes can be exceeded at the bounding K^+ aqueous concentration if the temperature falls below 20°C. Hence, this property sets the lower operating limit of the process at 20°C. If it is desirable to operate at a lower temperature for seasonal reasons, then feed blending or other control of the potassium concentration is needed. The process could be operated down to 15°C with 0.75 M Cs-7SB.

7.3.3.2.6 Solvent Cleanup

Solvent cleanup is based on NaOH washing. The presence of lipophilic anionic species in the solvent as extracted from the waste or as formed upon degradation of the solvent components represents no particular risk. However, ample evidence was gathered to show that lipophilic anions at sufficient concentration in the solvent overwhelm the tolerance provided by the TOA suppressor and impair stripping. The relative rate of buildup of lipophilic anions in the solvent based on their concentration in the feed or their formation rate (in the case of degradation products) must be compared to how fast they will be removed from the system by partitioning to process aqueous solutions and wash solutions.

A systematic test of the individual organic components of the full simulant revealed dibutylphosphate (DBP) to be the only organic component having a deleterious effect on stripping. Its partition ratio D_{DBP} was found here to be 2.3 between the baseline solvent and

full simulant at 25°C. At O:A = 0.33, this partioning result implies that only a modest buildup to 0.27 mM in the solvent is possible. Although this concentration is just enough to start to impair the function of the TOA, any NaOH concentration from 10 mM to 1 M efficiently washes out the DBP ($D_{DBP} \leq 0.01$).

4-*sec*-butylphenol (SBP) is one of the two major solvent degradation products, the other being the breakdown product of TOA, dioctylamine (DOA). At concentrations of greater than 3 mM, SBP in the solvent begins to interfere with stripping, but conservative estimates set the annual production of SBP in the solvent at less than 0.3 mM. Hence, solvent washing to remove SBP is not needed. Moreover, partitioning data show that the waste raffinate washes out the SBP weakly (est. 6% per solvent cycle, D_{SBP} ~50), sufficient to keep the SBP at trace levels (est. 0.002 mM) in the solvent.

Although surfactant anions have not been specifically identified as waste components, results showed that they have significant potential to impair stripping performance. TOA negates their effect at trace levels, but it is important to understand the partitioning of typical surfactant anions so that their buildup in the solvent could be predicted and washing methods optimized should this problem be encountered later. It was found that the 12-carbon surfactant anions dodeconoate (laurate) and dodecylsulfate and the 18-carbon surfactant octadecanoate (stearate) partition strongly to the solvent in contact with the simulant, scrub, or strip solutions. Partitioning is driven by the sodium concentration in the aqueous phase, making it desirable to minimize the aqueous sodium concentration. On the other hand, sufficient alkalinity is needed to deprotonate the acid forms of the surfactants. For the carboxylate surfactants, the optimum NaOH concentration for washing was found to be 3 mM ($D_{laurate} = 0.072$, $D_{stearate} = 96$). For dodecylsulfate (and presumably related sulfonate surfactants), the optimum is less than 0.001 M. As coalescence problems increase with decreasing NaOH concentration, 0.01 M NaOH was accepted as the best compromise for washing and recommended for use in the extended contactor tests at ANL and SRTC. At this concentration of NaOH at 25°C, $D_{laurate} = 0.12$, $D_{stearate} = 150$, and $D_{dodecylsulfate} = 1.7$. Using a 0.01 M NaOH wash at O:A of 5 and 25°C, these D values correspond respectively to 62%, 0.13%, and 10% removal of these surfactant anions. Assuming the feed has 1×10^{-5} M of any of these anions, estimated steady-state concentrations in the solvent correspond respectively to 4.8×10^{-5} M, 0.023 M, and 3.0×10^{-4} M. Such a buildup could be tolerated in the case of the 12-carbon surfactants, but not the 18-carbon surfactant. For this reason, it was judged prudent to demonstrate an effective solvent-cleanup alternative, and anion-exchange resin was shown to offer the requisite capability. Resins in the hydroxide form contacted directly with solvent spiked with stearic acid and sodium dodecylsulfate were particularly effective, with K_d values greater than 1000 mL/g for three resins, including two commercially available resins. Possibly other aqueous washing strategies could be used, but their development awaits further investigation.

The other major solvent degradation product, DOA does not partition to either the simulant or to 0.01 M NaOH wash solution, but it does partition weakly to the strip solution, where $D_{DOA} = 4.7$. At O:A = 5, loss of DOA to the strip effluent would be expected to be 4% per

solvent cycle, and the estimated steady-state concentration is 9×10^{-7} M based on 0.1 mM DOA per year as the rate of production due to thermal or radiolytic degradation of TOA.

7.3.3.2.7 Analytical Methods Development (CSSX SOWM 4.2, 4.4.2)

Methods to evaluate solvent quality were studied in order to specify the baseline pristine solvent quality assay, in-process monitoring requirements, and post-process monitoring. Two HPLC methods and one gas chromatography (GC) method were developed and implemented for the analysis of samples related to this project.[118] In addition, a solid phase extraction system was applied to the separation of organic compounds from aqueous materials, which come in contact with the solvent. The combination of these methods allows both quantitative analyses of the major components of the solvent, and visualization of any minor components, including breakdown products.

Off-line analyses for BOBCalixC6 and modifier were recommended using GPC-HPLC and reverse-phase HPLC with a dual detector for GPC HPLC. Gas chromatography coupled with mass spectrometry was recommended for analyses of trioctylamine, 4-*sec*-butylphenol and tributylphosphate.

7.3.4 Solvent Radiolytic Stability (CSSX SOWM 4.1.1, 4.1.2, 4.1.3, 4.1.4, 4.1.5, 4.1.6, 4.1.2.2)

The radiolytic stability of the solvent was not sufficiently understood. Degradation products could impact the extraction capabilities of the solvent matrix. These degradation products needed 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, were investigated.

7.3.4.1 Internal Irradiation

7.3.4.1.1 Previous Results

SRTC personnel performed a test to determine the extraction, scrubbing and stripping performance of the previous 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.[119] 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.

7.3.4.1.2 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.

The ORNL internal exposure tests used a simulant solution spiked with Cs-137. Experimental test plans were developed and approved.[120] 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 would receive an annual dose of 0.092 Mrad 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 the only nuclides contributing to the solvent dose are Cs-137 and Ba-137m (assuming the CSSX feed was subjected to the MST Sr and alpha removal process).

7.3.4.1.3 FY01 - Results

Studies of the effect of internal irradiation on the solvent were continued at both ORNL and SRTC during FY01. The ORNL test continued to use solvent loaded with Cs-137 from the CSSX simulant. Irradiation of the samples was completed in FY01. The sampling and analysis protocol was continued to obtain data corresponding to several times the expected annual dose the solvent will receive in the proposed process plant.

The ORNL tests involve exposing the solvent to internal radiation from Cs-137 while undergoing continuous agitation (see Reference 120). The organic to aqueous phase ratios agree with 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) were removed from the agitation

apparatus and evaluated by visually inspecting and determining the phase separation time. After the phases were separated, the organic and aqueous portions were analyzed for Cs content (allowing a calculation of D_{Cs}), solvent components, and solvent decomposition products to yield information as a function of dose.

During testing, the solvent received doses equivalent to approximately a decade of plant operation. Physical observations did not identify any dose-related impacts with no change in dispersed phase break times, no third-phase formation, and no interfacial crud formation. Chemical measurements did not identify any solvent performance issues. The D_{Cs} values are within the expected range of values for CSSX simulant.[121]

SRTC investigated the impact of radiation dose received from real waste on solvent performance using the samples acquired from 5 tanks in FY00. The tests examined the impact of dose on the extraction, scrub, and strip stages of the process. The test protocol mirrors the ORNL simulant test described in Reference 120.

The results of these tests with real waste samples are still in progress but initial results showed no measurable degradation of the primary solvent components, BOBCalixC6, Cs-7SB modifier, or TOA, at doses typical of approximately 1 year of facility operation. The primary degradation product of the modifier, 4-*sec*-butylphenol, was not detectable within the limits of the gas-chromatograph-mass spectroscopy (GC-MS) analysis of the organic phase after batch contact with aqueous waste solutions. TBP, DOA, and TOA were also below detection limits (<10 mg/L). However, a large dilution was required prior to removal of the samples from the shielded cells and may have led to the concentrations being below detection limits. Distribution coefficients (D_{Cs}) for the samples ranged from 9.2 to 25.5, which are above the design basis value of 8. There were, however, inconsistencies in the cesium mass balances based on the measured activities of the various waste solutions. Again, the large dilution required to remove the samples from the shielded cells may have introduced random errors in the reported results and giving poor mass balances for some of the samples. Complete results of this work will be reported later this fiscal year.

A yellow color has always been observed during batch and continuous contactor testing. The color is thought to be due to nitrated aromatics, but analyses have never been able to detect any nitrated organic products. The intensity of the yellow color is greatest at high radiation doses, but again nitration product concentrations have been below detection limits of the analytical methods.

7.3.4.2 External Irradiation

7.3.4.2.1 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 122. Results from those 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. Similar testing is needed for the new solvent system with Cs-7SB modifier.

7.3.4.2.2 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.[122] 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 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°C - 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.

The tests showed no significant degradation of the primary solvent components at radiation doses typical of the proposed facility lifetime of 10 years. Increased radiation can lead to degradation of solvent components. Less than 10% calixarene loss occurred at received doses up to 16 Mrad (a 160 year dose). No statistically significant loss of Cs-7SB modifier occurred at doses up to 16 Mrad, however, a 10% loss of modifier occurred at a dose of 50 Mrad. Less than 10% TOA loss occurred at doses up to 6 Mrad. TOA proved more susceptible to damage than the other components of the solvent. The only other significant

decomposition product identified was 4-*sec*-butylphenol, an expected decomposition product from the modifier. At 16 Mrad the concentration of 4-*sec*-butylphenol was ~0.4% of the initial modifier concentration. However, 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.

7.3.4.2.3 FY01 - Results

Results obtained in FY00 described above on the SRTC-batch external irradiations are documented in a report published in early FY01.[123]

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

7.3.4.3.1 Previous Results

Precipitate and Rag Layer Formation: Researchers at ANL performed a bench-scale solvent extraction test using 2-cm centrifugal contactors.[112] 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 (interfacial) 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.

Phase Separation: The ANL researchers performed three measures of phase separation.[114] 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 8×10^{-4}) were obtained. It should be noted 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. It should be noted 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.[107] 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 and 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.

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%.

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 tri-n-octylamine.

7.3.4.3.2 Contactor Tests using SRS Simulant Waste and Internal Cs-137 Irradiation (CSSX SOWM 3.1.1.3, 4.1.3, 4.1.5, 5.4)

7.3.4.3.2.1 FY00 - Results

Studies of the "second generation" CSSX solvent with 2-cm contactors were initiated in FY00 at ANL. Work with larger contactors was 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 used for these studies.

Throughput and phase separation: Initial hydraulic testing was performed using a single 5-cm centrifugal contactor stage.[124] 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.

The particular contactor used in these tests had curved vanes in the bottom of the housing, which is thought to significantly increase the rotor's pumping ability. All the tests showed low liquid levels in the mixing zone and reduced throughput to prevent other phase carry over. The low liquid levels in the mixing zone provided evidence of high pumping capacity. The high pumping action causes large amounts of air to be entrained in the dispersion in the mixing zone. These studies were repeated in FY01 with a contactor modified to reduce the rotor's pumping ability.

Mass transfer: Mass transfer studies were conducted in single- and four-stage contactor configurations.

The single-stage testing involved contacting a solute-containing phase with an opposing phase in a 5-cm centrifugal contactor.[125] 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 residence time effects 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 in order to determine stage efficiency values.

Acceptable stage efficiencies (~80%) were observed under extraction conditions for a variety of O:A ratios, V_{total}, and rotor speeds. Unacceptably low mass transfer efficiencies were observed in the scrub and strip test, and were a direct result of a very low liquid level in the mixing zone with an accompanying poor phase dispersion caused by the high pumping action of the rotor. Modifications to the contactor rotor and the contactor bottom plate to make the rotor partially pumping followed by a repeat of the single stage mass transfer tests were completed in FY01. The data showed improved mass transfer was obtained as a result of higher liquid levels in the mixing section.

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.[125] 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. The experimental data showed that steady-state conditions were not achieved.

Hydraulic performance: A test apparatus was designed, fabricated, and assembled for experiments designed to ascertain the impacts that solvent decomposition products from self-irradiation of the CSSX solvent spiked with Cs-137 may have on the hydraulic performance of the centrifugal contactors.[126] Leak testing, verification of the data acquisition software, and cold operational testing was completed.

7.3.4.3.2.2 FY01 - Results

Throughput and phase separations: The commercially procured 5-cm contactor used in the FY00 tests was designed for high phase separation efficiency, such as oil-water separations at a petroleum spill site, with little concern for mass transfer efficiency. Two simple modifications were made to the unit with the goal of achieving high mass transfer efficiency while still maintaining excellent phase separation capability. The modifications included replacing the curved vanes (impeller-like) on the contactor base plate with straight radial vanes and increasing the diameter of the opening at the bottom of the rotor. These two modifications converted the contactor to a partially pumping unit. The partial pumping characteristic results in higher liquid levels and improved phase dispersion in the mixing zone.

Throughput determinations were made under extraction and stripping conditions. A scrubbing mode throughput determination was not performed due to the similarity in flow conditions with the stripping mode parameters, and because the lower ionic concentration in stripping makes it the limiting condition. All throughput test data were obtained at the process baseline flowsheet O:A conditions, i.e., 0.31 for extraction and 5.0 for stripping.

Initial tests with the modified contactor revealed that the organic effluent stream contained small droplets of aqueous under all flow conditions. This phenomenon is related to the location of the aqueous interface inside the rotor. The problem was corrected by increasing the aqueous weir diameter from 22.22 mm (0.875 in.) to 24.13 mm (0.950 in.). Following the weir change both effluent streams were free of cross-phase contamination at V_{total} ranging from 490 to 635 mL/min at a rotor speed of 3600 rpm. At V_{total} greater than 635 mL/min cross-phase contamination was observed at all rotor speeds tested (3600-4800 rpm). Reducing the rotor speed to 3000 rpm reduced the maximum V_{total} to 550 mL/min.

Two general conclusions emerged from the follow-on throughput studies. First, the throughput curves for the partially pumping rotor are essentially horizontal lines. This result is not in agreement with current theoretical models used to estimate contactor throughput. Second, once the maximum flow capacity was exceeded, acceptable operation was re-established only after operating for an extended period at the reduced flow conditions. This observation differs from that made during tests using fully-pumping rotors, in which recovery from upset occurs quickly after re-establishing favorable flow conditions.

Mass transfer: Single-stage mass transfer tests were performed under extraction and stripping conditions. The flow rates used in the extraction phase of the testing were within the operating envelope that produced effluents that were free of cross-phase contamination. Stripping flow rates were scaled in accordance with the relative flows in the CSSX baseline process flowsheet. Stage efficiencies of ~90 % were observed in these tests.

Hydraulic operation throughout the testing was good, i.e., all samples collected for visual evaluation prior to sampling were free of cross-phase contamination.

These results showed that high stage mass transfer efficiencies and excellent phase separation can be achieved in all segments of the flowsheet contactor cascade with properly design rotors.

Hydraulic performance: The impact of solvent irradiation on contactor hydraulic performance involved operating a single centrifugal contactor in a manner that simulates the operation of a stage from the CSSX baseline flowsheet. Simulated process solutions with added Cs-137 and two different sets of flowsheet conditions were used to simulate one stage from each of the two major sections of the CSSX flowsheet (extraction and strip). The test apparatus was installed in a hot cell. The primary goal was 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) was also collected.

