Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

SRNL-STI-2008-00426

The Role of Liquid Waste Pretreatment Technologies in Solving the DOE Clean-up Mission

W. R. Wilmarth, Savannah River National Laboratory
M. E. Johnson, CH2M Hill Hanford Group Inc.
G. Lumetta, Pacific Northwest National Laboratory
M. R. Poirier, Savannah River National Laboratory
M. C. Thompson, Savannah River National Laboratory, Retired
N. Machara, DOE Office of Engineering and Technology

October 2008

Executive Summary

The improvement of liquid waste pretreatment technologies over the past fifty years has been remarkable, and the role of pretreatment technologies in accomplishing the Department of Energy's cleanup mission continues to evolve even as significant design and construction efforts are underway on large-scale projects such as the Waste Treatment Plant at Hanford and the Salt Waste Processing Facility at the Savannah River Site (SRS).

The selection of a pretreatment technology is a complex scientific and economic decision and must typically be made years ahead of the implementation date. In the interim, new pretreatment technologies emerge.

The Department of Energy's strategy for treating radioactive liquid waste stored in tanks at its Hanford and Savannah River sites consists of first separating the waste into high activity and low activity waste fractions through a pretreatment process. The high activity fraction is then immobilized in a glass form suitable for shipment to a national repository, while the low activity waste is immobilized in a waste form suitable for disposal at the respective site.

However, the specific technologies for pretreatment as well as immobilization differ at the two sites. At least four key factors have influenced the technology decisions regarding pretreatment of radioactive liquid waste at Hanford and Savannah River:

- First, requirements for low activity waste evolved differently at the two sites;
- Second, the tank wastes originated from different processes so have different compositions;
- Third, the time frame for technology decisions has been different, so the maturity of the technologies as well as other relevant information differs between the two sites.
- Fourth, the magnitude of the removal of a key radionuclide may not originate from a regulatory requirement. Instead, a specific facility design feature may drive the radionuclide decontamination factor.

Tables that summarize these factors are given below.

The general strategy for pretreatment involves a separation of insoluble solids from soluble salts, such as through dissolution and filtration, and then further treatment of the soluble fraction to remove key radionuclides such as cesium, strontium, actinides, and potentially technetium. The remaining soluble fraction, with radionuclides removed, is immobilized as low activity waste. The insoluble solids contain uranium and transuranics as well as Fe, Bi, Cr, Al, Mn, Hg and other elements, which in processing are combined with the cesium and other soluble radionuclides for treatment as high-activity waste.

The insoluble solids may be subject to caustic leaching to remove aluminum and chromium if economically advantageous, with the solubilized aluminum- and/or chromium-laden stream processed as low activity waste. Depending on the tank waste composition, a selective dissolution may be used during retrieval to reduce the processing requirements of some waste. Depending on the composition of certain saltcake tank wastes, a fractional crystallization process may be used to separate sodium from other constituents as a low-activity waste stream.

A number of technology options are available for these separations and are summarized in the table with the appropriate application.

Table 1. Summary of Low Activity Waste Requirements

Facility	**Basis**	**Target**	**Analyte Concentration in feed to Stabilization Facility**	**Requirements**
Savannah River: Saltstone Disposal Facility	Waste Determination	Cs-137	5.06E4 pCi/mL	90% Permit Limit
		Sr-90	2.87E5 pCi/mL (2.87 E-7 Ci/ml)	90% Permit Limit
		Total Alpha	2.5E4 pCi/mL (45 nCi/g)	94% Permit Limit NRC Class A
Hanford Site Integrated Disposal Facility	NRC agreement similar to WIR requirements: key radionuclide removal to the maximum extent technically and economically practical and Class C limits on waste per 10CFR part 61; contract requirements in addition: Cs < 3Ci/m^3; Sr < 20Ci/m^3; Bulk Vit feed spec Cs < 0.0012 Ci/mole Na, or DF > 50 to handle 200 West SST's.	Cs-137	1.05E5 pCi/L	ALARA Limit
		Sr-90	20 Ci/m^3	
		Total Alpha	100 nCi/g	

Table 2. Summary of Tank Waste Processes and Characteristics

	Hanford		**Savannah River**	
Number of Tanks	177		51	
Total Waste Volume	56.5 M gallons		36.5 M gallons	
Supernate Volume/Curies	21.9 M gal	47.7 MCi	16.9 M gal	200 MCi
Saltcake Volume/Curies	23.4 M gal	37.5 MCi	16.6 M gal	12 MCi
Sludge Volume/Curies	11.2 M gal	109 MCi	3.0 M gal	185 MCi
Radioactivity disposed as LAW (lifecycle)	5.3 M Ci		3-5 MCi (Waste Determination)	
Major Radiochemical separations facilities/ flowsheets and listing by area	7 flowsheets T, B BiPO$_4$ U uranium recovery S redox A PUREX Z Pu production/fab/recovery B Cs/Sr Encapsulation		2 flowsheets F PUREX/Pu production H PUREX/Pu-238 production	
Other Comparisons	Both ORP and SRS tanks contain viscous alkaline liquid, sludge, and saltcake. Hanford tanks have a greater diversity of waste composition because of the variety of fuels and processes used at Hanford. About 90% of the Cs and Sr were removed at Hanford, so generally Hanford tanks have less radioactivity than SRS. SRS waste contains zeolites that were used to remove Cs, and Hanford tanks contain diatomaceous earth that was added as a liquid sorbent. Tanks at both sites contain various proportions of key radionuclides (Cs-137, Sr-90, TRU, Tc-99, I-129, C-14, Se-79, Sn-126, H-3, U) as well as phosphates, carbonates, sulfates, nitrates and other chemicals as well as debris and contaminated or broken equipment.			

Table 3. Timeline for Cesium Removal Technology Selection

Facility	Technology	Selection Date	Rationale
Hanford Waste Tanks	Potassium Cobalt Ferrocycnide	1958-1962	Desired a removal method to precipitate Cs into the sludge so decontaminated supernatant solution could be placed in unlined underground cribs.
Savannah River Waste Tanks	Non-Elutable Zeolite Ion Exchange	1960-1965	Removal of Cs from high level waste evaporator overheads prior to disposal to seepage basins.
Hanford	Elutable Cation Ion Exchange	1978-1980	Recovery Cs to make Cs capsules for use for irradiation by universities and industry.
Savannah River	Elutable R-F Ion Exchange	1983-1985	Removal of Cs from low-level radioactive wastewater to below drinking water standards prior to release to environment.
Savannah River	In-Tank Precipitation (ITP)	1983	Demonstration of ITP Proof of Principle to remove Cs from HLW
West Valley	Non-Elutable Ion Exchange - IE-96	1988 - 1995	IE-95 and TIE-96 zeolites used in ion exchange columns to treat supernates and sludge wash solutions
ORNL Melton Valley	Non-Elutable Ion Exchange – Crystalline Silicotitanate (CST)	1996	Preferred technology during down selection between CS-100, CST, potassium cobalt hexacyanoferrate, resorcinol formaldehyde resin, SuperLig 644, and an organic resin bound in a proprietary organic web structure from 3M Corporation
Savannah River	In-Tank Precipitation	1995 - 1998	Demonstration of ITP on 450,000 gallons of salt solution; halted due to high benzene production in 1998; catalytic role of metals uncovered.
Waste Treatment Plant	Elutable Ion Exchange – SuperLig 644	2000	Preferred technology during down selection between CS-100, CST, and SuperLig 644 resins. Derived from BNFL Privatization Contract and was maintained into Bechtel-URS contract
Savannah River	Caustic-Side Solvent Extraction	1998 - 2002	Preferred technology selected for the Salt Waste Processing Facility during final down-selection between CSSX, Small-tank ITP, and CST; selection began with 144 alternatives and included NAS review before final selection
Savannah River	Caustic-Side Solvent Extraction	200X	ARP-MCU built as interim processing facility and pilot-plant for CSSX technology
Waste Treatment Plant	Elutable Ion Exchange – Spherical RF	2007	Cost reduction based on demonstrated performance of new resin.
Interim Pretreatment System	TBD	2009	Needed to support Early LAW Vitrification

Table 4. Technology Summary

	Technology	**Application – feed/product composition**	**Site**	**Comparative Effectiveness (reason selected, DF, maturity in appropriate environment, etc)**
cesium removal	Elutable Ion Exchange using Superlig 664 or RF resin	Cesium removal from aqueous LAW stream	Hanford (RF resin is current selection, Superlig was previous, now backup)	Process DF = 100,000 (remove up to 99.999%) as developed, tested and designed for Hanford waste; regenerable; column loading, gas generation properties.
	Non-Elutable Ion Exchange using crystalline silicotitanate	Cesium removal from aqueous LAW stream	Hanford (early backup medium); SRS (potential selection option); also Oak Ridge	Mature technology, can meet removal requirements, with drawback of requiring frequent removal of IX medium to dispose as HLW; requires additional processing (grinder) and produces additional waste
	Caustic Side Solvent Extraction (CSSX) with BOBCalix6	Cesium removal from aqueous LAW stream	Savannah River processing and Tank Farms; SRS designed for MCU; Hanford - potential for IPS	DF > 40,000 and CF = 15 as developed, tested and designed for SRS waste, using 30 stages. If used for IPS, would require 41 stages to achieve target DF of 5000 (with CF = 5) due to waste characteristics; other DF & CF combinations require different no. stages.
	Selective Dissolution	Cesium removal during retrieval to reduce processing requirements on salt waste	Hanford –SRS selected salt waste tanks	For specific tanks (practical criteria: Cs < 0.05 Ci/L and Na > 7 M), DF about 5-10.
Sr/Actininde removal	Monosodium Titanate (MST)	Sorbent for Sr & actinides	SRS in SWPF and ARP	Effective for SRS waste but not appropriate to Hanford waste, see below.
	Permanganate treatment	Destruction of complexants for Sr and actinides, and precipitation by saturation of less soluble salts (Sr carbonate; Mn oxides/hydroxides incorporate actinides on precipitation)	Hanford WTP	Organic complexants keep Sr and actinides in solution in Hanford waste, would not absorb to MST. Organic destruction is required, followed by precipitation.
Other Rads	Tc Removal by Ion Exchange	Ix removal of Tc from aqueous LAW stream	Hanford – WTP, may be removed from flowsheet for inefficiency	Only effective for removal of pertechnetate species, other oxidation states of Tc remain in the waste stream

Solid/liquid separations	Gravity Settling (Settle-Decant)	Sludge separation from salt waste	Hanford and SRS – Past use in tank farms; SRS for sludge washing upstream from DWPF	Slow settling times, downstream impact if flocculant were added; not used as a primary separation in flowsheets
	Dead-end filtration	Solid-liquid separation	Used at ETF for carbon fines removal	Generally not used in HLW processing because of rapid fouling; performance is not steady-state
	Cross flow filtration	Steady-state process for solid-liquid separation clarifying LAW streams and concentrating washed solids	SRS, Hanford processing – past and present flowsheets	Hanford pretreatment would use 0.1 micron filters for 99.99% solids removal.
	Rotary microfilter	Steady-state process for solid-liquid separation of entrained solids prior to downstream processing, deployable at-tank	SRS, Hanford - potential use in the tank farms as a supplement to processing	Commercially available, being tested at scale with 0.1 micron filter elements. Reasonable flux in testing.
	Sludge – Al/Cr Leaching	Removal of solids by dissolution with caustic and heating on select high Al/Cr waste streams	Hanford; WTP and tank farm for Al & Cr; SRS – carried out on several tanks successfully	Combination of caustic addition and heating, followed by solid/liquid separation (filtration, settle/decant); may be used if economically practical; 79% Al dissolved for select SRS tanks with considerable (~ 3M gal) liquid generation
Sodium Separation/ Removal	Fractional Crystallization	Decontamination technology to separate Na as LAW from other constituents	Hanford – potential supplemental treatment on select tanks	In lab tests, DF > 150; In eng tests, DF = 167; Modeling, DF = 110 – 270. Sodium retention in LAW 70 – 80% (target 50%)
	Electrochemical	Potential recycle of caustic for Al leaching	Hanford – potential flowsheet addition	This technology is under development and testing for the potential application

Note: At Hanford, a determination prepared by the U.S. Nuclear Regulatory Commission (letter from Bernero, NRC, to Lytel, DOE, March 2, 1993) forms the basis of treatment requirements. The NRC agreed that the LAW fraction of the double shell tank (DST) waste would not be subject to NRC licensing authority if the Department assured that the waste:

1. had been processed (or would be further processed) to remove key radionuclides to the maximum extent technically and economically practical;

2. would be incorporated into a solid physical form at a concentration that did not exceed the applicable concentration limits for Class C low-level waste as set out in the Code of Federal Regulations (CFR) Title 10, Part 61, and
3. would be managed, pursuant to the Atomic Energy Act, so that safety requirements comparable to the performance objectives set out in 10 CFR 61 were satisfied.

The agreement preceded the Waste Incidental to Reprocessing (WIR) provisions of DOE M 435.1, but it formed the basis for the WIR requirements. In June of 1997 (letter from Paperiello, NRC, to Kinzer, DOE, June 9, 1997), NRC provided a provisional agreement that the LAW portion of the Hanford tank waste planned for removal from the tanks and for disposal on-site was incidental and was, therefore, not subject to NRC licensing authority.

Table of Contents

List of Figures

List of Tables

Introduction

The objective of this report is to describe the pretreatment solutions that allow treatment to be tailored to specific wastes, processing ahead of the completion schedules for the main treatment facilities, and reduction of technical risks associated with future processing schedules.

Wastes stored at Hanford and Savannah River offer challenging scientific and engineering tasks. At both sites, space limitations confound the ability to effectively retrieve and treat the wastes. Additionally, the radiation dose to the worker operating and maintaining the radiochemical plants has a large role in establishing the desired radioactivity removal.

However, the regulatory requirements to treat supernatant and saltcake tank wastes differ at the two sites. Hanford must treat and remove radioactivity from the tanks based on the TriParty Agreement and Waste Incidental to Reprocessing (WIR) documentation. These authorizing documents do not specify treatment technologies; rather, they specify end-state conditions. Dissimilarly, Waste Determinations prepared at SRS in accordance with Section 3116 of the 2005 National Defense Authorization Act along with state operating permits establish the methodology and amounts of radioactivity that must be removed and may be disposed of in South Carolina.

After removal of entrained solids and site-specific radionuclides, supernatant and saltcake wastes are considered to be low activity waste (LAW) and are immobilized in glass and disposed of at the Hanford Site Integrated Disposal Facility (IDF) or formulated into a grout for disposal at the Savannah River Site Saltstone Disposal Facility.

Wastes stored at the Hanford Site or SRS comprise saltcake, supernate, and sludges. The supernatant and saltcake waste fractions contain primarily sodium salts, metals (e.g., Al, Cr), cesium-137 (Cs-137), technetium-99 (Tc-99) and entrained solids containing radionuclides such as strontium-90 (Sr-90) and transuranic elements. The sludges contain many of the transition metal hydroxides that precipitate when the spent acidic process solutions are rendered alkaline with sodium hydroxide. The sludges contain Sr-90 and transuranic elements.

