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7. Abstract

Clean Salt Process proof-of-principle experiments with actual waste from Tank 241-SY-101 (101-SY) have been completed. "Nonradioactive" sodium nitrate ($NaNO_3$) was recovered from a 101-SY composite sample. A ^{137}Cs decontamination factor of 14 million was achieved. Planning for tests with actual waste was based on flowsheet development work carried out using simulated 101-SY waste. Details of both the simulated waste development studies and the actual waste experiments are reported. The recovery of nonradioactive $NaNO_3$ from a 101-SY composite sample was a crucial step in demonstrating that the Clean Salt Process is technically feasible. Evidence is also presented that organics were being destroyed during the test process.

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LIST OF TERMS

AN	aluminum nitrate
ANN	aluminum nitrate nonahydrate
DF	decontamination factor
DSS	double shell slurry
DST	double shell tank
GEA	gamma energy analysis
GM	Geiger-Mueller
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetate (trisodium salt)
ICP	inductively coupled plasma
ISL	interstitial liquid component salts
NB	notebook
PUREX	Plutonium-uranium Reduction Extraction
SST	single shell tank
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
WHC	Westinghouse Hanford Company

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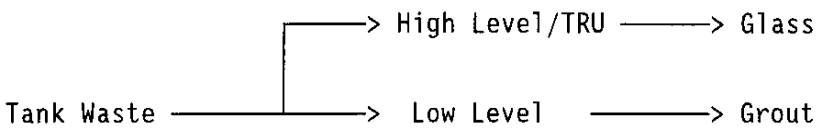
1.0 INTRODUCTION

"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 nonradioactive ("clean") sodium salts from the waste by fractional crystallization.

Waste storage in underground tanks has always been considered to be a temporary solution to the waste disposal problem. Plans for conversion to permanent storage have focused on two final waste forms: vitrification (glass) for high level and transuranic (TRU) waste, and grout for low level waste. Waste pretreatment is designed to fractionate the waste into the two feed streams as shown in Figure 1.1, in such a way as to send as much of the waste as possible to grout.

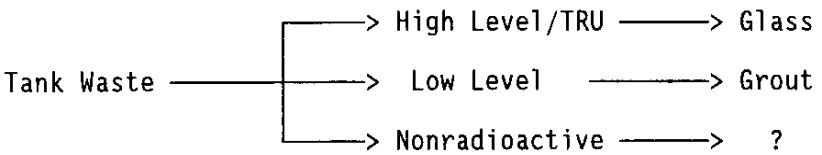
Figure 1.1. Waste Pretreatment for Final Disposal.



Pretreatment schemes to accomplish the desired fractionation into high level and low level streams are based on removal of radionuclides from the bulk of the waste so that the bulk becomes less and less radioactive (more low level). For example, ion exchange may be used to remove ^{137}Cs from the waste, and solvent extraction could be used to remove TRU isotopes.

The clean salt process represents an entirely different approach. Instead of removing radionuclides from the bulk of the waste, this process selectively removes the non-radioactive components. It opens up a possible new way of looking at waste pretreatment (Figure 1.2).

Figure 1.2. Waste Pretreatment with Clean Salt Process Incorporated.



The pretreatment scheme shown in Figure 1.2 could reduce the volume of grout at least by half, and perhaps by as much as a factor of ten. According to results presented in this document, it is technically feasible to recover nonradioactive salts from the waste. Process viability, then, depends in part on the final disposition of the recovered salt, for which a number of options might be considered. Commercial use of the salts by industry is within the

realm of possibility, but is highly unlikely to be approved simply because of the history of the salt. Conversion of the salt into process chemicals (nitric acid and sodium hydroxide) that could be re-used within the Department of Energy complex is an attractive possibility. Disposal of the salt as a chemical waste, rather than a radioactive waste, could be evaluated. And finally, it might be shown that a limited version of the clean salt process could be used to decontaminate the bulk of the waste to form grout feed. Instead of removing the radionuclides to leave a low level grout feed, the low level grout feed could be crystallized out of the waste, leaving the concentrated radionuclides. Instead of a series of radionuclide removal processes (ion exchange, solvent extraction, precipitation), a single process of fractional crystallization would accomplish the required decontamination.

2.0 SUMMARY

Clean Salt Process proof-of-principle experiments with actual waste from Tank 241-SY-101 (101-SY) have been completed. "Nonradioactive" sodium nitrate ($NaNO_3$) was recovered from a 101-SY composite sample. (In this context, "nonradioactive" means that the salt was sufficiently low in total activity to qualify for unconditional release from the radiation zone.) A ^{137}Cs decontamination factor of 14 million was achieved. Planning for tests with actual waste was based on flowsheet development work carried out using simulated 101-SY waste. Details of both the simulated waste development studies and the experiments with actual waste are reported in this document.

The recovery of nonradioactive $NaNO_3$ from a 101-SY composite sample was a crucial step in demonstrating that the Clean Salt Process is technically feasible. The separation of "clean" salt from double shell slurry (DSS) waste, as represented by 101-SY, is perhaps the most difficult test to which the process could have been put. However, there are other technical factors which make a viable process for application to DSS more complex than for other waste types, such as single shell tank salt cake. Development of the chemistry and flowsheets to incorporate these factors, which include aluminate and carbonate removal, was beyond the scope of the effort reported here. The factors are discussed in detail later in the report.

During simulated waste testing, it became apparent that organics were being destroyed during the process. Since organic destruction experimentation was beyond the scope of the funded study, little effort was made to pursue this finding. However, the limited amount of data available clearly show that the Clean Salt Process could be run under conditions that would provide organic destruction.

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3.0 SIMULATED WASTE STUDIES

A series of five batch tests of the Clean Salt Process (designated Tests A-E) was made using simulated 101-SY supernatant solution. Each test was run under somewhat different conditions. In Tests A, C, and E, the entire sample of simulated waste was acidified. In Test E, final filtrate solutions from Tests A and C were added to the acidified solution to simulate evaporator recycle. In Tests B and D, attempts were made to do a pre-acidification separation of the $NaNO_3$ and $NaNO_2$ from the other salts in solution. The same simulated waste was used for all five runs. The composition of the solution is shown in Table 3-1. The procedure and results for each of the five test runs are described below.

Table 3-1. Composition of Simulated 101-SY Supernatant Solution.

COMPONENT	CONCENTRATION, M
NaOH	2.0
$NaAl(OH)_4$	1.5
$NaNO_3$	2.6
$NaNO_2$	2.2
Na_2CO_3	0.42
Na_3HEDTA	0.20
Density, g/mL	1.36

3.1 TEST A

The first test was done using a procedure essentially similar to the one used previously for Tank 110-U sludge wash solution (Herting 1992a).

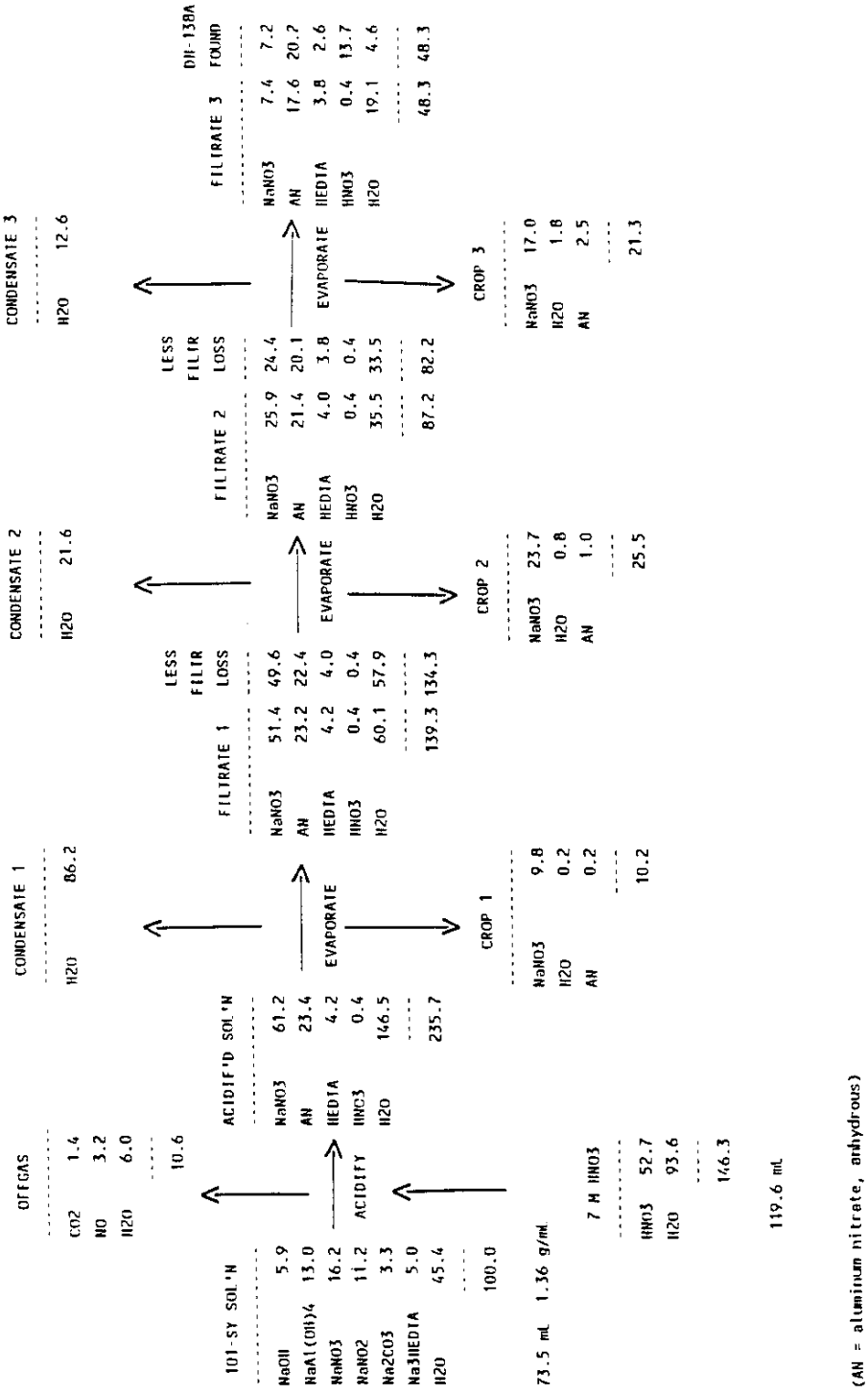
3.1.1 Procedure

A 100 g sample of simulated waste solution was acidified by adding 7M HNO_3 until all of the $Al(OH)_3$ had dissolved. The final pH was less than one. The total amount of HNO_3 solution added was 146.3 g (119.6 mL).

