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Subject: **Errata for Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 3 LA-UR-96-858**

To whom it may concern:

This letter is meant to provide corrections to the HDW Model Rev. 3 We have corrected the report and attached are the following updated sections. Please replace or update as appropriate.

In appendices C and E, not all the pages were updated, but we have provided you with complete sections for your convenience. The graphs and tables that were updated are signified with Rev. 3a and the graphs and tables that remain the same are signified with Rev. 3.

Sorry for the inconvenience. If there are any questions please feel free to call Steve Agnew at 505-665-1764.

Appendix A changes:
   1. Al and Zr clad fuel should be included with P2 waste for the period 1963-67.
   2. Al and Zr clad fuel should be included with P2 waste for the period 1968-72.
   3. All Zr clad fuel in Redox and Purex for the period 1966-67 should be assigned to CWZr1 for the period 1968-72.

Appendix C changes:
   1. Some of the TLM graphs were updated with the corrected data from the TLM spreadsheet.

Graphs

Page	Farm
C-66	B
C-67	BX
C-68	BY
C-69	C
C-70	S
C-73	T
C-74	TX
C-77	AW
C-78	AY
C-79	AZ
C-80	SY

Appendix E changes:

Inventory Estimate Tables

Page	Tank	Note #
E-1a	Total Site Inventory Rev.3a	1 - 9
E-40	BY-101	7
E-74	S-107	6
E-75	S-108	6
E-76	S-109	6
E-77	S-110	6
E-78	S-111	6
E-79	S-112	6
E-127	TX-101	5
E-128	TX-102	5
E-129	TX-103	5
E-130	TX-104	5
E-131	TX-105	5
E-132	TX-106	5
E-133	TX-107	5
E-134	TX-108	5
E-135	TX-109	5
E-136	TX-110	5
E-137	TX-111	5
E-138	TX-112	5
E-139	TX-113	5
E-140	TX-114	5
E-141	TX-115	5
E-142	TX-116	5
E-143	TX-117	5
E-144	TX-118	5

Note #

1. AN-103 SMM concentration for the density calculation contains a 3 instead of 4: =1+0.038*Na+0.07*Al-0.015*(OH-Al* **4**).
2. The molecular weight for DBP should be 210.2 instead of 161.01 in the HDW.
3. Total site calculation for crib and leaks utilized incorrect molecular weight of 55.847 for Al instead of 26.98.
4. Total site calculation for H_2O and TOC was incorrect; it included the 'All Quads' column along with the 'SST and DST' columns (double counting). (All quads + SST + DST + crib + leaks.)
5. TX farm TLM solids inventory for Sr-90 (Ci) used incorrect tank volume. (offset by one row).
6. S-107 through S-111 TLM solids total curie inventory for Sr-90 (Ci) and Cs-137 (Ci) incorrectly used the volume of tank S-106.
7. BY-101 Sr-90 and Cs-137 TLM solids concentration incorrectly used for calculation of the volume of tank BY-102.

Some minor errors were found in our report, but we only revised the tables that reflected the big errors. The explained corrections below 1 thru 3 reflect the minor errors reported. These corrections will be shown in the Rev. 4 document.

1. TLM ppm calculation referenced incorrect tank density in OH through FeCN analytes in tanks AW-105, AW-106, U-105, U-107, TY-106, B-105, B-106, and B-107.
2. Total ppm calculation referenced incorrect tank density in OH through FeCN analytes in tanks B-105, B-107, and TY-106.
3. Total concentration calculations for H20 and TOC excluded the density on B, U, and AW farms.

How to read this electronic version
of the
Hanford Tank Chemical and Radionuclide Inventories:
HDW Model Rev. 3a

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Contents and Report Text (00326134.pdf 180 Kb)
Appendices A, B - HDW List and Compositions (00326135.pdf 650 Kb)
Appendices C, D - TLM/SMM (00326136.pdf 1.3 Mb)
Appendix E - Inventory Estimates (00326137.pdf 2.5 Mb)
Appendix F - Glossary of Hanford Terminology (00326138.pdf 170 Kb)

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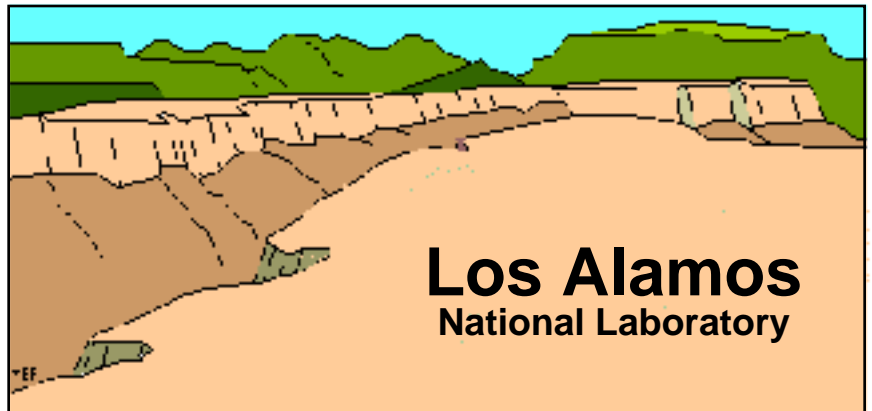
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Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 3

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Executive Summary

This estimate for the chemical and radionuclide compositions of the 177 Hanford High Level Waste storage tanks is the third major revision in a developing model called the Hanford Defined Waste (HDW) model. This model is composed of four parts:

1) a compilation of transaction records for all the tanks called the Waste Status and Transaction Record Summary (WSTRS);

2) a derivation called the Tank Layer Model (TLM) of solids histories for each tank based on primary additions of waste;

3) a calculation of supernatant blending and concentration with the Supernatant Mixing Model (SMM); and

4) a combination of process information along with some transaction information to derive compositions for about fifty Hanford Defined Wastes (HDW's), each of which has both sludge and supernatant layers.

All of this information is combined together in a spreadsheet to produce total chemical and radionuclide compositions for each tank's waste as well as a composition for its TLM and SMM blends. Furthermore, each tank's inventory is also represented by a linear combination of TLM sludges and SMM supernatants, each expressed in kgal of original waste. Thus, the genealogy of each tank's waste can be traced back to the plant and process from which it derived. These estimates comprise some 33 non-radioactive species and 4 radionuclides, Pu-239, U-238, Cs-137, and Sr-90. The 33 non-radioactive species in the model are Na, Al, Fe, Cr, Bi, La, Hg, Zr, Pb, Ni, Sr(stable), Mn, Ca, K, OH, nitrate, nitrite, carbonate, phosphate, sulfate, silicate, F, Cl, citrate, EDTA, HEDTA, glycolate, acetate, oxalate, DBP, butanol, ammonia, and ferrocyanide.

