

TECHNOLOGY DEVELOPMENT FOR ALTERNATIVE HIGH-LEVEL WASTE SALT PROCESSING FLOWSHEETS AT SAVANNAH RIVER SITE

Harry D. Harmon, PNNL; Steve N. Schlahta, PNNL; Samuel D. Fink, SRTC; Dennis W. Wester, PNNL; Kenneth J. Rueter, WSRC; Joe F. Walker Jr., ORNL; Tim E. Kent, ORNL; Leon Klatt, ORNL

ABSTRACT

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

The Tanks Focus Area (TFA), a program under DOE's Office of Science and Technology, was requested to review and revise the technology development roadmaps; develop down-selection criteria; and prepare a comprehensive Research and Development Program Plan for three candidate cesium removal technologies, as well as the alpha and strontium removal technologies that are part of the overall SPP. The three candidate cesium removal processes are Crystalline Silicotitanate Ion Exchange (CST), Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP).

The SPP research and development program is focused on resolving high-risk areas for each alternative cesium-removal process by mid-fiscal year (FY) 2001 to support a DOE process selection decision by June 2001. This paper describes the results of scientific research and technology development work conducted during FY 2000 and early FY 2001.

INTRODUCTION

SRS successfully demonstrated the In-Tank Precipitation (ITP) process for salt waste treatment both on a moderate and full-scale basis with actual SRS salt waste in the 1980's. The ITP process separates the cesium isotopes from the non-radioactive salts by tetraphenylborate precipitation. During radioactive startup of ITP in 1995, higher than predicted releases of benzene occurred. Westinghouse Savannah River Company (WSRC) studies of the chemical and physical properties of the ITP process showed that the benzene release rates associated with ITP facility operation at the required process throughput could exceed process safety limits. 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.

In 1999, DOE-Headquarters asked the National Academy of Sciences (NAS) to independently review the Department's evaluation of technologies to replace ITP. As a result of the NAS

review, DOE agreed that further research and development on each alternative was required to reduce technical risk prior to a down-select. In March 2000, DOE-Headquarters requested the Tanks Focus Area (TFA) assume management responsibility for the SPP technology development program at SRS. The TFA was requested to review and revise the technology development roadmaps, develop down-selection criteria, and prepare a comprehensive Research and Development Program Plan (1) for the three candidate cesium removal technologies, as well as the alpha and strontium removal technologies that are part of the overall SPP. The three candidate cesium removal processes are Crystalline Silicotitanate Ion Exchange (CST), Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipitation (STTP). The radionuclide removal requirements for the SPP are shown in Table I.

Table I. Radionuclide Removal Requirements

Component	Saltstone Waste Acceptance Criteria (nCi/g)	Required Decontamination Factor: Average/Bounding
Cesium-137	45	7,700/40,000
Plutonium/Americium	18 (total alpha)	12/55
Uranium	18 (total alpha)	1/1
Neptunium	0.03	1/33
Strontium	40	5/26

STRONTIUM (Sr) AND ALPHA REMOVAL

The program proposes addition of monosodium titanate (MST) to remove Sr and portions of the soluble uranium (U), plutonium (Pu), and neptunium (Np). Testing completed in FY 2000 and earlier helped to develop an understanding of the rate and equilibrium loading of these components as functions of temperature, ionic strength and mixing. While recent tests have shown that MST adequately meets the functional requirements for each process design, the use of alternate sorbents or technologies to remove the radionuclides of interest (i.e., Sr, Pu, and Np) may significantly improve some of the designs. Therefore, a portion of this research effort evaluated the use of alternate chemical means to remove these radionuclides. Similarly, the program has investigated means to improve cross-flow filtration performance by using chemical additives, as well as evaluating alternate solid-liquid separation technologies. The alternatives under study consider both the removal of MST and the removal of other sorbents that might replace MST.

MST Kinetics and Equilibrium

Research during FY 2000 examined MST sorption kinetics using 0.2 and 0.4 g MST/L in a 5.6 M sodium (Na) waste.(2) Results indicated intermediate removal of Sr and Pu from a 5.6 M Na solution compared to that observed for a 4.5 M and a 7.5 M Na solution. The Sr and Pu removal produced equilibrium concentrations that met process requirements under certain conditions, indicating that feed-blending strategies must consider the isotopic distribution of Sr and Pu. For Np, process requirements were not met at either MST concentration, although the addition of 0.4 g/L MST nearly achieved the limit. These results demonstrated that Sr and Pu removal rates decreased with increased Na concentration (i.e., ionic strength). The Np and U removal proved lower from the 5.6 M Na solution than the 7.5 M Na solutions. These results provided additional data for sizing Continuously Stirred Tank Reactors (CSTRs) for the STTP process and processing tanks for Sr and alpha removal unit operations in the CSSX and CST Non-Elutable Ion Exchange processes.

Alternative Alpha and Sr Removal Technologies

During FY 2000, Savannah River Technology Center (SRTC) conducted a review of available literature for data related to a number of actinide and Sr removal technologies. (3) This evaluation recommended the following sorbent materials for further testing to determine the rate and extent of removal: sodium nonatitanate (ST) in the form under development by Honeywell Performance Polymers and Chemicals (Morristown, New Jersey); SrTreat produced by Selion OY (Finland); and CST in various engineered forms, and pharmacosiderites as developed by researchers at Texas A&M University. The report also recommended evaluating precipitation with $\text{Sr}^{2+}/\text{Ca}^{2+}/\text{NaMnO}_4$. The study recommended not pursuing any testing of liquid/liquid extraction and polymer filtration methods at this time.

Physical and chemical characterization indicated that the ST samples exhibited similar particle volume distributions, which proved larger than that measured for the reference MST material. (4) In Sr and alpha removal testing, the samples exhibited lower removal capacities than MST (Figure 1). Texas A&M University review of the x-ray analyses for the ST suggests that the Honeywell samples represent a poor conversion of the sorbent to the desired structure. SRTC 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. (3) Initial results from those tests indicate much better performance of the ST and led researchers to review the earlier study. Chemical analyses indicate the vendor-defined titanium content of the samples used in the earlier study was incorrect and the experiments used less than the targeted amount of sorbent.

