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7. Abstract

Sodium nitrate crystallization studies were performed on nonradioactive solutions. Temperature had little effect on crystal size or shape. Solid/liquid separation efficiency was mainly a function of the weight percent solids in the slurry. Occlusion studies were done with sodium nitrate crystals taken from a tank 101-SY radioactive waste tank. After recrystallization and multiple washings, the sodium nitrate crystals retained 0.14% of the original Cs-137 activity, presumably trapped in occlusions within the crystals. Some data is presented on the sodium nitrate/alumninum nitrate/water solubility phase diagram.

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1.0 SUMMARY

"Clean Salt Process" is the name coined to describe a radically different approach to pretreatment of Hanford radioactive waste stored in underground tanks. The process recovers clear sodium salts from the waste by fractional crystallization. ("Clean" in this context means having total radioactivity on the order of ordinary environmental materials.)

This document describes laboratory studies done during fiscal year 1994. These studies support the development of detailed process flowsheets and preliminary plant design. They are funded by the U. S. Department of Energy under the Efficient Separations Processes Integrated Program (EM-50), Technical Task Plan (TTP) No. RL4-4-20-02, "Significant Volume Reduction of Tank Waste by Selective Crystallization". Transmittal of this document fulfills the requirements of Milestone 1 in the TTP.

In the laboratory, experiments with simulated waste were done to explore the effects of crystallization parameters on the size and crystal habit of product $NaNO_3$ crystals. Data were obtained to allow prediction of decontamination factor as a function of solid/liquid separation parameters. Experiments with actual waste from tank 101-SY were done to determine the extent of contaminant occlusions in $NaNO_3$ crystals. The occlusion rate determines the theoretical maximum decontamination factor for a single stage of crystallization, and therefore defines the size (number of required stages) of an operating plant.

A contract with the University of Arizona went into effect on May 1, 1994, to build a bench-scale continuous crystallizer using simulated Hanford waste. The principal investigator there is Dr. Alan Randolph. He is a world-class crystallization expert, and has expertise in Hanford waste chemistry through past consulting contracts here. He was instrumental in the selection of the design of Hanford's 242-A and 242-S evaporator/crystallizers that have been used here since the mid-1970's to reduce the volume of tank waste.

Solubility phase diagrams are crucial to the operation of any fractional crystallization plant. Laboratory studies were initiated on the solubility interactions between sodium nitrate and aluminum nitrate salts, since those interactions will be the dominant factors in an operating plant. More detailed studies will be done on this system at the University of Arizona later this year.

2.0 CRYSTAL STUDIES

2.1 Crystallization Parameters

The design of a crystallization plant is highly dependent on the ability to separate crystalline product from the mother liquor. In the clean salt process, nearly all of the radioactivity in the crystal slurry is in the liquid phase (see Section 2.2). Therefore, the decontamination factor that can be achieved with each solid/liquid separation is defined by the separation efficiency.

Using cold (nonradioactive) $NaNO_3$, a series of experiments was performed to test the effect of crystallization parameters on the size and habit of $NaNO_3$ crystals formed, and on the separation efficiency. The parameters that were varied were (a) evaporation temperature, (b) crystallization temperature, (c) volume percent solids in slurry before filtering or centrifuging, and (d) separation technique (filtration or centrifugation). The effects that were measured were (a) particle size, (b) weight percent filtered (or centrifuged) solids, and (c) weight percent water in the filter cake (or centrifuge cake). Results of the measurements were used to calculate the solid/liquid separation efficiency.

2.1.1 Experimental

The detailed procedure and data for these tests are recorded in controlled laboratory notebook WHC-N-624, pages 128-152.

The $NaNO_3$ used for these tests was the product of an earlier single-stage crystallization of a simulated tank 101-SY waste. A stock solution was prepared by dissolving 125.5 g of the impure $NaNO_3$ in 224.9 g water. The solution was filtered, then divided into nine 50 mL beakers, each containing a stirbar. The nine fractions were treated as shown in Table 1.

Table 1. Parameters for Crystallization Tests.

Fraction	Evaporation Temperature, °C	Crystallization Temperature, °C	Target Volume Percent Solids
1[a]	25	25	20
2, 7	25	25	20
3	25	25	50
4, 8	80	5	50
5	60	60	20
6, 9	60	60	50

[a] Fraction 1 undisturbed during evaporation; all other fractions stirred.

The evaporation temperature is the temperature at which the solution was held during the evaporation process. The crystallization temperature is the temperature the slurry was brought to before filtering.

All evaporations were done at atmospheric pressure in open beakers. The total time required to reach the target volume percent solids ranged from two hours at 80°C to 4 days at 25°C, and up to 9 days for the unstirred sample (Fraction 1). To determine whether the target volume percent solids had been reached, the stirrer was stopped periodically, and the solids were allow to settle.

When the target volume percent settled solids and crystallization temperature were reached, the slurry was filtered through a 0.45 micron filter. Weights of filter cake, filtrate, and total slurry were recorded. A sample of the filter cake was analyzed for percent water. Another sample of the filter cake was analyzed for particle size by polarized light microscopy.

The entire experiment was repeated using a laboratory-scale clinical centrifuge to perform the solid/liquid separation, rather than filtration.

2.1.2 Data

Measurements taken during the crystallization experiments are shown in Tables 2 and 3.

Table 2. Data from Crystallization Experiments; Separation by Filtration.

Fraction	Slurry Weight, g	Filter cake, g	% H_2O in filter cake	Average size, μm
1	24.2	3.0	4.4	370
2	22.0	5.1	8.6	190
7	24.8	3.2	10.0	120
3	19.7	7.6	9.2	90
4	20.5	6.2	7.6	70
8	20.9	7.7	10.9	90
5	21.1	3.9	5.4	80
6	20.2	4.9	6.9	140
9	21.0	4.9	7.7	150

2.1.3 Results

Crystallization temperature had surprisingly little effect on average crystal size. All of the size averages for the stirred samples fell within the rather narrow range of 50-190 micrometers. The variation between duplicate runs was almost as great as the differences between crystallizing conditions. The only factor that had a significant effect on crystal size was whether or not the solution was stirred during the evaporation. In the unstirred samples, the

crystals grew to be quite large. Some individual crystals as large as 7 mm in diameter were measured. In all cases, the crystals that formed were found to be very regular rhombohedra, indicating very low levels of occlusion or crystal defects.

Given that nearly all of the radioactivity in the slurry is in the liquid phase (see Section 2.2), the solid/liquid separation efficiency is a measure of how well the crystals can be decontaminated. The separation efficiency is measured by the amount of liquid phase retained in the filter cake (or centrifuge cake) relative to the total amount of liquid in the slurry. The total liquid in the slurry is equal to the amount retained in filter cake plus the amount of filtrate.

Table 3. Data from Crystallization Experiments; Separation by Centrifugation.

Fraction	Slurry Weight, g	Centrifuge cake, g	% H_2O in c'fuge cake	Average size, µm
1	21.9	5.2	8.6	3500
2	21.8	5.1	16.0	200
7	23.6	3.1	21.0	120
3	22.0	5.1	20.0	50
4	20.1	8.6	23.0	70
8	18.9	11.5	26.0	60
5	20.6	4.7	23.0	100
6	19.4	8.2	24.0	110
9	18.9	8.0	22.0	120

Tables 4 and 5 show the solid/liquid separation efficiency ("Wt % Liquid in Filter Cake") for each test. The weight of liquid in the filter cake was calculated from the measured %H_2O by assuming that the water was saturated in $NaNO_3$. For this purpose, a saturated solution was assumed to contain 0.45 g $NaNO_3$ per gram of solution, which is the approximate solubility of $NaNO_3$ at 25°C given in Reference 1, volume 2, page 1069. The weight of liquid in the filtrate was taken as the difference between the total slurry weight and the weight of filter cake. Then, the weight percent liquid in the filter cake (weight liquid in filter cake divided by total liquid) is a direct measure of the solid/liquid separation efficiency. To a very good approximation, the weight percent liquid in the filter cake is equal to the percentage of radioactivity that would be retained in the filter cake, and thus is directly related to decontamination factor.

The "Wt % Dry Solids in Slurry" in Table 4 is found by taking the weight of filter cake (Table 2), subtracting the weight of liquid in the filter cake (Table 4), and dividing by the total weight of the slurry before filtering (Table 2). As shown in Figure 1, there is a strong correlation between the weight percent solids in the slurry and the separation efficiency.