The wastes stored at each site have been generated and stored for over fifty years. Although the majority of the wastes were generated to support nuclear weapons production and reprocessing, the wastes differ substantially between the sites. Table 5 shows the volumes and total radioactivity (including decay daughters) of the waste phases stored in tanks at each site. At Hanford, there are 177 tanks that contain 56.5 Mgal of waste. SRS has 51 larger tanks, of which 2 are closed, that contain 36.5 Mgal. Mainly due to recovery operations, the waste stored at Hanford has less total curies than that stored at Savannah River. The total radioactivity of the Hanford wastes contains approximately 190 MCi, and the total radioactivity of the Savannah River wastes contains 400 MCi.

Table 5. Summary of Wastes Characteristics

	Hanford (System Plan, rev. 3)	Savannah River Site (LWO-PIT-2007-00062, Rev. 14)
Number of Tanks	177	51
Total Waste Volume	56.5 M gallons	36.5 M gallons
Supernate Volume/Ci	21.9 M gal / 47.7 M Ci	16 M gal / 200 M Ci
Saltcake Volume/Ci	23.4 M gal / 37.5 m Ci	16.6 M gal / 12 M Ci
Sludge Volume/Ci	11.2 M gal / 109 M Ci	3.0 M gal / 185 M Ci
Radioactivity disposed via LAW (Lifecycle)	5.3 M Ci	2.2 M Ci
Major Radiochemical Separations Facilities	7	2
Listing of Separations Flowsheets	T, B Bi PO_4 U Uranium Recovery S Redox A PUREX Z Pu Prod/Fab/Recovery B Cs/Sr Encapsulation	F PUREX/ Pu Production H PUREX/Pu-238 Production

Seven major facilities and six flowsheets were used at the Hanford Site for separations of plutonium, uranium, and fission products, whereas only two facilities and flowsheets were used at SRS for separations and recovery of plutonium and uranium. Figure 1 shows a timeline for the several chemical processes that were used over the history of the Hanford Site. Appendix A contains a description of these processes and their impacts on waste chemistry. The historical use of different flowsheets has led to significant differences in the compositions of tank wastes between the two sites.

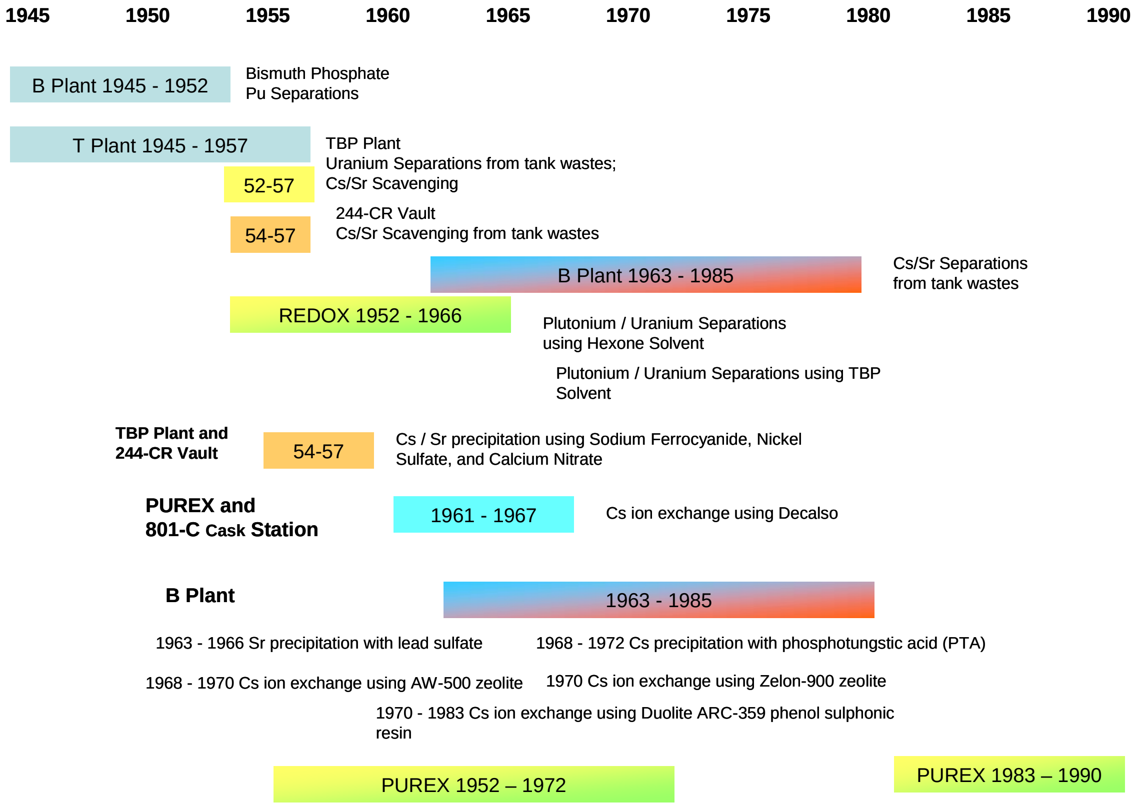


Figure 1. Timeline for Hanford Processing

At the Savannah River Site, all of the supernate and dissolved saltcake waste requires cesium removal prior to immobilization in grout in the Saltstone Processing Facility and disposal at the Saltstone Disposal Facility. According to the permits for Saltstone, cesium is limited to 45 nCi/gm of grout. Therefore, the Salt Waste Processing Facility (SWPF) is being designed to decontaminate feeds to 2.1E-04 Ci/gal. This cesium concentration is lower than the ALARA limit for Hanford feed to WTP LAW vitrification. Table 6 summarizes the cesium requirements for the Hanford LAW Waste Treatment Plant (normalized to 6M sodium) and the SRS SWPF, including the average and maximum decontamination factor (DF).

Table 6. Major Facility Cesium Requirements

Hanford Glass

Facility	Target Cs^{137} in feed and Immobilized LAW Product	Feed Source	Cs DF		Primary Driver for Pretreatment Target
			Average	Design Max	
WTP Pretreatment to LAW Glass	**3.4 E-04 Ci/gal Feed (0.3 Ci/m^3 in glass)**	**All Hanford Supernate, Saltcake, and HLW Sludge**	**1,110**	**24,400**	**WTP LAW Facility ALARA** Contact Maintenance of LAW Melters (e.g., bubler replacement) Contact Operation of LAW (e.g., Canister Closure and Handling)

SRS-Saltstone

Facility	Target Cs^{137} in feed and Immobilized LAW Product	Feed Source	Average	Design Max	Primary Driver for Pretreatment Target
SWPF Pretreatment to Saltstone	**2.1 E-04 Ci/gal Feed (45 nCi/g in Saltstone)**	**All SRS Supernate and Saltcake**	**17,000**	**40,000**	**Disposal Waste Form Criteria Section 3116 Determination for Salt Waste**

Due in part to the design and construction durations of major new DOE facilities such as WTP and SWPF and the limitations of space existing in the tank farms at Hanford and SRS, DOE initiated interim processing at SRS and has been examining alternative means of processing waste ahead of the start of WTP in 2019 and SWPF in 2012. Table 7 summarizes the cesium requirements for a number of processing options at Hanford and SRS.

Table 7. Interim Facility Cesium Requirements

Hanford Glass

Facility	Target Cs^{137} in feed and Immobilized LAW Product	Feed Source	Cs DF		Primary Driver for Pretreatment Target
			Average	Design Max	
Selective Dissolution to DBVS	**2.3E-02 Ci/gal**	**S-109/S-105**	**5**	**10**	**DBVS Contact Maintained Facility ALARA**
IPS to West Area Bulk Vitrification	**2.3E-02 Ci/gal**	**West SSTs/ SY-103**	**14**	**300**	**BV Contact Maintained Facility ALARA**
IPS to East Area Bulk Vitrification - SSTs	**2.3E-02 Ci/gal**	**East SSTs**	**10**	**400**	**BV Contact Maintained Facility ALARA**
IPS to Early LAW Vitrification	**3.4E-04 Ci/gal**	**Selected DST Supernates**	**2,350**	**5,000**	**WTP LAW Vitrification Facility ALARA**

SRS-Saltstone

Facility	Target Cs^{137} in feed and Immobilized LAW Product	Feed Source	Average	Design Max	Primary Driver for Pretreatment Target
DDA to Saltstone	**0.2 Ci/gal**	**Tank 41**	**~ 2**		**Negotiated Disposal Criteria - limited feed**
ARP-MCU to Saltstone	**0.09 Ci/gal (01 Ci/gal at 5.6 M Na)**	**Tank 24, 25 and 41**	**> 12**	**Not Specified (expect higher separations performance)**	**Negotiated Disposal Criteria - limited feed** **Shielding upgrades to Saltstone Required**

Hanford's Selective Dissolution process is intended to supply pretreated LAW solution to the demonstration bulk vitrification system (DBVS). Water is added to saltcake to displace the cesium-rich interstitial liquid. The cesium-rich interstitial liquid and some dissolved salt brine are transferred to the double-shell tank system for future processing.

The cesium-depleted saltcake is dissolved and transferred to the DBVS for vitrification. The DBVS uses an in-container vitrification unit which consists of a refractory lined steel box equipped with graphite electrodes and an off-gas hood and treatment system. The vitrified waste is contained in the refractory-lined steel box, which is disposed of along with the off-gas hood and remnants of the graphite electrodes.

The refractory-lined steel box provides additional radiation shielding, which enables a higher concentration of Cs-137 to be present in the pretreated LAW solution than allowable for the WTP LAW vitrification facility, while still meeting ALARA goals. The maximum allowable Cs-137 concentration in the feed to the DBVS is 2.3E-02 Ci/gal. Similarly, if the Hanford Interim Pretreatment System (IPS) were to supply pretreated LAW feed to a full-scale bulk vitrification (BV) process in either the 200-West or 200-East Areas, the maximum allowable Cs-137 concentration in the feed is 2.3E-02 Ci/gal. Again, the ALARA goals would be met as a result of the increased radiation shielding provided by the refractory lined steel box used in the BV system.

The maximum allowable Cs-137 concentration in the pretreated LAW feed to the WTP LAW vitrification facility is 3.4 E-04 Ci/gal, the same as during full operation of the WTP. The sodium concentration in the IPS pretreated LAW solution is anticipated to be 5 to 7 M. Therefore, the Cs-137 concentrations in Table 7 have been normalized to 6M Na.

Note that in all situations, the maximum Cs-137 concentration in the feed to the LAW immobilization processes is less than the waste incidental to reprocessing determination requirement of 0.162 Ci/gal, normalized to 6 M Na (or 0.189 Ci/gal normalized to 7 M Na).

The Deliquification, Dissolution and Adjustment (DDA) process used at SRS is similar to the Selective Dissolution process used at Hanford. In the DDA process, the interstitial liquid is removed via salt well pumping. The drained saltcake is then dissolved and retrieved. The retrieved saltcake is then adjusted with other wastes to prepare feed to the Saltstone plant.

Technological Solutions Past and Present

The development of technologies to support chemical processing flowsheets for treating HLW has challenged the scientists and engineers of the DOE community for decades. In the case of removing solid particulates from the tank wastes, for example, technology has matured from simply allowing the particulates to settle and decanting the clarified liquid to another process vessel. Although this technology has been used from the operational beginnings to the present day, other more sophisticated technologies have been developed, such as crossflow filtration, which has been used internationally and at almost all major DOE sites. Further advances are currently being investigated.

Cesium removal has been performed at different sites by different methods since the 1950's. The methods available were different depending on the pH and other metal ions in the solutions being treated for Cs removal. There were few alternatives initially that were selective for Cs except those developed for analytical separations. For example, potassium cobalt ferrocyanide was used at Hanford from 1958 to 1962. The specifications or limits were site-specific because clearly defined limits had not been developed for the entire industry. Over the years, national limits or specifications have been developed to define different wastes and ways they can be handled and disposed of.

Research and development of new materials and processes specific to Cs and Sr removal were pursued from 1970 to 1985 in support of high level waste treatment. Technologies using elutable cationic ion exchange resins were used by Hanford to remove cesium, and complexing agents were used to recover strontium.

The technical problem for Cs removal from DOE high level wastes at Hanford, Oak Ridge, and Savannah River is the high concentration of sodium in the wastes. The chemistry of Na and Cs are similar, so very high selectivity is needed to minimize the volume of the resulting Cs stream. From the early 1990's to the present time, research and development (R&D) projects supported by DOE's Office of Environmental Management (EM) have produced a number of improved materials and processes for treatment of waste, especially of Cs. Almost all the technologies adopted or considered at the different sites in recent years have come from EM's R&D program. The new technologies are much more selective toward Cs than any of the earlier technologies.

Table 8 lists sites and technologies for cesium removal through the years.

Table 8. Timeline for Cesium Removal Technology Selection

Facility	Technology	Selection Date	Rationale
Hanford Waste Tanks	Potassium Cobalt Ferrocyanide	1958-1962	Desired a removal method to precipitate Cs into the sludge so decontaminated supernatant solution could be placed in unlined underground cribs
Savannah River Waste Tanks	Non-Elutable Zeolite Ion Exchange	1960-1965	Removal of Cs from high level waste evaporator overheads prior to disposal to seepage basins
Hanford	Elutable Cation Ion Exchange	1978-1980	Recovery of Cs to make Cs capsules for use for irradiation by universities and industry
Savannah River	Elutable R-F Ion Exchange	1983-1985	Removal of Cs from low-level radioactive wastewater to below drinking water standards prior to release to environment
West Valley	Non-Elutable Ion Exchange - IE-96	1988 - 1995	IE-95 and TIE-96 zeolites used in ion exchange columns to treat supernates and sludge wash solutions
ORNL Melton Valley	Non-Elutable Ion Exchange - CST	1996	Preferred technology during down selection between CS-100, CST, potassium cobalt hexacyanoferrate, resorcinol formaldehyde resin, SuperLig 644, and an organic resin bound in a proprietary organic web structure from 3M Corporation
Waste Treatment Plant	Elutable Ion Exchange – SuperLig 644	2000	Preferred technology during down selection between Rohm & Haas CS-100, CST, and SuperLig 644 resins. Derived from BNFL Privatization Contract and maintained into Bechtel-URS contract
Salt Waste Processing Facility	Caustic-Side Solvent Extraction	2002	Preferred technology during down selection between CSSX, Small-tank ITP, and CST
ARP-MCU	Caustic-Side Solvent Extraction	2004	Built as pilot plant to scale-up CSSX technology
Waste Treatment Plant	Elutable Ion Exchange – Spherical RF	2007	Cost reduction based on demonstrated performance of new resin
Interim Pretreatment System	TBD	2009	Needed to support Early LAW Vitrification

Summary of Current Technologies

Solid-Liquid Separation Technologies

In recent years, several technologies have been demonstrated by the DOE for separating entrained solids from solutions. These solid separation technologies include:

- Gravity settling
- Filtration
- Rotary microfiltration.

