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Fractional Crystallization of Hanford Single-Shell Tank Wastes From Concept to Pilot Plant

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

CH2MHILL
Hanford Group, Inc.

P.O. Box 1500
Richland, Washington

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ABSTRACT

The Hanford site has 149 underground single-shell tanks (SST) storing mostly soluble, multi-salt, mixed wastes resulting from Cold War era weapons material production. These wastes must be retrieved and the salts immobilized before the tanks can be closed to comply with an overall site-closure consent order entered into by the U.S. Department of Energy, the Environmental Protection Agency, and the State of Washington. Water will be used to retrieve the wastes and the resulting solution will be pumped to a proposed pretreatment process where a high-curie (primarily ^{137}Cs) waste fraction will be separated from the other waste constituents. The separated waste streams will then be vitrified to allow for safe storage as an immobilized high-level waste, or low-level waste, borosilicate glass.

Fractional crystallization, a common unit operation for production of industrial chemicals and pharmaceuticals, was proposed as the method to separate the salt wastes; it works by evaporating excess water until the solubilities of various species in the solution are exceeded (the solubility of a particular species depends on its concentration, temperature of the solution, and the presence of other ionic species in the solution). By establishing the proper conditions, selected pure salts can be crystallized and separated from the radioactive liquid phase. The aforementioned parameters, along with evaporation rate, proper agitation, and residence time, determine nucleation and growth kinetics and the resulting habit and size distribution of the product crystals. These crystal properties are important considerations for designing the crystallizer and solid/liquid separation equipment

A structured program was developed to a) demonstrate that fractional crystallization could be used to pre-treat Hanford tank wastes and, b) provide data to develop a pilot plant design.

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INTRODUCTION

The Department of Energy-Office of River Protection (DOE-ORP) is responsible for the remediation of the Hanford Site tank farms that encompass 149 single-shell tanks (SST) and 28 double-shell tanks (DST) containing approximately 53 million gallons of mixed waste (waste with both hazardous and radioactive components). In the current remediation approach mandated by the Hanford Federal Facility Agreement and Consent Order jointly agreed to by the Washington State Department of Ecology (Ecology), the U.S. Environmental Protection Agency (EPA), and the DOE-ORP, all Hanford underground tank wastes must be treated by 2028. Recognizing that the Hanford Waste Treatment Plant (WTP) design wasn't adequate to treat all the tank wastes, the Mission Acceleration Initiative (MAI) was developed to help ensure that the year 2028 tank waste treatment milestone would be met. A key element of the MAI is the testing, evaluation, design and deployment of supplemental pretreatment and treatment technologies to treat and immobilize the low activity wastes (LAW).

In December 2004 CH2M HILL Hanford Group (CH2M HILL - the DOE-ORP prime contractor) selected a team led by COGEMA, Inc. (now AREVA NC) and including Georgia Institute of Technology (Georgia Tech), Swenson Technology, Inc. (Swenson), and Framatome NP (now AREVA NP) to demonstrate fractional crystallization as a potential pretreatment system for the Hanford tank waste. Fractional crystallization had been proposed because it is a mature industrial process typically used for crystallizing many of the sodium salts found in the Hanford tank waste. The main differences between the commercial applications and the proposed application were the complex mix of salts in the feed stocks and the presence of some radioactive species, especially ^{137}Cs , ^{129}I , and ^{99}Tc . The radioactive species, being far below their saturation limits, were expected to remain in the mother liquor and not become included in the separated salts. The process was to be evaluated by a two-phased program consisting of extensive simulant testing and thermodynamic model (chemical process simulation) development in Phase I followed by a similar program in Phase II, that included testing actual tank waste.

The intent of this paper is give the reader an overview of Hanford tank waste fractional crystallization and describe how the concept of fractional crystallization evolved from theory to pilot design work through a structured testing and demonstration program.

BACKGROUND

Crystallization can be considered a two-step process beginning with the "birth" of crystals from a supersaturated solution followed by growth of the crystals to larger sizes. These processes are called nucleation and crystal growth, respectively and can occur simultaneously to relieve supersaturation and thereby attain solution equilibrium. It is the relation between the extent of nucleation to crystal growth that controls the final crystal size and size distribution and thus is a crucial control aspect of the crystallization process.

Crystal habit refers to the external appearance (shape, size) of a crystal and is not only controlled by its internal structure, but also by the conditions at which the crystal grows. The rate of growth, the solvent used, and the impurities present can have a major impact on crystal habit. Crystal habit will affect the rheological properties of the suspension, the solid-liquid separation efficiency, the bulk density of the dry solid, and the flow properties of the dry solid.

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Consequently control of crystal habit, along with crystal size distribution (CSD), is also an important part of the crystallization process.

When a saturated solution has a single species that can be crystallized by cooling, evaporation, addition of a non-solvent or some other means of concentrating the solution, such an operation may be thought of as simple crystallization. However, when a solution contains multiple solutes, fractional crystallization occurs as the solutes are progressively removed from solution upon cooling, evaporation, etc. If the solutes come out of solution one at a time, then the result is a series version of simple crystallization. For example, suppose a solution contains four solutes, A, B, C, and D, and that all of them saturate the solution as solvent is evaporated from a solution. Figure 1 illustrates the hypothetical distribution of products if the solution is progressively saturated with A, then B, then C, and finally D in the course of evaporating solvent from the solution.

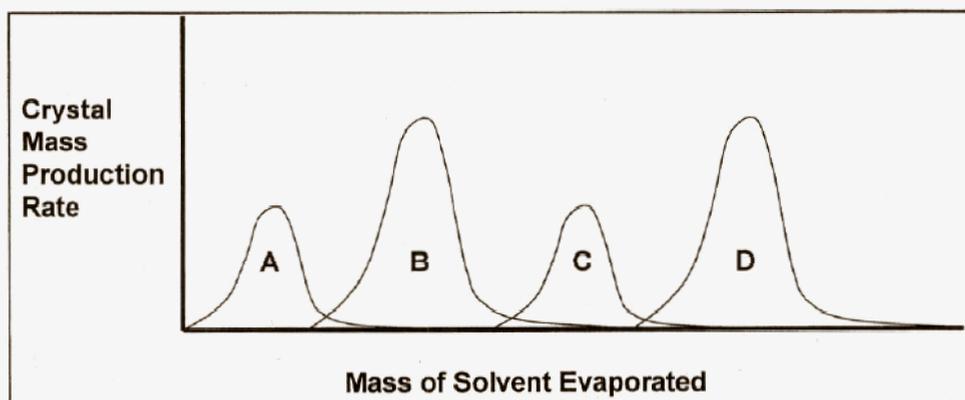


Fig. 1. Hypothetical product distribution from fractional crystallization: solution becomes saturated with solutes at different times in the evaporation.