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 ST. (5) Testing identified no correlation between MST or ST particle size and filter flux. Any potential filtration gains from differences in particle size between the MST and ST appeared offset by changes in filter cake porosity. The dispersion of the particle size for these samples likely contributed to this behavior.

MST Filtration and Settling

Cross-flow filter testing in FY 2000 included tests at the University of South Carolina with equipment representing about $\sim 1/20^{\text{th}}$ scale (based on filter area) of the filter used in the ITP facility at SRS. (6) 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.

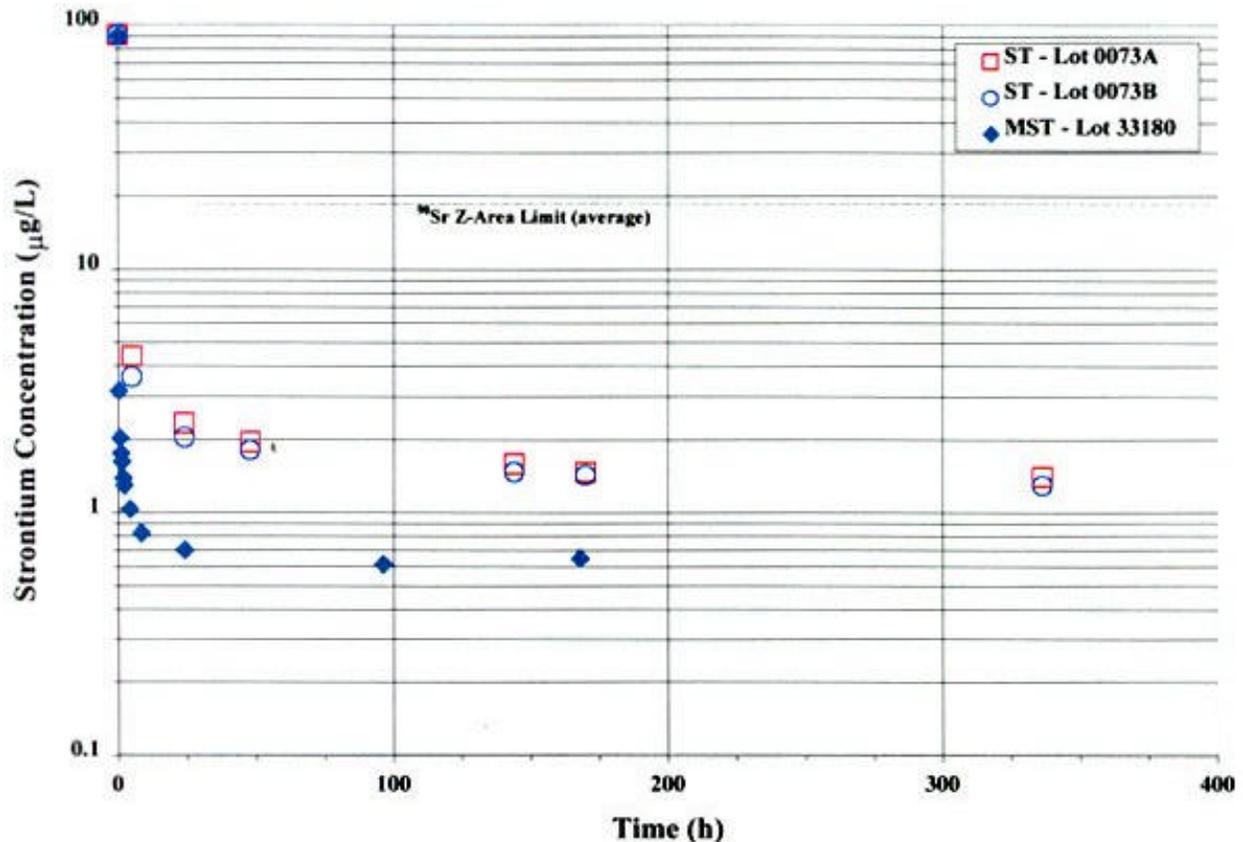


Fig. 1. Strontium Removal with Sodium Nonatitanate and Monosodium Titanate

In general, the measured flux equaled or exceeded the value determined in smaller scale tests. The data from the entire range of operating conditions was used 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.

Late in FY 2000, SRTC started additional experiments to examine the use of flocculating agents or filter aids to improve separation efficiency. (7) The studies examined individual additives and blends based in part on past experiments and using recommendations from various consultants. Testing identified six promising additives 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.

Feed Clarification Alternatives

During FY 2000, SRTC conducted an evaluation of alternate methods for achieving the required separation of solids from liquid. (8) The review included examination of literature, discussions with vendors, and review with researchers from within the DOE complex who possess extensive experience in solid-liquid separation technologies or processes. Finally, a workshop was conducted with representatives from SRS 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 remains 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 will examine improvements in filtration by combining the two separation stages as well as the addition of flocculating additives. If flocculation with cross-flow filtration proves ineffective, the program will investigate high shear filtration as well as flocculation in combination with centrifugation.

CST NON-ELUTABLE ION EXCHANGE

In the CST Non-Elutable Ion Exchange process, after alpha and Sr-90 removal, the salt solution is processed through an ion exchange column loaded with CST to remove Cs. The ability of CST to remove Cs from aqueous solutions as a function of temperature and waste composition has been investigated. Potassium (K), Sr, nitrate, and hydroxide (OH) are known to impact the equilibrium loading of Cs on CST. The most significant CST issue is its stability in highly alkaline solutions. Leaching of materials used in manufacturing the resin and column plugging have been observed in previous testing. This has led to a program to evaluate re-engineering the resin manufacturing process. Also, loaded CST must be transferred as slurry to DWPF, and the sludge, CST, and glass frit mixture must be homogeneously mixed and accurately sampled prior to feeding the melter.

CST Chemical and Thermal Stability

Recent CST batch and column tests at SRS and Oak Ridge National Laboratory (ORNL) have suggested that CST performance is degraded by contact with waste simulants and have demonstrated column plugging. These results led to concerns about the operability regime of the sorbent materials. These tests include:

- 1) IONSIVTM IE-911 pretreated with sodium hydroxide (NaOH) formed niobium (Nb)-rich solids that plugged the top layer (i.e., entrance region) of a column. Analyses of the pre-wash solutions also showed high concentrations of Nb.
- 2) IE-911 exposed to alumina-containing simulant (i.e., average salt simulant) nucleated the growth of the sodium aluminosilicate phases, such as cancrinite, on the surface of the bound pellets, thus cementing the pellets together and filling interstitial spaces.
- 3) High temperature exposure (50-120°C) of IE-911 resulted in loss of Cs capacity (9) and almost complete degradation of CST at 120°C.