Gravity Settling

In this technique, the insoluble solids are allowed to settle, and the supernate is then decanted and processed through the ion exchange or solvent extraction systems without any additional treatment.

SRS and Hanford have used settling and decanting to separate the insoluble sludge from the salt solution that is stored in their Tank Farms. SRS has used the process to wash sludge prior to vitrification at the Defense Waste Processing Facility.

In theory, the sludge solids in a slurried waste stream settle very slowly (i.e., they do not settle out in the waste tanks and are carried forward with the salt solution). Very long settling times may be required to achieve the solids removal required. SRNL (formerly SRTC) measured settling rates of insoluble solids in an actual Tank 41H sample [Hobbs 1995]. The measured settling rates for the smallest particles (< 4 μ) were less than 4 in/day. If the particles in the feed to this process have similar settling rates, settling and decanting alone are unlikely to be effective at removing a significant fraction of particles.

The settling rates could be improved by the addition of flocculants and additives. SRNL investigated flocculants to increase settling rates. Several flocculants were successful, but they had downstream impacts (e.g., to DWPF).

Because of the slow settling rate of the small particles, the gravity settling process may be improved by a polishing filtration step. The polishing filter could be a dead end filter or a crossflow filter.

Filtration

A filter separates solids from liquid with a semi-permeable barrier. The barrier contains pores that allow liquids and dissolved solids to pass but block insoluble solids that are larger than the pore.

As the filter rejects particles, some accumulate on the surface, forming a filter cake. The filter cake increases the resistance of the filter. The filter cake can be removed and the cake resistance reduced by periodic back washing. If the filter cake thickness can be reduced, the filter flux will increase.

Using settling and decantation in waste tanks as pretreatment steps to a filter would decrease the solids loading on the filter, which should lead to a longer operating time between back-pulses. If 90% of the solid particles could be removed by settling, the improvement in operating time could be as much as 10X. If 99% of the solid particles could be removed by settling, the operating time between back-pulses could be as much as 100X.

The decanted supernate may contain more very fine particles that could foul the filter more severely than simulated sludge feeds. Additionally, the process would need to be designed so the settled solids could be re-suspended.

Dead-end Filtration

One approach to employing filtration is dead-end filtration. In dead-end filtration, fluid flows at a constant flow rate from the outside to the inside of a cylindrical filter approximately 2 inches in diameter and 10-50 inches long. As the solids are rejected by the filter, they form a filter cake and increase the pressure drop across the filter. When the pressure drop reaches a certain value, the filter is back washed. If the time between back washes is long, this filter is a viable option. If the time between backwashes is short, the dead-end filter is not desirable.

SRNL testing evaluated a Pall porous metal filter as a replacement for the ceramic crossflow filters at the Effluent Treatment Facility (ETF) [Georgeton and Poirier 1990]. During testing, the filters fouled vary rapidly, and the time between back-washes was typically 5-6 minutes, and about 50 % of the filtrate was needed to back-wash the filter. The filter had a pore size of 5 μ and was fouled by small, colloidal particles. If a filter with smaller pore size could be found, it might operate longer between back-washes.

The performance of the dead-end filter in that application might be improved with the addition of a filter aid [McCabe 1995]. Diatomaceous earth is commonly used but would not be suitable for this waste stream. Any filter aid would need to be evaluated for compatibility with the high-pH, high-ionic-strength radioactive stream as well as compatibility with down-stream processes (e.g., DWPF).

In earlier Tanks Focus Area (TFA) investigation of solid-liquid separation technologies, SRNL [McCabe 1995] found dead-end filtration to work best with low concentrations of large particles. In a study to treat Hanford Cladding Removal Waste, scientists investigated crossflow and dead-end filtration. The simulated waste contained 1000 – 2100 ppm solids with a mean particle size of 1.2 μ. The 0.5 μ Mott crossflow filter performed better than the 0.5 μ dead-end filter tested.

The SRS Effluent Treatment Facility currently uses dead-end filters to remove carbon fines from a feed stream to a reverse osmosis process. Those filters are not backwashed.

Crossflow Filtration

Another approach to improving filtration is to employ crossflow filtration. Crossflow filters occur in a variety of designs. Common designs include plate and frame, hollow fibers, spiral wound, and tubular. Tubular design is the most common for DOE site radioactive waste treatment.

As shown in Figure 2, slurry flows through filter tubes through the center of a cylinder [Porter 1990]. A pressure gradient extracts slurry liquid through the filter-tube barrier, which blocks the solids. The rapid fluid motion through the filter tube sweeps the solid particles away from the surfaces, retarding cake buildup. The fluid containing the solids (concentrated slurry) exits the other end of the tube. The permeate liquid is removed from the cylinder through a separate outlet.

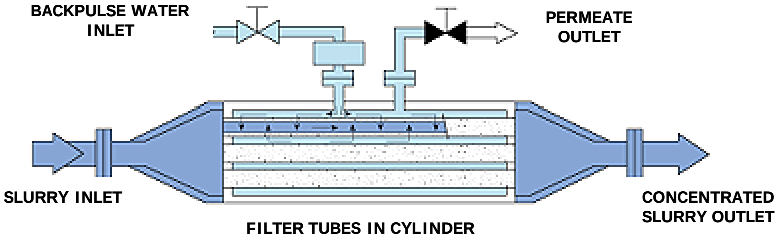


Figure 2. Schematic Drawing of a Crossflow Filter

As solid particles build up on the filter surface, they can be removed by backpulsing. In backpulsing, water is injected into the cylinder to increase the pressure on the filtrate side to displace the filter cake from the feed side of the filter tube. This reverse flow removes particles from the inner surface of the filter tube.

Fine particles that are smaller than the pore opening can become trapped in the filter pores. These particles decrease the porosity of the filter and filter flux. Pore fouling is generally not alleviated by backpulsing. Filter flux can be restored by cleaning particles from the filter pores, often with oxalic acid.

Crossflow filtration has been used successfully to separate entrained solids for the following radioactive waste services:

- Melton Valley Storage Tank (MVST) wastes at the Oak Ridge National Laboratory (ORNL)
- Waste processing at the West Valley Demonstration Project
- In-tank precipitation process demonstration at SRS (1983).

Both the West Valley Demonstration Project and the SRS demonstration used crossflow filters inserted through tank risers.

The crossflow filter unit used at ORNL was part of the Wastewater Triad Project, which included a cesium removal system (ion exchange columns) and an out-of-tank evaporator system. The crossflow filter unit consisted of two 5-ft long tube bundles (thirty-one 0.5-µm filter elements each connected in series and installed within a separate shielded structure). The feed pumps for the crossflow filter were installed within an existing process pump and valve vault. The ORNL crossflow filter unit was designed and fabricated from September 1997 through November 1998. The Melton Valley Storage Tank (MVST) feed to the crossflow filter unit contained up to 22 wt % solids. The filtrate production rate for the ORNL crossflow filter was 1 to 5 gpm, with a solid slurry recirculation rate of 30 to 50 gpm. The alpha concentration (primarily associated with the solids) in the MVST feed to the crossflow filter was reduced by >99.9%, and solids content of the filtrate was approximately 0.02 wt % during initial testing in 1999.

The WTP Pretreatment facility at Hanford includes an ultrafiltration process (crossflow filter), which uses 0.1-µm filter elements to achieve 99.99% solids removal. The WTP ultrafiltration process is using both for clarifying the LAW feed to the cesium removal ion exchange process for washing and leaching HLW solids. The average filter flux is assumed to be a minimum of 0.03-gpm/ft^2 based on crossflow filter test results reported in the WTP flowsheet bases document. The WTP flowsheet bases document includes test results for lab-scale tests with actual LAW and HLW samples and a pilot-scale test with simulants, and it also provides a description of the WTP crossflow filter system. Excluding Sr/TRU precipitation and filtration tests, only two crossflow filtration tests have been conducted with actual LAW solutions from tanks AW-10117 and AN-10418. Both tank waste samples were diluted to 5M Na and then concentrated using a lab-scale crossflow filter unit. The initial solids content of the AW-101 and AN-104 diluted waste samples was less than 0.1 wt % and 0.07 wt %, respectively. The diluted AW-101 sample was concentrated to less than 0.1 wt % and produced an average filter flux of 0.05-gpm/ft^2, at an axial velocity of 11 ft/sec and a transmembrane pressure of 60-psi. The diluted AN-104 sample was concentrated to 0.9 wt % and produced an average filter flux of 0.085-gpm/ft^2, at an axial velocity of 11 ft/sec and a transmembrane pressure of 40-psi. The crossflow filtration unit for use in processing LAW solution will process diluted tank waste similar to the diluted tank AW-101 and AN-104 waste samples tested by the WTP. The crossflow filtration unit is assumed to achieve an average filter flux of 0.05-gpm/ft^2, at an axial velocity of 11 ft/sec and a transmembrane pressure of 60-psi. This average filter flux is the least of the measured filter fluxes during testing with actual waste samples from tanks AN-104 and AW-101, as stated above.

Rotary Microfilter

The SpinTek ST-II rotary microfilter (RMF) is a compact filtration system that uses membrane filters mounted on rotating disks. The vendor states that the equipment can produce high filtrate flow rates with stable performance even when operating on slurries with high solids content. The vendor conducted tests for Los Alamos National Laboratory (LANL) with 10.5 – 42 wt % titanium dioxide slurries.

The flux advantage of the RMF compared to other membrane processes results from the high shear and centrifugal force acting on the boundary layer next to the membrane. This shear greatly reduces fouling of the membrane surface and increases fluid flow through the membrane. Pressure is decoupled from the feed flow rate, allowing more control over the driving force pressure and independent control of the shear applied to the filter cake. This feature allows the direct application of shear force with a magnitude significantly greater than that available in conventional membrane systems.

The membranes rotate at a top speed of 60 ft/s, which effectively cleans and sweeps solids from the membrane surface with a stable filtrate throughput. For comparison, previous cross-flow filter testing used axial velocities ranging from 3 to 25 ft/s. The SpinTek RMF unit uses 1 to 25 eleven-inch diameter disks covered with filter membranes. The disks are physically mounted and are hydraulically connected to a common hollow rotating shaft. The entire stack of membrane disks is enclosed within a vessel. The feed fluid enters the vessel and flows across the membrane surface, where permeate flows through the membrane and exits through the hollow shaft. The concentrated slurry is pumped from the chamber. Stationary surfaces, or turbulence promoters, oppose the rotating membrane disks, generating large fluid shear rates across the membrane surface. Volumetric hold-up is approximately 0.9 gallons for the single-disk unit, and up to 4 gallons for a 25-disk unit. Personnel may find this value useful in determining maximum loading during maintenance periods. Figure 3 illustrates the flow paths during filtration.

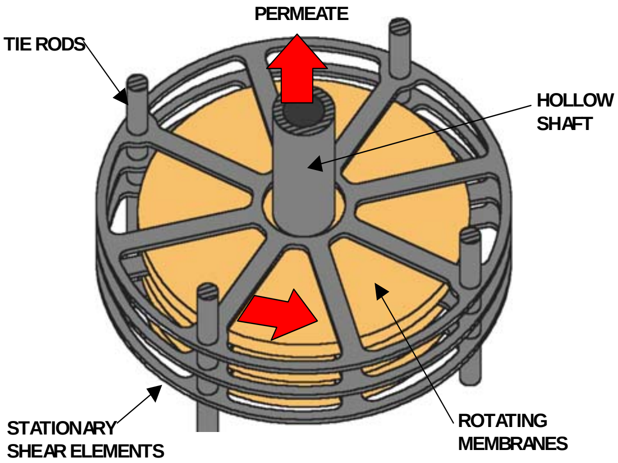


Figure 3. Illustration of SpinTek Rotary Filter with Three Filter Disks

The unit typically operates in a semi-batch mode with feed recirculated through the system and concentrated filtrate withdrawn. Eventually, the batch concentrates to a target insoluble solids level, and the concentrated material is replaced with a new batch of feed.

A SpinTek ST-II has been purchased for testing as an off-the-shelf item, and modifications for radioactive service have been performed. SRNL has modified the electrical, plumbing, and instrumentation systems. Modifications include the addition of calibrated manual pressure gauges for data collection as well as to aid in resolving potential system upsets. As testing started, SRNL discovered the need to modify the prototype filter disk.

There are a number of potential uses for the RMF at Hanford, including use in the Interim Pretreatment System (IPS) for starting LAW early or in selective dissolution of tank waste for processing through Bulk Vitrification. In both of these operations, the RMF would be used to remove sludge solids. SRNL [Poirier et al. 2008] performed rotary filter testing with a full-scale, 25-disk unit equipped with 0.5 micron filter media manufactured by Pall Corporation using a Hanford AN-105 simulant at solids loadings of 0.06, 0.29, and 1.29 wt %. The rotary filter produced a flux that was 1 – 3X higher than the flux produced with a crossflow filter using the AN-105 simulant. This improvement is less than observed with testing using SRS simulant. One likely cause is that the median particle size was 40% less in the rotary filter testing than in the crossflow filter testing. Filtrate turbidity measured < 4 NTU in all samples collected. The filter flux at 0.06 wt %, 0.29 wt %, and 1.29 wt % solids reached a near constant value at an average of 0.25 gpm/disk (6.25 gpm total), 1.29 wt %, and 0.10 gpm/disk (2.4 gpm total), respectively. Inspection of the seal faces after ~ 140 hours of operation showed an expected amount of initial wear, no passing of process fluid through the seal faces, and very little change in the air channeling grooves on the stationary face.

Cesium Removal Technologies

The removal of cesium from the alkaline wastes stored at Hanford and SRS has been studied by the DOE and its predecessor agencies for over 50 years. As discussed previously, several factors have significantly influenced the technology selections for the SWPF at Savannah River and the WTP at Hanford.

At SRS, caustic-side solvent extraction (CSSX) is the core technology for the interim Modular CSSX Unit (MCU) as well as the SWPF. The MCU underwent a successful startup during the spring of 2008.

The technology selection for the interim pretreatment at Hanford has not been made. There are several cesium removal technologies being considered:

- Selective Dissolution
- Crystallization
- Ion exchange
    - Elutable resin
    - Non-elutable resin
- Solvent extraction.

Those technologies under consideration are capable of removing cesium from saltcake waste and supernate. However, the amount of cesium removed (i.e., decontamination factor) can vary significantly among these technologies.