Clearly, if the slurry is sent to a solid-liquid separator after most of each of the solutes is crystallized, then each solute can be recovered in concentrated form, in addition to removing a large fraction of the total solutes from the solution.

Now consider a different situation, one in which the solutes achieve saturation at roughly the same time in process. Assuming that all nucleate and grow as such conditions are achieved, the product generation is expected to look more like that in Figure 2. In this situation, separation of species from one another is not possible by the route suggested for a system following Figure 1. Instead, this instance of fractional crystallization only facilitates separation of a physical mixture of the crystalline solutes from the residual mother liquor.¹

¹ Ronald W. Rousseau, Hatem Alsyouri, George Dumont, and Laurent Nassif, *RPP-RPT-27239 Rev 0 PHASE I LABORATORY REPORT*, January 2006.

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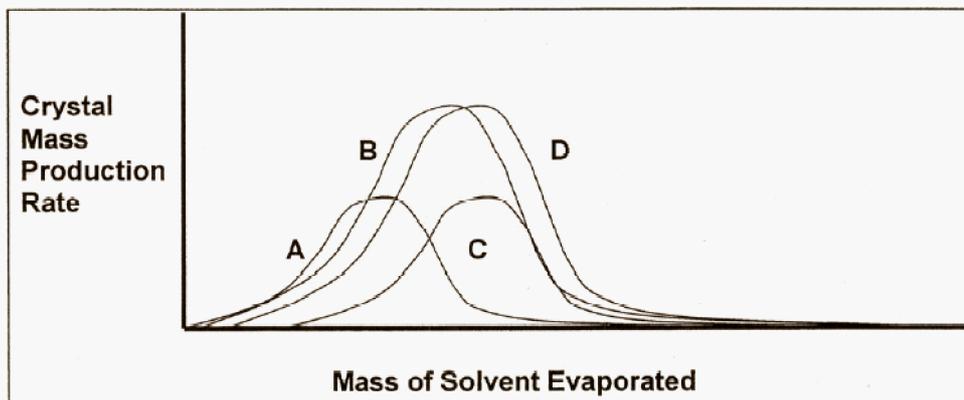


Fig. 2. Hypothetical product distribution from fractional crystallization: solution becomes saturated with solutes at roughly the same times in the evaporation.

In general, the chemical properties of the sodium salts occurring in Hanford waste have been well studied and well documented². The dominant ions (i.e. Na^{+1} , SO_4^{-2} , CO_3^{-2} , NO_3^{-1}) form common salts (i.e. NaNO_3 , $\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$) and double salts (i.e. $\text{Na}_6(\text{SO}_4)_2\text{CO}_3$ - burkeite) upon evaporation of water. The solubility of these salts behaves the same in radioactive and non-radioactive solutions alike. However, trace species may be present in various Hanford waste tanks that affect the formation and growth rates of sodium salt crystals³. For this reason, the proposed fractional crystallization process was developed using an incremental approach. That is, the simplest chemical systems were studied, tested, and validated against thermodynamic models, and then more and more complex systems were tested until the full representative SST/DST waste simulants were used.

Phase I Studies

Prior to initiating the incremental laboratory experiments at Georgia Tech a test plan⁴ was developed to guide the overall testing program and is illustrated in Figure 3.

² For example, "Crystal Properties and Nucleation Kinetics from Aqueous Solutions of Na_2CO_3 and Na_2SO_4 ," Shi, B., Rousseau, R., *Ind. Eng. Chem. Res.* 2001, 40, 1541-1547.

³ For example, "Effects of Calcium and Other Ionic Impurities on the Primary Nucleation of Burkeite," Shi, B., Frederick, J., Rousseau, R., *Ind. Eng. Chem. Res.* 2003, 42, 2861-2869.

⁴ Ronald W. Rousseau, *RPP-PLAN-24346, Rev 0, Hanford Medium/Low Curie Waste Pretreatment Project Phase I test and Demonstration Plan*, March 2005.

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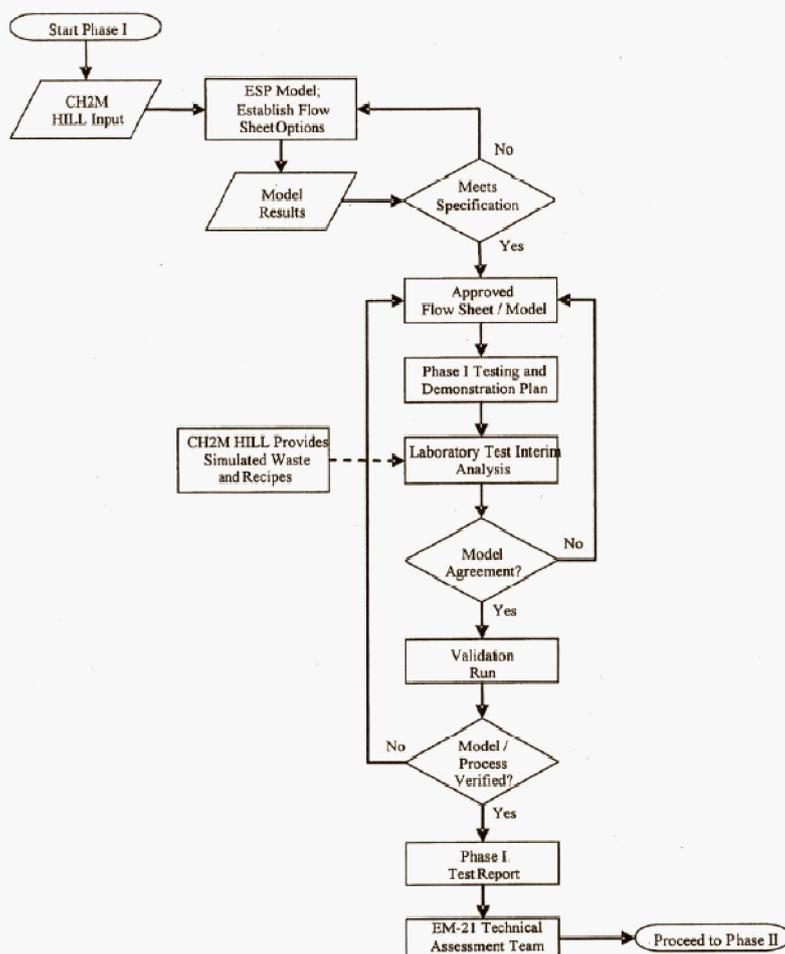


Fig. 3. Phase I project flow chart.

Each experiment was guided by a model developed with the Environmental Simulation Program/Mixed Solvent Electrolyte (ESP/MSE)⁵ software and since the thermodynamic parameters for a given temperature/pressure regime were fixed, only physical conditions such as evaporation rate, wash volumes, slurry density, etc. could be adjusted to gain correspondence between the model predictions and the laboratory observations. The incremental testing approach with “simple” solutions, e.g. Na_2CO_3 , Na_2SO_4 , NaNO_3 , etc. was also used to troubleshoot the laboratory test set-up and fine tune methods and procedures. Experiments with the full simulant were performed in a two-stage apparatus representative of the proposed crystallization process and it is shown schematically in Figure 4.