Also reported are total site inventories for DST's, SST's, as well as the total inventory of waste placed into cribs and trenches from the waste tanks during the history of Hanford. These estimates do not cover all waste additions to cribs since many streams went into the cribs directly from the plants. Such streams as stack scrubbing and process condensates were often sent directly to cribs from the plants.

Tank leaks represent a very small amount of the total waste. Many "leaks" are not actually measured volumes and are only assumed to have occurred at some nominal value. This is because ground activity occurred in the vicinity of a tank even though there was no measurable change in its inventory. HDW estimated leak inventory, then, does not provide for leaks that did not have a measurable effect on inventory. Only those leaks that actually resulted in a measurable volume loss from a tank are included in the leak estimate.

I. Background

One of the most important tasks involving the Hanford waste tanks is the estimation of those tank's contents. Such estimates are very important for three reasons: first, to establish safety limits during intrusive activities associated with these tanks; second, to establish a planning basis for future disposal; and third, to allow assays from one tank's waste to be used to validate, compare, and assess hazards among other tank's with similar waste inventories.

It is clear that direct assays of tank wastes will always be an important and ongoing need for the Hanford tanks. However, it is equally clear that it will be very difficult if not impossible to adequately address all issues with respect to waste tanks by sampling and assay alone. Representative sampling is undoubtedly the most difficult aspect of deriving tank inventories from assays alone. Both the extremely heterogeneous nature of tank waste and the limited access provided by riser pathways to waste in these seventy-five foot diameter underground tanks contribute to difficulties in using assays alone to derive tank inventories. Furthermore, there are safety issues, such as elevated amounts of soluble organic in dry nitrate waste, that are difficult to address by sampling alone since they could involve relatively small inaccessible regions of waste within a tank.

Finally, in order to make sense out of the highly variable results that often come from a tank's waste assays, it is necessary to couch those results in terms of the particular process and storage history of that tank. The HDW model estimates provide just such a needed sitewide framework for each of the 177 Hanford tanks.

II. Approach

The HDW model is described schematically in Fig. 1. The model begins with a process and transaction dataset that derives from a variety of sources. From this dataset, a balanced tank-by-tank quarterly summary transaction spreadsheet is derived called the Waste Status and Transaction Record Summary (WSTRS). At the end of each quarter, all tanks' volumes are reconciled with their reported status at that time and in the process, unknown transactions are recorded to accommodate otherwise unexplained gains or losses at the end of each quarter.

Using these fill records, the Tank Layer Model (TLM) provides a definition of the sludge and salt cake layers within each tank. The TLM is a volumetric and chronological description of tank inventory based on a defined set of waste solids layers. Each solids layer is attributed to a particular waste addition or process, and any solids layers that have unknown origin are assigned as such and contribute to the uncertainty of that tank's inventory. The TLM simply associates each layer of sludge within a tank with a process waste addition. As indicated in Fig. 1, the TLM analysis depends only on information from WSTRS.

The Supernatant Mixing Model (SMM) is an algorithm written in C++ and installed as a spreadsheet macro that describes the supernatant and concentrates within each of the tanks. The SMM uses information from both WSTRS and the TLM and describes supernatants and concentrates in terms of kgal (1 kgal = 1,000 gal) of each of the process waste additions.

Together the WSTRS, TLM, and SMM define each tank's waste in terms of a linear combination of HDW sludges and supernatants. In order to provide information on the elemental composition of each tank, the Hanford Defined Wastes (HDW's) compositions describes each of the HDW's based on process historical information. Each HDW has both supernatant and sludge layers, its total amount of waste set by WSTRS, and its sludge volume determined by the TLM. Thus, the HDW compositions depend on all prior model components—process/transaction dataset, WSTRS, TLM, and SMM.

Each tank's total inventory is calculated as

$$\mathbf{tank}_i = \frac{\sum\limits_j tlm_{ij}\mathbf{hdw}_j^{sl}}{slVol_i} + \frac{\sum\limits_j smm_{ij}\mathbf{hdw}_j^{su}}{suVol_i}$$
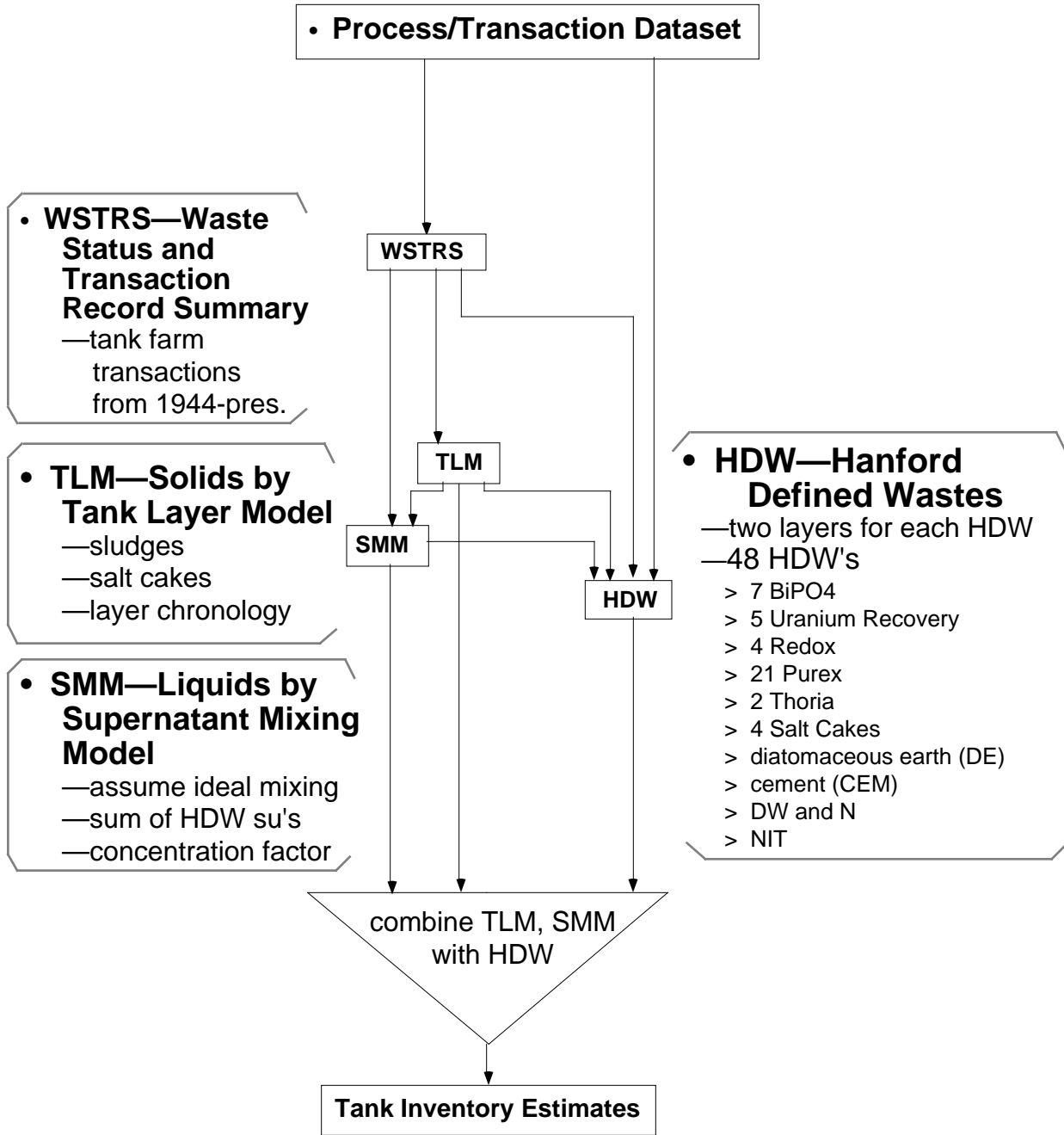
Fig. 1. *Schematic of overall strategy.*