Selective Dissolution

Selective dissolution is a straightforward technology that allows for the removal of cesium from saltcake wastes. Cs salts are soluble in alkaline media and reside in the free supernate and interstitial fluid in the pores of the saltcake. Saltcake is a porous media and has been modeled using geochemical techniques. The supernate is removed through normal pumping methods. A well is then mined into the saltcake using a hydro lance, and a well pump is installed. The interstitial fluid containing the Cs-137 (and Tc-99 as TcO_4^-) can then be removed. This draining of the saltcake is a tedious process as the well recovery rate is dictated by the porosity of the saltcake and the hydraulic conductivity of the saltcake media. The void fraction of the saltcake is typically about 40% of which 10% of the volume is occupied by various gases generated by radiolysis. Of the 30% remaining, most of this liquid fraction is removed in the well pumping. This leaves a small amount of Cs-137 in the saltcake.

Using selective dissolution, water is sprayed at 100 psi and up to 100 gpm onto the drained saltcake. This dissolves portions of the saltcake. With the force and the shear volume of water added to the tank, the freshly dissolved brine mixes with the interstitial liquid in the remaining saltcake. This will displace the cesium-137 in that saltcake. The liquids with the cesium are pumped out and transferred to other tanks for eventual processing at the Salt Waste Processing Facility at SRS and the Waste Treatment Plant at Hanford. The remaining saltcake can be further dissolved using water and retrieved as low-activity waste, which can be processed to immobilize the waste. The clarified salt solution (i.e., pretreated LAW) is sampled and analyzed to verify Na and Cs-137 concentration. After pumping a portion of the dissolved saltcake to another tank, the estimated Cs DF for the remaining dissolved saltcake solution coming from this selective dissolution process is 5 to 10. CH2M HILL [Barton 2006] demonstrated the selective dissolution technique in the tank S-112 waste retrieval project. At least 27 single-shell tanks at Hanford contain saltcake with mixtures of sodium nitrate, sodium carbonate, sodium phosphate salt crystals, and cesium-137. By removing the cesium-137 from liquids trapped within the salt matrix, the remaining saltcake is thought to meet Nuclear Regulatory Commission criteria for incidental waste.

SRS has already used the Deliquification, Dissolution and Adjustment (DDA) to process some of the lowest activity SRS salt waste before Salt Waste Processing Facility begins operation. The DDA process involves the following: 1) removing the supernate from above the saltcake; 2) extracting interstitial liquid within the saltcake matrix; 3) dissolving the saltcake and transferring the resulting salt solution to a settling tank; and 4) transferring the salt solution to the Saltstone Facility feed tank where, if required, the salt solution is aggregated with other Tank Farm waste to adjust batch chemistry. Chemistry adjustment may be required to ensure the salt solution feed stream meets processing parameters (e.g., sodium concentration, organic content, facility shielding limitations) for processing at the Saltstone Processing Facility. The deliquification and dissolution processes involved in DDA remove substantial amounts of Cs-137 as well as some insoluble Sr and actinides from this already relatively low-curie material. Through deliquification, DDA will remove approximately 50% of the Cs-137 and its daughter product Ba-137m from the saltcake targeted for dissolution.

Crystallization

Crystallization involves the formation of one or more solid phases from a fluid phase or an amorphous solid phase. It is applied extensively in the chemical industry, both as a purification process and as a separation process. Crystallization is one of the older operations in the chemical industry; therefore, practical experience can usually be used for the design and operation of industrial crystallizers. In addition, advances in the understanding of crystallization kinetics can be useful in the control, design, and scale-up of industrial crystallizers.

Fractional crystallization is a possible pretreatment technology to separate high-activity and low-activity waste for more efficient waste retrieval and processing. The science is well understood, and the process has an established track record in industries including salt and sugar refining, pharmaceutical production, and potash mining. Applied to Hanford’s tank waste, the process would dissolve solid tank waste in water and then, through filtration and evaporation, separate the waste into low-activity and high-activity waste streams. Highly radioactive isotopes such as cesium and technetium (i.e., the high-activity waste) would be maintained in the liquid portion, which could be pumped out and transferred to the double-shell tanks for eventual vitrification in the Waste Treatment Plant. The remaining low-activity waste, in the form of salt crystals and sludge, could be further dissolved and retrieved for processing to immobilize the waste.

The proposed system uses a two stage crystallizer system to crystallize salts from the LAW solutions as shown in Figure 4. The feed to the fractional crystallization process can be at any sodium concentration. The LAW feed is first processed to separate entrained solids that contain TRU and Sr-90. In the first crystallizer stage, the LAW solution is evaporated to remove excess water and result in a saturated salt solution containing salt crystals. The saturated salt solution is discharged from the crystallizer to a hydrocyclone for separation of the salt crystals from the mother liquor. The mother liquor is transferred to a feed vessel for the second stage crystallizer for additional salt removal. The salt crystals are transferred from the hydrocyclone to a centrifuge for washing with a saturated salt solution to remove interstitial liquid that contains soluble radionuclides. This wash solution is transferred to the feed vessel for the second stage crystallizer. The washed salt crystals are dissolved in water and combined with the salt crystals obtained from the second crystallizer stage.

The second crystallizer stage operates similarly to the first crystallizer stage. The mother liquor and wash solution from the first crystallizer stage is evaporated to remove excess water resulting in a saturated salt solution containing salt crystals. The saturated salt solution is discharged from the crystallizer to a hydrocyclone for separation of the salt crystals from the mother liquor. The mother liquor is transferred to another tank for interim storage and later processing in the WTP Pretreatment facility. The salt crystals are transferred from the hydrocyclone to a centrifuge for washing with a saturated salt solution to remove interstitial liquid that contains soluble radionuclides. This wash solution is transferred to another tank for interim storage and later processing in the WTP Pretreatment facility. The washed salt crystals are dissolved in water, combined with the salt crystals obtained from the first crystallizer stage, sampled, and analyzed to verify sodium and Cs-137 concentrations. The estimated Cs DF for the washed salt crystals is 300. A 1/9th scaled crystallizer has been installed at the Savannah River National Laboratory. As of the time of this report, testing was recently completed.

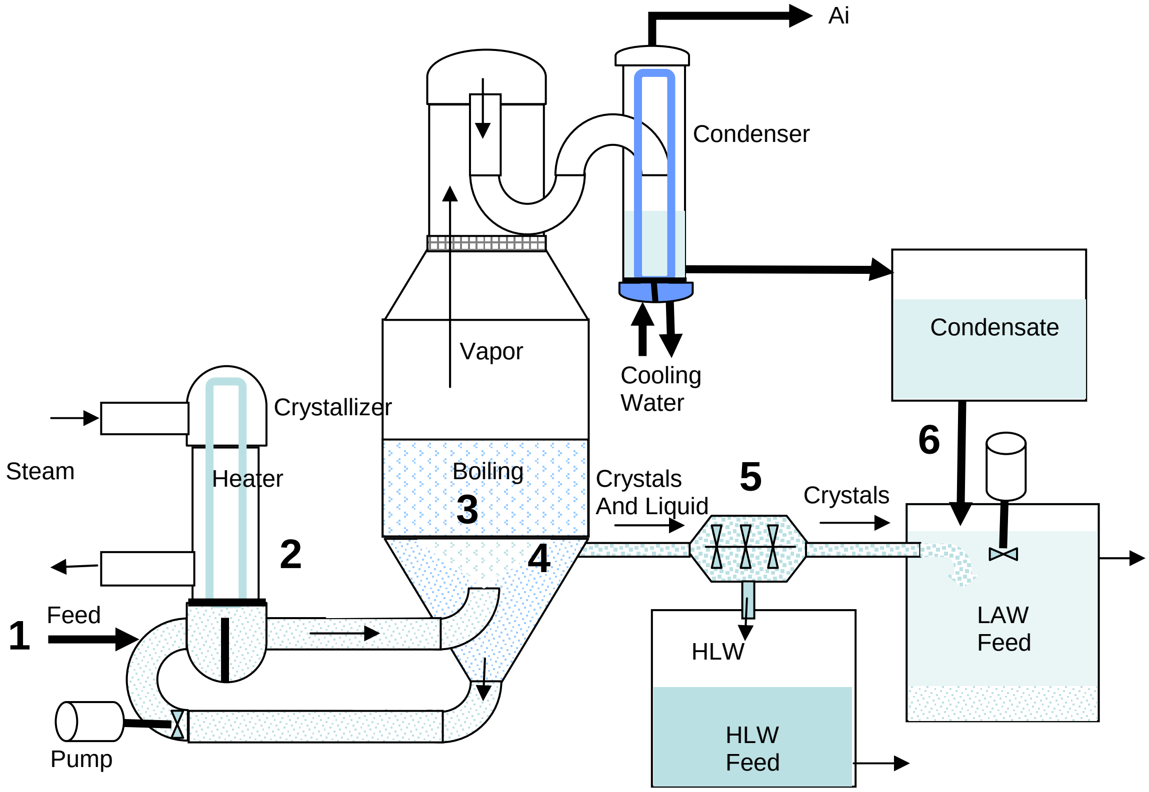


Figure 4. Fractional Crystallization Schematic

Laboratory-scale flowsheet tests [Herting 2006] of the fractional crystallization process were conducted with actual tank waste samples in a hot cell at the 222-S Laboratory at the Hanford site. The feed solutions were composite samples of dissolved saltcake from several S-farm and SX-farm tanks. Two composite samples were prepared: “SST Early,” representing the typical composition of dissolved saltcake early in the retrieval process, and “SST Late,” representing the typical composition during the later stages of retrieval. Prior reports on fractional crystallization include adequate descriptions of the historical background, theory, and application of the fractional crystallization process, details of which will not be repeated here. Analytical samples of process input and output streams allowed for evaluation of the process performance against the criteria established, such as cesium decontamination, product yield, etc. Favorably, all of the criteria for separations

(^{137}Cs removal, sulfate removal, and Na^+ separation) were exceeded in all three tests. Mass balance closure was acceptable for all system components except ^{90}Sr.

Ion Exchange

Ion exchange technology relies on exchanging one charged chemical species (i.e., either a cation or an anion) from a liquid phase for another charged species contained in a solid phase. In the case of cesium, the Cs^+ cation can be removed from alkaline waste streams by cation exchange, represented by the following general equation:

$$Cs^+(aq) + R^-M^+(s) \rightarrow M^+(aq) + R^-Cs^+(s) \tag{1}$$

where M^+ represents the exchanged cation and R^- represents a solid material having negatively-charge (anionic) sites to supply electroneutrality for the exchange of the positively charged cations. A variety of polymeric organic resins and inorganic materials have been evaluated for removing Cs-137 from alkaline liquid wastes at the Hanford and Savannah River sites (Bray et al. 1993, 1995; Brown et al. 1996; Wester et al. 2003). During the initial design of the Hanford Waste Treatment Plant, the contractor chose Cs ion exchange using SuperLig™ 644 as the baseline technology for removing Cs-137 from the LAW stream (Kurath, Blanchard, and Bontha 1999, 2000). More recently, a spherical resorcinol-formaldehyde resin has been investigated for the purpose of removing ^{137}Cs from Hanford LAW at the Hanford Waste Treatment Plant (Fiskum et al. 2006a-c).

Figure 5 schematically illustrates a generic Cs ion exchange process. In the first step of the process, the feed solution is passed through a column containing the Cs-selective ion exchange resin. Usually, two columns are employed in series. The first column (referred to as the "lead" column) retains most of the Cs-137 activity. The second column (the "lag" column) acts as a polishing step to remove any Cs-137 not removed in the first column. This results in a solution (column effluent) that is nearly free of Cs-137. The degree of Cs separation is expressed by the decontamination factor (DF) which is defined as the Cs-137 concentration (normalized to the mass of material dissolved in the solution) in the feed solution divided by that in the column effluent.

As more and more Cs is loaded onto the lead column, "breakthrough" of Cs will eventually occur. That is, eventually the lead column will reach its capacity to retain Cs, and any remaining Cs in the feed solution will pass through the column. The process is stopped before Cs breakthrough on the lead column occurs. In the second step of the process, the Cs loaded onto the lead column is eluted (removed) from the column, typically with a dilute nitric acid solution. The resulting solution containing the Cs-137 is then routed to HLW vitrification.

In practice, once the lead column is saturated and taken off-line for elution, the lag column illustrated in is reconfigured to be the lead column (with yet another column put in series to serve as the new lag column) and the process is continued. In this way, Cs removal can be continued while elution of the first lead column proceeds.

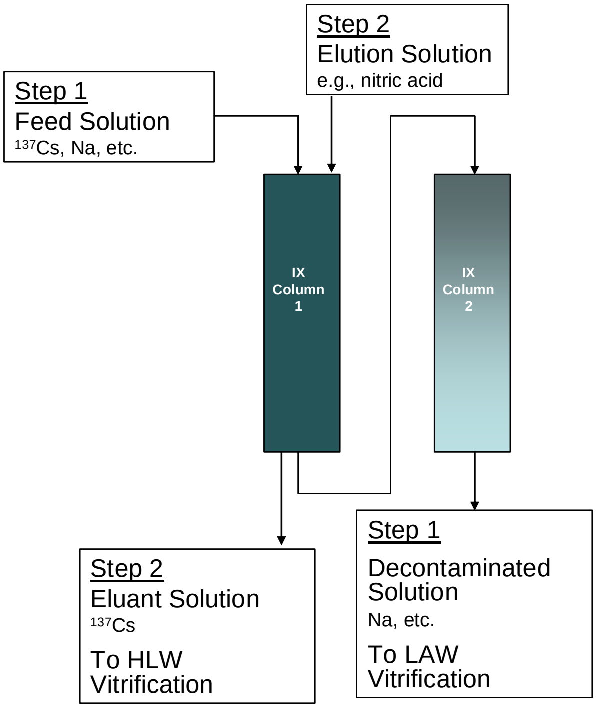
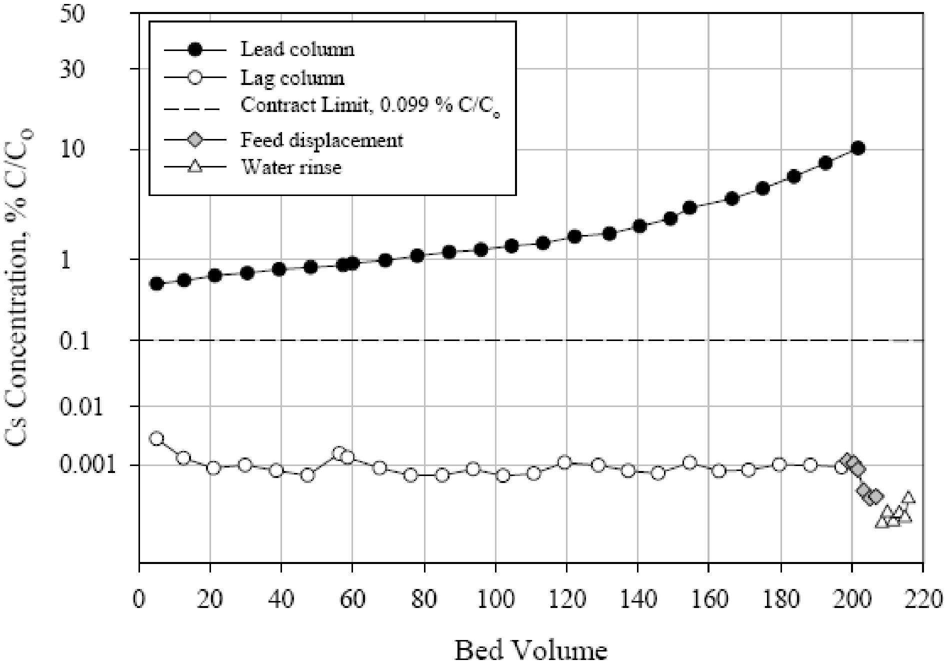


Figure 5. Schematic illustration of the Cs ion exchange process for an elutable ion exchange material; step 1 represents the loading cycle, while step 2 represents the elution cycle.

