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An Analysis of Alternative New Technical Strategy Flowsheets for Tank Waste Remediation System

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Abstract

This study examines the current New Technical Strategy flowsheet system with discrete event modeling. This modeling provides insight into:

- The total size of the system
- The amount of material, such as reagents and other added materials that must be supplied
- The final mass of waste that must be stored
- Areas within the system where a small change can greatly effect the total system

Some of the possible variations within that system are examined and compared. Further, an older, more complex system is examined.

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An Analysis of Alternative New Technical Strategy Flowsheets for Tank Waste Remediation System

Clay P. Booker
LANL TSA-3

I. INTRODUCTION

The Hanford Tank remediation plans have gone through a few revisions for the best waste processing system. Some designs have been complex while others have been fairly simple. One of the key means in understanding and selecting among the various proposed systems is a discrete events modeling of the system. This modeling provides insight into:

- The total required size of the system
- The amount of material, such as reagents and other added materials that must be supplied
- The final mass of waste that must be stored
- Areas within the system where a small change can greatly effect the total system

Discrete events modeling also provides the means by which various proposed systems may be compared. It is the framework in which variations within a particular system may be explored and compared to other instantiations.

This study examines the current New Technical Strategy flowsheet system with discrete event modeling. Some of the possible variations within that system are examined and compared. Further, an previously proposed, more complex system is examined.

II. ProMoS DISCRETE EVENT SIMULATION CODE

In analyzing the systems for this study, the ProMoS¹ code was used. This is a discrete-event simulation tool developed by the Technology Modeling and Assessment group (TSA-7) at Los Alamos National Laboratory. It has been used to examine DOE facilities and presently is used by several organizations in designing Complex-21.

The code has several features that are amenable to the analysis of production scale chemical processing systems. Some of these are relevant to this work are:

1. A scenario may be constructed so that the number of days worked per week and the number of shifts can be individually assigned to any single process. Accordingly, a particular process may be constrained to run on a 7 day/week, 3 shift/day work schedule while other process run under different work schedules. More importantly for the present analysis, the work schedule for the entire system may be altered by simply redefining the work-shift structure; this makes variations in a work schedule in a system simple to incorporate globally.
2. Each process in a system may be individually modeled by a combination of a Location and associated Workcenters.
 - A. A Location is analogous to the physical location for a process. The user may associate bulk-containers at a Location where material is to be received. In the simplest incarnation, a Location may just have a bulk-container which receives material but does not process it; such basic Locations are used as storage places to accumulate material.
 - B. Workcenters may be associated with any Location. A Workcenter is analogous to the actual process being modeled at the location. A Workcenter is specified with:
 - the batch size
 - the batch processing time which *may* be proportional to the available feed
 - the work schedule under which to run
 - the materials to be added to the batch in proportion to the total batch size or in proportion to particular materials in the feed
 - the individual destination of each material in the batch
 - the time remaining in the shift which will allow the process to run

Rather than just increasing the batch size to accommodate a larger or smaller through-put, the number of parallel, identical Workcenters associated with a Location may be increased or decreased.

Of course, the ProMoS code has several other features, but those delineated above are most relevant to this discussion. We have examined other commercially available codes, but none have the necessary features for this analysis which ProMoS possesses.

Beyond these attributes, the ProMoS code is installed and up and running on machines to which Los Alamos users have access. Various utilities to ease the burden of creating input files and extracting desired output data are available. Notably, a Macintosh Hypercard database manager allows the user to create a self-consistent input description that is internally checked; thus input errors are virtually eliminated, and the user is confident of having an input file that conforms to what is desired.

III. BASELINE

The baseline is predicated on the current New Technical Strategy flowsheet² ; It is depicted in Figure III.1..

Figure III.1. Pretreatment Block Diagram

At present only the liquid section has been developed with the sludge treatment section to be defined later. Farish³ has summarized the current proposals for the baseline processes. It is envisioned that the sludge washing and solid/liquid separation are performed within the tank. For **Cs Removal** ion exchange with CS-100 resin is being considered along with the alternatives, Resorcinol-Formaldehyde resin and Crystalline Silica-Titanates. Calcination is being considered for **Organic Destruction** with Hydrothermal processes as an option. A precipitation process is being considered for **Sr Removal**, and an ion exchange process is the primary alternative. **Tc Removal** is to be accomplished with anion exchange using Rellex-HPQ resin. The resulting Low-Level Waste (LLW) is reduced in volume with the **LLW Evaporator**; a concentrator is also considered for inclusion in this step. Finally the LLW is vitrified with the **LLW Vitrification** process. Note that Cs, Sr, and Tc are returned to the tank for later processing as High-Level Waste (HLW). Of course, the type and number of process steps are to be determined on a tank or farm basis.

A. Input Model Description

The liquid section section is treated in detail by the ProMoS code; the block diagram for the code model is shown below in Figure III.A.1.:

Figure III.A.1. Block Diagram of Baseline Overview

This model, with slight variations as noted below, is used to analyze:

- **The treatment of supernate only.** In this case it is assumed that the supernate is blended with the sludge. The sludge is allowed to settle and the supernate is *enriched* with materials of particular interest such as Cs, Sr, Tc, Na, and K; it is drawn off and run through the system in Figure III.A.1.. This is simplified from

the basecase and provides insight into initial operations.

- **The treatment of supernate and the sludge wash.** In this case the supernate is drawn off as it stands and run through the system; the supernate and the sludge are not blended so that as discussed below only a bit of Cs is the interesting constituent of the supernate. Then the sludge is washed with 4 times its mass of water, and the enriched water is drawn off and run through the system. This models the current baseline design.