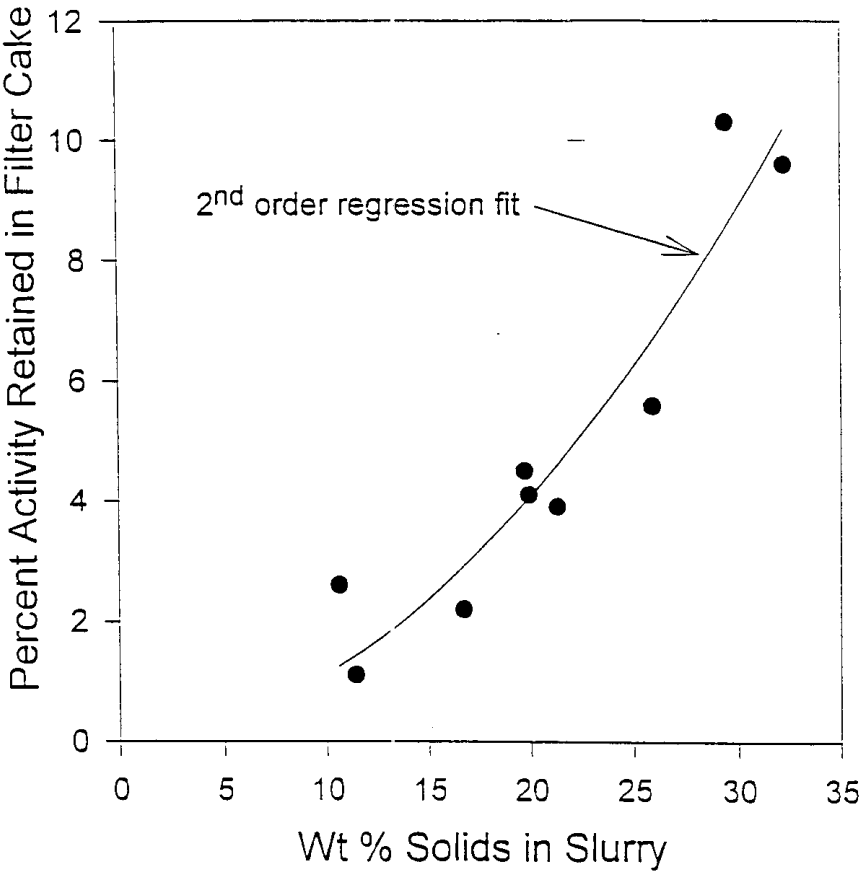
Table 4. Calculation of Solid/Liquid Separation (Filtration) Efficiency.

Fraction	Wt (g) Liquid in Filter Cake	Wt (g) Liquid in Filtrate	Wt % Liquid in Filter Cake	Wt % Dry Solids in Slurry
1	0.2	21.2	1.1	11.4
2	0.8	16.9	4.5	19.7
7	0.6	21.6	2.6	10.6
3	1.3	12.1	9.6	32.2
4	0.9	14.3	5.6	25.9
8	1.5	13.2	10.3	29.4
5	0.4	17.2	2.2	16.7
6	0.6	15.3	3.9	21.3
9	0.7	16.2	4.1	19.9

Table 5. Calculation of Solid/Liquid Separation (Centrifugation) Efficiency.

Fraction	Wt (g) Liquid in Centrifuge Cake	Wt (g) Liquid in Decantate	Wt % Liquid in Centrifuge Cake	Wt % Dry Solids in Slurry
1	0.8	16.8	4.6	20.2
2	1.5	16.8	8.1	16.5
7	1.2	20.5	5.5	8.1
3	1.8	17.0	9.8	14.7
4	3.6	11.5	23.7	24.8
8	5.4	7.4	42.3	32.0
5	1.9	15.9	10.9	13.2
6	3.6	11.2	24.3	23.9
9	3.2	10.9	22.7	25.4

Figure 1. Filtration Efficiency



2.2 Occlusion Testing

Due to the large difference in ionic radii of the Na^+ and Cs^+ ions, it is not possible for the cesium ion to replace sodium ion in the $NaNO_3$ crystal lattice. By their nature, however, crystals do have defects. One type of defect that can lead to crystal impurity is an occlusion, in which the $NaNO_3$ crystal grows "around" a pocket of foreign material. All foreign material present in the interstitial liquid can be removed by washing the crystals, but the material trapped in occlusions within the crystals cannot be removed. In our case, the foreign material contains radioactive contamination. Thus, the level of crystal occlusions sets the limit of decontamination that can be obtained in a single "stage", or crystallization. Of course, the contamination can be removed by recrystallization, or dissolving the contaminated crystals in water and forming new crystals (i.e., by adding "stages" to the process).

In order to determine the extent of occlusion-type contamination inherent for $NaNO_3$ crystals, two tests were done using $NaNO_3$ from tank 101-SY. The highly contaminated crystals were recrystallized from water, then washed repeatedly with a saturated $NaNO_3$ solution (to preclude dissolution of the crystals during the washing). Samples of the initial solution before crystallization, of each wash solution, and of the final washed crystals were analyzed to determine what happened to the ^{137}Cs.

2.2.1 Experimental

The detailed procedure and data for these tests are recorded in controlled laboratory notebook WHC-N-384-1, pages 145-148, and WHC-N-384-2, pages 3-7. The $NaNO_3$ crystals used for the tests were obtained from earlier clean salt process development tests on tank 101-SY sample. (See Section 4.2 in Reference 2.)

Recrystallization: The highly contaminated $NaNO_3$ (30.0 g) from tank 101-SY was dissolved in 60.0 g water. The solution was filtered through a 0.45 micron cellulose nitrate filter. (The same type of filter was used throughout these tests.) A small aliquot (5.0 mL) of the filtrate was analyzed for ^{137}Cs by gamma energy analysis (GEA). The solution was evaporated at 80°C until crystals were present, then the slurry was cooled to room temperature. The cooled slurry was allowed to settle to determine the volume percent settled solids, which was measured at 80%. The slurry was filtered, and the filtrate solution was analyzed by GEA.

Wash #1: The crystals were transferred from the filter to a plastic beaker, where they were weighed (19.7 g). An equal weight (19.6 g) of a saturated $NaNO_3$ solution was added to the crystals in the beaker as a wash solution, to displace interstitial liquid contaminated with ^{137}Cs. The use of saturated $NaNO_3$ solution prevented the crystals from dissolving in the wash solution. The slurry was stirred for 5 minutes, then filtered. The filtrate was analyzed by GEA.

Wash #2: The crystals from the first wash weighed 17.1 g, and 20.0 g of saturated $NaNO_3$ solution was added. The slurry was stirred, filtered, and sampled as above.

Wash #3: The crystals from the second wash weighed 17.2 g, and 15.9 g of saturated $NaNO_3$ solution was added. The slurry was stirred, filtered, and sampled as above.

Crystal analysis: The filter cake (17.0 g) remaining from the third wash was dissolved in 28.2 g of water, and the solution was analyzed by GEA.

The entire experiment was repeated, using four washes instead of three. The following weights were recorded during the repeat experiment:

Initial weight of contaminated $NaNO_3$ crystals: 30.2 g
Initial weight of water added to dissolve crystals: 60.3 g
Weight of recrystallized $NaNO_3$ filter cake: 17.3 g
Weight of crystals after first wash: 16.9 g
Weight of crystals after second wash: 18.0 g
Weight of crystals after third wash: 17.4 g
Weight of crystals after fourth wash: 17.8 g

The small variations in weight from wash to wash most likely reflect changes in the amount of liquid retained in the filter cake, rather than actual changes in the weight of dry crystals.

2.2.2 Data

The distribution of ^{137}Cs among the various streams can be calculated from the recorded weights, analyzed (or calculated) densities, and activities. The appropriate data are shown in Table 6 for the first test and Table 7 for the second test.

Table 6. Data and Analytical Results for Occlusion Test #1.

Stream	Weight of Stream (g)	^{137}Cs Activity (μCi/mL)	Density (g/mL)
Initial filtered solution of contaminated $NaNO_3$ crystals	80.93	2.92	1.253
Filtrate from recrystallization	19.21	10.90	1.38
Filtrate from Wash #1	22.26	2.04	1.38
Filtrate from Wash #2	19.79	0.184	1.38
Filtrate from Wash #3	16.12	0.0201	1.38
Solution of washed $NaNO_3$ (16.96 g filter cake)	45.18	0.00825	1.260

2.2.3 Results

In both of the occlusion tests, the amount of ^{137}Cs that could not be washed away from the $NaNO_3$ crystals represented 0.14% of the total amount of ^{137}Cs in the slurry before filtering. This implies that the maximum decontamination factor for a single crystallization stage would be approximately 700. With this information, combined with the TWRS estimate of the ^{137}Cs activity in the stream that would be the feed for the clean salt process, the size of the processing plant (i.e., number of stages) can be designed to match the required decontamination factor.

Table 7. Data and Analytical Results for Occlusion Test #2.

Stream	Weight of Stream (g)	^{137}Cs Activity (μCi/mL)	Density (g/mL)
Initial filtered solution of contaminated $NaNO_3$ crystals	98.69	2.13	1.218
Filtrate from recrystallization	21.93	9.40	1.38
Filtrate from Wash #1	16.81	0.983	1.38
Filtrate from Wash #2	20.93	0.0476	1.38
Filtrate from Wash #3	18.59	0.00516	1.38
Filtrate from Wash #4	20.44	0.00089	1.38
Solution of washed $NaNO_3$ (17.81 g filter cake)	51.19	0.00572	1.243

The amount of ^{137}Cs in each stream is calculated by multiplying the activity of the sample (as analyzed by GEA) by the weight of the stream, and dividing by the density. For example, the number of microcuries of ^{137}Cs in the filtrate from recrystallization in test #1 is calculated as follows:

$$(10.90\ \mu Ci/mL)\times(19.21\ g)/(1.38\ g/mL) = 151.7\ \mu Ci\ ^{137}Cs$$

The results of these calculations for all the streams are shown in Table 8. By setting the amount of ^{137}Cs in the initial solution to 100%, the percentage of ^{137}Cs reporting to each of the exit streams can be calculated.

The stream in Table 8 labeled "^{137}Cs Unaccounted For" represents the difference between the initial $NaNO_3$ solution and the sum of all the other streams. In both tests, the amount of ^{137}Cs "lost" is well within the analytical uncertainty of the analyses for the initial solution and the recrystallization filtrate.

The ^{137}Cs distribution can be viewed graphically (see Figure 2) by converting the percentage values in Table 8 to the percentage of ^{137}Cs remaining in the crystals after each step. Thus, in the initial slurry before filtering, 100%

of the ^{137}Cs is associated with the crystals. After filtering, the amount of ^{137}Cs retained in the filter cake is represented by the difference between the initial amount and the amount in the filtrate. The values used for Figure 2 are shown in Table 9. The percentage values have been "normalized" to account for the missing ^{137}Cs, i.e. the sum of the amounts of ^{137}Cs in each stream were forced to add up to 100%.