Figure 6 shows a typical "breakthrough" curve for removal of Cs-137 from a Hanford tank waste using spherical resorcinol-formaldehyde resin (Fiskum, Steele, and Blanchard 2006b). The plot shows the ratio of the Cs concentration in the column effluent to the Cs concentration initially in the waste solution (expressed in terms of a percentage). This ratio is plotted as a function of bed volumes of solution processed (the bed volume is the volume occupied by the resin in the column). Breakthrough curves are plotted for both the lead and lag columns. As can be seen, even after processing 200 bed volumes of solution, the amount of Cs-137 in the lag column effluent (i.e., the low-activity waste solution) is very low—0.001% of the Cs that in the feed solution. Thus the spherical resorcinol-formaldehyde resin is very effective at removing Cs from this highly alkaline waste; decontamination factors on the order of 100,000 have been achieved in testing with this resin.



Conditions:

- Spherical RF Lot number 5E-370/641
- Process temperature = 26 to 27°C
- BV in 0.5 M NaOH feed condition = 11 mL
- Flow Rate = 2.95 BV/h
- ^{137}Cs C$_o$ = 143 µCi/mL
- Na concentration = 4.94 M

Figure 6. ^{137}Cs Breakthrough Curves for Liquid Waste from Hanford Tank AN-102

A recent study at SRNL [Smith 2008] examined the use of elutable ion exchange technology for supporting the proposed Interim Pretreatment System at Hanford. The volume of waste solution that can be processed during a single ion-exchange cycle varies from about 125,000 gallons for AP-103 up to almost 300,000 gallons for AN-104. Resin behavior is expected to degrade with repeated operating cycles from the effects of chemical and radioactive exposure. The model assumes clean fresh resin and does not account for resin degradation. Previously we noted that the product concentration is from 30 to 140 times lower that the LAW feed limit. It is estimated that increasing the product concentration by an order of magnitude might allow an additional 25,000 gallons of waste to be treated during each ion-exchange loading cycle.

Ion Exchange technology has been used in this load-elute style of processing in several nuclear waste operations and actinide processing throughout the history of the Department of Energy and its predecessor organizations. Likewise, ion exchange to remove cesium from aqueous streams has been used for decades without the elution step. In this manner, an ion exchange resin is simply loaded to capacity with cesium and then disposed of. The non-elutable ion exchange methodology has been used since the late 1950’s and early 1960’s and was even considered today.

Following a successful deployment at the Oak Ridge National Laboratory for the treatment of the Melton Valley Storage Tank waste, Savannah River Site personnel have examined the use of non-elutable crystalline silicotitanate (CST) for removing cesium from tank waste. The CST technology was researched thoroughly for possible selection as the cesium removal technology for the Salt Waste Processing Facility currently under construction. The solvent extraction technology was eventually chosen for this application.

However, researchers at the Oak Ridge National Laboratory and the Savannah River National Laboratory [Walker 2004] are examining the use of CST in a smaller, more modular design under funding provided by the EM-21 Office of Waste Processing. The design of this deployable system, known as Small Column Ion Exchange, is shown in Figure 7. The concept uses an ion exchange column placed inside a tank riser. Another in-riser deployment consists of pumps and rotary microfilters to remove entrained solids and to pump the retrieved waste through the ion exchange column(s). A third module consists of a grinder to reduce the particle size of the spent CST and render it compatible with downstream processing when mixed with sludge being readied for vitrification in SRS's DWPF. Switching the ion exchange media to spherical resorcinol-formaldehyde resin to increase efficiency and utility is currently being examined. Likewise, this modular approach is being considered for use at Hanford in the proposed Interim Pretreatment System.

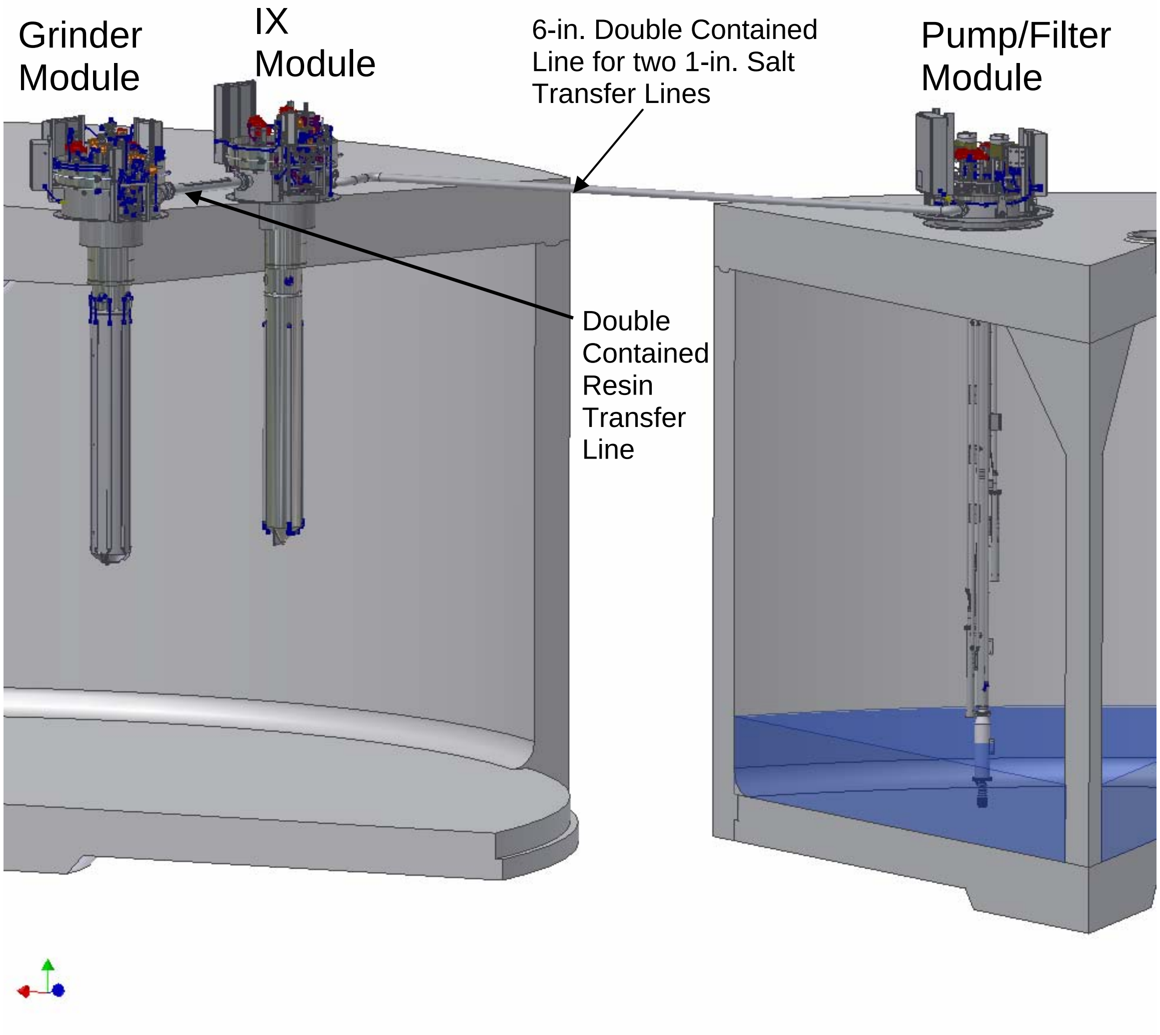


Figure 7. Small Column Ion Exchange Design

Similar to the work performed for the Hanford IPS, SRNL [Smith 2007] modeled the proposed small column ion exchange process for several SRS tank wastes. All of the calculations assume a two-column configuration. During the first cycle, both columns contain fresh media. In all subsequent cycles, the partially loaded second or lag column is placed into the lead position and a clean column is placed into the lag position at the start of the cycle. Since a partially loaded column is in the lead position, after the first cycle less waste volume is processed per cycle. Each cycle is run until the integral sum average cesium concentration in the effluent collected from the lag column reaches the Saltstone feed limit of 45nCi/g.

Bucket average breakthrough curves from VERSE-LC modeling for the nominal case (25 °C, 10 gpm, 15 ft column) for each of the five tanks were calculated. It has been noted that the breakthrough curves are relatively sharp. For Tanks 1-3, the width of the breakthrough from 1.0 nCi/g to 45 nCi/g is between 70,000 and 100,000 gallons while for tanks 37 and 41, the width is on the order of 160,000 gallons and 210,000 gallons, respectively. At a flow rate of 10 gpm, the corresponding breakthrough time is 117 hours for Tanks 1-3 and 267 hours for Tanks 37 and 41. To be conservative during actual operations, the run could be terminated at a lower bucket average effluent concentration without sacrificing much volume.

Solvent Extraction

Solvent extraction (or liquid-liquid extraction) is a mature technology that has been used in the nuclear industry for over 50 years. Adoption of solvent extraction methods for recovery of uranium and plutonium from irradiated nuclear fuel in the 1950's dramatically reduced waste volumes resulting from such operations. Solvent extraction involves mixing two immiscible liquid phases, so that the desired component(s) is transferred from one phase to another, while undesired components are retained in the original phase. Typically, an organic-based extractant is mixed with an aqueous feed solution containing multiple components. The extractant phase is designed so that it has an affinity for the target component to be separated, allowing for transfer of that component to the organic phase. Physical separation of the organic phase from the aqueous phase results in a separation of the target component from the other components in the aqueous phase. Figure 8 illustrates the concept of solvent extraction.

In the case of ^{137}Cs removal from alkaline tank waste solutions, the caustic-side solvent extraction (CSSX) process has been developed (Bonnesen et al. 2000). The CSSX process uses an extractant molecule (referred to as "BOBCalix6") that selectively binds cesium ions. Because this molecule binds cesium ions more strongly than sodium ions (which is present in great excess compared to cesium), it is able to extract cesium into the extractant organic phase, thereby separating it from the other waste components (which remain in the aqueous phase). The CSSX solvent also contains a modifier (which improves the solubility of BOBCalix6) and tri-octylamine (which mitigates the effects of acidic impurities in the solvent). These components are dissolved in a hydrocarbon diluent (Isopar® L).

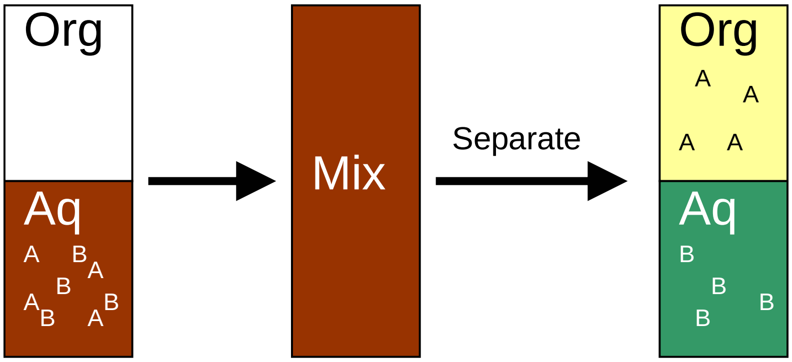


Figure 8. Schematic illustration of the principle of solvent extraction.

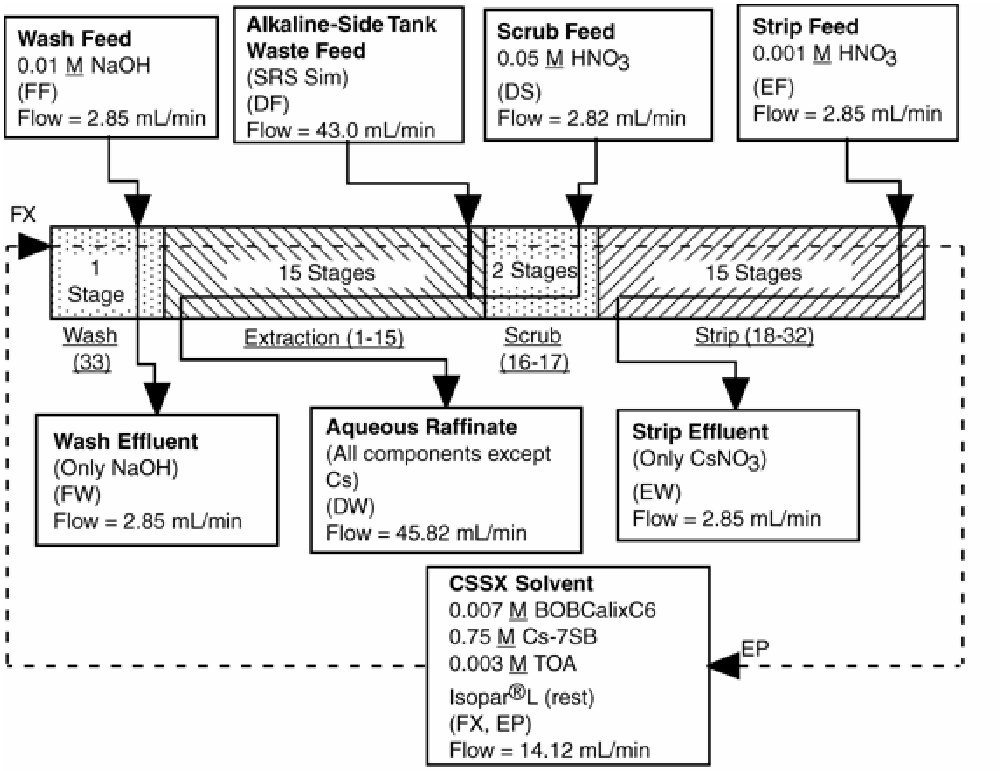


Figure 9. Example CSSX flowsheet for removing ^{137}Cs from Savannah River Site tank waste

As is the case with nearly all industrial applications of solvent extraction, the CSSX process is implemented in a counter-current flow configuration; that is, the organic solvent phase moves in a direction opposite to the aqueous phases. Figure 9 shows a sample CSSX flowsheet (Leonard et al. 2003).