⁵ Product of OLI Systems, Inc. Morris Plains, NJ.

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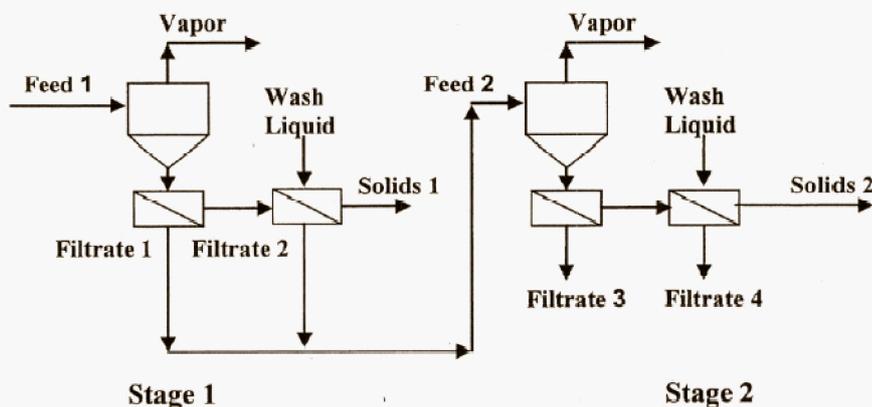
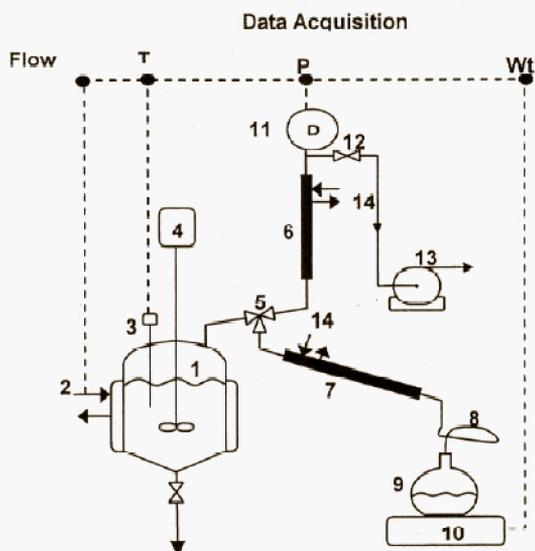


Fig. 4. Two-stage fractional crystallization schematic.

Each stage of evaporation was initially performed as a batch operation in the system shown schematically in Figure 5. Evaporation was performed until a specific slurry density was attained as indicated by a feed-to-condensate ratio predicted by the model. Difficulties encountered with ensuring proper mixing of the reduced slurry volume from a single charge and excessive build-up (encrustation) on the vessel walls led to developing a semi-batch process wherein the crystallizer operating level was held constant with intermittent addition of fresh feed. Following implementation of the semi-batch operation, encrustations were reduced and the quality of the results improved. The actual laboratory apparatus is shown in Figure 6.

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(1) Crystallizer, (2) Heating Fluid, (3) Thermocouple, (4) Motor to Drive Stirrer, (5) 3-Way Valve, (6) Reflux condenser [not used], (7) Product Condenser, (8) Flexible Tube Adapter, (9) Condensate Collection Flask, (10) Digital Balance, (11) Pressure Sensor, (12) On-Off Valve Plus Metering Valve, (13) Vacuum Pump, (14) Cooling Water.

Fig. 5. Evaporation stage schematic.

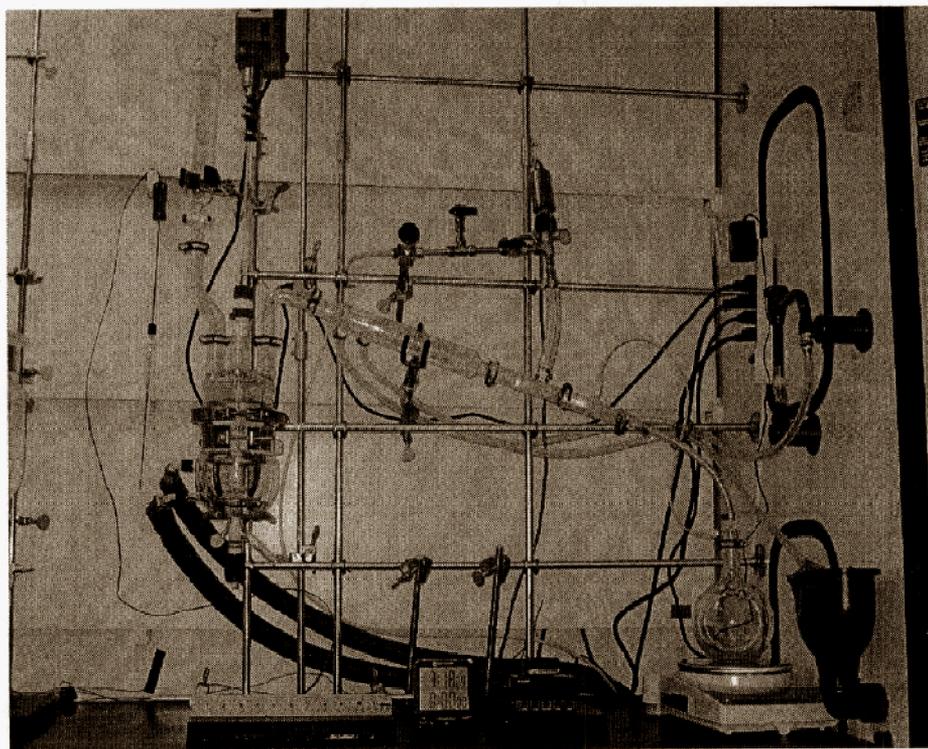


Fig. 6. Georgia Tech 300 mL crystallizing apparatus.

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As work progressed with the full simulant at Georgia Tech, it indicated that the predominant sodium salts crystallized contained nitrates, sulfates, and carbonates. With this information available a testing program was initiated at Swenson to duplicate the Georgia Tech results on a larger scale with these salts and to try to identify any design considerations that would need to be addressed prior to pilot phase activities. For this testing Swenson utilized their existing draft tube entry (DTE) crystallizer test loop. The DTE crystallizer is an evaporative (adiabatic cooling) crystallizer that circulates the magma in an external loop. Fines destruction is aided by incoming feed diluting the circulating slurry and also by the heater raising the temperature of the slurry (typically 25 – 50 % solids) in the range of 1° to 5° C. Temperature rise is limited to control the amount of supersaturation, and thereby limit the nucleation rate in the crystallizer (to favor crystal growth), and to also minimize any potential scaling tendencies. Subcooling in the heater is maintained by the static head provided by the crystallizer outlet column, but once the mother liquor re-enters the crystallizer body, boiling action is concentrated in the center of the vessel by the centrally located draft tube which evenly distributes the incoming mother liquor across the boiling surface. As accomplished at Georgia Tech, an incremental approach was used to work up to the three-salt combination using the same ESP/MSE model as a guide. The Swenson crystallizer system is illustrated in Figure 7 with actual photographs in Figures 8 and 9.

