Fractional Crystallization of Hanford Single-Shell Tank Wastes – Laboratory Development

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ABSTRACT

Laboratory studies demonstrate that fractional crystallization is a viable process for separating Hanford medium-curie waste into high-curie and low-curie fractions. The product salt from the crystallization process qualifies as low-curie feed to a supplemental treatment system (e.g., bulk vitrification). The high-curie raffinate is returned to the double-shell tank system, eventually to be sent as feed to the Waste Treatment and Immobilization Plant.

Process flowsheet tests were designed with the aid of thermodynamic chemical modeling. Laboratory equipment design and test procedures were developed using simulated tank waste samples. Proof-of-concept flowsheet tests were carried out in a shielded hot cell using actual tank waste samples. Data from both simulated waste tests and actual tank waste tests demonstrate that the process exceeded all of the separation criteria established for the program.

INTRODUCTION

The Hanford site has 149 single-shell tanks and 28 double-shell tanks storing approximately 53 million gallons of radioactive waste resulting from production of nuclear weapons material during the Cold War era. Current plans for disposal call for vitrifying the bulk of the waste at the Waste Treatment and Immobilization Plant (WTP). To reduce the burden on the WTP and speed up the disposal process, the Mission Acceleration Initiative (MAI) was implemented. The MAI plans call for sending a fraction of the waste, designated low-activity waste (LAW), to some form of supplemental treatment, e.g., bulk vitrification, rather than to the WTP. The amount of existing waste that could be classified as LAW is rather limited, but MAI plans include implementing a pretreatment process to convert medium-curie waste into LAW by reducing the radionuclide content of the waste (see Fig. 1). Fractional crystallization has been proposed as a candidate pretreatment process.

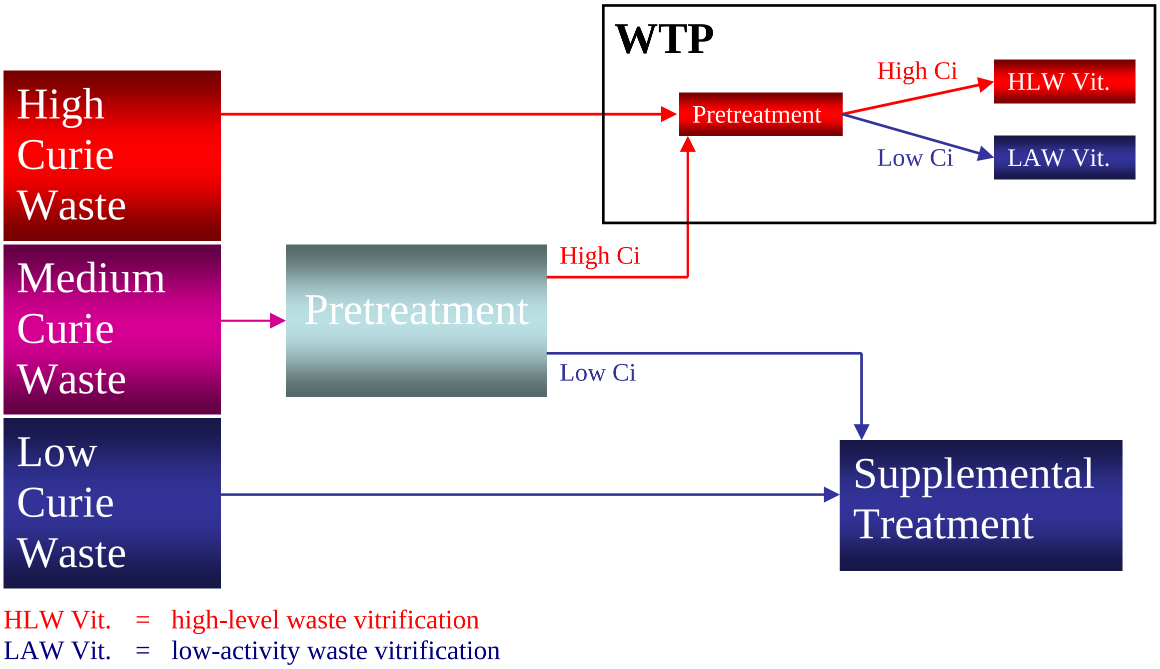


Fig. 1. Role of medium-curie waste pretreatment in Mission Acceleration Initiative program

Fractional crystallization is a common industrial practice but represents a radically different approach to radioactive waste pretreatment. Historically, cleaning up radioactive waste has meant finding ways to remove "the bad stuff" (i.e., the radionuclides) from the waste. Example methods include removing Cs-137 from the waste by cation exchange, removing Tc-99 by anion exchange, removing I-129 by precipitation in a silver reactor, or removing transuranic isotopes by solvent extraction, to name a few.