The irradiation tests were designed to simulate the effect of two years of continuous solvent irradiation under conditions present in the extraction and stripping sections of the CSSX cascade, based on the test duration and the amount of activity introduced into the aqueous test solutions. The irradiation test consisted of continuously mixing an aqueous process solution with the CSSX solvent. The aqueous solutions used in testing were spiked with Cs-137 at levels corresponding to the level expected in the contactor stage containing the highest cesium concentration in the extraction (Stage 15) and strip (Stage 18) segments of the 32-contactor cascade. During most of the test period CSSX solvent and spiked aqueous solution were continuously agitated in a small mixing tank. Periodically, the dispersed phases from the mixing tank were pumped to a sight glass. The phase separation parameters were measured at various time intervals as a means of quantifying changes in phase separation behavior. At each time interval, the dispersion from the mixing tank was processed through the 5-cm contactor to evaluate phase separation performance. Contactor effluent streams were collected in sight glasses, both to examine the effluents for cross-phase contamination and to collect samples for chemical analysis.

The organic samples were contacted with dilute nitric acid to remove the cesium, thereby halting the irradiation. These samples were assayed for the various solvent components, and analyzed for the modifier decomposition product. Gamma counting was performed on the aqueous samples. This activity data along with the initial Cs-137 activity were used to estimate the cesium distribution ratio under extraction and stripping conditions.

Under both extraction and stripping conditions, phase separation times under gravity conditions increased from the initial observations (i.e., the no-irradiation condition) to the final observation, but the increase was insufficient to affect phase separation in the centrifugal contactor. Contactor phase separations were performed at flow rates that were 75% – 80% of the contactor's maximum volumetric throughput capacity for the respective segment of the flowsheet. At no point was cross-phase contamination observed in either of the contactor effluent streams.

Assay results for the solvent components did not detect any concentration changes. The concentration of the modifier decomposition product, 4-*sec*-butylphenol, was less than the analysis method detection limit. These results are in agreement with results obtained from the solvent self-irradiation tests.

Extraction D_{Cs} values did not exhibit any trends with radiation dose, and the values were close to those expected for the experimental temperatures. The stripping D_{Cs} values were unacceptably high and showed an unexpected decreasing trend with time. During pre-installation of the test apparatus alkaline simulant was introduced in the system. The first element of the in-cell test involved the stripping condition. Because the buffer capacity of the strip solution is very low (0.001 M HNO_3), it is highly likely the apparatus contaminated the test solutions with alkali, thereby invalidating the estimated the stripping D_{Cs} values. A check of the aqueous phase pH of archived samples confirmed that the solutions were highly alkaline (pH >10).

Based on the results from this test, unacceptable phase separation conditions in centrifugal contactors were not observed.

Solids and contactor performance: Simulant solutions[103] 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 inter-process tank, the continued slow precipitation of salts may 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 indicates that they have adequate robustness.

Preliminary discussions concerning the possible placement of the CSSX system prior to the MST strontium and alpha removal process have indicated the MST elements of the process could be located in a contact maintenance area of the plant. This change in overall process configuration has the potential to substantially reduce plant construction and operating costs. However, this change in the overall process configuration could increase the potential for

waste sludge solids to remain in the CSSX feed stream. Filtration or some other solid/liquid separation step would be required to minimize the solids content of the feed stream.

Studies with 5-cm contactors to gain an understanding of the impact of solids on contactor performance are in progress.[127]

7.3.4.4 Degradation Products

7.3.4.4.1 FY00 - Results

Based on the data obtained on solvent samples externally irradiated at the SRTC, the stability of the solvent to external irradiation, both with regard to absolute breakdown rate and performance, is very good. No significant degradative loss of the primary solvent components or significant impairment of extraction, scrubbing, or stripping performance was observed over doses well exceeding an annual dose. For BOBCalixC6 and Cs-7SB, loss due to radiolytic breakdown was estimated to require less than 1% annual makeup. Even for TOA, the annual loss is conservatively expected to be 10%. The primary degradation product observed was 4-*sec*-butylphenol, due to breakdown of the modifier. Its rate of buildup, however, is low, less than 0.1 mM per annual dose. It was shown from partition ratios that this material would be washed out by the waste raffinate or NaOH wash solutions. Data from total organic carbon, solid-phase extraction, and NMR indicate that traces of organic products, especially fluorinated products from the modifier, report to the aqueous phases. By NMR, only under high (>6 Mrad) doses is any detectable sign of degradation observed, and even then the amount is small. Further, no changes between the irradiated samples and pristine solvent contacted with the full simulant, scrub, and strip solutions were observed by ES-MS. Interfacial behavior was also acceptable in the irradiated samples. Essentially no change in break time was observed. Interfacial tensions were all above 5 dyne/cm, and the response was either increasing with dose (scrub conditions) or decreasing with dose (extraction or stripping conditions). In batch tests, extraction and scrubbing behavior were not much affected by external irradiation and remained acceptable. Stripping was also acceptable for all but the highest dose (16 Mrad under stripping conditions), where it was clear that poor performance was related to the loss of 79% of the TOA. Unfortunately, it was not possible to restore performance of the most deteriorated solvent samples by solvent washing. However, replenishing lost TOA and caustic washing restored performance for solvent samples that were irradiated internally in batch tests performed at ORNL.

7.3.4.4.2 FY01 - Results

Samples from several areas of work in FY00 were received and subjected to analytical procedures and performance assessment. Analyses and tests were 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), Fourier transform infrared spectrometry (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 Real Waste Performance (CSSX SOWM 3.2.8, 3.2.8.2, 3.2.8.3)

One of the largest unknowns for any technology to be used for processing high level waste is whether the real waste solutions will give the same results as simulants. These studies were done to determine whether real waste solutions would behave in a similar manner to simulants used for process development up to this point. No testing with SRS real waste solutions was conducted prior to FY01.

7.3.5.1 FY01 - Results

7.3.5.1.1 Batch DF Extraction and Stripping Studies with High Activity Simulant (CSSX SOWM 3.2.2, 3.2.2.1, 3.2.2.2)

The purpose of this work was to demonstrate that realistic activity levels (0.325 Ci/L) can be fully decontaminated (DF >40,000) and that the loaded solvent also can be fully stripped. Contacts were performed in crosscurrent batch mode. No attempt was made to simulate counter-current conditions. Solution preparations for this test were completed in FY00. The actual contacting experiments were performed in FY01.

Prior laboratory measurements of fully stripped solvent were limited to low-activity tracer studies, and after a few strips the Cs-137 activity in the organic phase fell below the detection limit. This low current rate required respiking of the organic sample to measure the effectiveness of subsequent stripping tests. This experiment was designed to allow demonstration of the 40,000 DF without the need of the intervening spike.[123] The test involved cross-flow batch processing of an aqueous waste simulant through several extractions with fresh solvent, and a cesium loaded organic sample through one scrub and several strip contacts. The initial waste simulant was spiked with sufficient Cs-137 to yield an activity equivalent to 0.35 Ci/L. Because of this activity level, most of the work was performed in a hot-cell located in the Radioactive Materials Analytical Laboratory at ORNL. Once the activities in the solutions

were reduced to levels that could be handled in a radiochemical hood the solutions were transferred from the hot-cell and the batch contacts completed in the laboratory environment.

After 10-batch extraction contacts, the waste simulant decontamination factor was 280,000. The measured extraction cesium distribution ratio, corrected to 25°C, from the hot-cell portion of the work averaged 18.7 ± 2.9, which is in good agreement with the value of 16.4 ± 2.6 obtained in the laboratory environment.

After 9-batch strip contacts, the loaded solvent decontamination factor was 310,000. The cesium strip distribution ratios, corrected to 25°C, declined from 0.17 on the first strip to 0.11 as the infinite strip value. This behavior is in agreement with the general chemical behavior of the CSSX process. After correction to 25°C all of the observed cesium strip distribution ratios compared favorably with values measured with solutions spiked with tracer levels of Cs-137.

This experiment demonstrated that thermodynamic equilibrium exists for decontamination of the waste simulant and the loaded solvent from high activity levels to the analytical detection limits.

7.3.5.1.2 Real Waste Batch DF Extraction and Stripping Studies

Samples of HLW were obtained from 5 different SRS tanks in F and H tank farms during FY00. Portions of the samples are being treated by extracting Cs into solvent (O:A = 0.33), by scrubbing with 0.05 M acid (O:A = 5), and then be performing three consecutive strips with 0.001 M acid (O:A = 5) to determine, if the CSSX process can treat all wastes. Three of the samples have been treated thus far. The data indicate that the samples have extraction D_{Cs} values above the minimum value of 8 required for the baseline process. Scrub and strip D values for two of the samples are high compared to simulant solutions. The scrub and strip values were in the expected range for the third sample.

Prior to the real waste demonstration using the 32-stage centrifugal contactor cascade, the cesium distribution coefficients for the extraction, scrub and strip operations were performed as given above on the actual Tanks 37H/44F composite following the MST strike for alpha removal. The testing was performed in duplicate and targeted O:A ratios of 0.33 for the extraction step and 5 for the scrub and strip steps. The extraction D value was 27. The scrub distribution coefficient (2.93) was higher than expected. Higher scrub D values were also observed in the tests above. Difficulty was experienced in obtaining the correct pH of the scrub aqueous phase in the shielded cell environment. The pH was high (normally ~10) and indicated some aqueous carryover from the extraction step. The strip distribution values were 0.28, 0.15 and 0.11, respectively. These strip distribution values are in line with predictions for the temperature of the experiments, 20°C.

7.3.5.1.3 Real Waste 2-cm Contactor Flowsheet Test

A real waste test using 2-cm contactors was conducted at SRTC. The objectives of the real waste test are similar to 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 CSSX simulant. The duration of the real waste test allowed the solvent to be recycled ~25 times, which is almost 1% of the number of annual recycles that will occur in the proposed process plant. The number of solvent recycles was based on the waste feed volume (~130 L) and the desire for this test to represent a reasonable pre-pilot scale test.[129]

Two simulant tests were run in the 2-cm contactors after installation in the shielded cells. The first test used CSSX simulant, which included bounding concentrations of organic species possibly present in SRS waste. The same simulant was used at ANL for Proof-of-Concept and multi-day tests. The second test used Tanks 37H/44F waste simulant, without added organics. The tests ran very well hydraulically, with very little organic in the waste raffinate or strip raffinate decanters and little aqueous in the organic raffinate decanter. Analyses indicate steady state operation was not achieved during the first test with CSSX simulant, but the DF averaged 65,000 vs. goal of 40,000. Steady state operation was achieved during the second test, and DF averaged 110,000.

After the simulant runs, real waste from Tanks 37H/44F was run for 48 hours. During the flowsheet test, more than 105 liters of waste from Tanks 37H and 44F was treated using 1.5 liters of solvent. The solvent was recycled continuously (~25 times) to the process after passing through a single centrifugal contactor stage of 0.01 M NaOH wash solution. The DF for the waste raffinate was as high as 2 million during the first 24 hours of the test. A composite of all test samples (includes samples during upset conditions) showed an overall DF of 40,000 versus a requirement of 13,000 to meet the saltstone Waste Acceptance Criteria and a target of 40,000. The overall average DF for the spent solvent was 154,000 versus a target of 40,000. Problems were encountered in measuring the flow rate of the waste feed stream resulting in low feed flow rate in the first 24 hours of the test. Consequently, the CF averaged only 12.8 during that part of the test, which is lower than the target value of 15. Flow rate adjustments to the feed and strip streams resulted in varied, but higher CFs during the remainder of the test. The CF exceeded 15 for several hours during the test, but averaged 14.4 during the last 10.5 hours of good hydraulic operation. The operational upsets occurred three times when the feed flow was increased to raise the concentration factor from 12 - 13 to 15, causing the hydraulics of the contactor bank to become unstable. In analyzing the problem, the flows were found to approach the contactors' theoretical capacity. The total flow rate reached 55 mL/min vs. a maximum theoretical design of 60 mL/min. This hydraulic problem disappeared when we returned to the baseline flowsheet run in the first 24 hours – 52 mL/min total flow. Recovery from the upsets was demonstrated proving the robustness of the process. The laboratory-scale contactors are sensitive to interstage piping geometry for the high O:A ratios are required. Larger scale contactors will have increased head pressures so flow through the interstage piping will not be affected and will be designed (rather than modified) for the O:A ratios required.

7.3.6 Solvent Preparation and Commercialization (CSSX SOWM 4.2, 4.4.2, 6.1-6.3)

7.3.6.1 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 located in American Fork, UT, 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.

For the baseline CSSX plant with a solvent inventory of ~4000 L and assuming the baseline solvent composition 46 kg of BOBCalixC6, 677 kg of Cs-7SB modifier, and 1.4 kg of tri-n-octylamine are required.

7.3.6.2 Solvent Preparation (CSSX SOWM 3.1.3, 3.2)

7.3.6.2.1 FY00 - Results

In order to standardize the solvent matrix used in the 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.[130]

7.3.6.2.2 FY01 - Results

In FY01, the ORNL team prepared 18 L of solvent to support the testing of CSSX at ANL, ORNL, and SRTC. Such testing included flowsheet performance using both simulants and real waste in 32-stage centrifugal contactor cascades. It also included batch equilibration tests aimed at studying solvent stability (chemical, thermal, and radiolytic), and physical properties.

All solvent prepared and shipped to CSSX principal investigators was washed and tested in accordance with the solvent QA procedure.[130] Table 7.2 summarizes the solvent quality criteria from 21 determinations. All of the shipped solvent met the performance criteria. It is important to note that the solvent quality test does not involve sequential contacts of the solvent with the process solutions, rather the test involves a direct forward contact of the pristine solvent with the individual process solutions. Under this condition slightly different D_{Cs} values are obtained; thus the D_{Cs} values in Table 7.2 should not be directly compared with those obtained from sequential tests referenced in other sections of this report.

Table 7.2. Solvent QA Performance Criteria

Process	D_{Cs} (25°C)	95% Confidence Interval
Extraction	16.3	1.1
Scrub	1.46	0.12
Strip	0.028	0.005

Two 2-L lots of Isopar® L containing the modifier were prepared and shipped to SRTC. This material is being used to dilute organic phase samples prior to measurement of the gamma activity.

7.3.6.3 Extractant and Modifier Synthesis and Procurement

7.3.6.3.1 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 SRTC.[131] Work during FY98 indicated that the Cs-3 modifier showed significant chemical and some radiolytic decomposition.[132] 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.[131] 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.[9]

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

7.3.6.3.2 FY00 - Results

In FY00, IBC Advanced Technologies, Inc. successfully manufactured and delivered on schedule a 1-kg lot of BOBCalixC6; the material was of high purity. IBC Advanced Technologies, Inc. also expressed willingness and confidence in their ability to produce larger quantities of the material.[133]

7.3.6.3.3 FY01 - Results

To obtain information on the potential for competitive pricing, an Expression of Interest solicitation for the manufacture of 2 kg of modifier and 50 g of BOBCalixC6 was prepared. This solicitation was sent to 29 companies, and seven positive responses were received. Actual procurement of the materials was placed on hold until DOE completes the SPP technology selection decision.

Synthesis of ~11.3 kg of modifier was completed. This was accomplished in batch sizes of ~3.6 kg. Isolated yields were >95%, and the purity of the product was >97%. The synthetic procedure scaled well from the 100 to the 3.6 kg quantities; in fact, the yield at the larger scale was higher than that attained at the 100 g level.

The synthetic pathways of the modifier, Cs-7SB, and the extractant, BOBCalixC6, are outlined in Figures 7.4 and 7.5, respectively.

The carbon atoms denoted with an * in Figure 7.4 represent chiral centers in the molecules. The main structural isomer of the modifier is produced at >95% yield relative to the starting phenol.