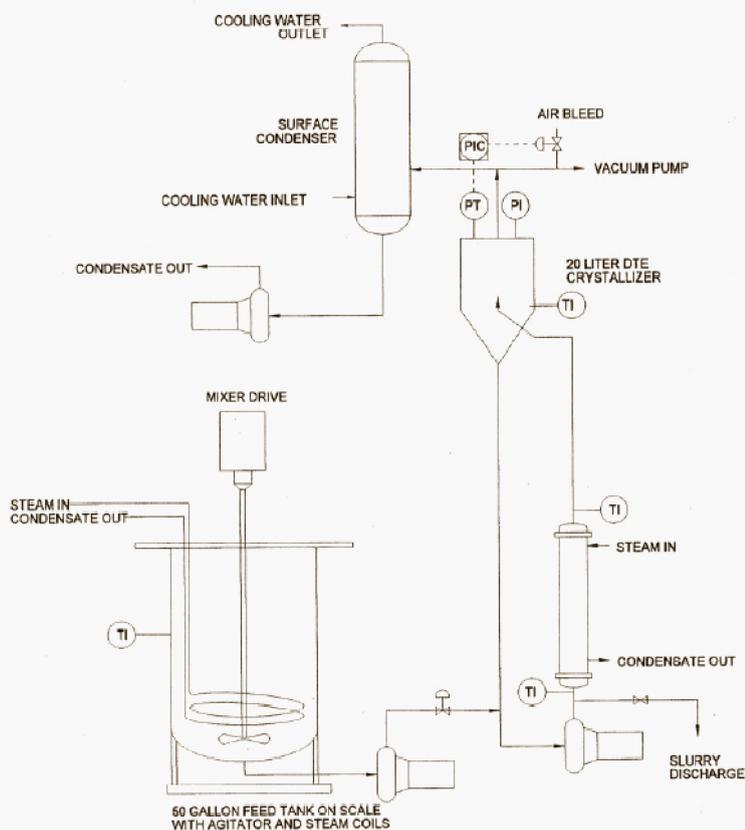


Fig. 7. Swenson DTE crystallizer system.

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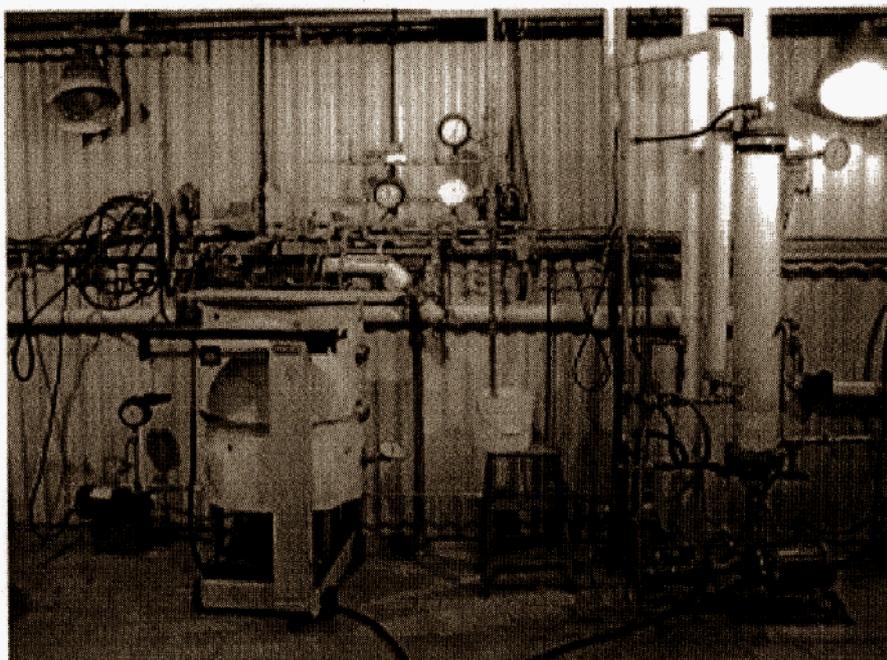


Fig. 8. Swenson DTE equipment – lower level.

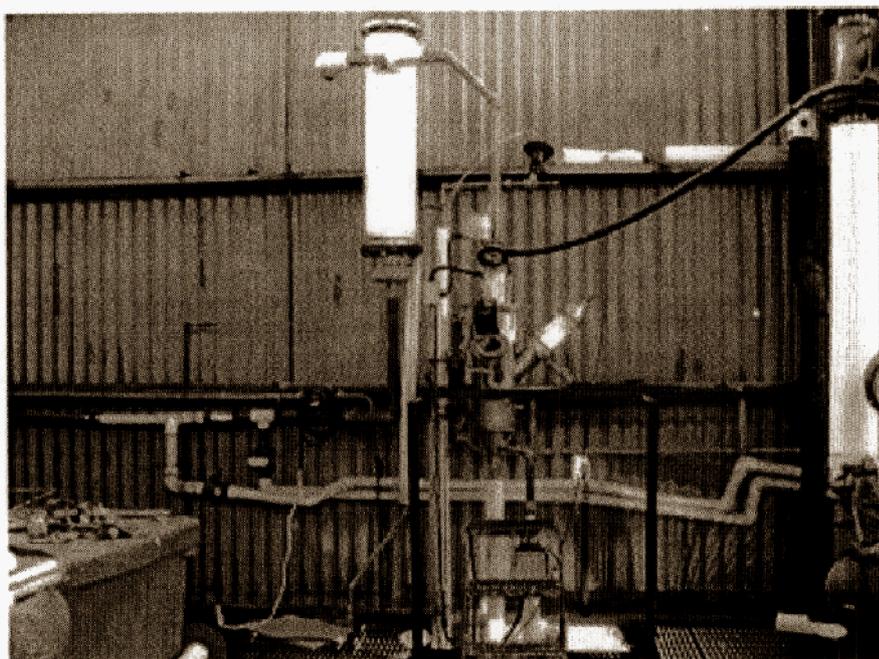


Fig. 9. Swenson DTE crystallizer and condenser – upper level.