The acidified solution was evaporated by stirring in an open beaker while heating the solution at about 60-80°C. After $NaNO_3$ crystals began forming, the solution turned from colorless to bright yellow, and the solution began to effervesce due to release of gas. When the slurry contained about 30% settled solids (by volume), the hot slurry was filtered to remove the first crop of $NaNO_3$ crystals, which weighed 10.2 g.

The filtrate was returned to the beaker for further evaporation. In similar manner, Crop 2 (25.5 g) and Crop 3 (21.3 g) of $NaNO_3$ crystals were recovered. See Figure 3.1 for a flow diagram summary of the process for

Figure 3.1. Mass Flow Diagram for Simulated Waste Test A.
(All quantities in grams except as noted)



Test A. Calculations used to derive the mass flow diagram are shown in Appendix A.

3.1.2 Results

The factor that stands out in Test A is the large amount of HNO_3 required to acidify the simulated waste solution. The amount is not unexpected, given the high concentrations of all the species in solution that consume acid. In fact, the amount required is in pretty good agreement with the amount calculated based on those concentrations. However, the final HNO_3 concentration is somewhat higher than it was in the 110-U experiments, which were run at pH 2. More importantly, the amount of HNO_3 required for the 101-SY acidification was higher in Test A than the amount that could be produced by recycle of the $NaNO_3$ product into HNO_3 and NaOH.

Each of the three crops of $NaNO_3$ crystals appeared under the microscope to be pure $NaNO_3$. However, it is very difficult to differentiate between $NaNO_3$ and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, or ANN) crystals. Therefore, a titration test was devised to assay the product for acidic impurity (i.e., ANN crystals) by adding NaOH to a sample of dissolved crystals until the solution reached pH 7. The titration method was calibrated using known mixtures of reagent grade $NaNO_3$ and ANN salts. The assay results showed the three crops to contain 4%, 7%, and 20% by weight ANN, respectively, for Crops 1, 2, and 3. It is not surprising that the relative amount of ANN increases with each successive crop, as the ratio of aluminum to sodium in solution increases each time $NaNO_3$ crystals are removed.

Depending on the final intended use or disposition of the "clean salt," the presence of ANN crystals in the $NaNO_3$ product may or may not be important. In any case, recrystallization of the product salt, which is necessary for achieving the required ^{137}Cs decontamination, would certainly remove the ANN contamination as well.

The effervescing of the concentrated slurry was undoubtedly due to the formation of gas resulting from destruction of the organic compounds (N-(2-hydroxyethyl)ethylenediaminetriacetate, trisodium salt (HEDTA), and its degradation products) in the simulated waste. The reaction is analogous to the PUREX sugar denitration reaction, where sucrose reacts with nitric acid to produce CO_2 and NO_x. In this case, HEDTA substitutes for the sucrose, and in terms of the desired outcome, the HNO_3 is destroying the organic, as opposed to the organic destroying the HNO_3 in the PUREX reaction. The HNO_3 concentration is lower in this case than in PUREX, but the proton activity may be as high due to the high ionic strength of the solution. These conclusions are supported by the total organic carbon (TOC) analysis of the final filtrate from Crop 3, where the amount of TOC reported in the analysis ("138-A found" in Figure 3.1) is lower than the amount calculated from mass flow in the system. Since the solution was still vigorously effervescing when the experiment was stopped, there is every reason to believe that much more of the organic could have been destroyed if efforts were made to optimize the organic destruction conditions. However, being outside the scope of this study, little additional work was done to address that issue.

One noteworthy observation about the organic destruction reaction was that the effervescence appeared to depend on the presence of crystals in the

slurry. In the absence of $NaNO_3$ crystals, the effervescence was slight, like a recently-poured glass of soda pop. As the number of $NaNO_3$ crystals increased, the speed of gas production increased, until a steady foam was present. When the stirrer was turned off and the crystals settled, the gas would build up in the crystal bed, which would expand in volume like rising bread dough until a "mini-burp" occurred, releasing the pent-up gas. When the crystals were filtered off and the clear liquid was returned to the beaker, the effervescence had virtually stopped, even when the liquid had returned to the same operating temperature. The effervescence resumed when new crystals had formed. It is possible that the HNO_3/organic reaction is catalyzed by $NaNO_3$ crystal surfaces, but that is only one possible explanation. The effect would have to be studied in more detail if this reaction were to be pursued as an alternative organic destruction method.

3.2 TEST B

In Test B, efforts were made to reduce substantially the amount of HNO_3 required by doing a pre-acidification separation of the $NaNO_3$ and $NaNO_2$ from the acid-consuming Na_2CO_3, $NaAl(OH)_4$ and NaOH. See Figures 3.2 and 3.3 for the flow diagram summary.

3.2.1 Procedure

A 100 g sample of simulated 101-SY waste solution (Table 3-1) was placed in an open beaker and heated to 70°C. Crystals of Na_2CO_3 began to form when about 10 g of water had evaporated. When 17 g of water had evaporated, the solution was cooled to room temperature, upon which it completely solidified to the consistency of mayonnaise. Examination of the slurry with the polarized light microscope revealed some $NaNO_3$ crystals mixed in with a sea of $Na_2CO_3 \cdot H_2O$ needles. Such needle-shaped crystals are notorious for their effect on slurry viscosity and their liquid retention properties.

The slurry was then reheated, upon which the $NaNO_3$ crystals dissolved and the $Na_2CO_3 \cdot H_2O$ needles were converted to anhydrous Na_2CO_3, which forms more equant (block-shaped) crystals. The slurry became quite fluid due to the change in crystal habit. Another 7 g water was evaporated, at which point the slurry was quickly centrifuged using a pre-heated centrifuge cone. The centrifuged solids (7.8 g) were dissolved in 10.6 g of water. A small sample of the solution was submitted for analysis (see "DH-131A found" in Figure 3.3). The remainder of the solution was cooled in an ice bath to form large, clear crystals of $Na_2CO_3 \cdot 10H_2O$, which were separated from the mother liquor by filtration, yielding 7.3 g of $Na_2CO_3 \cdot 10H_2O$ crystals and 9.8 g of mother liquor.

The 68.1 g of supernatant solution from the centrifuge cone was cooled to room temperature to precipitate $NaNO_3$ and $NaNO_2$ crystals, the identities of which were confirmed by microscopy. The slurry was centrifuged to separate 28.1 g of wet crystals from 35.5 g of supernatant liquid. A small sample of the liquid phase was diluted with water and submitted for analysis (see "DH-130A found" in Figure 3.2). After a period of a few days, the undiluted supernatant liquid solidified to face cream consistency, presumably due to precipitation of $Al(OH)_3$.

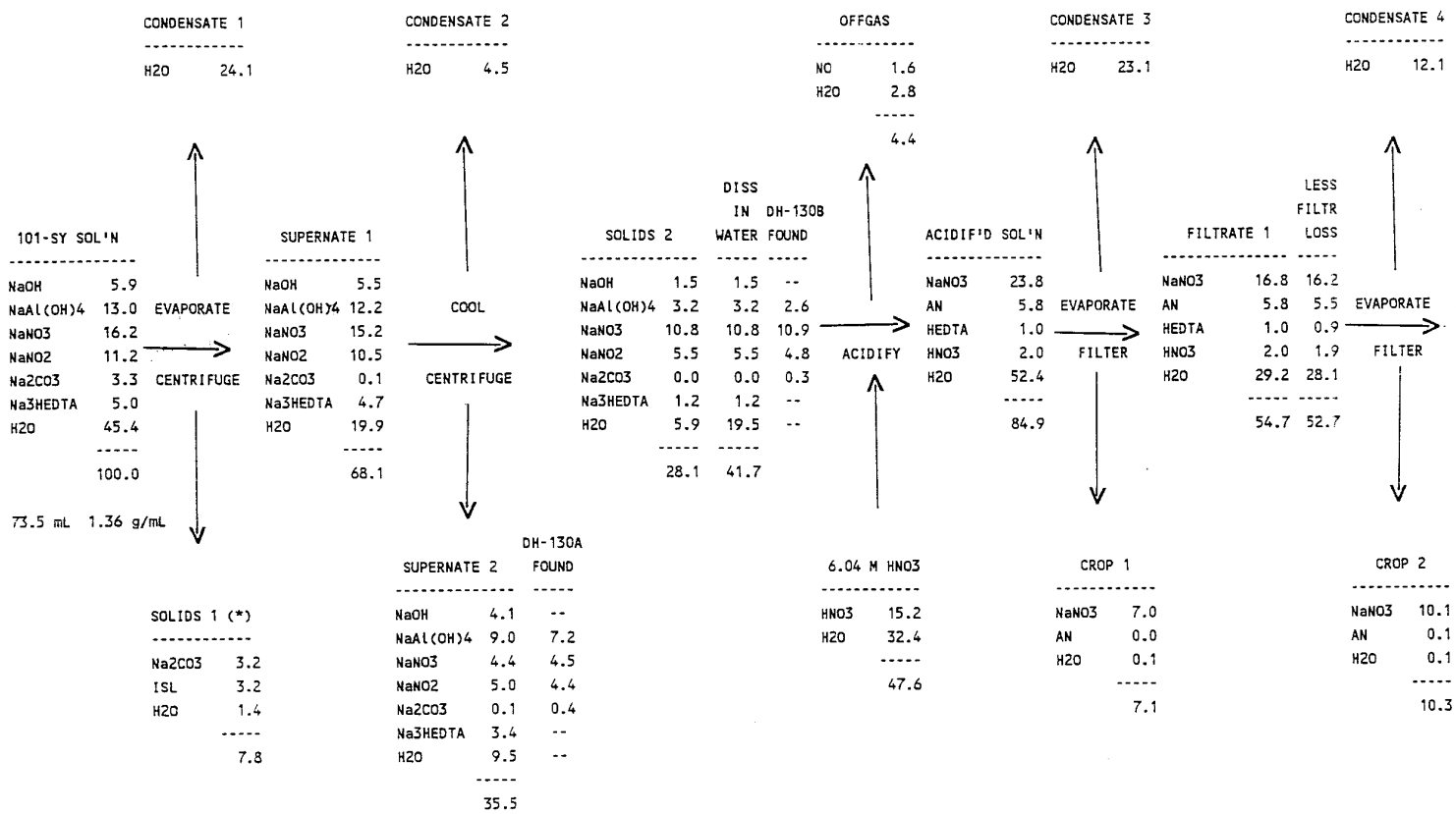


Figure 3.2. Mass Flow Diagram for Simulated Waste Test B.