Table 8. ^{137}Cs Distribution in Occlusion Tests.

Stream	Test #1		Test #2	
	Total μCi	% of total	Total μCi	% of total
Initial $NaNO_3$ solution	188.6	100.0	167.8	100.0
Recrystallization Filtrate	151.7	80.5	149.4	89.0
Wash #1 Filtrate	32.9	17.4	12.0	7.1
Wash #2 Filtrate	2.64	1.4	0.72	0.43
Wash #3 Filtrate	0.23	0.12	0.070	0.04
Wash #4 Filtrate	(0.04)[a]	(0.02)[a]	0.013	0.01
Washed Crystals	0.30 (0.26)[a]	0.16 (0.14)[a]	0.23	0.14
^{137}Cs Unaccounted For	0.79	0.42	5.38	2.62

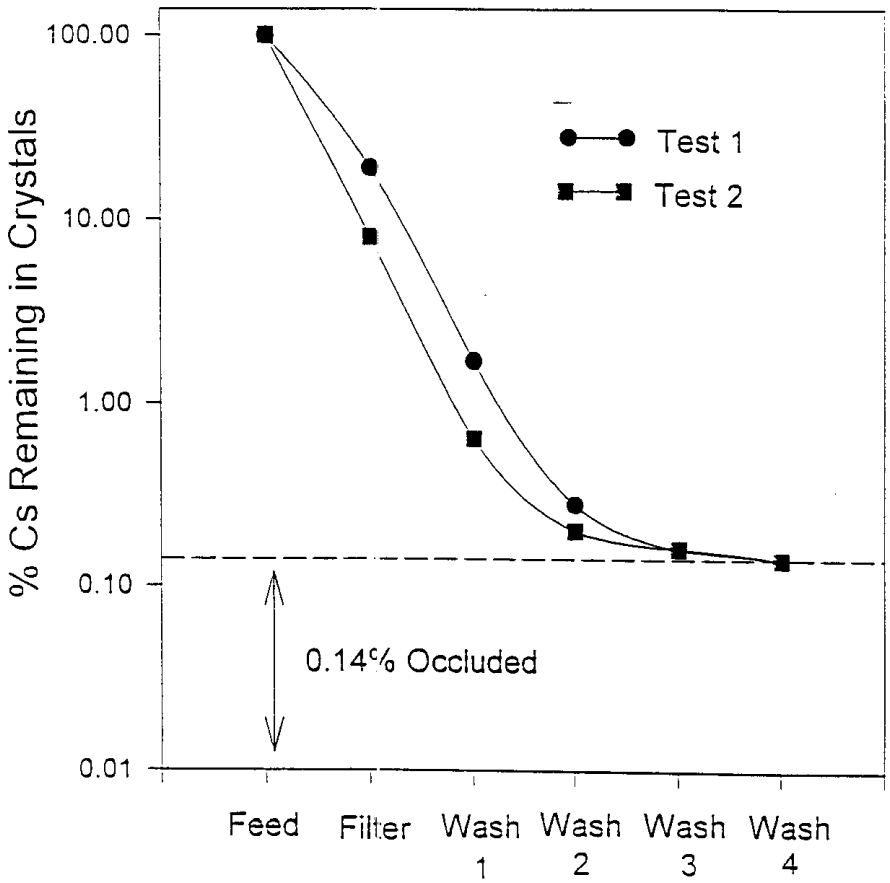
[a] Test #1 included only 3 washes. Values in parentheses are calculated assuming behavior analogous to Test #2 results.

Table 9. Percentage of ^{137}Cs Remaining with Crystals.

Stream	Test #1	Test #2
Initial $NaNO_3$ Solution (Feed)	100.00	100.00
Recrystallization Filtrate	19.16	7.98
Wash #1 Filtrate	1.69	0.64
Wash #2 Filtrate	0.28	0.20
Wash #3 Filtrate	0.16	0.16
Wash #4 Filtrate	0.14	0.14

From the graphic perspective of Figure 2, it is obvious that the effectiveness of the washing falls off rapidly after the second wash, and that the curve reaches a sort of asymptote that represents a level of contamination that can't be removed by washing. That amount is presumed to be held in occlusions within the crystals.

Figure 2. Occlusion Test Results



3.0 SOLUBILITY INTERACTIONS

Accurate solubility phase diagrams are essential to the operation of a fractional crystallization plant. In addition to solubility effects, trace components can sometimes have large effects on the crystal habit (and hence, solid/liquid separation efficiency) of major components.

Initial laboratory studies in the area of a solubility phase diagram for the sodium nitrate/aluminum nitrate system were performed at our in-house laboratory, and are reported below. A decision was made early in the fiscal year to "out-source" the bulk of the solubility interaction work to the University of Arizona. Work performed under that contract will include more detailed data on sodium nitrate/aluminum nitrate solubility interactions (see Task 1 in Section 4.0), as well as an investigation of the effects of minor Hanford waste components on $NaNO_3$ crystallization (Task 2).

3.1 Aluminum Nitrate

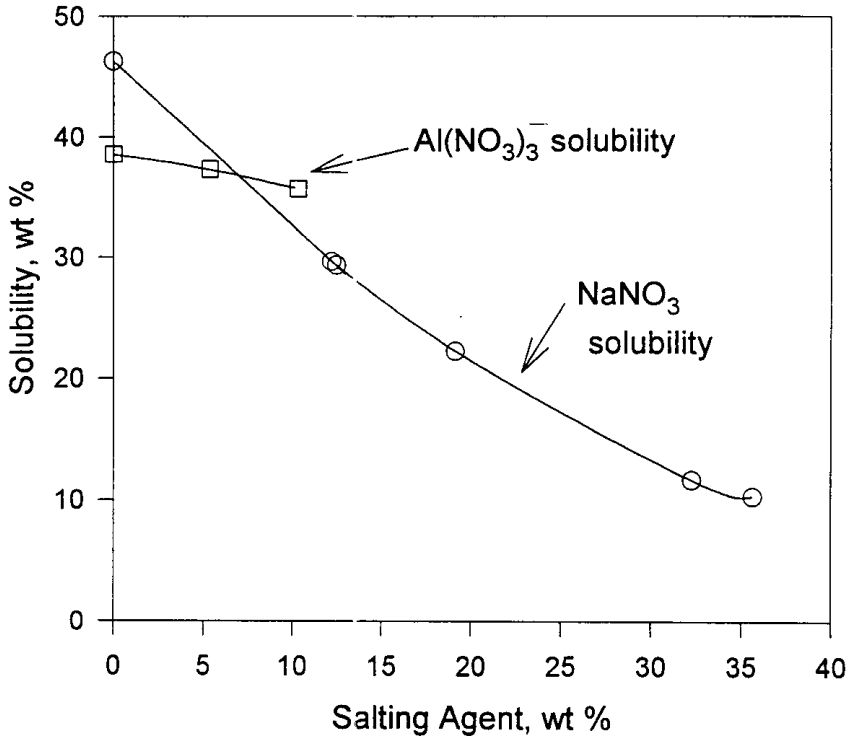
The first step in the clean salt process, as currently envisioned, is a water-wash of the waste sludge or saltcake, followed by solid/liquid separation and acidification of the aqueous solution (liquid phase). The acidified solution is then evaporated to produce crystalline $NaNO_3$. The most abundant salt in the acidified crystallizer feed solution, next to $NaNO_3$, is aluminum nitrate, $Al(NO_3)_3$. Therefore, the most essential solubility information required for plant operation is a phase diagram for the sodium nitrate/aluminum nitrate system.

Limited information is available from the literature. Solubility data for the system $NaNO_3/Al(NO_3)_3/H_2O$ at 20°C are compiled in Reference 1, volume 1, page 191. These data are plotted in Figures 3 and 4.

There are many ways to express solubilities of salts. In Figure 3, solubilities of $NaNO_3$ and $Al(NO_3)_3$ are shown as the weight percent of each salt in the three-component mixture (water being the third component). The y-axis on the graph represents the weight percent of the salt that is saturated. The x-axis represents the weight percent of the salt that is not saturated. Thus, it can be seen from the graph that $NaNO_3$ is saturated at approximately 47% when the $Al(NO_3)_3$ concentration is zero. As $Al(NO_3)_3$ is added to the solution, the $NaNO_3$ solubility drops sharply due to the salting out effect. At the last point on the $NaNO_3$ curve (at the lower right end of the curve), the solution is saturated in both $NaNO_3$ and $Al(NO_3)_3$.

From the same graph (Figure 3), the solubility of $Al(NO_3)_3$ in the absence of $NaNO_3$ is approximately 39%. As $NaNO_3$ is added to the solution, the solubility of $Al(NO_3)_3$ decreases just slightly. At the last point on the $Al(NO_3)_3$ curve, the solution becomes saturated in both salts.

Figure 3. Salting Effect, in Weight Percent



The crystallization plant will most likely operate at higher temperatures than 20°C. Figure 4 shows the 20°C Linke data from Figure 3 (in weight percent) plotted on a triangular solubility phase diagram. (Triangular diagrams are often used to show 3-component phase diagrams.) On the same graph, data are plotted from in-house studies on simulated 101-SY acidified solution at approximately 60°C, reported in Reference 2. The data were taken from Figures 3.1 and 3.5 in that document, and were normalized by dividing each weight by the sum of the three weights, so that the weight percents of the three components added up to 100%. The data for each end of the 60°C curve are taken from Linke for the respective 2-component systems (one salt plus water).