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Unlike the laboratory semi-batch glassware experiments, the Swenson test loop allowed the crystallization system to operate in a continuous mode, i.e. product crystals were withdrawn as fresh feed entered the system and the magma was recirculated. With this capability experiments were run to investigate the effects of residence time and evaporation rate on product crystals. Observing the process effects on CSD and crystal habit was important at this point to begin planning for the proper solid-liquid separation equipment that should be installed for the pilot. The net results of this preliminary work using only a three-salt simulant yielded useful observations:

- Temperature control of components/lines is important to avoid cooling crystallization where it is not desired, i.e. plugged sample lines and vessel encrustations. Ways to avoid this (heat tracing and insulation) should be provided along with ways to remove plugging/fouling once it occurs (flush lines, clean-out connections, and wash rings).
- Evaporation rate and residence time have significant effects on the types and habits of crystals produced. This confirmed similar work at Georgia Tech on the same three-salt solution as well as the full simulant.

Phase I Results

The Phase I experiments at Georgia Tech confirmed that the proposed fractional crystallization process could separate sodium salts from the simulated Hanford tank waste. The minimum sodium separation requirement was 50% and was achieved for the SST Early Feed (58.1 %) and the Late Feed (74.7%) however DST Feed could only achieve 43.9% to avoid alumina gel formation during the crystallization process. The minimum sulfate-to-sodium ratio (<0.01 for tank corrosion concerns) and cesium separation goals were also achieved (complete details of Phase I laboratory experiments and results can be found in Reference 1). With these favorable results CH2M HILL requested an independent review of the Phase I results by an external team of subject matter experts before deciding to proceed into the next phase of the project. This assessment was sponsored by the DOE Office of Environmental Management (EM-21) to verify that the Phase I results supported further investigation, identify potential risks faced by the project, and make recommendations regarding plans for Phase II including possible schedule acceleration.

After a review of the deliverables (References 1 and 2) and interviews with members of the project team, the Technical Assessment Team (TAT) agreed that fractional crystallization was a promising technology and recommended that the project should proceed to Phase II. Additionally the TAT recommended that:

- A suite of solid-liquid separation equipment must be demonstrated to evaluate performance, including suitable crystal habit, reliability, and maintenance to enable selection of the optimum system.
- Hot testing on real waste should be conducted in concert with matching simulant samples on the same apparatus using identical protocol. The validity of simulant testing can thus be established to enable further testing of simulants.

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- Pilot-scale testing of crystallizer and centrifuge separation equipment design by vendors is recommended to proceed in parallel with Phase II bench-scale testing of both simulants and real waste.
- Cold pilot-scale testing of system components (Phase III) should be accelerated.

The complete TAT report is Reference 3 and should be consulted for further details.

Phase II Work

The original project Phase II work scope was revised to incorporate the TAT recommendations noted above and since the first three bullet items would affect pilot design, immediate work had two goals related to hardware development:

1. Develop a new simulant based on the exact chemistry of actual tank waste to be tested, repeat flowsheet testing of the new simulant, then test the actual waste and compare the results to the simulant.
2. Test several methods of solid-liquid separation devices while also investigating factors affecting CSD using the new simulant.

New Simulant and Waste Testing. Item 1 was a parallel effort conducted at Georgia Tech and the Hanford 222-S Laboratory. The 222-S Laboratory used archived tank samples to make composite SST wastes representative of anticipated Early Feed and Late Feed compositions. Once mixed the samples were analyzed to provide a new simulant recipe and also provide the speciation inputs for new thermodynamic models. The new simulant testing program is depicted by the flow chart in Figure 10 (further details of the testing program are in Reference 4).

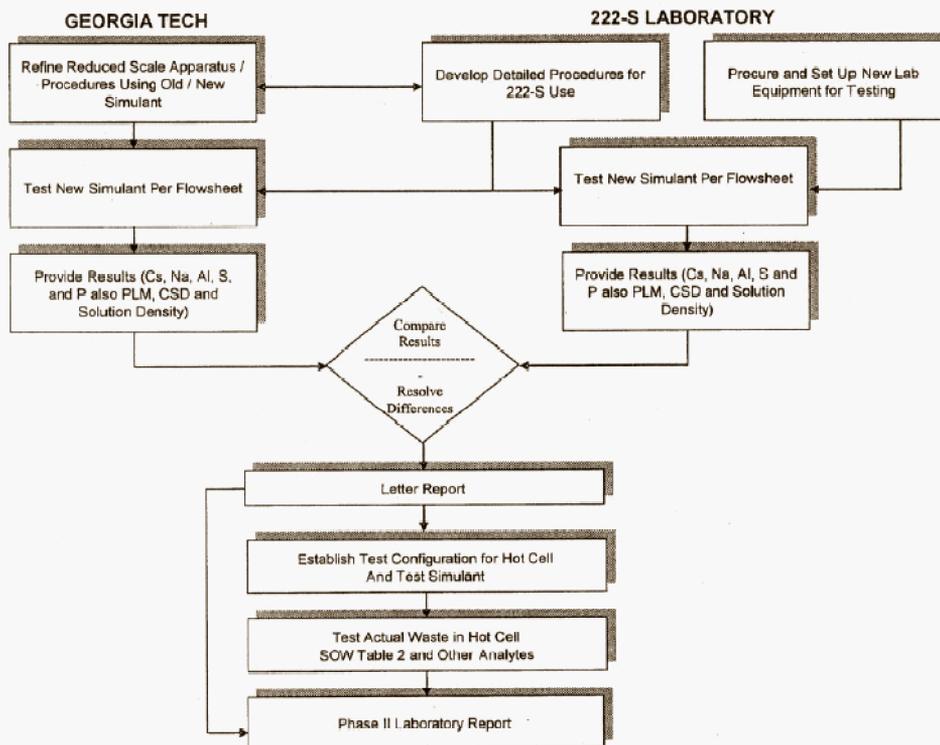


Fig. 10. Phase II laboratory work flow chart.

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During laboratory testing the new simulant behaved much like the original material in relation to model predictions and physical results however since the laboratory staffs had gained more experience operating the Georgia Tech crystallizer and washing apparatus, cesium removal efficiency (measured by decontamination factor, DF, the ratio of Cs in the feed to Cs in the washed crystals) improved markedly. Results of laboratory simulant and waste testing are summarized below, but full details of waste testing can be found in Reference 4.

Table I. Phase II Laboratory Testing Summary

Requirement	Goal	Model Prediction	Simulant Results	Actual Waste Results
Cs DF	50	110 - 270	> 150	153
Sodium in LAW	50%	70% - 80%	80%	73.5%

While actual waste testing proceeded at the Hanford 222-S Laboratory, additional simulant work continued at Georgia Tech to determine the effects of temperature, evaporation rates, and residence time on crystal type, crystal habit and CSD. In general the work proved that extending the residence time, i.e. reducing the evaporation rate to take a longer period of time to reach the model established condensate-to-feed ratio, increased the CSD and allowed more complete washing of the crystals.