The modifier synthesis is a single step process requiring only a clean-up and vacuum distillation of the product. The phenol starting material is available as a bulk chemical. However, the fluorinated epoxide is only available commercially as a specialty chemical, and the modifier manufacturer would need to develop the capability to prepare it in bulk quantities.

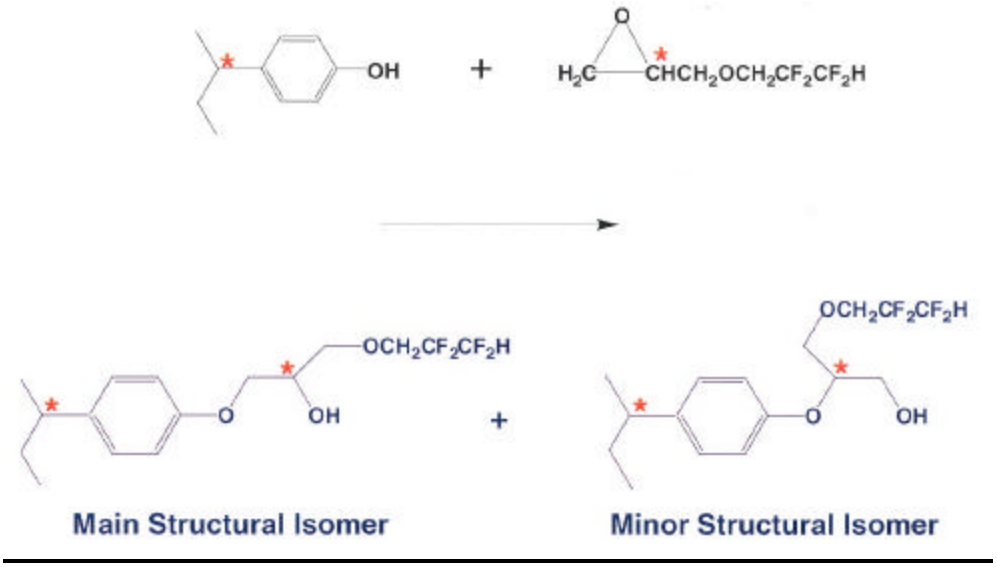

Figure 7.4. Modifier Synthesis Steps

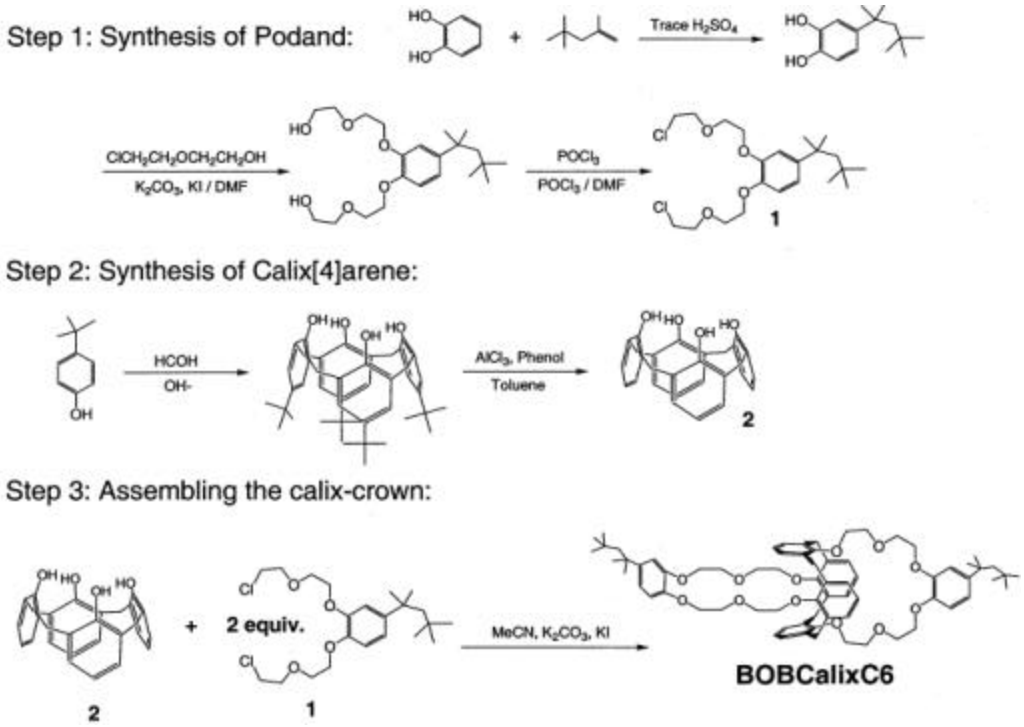

Figure 7.5. BOBCalixC6 Synthesis Steps

The BOBCalixC6 synthesis is a multi-step process requiring the synthesis of two precursor compounds. All of the starting materials for the precursor synthesis are available commercially in quantities sufficient to meet the projected BOBCalixC6 needs.

7.3.6.4 Technology Transfer

7.3.6.4.1 FY00 - Results

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.[134,135,136]

7.3.6.4.2 FY01 - Results

The patent entitled "Calixarene Crown Ether Solvent Composition and Use Thereof for Extraction of Cesium From Alkaline Waste Solutions," No. 6,174,503, was issued January 16, 2001. This patent covers the CSSX solvent composition and constituent concentrations, constituent composition, the process of extracting cesium from alkaline waste media, and the O:A ratio and composition of other process solutions necessary to implement the flowsheet. A patent application covering the second generation modifiers was filed with the US Patent & Trademark Office.

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

This science and technology roadmap for Small Tank TPB Precipitation (Figure 7.6) is a subset of the overall SPP roadmaps (see Appendix A of the R&D Program Plan[3] or SPP website at http://www.srs.gov/general/srtech/spp/progplan.htm). The STTP 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.

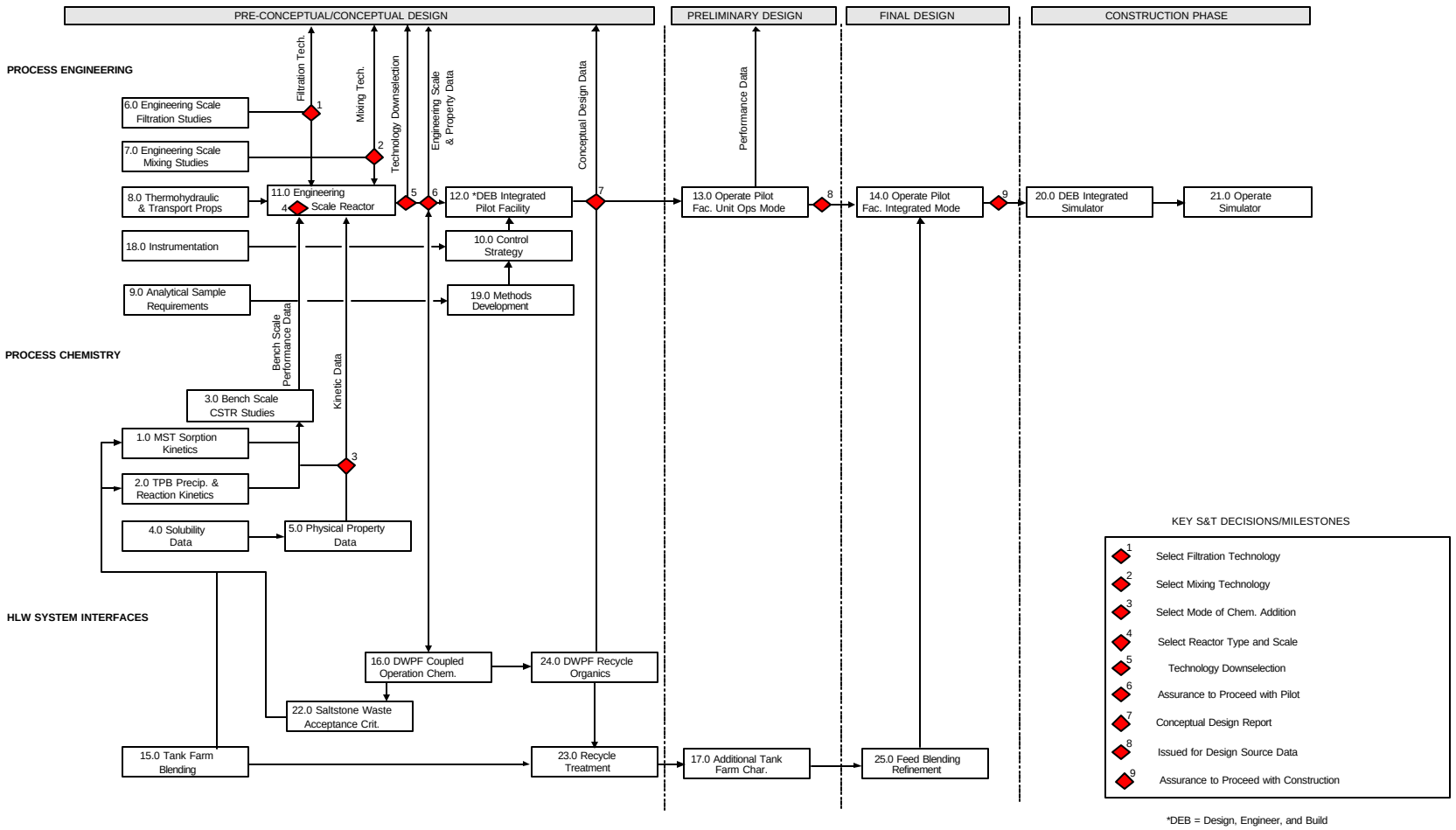

Figure 7.6. Science and Technology Roadmap for Small Tank TPB Precipitation Cs Removal Process

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.

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.

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. 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 decomposition of 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.[137] 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.[138] 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.[139] A series of tests were performed to determine the performance of the inhibitors 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.[140] 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.[141] As indicated above, there was considerable speculation about the role of oxygen in the activation of the Pd catalyst. 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.[142] 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.

Oak Ridge National Laboratory demonstrated the STTP process at the 1:4000 scale in FY99 using a 20-L capacity continuous stirred tank reactor (CSTR) system and a simulant of the salt waste traced with radioactive Cs, Sr, and U. Tests 1a and 2 were conducted in June and July 1999. The tests were conducted at 25ºC and DSS performance was achieved in both cases.[143] Catalyst components were not added to the simulant for Test 1a and no evidence of TPB decomposition was observed. Test 2 was conducted in closed-loop fashion (with recovery and recycle of unreacted NaTPB) and used a modified version of the "Enhanced Comprehensive Catalyst" system (ECC) to evaluate the impact on TPB degradation. TPB decomposition was not observed in Test 2, however, there was evidence that decomposition products intentionally added as components of the catalyst system (3PB, 2PB, and 1PB) were decomposing to lower phenylborate products.

7.4.2.2 FY00 – Results

During FY00 the workscope to address catalytic decomposition contained 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.

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 to metals in simulated waste to form nanoclusters; some of which incorporated Hg. The nanoclusters had a large surface area and were very reactive. Also, Pt(0) on alumina was shown to have reactivity similar to Pd(0) on alumina; however, the Pt concentration in the HLW tanks at SRS is minor relative to Pd. Ru(0) and Rh(0) 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 ions have been reduced to the metal forms which have been shown to be catalytically active. Studies are planned after downselect, if work on the STTP process continues, to determine conditions that may reduce Rh and Ru. These tests are also continuing to examine the potential mechanism for Pd catalysis, as suggested by a panel of experts.[144]

$$Pd^0 + TPB^- \longleftrightarrow Pd^- \cdot TPB$$

$$Pd^- \cdot TPB \longleftrightarrow PdH \cdot TPB + OH^-$$

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

Studies examined the catalytic activity of eight transition metals shown to be present in the SRS HLW at low concentrations. These transition metals demonstrated no tendency to increase the decomposition of TPB; however, the lack of reactivity may have been due to failure of the transition metals to reduce to the catalytically active form.[145]

Testing was also 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 Cu(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.

After review of the NMR test data, the STTP research team, along with consultants Dr. Boncella and Dr. King recommended that additional NMR tests be conducted in FY01.

Another method of exploring Pd speciation involved the use of electrochemical and spectroscopic techniques to evaluate the state of the aqueous phase Pd species. 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. These tests were initiated in FY00 and carried over into FY01.

The second aspect of this work continued to examine the catalytic activity of real waste. These tests were used to provide insight into the potential reaction rates that could be observed with real waste, as well as to 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 batch 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 completed in FY01. Information on these real waste batch tests is presented in FY01 results, below.

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 initiated 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 work to define this simulated catalyst system was completed and documented in early FY01 and the findings are reported in the FY01 results, below.

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, and (6) demonstrating that bi-metalic complexes between Pd and Cu, Fe, Rh, or Ru showed no significant synergistic effects.

7.4.2.3 FY01 – Results

Work in FY01 on TPB decomposition included tasks: (1) to develop an increased understanding of the catalyst system, (2) to evaluate the catalytic activity in HLW samples, and (3) to demonstrate the performance of the CSTR system in the presence of significant decomposition.

7.4.2.3.1 Understanding of the Catalyst System

Dr. James Boncella and Dr. Bruce King, consultants from the University of Florida and the University of Georgia, respectively, have continued to support the effort to develop an increased understanding of the catalyst system. Based on their review and recommendations, additional work was undertaken in FY01. This included follow up studies from FY00 to better define the properties of the palladium catalyst system as well as additional studies utilizing NMR spectrometry to answer questions regarding the role of lower phenylborates and mercury in the catalytic decomposition of TPB. Additional research is also being conducted using X-ray Absorption Fine-Structure (XAFS) and TEM to better view the structure of the Pd nanoparticles that are generated under catalytic conditions. This work includes actual sludge samples taken from SRS HLW tanks; however, the results from the HLW sludge samples may not be available until after down select. Finally Dr. Boncella and Dr. King continue to incorporate the results from the R&D work being conducted into reaction and catalytic mechanisms which are consistent with those identified in literature studies.

Additional testing undertaken at the SRTC during FY01 to better understand and define the properties of the palladium catalyst system included: (1) the need for mercury, intermediates, or benzene when utilizing a reduced Pd(0) catalyst, (2) the rate of phenylborate intermediate(s) in the catalytic reaction, (3) the influence of mercury concentration on palladium catalytic activity, (4) potential mercury surrogates, (5) possible high temperature Pd(0) activation in the absence of mercury, (6) the potential activation of rhodium and ruthenium at high temperatures, (7) potential palladium-metal synergisms, and (8) the effect of hydrogen on reactivity.[146] A summary of the observations and conclusions for these tests include the following:

- Tests indicate that mercury and phenylborate intermediates participate in the reaction cycle rather than just as an agent for reducing Pd(II) to Pd(0).

- The only tests exhibiting a reaction at the start of testing (i.e., no induction period observed) are those containing diphenylborinic acid, 2PB, in conjunction with Pd(0) on alumina, mercury, and benzene. The reactive step in the catalyst cycle that involves 2PB remains undetermined. The previously identified induction period identified by ORNL[147] is most likely a result of the time required to reduce Pd(II) or to form enough 2PB to initiate reaction.

- Palladium doped tests performed in the absence of mercury produced a small, but measurable degree of reaction. However, the extent of reaction was far below that observed when mercury is also present. The data support recent results from ORNL that reported reactivity in NMR vessels containing Pd(II) but no mercury.[147] The data, as a whole, demonstrate that reaction in the absence of mercury is possible under some conditions. However, the presence of mercury leads to increased reactivity under a wider (i.e., less stringent) set of conditions.

- Tests conducted with reduced ruthenium and rhodium resulted in a slight reaction. However, the reactivity of the two metals appears significantly less than that of palladium. The data support testing completed by SRTC earlier this year, which yielded the first demonstration of catalytic activity of these metals. An additional set of tests was conducted that sought to observe synergistic influences of the same metals with palladium. Tests show that the combination of Pd(0) with Ru(0) or Cu(II) proved only marginally more reactive than Pd(0) alone.