where

tank$_i$	= composition vector for tank i
hdw$_j^{sl}$	= composition vector for HDW sludge j
hdw$_j^{su}$	= composition vector for HDW supernatant j
tlm$_{ij}$	= kgal of hdw sludge j for tank i
smm$_{ij}$	= kgal of hdw supernatant j for tank i
slVol$_i$	= sludge kgal for tank i
suVol$_i$	= supernatant concentrate kgal for tank i.

The first term is the TLM solids inventory and is reported as

$$\mathbf{tank}_i^{sl} = \frac{\sum\limits_j tlm_{ij}\mathbf{hdw}_j^{sl}}{slVol_i}$$

while the second term is the SMM inventory reported as

$$\mathbf{tank}_i^{su} = \frac{\sum\limits_j smm_{ij}\mathbf{hdw}_j^{su}}{suVol_i}.$$

These inventory estimates for each tank also appear in the Historical Tank Content Estimate reports for each of four quadrants.[1]

IIa. Approach—Waste Status and Transaction Record Summary

The WSTRS is a spreadsheet of qualified fill records[2] with information extracted from Jungfleisch-83[3] and Anderson-91[4], and checked by Ogden Environmental and LANL against quarterly summary reports. The WSTRS reports, although largely representative of the waste histories of the tanks, are nevertheless incomplete in that there are a number of unrecorded transactions that have occurred for many tanks. Included within the WSTRS report, then, is a comparison of the tank volume that is calculated based on the fill records that are present in WSTRS with the measured volume of each tank. This comparison is made for each quarter to record any unknown waste additions or removals that may have occurred during that quarter.

The Rev. 3 estimates include new information from the Logbook Dataset[5] and have extensive revisions in the latter four evaporator campaigns: 242-S (S1 and S2) and 242-A (A1 and A2). The Logbook Dataset contains extremely detailed tank level information from about 1975 to 1992 and has allowed Rev. 3 to accomodate the blending that occurred during these campaigns. In Rev. 1, each campaign's waste was blended over many years of operation, then concentrated in one single step and distributed over all the bottoms receivers. In contrast, Rev. 3 blends the evaporator concentrates on about a quarterly basis thereby providing much better representation of these evaporator campaigns.

Transactions were added to WSTRS to resolve the many unknown level changes for each quarter according to a set of rules resulting in an updated WSTRS that is known as Rev. 3. This unknown transaction resolution was only completed for all unknowns larger than 50 kgal, although many smaller transaction unknowns were

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[1]Brevick, C. H., et al., "Historical Tank Content Estimate of the Northeast (Southwest, Northwest, Southeast) Quadrant of the Hanford 200 East Area," WHC-SD-WM-ER-349 thru 352, Rev. 0, June 1994.

[2] (a) Agnew, S. F., et al., "Waste Status and Transaction Record Summary for the NE Quadrant" WHC-SD-WM-TI-615, Rev. 1, October 1994. (b) Agnew, S. F., et al. "Waste Status and Transaction Record Summary for the SW Quadrant, " WHC-SD-WM-TI-614, Rev. 1, October 1994. (c) Agnew, S. F., et al. "Waste Status and Transaction Record Summary for the NW Quadrant, " WHC-SD-WM-TI-669, Rev. 1, October 1994.

[3](a) Jungfleisch, F. M. "Hanford High-Level Defense Waste Characterization—A Status Report," RH-CD-1019, July 1980. (b) Jungfleisch, F. M. "Supplementary Information for the Preliminary Estimation of Waste Tank Inventories in Hanford Tanks through 1980," SD-WM-TI-058, June 1983. (c) Jungfleisch, F. M. "Preliminary Estimation of Waste Tank Inventories in Hanford Tanks through 1980," SD-WM-TI-057, March 1984.

[4]Anderson, J. D. "A History of the 200 Area Tank Farms," WHC-MR-0132, June 1990.

[5]Brevick and Gaddis, "Tank Farm Logbook Dataset," in preparation.

accommodated as well. The following rules were used for unknown transaction resolution for the various tank categories.

Evaporator feed and bottoms receivers:
During an evaporator campaign, unknown waste transfers at the end of each quarter are resolved by sending wastes to or receiving wastes from an evaporator feed tank for tanks identified as either bottoms receivers or feed tanks for those campaigns.

Self-concentrating tanks:
Certain tanks in S, SX, A, and AX farms were allowed to self concentrate. Any losses or additions to these tanks are assigned to condensate or water, respectively.

Sluicing receivers:
For tanks associated with a sluicing campaign (either UR or SRR), unknown transactions are resolved by either sending or receiving from the sluicing receiver tank for that campaign. Unassigned losses from the sluicing receivers, then, are sent directly to the process.

Salt-well pumping and stabilization:
If an unknown loss occurs during salt well pumping stabilization of a tank, then the unknown is resolved by sending waste to the active salt well receiver at that time.

Historical use of tank:
If none of the above rules apply, then the historical use of the tank is used to assign the transaction. For example, C-105 was used as a supernatant feed tank for the CSR campaign and supplied ~1,500 kgal per quarter for several years. However, there is one quarter (1971q2) where C-105 loses 1,748 kgal without an assigned transaction. Because of C-105Õs process history, this transaction is assigned to CSR feed. Likewise, there are a number of large supernatant losses in A and AX Farms during sluicing for sludge recovery. These supernatant losses are assigned as feed to AR, which are the slurries transferred to AR Vault for solids separation, washing, dissolution, and feed to SRR.

The transaction data set has sometimes an arbitrary and non-unique order for transactions within each quarter. This transaction order has been largely resolved for the period 1975-present, but not for all of the remaining tanks for this estimate. Thus, a certain "historical" error is present in these DST estimates that is largely related to transaction ordering errors from 1945-1975. These errors are not very serious for the DST's, since much blending has occurred since 1981, butthis transaction ordering should be completed for the entire history of Hanford in order to determine how it will affect tank inventories.