To understand the cause and mechanism of these phenomena and thus avoid future performance degradation issues, a comprehensive series of pretreatment, simulant treatment, and column and batch studies were conducted in a multi-laboratory effort. The treatment experiments are being performed at SRTC, (10) ORNL, and Pacific Northwest National Laboratory (PNNL); and samples are being analyzed at Sandia National Laboratories (SNL).

Characterization studies (11,12) have shown:

- In addition to binder and CST, the as-received IE-911 contained three impurity phases including a niobium titanate. This phase may be the source of the niobium oxide-rich column plug, which formed during pre-treatment with recirculating NaOH.
- IE-911 pretreated with simulant exhibited cracking/exfoliation upon preparation for electron-microscopy studies. Increased temperature or time of exposure of IE-911 to simulant (both aluminum containing and aluminum-free) resulted in accelerated morphology (cracking/exfoliation) changes. Subsequent studies showed that the cracking/exfoliation occurred as a result of heating under applied vacuum during sample preparation. In any case, the cracking/exfoliation did not appear to affect Cs distribution coefficient values.
- IE-911 treated with alumina-containing simulant resulted in hexagonal nitrate cancrinite-type sodium aluminosilicate formation on pellet surfaces. Cancrinite formation increased with increasing temperature and time of simulant exposure. Cancrinite deposition correlated with Cs distribution coefficient drop.
- Exposure of IE-911 to simulant at 23-80°C did not significantly change the composition of the pellets. Exposure to simulant at 120°C resulted in almost complete decomposition of the CST.

Future work includes characterization of the short-term exposure samples from PNNL; characterization of simulant-treated samples from SRTC, ORNL, and PNNL; and confirming the identity of the niobium titanate impurity as a source of Nb oxide in plug formation.

Alternative Pretreatment of IE-911

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

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

These results (13) 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. (14)

Revised Manufacturing Process

Collaboration with UOP LLC (UOP) to develop an engineered form of CST (IE-911) compatible with SRS waste continues in FY 2001. A schedule for production of test batches of reformulated materials and for holding project review meetings is being followed. Product specifications (target definition) were defined for these test batches.

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

Initial efforts to improve IE-911 by UOP are focusing on the post-treatment step. The goal is to reduce the quantity of leachable components from the product. A test batch of 100 g was sent to SRTC in mid-November 2000, for testing and characterization.

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

Cs Loading Under Irradiation

One concern associated with deployment of CST is the effect of gas generation from radiolysis of water within the operating CST flow-through column. Calculations and testing were performed in FY 2000 to determine the effect of gas generation on the performance of CST in a flow-through column. The calculations indicated that the formation of gas bubbles within the small pores of CST (i.e., intraparticle bubble formation) was not likely. (15,16)

Batch tests performed by SRTC in FY99 indicated that a loss of CST capacity could be expected when irradiated under processing conditions. Additional testing examined this aspect of Cs-removal performance in the presence of gas generation. (17) A spent-fuel element in the High Flux Isotope Reactor pool was used for a radiation exposure test. This test measured Cs absorption in the presence of a radiation field and the associated radiolytic gas generated.

A test capsule containing a small flow-through column packed with ~20 mL of CST was designed and fabricated for insertion and irradiation in a spent fuel element of the High Flux Isotope Reactor test facility. The column was connected to simulant feed and coolant transfer lines were routed vertically upward through and out of the pool via an access port to the feed station transfer pumps and holding vessels. Simulant containing non-radioactive Cs was pumped to the CST column using low-pulsation gear pumps in order to load the Cs onto the CST. The

radiation dose received by the column of CST was representative of that expected for treatment of SRS HLW supernate. The test system was designed for continuous feed of simulated HLW supernate containing nonradioactive Cs and included a cooling system to maintain the temperature of the column below 35°C. Samples of the supernate were collected every 4 hours for Cs analysis and a Cs-loading curve was generated from the data. The loading curve was compared to baseline column performance data to determine the effect of radiolytic gas generation on CST loading capacity and mass-transfer zone length. The results indicated no significant effect of the radiation field on Cs loading (Figure 2).