(*) - See Figure 3•3 for recrystallization of carbonate solids. ISL = interstitial liquid salts.

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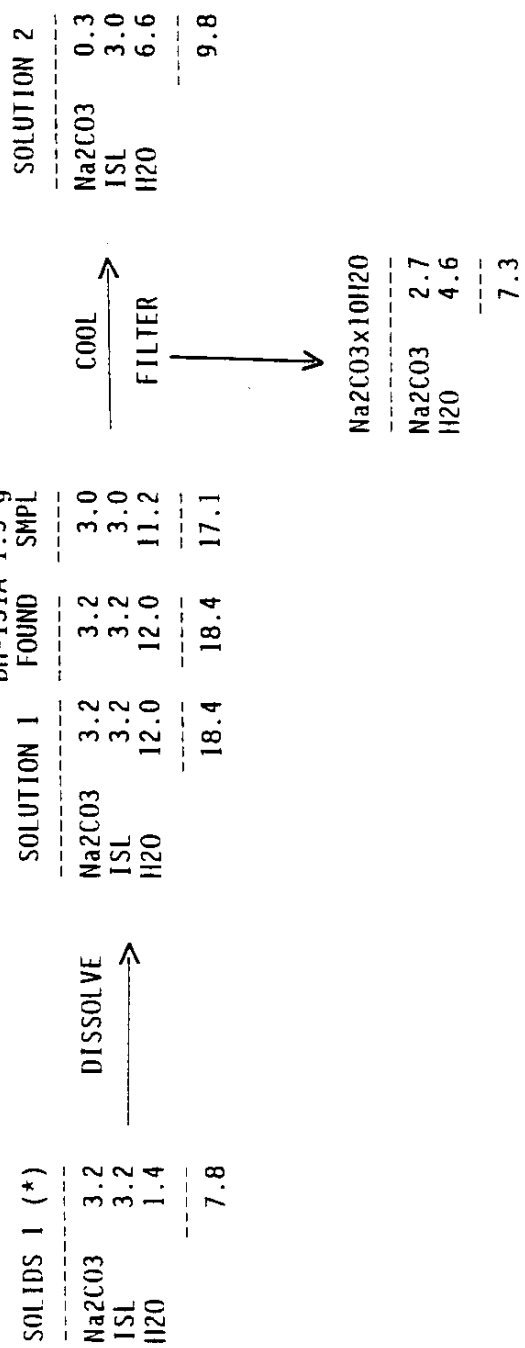
Figure 3.3. Mass Flow Diagram for Test B, Recrystallization of Sodium Carbonate.



(8) - From Figure 3.2.

The 28.1 g of centrifuged solids were dissolved in 13.6 g of water. A small sample of this solution was diluted with water and submitted for analysis (see "DH-130B found" in Figure 3.2). The solution was then acidified by adding 6.04 M HNO_3 until the initial $Al(OH)_3$ precipitate had redissolved, and there was no more gas (CO_2 and NO_x) evolution. The final pH was less than one. A total of 47.6 g of HNO_3 was added, about one-third the amount used in Test A.

The acidified solution was left sitting undisturbed (unstirred) in an open beaker for six days, during which time several very large (up to 1.0 cm wide) rhombohedral crystals of $NaNO_3$ were formed. The crystals removed by filtration weighed 7.1 g, and contained less than 2% by weight ANN as determined by titration.

The filtrate (denoted "Filtrate 1" in Figure 3.2) was evaporated further at room temperature with stirring. After 24 hours, a second crop of $NaNO_3$ crystals, very much smaller in crystal size than the first crop, was removed by filtration. The second crop weighed 10.3 g, and contained 2% by weight ANN.

The final filtrate ("Filtrate 2" in Figure 3.2) was sampled for analysis. See "DH-143 found" in Figure 3.2.

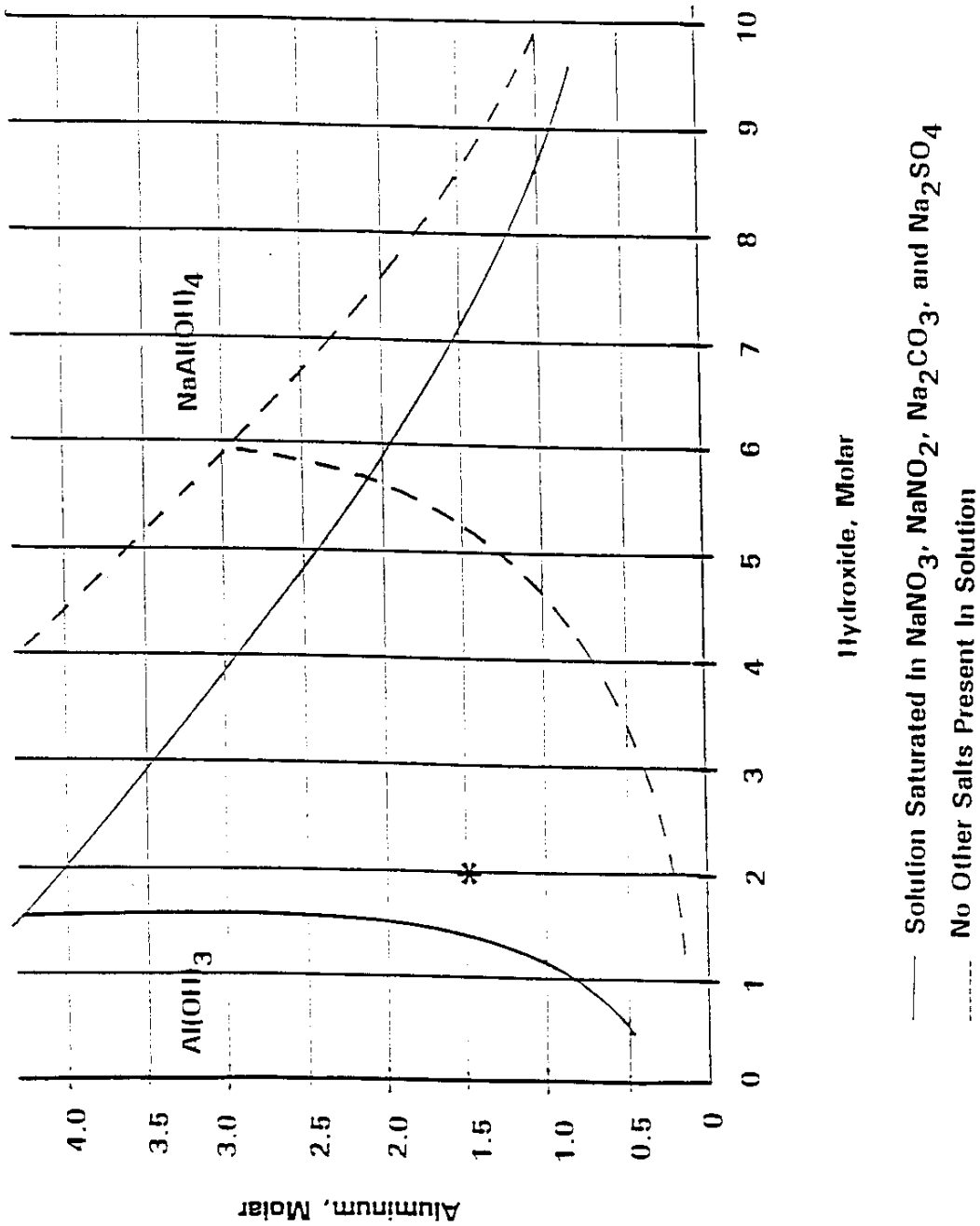
3.2.2 Results

Efforts to reduce acid requirements were partially successful. Removal of Na_2CO_3 appears to be very feasible. In the high ionic strength simulated waste solution, the only Na_2CO_3 crystal forms that are accessible are the anhydrous and monohydrate forms. (See Herting (1985) for more information on Na_2CO_3 crystal hydrates in simulated waste solutions.) By keeping the slurry warm, the much preferred anhydrous salt can be assured. When that salt is dissolved in water, the decahydrate crystal form becomes accessible due to the lower ionic strength of the solution. Therefore, conditions are favorable for clean recrystallization of the initial precipitate. While carbonate removal was not attempted with the subsequent tests with actual waste, it should be considered a viable option.

The attempt to separate $NaNO_3$ and $NaNO_2$ from the remainder of the waste solution was less successful, due mainly to the behavior of aluminum. Figure 3.4, which is taken from Barney (1976), shows an aluminum solubility diagram (aluminum concentration plotted against hydroxide concentration) that helps to understand what happens to the aluminum. The solid lines in the figure form a "hat" showing the aluminum solubility in sodium hydroxide solution that is saturated with $NaNO_3$, $NaNO_2$, Na_2CO_3, and Na_2SO_4. If a plotted composition falls under the "hat", as does the composition of the simulated 101-SY waste solution shown as the data point at 1.5 M Al/2.0 M NaOH, then the aluminum is in solution as the aluminate ion. If the composition falls to the left of the "hat", then $Al(OH)_3$ solids will be present when the system is at equilibrium. If the composition falls to the right of the "hat", then the system will include $NaAl(OH)_4$ solids.

The dashed line in Figure 3.4 represents the solubility curve for a solution containing only aluminum and sodium hydroxide, without the added ionic strength from the other sodium salts. The effect of the ionic strength

Figure 3.4. Aluminum Solubility Diagram.



on the solubility of aluminum is quite dramatic. In the present case, when the $NaNO_3$ and $NaNO_2$ salts are removed from solution by precipitation, the aluminum solubility curve shifts from the solid line in Figure 3.4 toward the dashed line, while the composition of the solution (the data point on the figure) shifts very little. Therefore, the data point winds up to the left of the dashed line "hat", and $Al(OH)_3$ will precipitate until equilibrium is reached. The resulting slurry has properties that are very undesirable for waste tank storage or further treatment. Therefore, this method of separating $NaNO_3$ and $NaNO_2$ from the pre-acidified solution is not recommended.