In this example, the alkaline tank waste feed (containing ^{137}Cs) enters the process at stage #15, it then flows left towards stage #1. The solvent phase enters at stage #1 and flows to the right (counter-currently) to the aqueous solution. During this process, cesium is efficiently transferred into the organic phase, such that by the time it reaches stage #1, the aqueous phase has very little cesium remaining (this is the aqueous raffinate). The Cs-loaded solvent is subjected to a scrub step to remove non-radioactive components that partially distribute to the organic phase and is then contacted with dilute nitric acid to strip the ^{137}Cs from the solvent phase. The solvent phase is then washed and recycled back to the extraction stages. The strip effluent contains the ^{137}Cs; this is destined for high-level waste vitrification. One of the major advantages of the CSSX process is that a nearly pure stream of $CsNO_3$ is provided to HLW vitrification (with only a small amount of nitric acid accompanying the $CsNO_3$).

As is the case with ion exchange, the decontamination factor is determined by dividing the amount of ^{137}Cs entering the process by the amount in the aqueous raffinate. Tests with actual Savannah River Site high-level tank waste have produced decontamination factors in excess of 100,000 using the CSSX process (Norato et al. 2003). These decontamination factors are well above the target value of 40,000, and the testing done to date has indicated the process to be very robust in maintaining these very high decontamination factors.

DOE-SR proceeded with the design and construction of a modular CSSX unit (MCU), and the MCU began operations in April 2008. The MCU is designed to process 4 gpm (~15.1 lpm) of 5.6M Na feed at 75% attainment. The MCU uses eighteen 12-cm diameter centrifugal contractors. Seven of the centrifugal contactors serve to extract cesium from the actinide decontaminated tank waste; two contactors are the acid (0.05 M nitric acid) scrub section; cesium is stripped from the solvent using 0.001 M nitric acid in seven contactors, and two contactors are used for solvent washing with 0.01M sodium hydroxide. The MCU design basis assumes the Cs DF is at least 12; however, the seven extraction contactors are capable of achieving a much higher Cs DF. The MCU design (as shown in Figure 10) includes additional process vessels such as salt solution (LAW) receipt vessels, salt solution feed tank, solvent hold tank, caustic wash tank, decontaminated salt solution (pretreated LAW) hold tank, strip effluent hold tank, contactor drain tank, solvent recovery tank, and cold chemicals storage tanks. The MCU receives SRS tank wastes that has been treated to separate soluble actinides and has been filtered. The actinide separation and filtration process is not part of the MCU scope.

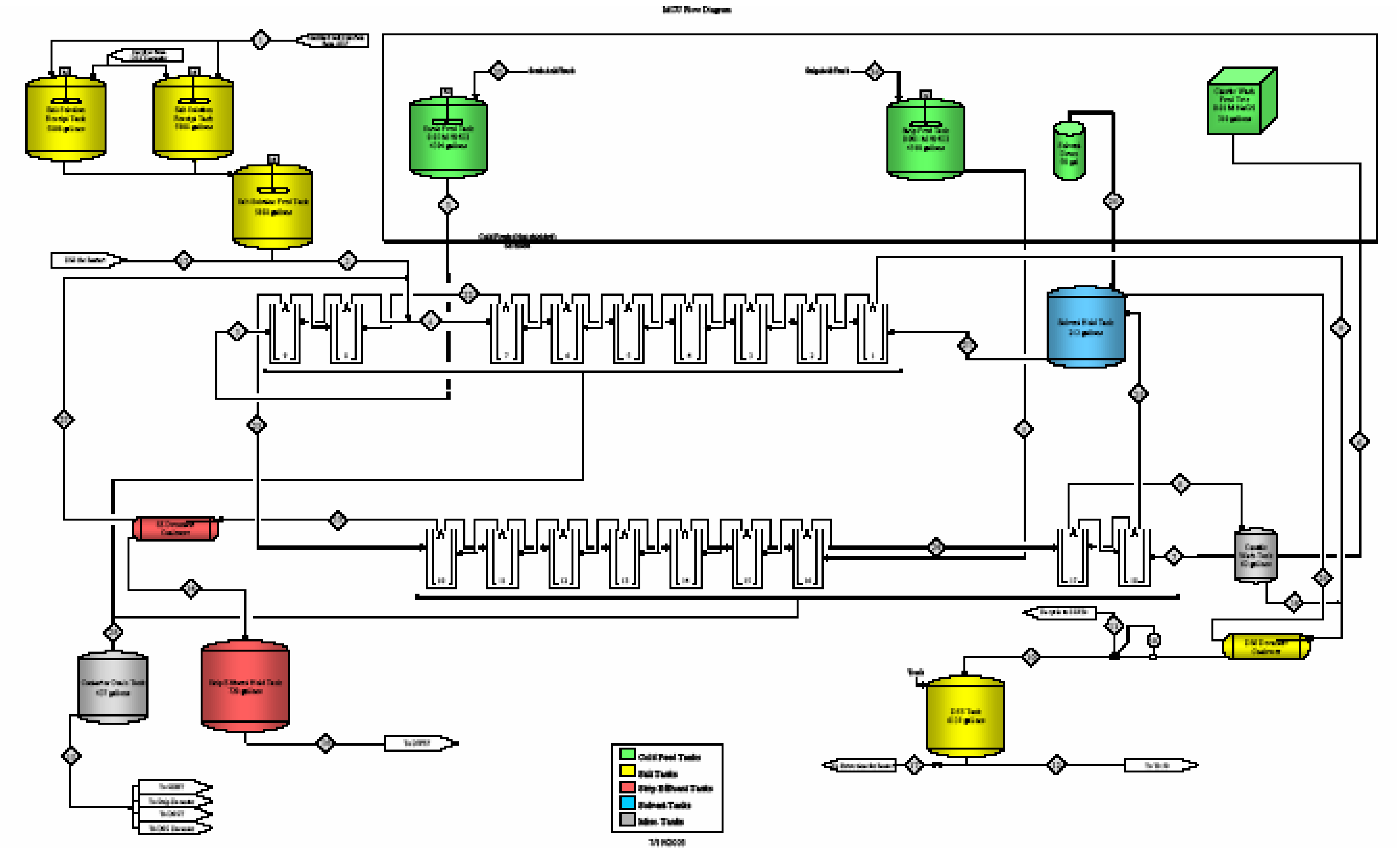


Figure 10. Schematic Drawing of the Modular Caustic-Side Solvent Extraction Unit

In support of the proposed Interim Pretreatment System, researchers at ORNL [Moyer et al. 2008] performed experimental measurement and performed solvent extraction process modeling to determine the ability of the current CSSX solvent and newly improved extractant chemistry on removing cesium from a variety of anticipated Hanford waste chemistries. Batch solvent extraction tests were required to expand the CSSX process model to higher potassium concentrations expected in the IPS feeds. Flowsheet design was performed using a computer simulation based on the SEPHIS (Solvent Extraction Processes Having Interacting Solutes) code that was developed at ORNL. Basic stage calculation equations used in SEPHIS were utilized to determine the number of extraction and stripping stages required to achieve target decontamination (DF) and concentration factors (CF), the former being the quotient of the Cs concentration in the feed divided by the concentration in the raffinate, the latter being the quotient of the product stream Cs concentration divided by the feed stream concentration.

Flowsheet calculations were performed for all combinations of solvent (BOBCalixC6-, the current cesium extractant, and BEHBCalixC6-based, the newer extractant) and the four simulants for which distribution ratios were determined. The four simulants bracket the highest and lowest D_{Cs} values, obviating the need to run all eight simulant cases. Under the assumptions made, the calculations show that up to 41 stages of contactors will be needed to achieve DF and CF targets of respectively 5000 and 5 for the current CSSX solvent (BOBCalixC6-based) and the most challenging waste composition. The magnitude of CF is the more influential goal parameter. If the CF requirement is relaxed to 2, the number of stages drops to 31, whereas if the CF requirement increases to 15, the number of stages more than doubles to 74. Dropping the CF requirement compromises IPS goals, however, as treated LAW will be returned to the tanks, making reduction of the volume of the return flow highly desirable. If the required DF is raised to 40,000, the number of stages increases only to 45. While the number of stages is fairly high if a limited footprint is available, considerable improvement in solvent performance is predicted if the BEHBCalixC6-based solvent system and stripping method is employed. In this case, the most challenging waste feed and the most ambitious goals (DF = 40,000 and CF = 15) require only 19 stages. These results and those obtained from ion exchange modeling for the resorcinol-formaldehyde resin application and that of fractional crystallization pilot testing will be factored into the technology selection for the proposed Interim Pretreatment System.

Additional Key Separations Technologies

So far in this report, the removal of key radionuclides from HLW has been discussed. Concentrating the sludge fraction into a small volume component that can be vitrified into a product canister for ultimate disposition in a federal repository removes a significant fraction of the alpha and strontium radioisotopic inventories of the waste. With the addition of cesium removal, the partially decontaminated waste stream provides the opportunity for removal of other key radioisotopes and non-radioactive metals. In the following sections of this report, discussions of these technologies are provided.

Strontium/Alpha Removal Technologies

The pretreatment of HLW prior to vitrification as described above necessitates the removal of cesium. Other radionuclides also must be removed, with the most notable being the actinides and strontium. At Hanford, the WIR dictates that the alpha content of the LAW glass must be less than 100 nCi/g, whereas at Savannah River, the WD requires that the Saltstone grout be less than 45 nCi/g. Likewise, the strontium content of the disposed LLW products is different. The Hanford LAW glass is limited to 20 Ci/m^3, and the SRS grout has a strontium limit of 2.5E-5 Ci/L in the feed. These requirements impose processing requirements for most of the Savannah River waste, but only the Hanford complexant concentrate wastes (241-AN-102 and 241-AN-107) need strontium and alpha removal.

Monosodium Titanate

Monosodium titanate (MST) is an inorganic sorbent material that exhibits high selectivity for strontium and actinide elements in the presence of strongly alkaline and high sodium containing salt solutions. Original development of MST at Sandia National Laboratory (SNL) produced a dried powder [Lynch 1976 and Dosch 1978]. The Savannah River Site selected this material for strontium and plutonium removal from high-level waste solutions in the early 1980s as part of the In-Tank Precipitation (ITP) process. SRNL modified the synthesis of the MST to optimize performance and transferred this technology to commercial vendors (Hobbs et al. 2005 and Peters et al. 2006]. Figure 11 shows a Scanning Electron Microscope (SEM) image of MST particles.

Figure 11. SEM Photograph of MST

In 2001, the Department of Energy (DOE) selected MST for the strontium/actinide separation step within the Salt Waste Processing Facility (SWPF). Subsequently, Salt Processing Program Engineering selected MST for use in the Actinide Removal Process

(ARP) to treat waste solutions low in cesium activity in a treatment facility located in Building 512-S. Figure 12 shows a graph of the change with time in solution concentrations (μM) of strontium, plutonium and neptunium upon contact with MST at the planned concentration of 0.4 g/L MST. Strontium removal is very rapid, whereas sorption of the plutonium and neptunium occurs at slower rates from the strongly alkaline and high ionic strength waste solutions [Hobbs 1999].

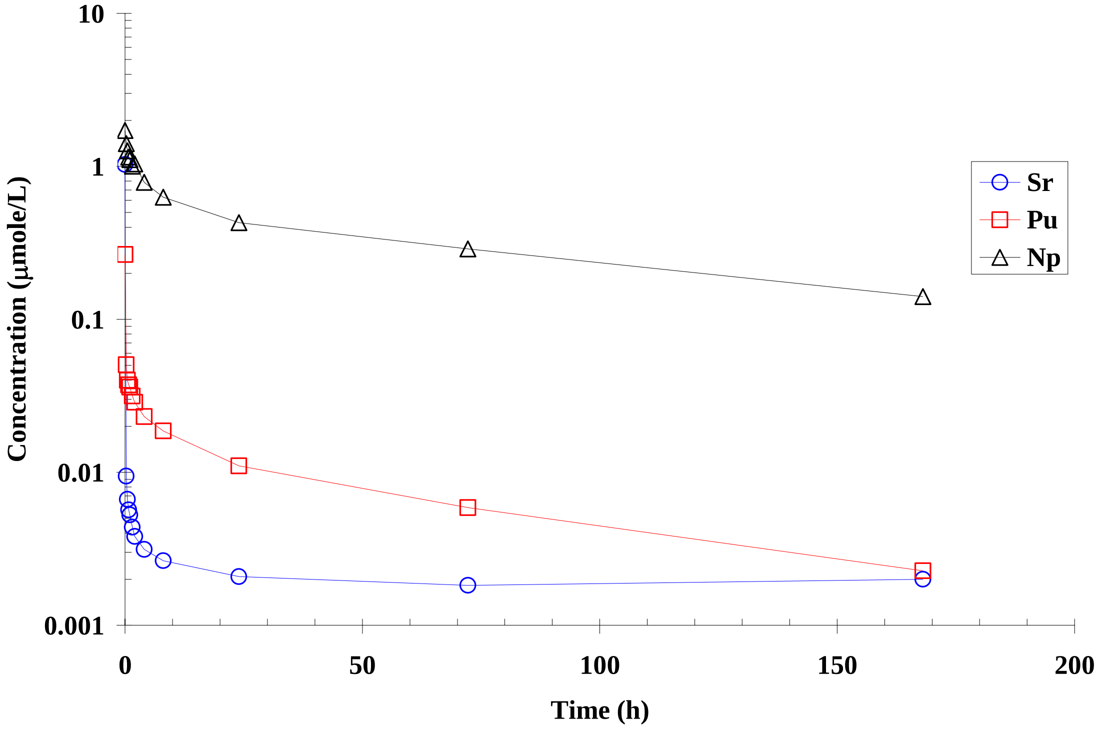


Figure 12. Typical Absorption Plot as a Function of Time for MST Treatment

Figure 13 shows a layout of a typical strontium and alpha removal process that would use the MST sorbent. Salt solution is transferred into one of two MST strike tanks at a sodium concentration of approximately 6.44 M in sodium. The sodium concentration is adjusted to ~5.6 M and the MST added. After the appropriate agitation time (baseline is 24 hrs), the MST suspension is filtered through a cross-flow filter to separate the strontium and actinide-loaded MST and any entrained sludge solids from the liquid. The concentrated MST/sludge solids accumulate until the solids inventory reaches ~5 wt % solids. At that point, the solids are washed with process water to reduce the sodium concentration to about 0.5 M. The washed MST/ sludge solids are then sent to DWPF for processing into borosilicate glass.