Fractional crystallization takes a different approach. Instead of removing radionuclides from the waste, fractional crystallization removes "the good stuff"—nonradioactive salts, e.g., sodium nitrate, carbonate, sulfate, etc. The nonradioactive salts are precipitated from the waste by evaporation of water, leaving the radionuclides in the residual solution. The precipitated salts are redissolved in water to form the LAW stream that becomes the feed to the supplemental treatment process. The end result is the same as the application of multiple radionuclide removal operations—a salt waste depleted of radionuclides—but the goal is accomplished with one process instead of several.

In addition to its simplicity, fractional crystallization has a number of other advantages over the traditional multi-process approach:

a. No chemicals are added to the waste or used in the process.
b. No secondary waste streams (e.g., spent resins) are generated by the process.

c. Dose rates in the facility remain low because there is no buildup of radionuclides, e.g., as with loaded resins, so less shielding is required.
d. The process has a long and diverse history of successful industrial applications.

Theory

The scientific theory behind the fractional crystallization process is simple. The medium-curie feed arrives at the facility as an aqueous salt solution. Water is evaporated at reduced temperature and pressure until sodium salts precipitate from solution. Fig. 2 shows an example of the formation of various salt phases as water is evaporated from a typical medium-curie feed solution.

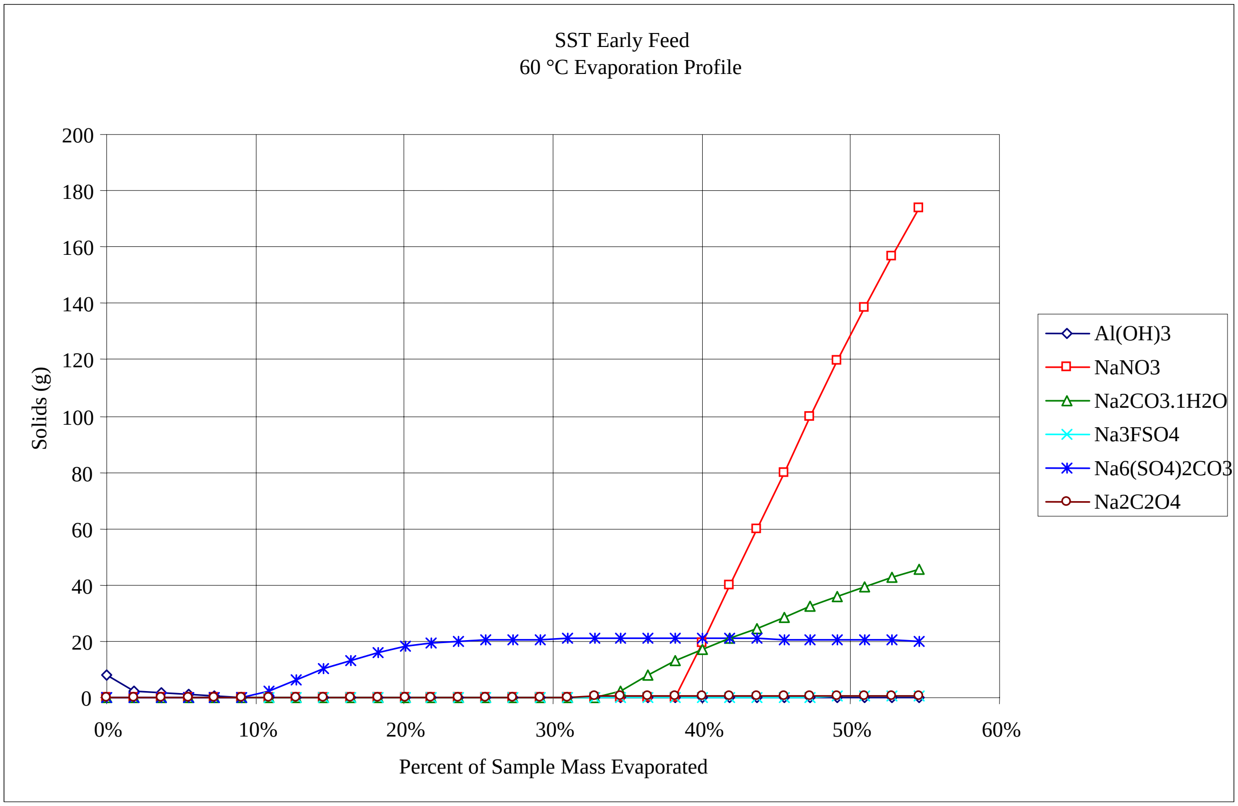


Fig. 2. Typical evaporation profile