As mentioned in the experimental section, the amount of HNO_3 required for the acidification in Test B was about one-third of that required in Test A. However, the amount of $NaNO_3$ recovered was also reduced by about one-third. The amount of HNO_3 that could be produced by "salt splitting" of $NaNO_3$ was still less than the HNO_3 required, though the gap was reduced somewhat. ("Salt splitting" means conversion of $NaNO_3$ into HNO_3 and NaOH by membrane electrolysis or thermal decomposition.)

3.3 TEST C

Test C (Figure 3.5) was a repetition of Test A except that the acidification was done by reverse strike, i.e., the waste solution was added to the HNO_3.

3.3.1 Procedure

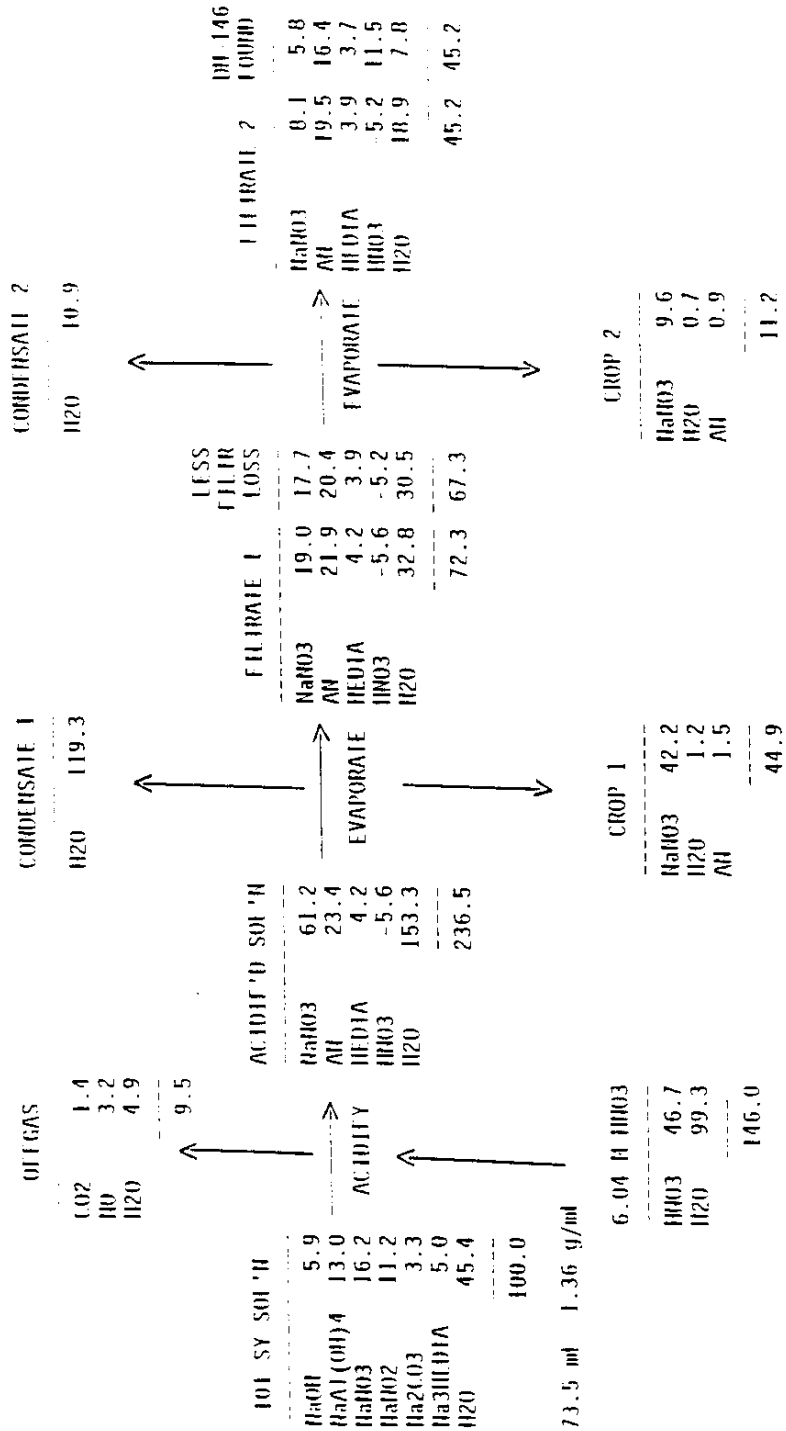
A 100 g sample of simulated 101-SY waste solution was added in small portions to 146.0 g of 6.04 M HNO_3. The solution turned cloudy near the end of the addition, but cleared up when the solution was heated to begin the evaporation. The solution was evaporated over the next six days, with occasional brief periods of heating. Then the slurry was heated to 70°C and filtered to remove the first crop of $NaNO_3$ crystals. The relatively large crop of crystals weighed 44.9 g, and contained 6% by weight ANN. The second crop of $NaNO_3$ crystals obtained by further evaporation of the filtrate weighed 11.2 g, and contained 14% by weight ANN. The filtrate from the second crop was sampled for analysis. See "DH-146 found" in Figure 3.5.

3.3.2 Results

The purpose of the reverse strike acidification was to alleviate the problems associated with foaming due to rapid gas evolution, and with high viscosity through the $Al(OH)_3$ precipitation region as the pH dropped through neutral. Both problems were essentially erased by the reverse strike, since the vessel where the mixing occurred started and remained acidic throughout the procedure. The few solids that formed upon addition of an aliquot of simulated waste solution would immediately dissolve, so the solution viscosity never increased. Gas was produced and evolved continuously as the waste was added, rather than suddenly when the pH dropped sufficiently low.

The total moles of HNO_3 used in Test C was about 11% less than in Test A. The total amount of $NaNO_3$ recovered was almost identical (50.5 g in Test A vs. 51.8 g in Test C). The amount of organic destruction that occurred in Test C was much less than in Test A because much of the evaporation was

Figure 3.5. Mass Flow Diagram for Simulated Waste Test C.



done at room temperature in Test C, and because the acid concentration was lower in Test C. (See "DH-146 found" in Figure 3.5 for the HEDTA analysis derived from a TOC measurement on the final filtrate.)

3.4 TEST D

Test D (Figure 3.6) was a repetition of Test B with a few exceptions. No attempt was made to recrystallize the anhydrous Na_2CO_3 crystals. The $NaNO_3/NaNO_2$ separation was made by rapid cooling rather than slow cooling. Only one crop of $NaNO_3$ crystals was recovered.

3.4.1 Procedure

A 100 g sample of simulated 101-SY waste solution was heated to 84°C until 24 g of water had evaporated and anhydrous Na_2CO_3 crystals were abundant. The slurry was then vacuum filtered. The filtrate, surprisingly, took on a deep reddish brown color. The filtrate later paled to the color of whiskey, but never returned to the original pale yellow. The filtered solids were weighed (4.4 g) and then discarded. The filtrate was left stirring overnight in an open beaker, and allowed to cool to room temperature.

The following day, the filtrate had become a thick slurry. The slurry was heated to redissolve the crystals, and 9 g water was added. All solids dissolved at 50°C. The solution was heated at 68°C until the added water had evaporated, and was then placed in an ice bath. When the slurry had reached 20°C, and microscopic observation revealed only $NaNO_3$ and $NaNO_2$ crystals, the slurry was removed from the ice bath and filtered. The liquid phase was sampled for analysis (see "DH-150 found" in Figure 3.6).

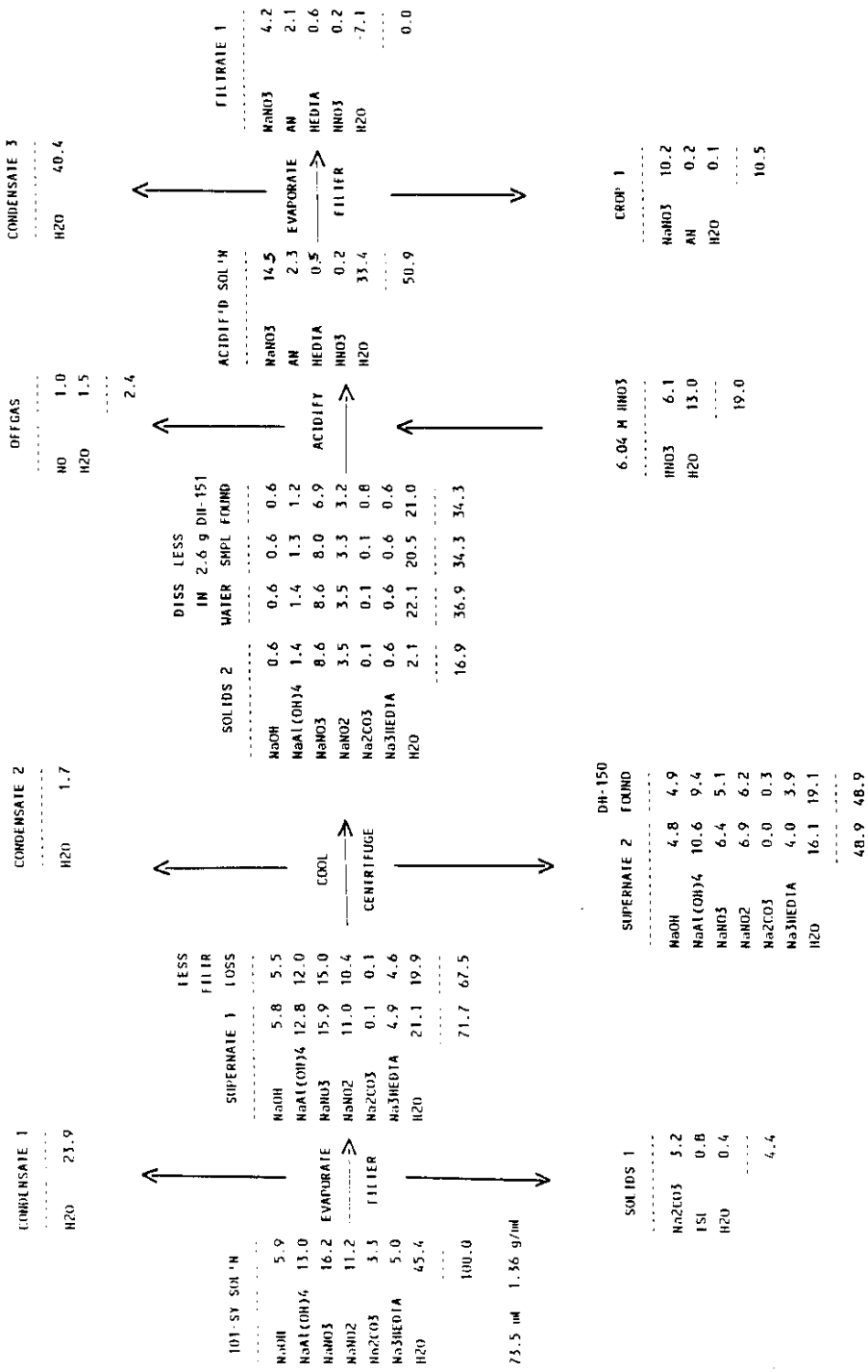
The 16.9 g of filtered solids were dissolved in 20.0 g of water, and the solution was sampled for analysis. (See "DH-151 found" in Figure 3.6.) The solution was acidified by adding 6.04 M HNO_3 until the $Al(OH)_3$ solids had dissolved and no more gas was being evolved. The total weight of HNO_3 solution added was 19.0 g. The clear solution was left in an open beaker to evaporate undisturbed (without stirring). After 25 hours, some very large (up to 4 mm) $NaNO_3$ rhombs were removed with a pair of tweezers. The remaining solution was left undisturbed for another 24 hours, during which a mixture of large and small crystals formed. The slurry was filtered, yielding a total of 10.5 g of crystals, including the large rhombs removed with a tweezers after the first day. The crystals contained 3% by weight ANN.