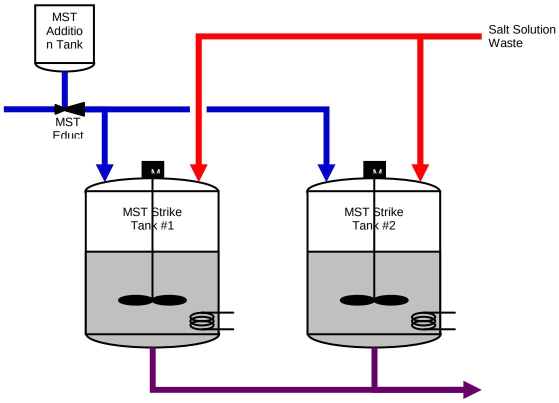


Figure 13. Typical MST Process without Filtration

Permanganate Treatment

The actinide elements plutonium and americium are present in the High Level Liquid Waste in Hanford tanks 241-AN-102 and 241-AN-107 due to the presence of complexing agents used in the processes within B Plant. The mission of B Plant from 1967 through 1985 was to recover Sr-90 from PUREX Acidified Sludge (PAS) and PUREX Current Acid Waste (CAW). B Plant was used to recover Cs-137 from Redox Neutralized Supernate (RNS), PUREX Neutralized Supernate (PNS), PUREX Sludge Supernate, and CAW. Sr-90 was separated from the PAS and CAW solutions using a solvent extraction process. The solvent extraction process used di-(2-ethylhexyl) phosphoric acid (D_2EHPA) and tributylphosphate (TBP) as the extractant in a normal paraffin hydrocarbon (NPH) diluent. The process was pH sensitive and required a buffering agent. Hydroxyethylene diamine triacetic acid (HEDTA), ethylene diamine tetraacetic acid (EDTA), and citric acid were added to complex many of the di- and trivalent metals in order to prevent their extraction from the aqueous phase into the organic solvent. The D_2EHPA-TBP-NPH solvent was then washed in several stages before recycle. Among the many species present during these stages were glycolic acid, sodium gluconate, and sodium hydroxide. The cumulative effect of these process conditions is the presence of species of strontium, plutonium and americium that are stabilized by complexing agents. These complexed species will not readily sorb to monosodium titanate; therefore, a different flowsheet was required.

SRNL [Wilmarth, et al. 2001, Nash et al. 2003] and Battelle personnel (Hallen, et al. 2002] demonstrated a process for separating the Sr-90 and TRU components from the Envelope C wastes (also called complexant concentrate waste). This new process uses addition of a strontium nitrate solution to precipitate strontium carbonate following a caustic adjustment step. The strontium addition imparts an isotopic dilution for the radioactive strontium. This is followed by an addition of a sodium permanganate solution that forms a precipitate of manganese oxides or hydroxides that incorporates the transuranic components in the waste. The process was scaled to the multi-liter volume and was shown by SRNL and Battelle to successfully decontaminate wastes removed from each of the identified tanks. Furthermore, work at Battelle with AN-102 material showed lowering the strontium could further optimize decontamination and permanganate concentrations to 0.02 M and with no added hydroxide or use of elevated temperature.

Technetium Removal

Technetium is a long-lived radionuclide that is present in tank waste in both the sludge and supernate. In the supernate, technetium is present as the pertechnetate ion (TcO_4^-). It is possible to remove this radionuclide through a number of processes, such as ion exchange, solvent extraction, crystallization, or precipitation. However, ion exchange has probably been studied to the highest degree. Ion exchange was used in 1963 to separate technetium from alkaline tank wastes at the Hanford site. Alkaline tank wastes were initially passed at ~3-gpm through a cask containing an inorganic ion exchange material to separate cesium and then through a cask containing ~400-gallons (1,5200 liters) of IRA-401 resin to separate technetium. Approximately 23,500-gallons of waste were passed through the cask containing IRA-401 resin for an average technetium recovery of 70% and approximately 1.1-kg of technetium. The resin was approaching 50% breakthrough of technetium at the conclusion of the load. The IRA-401 resin was washed and eluted with 6M nitric acid. The technetium eluate was steam stripped, concentrated to 25-gallons and shipped in a cask to the Hanford Laboratories (now known as Pacific Northwest National Laboratory).

In the early 1990's, the DOE conducted extensive testing of commercial and developmental ion exchange materials to determine suitable materials for separating various radionuclides from Hanford site tank waste solutions. These tests were conducted as part of the Tank Waste Remediation System (TWRS) Program, a predecessor organization to the WTP project. The tests conducted by the TWRS Program demonstrated acceptable technetium batch distribution coefficients (500 to 1500ml/gm) for six ion exchangers: Purolite A-520E, Ionac SR-6, Reillex HPQ, n-butyl-Reillex HP, TEVA ScintilEx, and Aliquot 336 beads. It should be noted that SuperLig® 639 resin was not being manufactured at the time the TWRS Program conducted these tests.

In addition to the above, the WTP project conducted extensive testing of SuperLig® 639 resin [Johnson 2000]. Lab-scale and pilot-scale column tests have been conducted using simulants and actual tank waste samples [King et al, 2001 and McCabe 2000]. In 1996 – 1997, SRNL personnel separated technetium from three samples of LAW material (from tanks AN-105, AN-107 and AW-101) using two columns (~10-ml each) in series containing SuperLig® 639 resin. The same columns were used for processing all three LAW solutions. In 1998 – 2001, SRNL and PNNL conducted additional testing of SuperLig® 639 resin using candidate LAW solutions from tanks AN-102 [Hassan 2000a], AN-103 [Hassan 2000b], AN-107 [Kurath 2000b] , AP-101 [Burgeson 2002], and AW-101 [Hassan 2003]. These tests were conducted using small columns (5 to 15-ml). SRNL personnel conducted tests using two ~25 to 100-ml columns of SuperLig® 639 resin to separate cesium and technetium from AZ-102 and AN-102 solutions. These tests provided information on repetitive loading and elution of the ion exchange resins as well as loading and elution profiles. In addition to laboratory-scale column tests, chemical and radiation stability testing of SuperLig® 639 resin have been conducted. SRNL personnel have also developed a preliminary ion exchange model that contains information useful for design and operation of a technetium ion exchange process using SuperLig® 639 resin [Hamm 2000].

For the WTP, technetium ion exchange was originally included as a contingency. Once the glass leach rates were established and the Performance Assessment indicated technetium removal was not needed, the ion exchange process was removed from the WTP. There was also a cost savings of several hundred million dollars with the removal of this process. Washington state objected to the removal of the technetium IX process, but eventually (about 3 years after the event) granted the RCRA permit modification to DOE. For Savannah River, technetium was evaluated in the Waste Determination process along with other radionuclides. In responses to the Nuclear Regulatory Commission's Requests for Additional Information, DOE [DOE, 2006] showed that the concentrations of Se-79, Tc-99 and I-129 in the SRS salt waste are such that they have low associated risks in the expected case based on DOE's analysis premised on the updated Special Analysis for Saltstone.

Aluminum and Chromium Removal

Leaching of non-radioactive constituents from the sludge waste can reduce the burden of material that must be vitrified in the melter systems, resulting in reduced glass waste volume, reduced disposal costs, shorter processing schedules, and higher facility throughput rates. This leaching process is estimated to reduce the Defense Waste Processing Facility (DWPF) operating life cycle at Savannah River Site (SRS) by seven years and to decrease the number of canisters to be disposed in the Repository by 1000 [Gillam et al., 2006]. Comparably, the aluminum and chromium leaching processes are estimated to reduce the operating life cycle of the Waste Treatment Plant (WTP) at Hanford by 20 years and to decrease the number of canisters to be disposed in the Repository by 15,000 - 30,000 [Gilbert, 2007].

Two primary constituents targeted for removal by leaching are aluminum and chromium. It is desirable to have some aluminum in glass to improve its durability; however, too much aluminum can increase the sludge viscosity and glass viscosity and reduce overall process throughput. Chromium has a finite solubility in glass, with excessive amounts causing formation of spinels or eskolaite that can settle in the melter or clog melter pour spouts [Perez et al., 2000]. Aluminum leaching is important to both sites, but chromium removal is important only at Hanford because a higher fraction of the chromium is insoluble in the Hanford sludge than in the sludge at SRS. As long as the chromium concentration can be maintained at less than 0.5 wt % in the glass, removal has little impact on sludge mass and no impact on glass quality.

A full-scale aluminum dissolution was performed in a waste tank at SRS in 1982 [Gillam, 2006b, Ator, 1984]. Sludge from Tank 15H was transferred to Tank 42H and settled to a final volume of about 64,000 gallons. Sodium hydroxide solution was added over a period of 21 days, and some salt solution was added as a source of liquid and caustic to minimize added caustic. The tank was heated with steam and mixed with slurry pumps for five days at 83 – 85 °C. The slurry was then settled, and the leachate liquor was decanted. The slurry was washed three times. The mixing pumps leaked a substantial amount of water into the tanks as well, enough to nearly double the volume of liquid during the dissolution step. The process successfully removed 79% of the aluminum from the sludge, but it generated 2,975,000 gallons of liquid. Other issues at the time included difficulty of the ventilation system in handling the excessive amount of liquid in the vapor and slower than expected settling of the resulting sludge.

At SRS, there are a limited number of tanks that contain appreciable amounts of high aluminum sludge [Gillam, 2006; Hamm et al., 2006]. Tanks 12H, 13H, 15H, 32H, 35H, and 39H together contain about 1000 metric tons of aluminum, which represents 61% of the total aluminum in all the waste tank sludge. At SRS, the conceptualized process is to dissolve the aluminum in a dedicated Type III waste tank outfitted with up to four mixer pumps. This tank (assumed to be Tank 42H) is a 1.3 million gallon waste storage tank, equipped with a fully active ventilation system and cooling coils. The first step is to transfer unwashed sludge slurry (~15 wt % solids) into the process tank. With mixing, the sodium hydroxide solution is added, and the tank is heated using steam sparging to 85 °C. Temperature is maintained, and the tank is continuously mixed for several days, with the duration dictated by composition and conditions. The tank contents are then allowed to cool and settle for at least fourteen days. The aluminum-rich supernate is then decanted and sent to another tank. The remaining sludge is rinsed with another more dilute sodium hydroxide solution, mixed, settled for at least fourteen days, and decanted. This rinsing, mixing, and settling is then repeated again, with an even lower concentration of sodium hydroxide solution. The aluminum-depleted sludge is then ready for transfer to the sludge washing tank, where more water is added to remove the soluble salts to meet the DWPF feed requirements, and mixing and settling are repeated.

A recent effort was completed at SRS to dissolve aluminum from the remains of Sludge Batch 4 stored in Tank 51. The sludge stored in Tank 51 contained sludge retrieved from Tank 11, which contained a large inventory of aluminum. This plant evolution occurred from October 2007 to February 2008. The process used was Low Temperature Aluminum Dissolution (LTAD). In this process, nearly 130 kgal of 50 wt % sodium hydroxide was added from 43 tanker trailers. Two slurry pumps were used to agitate the sludge-caustic mixture. The pump energy was sufficient to raise the tank content to between 55 and 64 °C. After approximately 45 days, nominally 307 kgal of aluminum-rich supernate was decanted to Tank 11. Analytical results indicated that ~ 60% of the available aluminum dissolved. This successful demonstration reduced the DWPF canister count by approximately 110 cans.

In the WTP baseline flow sheet, sludge solids are first recovered from various single shell and double shell tanks. During the retrieval process, incidental blending of the sludge occurs, resulting in blending of the gibbsite, boehmite and various chromium phases. This blended feed slurry is then delivered to the WTP at a nominal solids concentration of 6 wt % (though this value may vary up to 16 wt %). This slurry is then further blended with supernate retrieved from other tanks and the resultant blended slurry is concentrated to 20 wt % solids by filtration. After concentration, caustic is added, and the stainless steel tank is heated with steam to 100 ºC to dissolve the aluminum. The tank is held at temperature for at least eight hours. This process effectively dissolves all the gibbsite and roughly half the boehmite. Gibbsite and boehmite are two of the main Al-containing components in Hanford tank wastes. The slurry is then cooled and re-concentrated by filtration. Then the slurry is washed to dilute the caustic concentration. This washing step effectively removes the solubilized aluminum from the insoluble solids and is needed to prevent the potential solubilization of plutonium during the subsequent oxidation of chromium. (This solubilization of plutonium occurs under strongly oxidizing conditions if it is also in the presence of high hydroxide concentrations). After washing, sodium permanganate is added to oxidize the Cr(III) to Cr(VI). This slurry is allowed to react for six hours; then the slurry is again washed to separate the solubilized Cr(VI) from the sludge solids. This treatment dissolves approximately 80% of the chromium, which is sufficient. All of the filtered liquid phases are sent to ion exchange for cesium removal, and the insoluble solids are sent to the HLW melter system

List of Acronyms and Abbreviations

ALARA	As Low As Reasonably Achievable
ARP	Actinide Removal Process
BV	bulk vitrification
CAW	PUREX Current Acid Waste
CF	concentration factor
CFR	Code of Federal Regulations
CSSX	Caustic-Side Solvent Extraction
CST	crystalline silicotitanate
DBVS	demonstration bulk vitrification system
DDA	Deliquification, Dissolution and Adjustment
DF	decontamination factor
DOE	Department of Energy
DST	double shell tank
DWPF	Defense Waste Processing Facility
EDTA	ethylene diamine tetraacetic acid
EM	Environmental Management
ETF	Effluent Treatment Facility
HEDTA	Hydroxyethylene diamine triacetic acid
HLW	high level waste
IPS	Hanford Interim Pretreatment System
ITP	In-Tank Precipitation
LANL	Los Alamos National Laboratory
LAW	low activity waste
LDRD	Laboratory Directed Research & Development
LLW	low-level waste
LTAD	Low Temperature Aluminum Dissolution
MCU	Modular Caustic Side Solvent Extraction Unit
MST	monosodium titanate
MVST	Melton Valley Storage Tank
NPH	normal paraffin hydrocarbon
NRC	US Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
ORP	Office of River Protection
PNNL	Pacific Northwest National Laboratory
PNS	PUREX Neutralized Supernate
PUREX	Plutonium and Uranium Extraction
RMF	rotary microfilter
RNS	Redox Neutralized Supernate
RPP	River Protection Program
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscope
SEPHIS	Solvent Extraction Processes Having Interacting Solutes
SNL	Sandia National Laboratory

SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SST	single shell tank
SWPF	Salt Waste Processing Facility
TFA	Tanks Focus Area
TBP	tributyl phosphate
TRU	transuranic
TWRS	Tank Waste Remediation System
WIR	Waste Incidental to Reprocessing
WSRC	Washington Savannah River Company
WTP	Hanford Tank Waste Treatment and Immobilization Plant

References

Ator, R. A., *"In Tank Sludge Processing Demonstration Technical Summary,"* DPSP 83-17-14, September 13, 1984.

Barton, B. *"S-102/S-112 Limits of Technology Retrievals," Presented to: 2006 Hanford/SRS/Idaho Technical Exchange,"* May 2006.

Bonnesen PV, LH Delmau, BA Moyer, and RA Leonard, *"A Robust Alkaline-Side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste," Solvent Extr. Ion Exch.*, 18**:**1079-1107, 2000.