The fact that the 20°C and 60°C solubility curves in Figure 4 are more-or-less parallel lends credence to the higher temperature data. It is also comforting that the 60°C data from Reference 2 "fit" in between the literature values for the two endpoints at 60°C. The in-house data are derived from flowsheet calculations, rather than actual measurements of saturated solution compositions. That is to say, the composition of the initial solution was known, the amounts of water and crystals removed by evaporation were measured, and the composition of the saturated solution was calculated by mass balance.

3.2 Other Components

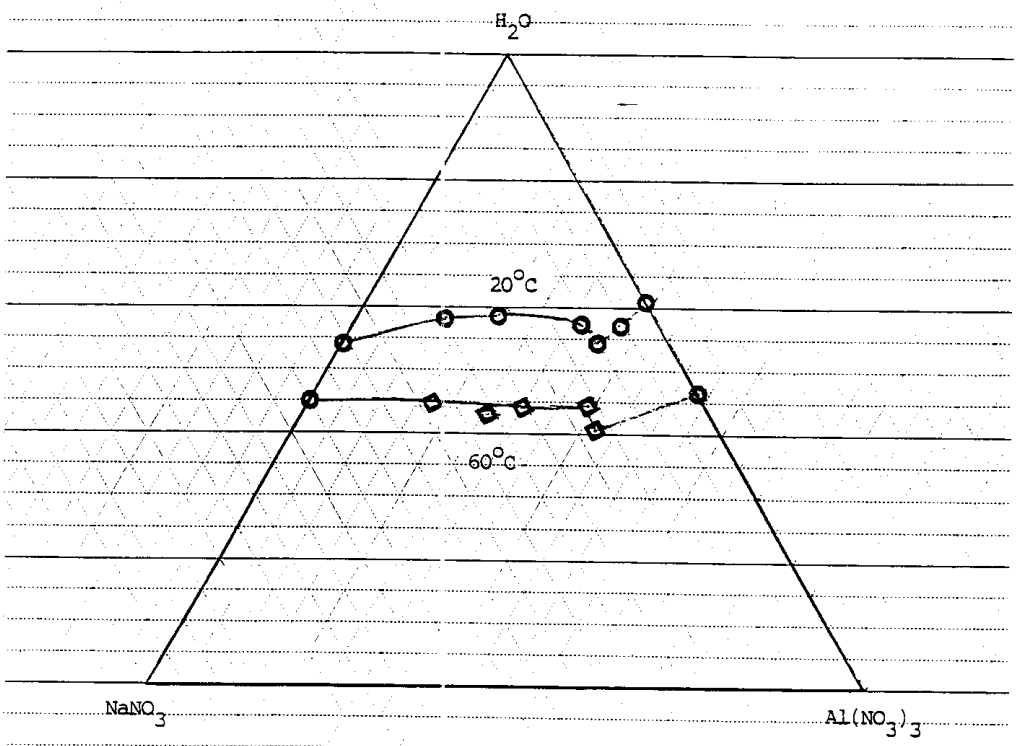
Other waste components are important for two reasons. As mentioned earlier, minor components can have a large effect on crystallization of $NaNO_3$ or other salts, and those effects need to be investigated. That task has been "out-sourced" to the University of Arizona.

In addition to their effects on the major components, some of the minor components could be of interest in terms of removing them from the waste stream as clean salts. Of particular interest are those components that have a deleterious effect on vitrified waste forms. Key examples include sulfate, phosphate, and fluoride.

A proof-of-principle test of the clean salt process was performed in 1992 using sludge from tank 241-U-110 (report attached as Appendix A). In that test, a fluoride/phosphate double salt was separated from the aqueous waste before acidification. The salt precipitated as large octahedral crystals that were identified as $Na_7F(PO_4)_2 \cdot 19H_2O$, sodium fluoride diphosphate. The unrecrystallized double salt contained 85% of the Na_3PO_4 present in the aqueous waste from the sludge wash, along with 33% of the NaF, and only 0.1% of the ^{137}Cs.

Properties of the sodium fluoride diphosphate salt (such as solubility vs. temperature, pH, etc.) are largely unknown. Given the potential for removing fluoride and phosphate from the vitrification plant feed solution, further study of the double salt system is called for, and is proposed for work to be done under this project in fiscal year 1995. Other methods of precipitating fluoride, phosphate, and sulfate will also be pursued next fiscal year.

Figure 4. Ternary Solubility Diagram (in weight percent) for the System $NaNO_3$ - $Al(NO_3)_3$ - H_2O.



○ = Literature data — see text

□ = Data from WHC-SD-WM-DTR-029

4.0 UNIVERSITY OF ARIZONA CONTRACT

On May 1, 1994, Westinghouse Hanford Company (WHC) established a contract with the University of Arizona to develop a continuous crystallization process and to make scale-up recommendations. Dr. Alan Randolph, a world renowned crystallization expert, is overseeing the work. The contract was let for $94K and was given a term of one year.

Researchers at the University of Arizona are tasked with building a mixed slurry/mixed product removal (MSMPR) crystallizer to investigate various crystallization parameters. Studies to be performed with the MSMPR crystallizer fall under three tasks:

Task 1. Growth rates and nucleation rates will be determined for sodium nitrate/aluminum nitrate solutions at a variety of Na/Al ratios.

Task 2. Studies will be performed on more complex aqueous mixtures representing Hanford tank waste. These studies will focus on possible effects of minor chemical constituents on the crystallization process.

Task 3. The researchers will investigate various techniques for crystallization and fines recovery.

More details of the contract and the specific tasks can be found in the Statement of Work, which is attached as Appendix B.

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APPENDIX A

Clean Salt Process End-of-Fiscal-Year [1992] Report

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Westinghouse Hanford Company — **Internal Memo**

From: Process Chemistry Laboratories — 12110-PCL92-078
Phone: 3-2532 T6-50
Date: October 1, 1992
Subject: CLEAN SALT PROCESS END-OF-FISCAL-YEAR REPORT

To: W. C. Allan L5-63

cc: J. N. Appel S4-58
J. W. Bailey S4-55
G. S. Barney T5-12
W. B. Barton L4-75
R. G. Cowan L5-31
J. J. Holmes L5-55
G. Jansen L0-14
J. R. Jewett T6-50
J. P. Sloughter T6-07
R. E. Van der Cook S6-07
DLH File/LB

Reference: Internal Memo, D. L. Herting to J. P. Sloughter, "Sodium Nitrate Recovery Test Plan," dated April 29, 1992.

1.0 INTRODUCTION

Clean Salt Process is the name coined to describe the proposed waste treatment process designed to recover inorganic salts of very low specific activity from the single shell and double shell tank waste. The objective of the process is to lower the bulk volume of waste destined for final disposal in grout vaults. Over 90% of the waste currently stored in the waste tanks, not counting water, is made up of water-soluble inorganic salts, most of which are recoverable as "clean salts". The recovered inorganic salts can be recycled in some cases ($NaNO_3$ converted to HNO_3 and NaOH for re-use as process chemicals), or disposed of in 55 gallon drums as low level waste.

Initial development and proof-of-principle testing of the process was funded this year by the Westinghouse Hanford Company (WHC) Development Steering Board. This report describes the laboratory studies that were carried out on simulated sludge and actual sludge from Tank 110-U.

2.0 RESULTS

The results of the proof-of-principle test using actual sludge from Tank 110-U were very encouraging. Two clean salt products were obtained from the 100 gram sludge sample. Out of a starting inventory of 1700 μCi of ^{137}Cs in the sludge sample, the first clean salt (sodium monofluoride diphosphate) contained 0.1 μCi ^{137}Cs without recrystallizing, and the second salt ($NaNO_3$) contained 0.05 μCi ^{137}Cs after one recrystallization. Details of the proof-of-principle test are shown in the attached process flowsheet

(Figure 1), and are described in more detail in the appropriate section later in this report.

3.0 SIMULATED SLUDGE PROCESS DEVELOPMENT TESTING

A number of scouting studies were carried out in order to select a baseline process out of a number of options that were available. A simulated waste was used for these studies. Since Tank 110-U had been selected as the waste tank that would be used for the proof-of-principle test with actual waste, the composition of the simulated waste was selected to match the composition of Tank 110-U as closely as possible.

Table 1 shows the chemical composition (by species) of actual waste from Tank 110-U, based on core composite data from the core samples taken