The process descriptions for each of the boxes in Figure III.A.1 are drawn from previous work in analyzing the various designs for Complex-21 and from study of the Clean option (see Section 4 below). These process descriptions are given below, but specific details are given in the appropriate section:

- **Tank:** This process in the ProMoS model is only a bulk container where the specific materials are held and then passed quickly to the next process. At the next process it waits until it can be processed by that process at the specified rate. For this analysis the tank contents are based on tank 101-SY because the best data is available for it. The contents⁴ are:

Table III.A.1. Tank 101-SY Contents

<u>Material</u>	<u>Amount (kg)</u>
Al	17,636.72
Am	3.53
Pu	43.55
Th	1,838.14
U	1,885.67
Tc	7.00
Cs	0.90
Na	54,642.55
K	1239.09
Fe	9,955.53
Sr	34.71
Zn	181.30
Np	0.79
Ce	388.56
Other Sludge Solids	574,043.29
Supernate	2,220,525.50

- **Solid/Liquid Separation:** This process is not used in all models since it is not required for simply drawing off the supernate. It is operated with a batch size of 880 kg with 1 hour per batch. Here the materials of interest may be split between the supernate and the sludge sections; specific splits, as appropriate, are mentioned below.
- **Cs Removal:** This process is based on the Resorcinol-Formaldehyde Ion Exchange Resin developed for the Clean Option study because data for the competitors is not available; when the data for the Baseline choice of CS-100 Resin becomes available, it will be interesting to rerun the analysis. **Cs Removal** has a 900 kg batch size with 8 hours per batch. Water, 2M NaOH, and 1M Formic Acid are added in this step in proportion to the mass of the bulk input. It generates 1 resin as waste for 180,000 kg of throughput; the waste resin which is assumed to be 100 kg is directed to the process **Resin Oxidation** (not shown). 0.01% of the Cs, Sr, and Tc in the stream are also directed to **Resin Oxidation**; this assumes that traces of these are trapped in the resin. The rest of the Cs and the Formic Acid are directed to **Tank Storage**. The remainder passes on to **Organic Destruction**.
- **Organic Destruction:** This is a calcination step, and no material is added here. It is operated with a 750 kg batch size and 4 hours per batch based on previous experience with Complex-21 analysis.
- **Sr Removal:** The chelating cation exchange process created for the Clean Option study is used here again because data is available for it. It is operated with a 900 kg batch size and 8 hours for each batch. Water, 2M NaOH, and 1M Nitric Acid are added in proportion to the mass of the bulk input. As with **Cs Removal** it generates waste resin with 0.01% of the Sr and Tc which is then fed to **Resin Oxidation**. The remainder of the Sr goes with the Nitric Acid 1M to the **Sr Evaporator**. The balance of the batch is directed to **Tc Removal**.
- **Tc Removal:** The Strong Base Anion Exchange process created for the Clean Option is used for the Tc Removal process in absence of data on the Reillex-HPQ resin anion exchange. It has a 900 kg batch size with 8 hours per batch. Water, NaOH 2M, Nitric Acid 0.25M, and Nitric Acid 6M are added here in proportion to the mass of the feed. As with **Cs Removal** and **Sr Removal** waste resin with 0.01% of the Tc is generated and directed to **Resin Oxidation**. The rest of the Tc follows the Nitric Acid 6M to **Acid Distillation** while the remainder of the batch goes to **LLW Evaporation**.
- **LLW Evaporation:** This process has a 340 kg batch size with 1 hour per batch based on data supplied by D. Chamberlain⁵. No material is added in this step. Evaporation with 60% to 70% of the feed to **LLW Vitrification** being water is

the basic model for this process. However, an option where this process is operated as an Evaporator plus Concentrator with only about 20% of the mass of the feed to the **LLW Vitrification** as water is included in this study; the batch size and process time are assumed the same as the evaporator alone. In either case, the balance of the water is directed to a location called **Off-gas Treatment**.

- **LLW Vitrification:** This process is operated with a batch size of 566.89 kg for 4 hours based on previous Complex-21 work. All water in the feed is assumed to be driven off and is directed to the location, **Off-gas Treatment**. Glass formers are added to the batch at 4 kgs of Glass Formers per kg of feed.
- **Sr Evaporator:** Here the 1M Nitric Acid bearing the Sr is reduced in volume. The resulting concentrated acid which is around 6.5M with the Sr is fed to the Location, **Tank Storage**. The remaining dilute acid is directed to the Location, **Acid Recovery**. No material is added in this process. The batch size is 75 kg processed in 4 hours.
- **Acid Distillation:** The 6M Nitric Acid bearing the Tc is reduced in volume here. Half of the acid with the Tc is fed to the location, **Tank Storage**, while the rest of the acid is fed to **Acid Recovery**. The 750 kg batch is processed in 4 hours.
- **Resin Oxidation:** This process is omitted from Figure III.A.1. It simply collects all the waste resin and converts it to an equal mass of ash that is then given to the *as yet* undefined sludge treatment section. It has a batch size of 100 kg, about 1 resin, and processes that in 1 hour.
- **Glass Storage:** This is just a Location where the glass from **LLW Vitrification** are collected.
- **Acid Recovery:** This is a Location where clean acid from **Sr Evaporator** and **Acid Distillation** are collected.
- **Off-gas Treatment:** This is a Location where clean water from **LLW Evaporation** and **LLW Vitrification** are collected.
- **Tank Storage:** In Figure III.1., Cs, Sr, Tc are routed back to the tank for later HLW processing. In the code model, the "Tank" actively feeds the liquid stream. Accordingly, reality is approximated by the Location, **Tank Storage**, where the extracted HLW can reside

It should be noted that the *primary path*, the path of the bulk of the feed is:

**Cs Removal → Organic Destruction → Sr Removal → Tc Removal → LLW Evaporation
→ LLW Vitrification**

B. Modeling Considerations

There are some concessions made for the ProMoS code used in this study. They were evaluated early on and appraised as being of little consequence.

- One difficulty with ProMoS is that at the end of the run, it is typically not practical to force the majority of the Bulk Containers to empty their contents *which is less than a specified batch size* into the appropriate Workcenter. As a result, there is some hold-up in most of the process at the end of the simulation. This does not seriously impact the system design or behavior.
- While it is capable of handling Workcenters with smaller batch sizes than those noted in section III.A. above, cutting them by a factor of 10 *and increasing the number of parallel units by 10* dramatically increases the code run time and memory usage. Accordingly, the batch sizes are, for the most part, a factor of 10 higher than desired to yield an acceptable use of computer resources. For example, a more realistic batch size for Cs Removal is 90 kg while on the other hand, a batch size of 75 kg for Sr Evaporation is reasonable. This compromise with respect to batch size does not significantly effect the analysis; multiplying the batch size by 10 is tantamount to having 10 times the number of properly sized units. The only adverse consequence is that it increases the hold-up in the process at the end of the simulation.