Bray, LA, KJ Carson, and RJ Elovich, "*Initial Evaluation of Sandia National Laboratory-Prepared Crystalline Silico-Titanates for Cesium Recovery,"* PNL-8847, 1993..

Bray, LA, JE Amonette, GN Brown, TM Kafka, and SF Yates, "E*fficient Separations and Processing Crosscutting Program: Develop and Test Sorbents",* PNL-10750, 1995.

Brown, GN, LA Bray, CD Carlson, KJ Carson, JR DesChane, RJ Elovich, FV Hoopes, DE Kurath, LL Nenninger, and PK Tanaka, "C*omparison of Organic and Inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste,"* PNL-10920, 1996.

Burgeson, I. E., et al, *"Small-Scale Column Testing of SuperLig 639 for Removing* ^{99}*Tc from Hanford Tank Waste Envelope A (241-AP-101),"* PNWD-3222, 2002

Department of Energy, *"Basis for Section 3116 Determination for Salt Waste Disposal at the Savannah River Site"*. DOE-WD-2005-001. January 2006.

Dosch, R. G., *"The Use of Titanates in Decontamination of Defense Wastes,"* Technical Report SAND-78-0710, Sandia Laboratories, Albuquerque, NM, June 1978.

SK Fiskum, ST Arm, MS Fountain, MJ Steele, and DL Blanchard, Jr. "*Spherical Resorcinol-Formaldehyde Resin Testing for* ^{137}*Cs Removal from Simulated and Actual Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A) Using Small Column Ion Exchange*," PNWD-3697, 2006a.

SK Fiskum, MJ Steele, and DL Blanchard, Jr., "S*mall Column Ion Exchange Testing of Spherical Resorcinol-Formaldehyde Resin for* ^{137}*Cs Removal from Pre-Treated Hanford Tank 241-AN-102 Waste (Envelope C)*, PNWD-3751, 2006b.

Fiskum, SK, IE Burgeson, OT Farmer, III, LR Greenwood, CZ Soderquist, MJ Steele, and MP Thomas, "*Spherical Resorcinol-Formaldehyde Resin Analysis Following Actual Hanford Tank Waste Processing,"* PNWD-3752, 2006c.

Georgeton, G. K., and M. R. Poirier, *"Alternative Filtration Testing Program: Preliminary Evaluation of Filter Test Results"*, WSRC-RP-90-1145, September 28, 1990.

Gilbert, R., *"Caustic and Oxidative Leaching to Solubilize Aluminum and Chromium,"* January 23, 2007 Workshop presentation.

Gillam, J., H. Shah, M. Rios-Armstrong, *"Sludge Batch Plan,"* CBU-PIT-2005-00144, Rev. 1.August 7, 2006.

Gillam, J. M., *"Aluminum in Waste Tank Sludge: History and Status,"* CBU-PIT-2006-00068, July 11, 2006b,

Hallen, R. T.,I. E. Burgeson,F. V. Hoopes, and D. R. Weier, *"Optimization of Sr/TRU Removal Conditions with Samples of AN-102 Tank Waste,"* RPP-WTP-RPT-029 Rev. 0, February 2002.

Hamm, L. L., et al, *"Preliminary Ion Exchange Modeling for Removal of Technetium from Hanford Waste Using SuperLig® 639 Resin,"* WSRC-TR-2000-00305, 2000.

Hamm, B.A., H.H. Elder, *"Savannah River Site Sludge Characterization Model Using Dial-up Factors,"* CBU-PIT-2006-00058, March 28, 2006.

Hassan, N. M., et al, *"Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-102,"* BNF-003-98-0219, 2000.

Hassan, N. M, et al., "*Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-103*," BNF-003-98-0146, 2000.

Hassan, N. M., et al, "*Multiple Ion Exchange Column Tests For Technetium Removal From Hanford Tank Waste Supernate (U)*," WSRC-MS-2003-00789, 2003.

Herting, D. A., "*Fractional Crystallization Flowsheet Tests with Actual Tank Waste,*" RPP-RPT-31352, Revision 0, October 2006.

Hobbs, D. T., "*Particle Size and Settling Velocity of Tank 41H Insoluble Solids"*, WSRC-TR-95-0249, May 30, 1995.

Hobbs, D. T., R. L. Pulmano, "*Phase IV Testing of Monosodium Titanate Adsorption with Radioactive Waste",* WSRC-TR-99-00286, Rev. 0, September 3, 1999.

Hobbs, D. T.; Barnes, M. J.; Pulmano, R. L.; Marshall, K. M.; Edwards, T. B.; Bronikowski, M.G.; Fink, S. D , *"Strontium and actinide separations from high level nuclear waste solutions using monosodium titanate 1. simulant testing," Separation Science and Technology*, 2005, 40(15), 3093-3111.

Johnson, M. E. and T. W. Crawford, PL, "*TWRS- P Project Development Requirements Document*," PL -W375-TE00002, Rev. 1, 2000.

King W. D. et al, "*Technetium Removal from Hanford and Savannah River Site Actual Tank Waste Supernates with SuperLig® 639 Resin*," WSRC-MS-2001-007609, 2001

Kurath, DE, DL Blanchard, and JR Bontha, "*Ion Exchange Distribution Coefficients for ^{137}Cs and ^{99}Tc removal from Hanford Tank Supernatants AW-101 (Envelope A) and AN-107 (Envelope C)*," PNWD-2467, 1999.

Kurath, DE, DL Blanchard, and JR Bontha., "*Small Column Ion Exchange Testing of Superlig 644 for Removal of ^{137}Cs from Hanford Tank Waste Envelope A (Tank 241-AW-101)*," PNWD-3001, 2000.

Kurath, D. E., *"Small-Scale Column Testing of SuperLig 644 for Removal of Cs from Hanford Tank Waste Envelope C (241-AN-107)*," PNWD-3039, 2000.

Leonard RA, SB Aase, HA Arafat, C Conner, DB Chamberlain, JR Falkenberg, MC Regalbuto, and GF Vandegrift, *"Experimental Verification of Caustic-Side Solvent Extraction for Removal of Cesium from Tank Waste," Solvent Extr. Ion Exch.*, **21:**505-526, 2003.

Lynch, R.; Dosch, R.; Kenna, B.; Johnstone, J; Nowak, E., *"The Sandia Solidification Process – a Broad Range Aqueous Solidification Method. IAEA Symposium on the Management of Radioactive Waste,"* Vienna, Austria, 1976, 360-372.

Moyer, B. A., J. F. Birdwell, Jr., L. H. Delmau, and J. McFarlane, *"Caustic-Side Solvent-Extraction Modeling for Hanford Interim Pretreatment System,"* ORNL/TM-2008/073, June 2008.

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

McCabe, D. J. et al, "*Comprehensive Scale Testing of the Ion Exchange Removal of Cesium and Technetium from Hanford Tank Wastes*," WSRC-MS-2000-00499, 2000.

Nash, C. A., H. H. Saito, and W. R. Wilmarth, *"Precipitation of Strontium and Transuranics and Cross-Flow Filtration of a Sample from Large Hanford Tank 241-AN-102,"* J. of Sep. Sci and Tech., 38, 3289, 2003.

Norato MA, MH Beasley, SG Campbell, AD Coleman, MW Geeting, JW Guthrie, CW Kennel, RA Pierce, RC Ryberg, DD Walker, JD Law, and TA Todd, *"Demonstration of the Caustic-Side Solvent Extraction Process for the Removal of ^{137}Cs from Savannah River Site High Level Waste," Sep. Sci. Technol.*, 38:2647-2666, .2003.

Poirier, M. R., D. T. Herman, D. B. Stefanko, and S. D. Fink, *"Testing of a Rotary Microfilter to Support Hanford Applications,"* in preparation.

Porter, M. C., Ed., *"Handbook of Industrial Membrane Technology,"* Park Ridge: Noyes, 1990.

Perez, J. M., D.F. Bickford, D.E. Day, D.S. Kim, S.L. Lambert, S.L. Marra, D.K. Peeler, D.M. Strachan, M.B. Triplett, J.D. Vienna, R.S. Wittman, *"High-Level Waster Melter Study Report,"* PNNL-13582, July, 2001. Rapko, B.M., G.J. Lumetta, Status Report on Phase Identification in Hanford Tank Sludges, PNNL-13394, 2000.

Peters, T. B.; Barnes, M. J.; Hobbs, D. T.; Walker, D. D.; Fondeur, F. F.; Norato, M. A.; Fink, S. D , "*Strontium and actinide separations from high level nuclear waste solutions using monosodium titanate 2. actual waste testing,", Separation Science and Technology*, 2006 (41), 2409 - 2427.

Smith, F. G., "*Modeling of Ion-Exchange for Cesium Removal from Dissolved Saltcake in SRS Tanks 1-3, 37 and 41,"* WSRC-STI-2007-00315, Rev. 0, August 2007.

Smith, F. G., *"Modeling of Ion-Exchange for Cesium Removal from Hanford Interim Pretreatment System Feeds,"* WSRC-STI-2008-00232, Rev. 0, May 2008.

Walker, J. F. Jr., et. al., "*Small Column Ion Exchange (SCIX) Alternative To Remove 137cs From Low Curie Salt Waste: Summary of Phase 1,"* ORNL/TM-2003/287, Oak Ridge National Laboratory, Oak Ridge, TN March 2004.

Wester, DW, DL Baldwin, P Berry, KJ Carson, BJ Cook, LP Darnell, JR DesChane, TG Levitskaia, BM Rapko, and CZ Soderquist, "*Ion-exchange Research in Support of Modular Treatment of Savannah River Site Tank Wastes,"* PNNL-45344, 091103B, 2003.

Wilmarth W. R., S. W. Rosencrance, C.A. Nash, D. P. DiPrete, and C. C. DiPrete, *"Transuranium removal from Hanford High Level Waste simulants using sodium permanganate and calcium,"* J. Radioanal. and Nucl. Chem., 247, 2001, p. 501**.**

Appendix A

Seven major facilities and six chemical processing flowsheets were used at the Hanford Site for separations of plutonium, uranium, and fission products, whereas only two facilities and flowsheets were used at the Savannah River Site for separations and recovery of plutonium and uranium. The historical use of different flowsheets at each site has lead to significant difference in the composition of tank wastes. For example, the Hanford Site used the bismuth phosphate ($BiPO_4$) process from 1945 through 1952 at B Plant and from 1945 through 1956 at T Plant to separate plutonium (and small amounts of neptunium) from irradiated aluminum-coated metal uranium fuel elements. The $BiPO_4$ process did not recover uranium from the fuel elements. Instead, the uranium was discharged along with large quantities of chemicals to the underground storage tanks. The wastes in the storage tanks formed precipitates containing primarily Al, Bi, Cr, Fe, Pb, Mn, Hg, PO_4, Na, SO_4, Sr, and Zr. The majority of the soluble chemicals and less than 10% of the long-lived radionuclides were subsequently discharged from the underground storage tanks to subsurface cribs and trenches.

The uranium partially precipitated in the storage tanks and was subsequently removed using hydraulic mining techniques (i.e., sluicing). The recovered uranium slurries were processed in U Plant from 1952 through 1957 using a tributyl phosphate (TBP) solvent extraction process to separate uranium from fission products and chemicals. The U Plant wastes were returned to the underground storage tanks. Cesium and strontium present in the U Plant wastes were precipitated using sodium ferrocyanide (FeCN), nickel sulfate, and calcium nitrate. This so-called FeCN precipitation process was conducted from 1954 through 1957 and is one of the major sources of Ca, Fe, and Ni present in the Hanford Site tank sludges.

The $BiPO_4$ processing facilities were replaced by the more efficient REDOX (1952 – 1967) and PUREX (1956 – 1972 and 1983 – 1990) Plants. The 202-S REDOX Plant was also unique to the Hanford Site. The REDOX process used packed pulse columns to separate uranium, plutonium, and neptunium from irradiated aluminum-coated metal uranium fuel elements using hexone as the solvent. The REDOX process was the major source of Cr and Al present in the Hanford Site tank sludges.

The Hanford Site 202-A PUREX Plant used solvent extraction columns, whereas mixer settlers were used in the 221-F and 221-H PUREX Plants at the Savannah River Site. In general, the PUREX flowsheets used at each site are similar; however, the quantities of chemicals used varied due to the different equipment used and different fuels processed. For example, the Hanford Site 202-A PUREX Plant processed irradiated aluminum-coated and Zircaloy-clad metal uranium fuel elements. The processing of the Zircaloy-clad fuel elements added zirconium, fluoride, and potassium to the tank wastes.

The $BiPO_4$, TBP, FeCN, and REDOX processes were unique to the Hanford Site and were not performed at the Savannah River Site. Each of these processes used chemicals that added to the inventory of wastes stored in the Hanford Site tanks. The $BiPO_4$, TBP, FeCN, and REDOX processes formed precipitates or metal sludges in the Hanford Site underground storage tanks. Therefore, the Hanford Site tanks contain sludges with concentrations of chemicals (e.g. Bi, Cd, Cr, Ni, etc.) that are different from the sludges stored in the Savannah River Site tanks.

The ultimate goal of waste pretreatment is to remove the highly radioactive species to an extent necessary for disposal of the bulk of the waste as low activity waste (LAW). At Hanford, the tank waste sludges, entrained solids and Cs-137 are the high level waste (HLW) fraction of the tank wastes and will be immobilized in glass in the Waste Treatment Plant currently under construction for disposal at the national repository.

The waste incidental to reprocessing determination also established a technical and economical processing limit of 0.05 Ci/L or 0.189 Ci/gal (normalized to 7 M sodium) for the Cs-137 concentration in LAW. Wastes with a Cs-137 concentration less than 0.05 Ci/L (normalized to 7 M sodium) do not require cesium removal to be considered waste incidental to reprocessing. While the Cs-137 concentration in some of the SST saltcake wastes is lower than this limit, the Cs-137 concentrations in all of the DST supernatants exceed this limit. Further reduction of the Cs-137 concentration in LAW processed by the WTP LAW facility is required based on the facility design and operating concept in order to maintain personnel radiation exposure As Low As Reasonably Achievable (ALARA). The maximum Cs-137 concentration in wastes processed by the WTP LAW facility is ~1.05E-04 Ci/L[1] (normalized to 7 M sodium) to meet ALARA goals for personnel radiation exposure. In order to comply with the above requirements, DST supernatant wastes must be treated to separate entrained solids and Cs-137 prior to processing in the WTP LAW facility. SST saltcake wastes must be treated to separate entrained solids to meet the waste incidental to reprocessing determination requirements and must be treated for removal of Cs-137 and/or diluted (if Cs-137 concentration less than 0.05 Ci/L normalized to 7 M sodium) to meet ALARA goals for the WTP LAW facility.

---

[1] Actual limit is 1.17E-04 Ci/L assuming 20 wt% sodium oxide loading in the ILAW glass. The value used is 90% of the WTP limit.