Table 1. Composition of Simulated and Actual Tank 110-U Sludge

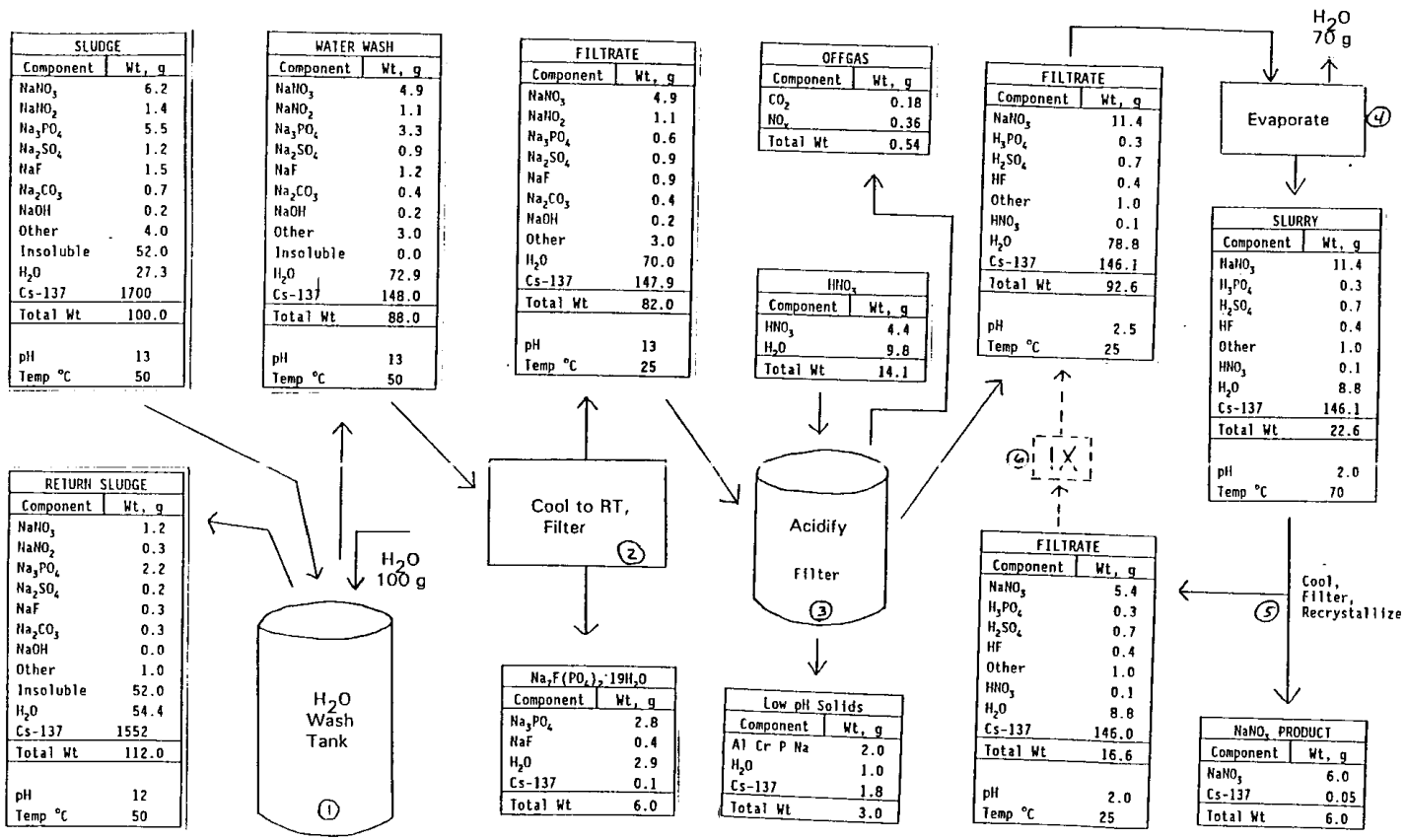
Actual Sludge		Simulated Sludge		
Species	Wt %	Wt %	Compound	Wt %
Na	9.0	9.0	$NaNO_3$	8.50
Al	9.0	9.0	$Al(OH)_3$	23.39
Fe	1.0	1.0	$BiPO_4$	2.74
Bi	1.9	1.9	Fe_2O_3	1.44
F^-	0.7	0.7	$NaAl(OH)_4$	4.13
NO_3^-	4.5	6.2	$Na_3PO_4 \cdot 12H_2O$	9.50
NO_2^-	0.9	0.9	NaF	1.55
PO_4^{3-}	3.2	3.2	$NaNO_2$	1.38
SO_4^{2-}	0.8	0.8	Na_2SO_4	1.14
CO_3^{2-}	0.4	0.4	Na_2CO_3	0.74
TOC	0.1	0.1	$Na_2C_2O_4$	0.13
Si	4.1	4.1	$Na_3Citrate \cdot 2H_2O$	0.29
H_2O	34.8	40.0	$Na_2SiO_3 \cdot 9H_2O$	11.93
M - OH[a]	22.3	22.5	SiO_2	6.19
C - OH[a]	0.2	0.2	NaOH	0.20
			H_2O	26.75
Total	92.9	100.0	Total	100.00

[a] M - OH and represents the weight of O and H associated with the metals Al, Fe, and Si; C - OH represents the weight of O and H associated with oxalate and citrate.

W. C. Allan
Page 3
October 1, 1992

12110-PCL92-078

CLEAN SALT PROCESS, PROOF-OF-PRINCIPLE TEST RESULTS, TANK 110-U SLUDGE



in 1989. The same table shows the chemical composition (by species and by compound) of the simulated sludge. Since the mass balance of the actual waste added up to less than 100%, some adjustment was necessary in preparing the simulant. The additional mass was achieved by increasing the amount of $NaNO_3$ and H_2O in the simulated sludge.

3.1 WATER-WASH STEP

The first step in the process is washing the sludge to dissolve the water-soluble fraction. Several small (5-10 g) samples of simulated sludge were used to evaluate processing options, including use of water vs. dilute (0.01 M) NaOH, water:sludge ratio, contact time (kinetics), and single vs. multiple contacts.

In each test, the supernatant solution (after centrifuging) was analyzed by ion chromatography (IC - for F^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}) and inductively coupled plasma spectroscopy (ICP - for Na, Al, and Si). Evaluations of optimum washing conditions were based on the concentrations of key species in the water wash solution (the supernate).

Tables 2-5 show the results of the analyses of the water wash solutions. The important findings can be summarized as follows:

1 - There was no difference between water and 0.01 M NaOH in washing efficiency.

2 - The 2:1 (water:sludge) wash dissolves more total salt out of the sludge than the 1:1 wash, but the water wash solution is more dilute. The 2:1 wash dissolves about 80% of the total sludge inventory of $NaNO_3$, $NaNO_2$, Na_2SO_4, and NaF, compared to about 60% for the 1:1 wash.

3 - Phosphate behaved differently than the other water-soluble salts. It was actually more concentrated in the 2:1 wash solution than in the 1:1 wash solution. The 1:1 wash dissolved only about 18% of the phosphate present in the sludge, while the 2:1 wash dissolved about 55%. The apparent reason is the strong dependence of phosphate solubility on the ionic strength of the solution. It could also be related to the pH of the solution, which controls the relative amounts of Na_2HPO_4 and Na_3PO_4.

4 - Because phosphate is the most abundant salt in the waste next to nitrate, the 1:1 wash gives a solution that has a much higher percentage of nitrate (relative to total dissolved salt) than the 2:1 wash.

5 - Two successive washings at 1:1 ratio gave very similar results to a single 2:1 wash. The second 1:1 wash contained as much phosphate (on a weight basis) as it did nitrate. The third successive wash at 1:1 ratio dissolved very little additional salt.

3.1.1 Water-Wash Step, Data Analysis and Experimental Details

In one series of tests the diluent:sludge weight ratio was evaluated. Table 2 shows the actual concentration of each species brought into solution in these tests.

The data in Table 3 are derived from the Table 2 data by the following calculation, using the Na in the first column as an example:

$$\frac{44{,}800\ \mu g\ \text{dissolved Na}}{\text{mL wash}} \cdot \frac{7.80\ \text{mL wash}}{7.99\ \text{g sludge}} \cdot \frac{1\ \text{g sludge}}{90{,}000\ \mu g\ \text{original Na}} = 49\ \%\ \text{dissolved}$$

Table 3 shows the percent of each component that dissolved out of the sludge into the water wash solution. The 90,000 µg Na is the total Na in one gram of unwashed sludge (see Table 1).

Tables 4 and 5 are analogous to Tables 2 and 3, but they show the data for the tests that were done to evaluate successive washes at 1:1 diluent:sludge ratio. Included in Table 4 is the analytical data for the one test done at

Table 2. Effect of Diluent and Diluent:Sludge Ratio. Concentrations (ppm) of Species Dissolved in Water Wash Solution.

Diluent:	H_2O	H_2O	NaOH	H_2O	NaOH	NaOH
Diluent:Sludge (wt:wt)	1:1	1:1 dupl.	1:1	2:1	2:1	2:1 dupl.
Supernate Volume, mL	7.80	7.80	7.80	10.20	10.30	10.50
Sludge Wt, g	7.99	7.93	8.08	4.92	5.10	5.15
Na	44800	44500	43200	31600	30900	30700
Al	142	142	139	88	90	98
Si	908	970	938	578	584	592
F^-	3580	3670	3790	2610	2760	2810
Cl^-	68	66	62	46	50	44
NO_2^-	5670	5630	5780	3340	3240	3550
NO_3^-	37700	38400	38800	21600	29100	23000
PO_4^{3-}	5980	5930	6200	8440	8750	8900
SO_4^{3-}	4820	4640	4680	2750	2770	2960
Solution SpG	1.07	1.10	1.09	1.04	1.05	1.05

a contact time of 20 hours, compared to the three hour contact time used for all of the other studies. There is no apparent difference between the three hour contact time and the 20 hour contact time.

For the successive wash tests, a single sludge sample was used for the three washes. Therefore, the data in Table 3 can be compared to the data in the first two columns of Table 2, where the first wash is shown. (The first wash data are repeated in Table 5 for ease of comparison.) The data for the longer contact time experiment (Table 4) should also be compared to the first two columns of data in Table 2.

Table 3. Effect of Diluent and Diluent:Sludge Ratio. Amount dissolved as percent of total amount in original sludge.

Diluent:	H_2O	H_2O	NaOH	H_2O	NaOH	NaOH
Diluent:Sludge	1:1	1:1 dupl.	1:1	2:1	2:1	2:1 dupl.
Na	49	49	46	73	69	70
Al	0	0	0	0	0	0
Si	2	2	2	3	3	3
F^-	50	52	52	77	80	82
Cl^-	--	--	--	--	--	--
NO_2^-	62	62	62	77	73	80
NO_3^-	59	61	60	72	95	76
PO_4^{3-}	18	18	19	55	55	57
SO_4^{3-}	59	57	56	71	70	75

Table 4. Effect of Successive Washes at 1:1 Ratio. Concentrations (ppm) of Species Dissolved in Water Wash Solution.