The radionuclides remain in the liquid phase for two reasons: (1) The concentrations of radionuclide salts in solution are so low that they never approach saturation; e.g., the concentration of Cs-137 in a typical feed solution is 1 x 10^{-5} M while the solubility of $CsNO_3$ in water is about 1 M, and (2) the radionuclide ions are too large to substitute for the nonradioactive ions in the salt crystals; e.g., the ionic radii of Na^+ and Cs^+ are 0.95 Å and 1.69 Å, respectively. Fig. 3 shows a space-filling model of a $NaNO_3$ crystal structure next to individual Na^+ and Cs^+ ions. It is clear that there is insufficient room in the crystal structure for a Cs^+ ion to substitute for a Na^+ ion without great stress being placed on the crystal lattice.

The precipitated low-activity sodium salts are separated from the high-activity mother liquor by centrifugation or filtration, washed with saturated salt solution to remove residual mother liquor, and redissolved in water to form the LAW stream. The contaminated wash solution is recycled to the evaporator. The high-activity mother liquor is returned to the tank farm for storage in a double-shell tank until it becomes feed for the WTP.

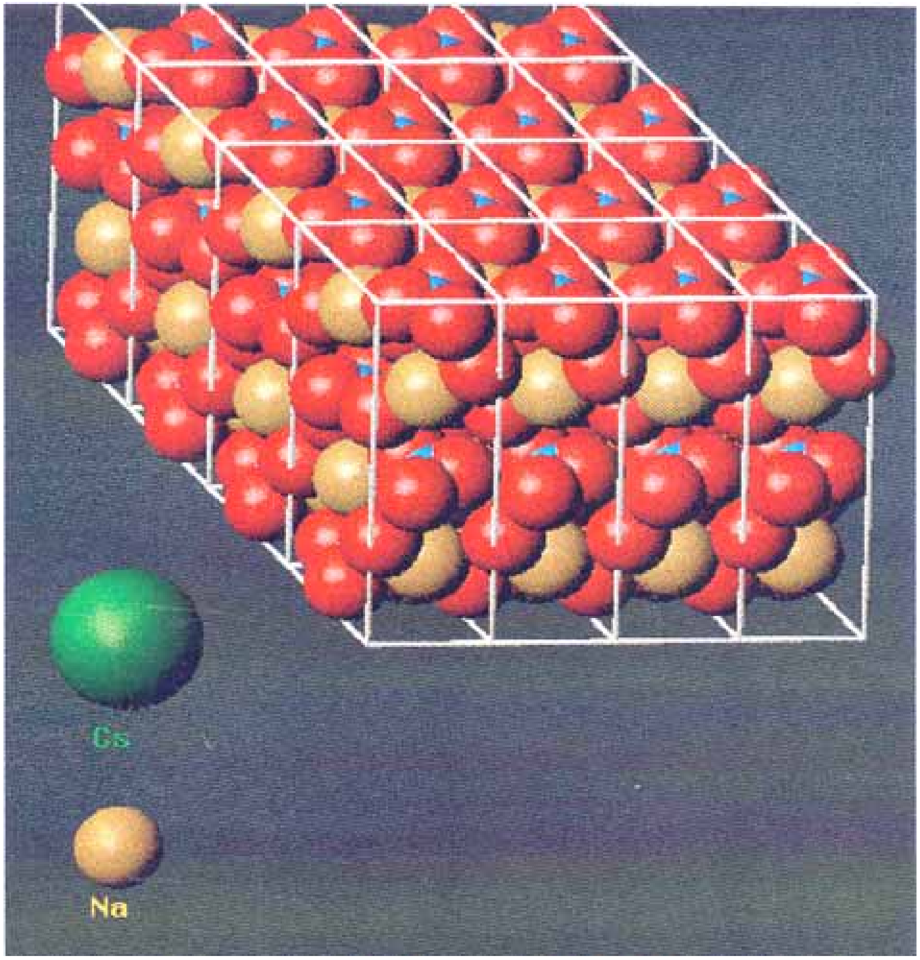


Fig. 3. Sodium nitrate crystal structure
(O = red, N = blue, Na = brown, Cs = green)

Process Feed

The medium-curie feed solution comes about as a result of saltcake retrieval operations. Of the 53 million gallons of waste stored in the underground tanks, nearly half is saltcake. Saltcake is retrieved from single-shell tanks by pumping water into the tank, dissolving the salt, and pumping the resulting brine out of the tank. This brine, which may be filtered to remove trace solids, becomes the medium-curie feed to the pretreatment process.