Solid-Liquid Separation Studies. The Phase II work at the Swenson Test Facility built on the preliminary study work mentioned previously. To ensure that the future testing results would be relevant to equipment design activities the three-salt solution used for Phase I was fortified with additional salts to make it behave similar to the new waste simulant. Sodium nitrite, sodium hydroxide, and sodium chromate were added along with non-radioactive cesium nitrate. To determine solid-liquid separation efficiency (including necessary washing steps) the cesium concentration in the feed would be compared to the cesium concentration in the product crystals. Since a cesium analysis must be done using an inductively coupled plasma-mass spectrometer (ICP-MS), and is a time consuming analysis not suitable for making in-process evaluations, a qualitative technique used during Phase I laboratory work was enhanced to provide a better basis for comparison.

For this early qualitative method crystals recovered from a run using an SST simulant were washed and filtered four times in series. Figure 11 displays the change in color of crystals at the bottom of the sample bottles (from left to right) as the product crystals were washed. The sample labeled -1 corresponds to the filtered slurry removed from the crystallizer and bottle 0 is a sample of the washed crystals produced in the experiment. Bottles 1 through 4 are samples taken after each of four additional wash steps. Each wash was performed by slurrying the crystals in a saturated solution of sodium nitrate. The experiment was stopped when, as determined by visual observation, the color between two successive samples remained unchanged. At this point the amount of adhering mother liquor and its associated impurities was assumed to be negligible and the remaining color was the result of the crystal inclusions. To check the accuracy of this visual method, the crystals were analyzed for chromium.

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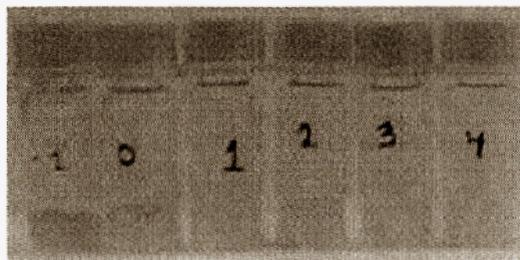


Fig. 11. Effects of washing on crystal color.

Figure 12 shows the chromium analyses of the washed crystals and it can be seen that the residual chromium is removed by each successive wash. Clearly, the expected coloration of the crystals due to the presence of chromium corresponds to the visual observations described above and the quantitative analysis shown on the graph.

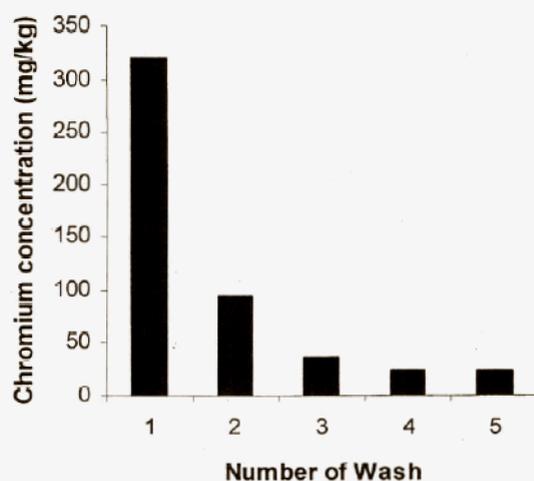


Fig. 12. Residual chromium after washing crystals.

To improve upon this technique, to make it more quantitative for the Phase II work, a colorimeter technique was developed at the Swenson laboratory. Although it was not an accurate comparison, i.e. chemical analyses indicated that cesium and chrome concentrations didn't always "follow" each other, the colorimeter was "good enough" for a rapid assessment of washing efficiency.

Another preliminary activity at Swenson was to determine crystal settling velocity to size the elutriation leg that would be used for wash column studies. For this testing sodium nitrate crystals, with a representative CSD, were dropped into a graduated cylinder containing saturated sodium nitrate solution and timed while they settled to the bottom. Figure 13 shows the heated bath/cylinder set-up for determining crystal settling rates. Figure 14 is the settling rate curve developed for the sodium nitrate crystals – the crystals used for the settling tests were representative of sieve screen samples used to determine size distribution.

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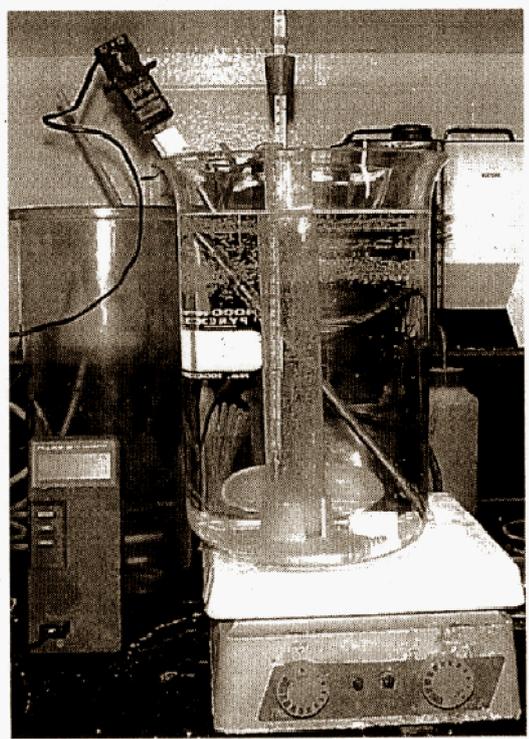


Fig. 13. Settling velocity test apparatus.

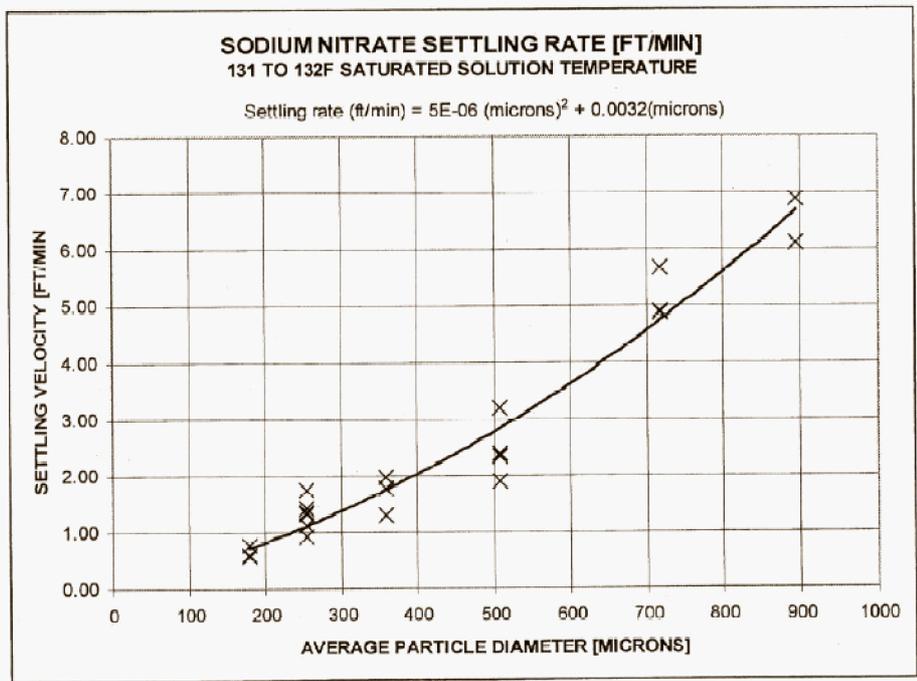


Fig. 14. Settling rate curve for sodium nitrate crystals.