	Second Wash		Third Wash		20 hour Contact
	Sample	Duplicate	Sample	Duplicate	
Sample Wt, g:	7.45	7.30	6.82	6.69	8.03
Supernate Volume, mL:	7.80	7.70	7.00	6.70	7.50
Na	23300	23400	8080	8660	42300
Al	55	57	37	32	101
Si	411	413	168	164	1020
F^-	2190	2380	790	730	3870
Cl^-	4	<20	<20	<20	43
NO_2^-	1790	1960	672	622	5970
NO_3^-	12000	11800	4090	3900	36700
PO_4^{3-}	11700	11700	3940	3930	5510
SO_4^{2-}	1300	1200	561	541	4490

Table 5. Effect of Successive Washes at 1:1 Ratio. Amount dissolved as percent of total amount in original sludge.

	First Wash		Second Wash		Third Wash		Avg Total
	Smpl	Dupl	Smpl	Dupl	Smpl	Dupl	
Na	49	49	25	25	8	13	84
Al	0	0	0	0	0	0	0
Si	2	2	1	1	0	1	4
F^-	50	52	31	33	10	14	94
Cl	--	--	--	--	--	--	--
NO_2^-	62	62	19	21	7	9	90
NO_3^-	59	61	19	18	6	8	86
PO_4^{3-}	18	18	36	36	11	16	67
SO_4^{2-}	59	57	16	15	6	9	81

3.2 SOLUTION TREATMENT OPTIONS

The main goal of the scouting studies was to produce the cleanest possible $NaNO_3$ crystals in the best possible yield. With this in mind, several options were considered for separating the nitrate out from the other anions in the water wash solution. Precipitation of the $NaNO_3$ was also tried under different pH conditions. A series of eight tests under various conditions were carried out, each one starting with a water wash solution prepared by a 2:1 contact (water:sludge) with the simulated sludge. The test conditions can be summarized as follows:

Test 1 - Acidify to pH 1.5, then precipitate $NaNO_3$

Test 2 - Acidify to pH 1.5, add NaOH to pH 7.6, then precipitate $NaNO_3$

Test 3 - No pH adjustment; add $Ca(NO_3)_2$ to precipitate Ca salts, centrifuge, then precipitate $NaNO_3$ from the supernate

Test 4 - Acidify to pH 7.6, add $Ca(NO_3)_2$ and proceed as in Test 3

Test 5 - Acidify to pH 1.7, add $Ca(NO_3)_2$, centrifuge; add NaOH to supernate to pH 7.3, then precipitate $NaNO_3$

Test 6 - Acidify to pH 1.7, add NaOH to pH 7.7, add $Ca(NO_3)_2$ and proceed as in Test 3

Test 7 - Acidify to pH 7.6, then precipitate $NaNO_3$

Test 8 - No treatment; go directly to $NaNO_3$ precipitation

The concepts behind each of the treatment methods are discussed in the sections that follow. A modified version of the first test was selected as the most advantageous option for reasons outlined below.

3.2.1 Acidification

Acidification of the wash solution with nitric acid serves several purposes, all of which lead to a cleaner separation of $NaNO_3$ crystals. Sodium carbonate is converted to CO_2 gas plus recoverable $NaNO_3$. Nitrite ion is disproportionated into NO_x gas and nitrate ion. Certain organic salts which might be present in the waste (e.g., Na_4EDTA) are much less soluble in the acid form (H_4EDTA), and could be removed by filtration. The same behavior might apply to some silicate compounds. Other sodium salts that would co-precipitate with $NaNO_3$ under basic conditions are converted into their weak acid forms ($H_3PO_4/H_2PO_4^-$, HSO_4^-, and HF), and remain in solution when the $NaNO_3$ is crystallized at low pH. And finally, it was observed during the testing of the treatment options that precipitation of $NaNO_3$ under low pH conditions leads to crystals having relatively large size and clean habit, i.e., the crystals are very regular rhombohedra. Under neutral conditions, the crystals tended to be more irregular in shape, and were often dendritic. Such crystals are much more difficult to filter, or otherwise separate from the mother liquid.

There were enough advantages to acidification that it was selected as the most promising treatment method, and was used for the proof-of-principle test with actual sludge from Tank 110-U. One alternative that has not yet been addressed is reducing the amount of HNO_3 required by doing a basic side crystallization, then dissolving the precipitate in water and then acidifying. For tanks that are low in NaOH content, such as Tank 110-U and most of the single shell tanks, the reduction in HNO_3 would probably not be very significant. Most of the acid gets consumed in protonating the conjugate anions of the weak acids in solution (carbonate, phosphate, sulfate, fluoride, etc.), rather than in simply neutralizing NaOH. In any case, the nitrate that is added in the form of HNO_3 is later recovered with the $NaNO_3$ product.

3.2.2 $Ca(NO_3)_2$ Addition

The idea behind calcium nitrate addition was to precipitate calcium salts, since there are several in the solution. Calcium phosphate, sulfate, fluoride, oxalate, and citrate all have very low solubilities. The idea encountered insurmountable difficulties in two areas. First, the precipitates tended to be very flocculent, making solid/liquid separation very difficult and causing excessive liquid retention in the sludge. Second, some calcium salts tended to form of colloidal suspensions during all subsequent operations, so that the final $NaNO_3$ product was contaminated with calcium salt fines. The option of calcium nitrate addition has been abandoned.

3.2.3 No Treatment

Precipitation of the sodium salts under basic conditions is feasible if no separation of the salts is required. Decontamination of the salts from the ^{137}Cs is still possible, because the cesium stays in solution even when the solution is very concentrated in all other salts. (The molarity of cesium ion is quite low, so the ion product for cesium nitrate -- $[Cs^+]\bullet[NO_3^-]$ -- remains lower than the solubility product constant, K_{sp}.) Since the main goal of this project was to obtain the cleanest possible $NaNO_3$ product in the highest possible yield, the non-specific precipitation of sodium salts was not pursued.

3.3 LARGE SCALE TESTS WITH SIMULATED SLUDGE

In preparation for the proof-of-principle test with actual sludge, two large scale (125 gram) tests were carried out using simulated sludge in which the entire flowsheet was tested. Since the behavior of the simulated sludge was so closely parallel to the actual sludge, including precipitation of the sodium monofluoride diphosphate salt, it would be redundant to go into a lot of detail on the simulated sludge tests. Some of the analytical data for these tests are not yet available. The analytical data will help to refine the concentrations in each stream of the flowsheet shown in Figure 1. If significant alterations to the flowsheet are required based on these data, then a follow-up report will be issued.

4.0 PROOF-OF-PRINCIPLE TEST WITH TANK 110-U SLUDGE

In order to demonstrate the feasibility of the proposed process, a single large-scale (125 gram) test was carried out using sludge from the core sample taken from Tank 110-U in 1989. The sample used was a combination of two archived core composite samples representing Core 7 and Core 14.

The results of the proof-of-principle test are shown as a process flowsheet in Figure 1. The concentrations of species shown in the various streams in the process are based on a combination of analyses from the proof-of-principle test and the simulated sludge tests, as well as some solubility data from literature sources.

Tank 110-U was not the ideal tank to use for demonstrating the process, but it was the only tank for which sufficient sample was available to do a large scale test. Tank 110-U is, in one sense, a more difficult case than a more typical single shell tank because it is unusually low in sodium nitrate content. It contains only 6.2% $NaNO_3$ by weight, compared to the overall average of 25% for single shell tank sludges, and 80% for single shell tank salt cakes. On the other hand, Tank 110-U contains a relatively large fraction of insoluble ^{137}Cs. As a result, 90% of the ^{137}Cs content of the sludge is removed in the initial water wash. For some other single shell tank wastes, and certainly for double shell tank wastes, a much larger fraction of ^{137}Cs will stay in the supernate.

If funding is continued next fiscal year, testing will be done on more "typical" waste tanks, including the double shell tank 101-SY.

4.1 DISCUSSION OF RESULTS

Figure 1 is a standard process flowsheet diagram. The process steps are labeled with the circled numbers 1-5. (Step 6, the recycle via an ion exchange loop to remove cesium, is envisioned, but has not been tested.) The process begins with the sludge feed stream shown in the upper left corner of the diagram, and ends with the $NaNO_3$ product in the lower right corner. All other input and output streams are shown.

Two clean salts of known composition were recovered during the test. The first salt crystallized out when the original water wash solution was cooled from 50°C to room temperature. It was identified by x-ray diffraction as a mixture of $Na_7F(PO_4)_2 \cdot 19H_2O$ and $Na_6HF(PO_4)_2 \cdot 17H_2O$. Note that the only difference between the two salts is the replacement of one Na^+ ion by a H^+ ion, and a slight difference in the number of waters of hydration. The difference between the two salts is analogous to the difference between Na_3PO_4 and Na_2HPO_4. They are effectively the same salt, and I have referred to the pair throughout the body of this report as the sodium monofluoride diphosphate salt.

The crystals formed upon cooling of the solution were quite large, clear, and regular in shape (octahedral). The optical properties (isotropic) of

the salt matched the literature properties for the Na_7 salt. The filtered crystals were quite low in ^{137}Cs even though no attempt was made to recrystallize them.

The second clean salt was $NaNO_3$, which was recovered in approximately the anticipated yield. (Some of the product was inadvertently lost during a wash step -- see the experimental section 4.2.) The separation of the $NaNO_3$ crystals from the ^{137}Cs, which stayed in solution, was excellent, especially after the salt was recrystallized once. (Refer to the ^{137}Cs numbers in Figure 1, which are all given as total μCi of ^{137}Cs.)