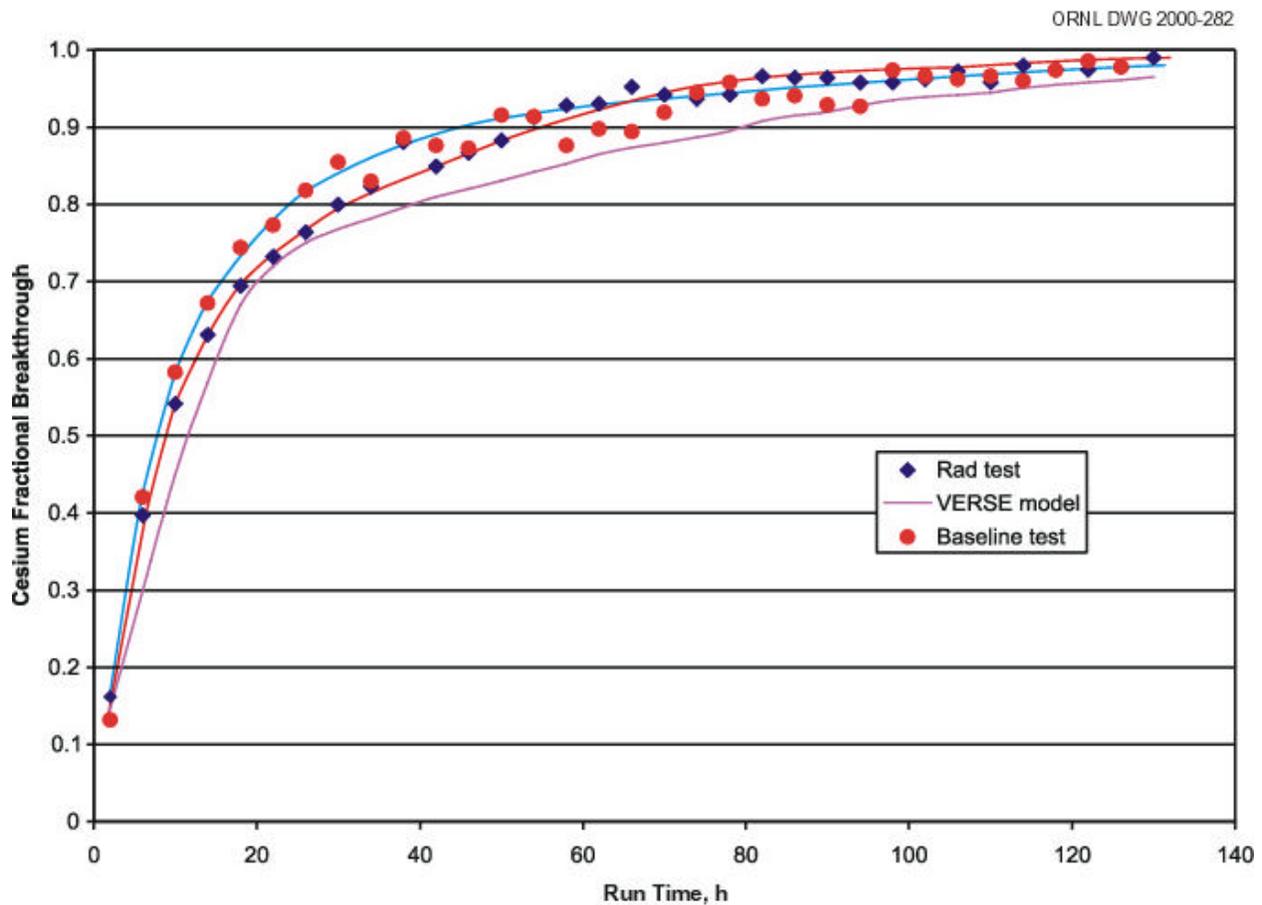


Fig. 2. Cesium Fractional Breakthrough Curves

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

Develop and Test Size-Reduction Method

Size reduction of CST particles is required to ensure that homogenous slurries can be produced and sampled representatively. FY 2000 CST grinding equipment tests ground approximately 50 pounds of solids at IKA Works and Micro Grinding Systems. The IKA equipment best satisfied the process selection criteria. Spent ion-exchange sorbent was expected to be significantly cleaner than similar zeolite slurry used at the DOE's West Valley Demonstration Project (WVDP) in New York. The spent CST sorbent should not contain tramp metal and should therefore be more suitable for size reduction with the IKA equipment. However, based on WVDP experience, it was also highly desirable to evaluate the Micro Grinding equipment for CST particle size reduction. It was also anticipated that it would be more difficult to control the particle size with the Micro Grinding system and that additional work would be required to establish optimum operating parameters, such as slurry concentration and flow. This equipment is mechanically very simple, however, which may facilitate its use in radioactive service.

The results of these preliminary experiments give a clear indication that size-reduction of CST particles presents little risk to their use. (18) According to data, it should be possible to reduce the size of CST particles so that homogeneous slurries can be produced and sampled representatively.

Develop Representative Sampling of CST/Sludge/Frit Slurry

Operation of the Hydragard® sampler, used in DWPF, with slurries of size-reduced CST was compared to operation with sludge/frit slurries in order to determine minimal size distributions for adequate CST slurry sampling. (19) Samples taken by the Hydragard® sampler showed a bias toward low frit with or without size-reduced CST present. Thus, the operation of the Hydragard® sampler itself will be re-assessed. However, it was concluded that CST was sampled using the same method as the sludge and that a representative sample would be obtained in the DWPF.

CAUSTIC SIDE SOLVENT EXTRACTION

The CSSX process uses a novel, four-component solvent to remove Cs from the alkaline salt stream in a series of countercurrent centrifugal contactors. Technology needs for CSSX are derived primarily from the immaturity of the solvent extraction process. Recent chemical and radiation stability measurements have shown that the solvent mixture is much more stable than originally anticipated. Extraction kinetics for solvent mixtures were found to be more than adequate for application to salt processing. Also, bench-scale extraction studies are being conducted to determine if the dual performance goals (decontamination factor [DF] of 40,000 and concentration factor [CF] of 12) can be simultaneously achieved, particularly with real waste.

Batch Equilibrium with External Irradiation of Solvent

The preliminary solvent irradiation tests were performed with simulated waste solution. These preliminary tests determined the susceptibility of a calixarene-based solvent system to radiation

damage.(20) A few limitations existed in these preliminary tests; the solutions were not continuously agitated, and irradiation exposure only occurred in the presence of simulated waste solution. The solvent matrix has since been changed 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. (21) These tests examined the impact of the following variables: modifier alkyl group structure, diluent, and mixing.

Four different solvents were studied in these experiments. All of these solvents employed calix[4]arene-bis(t-octylbenzo-crown-6) (BOBCalixC6) as the extractant and tri-n-octylamine as an additional modifier. 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 the 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, so 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. The organic-to-aqueous (O/A) ratios present in each test represented the O/A ratio anticipated in the proposed process. No significant degradation of the primary solvent components was observed for doses typical of the proposed facility lifetime. Less than 10% BOBCalixC6 loss occurred at doses up to 16 Mrad. No statistically significant loss of Cs-7SB modifier occurred at a dose of 16 Mrad. Less than 10% of the tri-n-octylamine degraded at a dose of 6 Mrad. At 16 Mrad the concentration of 4-*sec*-butylphenol was ~0.4% of the initial modifier concentration. It should be noted that the estimated annual dose that the solvent will receive in the proposed process plant is 0.1 Mrad.

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

Solvent Stability and Cleanup of Degraded Solvent

The chemical and thermal stability of the CSSX solvent have been studied. No degradation of the BOBCalixC6 was observed following continuous contact with alkaline nitrate simulant for up to 570 hours at $53 \pm 2^\circ\text{C}$. A thermal stability study spanning 110 days at 60°C showed no change in solvent performance, as measured by the Cs distribution coefficient determined from a batch extraction, scrub and strip protocol. Although the solvent in contact with the 0.05 M nitric acid scrub solution had a slight yellow tint, electrospray-mass spectroscopic measurements failed to detect any evidence of nitrated products. A trace amount of dioctylamine was detected, suggesting some decomposition of trioctylamine had occurred. Partitioning of solvent components and potential organic compounds contained in the waste were also studied. Annual solubility losses to the aqueous output streams will be <15% for the low cost modifier and <1% for the calixarene. Some organic compounds in the waste feed will partition to the organic

phase; however, these compounds remove easily by alkaline washing, suggesting that the extraction segment of the flow sheet may be self-purging.