C. Supernate mix with no dilution

It is of interest to consider the simple case where the supernate is drawn out of the tank leaving the sludge for later treatment. For this case, it is assumed that the supernate is first blended with the sludge so that some additional materials of interest are moved from the sludge into the supernate. The sludge is allowed to settle, and the supernate is decanted from the tank and processed as shown in Figure III.A.1.. Some of the specific process characteristics for those discussed in section A for this case are:

- **Tank:** Contains the sludge and supernate with materials of interest broken out for individual trace as in Table III.A.1..
- **Solid/Liquid Separation:** This process is used for this case to apply the appropriate split of materials given in Table III.C.1. 100% of the Tc, 90% of the Cs, 70% of the Al, 99% of the Na, and 99% of the K is passed through to the superante process steps while the rest is dumped in the location for sludge

treatment. The supernate that is processed then consists of :

Table III.C.1. Supernate Composition.

Material	Amount (kg.)
Al	12,345.70
Cs	0.81
K	1,226.70
Na	54,096.10
Sr	34.71
Tc	7.00
Supernate remainder	2,206,891.19

The balance of the system is as described in section III.A..

The system is allowed to process the material from the tank over the course of a year. With the above process descriptions and with 5 days/week operation and a single 8-hour shift per day, the system yields 5.8×10^6 kg of glass. The process attributes are shown in Table III.C.2.:

Table III.C.2. Process Descriptions.

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
Acid Distillation	750	3		
Cs Removal	900	12	Water	5,026
			Formic Acid 1M	11,417
			NaOH 2M	3,684
LLW Evaporation	340	30		
LLW Vitrify	566.89	2	Glass-Formers	2,546,470
Organic Destruction	750	15		
Resin Oxidation	100	1		
Sr Evaporator	75	1		
Sr Removal	900	13	Water	4,976
			Nitric Acid 1 M	11,503
			NaOH 2M	3,629
Tc Removal	900	13	Water	3,279
			NaOH 2M	3,643
			Nitric Acid 0.25M	1,595
			Nitric Acid 6M	546,555

In Table III.C.2. and subsequent such tables, the individual processes are listed in the first column; grey areas in that column indicate that the data to the right is associated with the above named process. The size column indicates the batch size for each Workcenter that models the process, and the Units column tells how many such Workcenters operating in parallel are required at that Location. The final two columns show the material added at each process; grey areas here indicate that no material is added for that process.

The material added usage for the entire system is summarized in Table 3.C.2.:

Table III.C.3. Material Added Usage.

Material	Amount (kg)
Formic Acid 1M	11,417
Glass Formers	2,546,470
NaOH 2 M	10,956
Nitric Acid 0.25M	1,595
Nitric Acid 1M	11,503
Nitric Acid 6M	546,555
Water	13,281

Finally, it is clear from several runs with variations in the feed that the number of units required in the primary path depends directly on the mass of the feed. Now, that feed is primarily liquid. Hence, if it is desired to reduce the size of the treatment system, an evaporator before the process, **Cs Removal**, scales the primary path by about the amount of liquid the Evaporator allows to pass through with the feed.

D. Supernate decant with subsequent sludge wash

This case closely approximates the anticipated treatment of the contents of the tanks. Here the supernate is not blended with the sludge to redistribute some of the materials of interest from the sludge to the supernate. The system is assumed to treat the supernate and the sludge wash over the course of a year; accordingly, the supernate-only treatment and the sludge-wash treatment are each allocated 6 months in which to complete the treatment.

In the first case, the supernate is decanted from the tank. For tank 101-SY, it is assumed that among the materials of interest, only a bit of the Cs resides in the supernate; the assumed composition is given in Table III.D.1.:

Table III.D.1. Supernate Composition.

Material	Amount (kg)
Cs	0.145
Supernate <i>remainder</i>	2,220,525.355

The resulting size and material added are summarized for this phase in Table 3.D.2.:

Table III.D.2. Process Descriptions — Supernate Decant.

Process	Size (kg)	Units	Material Added	
			Material	Amount (kg)
Acid Distillation	750	6		
Cs Removal	900	24	Water	4,907
			Formic Acid 1M	11,146
			NaOH 2M	3,597
LLW Evaporator	340	60		
LLW Vitrify	566.89	4	Glass Formers	5,079,330
Organic Destruction	750	29		
Resin Oxidation	100	1		
Sr Evaporation	75	2		
Sr Removal	900	25	Water	4,856
			NaOH 2M	3,542
			Nitric Acid 1M	11,227
Tc Removal	900	25	Water	3,287
			NaOH 2M	3,555
			Nitric Acid 0.25M	1,654
			Nitric Acid 6M	533,369

Notably, the primary path in this case is about twice the size of that of where the *enriched* supernate is treated (Section III.C. above). This is because they both are treating virtually the same mass of feed, but the present case is constrained to complete in half the time to accommodate the ensuing Sludge Wash treatment within the year period.

The Sludge Wash portion follows the Supernate Decant. The sludge is washed with 4 times the sludge mass of water. Here a solid/liquid separation section is required to direct the sludge to the sludge processing section, a Location, and to direct the wash to the liquid treatment section. As shown in Table III.D.3., the total mass to be run through the system is larger than that of the Supernate Decant; remaining materials of interest are washed out of the sludge into the wash:

Table III.D.3. Sludge Wash Composition.

Material	Amount (kg)
Al	12,345.70
Cs	0.6795
K	1,226.70
Na	54,096.10
Sr	34.71
Tc	7.00
Water added	2,647,600.00

Because of the larger mass of sludge wash, the expected size of the system is larger than that for Supernate Decant. The size of the system and the materials added are shown in Table III.D.4.:

Table III.D.4. Process Descriptions — Sludge Wash.