- The potential for palladium hydride formation in the waste has fueled speculation that the species may be an active participant in the catalytic cycle. Tests examined the influence of hydrogen gas on catalytic decomposition of NaTPB. The tests show that the continuously purged vessel containing hydrogen gas was less reactive than that of the static system in the absence of hydrogen gas. A significant and catalytic decomposition of NaTPB was observed in a mercury-hydrogen (palladium free) gas system. It was less reactive than a similar system containing Pd(0). A review of the organomercury literature suggests that the interaction of hydrogen gas with mercury may be responsible for the observed reaction.

- The current catalyst knowledge indicates that the minimum species required to catalyze NaTPB decomposition are a supported, reduced noble metal (e.g., Pd(0) on alumina) and 2PB. However, the most reactive system includes diphenylmercury (or Hg(II) salt) along with the other two components.

During FY01, NMR spectrometry was used at ORNL to investigate the mechanisms of TPB decomposition. These studies utilized boron-11 NMR spectrometry, with more detailed and controlled conditions, to repeat work that was performed in FY00 utilizing boron-10 spectrometry. The B-11 spectrometry allowed better integration of the lower phenylborate decomposition products (1PB, 2PB, and 3PB) because the B-11 is more spread out (128.33 MHz vs. 42.99 MHz for B-10). Also, reactions with carbon-13 labelled TPB and diphenylmercury were studied to determine the role of diphenylmercury in the catalytic decomposition of TPB.

A summary of the observations and conclusions for the FY01 tests utilizing NMR spectrometry included the following:[148]

- Pd(II) nitrate alone was confirmed to catalyze the decomposition of TPB, however, Pd(II) nitrate appears to be reduced to Pd(0) when added to alkaline phenylborate solutions under argon, as a gray metallic precipitate is observed to form. As a result, it appears that Pd(0) is the catalytically active component.

- Diphenylmercury alone does NOT catalyze the decomposition of TPB. There is no apparent decomposition after more than 600 hr in a 1 M NaOH solution at 45°C.

- Pd alone [from Pd(II) nitrate] degrades the phenylborates at different rates, with the rate constants for degradation being 2PB ≈ 3PB >> 4PB > 1PB. In the decomposition of TPB in the presence of Pd alone, this difference in rate constant for the decomposition of 3PB and 2PB is sufficiently large that only a trace of 3PB, and no 2PB, are observed as intermediates. Biphenyl, which could arise from the reaction of a Ph-Pd-X species with a phenylborate, is observed as a product.

- Since 2PB reacts more rapidly with both Pd alone and Pd/diphenylmercury than does TPB, the presence of small amounts of 2PB at the start of the reaction may lead to faster catalyst activation, and thus accelerate TPB decomposition. This has been observed in work at SRTC where 2PB has been shown to be the phenylborate necessary for catalytic activation. When large amounts of 2PB (equal to the TPB concentration) are present, the 2PB is degraded preferentially over the TPB, and a slight decrease in the TPB decomposition rate is observed.

- The TPB degradation rate appears to peak when the Hg:Pd ratio is about equimolar, then drops off upon increasing the Hg:Pd ratio; however, more data is needed to support this point. The ramifications for this result are that excess mercury may actually inhibit the degradation of TPB and the associated formation of benzene. (It should be noted that Hg inhibition has been observed at high Hg concentrations at SRTC.) This result is not unreasonable, given the information available regarding the observance of Hg/Pd nanoparticles – too much Hg may alter the composition of the nanoparticle, reducing the amount of Pd available to support the catalysis.

- Pd(II) nitrate with diphenylmercury (1:1 ratio) degrades the phenylborates at the same ordering (2PB ≈ 3PB > 4PB ≈ 1PB), but the relative rates as compared to Pd only catalyst are different. For this catalyst, 3PB and 2PB are clearly formed as intermediates. (This agrees qualitatively with the FY00 results.)

- The classic Suzuki reaction uses Pd as the catalyst to couple a phenyl group from an aryl halide with a phenyl group from a phenylborate. When labeled (carbon-13 enriched) diphenylmercury is used as the sole source of diphenylmercury, the formation of biphenyl is observed containing both a labeled phenyl group from the diphenylmercury and an unlabeled phenyl group from the TPB (cross-coupled product). This result suggests that a Suzuki-like reaction is occurring, whereby Pd is involved in coupling a phenyl group from diphenylmercury with a phenyl group from TPB. The role of diphenylmercury may be to accelerate the reaction by forming the reactive Pd phenylating agent (Ph-Pd-X) more readily that TPB alone. This would explain the large increase in catalytic activity in tests at ORNL and SRTC when diphenylmercury is used in conjunction with Pd.

Work was also completed in FY01 using XAFS spectroscopic techniques to obtain information on Pd and Hg in samples that were potentially supported on potassium tetraphenylborate (KTPB) and had been reacted with dissolved TPB and TPB decomposition

products (tri-, di- and mono-phenylborate and benzene). Palladium- and Hg-XAFS spectroscopic analyses were performed on several Pd and Hg-containing samples that had been equilibrated while being heated (about 45°C) with KTPB, dissolved TPB, and TPB decomposition products. The results from these studies have been documented by SRTC.[145] The primary findings from this study include the following:

- Palladium, initially added as Pd(II), forms metallic nanoclusters of face-centered cubic geometry, with and without Hg, in samples that have been incubated for more than 24 hours in the presence of TPB and TPB decomposition products at high pH.

- The HgPd clusters are closely associated with the KTPB solids (which were initially added) while Pd nanoclusters are not associated with the KTPB solids.

- For Pd, cluster formation is not highly influenced by radiation, Hg, or the presence of alumina.

- For Pd, early stages in cluster formation (i.e., before significant degradation of diphenylmercury) involves the formation of Pd-Hg and Hg-Hg bonds

- High levels of added diphenylmercury facilitate the reduction of Pd(II) during the cluster induction period.

- Samples that have been incubated for 12 hours in the presence of TPB and TPB decomposition products at high pH show evidence of Ru-Hg and Hg-Hg bonds. By analogy with Pd and Hg, this behavior may be evidence of bimetallic cluster formation between Ru and Hg.

It should be noted that work also is being conducted in FY01 using XAFS spectroscopic techniques to examine real HLW sludge samples for the presence of nanoclusters; however, this work will not be completed by down selection.

7.4.2.3.2 Evaluating the Catalytic Activity in HLW Samples

Work on evaluating the catalytic activity in SRS HLW samples has been completed and documented.[150] Batch testing of six different tank wastes for catalytic NaTPB decomposition was conducted. The wastes samples came from Tanks 7F, 13H, 26F, 30H, 35H, and 46F. Tests with the six wastes were performed at both ambient (22°C - 26°C) and 45°C. Testing lasted six months. Samples obtained from the tests yielded the following observations.

- Five tests exhibited rapid cesium decontamination. Three tests produced more moderate rates of cesium decontamination. The remaining four tests showed very slow rates of decontamination. The most probable cause of the low decontamination rates is inadequate mixing.

- Only six tests (representing four different tanks) showed detectable concentrations of soluble NaTPB.

- Both the low and high temperature tests with Tank 35H waste produced detectable concentrations of triphenylborane, an NaTPB decomposition product. No other test or waste showed evidence of NaTPB decomposition.

- The calculated maximum theoretical rate of benzene generation from the 45°C test with Tank 35H waste was less than 0.2 mg/(L-h). The lower temperature test yielded a substantially smaller rate.

- The low benzene generation rate is more than two orders of magnitude less than obtained in testing in 1997 with a high level tank waste composite with added sludge.

- The increased concentration of soluble mercury appears to be a significant difference between the Tank 35H sample and the other five tank waste samples.

In summary, catalytic decomposition tests were conducted on samples from several different HLW tanks and evidence of catalytic decomposition was detected in only one HLW sample. The rate of decomposition, based on the calculated maximum benzene generation rate in this sample, did not approach the maximum from surrogate tests and from those experienced in ITP. Therefore, in spite of what has been learned to date, exactly what activates the catalytic decomposition and leads to the high decomposition rates observed in real waste, is not fully known.

7.4.2.3.3 Demonstrating Performance During Significant Decomposition

Worked continued in FY01 at the SRTC on the development of a catalyst system which would allow evaluation of the performance of the STTP process during active catalytic decomposition in the 1/4000-scale CSTR system located at ORNL. Batch tests of sodium tetraphenylborate decomposition on reduced palladium catalyst were completed in FY00.[151] Results from these batch tests were used to formulate laboratory studies utilizing CSTRs. Results of these continuous laboratory studies were published.[152] The test system utilized a single (1-L) CSTR, with a residence time of 8 hours and a (1-L) concentration tank equipped with a Mott sintered metal filter. Tests were conducted at 25°C, 35°C, and 45°C. The catalyst system included reduced palladium on alumina powder, mercury(II) nitrate, benzene, phenylboronic acid, and IIT B52 antifoam. Testing utilized a salt solution with SRS "average waste" composition (i.e., the same solution as used in previous 1/4000-scale testing at ORNL). Testing, in the absence of the catalyst, produced potassium DFs of greater than 3000 (i.e., detection limited). In the presence of the catalyst, decomposition of soluble and insoluble NaTPB occurred in both vessels at temperatures as low as 25°C. The decomposition reaction, under the varying conditions, produced maximum benzene generation rates ranging from approximately 11 mg/(L-h) at 7.0 wt% solids (with 7.8 mg/L CSTR Pd concentration at 25°C) to greater than 35 mg/(L-h) at 2.5 wt% solids (with 26 mg/L Pd CSTR

concentration at 45°C) in the Concentrate Tank. Differences in reactivity were attributed to changes in insoluble catalyst concentration as well as temperature.

To evaluate performance of the STTP process during active catalytic decomposition in the 1/4000-scale system at ORNL, a catalyzed benzene generation rate of 10 mg/(L-h) in the Concentrate Tank at 10 wt% solids was targeted. The recommended catalyst system to meet this target, based on the laboratory scale CSTR tests, consisted of the following concentrations in the first CSTR at 25°C:

7.8 mg/L Pd (reduced) on alumina power,
80 mg/L mercury (II) nitrate,
720 mg/L benzene,
500 mg/L phenylboronic acid, and
1000 mg/L IIT B52 antifoam.

The ORNL catalytic decomposition demonstration (Test 4) was conducted in early October, 2000.[153] Antifoam, IIT B52, was added to the system vessels to minimize foam formation during the ~130 hour demonstration. The primary goal was to verify that the STTP process could achieve and maintain the necessary cesium decontamination while TPB was actively decomposing, with a targeted benzene generation rate of 10 mg/(L-h) in the Slurry Concentrate Tank at 10 wt% solids, at the STTP design temperature of 25°C. The plan was later revised to include an additional test phase to evaluate system performance at 45°C. The targeted benzene generation rate of 10 mg/L-h is equivalent to 2.5 mg/L-h if based only on the decomposition of TPB to 3PB. The above recommended catalyst system, consisting of Pd(0) on alumina powder, Hg(II) salt, phenylboronic acid (1PB), and benzene, along with IIT B52 for foam control was used for the test. TPB decomposition was successfully initiated and sustained during the test. The rate of TPB decomposition was determined by analysis of process samples for TPB degradation products using reverse-phase High Performance Liquid Chromatography (HPLC). The system vessels were controlled at 25°C during the first 76 hours of operation. During this period the benzene generation rate in the Slurry Concentrate Tank ranged from zero to 4.0 mg/(L-h) based on the decomposition of TPB to 3PB, which exceeded the target catalytic benzene generation rate. During this run at 25°C, the Cs-137 DF obtained for the filtrate from the Slurry Concentrating Tank ranged from 90,000 to 700,000 and the Sr-90 ranged from 100 to 200. The decontamination chemistry exceeded the DF goal of 40,000 (99.998% removal) for Cs-137 and 26 (96.15% removal) for Sr-90.

The temperature was increased to 45°C over the next 13 hours and then maintained at that temperature for the remainder of the test to determine the effect of the increased temperature on the catalytic decomposition rate and the decontamination factors. As expected, the TPB decomposition rate increased at the elevated temperatures with the benzene generation rate reaching values as high as 5.6 mg/(L-h) based on the TPB to 3PB reaction. At this elevated temperature the Cs-137 DF obtained for the filtrate from the Slurry Concentrating Tank ranged from 50,000 to 300,000 and the Sr-90 DF ranged from 100 to 200. Again, the decontamination chemistry exceeded the DF goal of 40,000 (99.998% removal) for Cs-137

and 26 (96.15% removal) for Sr-90 even at the elevated temperature with decomposition rates much greater than seen with real wastes.

Overall, the system control and hydraulic behavior was good, and the IIT B52 antifoam successfully prevented foam formation in all vessels. More than 162 L of radioactive, simulated waste was treated during the test and ~218 L of decontaminated filtrate was collected. About 13 L of 10 wt% TPB precipitate/MST slurry was collected and washed to recover the excess TPB (that not precipitated as K and Cs). Only about 10 to 15% of the available TPB was recovered during slurry washing with water. The problems with dissolving the excess NaTPB appears to be related to the use of the IIT B52 antifoam.

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.[154,155,156,158] 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, additional research was required 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 were obtained exploring a number of potential process variables.[158] 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.[159] 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.[160]

Based on the previous batch precipitation work, tests were performed to examine the performance of the precipitation process using the proposed CSTR configuration.[161] 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.[143] A 1/4000-scale, 20-L CSTR system including concentration and washing stages was fabricated at ORNL for this purpose. Two demonstrations (Tests 1a and 2) were performed in FY99 with this equipment. The first consisted of an "open-loop" test of the system, which did not include the recovery and recycle of TPB washed from the concentrated product. The second demonstration was a "closed-loop" test that 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; however, the addition of simulated sludge components interfered with the evaluation of Sr and U removal in the second test. The efficiency of excess NaTPB recovery was in the range of 9% - 20% of the available TPB, which was lower than expected for both of these tests.

The final element of the precipitation demonstration involved the continuous precipitation process using HLW from the SRS tank farm.[162] 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 for 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. The objective of the test was to examine the effectiveness of an improved antifoam (IIT B52) in minimizing foam formation and to determine if its presence had a negative impact on the removal of Cs, Sr and U from simulated waste. Additional runs with this system were conducted in FY01. The system used in the test for FY00 included two CSTRs and the slurry concentration system in an open-loop (no recycle of recovered TPB) configuration. The test was conducted for 72 hours with an 8-hour residence time in the CSTRs. The slurries in each vessel were mixed at 1200 to 1250 rpm, which is about twice the speed used in earlier tests. The temperature was maintained at 25°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. 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 22 hours to reach a DF of 2 for U in the Slurry Concentrating Tank. A DF of about 5 for U was obtained at the end of the test in the concentrate filtrate. A comparison of Test 1a and Test 3 data indicated that the increased mixing speed used in Test 3 for all process vessels not only enhanced the recovery of TPB in the washing process, but also improved the reaction rate and DF associated with the strontium and uranium removal. The DF values for Cs, Sr, and U exceeded the WAC standards needed for filtrate disposal in saltstone and indicated that IIT B52 antifoam had not interfered with the process performance. 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 was conducted in FY01, addressed the objectives necessary to demonstrate a sustained, steady state test with real waste.

7.4.3.3 FY01 – Results

Work in FY01 on cesium precipitation kinetics occurred in two major tasks: (1) completion of a 20-L CSTR (1/4000-scale CSTR) system run in a fully integrated, closed-loop operation with TPB actively decomposing and (2) completion of a CSTR real waste test.