3.4.2 Results

The amount of HNO_3 required in Test D was much smaller (about 60% less) than in Test B because a much cleaner separation was made between the $NaNO_3/NaNO_2$ crystals and the mother liquor containing the NaOH, $NaAl(OH)_4$, and other salts. Therefore, even though the total amount of $NaNO_3$ recovered (10.2 g) was less than in Test B (17.0 g), Test D was the only one in which the amount of $NaNO_3$ recovered could have been sufficient to produce the required HNO_3 by salt splitting.

After removal of the $NaNO_3$ and $NaNO_2$ crystals, the remaining aluminum-containing filtrate precipitated over a four day period, as had the

Figure 3.6. Mass Flow Diagram for Simulated Waste Test D.



analogous filtrate in Test B. Unlike the Test B filtrate, however, the Test D filtrate formed a crystalline precipitate that settled, leaving a clear, bright yellow supernatant solution.

3.5 TEST E

Test E (Figure 3.7) was performed according to the same procedure as Test C, except that the final filtrates from both Test A and Test C were incorporated to simulate a filtrate recycle stream in a plant scale operation.

3.5.1 Procedure

A 100 g sample of simulated 101-SY waste solution was added in small portions to 146.0 g of 6.04 M HNO_3. As in Test C, the cloudy solution cleared up when heated to 61°C. At that point, 46.6 g of final filtrate solution from Test A plus 36.7 g of final filtrate solution from Test C were added, along with 10 g of rinse water for each solution. A small sample of the resulting mixed solution was submitted for analysis to determine the starting composition. (See "DH-5 found" in Figure 3.7.)

The solution was left stirring at room temperature over the weekend, during which time some $NaNO_3$ began to crystallize. The crystals redissolved at 60°C while the solution was being heated to 70°C. Gas production was evident. When the slurry reached approximately 30% settled solids by volume, it was filtered. The weight of crystals recovered in Crop 1 was 35.2 g, and the ANN content was 12% by weight.

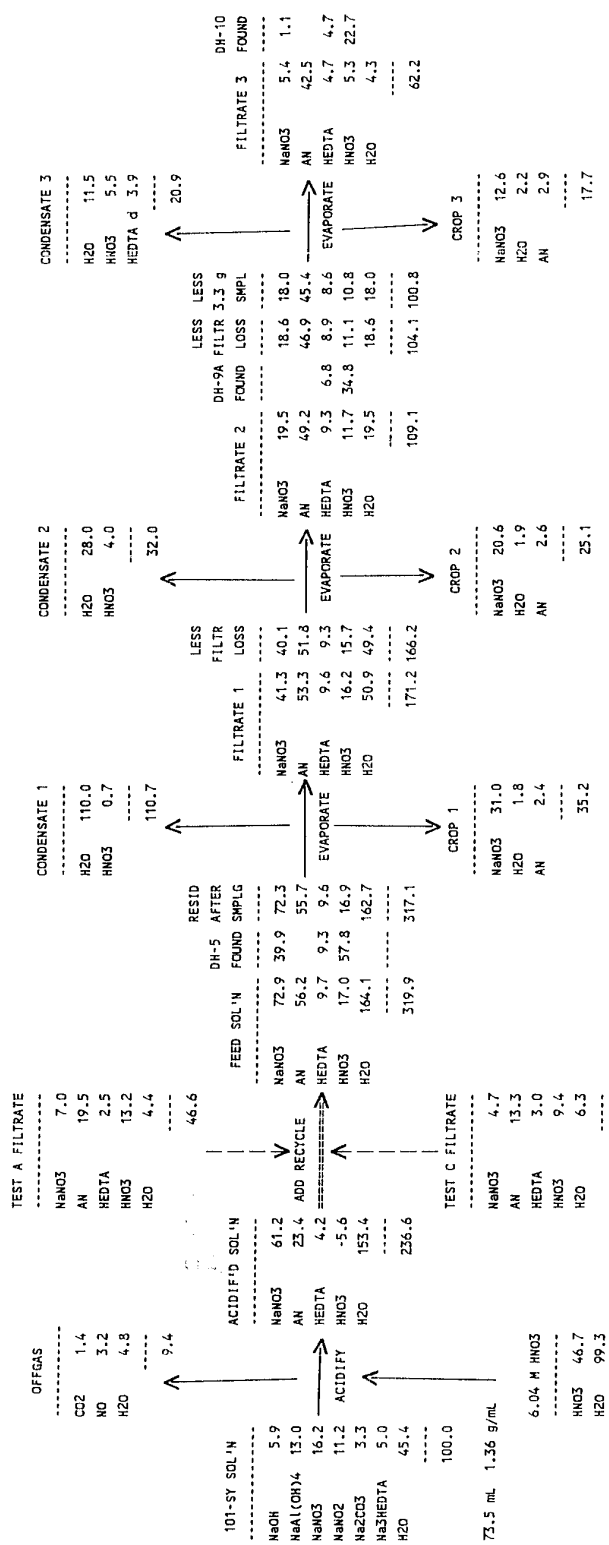
Evaporation of the filtrate continued. Gas evolution had nearly ceased when the $NaNO_3$ crystals were removed. By the time the amount of new $NaNO_3$ crystals had reached about 25% by volume, the gas production was fast enough to produce a stable "head" of foam about 4 mm thick on top of the slurry. At 70°C and 40% settled solids, the slurry was filtered. The weight of crystals recovered in Crop 2 was 25.1 g, and the ANN content was 18% by weight. A small sample of the filtrate was submitted for H^+ and TOC analyses in order to track the progress of the organic destruction reaction. (See "DH-9A found" in Figure 3.7.)

The gas production rate in the filtrate was considerably slowed, but not stopped. Even when the volume of new crystals had reached 40%, the gas production rate was still slower than it had been during the evaporation for Crop 2. The beaker was covered with a watch glass in order to slow the rate of evaporation, and the solution was heated up to 83°C. The gas production rate increased substantially, producing a stable head of foam nearly as thick as the solution. Small additions (1-2 mL) of water were made periodically to keep the gas production (organic destruction) reaction going for another 2 hours. Then the slurry was filtered to recover the third and final crop of crystals, which weighed 17.7 g and contained 29% by weight ANN. The final filtrate was sampled for analysis ("DH-10 found" in Figure 3.7).

3.5.2 Results

The total amount of $NaNO_3$ recovered in Test E (64.2 g) was higher than in any of the other tests, owing to the addition of the recycled filtrates

Figure 3.7. Mass Flow Diagram for Simulated Waste Test E.



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from Tests A and C. The amount of $NaNO_3$ recovered would have been just sufficient to cover the HNO_3 requirement if the salt splitting process could be operated at about 98% efficiency.

The TOC analytical data clearly show that organic destruction was going on during the evaporation steps. Total organic carbon analysis of Sample DH-9A (Figure 3.7) shows the HEDTA to be approximately 22% lower than calculated at that early stage in the evaporation. In the final filtrate (DH-10, Figure 3.7) the "calculated" and "found" values for HEDTA were forced to balance by adjusting the calculated value. The adjustment was made by adding "HEDTA d", which stands for HEDTA decomposition gases, to the condensate (or offgas) stream. The amount of HEDTA appearing in the offgas represents 45% of the total HEDTA in the system at that point. Therefore, 45% destruction of the organic (conversion to gaseous products) was achieved. Recall that the organic destruction reaction appeared to be still going at full speed when the reaction was terminated. This is clearly an interesting sidelight worthy of further study in relation to the overall tank farms issue of organic destruction.

3.6 FATE OF ALUMINUM

What happens to the aluminum? In all of the tests that were done, the aluminum is simply left in solution as either sodium aluminate (basic side) or aluminum nitrate (acid side). In an actual useful process, that would not be the end of the story. What options are available for disposition of the aluminum?

The most obvious option is precipitation of ANN, some of which occurred unintentionally in Tests A-E. The ANN could be considered another feed for a nitric acid recovery operation, in which the ANN could be calcined to yield nitric acid and alumina (Al_2O_3), the latter being a suitable final waste form.

A few experiments have been done by other WHC investigators to remove aluminum from the caustic solution by bubbling carbon dioxide gas through the solution. An insoluble sodium aluminum carbonate (Dawsonite) salt forms. There is a program just starting at the University of Texas to evaluate this process.