Process	Size (kg)	Units	Name	Material Added
Acid Distillation	750	8		
Cs Removal	900	28	Water	6,001
			Formic Acid 1M	13,631
			NaOH 2M	4,399
LLW Evaporation	340	60		
LLW Vitrify	566.89	3	Glass-Formers	782,308
Organic Destruction	750	30		
Resin Oxidation	100	1		
Solid/Liquid Separation	900	6	Water	2,647,600
Sr Evaporator	75	2		
Sr Removal	900	28	Water	5,941
			Nitric Acid 1 M	13,735
			NaOH 2M	4,333
Tc Removal	900	28	Water	4,021
			NaOH 2M	4,349
			Nitric Acid 0.25M	2,024
			Nitric Acid 6M	652,539

The Sludge Wash system is generally slightly larger than the Supernate Decant system

and thus the maximum size of the system is determined by the maximum number of units in column 2 of Table III.D.3 and Table III.D.4.. Note the contrast between the Glass Formers used in the two systems. This may be an artifact of the modeling assumptions. For the Supernate only system, the supernate is *replaced* by supernate-solids in the ratio of 5 to 1 in the LLW Evaporator; the supernate-solids are assumed to be 20% of the mass of the supernate. This assumption is also used in the Clean Option analysis below. However, in the treatment of the sludge wash, all of the solids are broken out in Table III.D.3. and they are only about 2.5% of the water. A different estimate of the solid mass fraction of supernate solids would, of course yield a different results.

The total amount of material added in both systems is shown in Table III.D.5.:

Table III.D.5. Total Material Added Usage.

Material Added	Amount (kg)		
	Supernate Decant	Sludge Wash	Both
Formic Acid 1M	11,146	13,631	24,777
Glass-Formers	5,078,330	782,308	5,860,638
NaOH 2M	10,694	13,081	23,775
Nitric Acid 0.25 M	1,654	2,024	3,678
Nitric Acid 1 M	11,227	13,735	24,962
Nitric Acid 6M	533,369	652,539	1,185,908
Water	13,050	2,663,563	2,676,613

The Supernate Decant system yields a total LLW glass mass of 5.5×10^6 kg while the Sludge Wash system yields a total LLW glass mass of 196,137 kg. The Glass Formers are added at the ratio of 4 to 1 based on mass. Again, the LLW waste in the Supernate-only section depends on the assumption that the supernate is reduced to 20% as a solid by an evaporator.

E. Options

For cases C. and D. above, the processes were analyzed with a work schedule of 7 days/week and 3 shifts/day for a year. As expected, the material added usage is the same as for the 5 days/week, 1 shift/day case. The number of units in the **primary path** is reduced by a factor of about 4. This means that a much smaller system could be used for each tank. Perhaps even a series of portable systems could be driven up to each tank for treatment with the continuous operation option.

Another option is to augment the **LLW Evaporator** with a Concentrator. Then it is assumed that the feed passed on to **LLW Vitrification** contains only 20% water rather than the

70% to 60% water from an evaporator alone. However, the assumption that the supernate is reduced by a factor of 5 to the nondescript supernate-solids, is not altered; in the case of supernate run through the system, the Concentrator only has a different effect on the water *added* in prior processes. The effect of the LLW Concentrator on the final waste is shown below:

Table III.E.1. Concentrator Reductions in LLW Waste

System	Amount of Glass (kg)	
	Evaporator	with Concentrator
Supernate mix with no dilution	5.768×10^6	3.056×10^6
Decanted Supernate before Sludge Wash	5.524×10^6	2.667×10^6
Sludge Wash after Decanted Supernate	850756	410882

Clearly, following the **LLW Evaporator** with a Concentrator can reduce the waste glass by almost a factor of 2. However, it should be noted that this estimate is sensitive to two features. As noted above, the reduction of the supernate to supernate-solids is the same for both the evaporator alone and with the concentrator. Also, it is assumed that **LLW Vitrification** adds Glass Formers based on the mass of the feed and ignores the composition of that feed.

E. Conclusions

From the above analysis several conclusions are apparent.

- An evaporator placed before the primary path, before **Cs Removal**, would reduce the amount of liquid traversing the primary path. As a result, the amount of material added in the primary path and the number of individual, parallel units required in the primary path would be reduced.
- Running any of the systems on a 7 day per week, 3 shift per day basis reduces the number of units required by a factor of about 4. Such a reduction makes a *portable* system more attainable. Also, for the same capital cost, more identical systems could be built to treat a number of individual tanks at the same time.
- If a Concentrator follows the **LLW Evaporator**, the amount of glass waste can be reduced by a factor of about 2 subject to the assumptions mentioned in section III.E..
- The system analyzed here was not designed to handle *just* the contents of tank

101-SY; rather it is set up with all the processes needed to extract the desired materials whether or not those materials are in the feed. Accordingly, this analysis is applicable to most other tanks on the reservation.

IV. CLEAN OPTION

The Clean Option has been suggested by J. L. Swanson⁶ in order to reduce the volume of the high-level waste, decrease the radioactivity and toxicity of the low-level waste to be left on site, and accomplish both without significantly increasing the total amount of waste for disposal. Since this proposal, matters have changed so that it is not longer anticipated that waste will be left on site; however, the Clean option is an interesting alternative and provides some attractive possibilities.

A. Clean System Description

This study is based on the original proposal and includes grouting of the LLW. If future analysis is done, it will undoubtedly include alternatives to the grout. This is a fairly complex system to model. The system is broken up into a considerable number of processes, and there is extensive recycling of material from one stream to another stream. The overview of the Clean option is shown in Figure IV.1.:

Figure IV.1. Overview of the Clean Option.

Water is added to the source tank in the ratio of 2.857 to the mass of the total contents and then water is added in the initial Solid/Liquid Separation at the ratio of 0.05 by mass.