Contactors Tests using SRS Simulant Waste and Internal Cs-137 Irradiation

Studies of the "second generation" CSSX solvent with 2-cm contactors were initiated in FY 2000 at Argonne National Laboratory. Work with large contactors is being performed at ORNL to increase the reliability of engineering design extrapolations. Prior to FY 2000, no studies with the CSSX solvent and contactors larger than 2-cm had been performed. Commercially available 5-cm contactors were procured for these studies.

Throughput and phase separation. Initial hydraulic testing was performed using a single centrifugal contactor stage.(22) 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.

Mass transfer. Testing also involved contacting a solute-containing phase with an opposing phase in a single, 5-cm centrifugal contactor and a four-stage contactor assembly. (23) 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 previous throughput/phase separation testing. Both flowrates and contactor speeds were varied to investigate possible effects of residence time on mass transfer performance. Prior to testing, samples of both feed solutions were collected and equilibrated under controlled conditions. Solute concentrations in the equilibrated phases were used to determine equilibrium distribution coefficients. These values were compared against results from contactor testing to determine stage efficiency values. Stage efficiencies > 80% were measured.

Hydraulic performance. A test apparatus was designed, fabricated, and assembled for experiments designed to ascertain the impacts that solvent decomposition products (from internal irradiation of the CSSX solvent) may have on the hydraulic performance of the centrifugal contactors. (24) Preliminary test results for a radiation dose equivalent to two years of plant operation have not identified any contactor hydraulic performance issues.

Waste Simulant 2-cm Contactor Flowsheet Tests

The CSSX process to remove Cs from SRS HLW was tested in a minicontactor (2-cm centrifugal contactor). In the first phase of this effort, the minicontactor stage efficiency was improved from 60 to 80% so that the complete CSSX flowsheet could be carried out in 32 contactor stages. Then, using a 32-stage unit, the CSSX flowsheet was demonstrated, first without solvent recycle, and then with solvent recycle. (25) Two tests of the CSSX process were made without solvent recycle. The first flowsheet test ran well early in the test, but the Cs

concentration in the aqueous raffinate concentration climbed with time. The decrease in the DF with time was attributed to a temperature rise in the extraction section.

In the second flowsheet test without solvent recycle, the feed temperature was controlled by: 1) cooling the laboratory from 25 to 18°C; 2) cooling the simulant feed to the contactor in an ice bath; 3) not turning on the rotors in the extraction section until they were needed; and 4) turning on the rotors in the scrub and strip sections one hour before the test. As shown in Figure 3, this second CSSX flowsheet test without solvent recycle worked very well over the entire two-hour test period. The CF quickly increased to 16.0 ± 0.9 . The stripping factor was high throughout

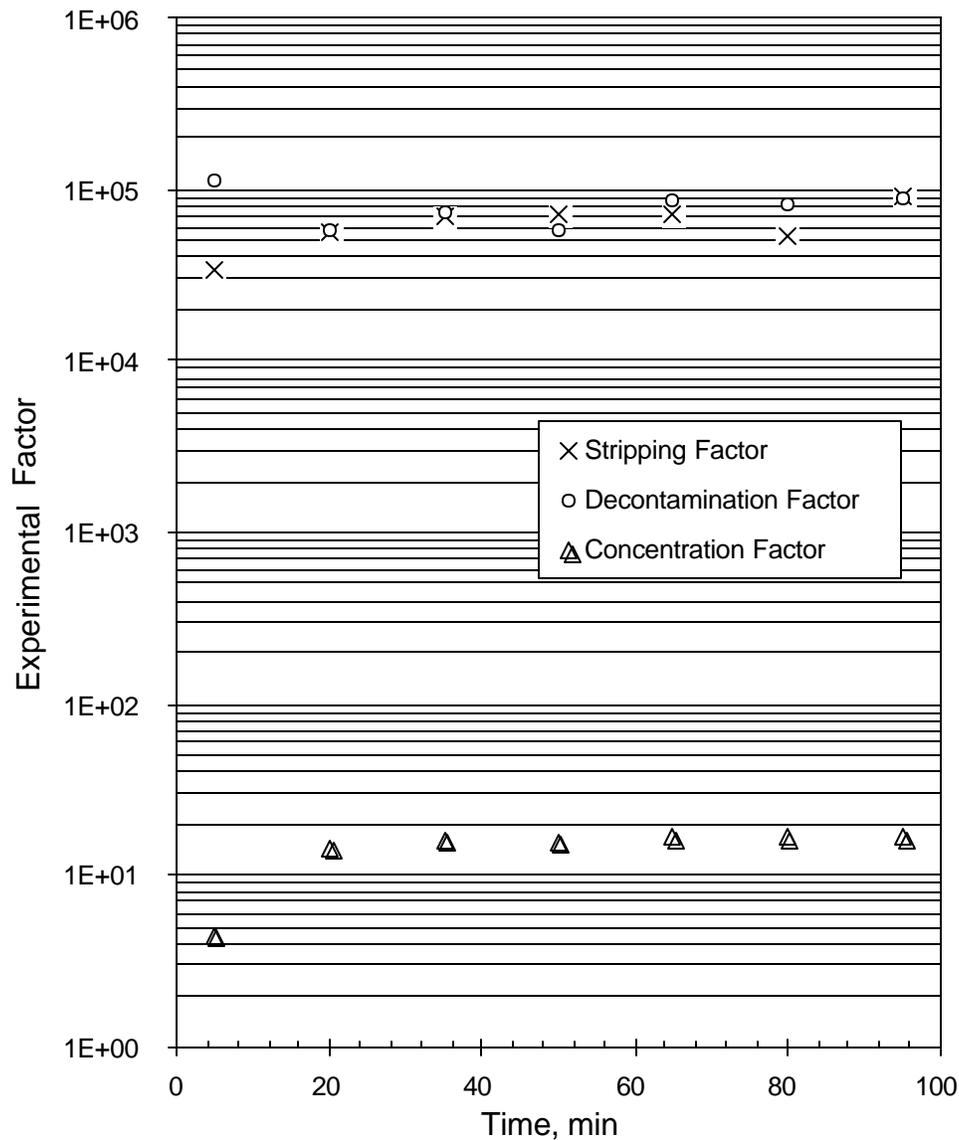


Fig. 3. Change in the Stripping, Decontamination, and Concentration Factors with Time for 2-cm Centrifugal Contactor Flowsheet Test without Solvent Recycle