Several experiments have been done, ranging up to pilot plant scale, on removing aluminum from the acid solutions as an alum salt. In some work done at Oak Ridge National Laboratory (Felker 1982), fly ash is leached with sulfuric acid to dissolve the aluminum, and the ammonium alum salt $NH_4Al(SO_4)_2 \cdot 12H_2O$ is formed by adding ammonium sulfate to the acid solution. The alum is calcined to yield alumina and regenerate the ammonium sulfate reagent. The U.S. Bureau of Mines (USBM 1976) reported on a process of leaching aluminum out of clay using ammonium bisulfate. The ammonium alum salt is precipitated from the solution, then decomposed into hydrated alumina by autoclaving the alum with aqueous ammonia, regenerating the leaching reagent. In our situation, the alum salt could be considered a suitable final waste form, or it could be decomposed by one of the above methods to yield alumina and regenerate the ammonium sulfate needed to precipitate the alum.

The alum precipitation process was tried in the laboratory using the final filtrate solution from Test E, which was calculated to contain 75% by weight aluminum nitrate (see Figure 3.7). In this test, 7.4 g of ammonium sulfate was dissolved in 15.3 g of water. Then 8.0 g of Test E final filtrate was added. The vial containing the resulting solution was placed in an ice bath. When the solution was seeded with ammonium alum crystals, nucleation occurred. The slurry was filtered, yielding 5.9 g (42% yield) of perfectly octahedral crystals of $NH_4Al(SO_4)_2 \cdot 12H_2O$. The same process was attempted using potassium sulfate to form the potassium alum salt, but it was much less successful, due in large part to the poor solubility of potassium sulfate.

4.0 ACTUAL WASTE STUDIES

Experiments with actual waste from Tank 101-SY were very significant because they produced the first portions of Hanford tank waste ever decontaminated sufficiently to allow unconditional release from the laboratory. They proved beyond a doubt that the proposal for extracting "nonradioactive" $NaNO_3$ from the waste in Hanford underground storage tanks was at least technically possible.

Three experiments (Runs 1, 2, and 3) were done with a Tank 101-SY composite sample containing a mixture of convective and nonconvective layer segment samples from Window C and Window E core samples. The segments were mixed in the composite sample in proportion to represent the relative amounts of convective and nonconvective layers in the tank. Therefore, the composite sample is considered a good representation of the overall composition of the waste in the tank.

4.1 RUN 1

4.1.1 Procedure

Step 1, Water Leach - In the 1E-1 hotcell (222-S Laboratory), tank 101-SY composite sample "101-SY Tank Comp 93B" was homogenized, and a 119.7 g aliquot of the sample was transferred to a 250 mL beaker, to which 120.3 g of water was added. The slurry was stirred for 22 hours at an average temperature of 60°C, during which time 58.6 g of water was lost to evaporation. Fresh water was added to return the slurry to the original total weight, and the slurry was heated for another 2 hours. The slurry was then transferred into four 50 mL centrifuge cones, which were spun in a heated centrifuge for about 1.5 hours each. The clear supernatant solution from each cone was transferred into a jar labeled "101-SY Water Wash." The total weight of the water wash solution was 196.7 g, and the total weight of centrifuged solids was 19.9 g. The water wash solution was sampled for analysis (CSP-43) to determine the starting composition.

Step 2, Titration - To determine how much HNO_3 would be needed to acidify the water wash solution, a small sample of the solution was titrated with HNO_3. A 2.0 mL (2.57 g) sample of the water wash solution was pipetted into 30 mL of water in a 60 mL glass jar. Nitric acid (0.499 M) was added in 1.00 mL increments, reading the pH after each addition, until the solution had reached a pH of less than 1.5. The "endpoint" of the titration, at 30 mL of HNO_3 added, was selected as the point at which the $Al(OH)_3$ solids had redissolved, and the pH of the solution had stopped drifting upwards following each HNO_3 addition.

Step 3, Acidification - In the 1E-1 hotcell, 109.2 g of 12.0 M HNO_3 was weighed out into a 400 mL beaker, to which 167.8 g of 101-SY water wash solution was added in small increments. The amount of acid needed was calculated from the titration results in Step 2 above. The acidified solution was stirred overnight at room temperature. The pale brown solution contained a few solids which were removed by vacuum filtration.

Step 4, Evaporation/Crystallization - The clarified acid solution was heated in an open beaker to 56°C to evaporate the water. The color of the solution gradually darkened from the color of weak tea to root beer. When the volume of precipitated $NaNO_3$ crystals had reached about 25%, the slurry was filtered. A saturated $NaNO_3$ solution was used to wash the filter cake. Just enough of the wash solution was added to cover the crystals, then the solution was pulled through the salt by vacuum. The wash solution was added to the filtrate, and the solution was returned to the beaker for further evaporation. The weight of crystals recovered in Crop 1 was 36.5 g.

Two more crops of crystals were recovered and washed in the same fashion. Crop 2 weighed 31.4 g, and Crop 3 weighed 8.0 g. The final filtrate was transferred to a labeled centrifuge cone and stored in the hotcell for possible future use.

Step 5, Recrystallization - The three crops of $NaNO_3$ crystals were combined into a single jar, which was transferred from the 1E-1 hotcell to a hood in Room 1GA. Approximately 110 mL of water was added to the jar to dissolve the crystals, and the solution was then filtered. The filtrate was transferred to a clean 150 mL beaker, where a dose rate of 60 mRAD/hr was recorded. (The dose rate of the initial 101-SY slurry is estimated at approximately 2 RAD/hr.) Due to an unfortunate spill while inserting a thermocouple into the beaker, about one fourth of the solution was lost.

The solution was heated at 60°C in the open beaker until crystals began to form, then the heat was turned off. When the temperature had reached 30°C, the slurry contained about 50% settled solids. The slurry was filtered, and the filtrate was transferred to a plastic beaker. The salt cake was washed with a saturated $NaNO_3$ solution, and the wash solution was discarded. The product $NaNO_3$ crystals weighed 22.4 g and had a dose rate of 0.1 mRAD/hr on a proportional counter (CP), and 3500 counts per minute (cpm) on a Geiger-Mueller (GM) counter. A small sample (0.13 g) of the crystals was dissolved in 9.9 mL water and submitted (CSP-50) for gamma energy analysis (GEA) and total activity.

The remaining 22.3 g of $NaNO_3$ crystals were dissolved in approximately 35 mL of water, and the solution was filtered. The filtrate was evaporated at 60°C until solids formed, and the slurry was cooled to 30°C before filtering. The filtrate was combined with the previous filtrate in the plastic beaker. The salt cake was washed as before, and the wash solution was discarded. The total weight of $NaNO_3$ crystals recovered was 11.1 g. The CP reading was not above background, and the GM reading was less than 50 cpm above background. A small sample (0.17 g) of the crystals was dissolved in 10.0 mL water and submitted (CSP-51) for GEA and total activity analyses.

The remaining 10.9 g of $NaNO_3$ crystals were dissolved in 15 mL water. The solution was recrystallized as the earlier stages, yielding 4.0 g of $NaNO_3$ crystals which had no detectable radioactivity on the laboratory GM counters. In order to check for total activity, 0.73 g of the crystals were dissolved in 1.12 g of water, and the solution was submitted (CSP-53) for total activity analysis. The result (58 pCi/g in the solid sample, virtually all beta-gamma) was well below the limits for allowing unconditional release of the remaining 3.3 g of $NaNO_3$ from the radiation zone (which are 50 pCi/g alpha plus 200 pCi/g beta-gamma).

4.1.2 Results

Run 1 produced the first portion of Hanford tank waste ever decontaminated sufficiently to allow unconditional release from the laboratory.

The "devil's advocate" would be quick to point out that the experiment was flawed because of the way in which the filter cake wash solutions were combined with the filtrates during the initial stage of $NaNO_3$ crystallization. Therefore, some $NaNO_3$ that started out as reagent $NaNO_3$ crystals was intentionally added to the 101-SY sample, and corrupts any conclusions that could otherwise be drawn. This criticism was dealt with in Run 3, which was completed without recycling the filter cake wash solutions.

Analytical results for the initial water leach solution (CSP-43) were consistent with the composition calculated from the known composition of the 101-SY composite sample. The analytical result for each component was within the normal tolerance range for analytical error. The calculated starting composition is considered more accurate than the analytical results, because the calculations are based on multiple samples analyzed during the Window E core sample analysis effort (Herting 1992b). Actual laboratory analytical results are shown in Appendix B.

Table 4-1 contains a summary of the ^{137}Cs and total activity analyses of the $NaNO_3$ crystals at each stage of crystallization. A stage is defined by the separation of $NaNO_3$ crystals from their mother liquor, and may include any number of individual crops. Thus, stage 1 in Run 1 included the three crops of $NaNO_3$ that were recovered from the acidified, evaporated 101-SY water leach solution. Stages 2-4 represent successive recrystallizations of the $NaNO_3$ recovered in stage 1.

Table 4-1. ^{137}Cs and Total Activity Analyses.
(All results given in pCi/g)

Sample	^{137}Cs	Total Activity
101-SY Slurry (Herting 1992b)	3.5×10^8	(4.0×10^8)[a]
Stage 1 $NaNO_3$	not analyzed	not analyzed
Stage 2 $NaNO_3$ (CSP-50)	5.3×10^4	6.0×10^4
Stage 3 $NaNO_3$ (CSP-51)	1200	(1400)[a]
Stage 4 $NaNO_3$ (CSP-53)	(51)[a]	58

[a]Values in parentheses were calculated, either because the analysis was not done (101-SY slurry sample) or because the value was reported as a "less than" by the laboratory; calculations were made using the same ratio of ^{137}Cs to total activity as found in Sample CSP-50.

Decontamination factors (DF's) can be calculated from the data in Table 4-1. A DF is defined, in this case, as the specific activity of ^{137}Cs in a given sample divided by the specific activity of ^{137}Cs in another sample further along in the process. For example, the overall DF for the entire process is defined as the specific activity of ^{137}Cs in the 101-SY slurry (3.5×10^8 pCi/g) divided by the specific activity of ^{137}Cs in the stage 4 $NaNO_3$ product (51 pCi/g), or DF = 6.9×10^6.

Decontamination factors can also be measured across stages 2 and 3 (DF = 42), or across stages 3 and 4 (DF = 25). Decontamination factors cannot be measured directly across the slurry and stage 1, or across stages 1 and 2, because the stage 1 analysis is missing. If one were to speculate that the DF decreases with each successive stage, such a progression could be achieved by assigning a value of 3.5×10^6 pCi/g for the stage 1 $NaNO_3$ crystals, which would give DF's of 100, 66, 42, and 25 for the individual stages 1 through 4. One could also make a case that the DF ought to be more or less the same for each successive stage, and calculate a constant DF by taking the overall DF to the one-fourth power, which would give DF = 51 for all stages.