B. Sludge Processing stream

The Sludge Processing stream has several possible variations. For this study, it is assumed that all of the sludge is *eventually* dissolved or suspended and sent on to the Basic Side or to the Acid Side. An interesting variation is to provide an outlet to Acid Dissolution to Vitrification and reduce the cycles of attempted dissolution/suspension. The Sludge Processing stream sends material to both the Basic Side stream and the Acid Side stream contributing to the complexity of the system. The Sludge Processing section is shown in detail in Figure IV.2.:

Figure IV.2. Clean Option: Sludge Processing.

The individual processes for the Sludge Processing stream are:

- **Caustic Leach:** Here the sludge is washed with Water and 7M NaOH in the ratio of the feed mass of 2.05 and 3.19 respectively. Besides feed from the initial

Solid/Liquid Separation, it is also supplied from **Acid Dissolution 2**, **Cs Removal** in the Acid Side stream, and **Resin Oxidation**. It is run with an 880 kg batch size at 8 hours for each batch.

- **Solid/Liquid Separation-2:** Water is added to the output of **Caustic Leach** in the ratio of 0.5128 by mass of the output. The liquid is directed to the Basic Side **Evaporator** while the solids are fed to **Acid Dissolution 1**. The 880 kg batch is processed in 8 hours.
- **Acid Dissolution 1:** Water is added at the ratio of 0.69, 1M Oxalic Acid is added at the ratio of 0.82, 4.5M Nitric Acid is added at the ratio of 0.02, and 12M Nitric Acid is added at the ratio of 1.55 all based on the mass of the feed. 30% of the input, except the Water, Nitric Acid, and Iron, is directed to **Acid Dissolution 2**. The remainder is given to the Basic Side **Evaporator**. 8 hours is allocated to process the 880 kg batch.
- **Solid/Liquid Separation-3:** This process is fed by both **Acid Dissolution 1** and **Acid Dissolution 2**. 5% of the batch plus 100% of the water, Nitric Acid, Formic Acid, APM, and HF go to **TBP 1 Extr/Scrub**. The remainder is sent back to **Acid Dissolution 1**. The batch size is 880 kg and it is processed in 8 hours.
- **Acid Dissolution 2:** Here the sludge is treated with 10M HF in the ratio of 0.08 and 12M Nitric Acid in the ratio of 0.44 both relative to the mass of the feed. 10% of the output, except for the water, Nitric Acid, Formic Acid, and Iron, is sent to **Caustic Leach** while the remainder goes to **Solid/Liquid Separation-3**. The 880 kg batch is processed in 8 hours.

C. Basic Side Processing stream

The Basic Side is fairly simple and is similar to the Supernate/Sludge Wash section envisioned for the Baseline. Note the Sr Evaporator and Resin Oxidation feed the Sludge Processing stream; this contributes to the complexity of the system. The Basic Side Processing is shown in Figure IV.3.:

Figure IV.3. Clean Option: Basic—Side Processing.

The Basic Side processes are:

- **Evaporator:** This process receives material from the **Initial Solid/Liquid Separation**, the **Sludge Processing Solid/Liquid Separation-2**, and **Offgas Scrub** in the HLW stream. It is assumed here that 20% of the supernate is reduced to supernate-solids and the remainder of the supernate is driven off. 62% of the incoming water is passed with the solids to **Resorcinol-Formaldehyde Ion Exchange Resin**. The batch size is 7500 kg which is processed in 4 hours; this is 100 times the desired size, but necessary to yield a tractable code running time.
- **Resorcinol-Formaldehyde Ion Exchange Resin:** This is the same process as **Cs Removal** for the Baseline in Section III; because the data for the CS-100 Resin

was not available, the Clean Option and the Baseline analyzed in this study use the same Cs removal process. The Cs and Formic Acid go to **HLW-Denitration**, the resin goes to **Resin Oxidation**, and the primary stream continues to **Chelating Cation Exchange Resin**. 2M NaOH is added in the ratio of 0.0016, water in the ratio of 0.002, and 1M Formic Acid in the ratio of 0.005 in relation to the mass of the feed. 8 hours is required for each 900 kg batch. 0.01% of the Cs, Tc, and Sr is assumed to be trapped in the resin and thus periodically sent to **Resin Oxidation**.

- **Chelating Cation Exchange Resin** adds Nitric Acid 1M, water, and 2M NaOH in the ratios of 0.005, 0.002, and 0.0016 to the mass of the feed. 99.99% of the Sr follows the Nitric Acid to the **Sr Evaporator**. 0.01% of the Tc and Sr follows the Resin to **Resin Oxidation**. The remainder goes to **Strong Base Anion Exchange Resin**. The batch size is 900 kg and completes in 8 hours. This process is identical to **Sr Removal** in the Baseline, Section III.
- **Strong Base Anion Exchange** removes Tc from the primary stream. It is the same as **Tc Removal** for the Baseline in Section III. 2M NaOH, 6M Nitric Acid, and 0.25M Nitric Acid are added in proportion to the mass of the feed with the ratios: 0.00159, 0.23858, and 0.00074 respectively. 0.01% of the Tc follows the resin to **Resin Oxidation**. The balance of the Tc follows the 6M Nitric Acid to **Acid Distillation**. The rest goes to **Basic LLW Evaporator**.
- **Resin Oxidation** is fed by all of the exchange processes. It has a batch size of 100 kg, about 1 resin and completes in 1 hour. The resin is converted to ash and sent on to **Caustic Leach**.
- **Sr Evaporator** has a batch size of 75 kg which is assumed to be a reasonable size for this process; it receives so little feed that it is not necessary to inflate it for code running concerns. The batch completes in 4 hours. The Sr and 6M Nitric Acid is sent to **Acid Dissolution 1** while the balance of the dilute acid goes to **Acid Recovery** which is just a Location.
- **Acid Distillation** receives Tc and 6M Nitric Acid from **Strong Base Anion Exchange Resin**. It processes a 750 kg batch in 4 hours. Half of the acid and the Tc goes to **HLW Evaporator** and the rest of the acid goes to the Location, **Acid Recycle**.