IIb. Approach—Tank Layer Model (TLM)

The TLM a solids layer model that uses the past fill history of each tank to derive an estimate of the types of solids that reside within those tanks. The TLM[6,7] is generated by reconciling the reported solids levels from WSTRS for each tank (as shown in App. C) with the solids volume per cent expected for each primary waste addition (see App. A). Note that a solid's model has already been extensively used at Hanford to estimate sludge and salt cake accumulation, the results of which are reported[8] monthly.

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[6](a) Brevick, C. H., et al., "Supporting Document for the Historical Tank Content Estimate for A Tank Farm," WHC-SD-WM-ER-308, Rev. 0, June 1994. Likewise, reports and numbers for each farm are as follows: AX is 309, B is 310, BX is 311, BY is 312, C is 313, S is 323, SX is 324, and U is 325. These supporting documents contain much of the detailed information for each tank farm in a concise format, all released as Rev. 0 in June 1994.

[7]Agnew, S. F., et al. "Tank Layer Model (TLM) for Northeast, Southwest, and Northwest Quadrants," LA-UR-94-4269, February 1995.

[8]Hanlon, B. M. "Tank Farm Surveillance and Waste Status and Summary Report for November 1993, "WHC-EP-0182-68, February 1994, published monthly.

There are some tanks that the HDW model assumes a different waste inventory than that reported in Hanlon. This differences come aboutbecause of the difficulties that are often encountered in determining the remaining inventory in tanks with large surface heterogeneities. Also shown in App. C, then, are a list of tanks for with their Hanlon volumes and their adjusted volumes used for the HDW estimates. The sources of these discrepancies are a series of reports about stabilized tanks.[9]

The TLM is a volumetric and chronological description of tank inventory based on the HDW sludges and salt cakes. Each solids layer is attributed to a particular waste addition or process, and any solids layers that have unknown origin are assigned as such and contribute to the uncertainty of that tank's inventory. The TLM simply associates layers of solids within each tank with a waste addition or a process campaign.

The TLM uses the information obtained from the transaction history for each tank to predict solids accumulations. These predictions are made for three categories of waste tanks. The first category involves primary waste additions, which are the waste additions from process plants directly into a waste tank. The primary waste transactions are used along with solids volume reports for each tank to derive an average volume per cent solids for each HDW type. The solids accumulations are, then, also assigned to a particular HDW for the tanks where the solids information is missing or inconsistent.

A second category of waste is that where solids accumulate as a result of evaporative concentration of supernatants. All solids that accumulate in such tanks occur after they have been designated as "bottoms" receivers. These solids are assigned to one of four salt cakes, which are defined as blends over entire evaporator campaigns. The four salt cakes are BSltCk, T1SltCk, BYSltCk and RSltCk, are all defined as HDW's. The latter five evaporator campaigns T2, S1, S2, A1, and A2 all result in waste concentrates that are defined differently for each tank within the SMM.

The third category of waste is that where solids accumulate due to tank to tank transfers of solids. This category allows solids to cascade from tank to tank, for example, or accounts for solids lost during routine transfers, as was common with decladding wastes CWR and CWP, 1C , or FeCN sludges.

The results of the TLM analysis are a description of each tank's solids in terms of sludge and salt cake layers. Although interstitial liquid is incorporated within the composition for sludges and salt cakes, any residual supernatants that reside in these tanks above the solids are described by the SMM. The output of the TLM, then, can only be used to predict the inventory of the sludges and each of four salt cakes that reside within waste tanks. These TLM results are inserted into the WSTRS record and are used by the SMM in considering excluded volumes for mixing of waste supernatants.

Not all of the transactions that have occurred in the past are faithfully recorded by the WSTRS data set. Therefore, WSTRS is an incomplete document with many missing transactions. However, the two critical pieces of information that are used in the TLM analysis are the primary waste additions and the solids level measurements, both of which are well represented in WSTRS.

The missing transactions largely involve tank-to-tank transfers within WSTRS. These missing transactions, which are salt cake, salt slurry, and supernatant, do lead to a larger uncertainty for the compositions of the concentrated products from evaporator operations. As many as 25% of all transactions may be missing from this data set, perhaps as many as 60-80% of these missing transactions are associated with the evaporator operations. Although this information might be recovered in the future, the HDW model strategy at this time resolves as many of these unknown transactions as possible with the rules stated above.

Sludge Accumulation from Primary Waste
The TLM analysis associates a solids volume percent (vol%) with each primary waste stream. These solids vol% are those that are consistent with the solids volumes reported in Anderson-91 by comparing those solids accumulations with the primary waste additions that are recorded in WSTRS. The result of this analysis is a solids

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[9] (a) Swaney, S. L. "Waste Level Discrepancies between Manual Level Readings and Current Waste Inventory for Single-Shell Tanks," Internal Memo 7C242-93-038, Dec. 10, 1993. (b) Boyles, V. C. Boyles ÒSingle Shell Tank Stabilization Record,Ó SD-RE-TI-178 Rev. 3, July 1992. (c) Welty, R. K. ÒWaste Storage Tank Status and Leak Detection Criteria,Ó SD-WM-TI-356, September 1988.

volume percent for each waste type with a range of uncertainty associated with the inherent variability of the process.

Not all of the waste types have adequate solids reports associated with them. For these waste types, a nominal value is assigned based on similarity to other waste types where there exists a solids vol%. For example, a total of 810 kgal of Hot Semi-Works waste (HS) was added to several tanks in C Farm, but these additions only constituted a small fraction of the total solids present in any of these tanks. Therefore, a nominal 5 vol% solids is assigned for that waste type.

Each TLM spreadsheet table shows the primary waste additions and the solids from those additions based on the characteristic vol% for that waste type. The TLM compares this prediction with the solids level reported for the tank and indicates either an unknown gain or loss for this tank. Once a layer is "set" in the tank, its volume appears in "Pred. layer" and type in "Layer type", thus comprising a chronological layer order from the bottom of a tank to the top, where each layer is described in terms of a volume and a type. Note that lateral variations are not accounted for in this model, and therefore this model only derives an average layer thickness. The TLM does not include any lateral distribution of those layers, which can in some cases can be quite extreme.

There are two main sources for variations in the solids vol% for each waste type. First, there is an inherent variability in each process stream, which is largely attributable to process variations. Second, solids can be added to or removed from tanks by inadvertent (or purposeful) entrainment during other supernatant transfers. In addition to these sources of variation, there are a number of other minor sources of solids changes such as compaction, subsidence following removal of salt well liquid, and dissolution of soluble salts by later dilute waste additions. Other solids variations may be due to metathesis and other chemical reactions within the tanks, such as degradation of organic complexants over time.