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With this preliminary work out of the way, along with some system maintenance items, solid-liquid separation work began.

Hydraulic Wash Column. A hydraulic wash column is typically well suited for the purification and solid-liquid separation of crystals from a melt (a melt being a pure molten solid, e.g. silicon, as opposed to a solution such as the SST waste simulant). Wash columns have also been used in association with freeze concentration and eutectic freeze crystallization processes for water purification/waste water treatment. In principle they work by subjecting a sinking bed of crystals to a rising flow of clean water (solvent) to wash off contaminants and leave pure crystals. For use with this project the intent was to modify the concept to not only wash the crystals with a counter-flow of clean condensate, but to dissolve the clean crystals to provide a saturated feed for the downstream treatment process (currently designated as bulk vitrification). If feasible, this one-step operation would eliminate several components from the system and thereby reduce maintenance requirements. The column is shown in Figure 15 with a draft tube take-off line for the up-flowing, clean, saturated solution. Crystals falling from the crystallizer elutriation leg (Figure 16) would accumulate in the annular area created by the retention screen.

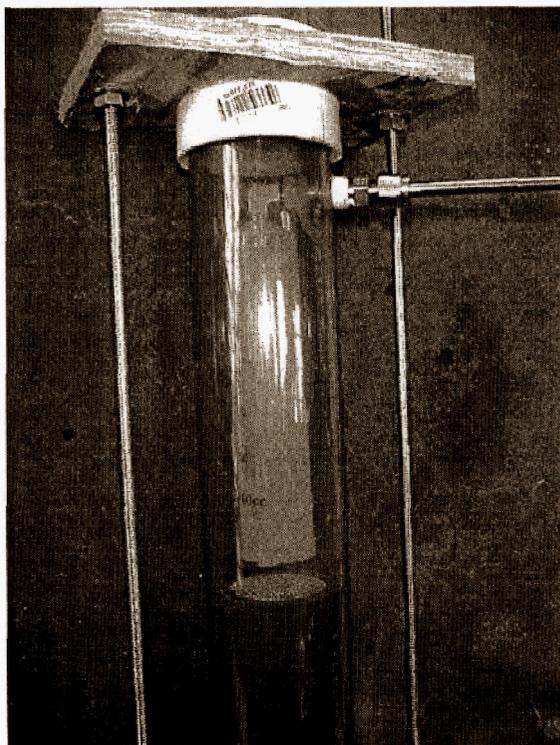


Fig. 15. Wash column lower end.

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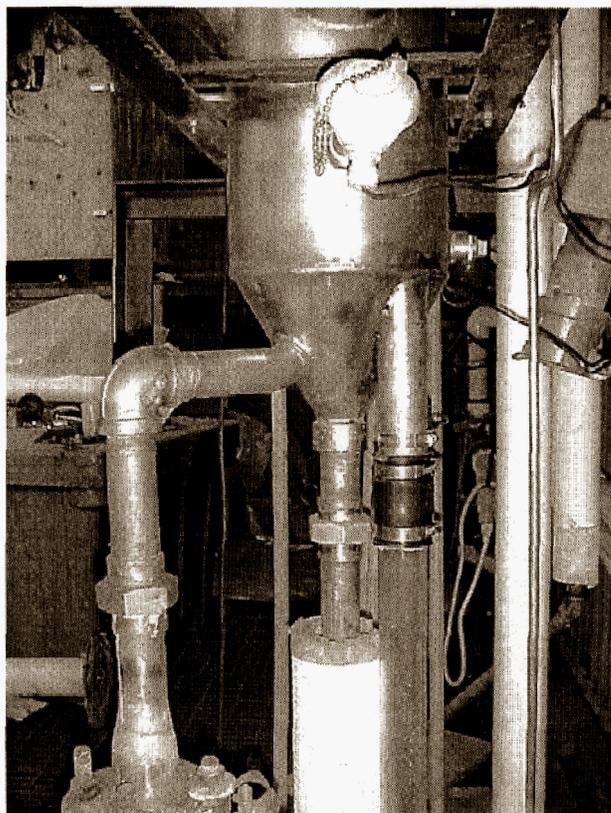


Fig. 16. DTE crystallizer with new elutriation leg.

Several weeks of testing yielded multiple problems with maintaining a balanced crystal production rate, dissolving water flow rate, and wash column outlet flow rate. If the liquor flow rate up the column was too high, the bed of crystals tended to fluidize resulting in intermixing of the crystals with a subsequent rise in the chromium concentration in the wash column outlet stream. If the liquor flow rate up the column was too low, the bed of crystals tended to pack together forming a bridge that could usually be dislodged with gentle rapping on the side of the column, but in 10 to 20 minutes the bridging would reoccur. Other problems involved temperature control within the column caused by varying condensate temperatures and crystal dissolution (endothermic reaction). A heater was installed in the condensate line to the column, but adequate control was never accomplished. While the wash column was able to achieve reasonably high decontamination factors (as high as 62), there were too many operational issues with the small scale equipment to resolve in the time allotted for the solid-liquid separation investigations. Further investigation of wash column testing was stopped and this method would not be considered for pilot use.

Filtration. Filtration for use with fractional crystallization would require a way to wash, dry (remove interstitial liquid from washing or the mother liquor from the original slurry), and harvest the crystals. To accomplish this only a rotary drum or belt type filter could be utilized since both of these units work by applying a vacuum below the filter media (drum fabric or belt). Residual mother liquor or the wash solution is drawn through a layer of deposited crystals (filter cake) which is removed from the media by a knife assembly scraping off a portion of the cake as

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the belt moves or the drum rotates. Neither unit could be obtained at the scale necessary for the test loop so a Büchner funnel apparatus was used to simulate the effect of the filter media. Büchner funnel testing is the common industry test method for designing rotary drum or belt filters and was also the filtration method used throughout all laboratory crystallization experiments. During the tests it was learned that the funnel filter media was prone to blinding, i.e. restricting flow, when a large number of fine crystals were in the slurry. This was thought to be the result of the finer crystals packing the interstitial spaces created by the larger crystals as they settled. One other observation made was that even during times when liquid (mother liquor or saturated wash solution) was being removed from a mass of predominantly large crystals, partial plugging (evidenced by long filtration times) occurred. This was thought to be the result of cooling crystallization of the saturated liquid (wash solutions were typically applied at the same temperature as the mother liquor in the crystallizer, but cooled as air was drawn through the media).