D. Acid Side Processing stream

The Acid Side is complex. Pu, Np, and Th are extracted with the U in the first TBP stream; the second TBP stream only extracts the U for the stockpile. Certainly an option here is to omit the U processing *and thus the second TBP stream*, and send the U to waste. The Acid Side stream is shown in Figure IV.4.:

Figure IV.4. Clean Option: Acid Side Processing.

The Acid Side Processing processes are:

- **TBP 1 Extr/Scrub** is an extraction and scrub process. The U, Pu, Np, and Th follow the TBP to **TBP 1 Reduc Strip** while the balance goes to **CMPO Extr/Scrub**. The 880 kg batch completes in 4 hours. 1.1M TBP is added in the ratio of 0.195 to the mass of the feed, and 1M NaNO₂ is added in the ratio of 0.00021; 4M Nitric Acid is added in the ratio of 0.088.
- **TBP 1 Reduc Strip** sends the U along with the TBP to **TBP 1 Final Strip** and sends the Pu, Np, and Th to **HLW Evaporator**. 4 hours is required for each 880 kg batch. 0.2M Nitric Acid and 0.1M NH₂OH are added in the ratios 0.458 and

0.458 respectively to the mass of the feed.

- **TBP Final Strip** directs the TBP to the Location **TBP 1 Wash** and sends the U and water to **U Evaporator**. The batch size is 880 kg and requires 4 hours. HEDPA is added in the ratio of 0.175 and water is added in the ratio of 0.8 to the mass of the feed.
- **U Evaporator** removes 40% of the received water and sends it to the Location, **Water Recycle**. The U, HEDPA, and the rest is sent to **TBP 2 Extr/Scrub**. The 880 kg batch requires 4 hours.
- **TBP 2 Extr/Scrub** adds 12M Nitric Acid, 1.1M TBP, and 0.007M $\text{NH}_2\text{-OH-HNO}_3$ by the mass of the feed in the ratios 1.25, 4.075, and 0.61 respectively. The batch size is 880 kg and completes in 4 hours. The U follows the TBP to **TBP 2 Strip** and the balance heads to **Backcycle evaporator**.
- **TBP 2 Strip** adds 0.01M Nitric Acid in the ratio of 1.67 to the mass of the feed. The U and the acid are sent to **U Product Evaporator** while the TBP goes to the Location, **TBP 2 Wash**.
- **U Product Evaporator** sends U and concentrated Nitric Acid to **U Calcination** and the water is sent to the Location, **Water Recycle**. The 750 kg batch requires 4 hours.
- **U Calcination** completes a 750 kg batch in 4 hours. It sends the U to the **Stockpile Location**, and the balance is sent to the Location, **Water Recycle**.
- **Backcycle Evaporator** recycles any U and almost half of the water to **TBP 1 Extr/Scrub** and the balance is sent to the Location, **Water Recycle**. 4 hours is required for the 750 kg batch.
- **CMPO Extr/Scrub** sends the Am, Ce, Sm, and Bi along with the CMPO to **CMPO Strip**. The remainder is sent to **CE Extr/Scrub**. The 880 kg batch completes in 4 hours. Complex Adjusting Solution and 0.2M CMPO are added in the ratios 0.054 and 0.246 to the mass of the feed.
- **CMPO Strip** lets the Bi follow the CMPO to **CMPO Wash** and directs the Am, Ce, and Sm to **Am/La Removal** with an 880 kg batch completing in 4 hours. 0.05M Nitric Acid is added in the ratio of 2.08 to the mass of the feed.
- **CMPO Wash** runs with an 880 kg batch that requires 4 hours. The Bi goes to **Acidic LLW Evaporator** while the CMPO goes to a Location for later reuse.
- **Am/La Removal** completes a 900 kg batch in 8 hours. It adds water, 0.05M Na_3DTPA , 0.3M Na_3DTPA , 6M Nitric Acid, and 1.5M Zinc Nitrate in the ratios 0.026, 0.114, 0.03375, 0.004, and 0.00056 to the mass of the feed. Ce is sent to **Acid LLW Evaporator**, Am is sent to **HLW Evaporator**, and resin is periodically sent to **Resin Oxidation**.
- **CE Extr/Scrub** sends Sr, Ba, and Tc along with the CE to **CE Strip**. The rest

- goes to **Cs Removal**. It requires 4 hours for an 880 kg batch. 0.2M CE and 1M Nitric Acid are added in the ratios of 1.0 and 0.34 to the mass of the feed.
- **CE Strip** needs 4 hours for an 880 kg batch. It adds 0.01M Nitric Acid in the ratio of 1.38 to the mass of the feed. Sr, Ba, and Tc go to **Sr/Ba/Zn Removal**. The CE goes to a Location.
 - **Sr/Ba/Zn Removal** has a 900 kg batch that takes 4 hours. It adds water, 6M Nitric Acid, 1.5M Zinc Nitrate, and 0.05M Na₃EDTA in the ratios 0.05, 0.0036, 0.0024, and 0.88 respectively to the mass of the feed. Ba and Zn go to **Basic LLW Evaporator**, Sr and Tc go to **HLW Evaporator**, and resin is generated that goes to **Resin Oxidation**.
 - **Cs Removal** directs Al, APM, and Cs to **Caustic Leach**. Resin is generated that goes to **Resin Oxidation**, and the balance goes to **Acidic LLW Evaporator**. The 900 kg batch takes 8 hours. Water, APM, and Al₂O₃ are added in relation to the mass of the feed by the ratios 0.0004, 0.000004, and 0.000036 respectively.

E. LLW Treatment stream

The LLW Treatment stream is fairly simple. However, there are two input streams. One is for the LLW waste of the Acid Side and another for the LLW waste of the Basic Side; the Acid Side waste stream includes a Denitration step after the evaporator before the two streams are merged. For this study, the LLW Treatment stream results in grout formation based on the original concept for the Clean Option; an apropos alternative is to send the LLW waste to glass formation. The LLW Treatment is shown in Figure IV.5.:

Figure IV.5. Clean Option: LLW Treatment.