The main objective of Run 1 was to isolate a nonradioactive product salt. Obtaining sufficient quantitative data to allow mass flow calculations was an objective that was not fully pursued until Run 3. Therefore, the discussion of the mass flow is presented later in the report under the heading "Run 3 - Results."

4.2 RUN 2 - SUMMARY

Run 2 was essentially a repeat of Run 1, and was terminated at the end of the hotcell portion of the experiment due to a procedural error that had occurred during the $NaNO_3$ crystallization step. Three crops of $NaNO_3$ crystals, with a total weight of 122.3 g, were obtained. The crystals were saved for possible future use in studies designed to identify and optimize recrystallization parameters.

4.3 RUN 3

The procedure used for Run 3 was essentially the same as for Run 1, but with two important differences. First, the filter cake wash solutions in step 4 were discarded, rather than being combined with the filtrates. Therefore, no "cold" $NaNO_3$ could have been added to the sample as it was processed. Second, much more extensive weight measurements were taken during every step of the procedure, allowing detailed mass flow measurements to be calculated. These measurements are shown in detail in Appendix C.

4.3.1 Results

Sixteen grams of nonradioactive $NaNO_3$ (total activity 25 pCi/g) were recovered in Run 3. The overall DF for ^{137}Cs was 14 million. The increase in product yield (16 g in Run 3 vs. 4 g in Run 1) was due mainly to improvements in laboratory technique.

Figure 4.1, which is derived from the mass flow measurements and calculations in Appendix C, shows the overall process input and output streams for Run 3. The numbers have been adjusted to account for experimental losses. It is apparent from this figure that the prospects for applying the Clean Salt Process in its current state of development are not very attractive for double shell slurry waste. There is simply not enough reduction in waste volume to merit running the plant. (Compare 120 g of waste feed with 94 g radioactive waste output.) Clearly, the process must incorporate a method for disposing of aluminum if it is to be economically feasible.

Figure 4.2 shows a hypothetical overall mass flow for a process in which carbonate and aluminate are removed by precipitation prior to the acidification step. Values shown are derived from calculations shown in Appendix C. The amount of undissolved sludge would be unchanged in this hypothetical process, but the acid requirement would be much lower, and the final filtrate volume would be much lower. The input/output ratio would be 120 g/53 g, corresponding to a factor-of-two reduction in the volume of radioactive waste.

Figure 4.1. Overall Mass Flow for Run 3.

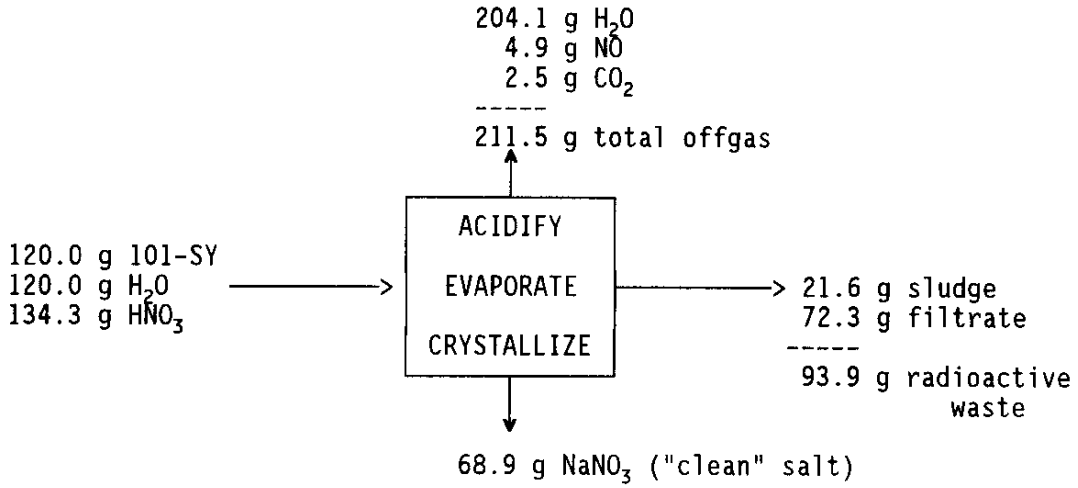
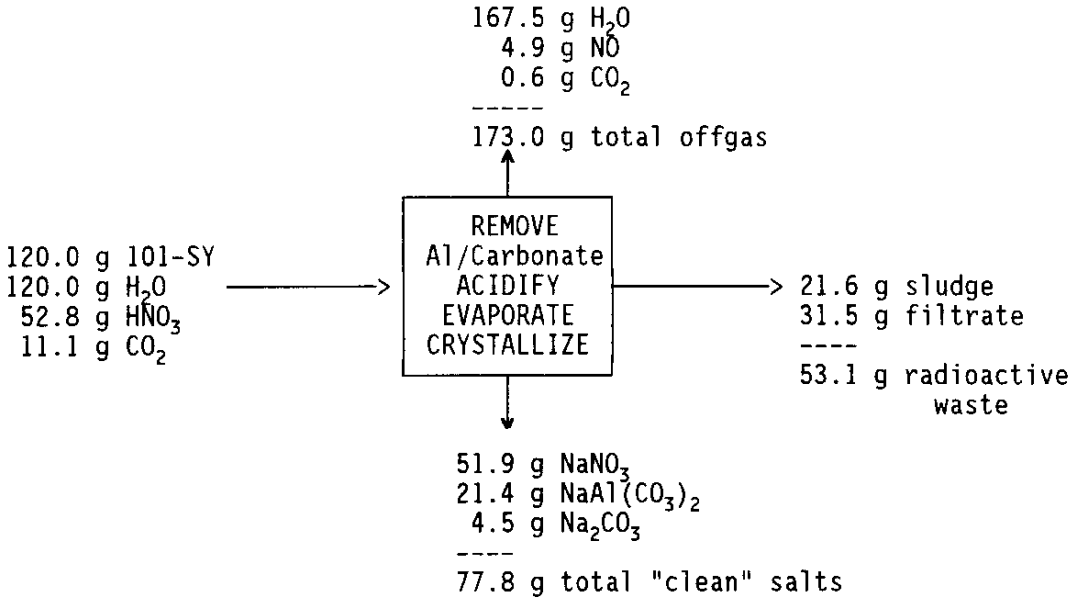


Figure 4.2 - Mass Flow for Hypothetical Process with Carbonate/Aluminate Removal



5.0 CONCLUSIONS

Sodium nitrate crystals make up an estimated 67% of the entire inventory (not including water) of radioactive waste stored in the 149 single shell and 28 double shell tanks at Hanford (see Table 5-1). Recovery of most of the $NaNO_3$ as a nonradioactive salt would dramatically reduce the volume of mixed waste destined for grout disposal. The political and economic benefits are obvious. The recovery of nonradioactive $NaNO_3$ from a 101-SY composite sample, as presented in this report, proved beyond a doubt that the proposed process for extracting $NaNO_3$ from the waste in Hanford underground storage tanks is at least technically possible.

Table 5-1. Hanford Tank Waste Inventory (water not included). Values given in 10^3 Metric Tons.

Component	SST Sludge	SST Salt Cake	DST Waste	Total
$NaNO_3$	20	110	15	145
Other Soluble Salts	24	11	20	55
Insolubles and Radionuclides	9	1	5	15
Total	53	122	40	215

Tank 101-SY contains only 23% $NaNO_3$ (on a dry weight basis), in contrast to single shell tank (SST) salt cake, which contains 90% $NaNO_3$. Thus, it is obvious that some waste types are more amenable than others to volume reduction by extraction of clean $NaNO_3$. Of course, the process is not necessarily limited to $NaNO_3$ extraction. Depending on the type of waste being processed, further volume reductions may be possible by recovering any of the common sodium salts that have the proper solubility characteristics to allow recrystallization from water.

Advantages of the Clean Salt Process may not be limited to volume reduction of the mixed waste. For example, the ^{137}Cs-bearing effluent from the process contains a much lower Na:Cs ratio than the feed solution, which should improve the efficiency of the ion exchange process used for ^{137}Cs removal.

There are a number of unanswered questions about how the Clean Salt Process fits in with the overall waste pretreatment program, as well as myriad technical details that have not yet been addressed. Given the potential benefits of Clean Salt Process, its technical simplicity, and the large amount of industrial experience in the field, it seems imperative that efforts continue to develop the process for future application.

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6.0 ACKNOWLEDGEMENTS

Funding for laboratory work on development of the clean salt process was provided during FY92 and FY93 by the Westinghouse Development Steering Board. Most of the laboratory work with radioactive samples, and all of the hotcell work, was performed by Wayne Edmonson. Tracy Harrison did her usual stellar job of formatting and editing the document.

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APPENDIX A

CALCULATION OF FLOWSHEET VALUES

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TEST A -- DIRECT ACIDIFICATION, NO RECYCLE

Figure 3.1 in the main body of the report shows the mass flow for each component of the system in Test A. Shown here are the calculations used to determine the weights shown in that figure. Each heading below corresponds to the title of one of the boxes in the figure.

"101-SY SOL'N"

Test A was conducted using a 100 g sample of simulated 101-SY waste solution having the composition shown in Table A-1. Molarities are taken from Notebook WHC-N-345-1, p. 121. Solution volume comes from p. 123 of the same notebook. Density used in the calculation (volume=mass/density) comes from analyses of the solution by Analytical Laboratories (see Samples DH-124A, DH-124B, DH-139C, and DH-139D in Notebook RHO-RE-NB-248).

Table A-1. Composition of Simulated 101-SY Supernate.