Because some saltcake components dissolve more readily than others—a process known as selective dissolution—the composition of the retrieved brine varies as a function of time during the retrieval process. For the purposes of the fractional crystallization project, the term “SST Early” applies to an average or typical composition of the retrieved brine during the early part of retrieval; the term “SST Late” refers to the composition of the brine near the end of the retrieval. Table I shows the concentrations of some key components of the two waste feed types based on analysis of solutions obtained by dissolving a composite sample of actual tank waste. Laboratory testing was done on both feed types to evaluate the ability of the fractional crystallization process to handle any type of medium-curie waste generated during saltcake retrieval.

Table I. Major Feed Components in Molarity

Component	SST Early	SST Late
Na^+	6.31	1.20
NO_3^-	3.28	0.53
NO_2^-	0.52	0.07
CO_3^{2-}	0.61	0.10
OH^-	0.62	0.10
SO_4^{2-}	0.13	0.02
Cs^+	1.0×10^{-5}	1.6×10^{-6}

Project Plan

In 2004, a Call for Proposals was issued by CH2M HILL Hanford Group, Inc. titled “Hanford Medium/Low Curie Waste Pretreatment Alternatives Project,” funded by the U.S. Department of Energy’s EM-20 program. In December of that year, a contract was awarded to a team led by COGEMA, Inc. (now AREVA NC), and including the Georgia Institute of Technology (Georgia Tech), Swenson Technology, Inc. (Swenson), and Framatome NP (now AREVA NP). A structured program was developed to (1) demonstrate that fractional crystallization could be used to pretreat Hanford tank wastes and (2) provide data to develop a pilot-plant design. The project plan was to evaluate the process by a two-phased program consisting of extensive simulant testing and thermodynamic model development in Phase I, followed by a similar program in Phase II that included testing actual tank waste.

This paper covers the laboratory development program with simulated and actual tank waste. Other papers being presented at this conference cover the thermodynamic model development (“Fractional Crystallization of Hanford Single-Shell Tank Wastes – A Modeling Approach,” paper 7230) and the overall fractional crystallization program (“Fractional Crystallization of Hanford Single-Shell Tank Wastes – From Concept to Pilot Plant,” paper 7227).

SIMULATED WASTE TESTING

An experimental semi-batch apparatus was designed and assembled to test the fractional crystallization process on SST Early and SST Late simulant solutions. Original designs were frequently modified to obtain the apparatus represented in Fig. 4. Key aspects include a jacketed crystallizer in which the contents were kept well mixed with motor-driven impellers. Fig. 4 shows a funnel that was used to add feed during a run to maintain a constant slurry level in the crystallizer, a heat exchanger that condensed the generated water vapor, a balance to determine the mass of collected condensate, a vacuum pump, and a data acquisition system to record process variables. A full test run involves two stages in which water is evaporated from the crystallizer at a specific rate until a predetermined condensate-to-feed ratio is achieved. This value is bounded by an objective to keep the solids content in the crystallizer slurry below a specified value (30 wt%).