7.4.3.3.1 20-L CSTR Closed Loop Test

The objective of the fifth 20-L CSTR system run was to demonstrate the acceptable performance of the system in a fully integrated, closed-loop operation (with TPB recovery and recycle) while TPB was actively decomposing under steady state conditions. To accomplish this, plans called for the production of 3 - 4 batches of slurry while recycling the slurry wash water. The slurry wash water from the fourth 20-L test demonstration, in which slurries were produced at both 25°C and at 45°C, was used early in Test 5. The slurry wash water from Test 5 was used later in the run when it became available for recycle. The run was completed in February, 2001.[17] The improved catalytic mixture, including palladium on alumina, phenylboronic acid, and inorganic mercury, was delivered to CSTR 1. The Pd and Hg were added to the MST/water and the 1PB was added with the NaTPB feed to CSTR 1. Benzene was not added as a component of the catalyst system in order to better monitor the progress of TPB decomposition through detection of benzene in the off-gas system. The cesium decontamination was maintained at >40,000 DF in the filtrate product for the duration of the test, exceeding the WAC treatment goals for the STTP process. TPB decomposition activity was observed in all vessels as evidenced by benzene detection in the vessel off-gas and by analysis of TPB decomposition products in the fluid samples.

An important objective of this test was to observe decomposition activity data for potential impact of recycling washwater that could contain (in addition to the recovered TPB) additional catalyst components and antifoam degradation products. In addition, it was important to determine the impact, if any, of changing the batch source of the IIT B52 antifoam. Although the data did not clearly show a direct impact by the wash water or antifoam, the results did show increased decomposition activity in CSTRs while changes in recycle wash water composition and antifoam batch were taking place. The fluctuation in the data and the time relationship of these changes complicated the ability to narrow the cause to any one factor. The increased decomposition activity could just as likely have been caused by the catalyst system with a prolonged induction period. The increased decomposition activity in the concentrate tank was most likely due to the increase in the Pd catalyst content caused by the filtration operation.

Operating data for Test 5 indicated that acceptable performance of the 20-L CSTR system could be maintained in closed-loop operation with TPB actively decomposing. However, the data trends for the TPB decomposition products detected in the process vessels did not support the achievement of steady state conditions in all cases. The concentration of 3PB in CSTRs 1 and 2 is reasonably consistent in the time frame of 100 to 186 hours. However, during generation of the second batch of concentrated TPB/MST slurry in the 70 to 130 time frame, the 3PB data for the filtrate from the Slurry Concentrate Tank indicated a clearly increasing rate of TPB decomposition corresponding with a clearly decreasing trend in soluble NaTPB. During the processing of the third batch of slurry (130 to 186 hour time frame), the trends in the 3PB and TPB filtrate concentrations were quite different. The 3PB showed a slightly decreasing trend and the TPB was fairly constant at a slightly higher concentration than was observed while processing the second slurry batch. To establish that

steady state conditions existed, it would have been necessary to observe consistent 3PB and TPB trends while processing an additional two or three batches of concentrated slurry.

There were few operational problems through most of the fifth campaign; however, the test had to be terminated 2.5 days prematurely due to the failure of the fluid seals on the Slurry Concentration System progressive cavity (Moyno) pump. The failure occurred while processing the third batch of slurry. Hydraulic behavior occasionally gave fluid flow problems in piping connections between the CSTRs, with the MST/Pd/Hg feed mixture, and with the IIT B52 antifoam feed. During the test, more than 300 kg (235 L) of radioactive, simulated waste was processed, and about 21 L of 10 wt% concentrated TPB/MST reaction product was produced and washed in three batches. More than 320 kg (267 L) of decontaminated filtrate was produced.

Although the system performance was acceptable throughout the operation, it is not possible to predict similar performance in a longer operation without observing consistent TPB decomposition behavior in all vessels. As such, should STTP be selected, it is recommended that an additional 20-L CSTR test be performed in order to verify acceptable performance for a longer-term operation.

7.4.3.3.2 Real Waste CSTR Test

SRTC personnel completed a successful demonstration of the STTP process option using SRS high-level waste in a system consisting of two CSTRs operating in series.[18] The test had five primary objectives which included:

1. Demonstrating that NaTPB can be used to continuously precipitate cesium at 25°C to levels that would meet the WAC for Saltstone with real waste for at least two system turnovers.

2. Demonstrating that monosodium titanate can be used to continuously remove strontium and various actinides (Pu, U) at 25°C to levels that would meet the WAC for Saltstone with real waste.

3. Demonstrating that the STTP test system can be operated stably.

4. Demonstrating the effectiveness of a proprietary antifoam, designated as IIT B52. with real waste.

5. Obtaining a measure of the catalytic activity of the real waste used in these tests at 45°C.

The HLW waste used for the test came from a mixture of samples from a number of different SRS tanks. The real waste CSTR test met all primary objectives for the test. The target cesium DF of 10,000 was exceeded. In fact, the ability of the system to remove cesium surpassed expectations, giving average DF values of 1.4 million over the entire experiment.

Furthermore, this process did not appear to have a high dependency on temperature effects from 25°C to 45°C. Cesium precipitation kinetics agreed well with expectations based on previous testing.

Regular MST additions successfully removed plutonium and uranium from the system. Plutonium removal achieved an average DF of 126, and uranium achieved an average DF of 2.36. Compared to the Saltstone limit of a total alpha activity of 20 nCi/g, on average the experiment achieved an activity of 0.214 nCi/g, which corresponds to a alpha removal DF of 115. Temperature change from 25°C to 45°C had no apparent effect on the removal of the alpha components.

Regular MST additions also successfully removed strontium from the system. Strontium removal achieved an average DF of 45.6, compared to the requirement to meet Saltstone limits of a DF of 19.3. Strontium sorption kinetics agreed well with expectations based on previous testing.

The IIT B52 antifoam was successfully demonstrated, as no debilitating problems were noted that could be directly traced back to foaming. The only visual evidence of foaming behavior was that some of the slurries taken from the sample port were slightly frothy when exiting the port. Stable operations were maintained throughout the experiment, with the exception of an overflow plug from CSTR 1 to CSTR 2 after 71 hours into the test. This problem was quickly and completely alleviated through the use of a backup pump. It should be noted that current design for the full-scale STTP facility specifies pumps, and not overflow lines, to regulate flow from the CSTRs. After starting the bypass pump, the test continued without interruption or further evidence of hydraulic instability. The exact cause of the plugging remains under investigation and no definitive link exists between the observed plugging and the antifoam addition.

Parallel antifoam tests injecting air into a graduated column containing a slurry of sodium tetrapheynlborate and real waste produced results very similar in nature to those from earlier tests with simulated waste. The IIT B52 additive worked effectively to break the foam in these column tests with real waste and controlled foam formation at concentrations similar to those used in earlier testing.

To obtain a measure of the catalytic activity of the HLW used in the CSTR real waste test, the amount of phenylborate species and soluble boron present in the CSTRs at both temperatures was measured. There was no evidence of TPB decomposition. At all times, in both tests, there were less than detectable amounts (<10 ppm) of TPB decomposition products; 3PB, 2PB, 1PB, or phenol. The increase in temperature from 25°C to 45°C caused no additional detectable decomposition of TPB. While there was a decreasing amount of TPB in solution, this was not attributed to decomposition, but to increasing sodium levels which caused a decrease in TPB solubility.

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 than those precipitates which were previously produced by batch processing. However, these lower yield stresses could not be directly attributed to the formation route of the precipitate material due to a number of other causes, including the presence of an antifoam agent and the prior shear history of the material.

Two 20-L CSTR demonstrations (Tests 1a and 2) were performed in FY99 that included tests of the washing process.[143] The efficiency of excess NaTPB recovery was in the range of 9% – 20% of the available TPB, which was lower than expected for both of these tests.

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 conducted 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 ~29% of the excess TPB was recovered. This recovery was superior to that achieved in earlier tests where the antifoam was not used; however, this was likely due to the higher mixing speed (1200 vs. 600 rpm) used in this test.

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 recovery of NaTPB will be conducted after the down-selection process has been completed.

7.4.4.3 FY01 – Results

Two 20-L CSTR demonstrations (Tests 4 and 5) were performed in FY01 that included tests of the washing process.[17] The analyses of the washed batches in Test 4 found that the recoveries of TPB were poor, with only 10 and 11% recovered. As in Test 3, antifoam IIT B52 was used in Test 4. Compared to Test 3, the Test 4 TPB recovery was significantly lower, probably due to the using a lower mixing speed (650 ± 50 rpm) than was used in Test 3. The washing conditions for the two batches of slurry in Test 4 were fairly comparable to those employed in the second wash cycle in Test 2 from the standpoint of available TPB (0.63 vs. 1.09 mol), washing time (28 vs. 30 h), washing rate (15 vs. 20 mL/min), and mixing speed (both 650 ± 50 rpm). Based on equivalent washing volume, TPB concentrations for Test 2 were much higher than those obtained for Test 4. This indicates that the addition of IIT B52 in Test 4 may have interfered with the TPB recovery.

Three batches of concentrated slurry were produced in Test 5, but only the first two were washed. Again, the recoveries were ineffective with about 11% of the available TPB recovered from the first batch and ~3% from the second. The washing conditions for Test 5 closely resemble those used in Test 4 and the second batch in Test 2. IIT B52 was used in Tests 4 and 5. The results for the first batch in Test 5 and the two batches in Test 4 indicate very similar washing efficiencies, in the range of 10 to 12%. Although the washing conditions for the second slurry batch in Test 5 were also very similar, the results showed the poorest TPB recovery at 3%. TPB recovery for Test 2 second batch, at 18%, was significantly higher than the recoveries achieved in Test 4 and 5 slurry washes. The results reinforce the likelihood that IIT B52 interfered with the TPB recovery.

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

7.4.5 Antifoam Development (STTP SOWM 5.1 - 5.7)

One of the prime needs for the STTP process was 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 to resolve a high risk technology area for the STTP process. 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 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 KTPB 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-radio-active 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 KTPB 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. 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, an 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 postulated mechanism for the action of IIT B52 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 – Results

Antifoam development was conducted in several areas during FY01. Analytical methods were developed for the chosen antifoam and these methods were used to conduct process simulation tests to determine the partitioning of the antifoam across the precipitation, concentration, washing, and hydrolysis cycles. Since phenylboric acid hydrolysis kinetics are key to insuring that an acceptable Precipitate Hydrolysis Aqueous Product (PHA) is produced, studies were conducted in FY01 to determine, if the selected antifoam has a significant impact on the phenylboric acid hydrolysis kinetics. Results on the impact of the antifoam on hydrolysis are reported in Section 7.4.7. In addition, the impact of irradiation on the chosen antifoam was determined by conducting a series of foam column experiments with irradiated and unirradiated antifoam. Also, antifoam experts from IIT are doing additional development work on the selected antifoam and the selected antifoam is being evaluated in CSTR studies using both simulated and actual SRS HLW.

7.4.5.3.1 Antifoam Analytical Technique Development

The IIT B52 antifoam is composed of a surfactant, namely bis(2-ethylhexyl) sulfosuccinate, sodium salt ($C_{20}H_{37}O_7SNa$) dissolved in a diluent such as ethanol or propylene glycol. The surfactant is used to prevent foaming during STTP processing. An analytical technique was needed to monitor the concentration of IIT B52 to determine the partitioning of the antifoam

across the precipitation, concentration, washing, and hydrolysis cycles in the STTP process. An analytical method using HPLC with an evaporative light scattering detector was developed to perform quantitative and qualitative analyses of the surfactant in the STTP.[163] The developed method can be successfully used to analyze the IIT B52 in high caustic media such as decontaminated salt solution and precipitate. The method also can be used to analyze acidic media such as the PHA product or organic phases such as benzene and TPB solids.

Degradation of the IIT B52 was observed in the high caustic precipitate samples analyzed. IIT B52 has an approximate half-life of 30 minutes in the 3M caustic precipitate. The rate of decomposition of IIT B52 in the PHA was not determined but was observed when performing recovery studies.

7.4.5.3.2 Antifoam Partitioning

Work on the partitioning of the IIT B52 antifoam has been completed.[164] The IIT B52 antifoam agent was tested on a laboratory scale with simulated KTPB slurry using the proposed STTP process precipitation, concentration, and washing steps. This test was compared to an identical test conducted without antifoam using simulated KTPB slurry. Even under extreme agitation, foaming did not occur in precipitate slurries produced with or without antifoam during the precipitation cycle. Foaming did not occur in the concentration and washing cycles conducted with antifoam. The formation of KTPB foam is not a recoverable event without the use of antifoam. If gas entrainment in the slurry is carefully avoided, little or no foam will be generated during normal operations while concentrating and washing the precipitate. Ultimately, the STTP process should be designed to minimize the introduction of gas into the slurry during concentration and washing. However, gas can become entrained in the process via several mechanism: (1) during startup and initial filling of the system, (2) by uncovering the agitator blades, (3) through the use of pneumatic level/density instrumentation, or (4) by entrainment of gas at the surface of the liquid during agitation. Therefore, antifoam will be required during concentration and washing.

All of the IIT B52 antifoam was consumed during the precipitation, concentration, and washing cycles. None of the active antifoam ingredient (bis(2-ethylhexyl) sodium sulfosuccinate) was detected in the dilute precipitate (0.6 wt%), concentrated precipitate (10 wt%), washed precipitate (10 wt%), or the permeate from concentration and washing. A brief literature search revealed that bis(2-ethylhexyl) sodium sulfosuccinate undergoes hydrolysis in strong basic conditions (saponification) to form sodium succinate and 2-ethyl-1-hexanol. Both bis(2-ethylhexl) sodium sulfosuccinate and 2-ethyl-1-hexanol have been used as antifoam agents in other industrial applications. Analytical results confirmed the presence of 2-ethyl-1-hexanol in the washed precipitate and in the filtrate collected during washing. Therefore, the resulting reaction products are likely to be present in the solids sent to hydrolysis and in the filtrate to be used for saltstone.

Insoluble aluminum formed during the washing cycle. Gibbsite was present in washed precipitate slurry at concentrations in excess of 940 mg/L. The insoluble aluminum

composes <1% of the total mass of solids produced. Since the STTP process is designed to handle solids, the small quantity of aluminum that precipitates should not have a significant effect on the overall STTP process.

The IIT B52 antifoam affects the settling characteristics of the precipitate slurries. The insoluble solids in slurries produced without antifoam floated at the surface, whereas the concentrated slurries produced with antifoam settled to the bottom of the test vessels and storage containers. Based upon this testing, as little as 100 ppm/v of IIT B52 causes a significant change in the slurry settling characteristics. The change in settling characteristics is explained by the fact that bis(2-ethylhexyl)sodium sulfosuccinate is a powerful and well characterized wetting agent. No gross differences were noted in the filterability between the precipitates made with and without antifoam. However, the antifoam may make it easier to maintain a homogenous slurry which could be easier to handle in the plant.

7.4.5.3.3 Irradiation Impact on Antifoam

IIT B52 antifoam is added to the CSTRs, the concentration tank, and the wash tank in the STTP process to control foam. The antifoam dissolved in a diluent, will be subject to the radiation dose from the waste, primarily Cs-137. During normal processing, the CSTR slurry has approximately a half-day residence time in each CSTR, a two-day residence time in the concentration tank and a two-day residence time in the wash tank. It will then have a four-day residence time in the product tank prior to hydrolysis of the precipitate. The impact of irradiation on IIT B52 antifoam effectiveness in laboratory scale foaming columns has been studied.[165]

A test program was designed to measure damage to the antifoam agent (i.e. its loss of effectiveness, if any, as an antifoam agent) caused by the irradiation during processing and storage. To simulate the radioactive dose, simulated KTPB precipitate (at an insoluble solids concentration of 9 - 11 wt%) was combined with IIT B52 antifoam (at concentrations of 300 ppm/v and 1000 ppm/v) and irradiated in the SRTC's cobalt well to match the expected dose in the STTP. In addition, test slurries without antifoam were irradiated and the antifoam added post irradiation at comparable levels. Foam column testing was used to measure the effectiveness of the antifoam in the precipitate.