(The reader might notice that the total amount of $NaNO_3$ in the crystalline product plus the filtrate is higher than the amount in the sludge at the beginning of the process. The reason is that nitrate is added in the form of HNO_3 during the acidification.)

A third product stream shown in Figure 1 is the "low pH solids" that formed when the water wash solution was acidified. The composition of these solids is not known, but the ICP analysis indicates that the main components are phosphorus, aluminum, and chromium. The ^{137}Cs in that stream is higher than in the other two product streams because the solids remain wet with interstitial liquid due to the small particle size of the solids.

4.2 EXPERIMENTAL DETAILS

Each of the process steps outlined in the Figure 1 flowsheet is described in detail below. The total weights used in the experimental description do not match the weights shown in Figure 1 because the weights in the figure have been "normalized" to a starting weight of 100 grams of sludge.

All of the laboratory work (procedures, observations, measurements) for the work with actual Tank 110-U sludge are recorded in laboratory notebook WHC-N-384 1. (The corresponding information for the simulated waste effort is recorded in laboratory notebook WHC-N-345 1.)

4.2.1 Water Wash of the Sludge (Flowsheet Step 1)

Two archived core composite samples from Tank 110-U, 72.0 g from Jar #390 plus 55.5 g from Jar #391, were combined with 128.3 g H_2O in a single jar. The archived samples were quite dry, chunky, and brittle, but they dispersed nicely in the water wash. The sample remained in the water at room temperature, unstirred, for about 3 weeks before proceeding with the experiment.

The sample was heated to 50°C for two hours with periodic agitation. In order to analyze the sample for starting composition, 5 g of the slurry at 50°C was added to 40 g H_2O. The diluted sample was centrifuged, and the supernate was submitted for analysis. The ^{137}Cs concentration shown in the flowsheet for the water wash is based on this analysis. The hydroxide and IC analyses for this sample have not yet been completed.

The remaining slurry was transferred into four 50 mL centrifuge cones. All four cones were centrifuged for one hour in a centrifuge which was maintained at 50°C with an external heating jacket. The supernatant solutions from all of the cones were decanted into a single 125 mL plastic bottle, which was removed from the hotcell. The supernatant solution contained a small amount (about 2% by volume) of floating organic liquid, which was presumed to be the normal paraffin hydrocarbon used as the hydrostatic fluid when the tank was core sampled.

Table 6 shows the breakdown of the cones into centrifuged solid and supernatant liquid fractions. It is noteworthy that the weight of centrifuged solids was greater than the starting weight of the sludge. That is because the starting sludge had dried out so much during three years of archival in the hotcell. Once the sludge was re-hydrated when the water was added, it could not be centrifuged back to its pre-hydrated level of water content. Comparing the compositions of "sludge" and "return sludge" in Figure 1 shows that the return sludge is lower in all of the soluble salts, but the added water more than compensates for the loss in salt content. This behavior is an artifact of the sample history, and is not expected to be observed under actual processing conditions.

Table 6. Centrifugation of Diluted Sludge

	Cone A	Cone B	Cone C	Cone D	Total
Diluted Sludge, g	60.85	55.42	53.53	60.02	229.82
Total Volume, mL	43.30	41.00	42.50	42.50	169.30
Bulk SpG	1.41	1.35	1.26	1.41	1.36
Supernate Wt, g	24.08	23.82	29.55	20.55	98.00
Supernate Vol, mL	21.80	21.50	27.25	20.00	90.55
Supernate SpG	1.10	1.11	1.08	1.03	1.08
Solids Wt, g	35.17	30.56	23.28	38.81	127.82
Solids Vol, mL	21.50	19.50	15.25	22.50	78.75
Solids SpG	1.64	1.57	1.53	1.72	1.62

4.2.2 Cooling the Water Wash Solution (Flowsheet Step 2)

When the water wash solution in the 125 mL plastic bottle cooled to room temperature, 6.0 g of sodium morofluoride diphosphate crystallized out of solution. A small sample of the crystals were submitted for x-ray diffraction. The x-ray spectrum (see Figure 2) showed a series of very sharp peaks, an indication of sample purity, that were clearly identifiable as the two salts $Na_7F(PO_4)_2 \cdot 19H_2O$ and $Na_6HF(PO_4)_2 \cdot 17H_2O$. The remainder of the crystals were filtered and washed once with water. A small sample of the

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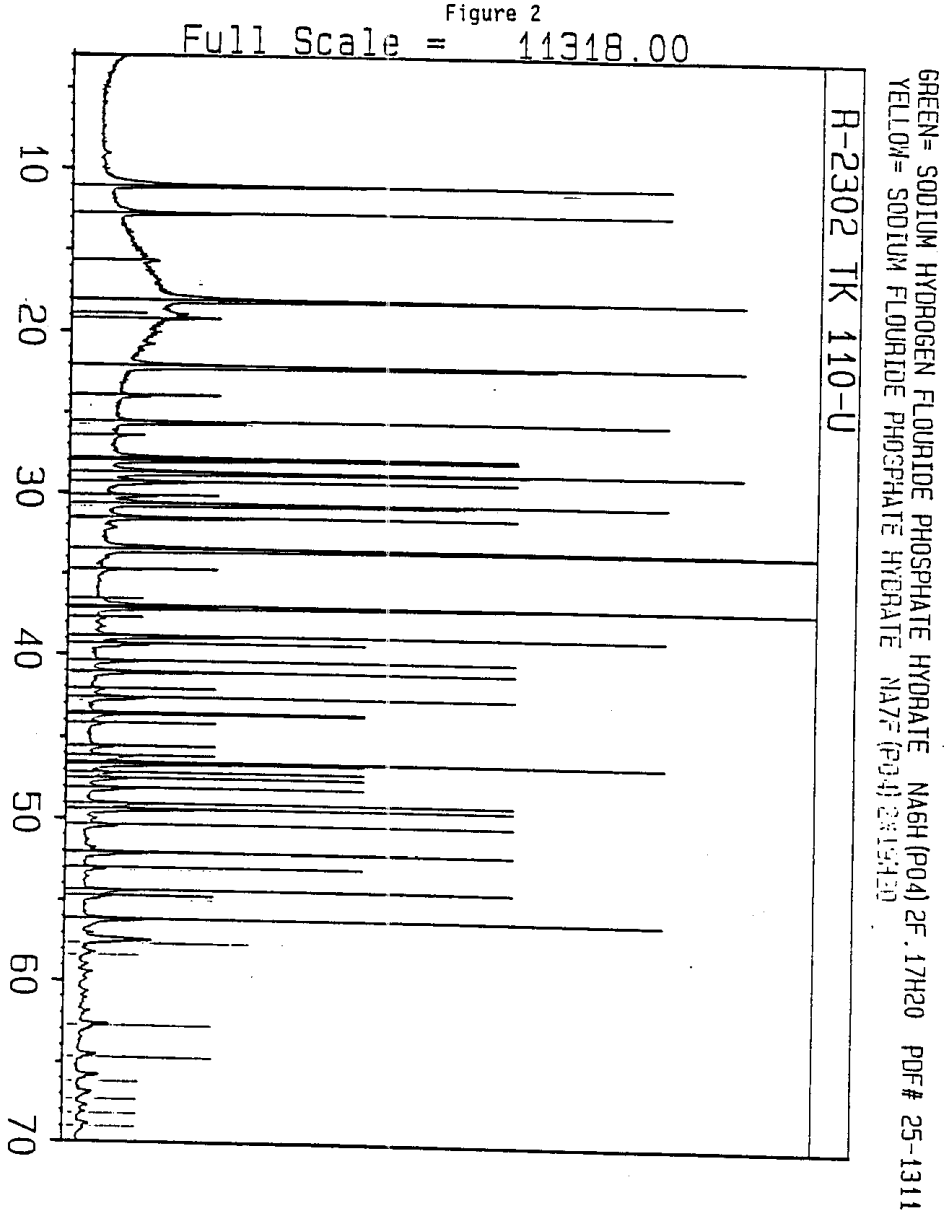
Figure 2



washed crystals (0.49 g) was dissolved in 9.61 g H_2O, and the solution was submitted for gamma energy analysis (GEA). The ^{137}Cs content of the salt shown in the flowsheet is based on the results of this GEA.

4.2.3 Acidification of Water Wash Solution (Flowsheet Step 3)

The filtrate from Flowsheet Step 2 was acidified with 6 M HNO_3. The titration curve for the acidification is shown in Figure 3. The solution was straw-colored at the starting pH of 12.6.—The solution began to turn slightly cloudy at pH 10.6, then became more yellow at pH 10.1. The color returned to straw at pH 8.7, but remained slightly cloudy throughout. Gas bubbles were first noted at pH 6.33. Gas production became more intense at pH 5.1, and subsided at pH 3.3. At the final pH of 2.5 the color changed to olive. The acidified solution was left for 10 days before proceeding with the experiment.

The acidified solution was transferred to two 50 mL centrifuge cones. After centrifuging, there was 3.5 g of centrifuged solids and 91.9 g of pale blue green supernate.