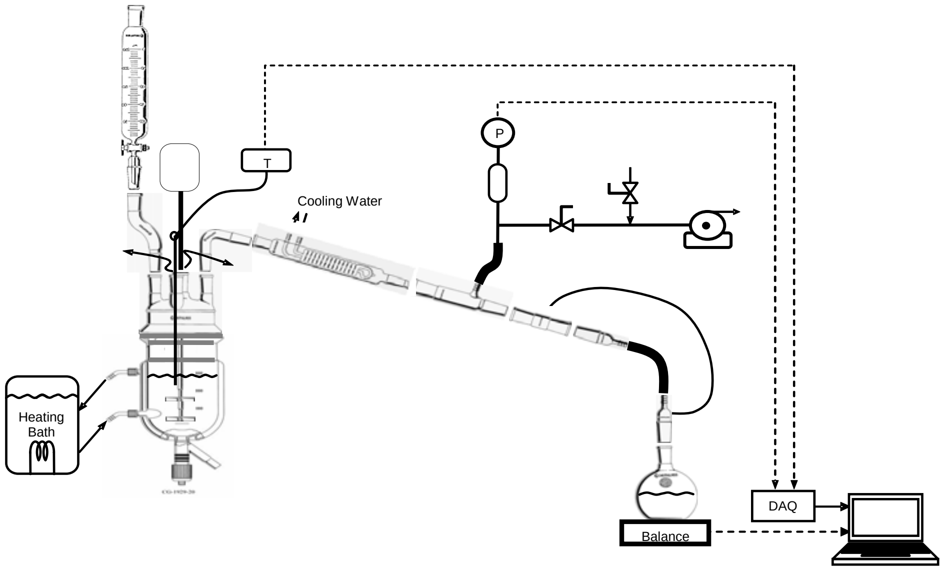


Fig. 4. Schematic drawing of semi-batch crystallization apparatus

When the operation of a stage is ended, the slurry is recovered, filtered, and washed. Samples are taken of the slurry for analysis by polarized-light microscopy (PLM), and the washed solids are dried and sieved. Samples of the sieved crystals also are analyzed by PLM. Filtrate obtained from the first stage is diluted slightly to prevent further crystallization and used as feed for the second crystallization stage.

Representations of the progress of a typical run are shown in Fig. 5. The graph on the left shows plots of the condensate recovery and feed added to the system, while that on the right shows measured temperatures and pressures. The temperature variation was maintained within ±1 °C by adjusting the system pressure to accommodate increases in the boiling point elevation.

The crystals recovered from a simulant run were essentially all sodium salts, with sodium nitrate, sodium carbonate monohydrate, and burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$). The largest of the crystals was sodium nitrate, which crystallizes in rhombohedral form and grows to sizes up to about 500 μm in the semi-batch run. Sodium carbonate forms elongated crystals, whose PLM images are colorful, with a dominant size in the range from about 15 μm to 250 μm. Burkeite crystals are significantly smaller with a dominant size ranging from 20 μm to 30 μm.

Samples of the solids were carefully taken and subjected to a refined sieving operation. The results included mass of crystals on each sieve and the sizes of all sieves. These were then transformed into fractional mass densities to obtain information on the product crystal size distribution for each stage of each run. Fig. 6 gives a plot for the first stage of Run 38b.