the test with an average value of $74,000 \pm 13,000$ after the first five minutes. The DF was high throughout the test with an average value of $69,000 \pm 14,000$ after the first five minutes. The temperature of the aqueous raffinate never exceeded 32°C ; it rose from 22 to 29°C during this second test.

The CSSX flowsheet with solvent recycle was very similar to the first two tests except that the solvent was recycled four times. To achieve this much recycle, the test lasted three hours. After correcting initial hydraulic problems, the process operated with a CF of 14.6 ± 1.1 , a DF of $82,000 \pm 17,000$, and a stripping factor of $117,000 \pm 20,000$. The stripping factor was obviously adequate for the solvent to be recycled. It kept the Cs concentration in the recycled solvent low and allowed the extraction section to perform well. The temperature management plan was also successful.

SMALL TANK TETRAPHENYLBORATE PRECIPITATION

The STTP is a continuous precipitation process that mixes salt solution, sodium tetraphenylborate (NaTPB), a slurry of MST, spent wash water, and dilution water in a Continuously Stirred Tank Reactor (CSTR). Under optimum conditions obtained in the CSTR, soluble Cs and K precipitate as tetraphenylborate (TPB) salts and MST sorbs Sr and actinides. The salts and MST solids are readily filtered to achieve the desired DF, but the process has inherent risks due to the catalytic decomposition of TPB (to form benzene) and foaming of the slurry. Extensive product decomposition studies were conducted to identify the key catalysts and reaction mechanism. Also, effective antifoam performance has been demonstrated in CSTR tests with radioactive simulant and real waste.

Tetraphenylborate Decomposition Studies

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. The workscope to address these issues contains three primary elements: 1) developing an increased understanding of the catalyst system, 2) evaluating the catalytic activity in HLW samples, and 3) demonstrating the performance of the CSTR system in the presence of a significant decomposition.

To develop an increased understanding of the catalyst system, experts in the field of catalysis 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 Palladium (Pd) and/or mercury (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;(26,27) additional tests are being conducted in FY 2001.

The second aspect of this work continues to examine the catalytic activity of real waste. These tests will not only provide insight into the potential reaction rates that may be observed with real waste, but will also provide insight into the catalytic mechanism based on extensive analysis of the waste composition. In FY 2000, six SRS waste tanks were sampled for characterization and testing. Based on historical knowledge, these tanks were selected to be representative of the SRS

storage tank waste and to bound the catalytic decomposition rates. Tests with these tank wastes were initiated in late FY 2000 and continue in FY 2001.

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 decontaminated salt solution even in the presence of a significant decomposition reaction. Work completed in FY 2000 defined a simulated catalyst system using reduced Pd supported on alumina, for use in the 20-L CSTR tests. An SRS average waste salt solution was used during these tests. The objective of the test, based on benzene generation data from studies of HLW Tank 48, was to achieve a benzene generation rate of 10 milligram per liter-hour (mg/[L-h]) at 10 wt% solids in the concentration tank. At 25°C and 7.5 wt% solids in the concentrate tank, a benzene generation rate of 15 mg/(L-h) was achieved. As a result, the following catalyst system was recommended for the 20-L test system at ORNL: 7.8 mg/L Pd(0) on alumina powder, 80 mg/L Hg(II) nitrate, 720 mg/L benzene, 500 mg/L phenylboronic acid, and 1000 mg/L IIT B52 antifoam.(28)

In summarizing work completed during FY 2000, substantial progress was made in characterizing and understanding the catalytic decomposition mechanism. Major progress included: 1) contracting experts 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), platinum(0), rhodium(0), and ruthenium(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 silver and cadmium did not; 6) demonstrating that bi-metallic complexes between Pd and copper, iron, rhodium, or ruthenium showed no significant synergistic effects; and 7) showing that Pd(II) reduced in simulated waste to form nanoclusters, some of which incorporated Hg.

Cs Precipitation Kinetics

A 20-L CSTR test of the STTP process to evaluate the decontamination and the antifoam efficiency was completed during FY 2000. (29) The system used in the test for FY 2000 included two CSTRs operating in series and was a single-pass, 72-hour test with an 8-hour residence time in the CSTRs. The slurries in each vessel were mixed at 1200 to 1250 rpm while maintaining the temperature at 25°C. In this test 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 DF values for Cs, Sr, and U exceeded the Waste Acceptance Criteria standards needed for filtrate disposal in saltstone (Figure 4). High-pressure liquid chromatography analyses showed that no measurable NaTPB decomposition occurred during the test.

An additional 20-L CSTR test was initiated in early FY 2001. The test used a simulated catalyst [Pd(0) on alumina], the new recommended antifoam, and did not recycle wash water. Run 4 was initiated at 25°C and benzene was not added to the system; this was done to determine if the decomposition reaction would initiate in the absence of benzene. After ~16 hours of operation, no benzene was detected in the headspace of any tanks in the system. Subsequently, benzene