	MW	Feed Conc [M]	Wt, g	mol Na	mol NO3
NaOH	40	2.0	5.88	0.15	0.15
$NaAl(OH)_4$	118	1.5	13.01	0.11	0.44
$NaNO_3$	85	2.6	16.24	0.19	0.19
$NaNO_2$	69	2.2	11.16	0.16	0.16
Na_2CO_3	106	0.42	3.27	0.06	0.06
Na_3HEDTA	344	0.20	5.06	0.04	0.04
H_2O	18	--	45.38	--	--
Total			100.00	0.72	1.05

"OFFGAS"

CO_2 weight assumes all carbonate becomes CO_2 during acidification:

$$3.3 \text{ g } Na_2CO_3 * (44 \text{ g } CO_2/106 \text{ g } Na_2CO_3) = 1.4 \text{ g } CO_2$$

NO weight assumes the following reaction occurs quantitatively:

$$3\ NaNO_2 + 2\ HNO_3 \text{ ---> } 2\ NO + 3\ NaNO_3 + H_2O$$

$$11.2 \text{ g } NaNO_2*(1 \text{ mol}/69 \text{ g})*(2 \text{ mol NO}/3 \text{ mol } NaNO_2)*(30 \text{ g/mol}) = 3.2 \text{ g NO}$$

Total weight of 10.6 g taken from experimental data -- p. 129 in Notebook WHC-N-345-1.

H_2O weight is total weight loss (10.6 g) minus CO_2 and NO.

"7 M HNO_3"

Total weight and volume are measured experimentally -- see p. 129 in NB 345-1. Weight of HNO_3 calculated from molarity and volume; H_2O by difference.

"ACIDIFIED SOL'N"

Assumptions include: All Na is $NaNO_3$. Water = feed water + acid water + water produced by the nitrite decomposition reaction shown above (1.0 g) + water from neutralization reactions (2.6 g from NaOH, 7.9 g from $NaAl(OH)_4$, 1.1 g from Na_2CO_3, and 0.8 g from Na_3HEDTA). Total weight of acidified solution comes from experimental data (p. 129). HNO_3 is the difference between the total weight and the sum of the other components. Thus:

0.72 mol $NaNO_3$ x 85 g/mol =	61.2 g $NaNO_3$
0.11 mol AN x 213 g/mol =	23.4 g AN (aluminum nitrate)
0.015 mol HEDTA x 278 g/mol =	4.2 g HEDTA
HNO_3 by difference =	0.4 g HNO_3
H_2O = 13.5 + FEED + ACID - OFFGAS =	146.5 g H2O

	235.7 g ACIDIFIED SOLUTION

"CONDENSATE 1"

Total weight comes from experimental data (p. 133), where the total slurry weight and weight of crystals are given; weight of filtrate is the difference between total slurry and crystals; condensate weight is the difference between the current total slurry and initial solution weight (p. 129). Water is assumed to be the only component in the condensate.

"CROP 1"

Total weight is determined experimentally (p. 133). Distribution into $NaNO_3$, H_2O and AN is based on analysis shown on pp. 12-14 in NB WHC-N-624, which shows Crop 1 is 4% ANN (aluminum nitrate nonahydrate), which breaks down into 0.2 g H_2O plus 0.2 g AN.

"FILTRATE 1"

Total weight is experimental (see "Condensate" above). $NaNO_3$ weight is difference between previous weight and Crop 1, as is AN weight. Weight H_2O is previous minus condensate and Crop 1.

"LESS FILTR LOSS"

This takes into account the amount of filtrate that gets "lost" in the glass frit filter. An estimated (occasionally measured) loss of 5 g occurs during each filtration, which is made up almost entirely of filtrate that gets caught in the pores of the glass frit and on the inside walls of the bottom part of the filter. Thus, each entry in this column is calculated from the weight of that component in the filtrate times 5 g less than the total filtrate weight divided by the total filtrate weight. For example, $NaNO_3$ = 51.4 * 134.3 / 139.3. The sum of the three outputs from the next evaporation step (Crop 2 plus Condensate 2 plus Filtrate 2) is equal to the sum of this column.

"CONDENSATE 2"

Total weight is 134.3 - 112.7 = 21.6 g (see p. 134 in NB 345-1), where 134.3 is the filtrate weight going into the evaporation step, and 112.7 is the weight of the total slurry before filtering.

"CROP 2"

Total weight 25.5 g -- see p. 134 in NB 345-1. Breakdown into components as in Crop 1 -- see p. 14 in NB 624 (7% ANN).

"FILTRATE 2"

Same calculations as Filtrate 1. Total weight is sum of components, and agrees with NB value (p. 134).

"CONDENSATE 3"

Total wt is 82.2 - 69.6 = 12.6 g (see p. 138 in NB 345-1), where 82.2 is the filtrate weight going into the evaporation step, and 69.6 is the weight of the total slurry before filtering.

"CROP 3"

Total weight 21.3 g -- see p. 138 in NB 345-1. Breakdown into components as in Crop 1 -- see p. 14 in NB 624 (20% ANN).

"FILTRATE 3"

Same calculations as Filtrate 1. Total weight is sum of components, and agrees with NB value (p. 138).

"DH-138A FOUND"

Values are derived from analysis of Sample DH-138A as follows:

Dilution factor derives from 1.00 mL filtrate dissolved in 9.00 mL H_2O.
Solution SpG comes from weight of 1.00 mL sample -- p. 138.
Total solution weight assumed to be as found, 48.3 g.

HNO_3 calculation based on H^+ analysis of 0.66 M as follows:

$$\frac{0.66 \text{ mol } HNO_3}{\text{L dil.}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{10 \text{ mL dil}}{1 \text{ mL conc}} \times \frac{1 \text{ mL conc}}{1.47 \text{ g con}} \times \frac{48.3 \text{ g conc}}{} \times \frac{63 \text{ g}}{\text{mol}} = 13.7 \text{ g } HNO_3$$

AN weight based on Al analysis by inductively coupled plasma (ICP):

$$\frac{7{,}800 \text{ ug Al}}{\text{mL dil}} \times \frac{10}{1} \times \frac{213 \text{ g AN}}{27 \text{ g Al}} \times \frac{1}{1.47} \times \frac{1}{10^6} \times 48.3 = 20.2 \text{ g AN}$$

HEDTA weight based on TOC analysis:

$$\frac{3{,}370 \text{ ug C}}{\text{mL dil}} \times \frac{10}{1} \times \frac{278 \text{ g HEDTA}}{120 \text{ g C}} \times \frac{1}{1.47} \times \frac{1}{10^6} \times 48.3 = 2.6 \text{ g HEDTA}$$

$NaNO_3$ weight calculated in two independent ways. First way is from Na analysis by ICP:

$$\frac{5{,}910 \text{ ug Na}}{\text{mL dil}} \times \frac{10}{1} \times \frac{1}{10^6} \times \frac{85 \text{ g } NaNO_3}{23 \text{ g Na}} \times \frac{1}{1.47} \times 48.3 = 7.2 \text{ g } NaNO_3$$

Second way is total nitrate minus the nitrate from HNO3:

$$\frac{56{,}900 \text{ ug } NO_3}{\text{mL dil}} \times \frac{10}{1} \times \frac{1}{1.47} \times \frac{1}{10^6} \times 48.3 = 18.7 \text{ g total } NO_3$$

$$(13.7 \text{ g } HNO_3) \times (62 \text{ g } NO_3/63 \text{ g } HNO_3) = 13.5 \text{ g } NO_3 \text{ from } HNO_3$$

$$18.7 - 13.5 = 5.2 \text{ g } NO_3 \text{ from } NaNO_3$$

$$5.2 \text{ g } NO_3 \times (85 \text{ g } NaNO_3/62 \text{ g } NO_3) = 7.1 \text{ g } NaNO_3$$

Water weight (found) is calculated by difference.

Overall, the agreement between "Calculated" and "Found" in Filtrate 3 is fairly good. The HEDTA found is expected to be low because of the organic destruction. Al is within analytical error. $NaNO_3$ is amazingly close. The major discrepancy is the distribution of HNO_3 and H_2O.

TEST B - PRE-ACIDIFICATION SEPARATION OF $NaNO_3$ AND $NaNO_2$

Figures 3.2 and 3.3 in the main body of the report show the mass flow for each component of the system in Test B. Shown here are the calculations used to determine the weights shown in those figures. Each heading below corresponds to the title of one of the boxes in the figures. Calculations are shown first for Figure 3.2, followed by calculations for Figure 3.3.

"101-SY SOL'N"

Same feed solution used in all Tests A-E; see Test A for full explanation.

"CONDENSATE 1"

This represents the total weight lost during the first evaporation. See page 127 of Laboratory Controlled Notebook WHC-N-345-1. (100.0 - 75.9 = 24.1)

"SOLIDS 1"

The total weight (7.8 g) comes from the weight of centrifuged solids recorded on page 127. The fraction represented by Na_2CO_3 is taken from Sample DH-131A (see below). The difference between the weight Na_2CO_3 and total weight is assumed to be interstitial liquid component salts (ISL) plus water from the interstitial liquid. The H_2O is calculated by taking that difference times 20/68.1 (the fraction of water in the supernatant solution). The remaining 3.2 g is assumed to be due to the ISL component salts. The results of DH-131A for ISL components (Al, Na, NO_3, NO_2) are consistent with this assignment. The amounts of ISL components found in DH-131A were 0.76 g Al, 0.54 g Na [excluding the Na from Na_2CO_3 and NaAl(OH)4], 0.83 g NO_3, and 0.48 g NO_2. Total = 2.61 g. This is about the right amount for 3.2 g ISL, the remainder being the un-analyzed OH and TOC.

"SUPERNATE 1"

Water and Na_2CO_3 weights are determined by difference ("101-SY SOL'N" minus "CONDENSATE 1" minus "SOLIDS 1"). All other components are reduced enough to compensate for the amount of ISL in "SOLIDS 1". This amount is found by adding all of the ISL components in "101-SY SOL'N" (51.4 g) and subtracting the 3.2 g ISL in "SOLIDS 1". Then each component in "101-SY SOL'N" is multiplied by the factor 48.2/51.4 to find the amount remaining. The column total (68.1 g) matches the expected total (100.0 - 24.1 - 7.8 = 68.1).

"SUPERNATE 2"

For NaOH, $NaAl(OH)_4$, Na_2CO_3, and Na_3HEDTA the weights are calculated by multiplying the weight in the feed supernate (after evaporate/centrifuge) by the factor 7.2/9.8, which is the amount of $NaAl(OH)_4$ found in DH-130A (7.2) divided by that amount plus the amount found in DH-130B. This factor is thought to be a fair representation of the distribution of liquid between the supernate and solids fractions (assuming Al stays in solution). $NaNO_3$ and $NaNO_2$ are calculated in the same way, but the fractions come from their specific analyses rather than Al. Their factors are thus 4.5/15.4 and 4.4/9.2 respectively. Water is found by difference, using the total supernate