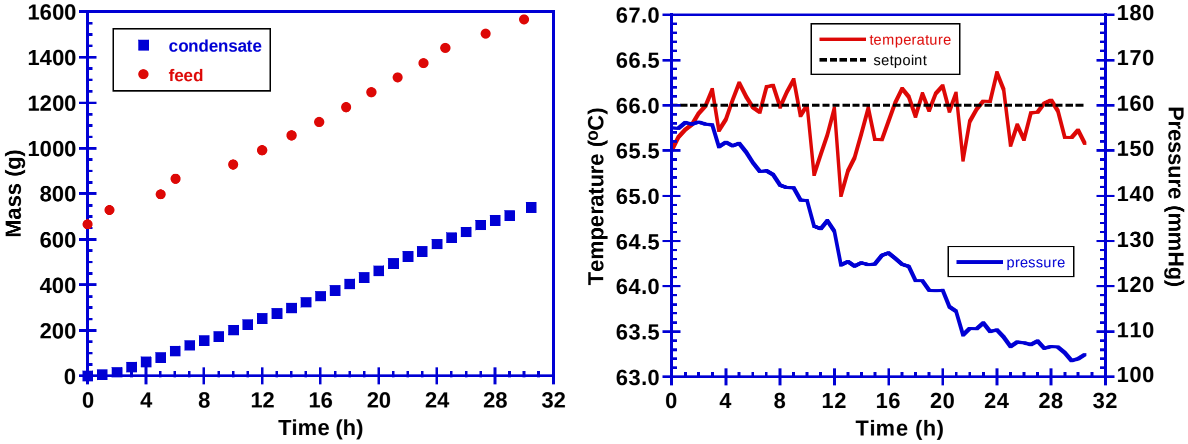


Fig. 5. Operating conditions during a typical simulant run

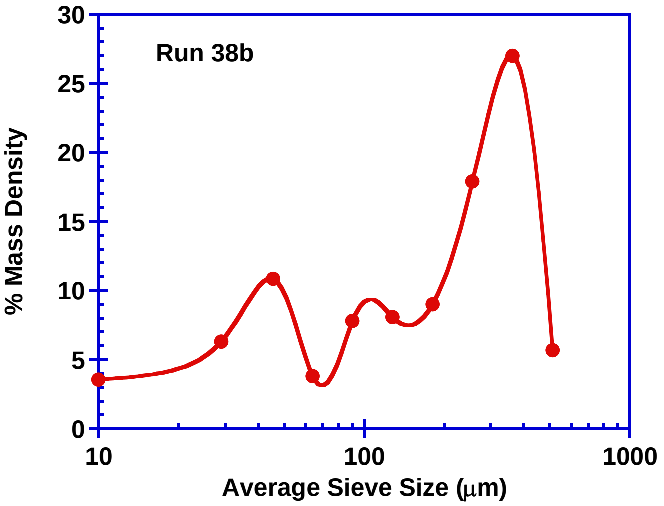
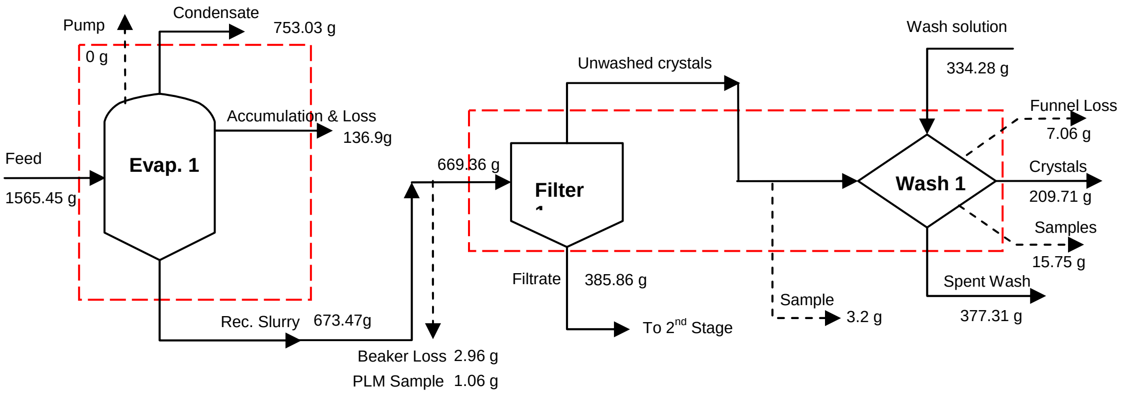


Fig. 6. Product crystal size distribution from Run 38b, Stage 1

The quality of data collected on each stage of each run was evaluated in terms of closure of mass balances. In performing this evaluation, great care was taken to be sure that materials were carefully weighed and to account for all known losses of material. Fig. 7 illustrates how a balance on total mass was performed; after accounting for known losses, the closure for this stage of Run 38b was within 0.4%.



Pump	Mass of the condensate collected in the cold trap protecting the vacuum pump.
Recovered Slurry	Mass of slurry recovered from the crystallizer.
Accumulation and Loss	Mass recovered by washing the vessel with a known amount of water.
Funnel Loss	Mass recovered by washing the funnel with a known amount of water and then drying with paper of a known weight. Performed after the filtration and washing operations.
Beaker Loss	Mass of slurry lost in the beaker necessary for the transfer from the vessel to the filter.
Sample	Mass collected from the unwashed crystals or washed crystals.
PLM Sample	Mass taken from the slurry for PLM imaging.

Fig. 7. Overall mass balance in Stage 1 of Early Feed Run 38b
(Solid arrows are the process streams and the dotted arrows represent the quantified losses. Closure on a total mass balance was performed for each dashed box around a process unit.)

ACTUAL TANK WASTE TESTING

There were two compelling reasons to perform laboratory flowsheet tests using actual tank waste feed samples. First, experience has shown that actual tank waste sometimes behaves differently than simulated tank waste. However, due to the order(s)-of-magnitude difference in cost, more extensive studies such as parametric effects on system performance are usually carried out with simulants. It was necessary to show that the actual tank waste samples behave the same as the simulants to establish the validity of process chemistry results based on simulated waste tests. Second, it was necessary to establish that the process separation criteria for sodium, Cs-137, and sulfate were achievable with actual tank waste. Both goals were achieved.