Cs DF

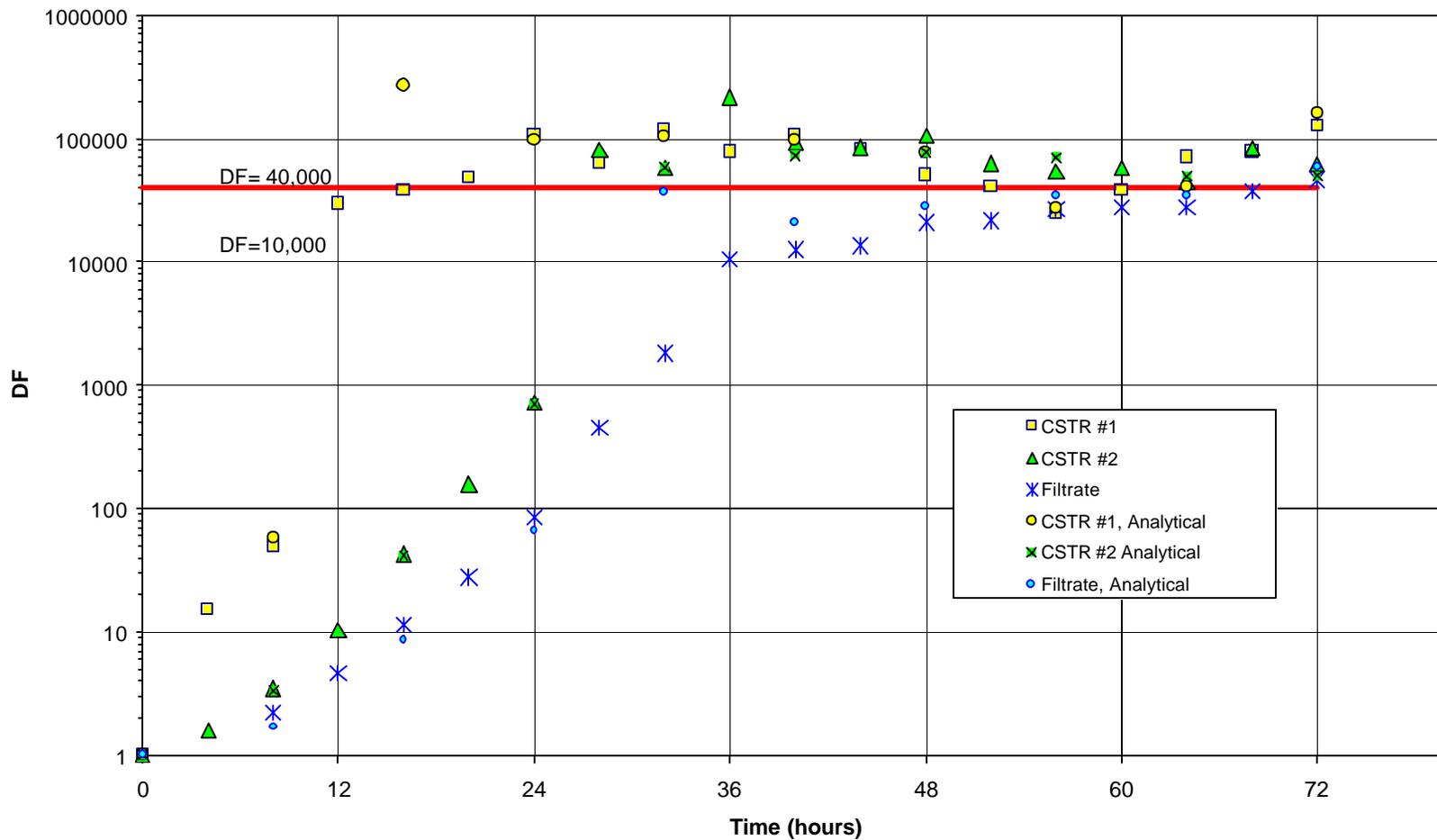


Fig. 4. Test 3 Cesium-137 DF

was added to the first CSTR. After ~30 hours of operation, in-cell counting indicated that Cs DF on the order of 40,000 was attained and the benzene generation rate was >30 mg/(L-h) in the first CSTR. During this period, the benzene generation rate was ~3 times the target value, indicating that tetraphenylborate (TPB) was actively decomposing. Operation at 25°C continued until a target value of ~10 wt% solids were obtained in the concentrate tank. During the entire 25°C operation, Cs DF was maintained between 15,000 and 40,000 in all tanks, which exceeds design requirement for a Cs DF >10,000 for the STTP process.

The temperature of the 20-L CSTR system was then raised to 45°C after reaching ~10 wt% solids in the concentrate tank. The increased temperature resulted in an increased benzene generation rate, indicating that the rate of decomposition increased. However, the DF was maintained during the entire 45°C operational period. This significant result indicates the robustness of the CSTR operation, even well above normal operating temperatures.

A real waste CSTR test will be conducted in FY 2001 utilizing two 1-L CSTRs in series. During initial operation at 25°C, it will be determined if the system can meet the design DF for Cs, Sr, and alpha emitters. The Cs DF must be maintained at >10,000 for at least two system turnovers. The antifoam developed and selected based on previous testing will be utilized in this real waste CSTR test and stable operation will be demonstrated. After operation at 25°C, the temperature will be raised to 45°C to determine the reactivity of catalysts present in the real waste sample and to evaluate the robustness of the process. This task will be conducted following the completion of 1/4000-scale CSTR testing.

Antifoam Development

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 a known expert in the field of foam formation at the Illinois Institute of Technology (IIT). IIT studied the foaming problem in a 10% potassium tetraphenylborate (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.(30) The IIT mechanism involves disintegration of the KTPB particle structure at the gas/liquid interface. After the IIT B52 was identified as the best performer in tests by IIT and SRTC,(31) it was recommended for demonstration in the 20-L CSTR test system at ORNL. The 20-L antifoam test demonstrated that the IIT B52 antifoam was effective at controlling the foam in both CSTRs and in the concentrate tank.

Washing and Filtration Studies

Bench scale tests were conducted during FY 2000 to determine the effect of the various antifoams on the recovery of NaTPB during the washing phase of the process.(31) Recovery of TPB with no antifoam typically averaged ~60%. With the IIT B52 antifoam (which gave the best results as an antifoaming and defoaming agent) the NaTPB recovery dropped to 13%. Washing tests were also used on the sludge from the third 20-L CSTR run at ORNL, which also

used the IIT B52 antifoam agent. These washing tests indicated that ~10% of the excess TPB was recovered.(29)

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 indicated that the low recovery of NaTPB was not a major impact on the economics of the STTP process. Additional work on the NaTPB will be conducted, if needed, after the down-selection process has been completed.