The LLW Processing processes are:

- **Basic LLW Evaporator** sends 37% of the water to a Location, **Water Recycle** and the balance to **LLW Calcination** . The 750 kg batch takes 4 hours.
- **Acidic LLW Evaporator** sends 36% of the water to a Location, **Acid Recovery** , and the rest to **Acidic LLW Denitration**. The 750 kg batch completes in 4 hours.
- **Acid LLW Denitration** adds 2M Sucrose in proportion to the mass of the feed by the ratio, 0.167. The 750 kg batch requires 2 hours and is passed on to **LLW Calcination**.
- **LLW Calcination** sends I, Na, and some Nitric Acid to **I Removal**, the rest goes to **Cr Reduction**. 4 hours is required for the 750 kg batch.
- **I Removal** takes 4 hours for the 750 kg batch. I is sent to a Location while NO₃

goes on to **NO_x Destruction**.

- **NO_x Destruction** adds NH₃ by the ratio of 0.275 to the mass of the feed. It has a 750 kg batch size that completes in 4 hours.
- **Condenser** takes 4 hours to complete a 750 kg batch. It releases N₂ and sends NaOH to **Cr Reduction**.
- **Cr Reduction** receives feed from **LLW Calcination** and **Condenser**. It adds 1.5M NH₂OH by the ratio of 0.0146 to the mass of the feed and sends the result to **Solid/Liquid Separation**. It has a 750 kg batch that runs in 4 hours.
- **Solid/Liquid Separation** requires 1 hour for the 880 kg batch. It routes liquids to a Location for possible reuse and sends the rest to **Grout Formation**.
- **Grout Formation** adds cement in the ratio of 7 kgs to each kg of feed. It completes a 566.89 kg batch in 4 hours. The grout is sent to a Location for storage.

E. HLW Treatment stream

The HLW Treatment stream is straightforward. Here the waste is embedded in glass. It is shown in Figure IV.6.:

Figure IV.6. Clean Option: HLW Process .

The process for the HLW process are:

- **HLW Evaporator** completes a 750 kg batch in 4 hours. It sends 36% of the water to a Location, **Acid Recovery**. The balance is sent to **HLW Denitration**.
- **HLW Denitration** adds 2M Sucrose in the ratio 0.0112 by mass to the input feed. It requires 4 hours for a 2142.86 kg batch. It feeds **HLW Vitrification**. Besides **HLW Evaporator**, it is also fed by **Resorcinol-Formaldehyde Ion Exchange Resin**.
- **HLW Vitrification** adds 4 kgs of Glass Formers to each kg of feed. All of the water goes to **Offgas Scrub** while the glass goes to a Location, **HLW Glass**. The 566.89 kg batch requires 1 hour.
- **Offgas Scrub** adds 0.6M NaOH in the ratio of 0.02344 to the mass of the feed. It has an 88 kg batch that completes in 1 hour. The result goes to **Evaporator** in the Basic Processing stream.

G. Results

As mentioned previously, the Clean Option has been analyzed with the original assumption of grout formation for LLW waste. However, it can still be compared to the Baseline. The actual mass of LLW waste received by **Grout Formation** is 1.851×10^6 kg while **LLW Vitrification** in Section III.C., Supernate mix with no dilution, receives 1.315×10^6 kg; the Clean Option produces about 1.4 times the LLW waste than that case.

The HLW waste production for the Clean Option is 1.25×10^6 kg of glass. Unfortunately, the HLW stream for the Baseline has not been defined so no comparison is possible here.

The size of the Clean Option for this study is shown in Tables IV.1 through IV.6:

Table IV.1. Initial Separation Description.

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
Solid/Liquid Separaton	880	8	Water	553,247

Table IV.2. Process Descriptions: Sludge Processing

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
Acid Dissolution 1	880	4	Water	452,055
			Oxalic Acid 1M	534,892
			Nitric Acid 4.5M	13,458
			Nitric Acid 12M	1,012,213
Acid Dissolution 2	880	2	Water	73,138
			HF 10M	16,134
			Nitric Acid 12M	84,861
Caustic Leach	880	4	Water	1,281,656
			NaOH 7M	1,996,172
Solid/Liquid Separation 2	880	24	Water	2,001,270
Solid/Liquid Separation 3	880	19		
Solid/Liquid Separation	900	6	Water	2,647,600

Table IV.3. Process Descriptions: Basic—Side Processing.

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
Acid Distillation	750	4		
Chelating Cation IX	900	15	Water	6,067
			NaOH 2M	4,425
			Nitric Acid 1M	14,025
Evaporator	7500	12		
Resin Oxidation	100	1		
Resorcinol-Formaldehyde IX	900	15	Water	6,134
			NaOH 2M	4,496
			Formic Acid 1M	13,934
Sr Evaporator	75	1		
Strong Base Anion Exchange	900	15	Water	4,106
			NaOH 2M	4,440
			Nitric Acid 0.25M	2,067
			Nitric Acid 6M	666,281

Table IV.4. Process Descriptions: Acid Side Processing.

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
Am/La Removal	900	11	Water	48,630
			Na ₃ DTPA 0.05M	213,247
			Na ₃ DTPA 0.3M	63,271
			Nitric Acid 6M	11,417
			Zinc Nitrate 1.5M	7,630
Backcycle Evaporator	750	9		
CE Extraction/Scrub	880	12	CE 0.2M	3,860,560
			Nitric Acid 1M	1,327,763
CE Strip	880	12	Nitric Acid 0.01M	5,340,463
CMPO Extraction/Scrub	880	12	CMPO 0.2M	901,972
			Cmplx. Adj. Sol'n	197,324
CMPO Strip	880	4	Nitric Acid 0.05M	1,874,428
CMPO Wash	880	6		
Cs Removal	900	24	Water	2,075
			APM	21
			Al ₂ O ₃	187
Sr/Ba/Zn Removal	900	28	Water	266,987
			Na ₃ EDTA 0.05M	4,698,396
			Nitric Acid 6M	19,116
			Zinc Nitrate 6M	13,029
TBP 1 Extraction/Scrub	880	16	TBP 1.1M	657,534
			NaNO ₂ 1M	708
			Nitric Acid 4M	296,566
TBP 1 Final Strip	880	7	Water	756,472
			HEDPA	165,044
TBP 1 Reducing Strip	880	4	TBP 1.1M	283,234
			NH ₂ OH 0.1M	302,670
			Nitric Acid 0.2M	302,570
TBP 2 Extraction/Scrub	880	3	TBP 1.1M	1,663,900
			NH ₂ -OH-HNO ₃	250,365
			Nitric Acid 12M	510,915
TBP 2 Strip	880	12	Nitric Acid 0.01M	2,777,551
U Evaporator	880	4		
U Product Evaporator	750	12		
U Calcination	750	1		

Table IV.5. Process Descriptions: LLW Treatment.