The addition of 1000 ppm/v of antifoam was more effective than the 300 ppm/v in testing. In addition, 1000 ppm/v of fresh antifoam added to irradiated precipitate without antifoam was slightly more effective than 1000 ppm/v of antifoam that had been irradiated with the precipitate. This was likely due to the degradation of the antifoam in the five days of storage post irradiation.

The antifoam was not effective in the washed precipitate as measured by the foam column testing. This suggests that the wash tank is the most likely source of foaming during normal processing. Because of the aggressiveness of this testing, it does not necessarily mean that there will be foam problems in a properly designed agitated tank. However, should STTP be selected, further testing should be completed to understand why the washed precipitate is so

much foamier. Consultants at IIT are currently working to develop a basic understanding of the poor performance of the IIT B52 in the washed precipitate.

One additional finding is that the irradiation of the precipitate decreases its foaming tendency. The foamiest mixture tested was an unirradiated precipitate with 1000 ppm/v of antifoam added five days before testing. This suggests that chemical degradation of the antifoam is much more significant to the antifoam's effectiveness than the irradiation expected during normal processing.[165]

7.4.5.3.4 IIT Antifoam Development

IIT is under a subcontract to do the basic research necessary to understand the foaming mechanism and explain the effectiveness of the IIT B52 antifoam agent in the STTP process. The work on this subcontract has been summarized in a WSRC report.[166]

During agitation in the STTP process, the KTPB particles can attach to the air/liquid surface of the foaming bubbles and form a particle structural stabilization barrier (PSSB), thereby lending stability to the foam lamella. The KTPB particles at high pH slowly decompose to benzene which is retained on the particle. With time, the KTPB particles aggregate to form a slurry. Benzene helps KTPB particles to aggregate and thereby stabilize the foam lamella. To eliminate the foaminess, it is necessary to disintegrate the particle foam lamella stabilization barrier. The IIT B52 does this in two way. First, by modifying the biphilic [partially wetted] surfaces of the KTPB particles by removing the benzene from the particle surfaces so that they become hydrophilic (water wetted). Second, by breaking the PSSB by generating a surface tension gradient (local instability) at the air/slurry surface.

IIT B52 has been demonstrated to be an effective antifoam in both column and CSTRs tests at SRTC and ORNL. Various batches of IIT B52 provided by different companies have utilized different solvents (i.e., ethanol, and propylene glycol) for dissolving the active ingredients in IIT B52. As a result, the batches have had different chemical properties, such as density, solubility in water, and flash point. There has also been differences in the performance of the different batches in column tests. If additional work is done on the STTP process after downselect, it is recommended that a short term study be conducted to select the best solvent for the IIT B52 in terms of its suitability to the STTP process.

7.4.5.3.5 CSTR Antifoam Test Results

Two tests of the 20-L CSTR system were conducted at ORNL in which the IIT B52 antifoam was used. IIT B52 Lot 7-31-2000 with Product Index ANAEPG was used in Test 4 with good results. Overall, the system control and hydraulic behavior for Test 4 was acceptable, and the IIT B52 antifoam successfully prevented foam formation in all vessels.

In the fifth 20-L CSTR demonstration run a newer lot of IIT B52 antifoam (Lot 10-05-2000, Product Index ANWEM) was used. In previous tests with the 20-L demonstration system, Lot 7-31-2000 with Product Index ANAEPG had been used. Frequent problems occurred

while trying to maintain consistent flow of the IIT B52 (Lot 10-05-2000, Product Index ANWEM) The lines to the process vessels were initially filled with non-diluted IIT B52 using 5 mL syringes in the syringe pumps. After the process fluids began overflowing from CSTR 2 into the Concentrate Tank, the syringes were refilled and the syringe pumps started at the desired rates. After 2.5 days of acceptable operation, the syringe pumps stopped pumping and could not be restarted. Cleaning and replacing the syringes did not correct the problem. SPP antifoam development personnel recommended trying to reestablish flow using antifoam diluted with water at a ratio of 9:1. A smaller, 1-mL glass syringe was used to apply greater pressure and the lines were flushed with a solution consisting of water and antifoam mixed in a ratio of 9:1. Subsequently, the antifoam (9:1) was placed in 30-mL syringes and the syringe pumps for feeding the antifoam to CSTR 1 and 2 restarted. After about 4 hours, the pumps failed again. The syringes were replaced with 5-mL syringes to provide greater pressure and flow was reestablished. After operating for 18 hours, all of these syringe pump lines became plugged. Visual inspection of the antifoam supply indicated that this particular batch appeared to be more viscous than the batch used in earlier testing. Diluting the antifoam 9:1 with water appeared to make the antifoam somewhat less viscous, but more gelatinous in nature. The SPP antifoam development personnel recommended the use of an earlier batch of antifoam, IIT B52 (Lot 7-31-2000, ANAEPG) that had successfully been used in undiluted form for Tests 3 and 4. The use of the IIT B52 (ANWEM) was discontinued. The lines were cleared once again, and five-mL syringes were used to pump the undiluted IIT B52 (Lot 7-31-2000, ANAEPG). The antifoam feed pumps operated well for the remainder of the test. The primary difference in the two lots of antifoam is that ANAEPG lot of antifoam used an ethylene glycol solvent and the ANWEM lot used an ethanol solvent. IIT is currently doing additional development with the IIT B52 antifoam to resolve the performance problem. Despite the difficulties encountered in Test 5 with antifoam addition, no foam related problems were experienced and no evidence of excessive foaming within the vessels was observed.

Based on the problems associated with the ANWEM lot of antifoam in the fifth 20-L demonstration run, it was decided by the SPP team that ANAEPG lot would be used in the real waste CSTR test at the SRTC. With the ANAEPG lot, the continuous real waste demonstration showed no appreciable signs of foaming at either 25°C or 45°C. The overflow tube between the first and second reactor vessel plugged after operation had been completed at 25°C and ~10 hours after the temperature had been raised to 45°C. Personnel quickly activated the bypass pump, which pumped the material from the two CSTRs, and bypassed the overflow lines. After starting the bypass pump, the test continued without interruption or further evidence of hydraulic instability. The exact cause of the plugging remains under investigation and no definitive link exists between the observed plugging and the antifoam addition.

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,[167] the benzene toxicity characteristics leach procedures (TCLP) results from saltstone,[168] and benzene generation rates from saltstone.[169] 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 – Results

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 if precipitate, either unirradiated or irradiated to a dose of 65.6 Mrad, could be processed.[170] 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 – Results

7.4.7.3.1 Impact of Antifoam on Hydrolysis Kinetics

The antifoam agent IIT B52 was found to have no detectable effect upon the rate of phenylboric acid (PBA) reaction during acid hydrolysis of a TPB simulant slurry containing 2000 ppm of the antifoam agent. Analysis of reactor contents at the completion of feeding revealed no detectable quantity of the antifoam agent. Analysis of all process streams at the completion of the hydrolysis cycle also revealed no detectable quantity of the antifoam agent. It is therefore concluded that the antifoam agent, IIT B52 rapidly decomposes in the feed slurry and/or during acid hydrolysis of the TPB feed.

Should the STTP process be selected as one of the salt processing processes, then future work is recommended to identify, quantify, and evaluate the impact of the decomposition products of IIT B52 antifoam agent. Future studies should incorporate all components and factors that are known to effect the properties of the precipitate slurry and the process chemistry: mercury, sludge solids, and radiation dose during slurry storage time.[171]

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.[172] In addition, these tests also explored varying levels of PHA on the glass properties. Three different glasses were formulated for these studies.[173,174,175] 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 process sludge, 30 wt% loading of sludge 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% sludge loading 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 – Results

During the first phase of the variability study on higher loading of PHA and MST, the Product Composition Control System models predicted 17 of the 23 glasses may be amorphously phase separated (i.e., the glasses may fail to meet the homogeneity constraint). No kinetic studies were conducted on any of these glasses, all of which were rapidly quenched and exhibited poor PCT leaching characteristics. These studies were completed during FY01 by cooling a limited number of glasses, using the canister centerline cooling profile, and then measuring PCT.

The impact of the cooling rate on the durability of PHA glasses has been studied and documented.[106] This study was conducted to determine the effect, if any, on the PCT responses of glasses cooled at different rates. Two bounding cooling profiles were used in this study: rapidly quenched and a canister centerline cooling curve. Glasses were selected based on a number of criteria, but mainly to challenge the regions where amorphous phase separation is expected. The current DWPF homogeneity constraint, imposed to preclude regions of phase separation, predicted that most of the glasses selected would be phase separated. It was, therefore, important to ensure that deleterious phase separation does not occur at either cooling profile. In this case, deleterious phase separation is defined as the formation of an amorphous phase in the glass that significantly decreases the glass durability as measured by the PCT response.

The results showed that there was no practical difference between the PCT responses for glasses subjected to the two cooling profiles. In fact, although to a small extent, the centerline-cooled (clc) glasses were generally more durable than the rapidly quenched glasses in this study. These results reveal that no deleterious (amorphous) phase separation occurred under either cooling regime.

All of the glasses readily satisfied the requirement that the PCT responses be at least two standard deviations below the PCT response of the standard environmental analysis glass. Furthermore, the PCT responses were almost entirely within the prediction intervals of the DWPF Durability Model. These results are detailed in the report.

X-ray diffraction and scanning electron microscopy were used to evaluate phases observed in the centerline cooled glasses. In one glass, pha17, a phase rich in copper was detected that had formed on the surface of trevorite crystals. trevorite crystals were also detected in several other clc glasses. A secondary phase precipitated out on the surface of trevorite crystals in glasses that had low sludge loadings (~22 wt% oxide) and high PHA (~13 wt% oxides in the glass). This phase was rich in potassium and titanium.

8.0 References

[1] M. Levenson and G. Choppin to E. J. Moniz, Letter dated October 14, 1999, Interim Report on Independent Technical Review of Alternatives for Processing the High-Level Radioactive Waste Salt Solutions at Savannah River Site.

[2] "Alternatives for High Level Waste Salt Processing at the Savannah River Site" by the Committee on Cesium Processing Alternatives for High Level Waste at the Savannah River Site, Board on Radioactive Waste Management, Board on Chemical Sciences and Technical, and National Research Council, 2000.

[3] "Savannah River Site Salt Processing Project Research and Development Program Plan", PNNL-132253, Rev. 1, November 2000.

[4] "High Level Waste Salt Disposition Systems Engineering Team Decision Phase Final -RP-99-00007, November 1999.

[5] "Supplemental Environmental Impact Statement Defense Waste Processing Facility", U. S. Department of Energy, DOE/EIS-0082-S, November 1994.

[6] H. H. Saito, M. R. Poirier, S. W. Rosencrance, and J. L. Siler, "Improving Filtration Rates of Monosodium Titanate (MST)-Treated Sludge Slurry with Chemical Additives", WSRC-TR-99-00343, September 15, 1999.

[7] H. H. Saito, M. R. Poirier, and J. L. Siler, "Effect of Sludge Solids to Monosodium Titanate (MST) Ratio on MST-Treated Sludge Slurry Cross-Flow Filtration Rates", WSRC-TR-99-00342, September 15, 1999.

[8] R. Haggard et al., "Final Report on the Crossflow Filter Testing for the Salt Disposition -FRED-PSP-RPT-09-0-010, Rev. 0, December 4, 1998.

[9] L. H. Delmau et al., "Improved Performance of the Alkaline-Side CSEX Process for Cs Extraction from Alkaline High-Level Waste Obtained by Characterization of the Effect of Surfactant Impurities", ORNL/TM-1999/209, November 1999.

[10] D. T. Hobbs, "Phase V Simulant Testing of Monosodium Titanate Adsorption", WSRC-TR-2000-00142, May 22, 2000.

[11] D. T. Hobbs and D. D. Walker, "Plutonium and Uranium Adsorption on Mono-Na Titanate", WSRC-RP-92-93, August 13, 1992.

[12] D. T. Hobbs and S. D. Fleischman, "Fissile Solubility and Mono-Na Loading Tests", WSRC-RP-92-1273, February 12, 1993.

[13] D. T. Hobbs, M. G. Bronikowski, T. B. Edwards, and R. L. Pulmano, "Final Report of Phase III Testing of Mono-Na Titanate Adsorption Kinetics", WSRC-TR-99-00134, Rev. 0, May 28, 1999.

[14] D. T. Hobbs and R. L. Pulmano, "Phase IV Simulant Testing of Mono-Na Titanate Adsorption Kinetics", WSRC-TR-99-00219, Rev. 0, June 29, 1999.

[15] J. W. McCullough, P. C. Suggs, and J. M. Reynolds, "DOE-SR Review Team Final Report in Phase IV of the HLW Salt Disposition Alternatives Evaluation", HLW-00-001, December 1999.

[16] D. T. Hobbs, T. B. Peters, and D. J. Wheeler, "Investigation of Savannah River Site High Level Waste Solutions for Evidence of Colloidal Plutonium, WSRC-TR-2001-00103, March 13, 2001.

[17] D. D. Lee and J. L. Collins, "Evaluation of the Small Tank Tetraphenylborate Process Using a Bench-Scale Continuous Stirred Tank Reactor System at Oak Ridge National Laboratory, Results of Test 5", ORNL/TM-2001/42, (April 2001, Draft-Official Use Only).

[18] T. B. Peters, M. J. Barnes, F. F. Fondeur, R. W. Blessing, R. Norcia, J. G. Firth, C. W. Kennell, and T. R. Tipton, "Demonstration of Small Tank Tetraphenylborate Precipitation Process Using Savannah River Site High Level Waste", WSRC-TR-2001-00211, May 1, 2001.

[19] D. D. Walker, M. A. Norato, R. A. Pierce, W. R. Wilmarth, R. A. Leonard, T. Todd, and J. D. Law, "Demonstration of Caustic-Side Solvent Extraction with Savannah River Site High Level Waste", WSRC-TR-2001-00223, April 19, 2001.

[20] D. T. Hobbs, T. B. Peters, and L. N. Oji, "Task Technical and Quality Assurance Plan for FY2001 Strontium and Actinide Removal Testing", WSRC-RP-2001-00188, January 18, 2001.

[21] D. T. Hobbs and David G. Karraker, "Recent Results on the Solubility of Uranium and Plutonium in Savannah River Site Waste Supernate", *Nuclear Technology*, 1996 (114), 318-324.

[22] C. H. Delegard, "Solubility of PuO_2xH_2O in Alkaline Hanford High-Level Waste Solution", *Radiochem. Acta*, **41** (1987), 11.

[23] D. T. Hobbs, "Evaluation of Alternate Materials and Methods for Strontium and Alpha Removal from Savannah River Site High-Level Waste Solutions", WSRC-TR-2000-00229, August 2000.

[24] D. T. Hobbs, M. S. Blume, and H. L. Thacker, "Screening Evaluation of Sodium Nonatitanate for Strontium and Actinide Removal from Alkaline Salt Solution", WSRC-TR-2000-00361, October 2, 2000.

[25] M. R. Poirier, "Filtration of Sludge and Sodium Nonatitanate Solutions", WSRC-TR-2000-00290, August 16, 2000.

[26] D. T. Hobbs, M. S. Blume, and H. L. Thacker, "Screening Evaluation of Alternate Sorbents and Methods for Strontium and Actinide Removal from Alkaline Salt Solution", WSRC-TR-2001-00072, Rev. 0, February 2001.

[27] J. L. Collins and K. K. Anderson, "Development and Testing of Spheroidal Inorganic -96463, Oak Ridge National Laboratory, Oak Ridge, TN, January 29, 1998.