The TLM assigns solids changes to variability when they fall within the range established. If a change in solids falls outside of this range, the TLM associates the gain or loss of solids with a waste transfer to or from another tank or to dissolution of soluble salts in the upper existing solids layers.

Diatomaceous Earth/Cement

Diatomaceous Earth, an effective and efficient waste sorbent material, was added to the following waste storage tanks BX-102 (1971), SX-113 (1972), TX-116 (1970), TX-117 (1970), TY-106 (1972), and U-104 (1972). The additions of diatomaceous earth were used to immobilize residual supernatant liquid in tanks where the liquid removal by pumping was not feasible. The conversion factor in the TLM for Diatomaceous Earth (DE) is 0.16 kgal/ton and Cement (CEM) or (CON) is 0.12 kgal/ton. The CEM waste was only added to one tank, BY-105 (1977).

Salt Cake Accumulation

Once a tank becomes a "bottoms" receiver, the TLM assumes from that point on that any solids that accumulate are salt cake or salt slurry. Salt cake can be any one of four different types, depending on which evaporator campaign created it. These are B (242-B), T1 (early 242-T), BY (ITS #1 and #2 in BY Farm), and R (Redox self-concentrating tanks). **Table 2** describes the various evaporator campaigns that resulted in concentration of waste and precipitation of solids at Hanford. For salt cake accumulation, the TLM assumes that all of the solids reported are salt cake. Two other minor evaporation campaigns involved use of Redox and B Plant evaporators for tank wastes. These minor campaigns have been associated with T2 or S1 campaigns, respectively.

The HDW model assigns waste of the five later campaigns for 242-T, 242-S, and 242-A evaporators as concentrates within the SMM. These later concentrates correspond roughly to what is known as double-shell slurry (DSS) or double-shell slurry feed (DSSF), although their early concentrates are often referred to as salt cake as well.

IIc. Approach—Supernatant Mixing Model (SMM)

The third step is to describe the composition of supernatants and concentrates within each of the tanks (note that interstitial liquid is part of the TLM sludge and salt cake definitions, not the supernatant). To accomplish this, an ideal mixing model has been developed, called the Supernatant Mixing Model. This model describes supernatants in terms of original kgal (1 kgal = 1,000 gal) of each of the HDW supernatants. The SMM is a very critical part of the definition of waste in double-shell tanks (DST's) where a large fraction of the waste supernatants now reside. For single-shell tanks, the SMM contributes largely to the composition of concentrated wastes. A block diagram of the SMM approach is shown in Fig. 2. The fundamental assumptions used for this model are ideal mixing of each tank's free supernatant volume throughout its history. In particular, the volume of solids layers within each tank defined by

the TLM are excluded from mixing with any supernatant additions. In addition, all evaporator feed to and from 242-A, 242-S, and the latter 242-T operations are treated as free supernatant in all tank transactions.

The SMM calculation reads transaction information from WSTRS, sorts it to a date order, and performs a transaction by transaction accounting of all of the tank waste transactions for the history of Hanford. This algorithm accounts for residual solids accumulation as per the TLM above.

The SMM provides a description of each tank's free supernatant and supernatant concentrate based on a linear combination of Hanford Defined Waste (HDW) supernatants. The HDW supernatants have been reported in the Waste Status and Transaction Record Summaries for that tank. This linear combination of HDW supernatants represents a total volume that is usually larger (sometimes smaller) than the actual volume of free supernatant within each tank. This is because active evaporation (or dilution) of the waste during its history.

Each tank's SMM waste vector is expressed in terms of a linear combination of HDW supernatants, which in turn are used to predict a chemical and radionuclide inventory with compositions provided by the HDW (or other sources). The SMM does not allow mixing with TLM solids that have precipitated from primary waste streams. However, those solids that resulted from the later concentrator operations 242-A, 242-S, and latter 242-T, are treated as supernatants within the SMM.

SMM and TLM Output Tables

The output of the Supernatant Mixing Model is a table whose column headings are the HDW's and auxiliary wastes and whose rows are the waste tanks and processes. The auxiliary wastes are water, unk, swliq, and gas and do not appear on the HDW waste list. These auxiliary wastes are used for tracking of unknowns, evaporator runs, and gas retention in waste concentrates. The SMM table's columns (see App. D) show the HDW distribution among the tanks and processes for a particular time. These are given in kgal of original HDW supernatant. The linear combination of HDW supernatants represent a total volume that is usually larger (but sometimes smaller) than the actual volume of free supernatant or concentrate within each tank. The reason that the SMM volume differs from the tank volume is because of active evaporation or dilution of a tank's waste.

The TLM tables are also shown in App. C and follow roughly the same format as the SMM tables. There is no concentration effect with the TLM solids and so the row sum of the TLM for each tank is equal to the TLM volume for that tank.

IId. Approach—Hanford Defined Wastes (HDW)

The fourth step in the strategy is to provide chemical and radionuclide concentrations for each of the Hanford Defined Wastes[10] (HDW's). The HDW's begin with inputs of radionuclide and stable chemicals, both of which are used to define the total species in each waste stream (see Fig. 3, campaign and chemicals added). These total species are then separated into two layers, a sludge and a supernatant, that result in different concentrations of species for the two layers.

Each species is precipitated according to a single point solubility and ions precipitated in more than one salt are simply successively precipitated. Thus, the solids that precipitate are merely representative of the actual solids and are not meant to reflect the actual solids distribution. Because the supernatant is also present in the interstices of the sludge layer, this "supernatant" is included within the sludge composition. The solubility of each species is set by a macro that, when run on the HDW spreadsheet, adjusts the fraction precipitated parameter so that the supernatant concentration is equal to or less than the target solubility.

The sludge and supernatant compositions are each expressed in mol/L for the stable chemicals, with water and TOC as wt% and radionuclides in μCi/g and Ci/L, respectively. Each waste is kept in ion balance according to the oxidation states assumed for that species. The sludge and supernatant layers are also expressed in terms of ppm composition, for which are kept a mass balance as well. However, the
mass balances are limited by differences among water, oxide, and hydroxide with the various solids to only within ±2%.