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
Acidic LLW Evaporator	750	32	Al(NO ₃) ₃	180,410
Acidic LLW Denitration	750	20	Sucrose 2M	711,937
Basic LLW Evaporator	750	26		
Condenser	750	8		
Cr Reduction	750	30	NH ₂ OH 1.5M	108,060
Grout Formation	566.89	9	Cement	12,956,270
I Removal	750	4		
LLW Calcination	750	38		
NO _x Destruction	750	4	NH ₃	269,473
Solid/Liquid Separation	880	12		

Table IV.6. Process Descriptions: HLW Process.

Process	Size (kg)	Units	Material Added	
			Name	Amount (kg)
HLW Denitraton	2142.86	1	Sucrose 2M	3,432
HLW Evaporator	750	35		
HLW Vitrification	566.89	4	Glass Formers	1,238,090

It would be interesting to run the Clean Option with Concentrators following some or all of the Evaporators. Certainly, the key places where a Concentrator could have a large effect in following an Evaporator are: **Evaporator**, **Acidic LLW Evaporator**, **Basic LLW Evaporator**, and **HLW Evaporator**. It would also be interesting to place an Evaporator before the first process in the Acid Side Processing; the feed to **TBP 1 Extr/Scrub** is overwhelmingly water so that a reduction in the mass here could reduce the size of the downstream processes.

The total material usage for the Clean Option is shown in Table IV.7.:

Table IV.7. Material Added Usage.

Material	Amount (kg)
Al(NO ₃) ₃	180,410
Al ₂ O ₃	187
AMP	21
CE 0.2M	3,860,560
Cement	12,956,270
Cmplx. Adj. Sol'n	197,324
CMPO 0.2M	901,972
Formic Acid 1M	13,934
Glass Formers	1,238,090
HEDPA	165,044
HF 10M	16,134
Na ₃ DTPA 0.05M	213,247
Na ₃ DTPA 0.3M	63,271
Na ₃ EDTA 0.05M	4,698,936
NaNO ₂ 1M	708
NaOH 2M	13,361
NaOH 7M	1,996,172
NH ₂ -OH-NHO ₃	250,365
NH ₂ OH 0.1M	302,670
NH ₂ OH 1.5M	108,060
NH ₃	269,473
Nitric Acid 0.01M	8,118,014
Nitric Acid 0.05M	1,874,428
Nitric Acid 0.25M	2,067
Nitric Acid 0.2M	302,570
Nitric Acid 12M	1,607,989
Nitric Acid 1M	1,341,788
Nitric Acid 4.5M	13,458
Nitric Acid 4M	396,566
Nitric Acid 6M	698,814
Oxalic Acid 1M	534,892
Sucrose 2M	715,369
TBP 1.1M	2,604,668
Water	8,099,437
Zinc Nitrate 1.5M	7,630
Zinc Nitrate 6M	13,029

V. CONCLUDING REMARKS

It is clear that the supernate/sludge wash stream of the Baseline processing system will involve a large apparatus but is relatively straightforward in design. The size of the system can be greatly reduced by simply operating it on a 7 day per week, 3 shift per day basis. Alternately or in tandem with such a work schedule, it appears that an evaporator placed at the beginning of the primary path can substantially reduce the size of this system. It is also apparent that augmenting the Evaporator with a Concentrator in the final LLW treatment stages can greatly reduce the final mass of glass produced.

While the processes descriptions used for this study are valid for use in the Baseline, it is important to analyze the data from primary process selections when this data becomes available; this would necessitate using the data from the CS-100 ion exchange for the Cs Removal process, the desired precipitation process for Sr Removal, and Rellex-HPQ resin for Tc Removal.

The analysis of the Clean Option provides some valuable insight. It is more complex and uses considerably more added material than the Baseline. On the other hand, it *may* actually reduce the amount of HLW waste compared to the Baseline; when the Baseline HLW stream is defined, it will make an interesting comparison. The LLW waste production for the Clean Option exceeds that of the Baseline; however, there is ample opportunity to reduce this by following Evaporators with Concentrators. Moreover, the Clean Option seems to present the chance for large scale recycling of materials so that the added material usage could be greatly reduced; this aspect was not analyzed in this study.

- 1 H. W. Egendorf: Lisp and Portability: The Process Modeling System, Lisp User's and Vendors '92 Conference, San Diego, CA, 1992 August 10-13, LA-UR-92-2780.
- 2 Private Communication to Thomas J. Farish, 2/2/94.
- 3 Thomas J. Farish, Experimental Infrastructure and Logistics Required to Support TWRS Technology Development, LAUR-94-1140, 1994 March 25, Los Alamos National Laboratory.
- 4 S. L. Yarbrow, W. A. Punjak, S. B. Schreiber, S. L. Dunn, G. D. Jarvinen, S. F. Marsh, S. Agnew, E. Birnbaum, K. W. Thomas: Status of Tank 101-SY Remediation Flowsheet Development at LANL, LA-UR-92-1725, 1993 April 30, Los Alamos National Laboratory.
- 5 Private Communication to Thomas J. Farish, 2/1/94.
- 6 J. L. Swanson: Clean Option: An Alternative Strategy for Hanford Tank Waste Remediation, Volume 2: Detailed Description of First Example Flowsheet, September 1993, Pacific Northwest Laboratory, PNL-8388 Vol. 2, UC-721.

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