SUMMARY

Evaluation of technical issues and concerns identified in previous phases of SPP led to a narrowed list of issues that are believed to represent high technical risks to implementation of the three alternative Cs removal processes and the required Sr and actinide removal. The Tanks Focus Area prepared an integrated Research and Development Program Plan(1) describing the activities required to satisfactorily resolving these issues prior to a technology down-selection decision. Tests to resolve these issues have been conducted with simulated wastes. Final confirmations of key parameters and flowsheet demonstrations have been conducted with real waste samples. The program remains focused on providing the needed results to support a DOE down-selection decision by June 2001.

REFERENCES

1. "Savannah River Site Salt Processing Project Research and Development Program Plan", PNNL-1253, Rev. 1, Pacific Northwest National Laboratory (2000).
2. D. T. HOBBS, "Phase V Simulant Testing of Monosodium Titanate Adsorption", WSRC-TR-2000-00142, Westinghouse Savannah River Company (2000).
3. 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, Westinghouse Savannah River Company (2000).
4. 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, Westinghouse Savannah River Company (2000).
5. M. R. POIRIER, "Filtration of Sludge and Sodium Nonatitanate Solutions", WSRC-TR-2000-00290, Westinghouse Savannah River Company (2000).
6. V. VAN BRUNT et al., "Final Report on the Crossflow Filter Optimization with 5.6 M Salt Solution", USC-FRED-PSP-RPT-09-A-015, University of South Carolina (2001).
7. M. R. POIRIER, "Task Technical and Quality Assurance Plan for the Sludge/Mono-Na Titanate (MST) Filtration Test Program", WSRC-TR-99-00483, Westinghouse Savannah River Company (1999).
8. M. R. POIRIER, "Evaluation of Solid-Liquid Separation Technologies to Remove Sludge and Monosodium Titanate from SRS High Level Waste", WSRC-TR-2000-00288, Westinghouse Savannah River Company (2000).

WM'01 Conference, February 25-March 1, 2001, Tucson, AZ

9. P. A. TAYLOR and C. H. MATTUS, "Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent - Interim Report, ORNL-TM-2000/307, Rev. 0, Oak Ridge National Laboratory (2000).
10. 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, Westinghouse Savannah River Company (2000).
11. M. NYMAN, et al., "Characterization of As-Received, Pre-Treated, and Simulant-Treated IE-911 (UOP Batches 98-5, 99-7, and 99-9)", Interim Report, Westinghouse Savannah River Company (2000).
12. Y. SU, et al., "Chemical and Thermal Stability Studies of Cs-Loaded IE-911 (Interim Report)", PNNL-13392, Pacific Northwest National Laboratory (2000).
13. 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, Westinghouse Savannah River Company (2000).
14. J. L. KRUMHANS�, et al., "A Preliminary Assessment of IE-911 Column Pretreatment Options", Sandia National Laboratory (2000).
15. T. HANG and D. D. WALKER, "Gas Generation and Bubble Formation Model for Crystalline Silicotitanate Ion Exchange Columns", WSRC-TR-2000-00177, Rev. 0., Westinghouse Savannah River Company (2000).
16. F. F. FONDEUR, D. D. WALKER, W. R. WILMARTH, and S. D. FINK, "Bubble Formation Modeling in IE-911", WSRC-TR-2000-00177, Rev. 0, Westinghouse Savannah River Company (2000).
17. A. J. MATTUS, et al., "Study of the Potential Impact of Gamma-Induced Radiolytic Gases Upon Loading of Cesium Into Crystalline Silicotitanate Sorbent at the High Flux Isotopes Reactor", ORNL/TM-2000/362, Oak Ridge National Laboratory (2000).
18. R. C. ODOM and F. G. SMITH, III, "CST Particle Size Reduction Tests", WSRC-TR-2000-00350, Rev. 0, Westinghouse Savannah River Company (2000).
19. T. B. EDWARDS, et al., "Hydragard Sampling of Melter Feed Slurry Containing CST (U)", WSRC-TR-2000-0378, Rev. 0, Westinghouse Savannah River Company (2000).
20. C. L. CRAWFORD, et al., "Radiation Stability of Calixarene Based Solvent System", WSRC-TR-98-00371, Westinghouse Savannah River Company (1998).
21. R. A. PETERSON, et al., "Solvent Extraction External Radiation Stability Testing", WSRC-TR-2000-00413, Rev. 0, Westinghouse Savannah River Company (2000).
22. 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, Oak Ridge National Laboratory (2000).
23. 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, Oak Ridge National Laboratory (2000).
24. D. E. BENKER, "Experimental Test Plan for Contactor Loop Tests Using SRS Simulant Waste with ¹³⁷Cs Internal Irradiation", Experimental Test Plan No. 3 for TTP ORNL-CTD-2, Rev. 0, Oak Ridge National Laboratory (2000).

WM'01 Conference, February 25-March 1, 2001, Tucson, AZ

25. R. A. LEONARD, et al., "Proof-of-Concept Flowsheet Tests for Caustic-Side Solvent Extraction of Cesium From Tank Waste", ANL-00/30, Argonne National Laboratory (2001).
26. R. A. PETERSON and M. J. BARNES, "Results of Experimental Investigation into Noble Metal Catalyzed Decomposition of Sodium Tetraphenylborate", WSRC-TR-2000-00230, Westinghouse Savannah River Company (2000).
27. L. J. OJI and M. J. BARNES, "Batch Studies of Sodium Tetraphenylborate Decomposition on Reduced Palladium Catalyst" (WSRC-TR-2000-00459), Rev. 0, Westinghouse Savannah River Company (2000).
28. M. J. BARNES, et al., "Tetraphenylborate Catalyst Development For the Oak Ridge National Laboratory 20-L Continuously Stirred Tank Reactor Demonstration", WSRC-RP-2000-00457, Rev. 0, Westinghouse Savannah River Company (2000).
29. D. D. LEE, "Test Results for CSTR Test 3", Workaid Number: CERS/SR/TPB/011, Oak Ridge National Laboratory (2000).
30. D. P. LAMBERT, "Final Report: Illinois Institute of Technology Antifoam Recommendation to SRTC", WSRC-TR-2000-00297, Rev. 0, Westinghouse Savannah River Company (2000).
31. M. A. BAICH, et al., "Laboratory Scale Antifoam Studies for the STTPB Process (U)", WSRC-TR-2000-00261, Rev. 0, Westinghouse Savannah River Company (2000).