Preparations

The first step in the actual tank waste testing was to generate samples of SST Early and SST Late feed solutions from actual tank waste. Archived single-shell tank core samples were used for this purpose. Sixty-three archive samples from seven tanks in Hanford’s S-farm and SX-farm were combined to form (in effect) one large composite sample weighing 2.9 kg. An equal weight of water was added to the composite, and the slurry was stirred to dissolve solids. After the slurry settled, 4.7 kg of clear supernatant liquid was decanted into a container labeled SST Early feed. The settled solids were treated with 2.9 kg fresh water. The new mixture was stirred and settled as before, and 3.1 kg of clear supernatant liquid was decanted into a container labeled SST Late feed. Compositions of the two feed solutions are shown in Table I.

The second step was to build a crystallizer system at Hanford’s 222-S Laboratory duplicating the one that had been used for the simulated waste tests at Georgia Tech and to establish equivalent procedures for its use. To that end, personnel traveled from Hanford to Georgia Tech to examine the system first-hand before attempting the construction at 222-S Laboratory. Subsequently, personnel traveled from Georgia Tech to Hanford to examine the completed system and to ensure that operating procedures were the same at both laboratories.

The third step was to perform simulated waste tests at Hanford to familiarize operators with the system and to evaluate areas that might be problematic when the system was moved into the hot cell for the actual tank waste studies. Several minor design changes were implemented to make the system more “hot cell friendly.”

The fourth step was to perform flowsheet tests with the redesigned system using the same simulated waste samples that had been used at Georgia Tech to demonstrate the same results could be achieved at either laboratory.

The fifth—and major—step was to load the crystallizer system into a hot cell at the 222-S Laboratory. This step required the coordinated efforts of literally dozens of 222-S Laboratory personnel in the planning and execution of the task.

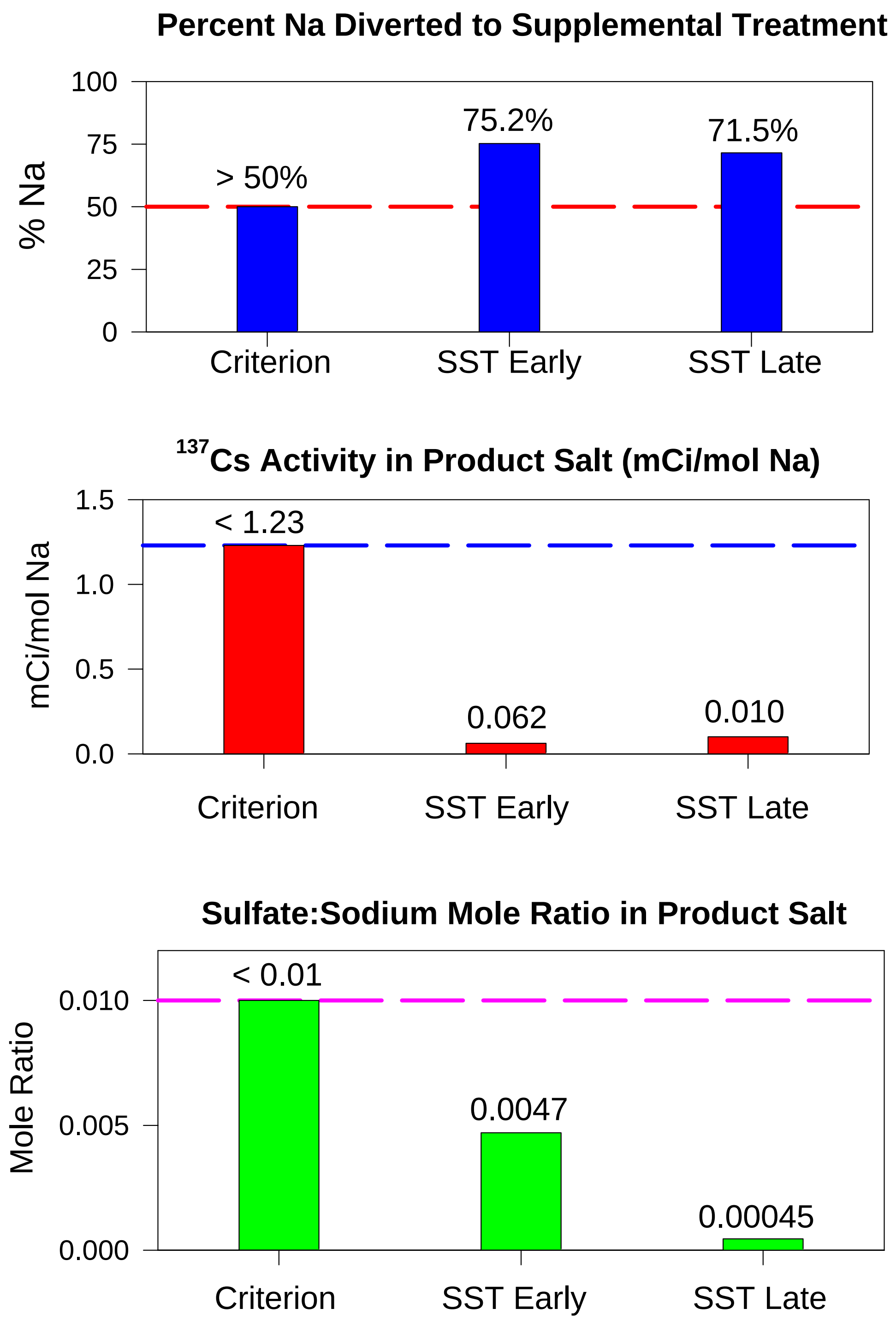
The sixth step was to run a flowsheet test inside the hot cell using simulated waste to allow personnel to become familiar with operating the crystallizer system, as well as the slurry filtration and filter cake wash steps, using hot cell master-slave manipulators.