Looking ahead to actual equipment, rotary drum units could not be considered because of containment issues related to radioactive service (a total enclosure could be constructed, but this would not be practical for an operating system). Totally enclosed belt filters are available however the belt and all the rotating parts (rollers, sprockets, idlers, etc.) would also be a maintenance problem with the contaminated service. A final consideration was that the rotary drum or belt media, like the Büchner funnel media, would be prone to plugging from cooling crystallization and therefore require frequent washing with unsaturated solution to dissolve the crystal build-up. For these reasons rotary drum and belt filters were eliminated from pilot consideration.

Centrifugation. Centrifuges are typically classified as either filtering or decanting and for this project only the filtering type was considered because it allows the product crystals to be washed. In a full size application the product slurry is introduced in the centrifuge and is accelerated to many times the force of gravity ("g" forces) by the rotating basket. Similar to the principle of filtration discussed above, the crystals build up a cake that is retained by a screen or cloth as the liquid moves through it and is discharged. Wash solution is introduced through a separate nozzle from the feed and is directed uniformly along the cake to achieve near plug-flow conditions. A knife assembly scrapes off the excess cake to a predetermined depth leaving a heel (thin coat of crystals) behind. Since centrifuges are typically capable of removing > 90% of the interstitial liquid, a gain in crystal DF over vacuum filters is "automatic" because the liquid contains the soluble radionuclides of interest. For the laboratory work the small unit and ancillary equipment shown in Figures 18 through 23 were used. Slurry was manually added to the basket as was the heated, saturated solution used for washing.

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Fig. 18. Centrifuge basket.

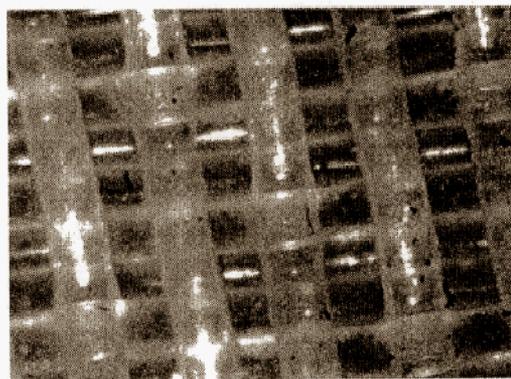


Fig. 19. Basket internal mesh.



Fig. 20. Centrate pail.

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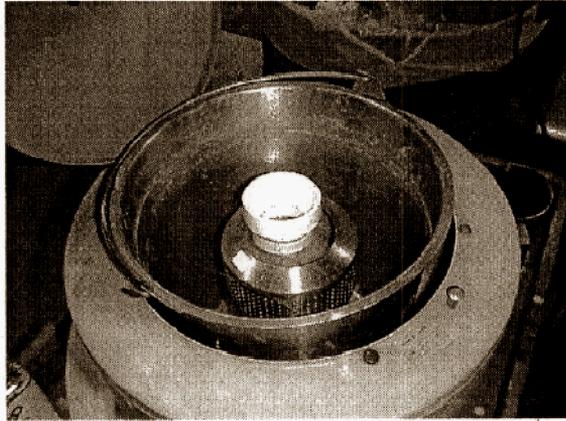


Fig. 21. Centrifuge assembly.

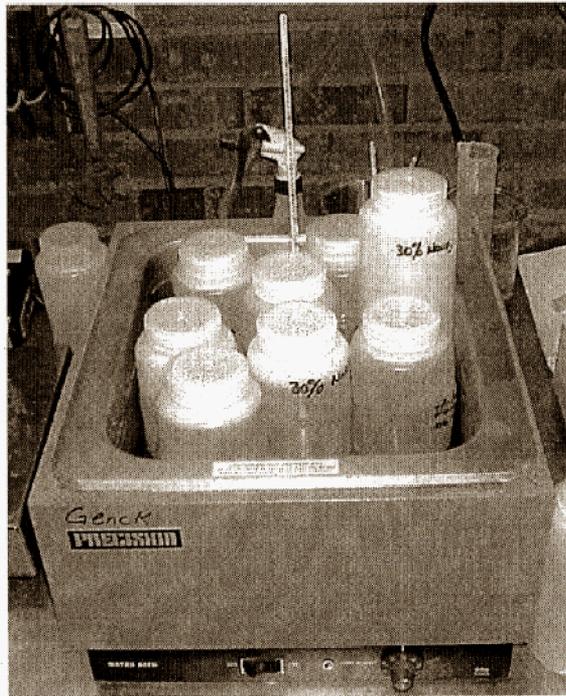


Fig. 22. Heated water bath for samples and wash.

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Fig. 23. Slurry container with agitator in heated bath.

Concurrent with centrifuge work, the DTE crystallizer was being operated at varying residence times to grow the best crystals for deliquoring/washing. As with any crystallizer installation, the crystallizer and downstream processing unit(s) must be designed in parallel for best results. With residence times varying between two to twelve hours, the best results were found to occur in the four to eight hour range. Initial laboratory analyses of the centrifuged samples yielded chromium levels below the quantitation limits of the analytical equipment so the cesium level was increased to 1000 times the value typically found in the simulant. With the higher cesium concentration, a DF of 167 was obtained.

Current Project Status. The testing program and laboratory experiments detailed above have allowed the project to proceed into the pilot testing phase. Using the data gathered a custom DTE evaporative crystallizer unit has been designed and will operate as a single stage (see Figure 24). The system will operate in a continuous mode and utilize a peeler centrifuge for crystal separation and washing. Once installed in the testing facility at the Savannah River National Laboratory (SRNL) flowsheet tests similar to the original laboratory experiments will be performed using the new simulant and compared to the thermodynamic model predictions. Once "baseline" operations are confirmed, additional testing will be performed with upset conditions such as higher concentrations of organics or solids in the feed. The data gathered by the pilot testing program will be compiled and evaluated to determine equipment scale-up to full size for Hanford processing needs and establish overall system design requirements.

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CONCLUSION

The Hanford Medium/Low Curie Pretreatment Project has followed a structured program to demonstrate fractional crystallization as a potential pretreatment process from its inception to its current status. Briefly stated the progression has been:

- Develop a concept and test its theoretical viability with a thermodynamic model.
- Develop and perform laboratory experiments based on the model using first, simple solutions to balance theory against reality, then progressing to the full simulant.
- Develop and perform a laboratory testing program, based on model predictions, to validate that the simulant and the actual waste perform similarly.
- Develop and perform a testing program to establish process and equipment requirements.
- Develop a pilot plant design based on the above.

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