[28] R. A. Peterson, C. A. Nash, and D. J. McCabe, "Correlation of Filtrate Flow Rate for Irradiated and Unirradiated Tetraphenylborate Slurries", *Separation Science and Technology* 32(1-4) (1997), pp. 721-736.

[29] D. J. McCabe, "Evaluation and Ranking of the Tank Focus Area Solid Liquid Separation Needs", WSRC-TR-95-0337, August 17, 1995.

[30] D. J. McCabe, B. W. Walker, and R. A. Peterson, "Oak Ridge Gunite Simulant Filtration -TR-96-0234, September 30, 1996.

[31] R. A. Peterson and D. J. McCabe, "Hanford and Oak Ridge Underground Storage Tank Waste Filtration Process Evaluation", WSRC-TR-96-0232, July 30, 1996.

[32] B. W. Walker and D. J. McCabe, "Hanford Phosphate Precipitation Filtration Process C-TR-97-00352, September 30, 1997.

[33] B. W. Walker and D. J. McCabe, "Hanford Underground Storage Tank Waste Filtration -TR-97-00353, September 30, 1997.

[34] B. W. Walker and D. J. McCabe, "Oak Ridge National Laboratory Melton Valley Storage Tank Waste Filtration Process Evaluation", WSRC-TR-97-00354, September 30, 1997.

[35] D. J. McCabe, "Technology Status Report of the Applicability of Solid-Liquid Separation Methods to Radioactive Tank Wastes", WSRC-TR-97-0398, December 22, 1997.

[36] P. A. Taylor and C. H. Mattus, "Resuspension and Settling of Mono-Na Titanate and Sludge in Supernate Simulant for the Savannah River Site", ORNL/TM-1999/166, October 1999.

[37] H. H. Elder and J. R. Fowler, "Alternatives for Feed Clarification Study", HLW-SDT-99-00289, September 14, 1999.

[38] M. R. Poirier, "FY2000 FRED Test Report", WSRC-TR-2001-00035, January 11, 2001.

[39] M. R. Poirier, "Task Technical and Quality Assurance Plan for the Sludge/Monosodium Titanate (MST) Filtration Test Program", WSRC-TR-99-00483, December 17, 1999.

[40] M. R. Poirier, "Evaluation of Flocculation and Filtration Procedures Applied to WSRC Sludge: A Report from B. Yarar, Colorado School of Mines", WSRC-TR-2001-00213, April 16, 2001.

[41] L. O. Dworjanyn, "Monosodium Titanate Sludge Filtration", WSRC-RP-2000-00685, Rev. 0, August 18, 2000.

[42] M. R. Poirier, "Mark Clark Consultation on Role of Tetraphenylborate in Filtration", WSRC-TR-2000-00270, July 31, 2000.

[43] V. Van Brunt, R. Haggard, T. Deal, C. Stork, M. Poirier, and S. D. Fink, "Cross-Flow Filtration of Simulated High-Level Waste Sludge (Tank 8F)", WSRC-TR-2001-00195, April 20, 2001.

[44] M. R. Poirier, F. F. Fondeur, T. L. Fellinger, and S. D. Fink, "Cross-Flow Filtration Demonstration for Slurries Containing High Level Waste Sludge and Monosodium Titanate", WSRC-TR-2001-00212, April 11, 2001.

[45] M. R. Poirier, "Evaluation of Solid-Liquid Separation Technologies to Remove Sludge and Monosodium Titanate from SRS High Level Waste", WSRC-TR-2000-00288, August 16, 2000.

[46] S. G. Subosits, "Alpha Sorption Process Alternatives Studies", HLW-SDT-2000-00296, August 2000.

[47] W. B. Van Pelt, "Dr. Baki Yarar Consultation on Salt Alternatives Solid-Liquid Separations", WSRC-TR-2000-00287, September 15, 2000.

[48] M. R. Poirier, "Improving the Filtration of Sludge/Monosodium Titanate Slurries by the -TR-2001-00175, March 27, 2001.

[49] M. R. Poirier, "Filtration Systems, Inc. Report for SRS SpinTek Rotary Microfilter -TR-2001-00214, Rev. 1, May 4, 2001.

[50] M. R. Poirier, "Vendors Declining to Participate in Alternative Solid-Liquid Separation Technology Evaluation", WSRC-RP-2001-00190, January 22, 2001.

[51] C. J. Martino and M. R. Poirier, "Task Technical Plan and Quality Assurance Plan for the Settle and Decant Testing of MST in Salt Simulant", WSRC-TR-2001-00030, March 5, 2001.

[52] L. Harkey, "In-line/On-line Radionuclide Detection Monitor", J-SPP-H-00222, June 29, 2000.

[53] A. O. Delley, "Task Requirement and Criteria Salt Waste Processing Facility In-Line/On-Line Radionuclide Detection Monitor", G-TC-H-00030, Rev. 1, July 19, 2000.

[54] D. J. McCabe, "Crystalline Silicotitanate Examination Results", WSRC-RP-94-1123, Rev. 0, May 18, 1995.

[55] D. J. McCabe, "Examination of Crystalline Silicotitanate Applicability in Removal of Cs from SRS High Level Waste", WSRC-TR-97-0016, Rev. 0, April 25, 1997.

[56] D. D. Walker, et al., "Cs Removal from Simulated SRS High-Level Waste Using Crystalline Silicotitanate", WSRC-TR-98-00344, Rev. 1, October 16, 1998.

[57] Z. Zheng, R. G. Anthony, and J. E. Miller, "Modeling Multicomponent Ion Exchange Equilibrium Utilizing Hydrous Crystalline Silicotitanates by a Multiple Interactive Ion Exchange Site Model", *Ind. Eng. Chem. Res*., **36**, No. 6, 2427-2434 (1997).

[58] J. A. Berninger, R. D. Whitley, X. Zhang, and N.-H. L. Wang, "A Versatile Model for Simulation of Reaction and Non-Equilibrium Dynamics in Multicomponent Fixed-Bed Adsorption Processes", *Computers Chem. Eng.*, **15**, No. 11, 749-768 (1991). Whitley, 1990; "Dynamics of Nonlinear Multicomponent Chromatography Interplay of Mass Transfer, Intrinsic Sorption Kinetics, and Reaction", Ph.D. Thesis, Purdue University, West Lafayette, IN.

[59] Ernest et al., 1997; "Development of a Carousel Ion-Exchange Process for Removal of Cs-137 from Alkaline Nuclear Waste", *Ind. Eng. Chem. Res.*, **36**, 2775. Koh et al., 1998; "Pore and Surface Diffusion and Bulk-Phase Mass Transfer in Packed and Fluidized Beds", *Ind. Eng. Chem. Res.*, **37**, 228. Ma et al., 1996; "Pore and Surface Diffusion in Multicomponent Adsorption and Liquid Chromatography Systems", *AlChE J*., **42**, 1244.

[60] D. D. Walker, "Modeling of Crystalline Silicotitanate Ion Exchange Columns", WSRC-TR-98-00343, Rev. 0, October 2, 1998.

[61] W. R. Wilmarth, T. Hang, J. T. Mills, V. H. Dukes and S. D. Fink, "The Effect of Pretreatment, Superficial Velocity, and Presence of Organic Constituents on IONSIV® IE-911 Column Performance", WSRC-TR-99-00313, August 31, 1999.

[62] D. D. Walker, et al., "Cs Removal from Savannah River Site Radioactive Waste Using Crystalline Silicotitanate (IONSIV® IE-911)", WSRC-TR-99-00308, Rev. 0, September 18, 1999.

[63] F. F. Fondeur, T. Hang, D. D. Walker, W. R. Wilmarth, M. Bussey, and S. D. Fink, "The Effect of Carbonate, Oxalate and Peroxide on the Cesium Loading of IONSIV® IE-911", WSRC-TR-2000-00344, October 30, 2000.

[64] F. F. Fondeur, "Crystalline Silicotitanate Ion Exchange Support for Salt Alternatives", SRT-LWP-2000-00189 (Texas A&M University Final Report KE-49242-0), December 12, 2000.

[65] F. F. Fondeur, T. Hang, D. D. Walker, W. R. Wilmarth, and S. D. Fink, "The Effect of Alkaline Earth Metal on the Cesium Loading of IONSIV® IE-910 and IE-911", WSRC-TR-2000-00406, December 2000.

[66] M. H. Beasley, A. D. Coleman, B. H. Croy, S. D. Fink, and D. D. Walker, "IONSIV® IE-911 Performance in Savannah River Site Radioactive Waste", WSRC-TR-2000-00526, Rev. 0, April 10, 2001

[67] S. N. Yen, J. A. Pike, R. A. Jacobs, M. R. Poirier, B. M. Sahawneh, and R. K. Leugemors, "Evaluation of Alternate Ion Exchange Designs for CST Non-Elutable Ion Exchange Process", WSRC-TR-2001-00133, Rev. 0, April 10, 2001.

[68] J. A. Pike and B. M. Sahawneh, "Process Impacts of Alternate Fixed Bed Column Conceptual Designs for CST Ion Exchange", HLW-SDT-2001-00033, January 24, 2001.

[69] B. B. Spencer, H. Wang, and K. K. Anderson, "Thermal Conductivity of IONSIV® IE-911 Crystalline Silicotitanate and Savannah River Waste Simulant Solutions", ORNL/TM-2000/285, November 2000.

[70] S. Y. Lee, "Heat Transfer Calculations for a Fixed CST Bed Column", WSRC-TR-2000-00522, January 15, 2001.

[71] D. D. Walker, "Crystalline Silicotitanate Column Plugging Incidents", SRT-LWP-2000-00136, August 22, 2000.

[72] W. R. Wilmarth, V. H. Dukes, J. T. Mills, and F. F. Fondeur, "Effect of Sodium Hydroxide Pretreatment of UOP IONSIV IE-911 Crystalline Silicotitanate Sorbent", WSRC-TR-2000-00167, April 24, 2000.

[73] J. L. Krumhansl, C. Jove-Colon, P.C. Zhang, R. C. Moore, T. M. Nenoff, D. A. Lucero, F. M. Salas, and H. L. Anderson, "A Preliminary Assessment of IE-911 Column Pretreatment Options", SAND-2001-1002, 2001.

[74] J. L. Krumhansl, P.C. Zhang, C. Jove-Colon, and H. L. Anderson, "General Stability Models for Potential IE-911 Column Plugging Materials", SAND-2001-1001, 2001.

[75] P. A. Taylor and C. H. Mattus, "Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent", ORNL/TM-2001/39, March 2001.

[76] P. A. Taylor and C. H. Mattus, "Thermal and Chemical Stability of Crystalline -1999/233, October 1999.

[77] D. D. Walker, "Cesium Sorption/Desorption Experiments with IONSIV® IE-911 in Radioactive Waste", WSRC-TR-2000-00362, Rev. 0, December 13, 2000.

[78] W. R. Wilmarth, J. T. Mills, and V. B. Dukes, "Results of Sorption/Desorption -911 Crystalline Silicotitanate", WSRC-TR-2000-00394, August 31, 2000.

[79] M. Nyman, T. Headley, and T. M. Neoff, "Characterization of UOP IONSIV® IE-911: Part 2 Final", SAND-2001-0999, April 2001.

[80] Y. Su, L. Li,J. S. Young, and M. L. Balmer, "Investigation of Chemical and Thermal Stabilities of Cs-Loaded UOP IONSIV® IE-911 Ion Exchanger" (Final Report), PNNL-13392-2, March 2001.

[81] D. D. Walker, "Stability and Solubility Tests with SRS Simulated Wastes", WSRC-TR-2000-00273, Rev. 0, November 6, 2000.

[82] G. Eriksson, "Thermodynamic studies of high-temperature equilibriums. XII. SOLGASMIX, a computer program for calculation of equilibrium compositions in multiphase systems", *Chem. Scripta*, **8**, 1000 (1975); C. F. Weber, "Convergence of the equilibrium code SOLGASMIX", *J. Comp. Phys.*, **145**, 655 (1998).

[83] H. Park and P. Englezos, "Thermodynamic Modeling of Na Aluminosilicate Formation in *Ind. Eng. Chem. Res.*, **38**, 4959-4965 (1999).

[84] D. D. Walker, "Preparation of Simulant Waste Solutions -TR-99-00116, April 15, 1999.

[85] K. S. Pitzer, Activity Coefficients in Electrolyte Solutions, 2nd Ed., CRC Press, Boca Raton, FL (1987).

[86] W. F. Steele, C. F. Weber, and D. A. Bostick, "Waste and Simulant Precipitation Issues, -2000/348, January 2001.

[87] K. Zheng, R. St. C. Smart, J. Addai-Mensah, and A. Gerson, *J. Chem. Eng. Data*, **43**, 312-317 (1998); K. Zheng, J. Addai-Mensah, A. Gerson, and R. St. C. Smart, *J. Crystal Growth* **171**, 197-208 (1997); M. C. Barnes, J. Addai-Mensah, and A. R. Gerson, *Collids Surfaces A: Physicochem. Eng. Aspects* **157**, 101-116 (1999).

[88] R. G. Anthony and Z. Zheng, CST Ion Exchange Version 5 (CSTIXE5)", Department of Chemical Engineering, Texas A&M University, College Station, Texas.

[89] W. R. Wilmarth, D. D. Walker, F. F. Fondeur, S. D. Fink, M. Nyman, J. Krumhansl, J. T. Mills, V. H. Dukes, and B. H. Croy, "Examination of Pre-Production Samples of UOP IONSIV® IE-910 and IE-911", WSRC-TR-2001-00221, April 18, 2001.

[90] D. D. Walker, "Radiolytic Gas Generation in Crystalline Silicotitanate Slurries", WSRC-TR-99-00285, September 1, 1999.

[91] High Level Waste Salt Disposition Systems Engineering Team, "Position Paper on Performance of Small CST Column Gas Generation Test in Radiation Field", HLW-SDT-99-0257, Rev. 0, August 30, 1999.

[92] T. D. Welch and K. K. Anderson, et al., "Hydraulic Performance and Gas Behavior of a Tall Crystalline Silicotitanate Ion-Exchange Column", ORNL/TM-1999/103, February 2000.

[93] B. B. Spencer, K. K. Anderson, H. L. Jennings, T. E. Kent, P. A. Taylor, M. W. Geeting, "Evaluation of Gas Disengaging Equipment Supporting a Crystalline Silicotitianate Ion-Exchange Column System", ORNL/TM-2001/46, March 2001.

[94] T. Hang and D. D. Walker, "Gas Generation and Bubble Formation Model for Crystalline Silicotitanate Ion Exchange Columns", WSRC-TR-2000-00177, Rev. 0, June 16, 2000.

[95] F. F. Fondeur, D. D. Walker, W. R. Wilmarth, and S. D. Fink, "Bubble Formation Modeling in IE-911", WSRC-TR-2000-00161, Rev. 0, June 16, 2000.

[96] A. J. Mattus, T. E. Kent, and P. A. Taylor, "Study of the Potential Impact of Gamma-Induced Radiolytic Gases Upon Loading of Cesium onto Crystalline Silicotitanate Sorbent at the High Flux Isotope Reactor", ORNL/TM-2000/362, January 2001.

[97] R. C. Odom and F. G. Smith, III, "CST Particle Size Reduction Tests", WSRC-TR-2000-00350, Rev. 0, July 14, 2000.

[98] Z. H. Qureshi, "Mixing and Sampling of Sludge-Frit CST Slurries", WSRC-TR-99-00309, September 1999.

[99] M. A. Baich, "CST/Water Slurry Mixing and Resuspension", WSRC-TR-2000-00370, Rev. 0, September 20, 2000.