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[10]Agnew, S. F., et al., "Hanford Defined Wastes: Chemical and Radionuclide Compositions," LA-UR-94-2657, Rev. 2, September 1995.
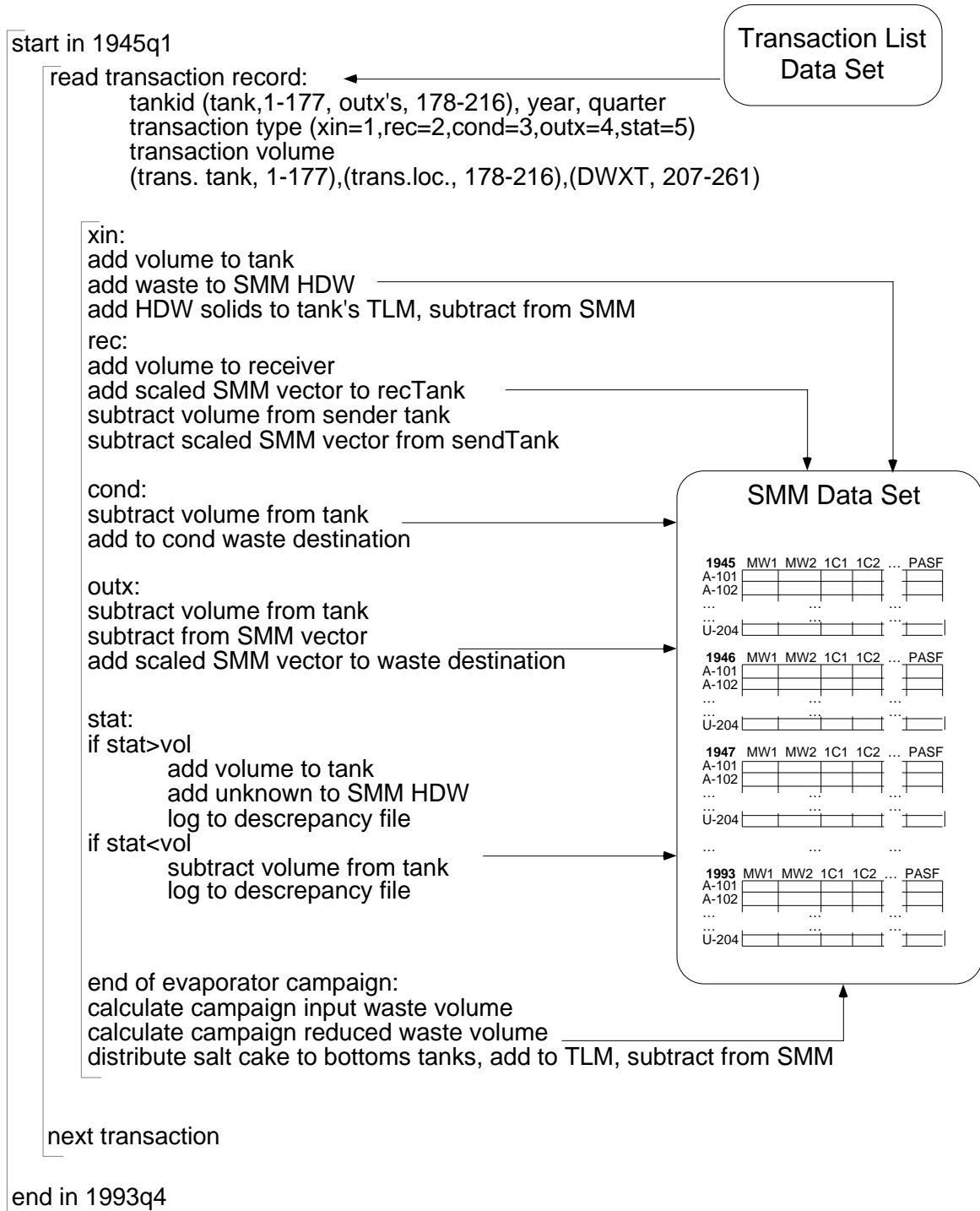
Supernatant Mixing Model
Block Diagram

Transaction List Data Set

start in 1945q1

read transaction record:
tankid (tank,1-177, outx's, 178-216), year, quarter
transaction type (xin=1,rec=2,cond=3,outx=4,stat=5)
transaction volume
(trans. tank, 1-177),(trans.loc., 178-216),(DWXT, 207-261)

xin:
add volume to tank
add waste to SMM HDW
add HDW solids to tank's TLM, subtract from SMM

rec:
add volume to receiver
add scaled SMM vector to recTank
subtract volume from sender tank
subtract scaled SMM vector from sendTank

cond:
subtract volume from tank
add to cond waste destination

outx:
subtract volume from tank
subtract from SMM vector
add scaled SMM vector to waste destination

stat:
if stat>vol
add volume to tank
add unknown to SMM HDW
log to descrepancy file
if stat<vol
subtract volume from tank
log to descrepancy file

end of evaporator campaign:
calculate campaign input waste volume
calculate campaign reduced waste volume
distribute salt cake to bottoms tanks, add to TLM, subtract from SMM

next transaction

end in 1993q4

SMM Data Set

1945 MW1 MW2 1C1 1C2 ... PASF
A-101
A-102
...
U-204

1946 MW1 MW2 1C1 1C2 ... PASF
A-101
A-102
...
U-204

1947 MW1 MW2 1C1 1C2 ... PASF
A-101
A-102
...
U-204

1993 MW1 MW2 1C1 1C2 ... PASF
A-101
A-102
...
U-204

Fig. 2. *Block Diagram of SMM algorithm.*

—10—

Block Diagram of HDW Spreadsheet

Campaign Information, pp. 1*-3
—fuel processed
—exposure
—total waste
—average waste rate
—Pu extraction efficiency
—nuclide source terms
—solids vol%
—CSR input

Chemicals Added, pp. 4-6
—mostly based on tons fuel
—others concentration
—NaOH added to neutralize

**p. 1 refers to Appendix pages
with HDW spreadsheets.*

Species Total (mol/L), pp. 7-9

Sludge (mol/L), pp. 10-12

Supernatant (mol/L), pp. 13-15

Solids Conc. (mol/L), pp. 16-18

repeat until
su‡ species
match targets

Solids Volume (cc/L), pp. 19-21

solubility macro
or by hand

(‡su = supernatant)