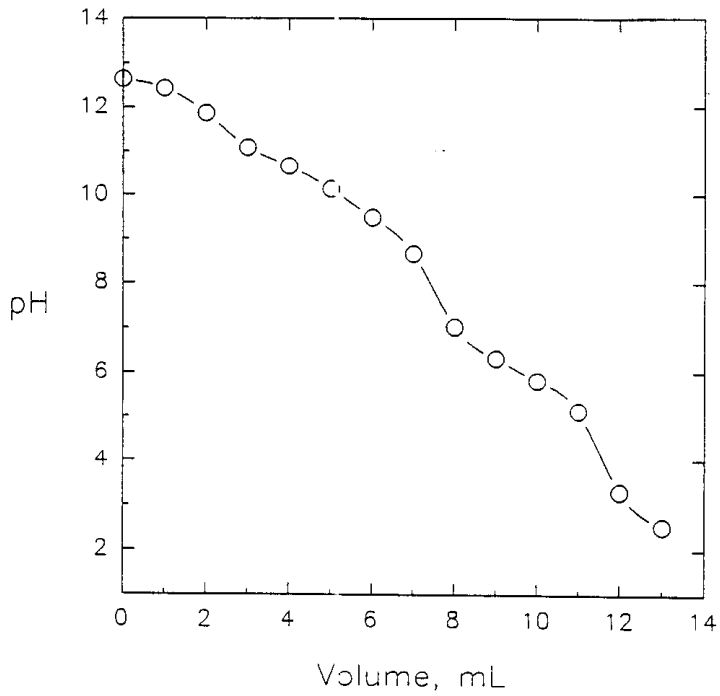
4.2.4 Evaporation and Crystallization (Flowsheet Steps 4 and 5)

The 91.9 g of supernatant solution was evaporated at low heat (about 50°C) until the total weight was 20.8 g and $NaNO_3$ crystals (identified by polarized light microscopy) had formed. The slurry was filtered. The filtrate was transferred back to the beaker in which it had been evaporating. The crystals were washed with a concentrated but not saturated solution of $NaNO_3$. (The solution contained 42% by weight $NaNO_3$, compared to saturated which has 47%.) The volume of wash solution used was too large, and the rate of dissolution of the product $NaNO_3$ crystals into the wash solution was surprisingly fast, so much of the product from the "first crop" was lost. It was quite apparent, though, that the crystals were very white. There was also a small amount of fine, dark green solids that were filtered out of solution along with the $NaNO_3$ product.

The filter paper was washed with 50 mL water to remove all traces of $NaNO_3$. The dark green solids remaining on the filter paper were then dissolved by adding 15 mL of 6 M HNO_3 to the filter. The resulting solution was filtered, and the filtrate was analyzed by ICP in an attempt to identify the dark green solids. The major elements detected by ICP in the sample were: 3210 ppm Na, 700 ppm P, 360 ppm Al, and 190 ppm Cr. These are presumed to be the same type of solids removed earlier, but incompletely, by centrifugation.

The pretty bluish green filtrate that was returned to the beaker was evaporated further until the total slurry weight was 12.5 g, and the slurry was fairly thick with precipitated $NaNO_3$. When the slurry was filtered, the solids were white with a very faint greenish tint. The filtrate was transferred to a vial for analysis by IC, ICP, and GEA. The ^{137}Cs value shown in Figure 1, step 5 filtrate, is based on this analysis. Other analyses are still pending.

Figure 3. Titration Curve for Acidification



6 M HNO_3 added to 92.0 g Water Wash Solution

4.2.4.1 Recrystallization of NaNO3 Product

The solids on the filter were carefully washed with a minimum amount of concentrated $NANO_3$ solution. The washed crystals were then transferred to a vial, weighed (3.7 g), re-dissolved in 5.9 g water, and filtered. The 9.0 g of filtrate (0.6 g lost in the filter) was evaporated down to 4.8 g, then cooled and filtered. The snow-white crystals were washed with $NANO_3$ solution, then air-dried. The actual weight of recrystallized, washed, dried crystals recovered was 1.9 g. A sample of the crystals examined with the polarized light microscope showed a homogeneous sample with no apparent contamination. The sample contained very clean, uniform, well-shaped rhombohedral crystals, ranging in size from about 10 μm to 200 μm, with an average size of about 30 μm (as estimated from polarized light microscopy).

The remaining crystals were dissolved in 9.8 g H_2O and submitted for GEA analysis. The ^{137}Cs value shown in Figure 1, $NaNO_3$ product, is based on this analysis.

5.0 RECYCLE STREAMS

The flowsheet shown in Figure 1 has several opportunities for recycling of streams, not all of which are shown on the flowsheet. For example, the condensate from the evaporation process (step 4) can be used for input to the sludge wash tank in the beginning of the process (step 1). A fraction of the nitric acid used in the acidification (step 3) can be obtained from recovery of No_x offgas from previous cycles. The remainder of the HNO_3 can be obtained from decomposition of the $NaNO_3$ product (step 5) into HNO_3 and NaOH by either electrolytic or thermal means.

The recycle stream which is essential to the success of the process is the return of the final filtrate (step 5) to the evaporator feed stream. By the nature of the high solubility of $NaNO_3$, it is necessary to crystallize only about 50-60% of the amount of $NANO_3$, in a given batch of slurry. The large fraction of $NaNO_3$ that remains in solution must be returned to the evaporator if the process is to be efficient.

The obvious problem with routing the final filtrate back to the evaporator is that the concentration of other soluble species (most notably ^{137}Cs) Will build up with each succeeding process cycle. Therefore, an ion exchange step is proposed (step 6) in order to remove the ^{137}cs from the recycle stream. This proposed process is shown with dotted lines in Figure 1 because no actual laboratory work has been done on that portion of the flowsheet.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The proof-of-principle test with actual sludge from Tank 110-U was an unqualified success. The isolation of snow-white $NANO_3$ crystals of very low activity with just one recrystallization was very exciting.

While the Clean Salt Process lacks the glamour of cutting-edge technology, it has the advantage that it uses very simple processes that have had many decades of proven use throughout industry. At this very early stage of flowsheet development, it is easy to point out areas of difficulty. However, the potential economic and political advantages of the process are obvious, and merit continuation of the experimental work into the next fiscal year.

If you have any questions please feel free to call.

for D. L. Herting, Scientist
Process Chemistry Laboratories

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APPENDIX B

Statement of Work

University of Arizona Contract

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STATEMENT OF WORK PO #352167

STATEMENT OF WORK SUMMARY

Westinghouse Hanford Company (WHC) is investigating removing sodium nitrate and other non-radioactive salts from Hanford tank waste. This effort is currently being funded by the Department of Energy's (DOE) Office of Technology Development under the Efficient Separations Processing Integrated Program (ESPIP). An individual or organization with crystallization expertise is required to perform several engineering studies. These studies are needed to support a DOE-HQ decision at the end of FY 1994 of whether to pursue pilot-scale development of this process. Copies of all existing work to date on sodium nitrate recovery will be provided to the researchers.

INTRODUCTION

The Clean Salt process being developed by WHC involves crystallizing essentially pure sodium nitrate from a complex low-level aqueous waste matrix. Successful development of the Clean Salt process could significantly decrease the volume of radioactive waste, saving millions of dollars in disposal costs.

Crystallization is an art as well as a science and the crystallization process can be affected by any number of seemingly insignificant factors. The successful design of a salt recovery process needs to be developed and tested under carefully controlled conditions that are scaleable to pilot and full scale systems. To accomplish this, the studies conducted by the expert researchers need to demonstrate mixed slurry, mixed product reactor (MSMPR) crystallization, and efficient fines recovery.

OBJECTIVE/PURPOSE

The objective/purpose of this research effort will be to provide WHC with data from which the viability of scaling the process can be evaluated. Key studies to be performed are Mixed Slurry Mixed Product Reactor (MSMPR) crystallization studies, fines recovery, and different crystallization techniques.

The researchers will provide information and reports to support the outlined tasks. All tests will be non-radioactive. Non-radioactive stand-ins will be substituted for radioactive species whenever possible.

TASK OUTLINE

Task 1: Growth Rate Studies for Single Component and Simple Mixture Systems.

The researchers shall perform simple growth rate studies for single component sodium nitrate and aluminum nitrate. The researchers will perform at least four bi-component studies for sodium nitrate and aluminum nitrate at various relative concentrations. Aluminum concentrations will be varied between 0.5 and 17 weight percent on a cation basis and the sodium concentrations will be varied between 83 and 95.5 weight percent on a total cation basis. These studies will establish the MSMPR crystallization growth rates and nucleation rates for these components. Westinghouse Hanford will provide the researchers with the necessary chemical reagents.

Task 2: Crystallization Studies for Complex Mixture Systems.

The researchers will perform crystallization studies for complex aqueous solutions that represent Hanford tank waste. Minor chemical constituents can adversely affect the crystallization process. These studies will provide information on solubility interactions and on the process dynamics for MSMPR crystallization. Westinghouse Harford will either provide the experimenter with the complex aqueous solutions, or with the recipes and necessary chemical reagents. The researchers will need to allow for trace component analyses to support their conclusion.

Task 3: Fines Recovery and Crystallization Technique

The researcher will investigate different fines recovery and crystallization techniques. The efficient recovery of sodium nitrate and other non-radioactive salts depends on the ability to grow sufficiently large particles. Researchers will study the various techniques and make a recommendation to WHC as to which techniques would be apply to the Clean Salt process. Westinghouse Hanford will provide the researchers with the necessary chemical reagents.

DELIVERABLES

Interim Reports/Technical Briefs

Interim reports are required to document completion of each task. The interim reports will detail findings for each particular task. A technical brief for fiscal year 1994 activities is required. Letters from the experimenters will suffice for the interim reports and technical brief.

Final Report

A final report is due upon completion of all of the tasks. The report will contain a detailed summary of the interim reports.

All reports prepared by the researchers shall be reviewed and approved by WHC prior to acceptance.

REQUIRED SCHEDULE

The completion date for this project is one year from the date the contract is awarded. The schedule for interim reports for each task is flexible. The technical brief needs to be submitted by September 15, 1994 for inclusion in a WHC report due September 30, 1994.