[100] T. B. Edwards, Z. H. Qureshi, J. R. Harbour, and F. G. Smith, III, "Hydragard® Sampling of Melter Feed Slurry Containing CST: A Nonproprietary Summary", WSRC-TR-2000-00433, Rev. 0, October 25, 2000.

[101] D. C. Koopman and D. L. Lambert, "Hydrogen Generation and Foaming During Tests in the GFPS Simulating DWPF Operations With Tank 42 Sludge and CST", WSRC-TR-99-00302, September 3, 1999.

[102] W. E. Daniel, "Hydrogen Generation Rate During Melter Feed Preparation of Tank 42 Sludge and Salt Washed Loaded CST In The Defense Waste Processing Facility (DWPF)", WSRC-TR-99-00277, August 23, 1999.

[103] M. K. Andrews, T. B. Edwards, J. R. Harbour, D. M. Marsh, and P. J. Workman, "Results of the CST/Sludge Variability Study", WSRC-RP-98-01142, October 1, 1998 (Official Use Only).

[104] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Summary of Results for CST Glass Study: Composition and Property Measurements", WSRC-TR-99-00324, Rev. 0, September 7, 1999 (Official Use Only).

[105] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Impact of Cooling Rate on the Durability of CST Glasses: A Nonproprietary Summary (U)", WSRC-TR-2001-00125, Rev. 0, March 8, 2001.

[106] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Impact of Cooling Rate on the Durability of PHA Glasses (U)", WSRC-TR-2001-00123, Rev. 0, March 8, 2001.

[107] R. E. Eibling and D. C. Koopman, "CST Melter Feed Characterization in Support of the 1999 and 2000 Thermal Fluids Lab Hydragard Testing", WSRC-TR-2000-00445, Rev. 0, December 31, 2000.

[108] E. K. Hansen, D. C. Koopman, and P. R. Monson, "Impact of CST on the Rheological Characteristics of DWPF Melter Feed', WSRC-TR-2001-00069, Rev. 0, March 7, 2001.

[109] D. C. Koopman, "Sludge Batch 2 (Macrobatch 3) Flowsheet Studies with Simulants", WSRC-TR-2000-00398, Rev. 0, October 9, 2000.

[110] C. A. Shook and M. C. Roco, Slurry Flow – Principles and Practice, Butterworth – Heinemann, 1991, pp. 61-64.

[111] Rutland, P. L., "Position Paper on the Simulant for the Caustic Side Solvent Extraction Research and Development", HLW-SDT-2000-00134, May 2000.

[112] R. A. Leonard, et al., "Evaluation of an Alkaline-side Solvent Extraction Process for Cs Removal from SRS Tank Waste Using Laboratory-scale Centrifugal Contactors", ANL-99/14, August 1999.

[113] R. A. Leonard, S. B. Aase, H. A. Arafat, C. Conner, J. R. Falkenberg, and G. F. Vandegrift, "Proof-of-Concept Flowsheet Tests for Caustic-Side Solvent Extraction of Cesium from Tank Waste", ANL-00/30, November 2000.

[114] R. A. Leonard ,S. B. Aase, H. A. Araft, C. Conner, D. B. Chamberlain, M. C. Regalbuto, and G. F. Vandegrift, "Interim Report on Multi-day Test of the Caustic-Side Solvent Extraction Flowsheet for Cesium Removal from a Simulated SRS Tank Waste", ANL/CMT/CSSX-2001/01, April 24, 2001.

[115] B. A. Moyer, S. D. Alexandratos, P. V. Bonnesen, G. M. Brown, J. E. Caton, Jr., L. H. Delmau, C. R. Duchemin, T. J. Haverlock, T. G. Levitskaia, M. P. Maskarinec, F. V. Sloop, Jr., and C. L. Stine, "Caustic-Side Solvent Extraction Chemical and Physical Properties Progress in FY 2000 and FY 2001", CERS/SR/SX019, Rev.0, April 2001.

[116] P. V. Bonnesen, "Alkaline-Side Extraction of Cs from Savannah River Tank Waste Using a Calixerene Crown Ether Extractant", ORNL/TM-13704, December 1998.

[117] L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, F. V. Sloop, Jr., and B. A. Moyer, "Caustic-Side Solvent Extraction Chemical and Physical Properties: Equilibrium Modeling of Distribution Behavior", Technical Report: CERS/SR/SX/018, Rev. 0, April 16, 2001.

[118] M. P. Maskarinec, J. E. Caton, T. L. White, "Analytical Methods Development in Support of the Caustic Side Solvent Extraction System", CERS/SR/SX/022, Rev. 0, March 2001.

[119] P. V. Bonnesen, L. H. Delmau, B. A. Moyer, and R. A. Leonard, "A Robust Alkaline-Side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste", *Solvent Extr. Ion Exch.* 18(6), 1079-1108 (2000).

[120] R. D. Spence, "Experimental Test Plan for Batch-Equilibrium Hot-Cell Tests with SRS Simulant Waste and Internal ^{137}Cs Irradiation", Test Plan No. 2 for TTP ORNL-CTD-1, Rev. 0, June 14, 2000.

[121] R. D. Spence, L. H. Delmau, L. N. Klatt, F. V. Sloop, Jr., P. V. Bonnesen, and B. A. Moyer, "Batch-Equilibrium Hot-Cell Tests of Caustic-Side Solvent Extraction (CSSX) with SRS Simulant Waste and Internal Cs-137 Irradiation", CERS/SR/SX/021, April 2001.

[122] C. L. Crawford, et al., "Radiation Stability of Calixarene Based Solvent System", WSRC-TR-98-00371, October 2, 1998.

[123] R. A. Peterson, T. L. White, S. Crump, and L. H. Delmau, "Solvent Extraction External Radiation Stability Testing", WSRC-TR-2000-00413, Rev. 0, November 20, 2000.

[124] J. F. Birdwell, Jr. and D. E. Benker, "Throughput and Phase Separation Evaluations of 5-cm Contactors for CSSX Processing", Experimental Test Plan No. 1 for TTP ORNL-CTD-2, Rev. 0, June 26, 2000.

[125] J. F. Birdwell, Jr. and D. E. Benker, "Test Instruction for One- and Multi-stage CSSX Process Mass Transfer Evaluations in 5-cm Centrifugal Contactors", Experimental Test Plan No. 2 for TTP ORNL-CTD-2, Rev. 0, June 27, 2000.

[126] D. E. Benker, "Experimental Test Plan for Contactor Loop Tests Using SRS Simulant Waste with ^{137}Cs Internal Irradiation", Experimental Test Plan No. 3 for TTP ORNL-CTD-2, Rev. 0, June 6, 2000.

[127] J. F. Birdwell, Jr., "Test Plan for Evaluation of Solids Transfer and Accumulation in 5-cm Centrifugal Contactors", CERS/SR/SX/020, Rev. 0, April 24, 2001.

[128] R. D. Spence, "Test Plan for Hot-Cell Contacting Demonstration with High Activity Cs-137 in Support of Workscope Matrix Task 5.1.7", Test Plan No. 1 for TTP ORNL-CTD-1, Rev. 0, May 31, 2000.

[129] R. Blackmon, et al., "Real Waste Feasibility Study for Caustic Side Solvent Extraction -SDT-2000-00251, Rev.0, July 2000.

[130] T. J. Keever and P. V. Bonnesen, "Method for Evaluating CSSX Solvent Quality", CERS/SR/SX/005, Rev. 0, June 23, 2000.

[131] B. A. Moyer, et al., "Development of an Alkaline-Side Cs SX Process Applicable to Savannah River HLW Using A Calixarene-Crown Extractant FY98 Report", October 1, 1998.

[132] R. A. Peterson, "Solvent Extraction Phase III Research Summary", WSRC-TR-98-00370, October 2, 1998 (Withdrawn from reference).

[133] P. V. Bonnesen, "Letter Report on Candidate Calix Producers", CERS/SR/SX/008, September 22, 2000.

[134] P. V. Bonnesen, "Letter Report on Acceptable Diluent, Diluent Suppliers, and Tri-n-octylamine Suppliers", CERS/SR/SX/006, September 22, 2000.

[135] P. V. Bonnesen, "Letter Report on Minimum Purity Requirements and Product Specifications for CSSX Solvent Components", CERS/SR/SX/007, September 21, 2000.

[136] P. V. Bonnesen, "Letter Report on FY00 Technology Transfer Activities for the CSSX Process", CERS/SR/SX/010, September 29, 2000.

[137] W. R. Wilmarth and C. L. Crawford, "The Influence of High Temperature and Radiation on Inhibiting Agents for the Decomposition of Na Tetraphenylborate", WSRC-TR-98-00232, August 3, 1998 (Official Use Only).

[138] D. D. Walker, "Low Temperature Decomposition Rates for Tetraphenylborate Ion", WSRC-TR-98-00342, October 2, 1998.

[139] R. A. Peterson, "Catalyst Removal Demonstrations using Radioactive Waste", WSRC-TR-99-0208, June 21, 1999 (Official Use Only).

[140] D. T. Hobbs, "Radioactive Testing Results in Support of the In-Tank Precipitation Facility-Filtrate Test", WSRC-TR-98-00250, August 28, 1998.

[141] D. D. Walker, "Effects of Oxygen and Catalyst on Tetraphenylborate Decomposition -TR-99-00279, September 7, 1999.

[142] R. B. King and N. Bhattacharyya, "A Preliminary Spectrophotometric Study of the Reduction of Palladium with Phenylboron Compounds in Simulated High Level Wastes", September 30, 1998.

[143] D. D. Lee and J. L. Collins, "Continuous Flow Stirred Tank Reactor 20 Liter Demonstration Test: Final Report", ORNL/TM-1999/234, September 30, 1999.

[144] R. J. Hanrahan, E. J. Lahoda, R. B. King, R. A. Smiley, and G. W. Parshall, "Report on March 17, 18 and 19, 1998 ITP Process Chemistry and Mechanisms Panel Meeting", SRT-WPT-98-0005, March 24, 1998.

[145] L. N. Oji, R. A. Peterson, and M. J. Barnes, "Small Tank Tetraphenylborate: Catalyst Influence of Selected Metals", WSRC-TR-2000-00276, July 31, 2000.

[146] M. J. Barnes and L. N. Oji, "Small Tank Tetraphenylborate Catalyst Studies", WSRC-TR-2001-00180, Rev. 0, March 28, 2001

[147] P. V. Bonnesen, L. H. Delmau, and F. V. Sloop, "Investigating the Mechanism of Catalytic Tetraphenylborate Decomposition Using Nuclear Magnetic Resonance Spectrometry: Initial Studies in FY00", ORNL/TM-2000/279, December 2000.

[148] P. V. Bonnesen and G. M. Brown, "Investigating the Mechanism of Catalytic Tetraphenylborate Decomposition Using Nuclear Magnetic Resonance Spectrometry: FY01 Interim Report", ORNL/CS-01, April 30, 2001.

[149] M. C. Duff, D. B. Hunter, and J. Urbanik-Coughlin, "Sample Characterization of Palladium Supported on Tetraphenylborate", SRT-LWP-2000-00187, December 12, 2000.

[150] M. J. Barnes, L. N. Oji, T. B. Peters, and F. F. Fondeur, "Tetraphenylborate Catalyst Development for the Oak Ridge National Laboratory 20-L Continuously Stirred Tank Reactor Demonstration", WSRC-TR-2000-00457, Rev. 0, November 29, 2000

[151] M. J. Barnes, B. B. Anderson, T. L. White, and K. L. Martin, "Tetraphenylborate Decomposition Testing Using Actual Savannah River Site High Level Waste", WSRC-TR-2001-00251, May 2, 2001.

[152] L. N. Oji and M. J. Barnes, "Batch Studies of Sodium Tetraphenylborate Decomposition on Reduced Palladium Catalyst", WSRC-TR-2000-00459, Rev. 0, October 28, 2000.

[153] D. D. Lee and J. L. Collins, "Test Results for CSTR Test 4", ORNL/TM-2001/8, (April 2001, Draft-Official Use Only).

[154] L. Lee and L. Kilpatrick, "A Precipitation Process for Supernate Decontamination", DP-1636, November 1982.

[155] M. J. Barnes, R. A. Peterson, R. F. Swingle, and C. T. Reeves, "Na Tetraphenylborate Solubility and Dissolution Rates", WSRC-TR-95-0092, March 7, 1995.

[156] D. J. McCabe, "Cs, Potassium, and Na Tetraphenylborate Solubility in Salt Solution", WSRC-TR-96-0384, December 16, 1996.

[157] S. M. Serkiz, J. D. Ginn and A. R. Jurgensen, "Tetraphenylborate Solubility in High Ionic Strength Salt Solutions", WSRC-TR-98-00103, April 3, 1998.

[158] M. J. Barnes, "Cs Precipitation Kinetic Studies", WSRC-TR-98-00367, October 2, 1998.

[159] R. A. Peterson and J. O. Burgess, "Co-precipitation and Solubility Studies of Cesium, Potassium and Sodium Tetraphenylborate", WSRC-TR-99-00216, Rev. 1, December 22, 1999.

[160] R. A. Peterson, "Idealized Mixing Impacts", WSRC-RP-99-00849, September 16, 1999.

[161] M. J. Barnes, R. A. Peterson, and S. R. White, "Cs Removal Kinetics and Equilibrium: -TR-99-00325, September 8, 1999.

[162] R. A. Peterson and J. O. Burgess, "The Demonstration of Continuous Stirred Tank Reactor Operations with High Level Waste", WSRC-TR-99-00345, Rev.1, February 15, 2000.

[163] D. R. Best and T. L. White, "IIT B52 Antifoam Analytical Technique Using High Performance Liquid Chromatography and a Evaporative Light Scattering Detector", WSRC-TR-2001-00135, Rev. 0, March 16, 2001.

[164] T. B. Calloway, M. A. Baich, and D. P. Lambert, "Fate of IIT B52 Antifoam Agent Across the Small Tank TPB Process", WSRC-TR-2001-00102, Rev. 0, March 31, 2001.

[165] I. Hickson, "Impact of Irradiation on IITB52 Antifoam Effectiveness in Laboratory Scale -TR-2001-00128, Rev. 0, April 12, 2001

[166] D. P. Lambert, "Illinois Institute of Technology Report: IITB52 Antifoamer for Alternative Salt Processes", WSRC-TR-2001-00237, Rev 0, May 1, 2001.

[167] M. R. Poirier, "Benzene Evolution Rates from Saltstone Prepared with 2X ITP Flowsheet Concentrations of Phenylborates and Heater to 85°C", WSRC-TR-99-00155, May 21, 1999.

[168] M. R. Poirier, "Benzene TCLP Results from Saltstone Prepared with 2X ITP Flowsheet Concentrations of Phenylborates", WSRC-TR-99-00156, May 21, 1999.

[169] M. R. Poirier, "Benzene Generation from Phenylborate Decomposition in Saltstone", WSRC-TR-99-00154, May 21, 1999.

[170] P. R. Burket, "Hydrolysis Test Program in Support of Salt Disposition Activities", WSRC-TR-99-00272, September 17, 1999 (Withdrawn from reference).

[171] M. A. Baich, "IIT B52 Antifoam Impact Upon PBA Hydrolysis Kinetics (U)", WSRC-TR-2001-00167, Rev. 0, March 22, 2001.

[172] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Summary of Results for PHA Glass Study: Composition and Property Measurements", WSRC-TR-99-00332, September 9, 1999.

[173] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Composition and Property Measurements for PHA Phase 1 Glasses", WSRC-TR-99-00262, August 4, 1999.

[174] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Composition and Property Measurements for PHA Phase 2 Glasses", WSRC-TR-99-00290, August 18, 1999.

[175] T. B. Edwards, J. R. Harbour, and R. J. Workman, "Composition and Property Measurements for PHA Phase 3 Glasses", WSRC-TR-99-00292, August 18, 1999.