Finally, three flowsheet tests were performed in the hot cell using the actual tank waste composite feed samples: SST Early Stage 1 (Run 44 Stage 1), SST Early Stage 2 (Run 44 Stage 2), and SST Late Stage 1 (Run 46).

Results

The actual-waste test performance exceeded the separations criteria by a comfortable margin in all cases. Fig. 8 shows how each actual-waste feed stream fared with respect to the criteria for sodium, cesium, and sulfate separations.

Results of the actual-waste flowsheet tests matched the results of the corresponding simulated waste flowsheet tests in all respects. For example, Table II shows a chart comparing the measurements and observations for the SST Early Stage 1 flowsheet test. In all cases, the results for the actual-waste tests fell within the range of reproducibility for the simulated waste tests.



Percent Na Diverted to Supplemental Treatment

^{137}Cs Activity in Product Salt (mCi/mol Na)

Sulfate:Sodium Mole Ratio in Product Salt

Fig. 8. Performance criteria.

Table II. Comparison of Simulated vs. Actual Tank Waste Flowsheet Test Results (SST Early Stage 1)

Measurement/Observation	Average of Simulated Waste Tests Runs 38b, 41, 42)	Actual Waste Test
Initial pressure (torr)	140 ± 10	140
Endpoint pressure (torr)	90 ± 5	90
Foaming at liquid/vapor interface	Manageable	Manageable
Condensate rate (g/h)	25 ± 1	24
Nucleation point (g H_2O evaporated)	250 ± 20	240
Condensate/feed ratio (target 0.474)	0.474 ± 0.007	0.469
Mass of washed solids (as % of feed)	14.6% ± 1.3%	14.9%
Wt% SO_4 in washed solids	3.3% ± 0.5%	3.2%
Solid phases identified by PLM (in approximate order of abundance)	$NaNO_3$ > $Na_2CO_3 \cdot H_2O$ > $Na_6CO_3(SO_4)_2$ $\cong Na_2C_2O_4$	$NaNO_3$ > $Na_2CO_3 \cdot H_2O$ > $Na_6CO_3(SO_4)_2$ $\cong Na_2C_2O_4$ $\cong Na_3FSO_4$

CONCLUSIONS

Laboratory test results conclusively show, with both simulated and actual tank waste samples, that the desired separations are achievable. At least on a laboratory scale, the fractional crystallization process can provide a viable pretreatment method to convert medium-curie waste into low-curie feed for a supplemental treatment process.

Another vital conclusion that may be drawn from the hot cell tests is that the actual tank waste samples behaved the same as the simulated waste samples. There were no significant differences in the physical behavior of the actual vs. simulated tank waste during evaporation, filtration, and washing operations. There were no significant differences in the amounts and types of product salts. Therefore, one can conclude

a. Process parameters may be tested and evaluated in the laboratory using simulated tank waste samples with some assurance that the findings will be applicable to actual tank waste.

b. Pilot-scale work may be carried out with simulated tank waste with some assurance that the findings will be applicable to actual tank waste in the actual plant operation.