Fraction Precipitated as solids, pp. 22-24

Sludge (ppm), pp. 25-27

calculate blends
as weighted
averages of HDW
su's

Supernatant (ppm), pp. 29-30

Supernatant to Evaporator Campaigns,
Nitrate to Nitrite to Ammonia Radiolysis,
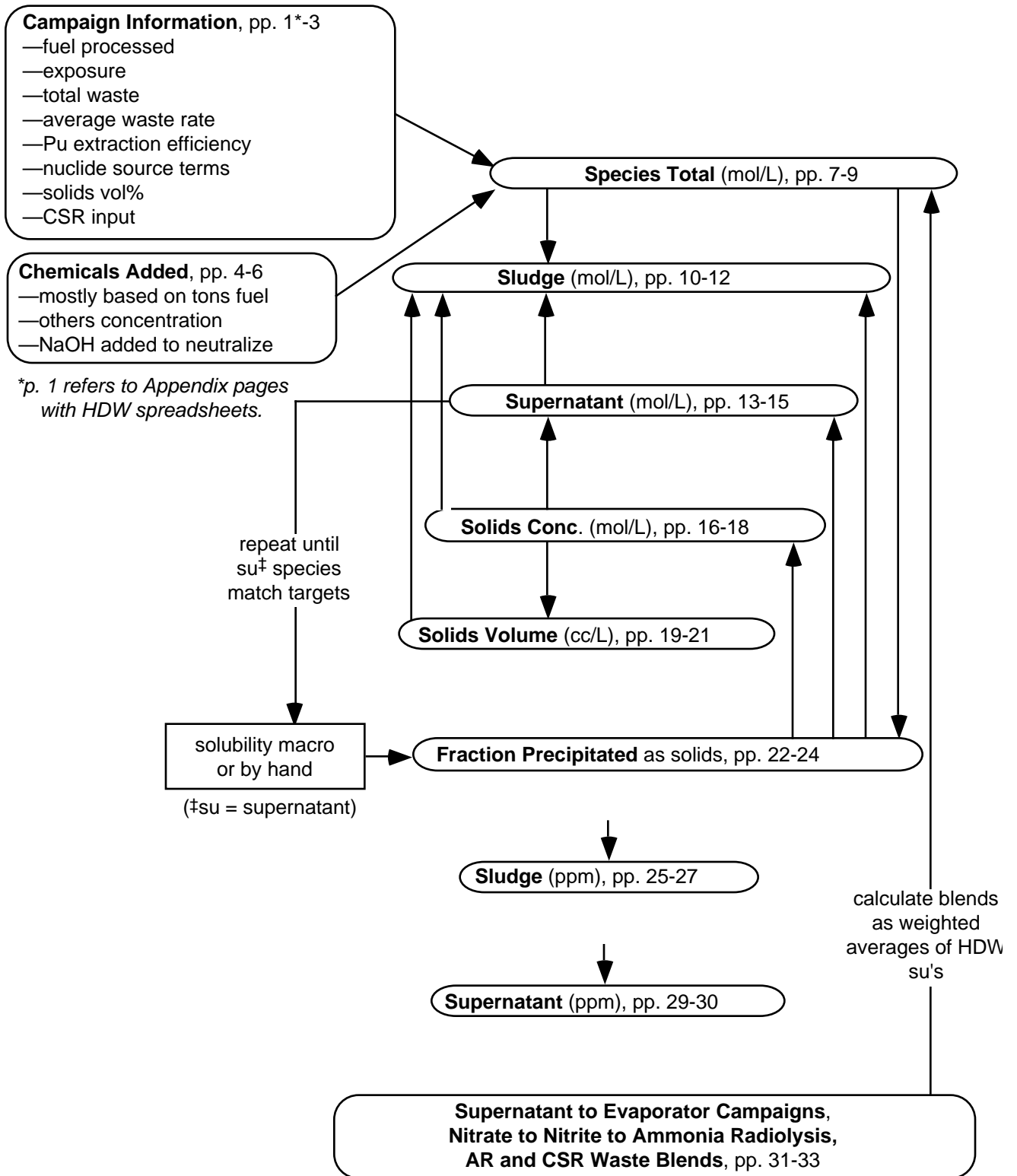**AR and CSR Waste Blends**, pp. 31-33

Fig. 3. *Block Diagram of HDW spreadsheet .*

III. Results and History of Revisions

Appendix E shows the composition and inventory for each of the 177 Hanford Waste tanks. Each tank is described by three tables and each table comprises three columns of information. Two columns describe the analyte concentrations as mol/L and ppm and the third column expresses the tank inventory in kg or MCi (1 MCi = 1e6 Ci). The three tables represent TLM solids blend, SMM liquids blend, and total composite tank concentrations and inventories. The TLM solids composition and inventory represents the volume average blend of all of the TLM solids layers. Note that among the TLM solids definitions are four salt cake concentrates: B, T1, R, and BY. Therefore, the TLM solids inventory definition includes sludges and some salt cake.

The second table for each tank represents the SMM composite inventory for liquids and concentrates. This table represents inventories from evaporator concentrates termed T2, S1, S2, A1, and A2. Note that these concentrates actually include a lot of solids but are treated nevertheless as homogeneous mixtures that can be pumped, blended, and moved to other tanks as though they were liquid.

The HDW model provided its first estimates in June of 1994 as Rev. 0 for the NE and SW quadrants. This early revision was based on single waste types for salt cake and salt slurry for the entire site. Revision 1 was actually the first complete site inventory and was completed in Fall of 1994 for the three SST quadrants, NE, SW, and NW, while Rev. 1 for the DST SE quadrant was completed in March 1995. These estimates included many bug fixes and other corrections and also included additions for process vessel corrosion source terms (adds Fe, Cr, and Ni) as well as a hard water Ca source term. However, the Cs-137 and Sr-90 inventories were calculated too high by about 20% and all evaporator campaigns were blended into multi-year composites. These evaporator blends were an improvement over the single waste types for salt cake and salt slurry in Rev. 0, but still represented an approximation for individual tanks. Essentially, these evaporator blends were excellent representations of the total waste into a campaign and its total volume reduction, but were distributed across perhaps ten or twenty different slurry receivers that were involved in each campaign.

The next step with the HDW Estimates, Rev. 2, was an attempt to express the five later evaporator campaigns on a tank by tank basis. The SMM provided the waste concentrate history step by step throughout each of the evaporator campaigns. Revision 2.1 represents a bug fix in the spreadsheet that incorrectly calculated water and TOC and another problem with miscalculation in SX Farm. This revision was based on the HDW Rev. 2 compositions, which had improved the Cs-137 and Sr-90 inventory calculation and had included chloride and potassium source terms that piggyback on the NaOH additions. Various other bug fixes and changes and additions were a mercury source term used in the decladding process, adjustments on the wastes from UR (Uranium Recovery), slight realignments of 1C and 2C waste campaigns, and other minor changes. Revision 2 also reduced the process vessel corrosion source term (Fe, Ni, Cr) for early BiPO4 wastes and decladding wastes consistent with the fact that these processes were much less corrosive than either Purex or Redox.

The Rev. 2.1 estimates nevertheless had some problems. The most significant problem was the incomplete transaction records for the later evaporator campaigns caused incorrect distribution of waste concentrates. In particular, some tanks were impossibly over concentrated (Na in excess of 16-17 mol/L), while other slurry receivers were more dilute than they should have been. It was clear that there were severe problems in waste misdirection with Rev. 2.

To correct these problems, the Rev. 3 estimates have extensively modified WSTRS by adjusting the evaporator transactions to blend on a per quarter basis and for some quarters, wastes have been blended on an even finer time scale. This improvement in the transaction record was largely accomplished by use of a draft version of the Logbook Dataset[5], constructed by ICF Kaiser for WHC and not yet published. Also used is an extensive set of reports from evaporator operations for 242-S and 242-T. Unfortunately, there was a lack of detailed information about the 242-T evaporator operation.

The overall inventories for the analytes have not changed significantly except for lead, manganese, and oxalate. Lead site inventories increased dramatically in Rev. 3 since these estimates included the lead coating that covered each fuel slug. This turns out to be a major source of lead in the waste tanks and the total lead inventory increased from 3 to 280 mT. There was also an error in the concentration of manganese in OWW2, which upon correction lowered the manganese site inventory from 219 to 39 mT. The oxalate inventory increased from 23 to 69 mT because of a decrease in its solubility limit. Since 224 waste supernatant was all cribbed, decreasing oxalate solubility retains more in the waste tanks and this was the only oxalate source term.

IV. Uses and Limitations of HDW Model Estimates

The HDW Model Rev. 3 estimates represent a Hanford site inventory based on process history that is compatible with the waste types, compositions, and processing history of the site. The total site estimates will not change appreciably in the future unless the wastse source terms for the various waste streams change, but it is still possible that changes in the transaction record will alter the inventory estimates of individual tanks. All estimates are valid as of 1-1-94 and Sr-90 and Cs-137 are both decayed to the same date. Therefore, these estimates do not account for the latest evaporator campaign in '95-'96, which moved and blended large amounts of waste supernatants in the DST's.

The HDW estimates are the first complete, total, ion and mass balanced inventory estimates yet provided on a per tank basis. As such, they have immediately shown that: site sodium inventory has been traditionally overestimated by about one third. Whereas previous site estimates for sodium were around 71,000 mT (mT = metric tonnes), the HDW estimate show only 40,000 mT are actually now in either the DST's or the SST's. This difference is largely due to the large amount of waste supernatant that was sent to crib, some 20,000 mT, but is also due to more subtle double counting of waste stream chemicals that has occurred in the past.

These estimates have also shown an increase in the iron inventory, which the HDW model now estimates at 1,830 mT (1,610 in the SST's and 220 in the DST's) as compared to previous estimates of 710-730 mT. These total site estimates are shown in App. E along with estimates for individual tanks.

The site inventory estimates include totals for waste sent to the cribs as well as totals for leaks with measurable volume losses. Note that the leaks from waste tanks are only a small fraction of the total inventory sent to the ground, constituting only 10% of the 2.2 MCi of Cs/Sr activity and only 2% of the 48 kg of Pu that was sent to the soil column. Thus, the amount of activity intentionally sent to the soil column dwarfs the activity inadvertently placed into the ground by leaks and spills.

There are still problems with these estimates. The evaporator blending and SMM approach naturally produce blending averages for waste supernatants that were processed during each quarter. The actual blending that occurred during these quarters may not be exactly represented in this approximation. This blending error then contributes to the overall variability in the waste predictions.

Another problem with the HDW model is that precipitated solids from waste concentration do not remain in the slurry receiver during evaporator runs. That is, liquid that is drawn from each bottoms tank following cooling is always removed as a blend of the total concentrate. This leads to an under concentration of the bottoms receiver and correspondingly an over concentration of tanks that receive and further blend and concentrate the recycled liquors. This effect systematically shifts concentrate from early receivers to later receivers and therefore increases the variability of the estimates by introducing a systematic bias in early versus late concentrates.

V. Uncertainty for the HDW Estimates

There are two main origins of variability within the HDW model—process variability (results in variability of hdw's) and transaction variability (results in variability in tlm and smm factors). Since process variability affects the HDW compositions and transaction variability affects the SMM/TLM factors, these two variabilities will be additive in the final inventory estimates.

Quantification of Process Variability

Starting with the hypothesis that the waste rate variability is the most direct measure of process variability and therefore of HDW compositional variability, the two sources of waste rate variability are:

1) Rework processing. For a given amount of fuel processed during a campaign, early batches needed to be reworked more often than later batches because the separations failed to achieve the necessary decontamination or separation factors. Note that for rework, the chemicals in the waste scale linearly with the waste volume but the radionuclides will be diluted by increasing rework;

2) Ancillary processing resulting in primary waste dilution. There are many ancillary waste streams that derive from various cell cleanup and vessel cleanout activities. These activities by and large add very little or no chemicals or radionuclides to the waste stream. Therefore, to a first approximation, this variability simply dilutes or concentrates the waste stream. This dilution or concentration simply changes the relative supernatant and sludge inventories of each component.

This approach completely neglects chemical source term variability, which derives from measurement errors during processing. This variability is in the range 3-5% and will therefore be bounded by the two main sources noted above.

The variability of every process waste rate will actually be a combination of rework and ancillary processing and there is little information about what this combination is. Assuming that the amount of chemicals used scales linearly with the volume of the waste produced for rework processing, the waste compositions within each tank will actually be independent of the amount of process rework (radionuclides, however, will be reduced in concentration by the increase in rework.)

This approach subtracts a linear trend from each waste rate due to rework over the period of a campaign and makes the assumption that the resultant variability of the waste composition is wholly attributable to ancillary processing. This results in waste composition variabilities that should be equal to or greater than the true waste composition variabilities. In principle, the HDW model would need more information to assign the correct fraction of waste rate variability to process rework.

With these assumptions in hand, an uncertainty for each HDW (Hanford Defined Waste) can be derived by resolving each HDW analyte for its upper and lower limits. An RSD (Relative Standard Deviation) for each HDW results in a set of upper and lower compositions for each component of each HDW. Note that these relative variabilities will be different in general from the overall RSD for each HDW. This is because of the fact that the solution concentrations of semi-soluble species are directly linked to their sludge inventories.

Finally, there is a fundamental correspondence that relates a tank's waste volume to a corresponding waste stream variability. That is, if a tank contains 75 kgal of a waste sludge, then the waste rate variability must be calculated for the time that it took to deposit that 75 kgal of sludge.

This is a very important point. A manifestation of waste heterogeneity within a tank is that the larger the waste sample taken from a tank, the more representative that sample will be to the mean value for that waste type. The waste rate variability quantitates that relationship. It means that the smaller the sample of waste in an assay, the less representative that assay will be for tha tank contents and therefore a larger margin will occur for comparison of that assay to the HDW estimates. Conversely, the larger the amount of waste sampled, the better it will represent the tank's waste and the smaller will be the margin for HDW estimate comparisons.

There are fourteen tanks in S and SX Farms that hold nearly all of the R1 sludge, averaging 75 kgal each. Thus, each tank's sludge represents about two quarters worth of accumulation, and the variability is 12%, ranging from 10-16% depending on exactly how much sludge is in a given tank.

Most of the R2 waste sludge is on average distributed 30 kgal each among 7 tanks. At 30 kgal, the variability will be 13%, and will range from 10-16% for that set of tanks as well. It is interesting to note that despite the very different Redox campaigns, the waste rate variabilities are very similar.

There are two basic parameters from this variability analysis; a waste rate variability and a waste rate trend. The waste rate variability represents a dilution of all species while the waste rate trend does not change the chemical composition at all, since chemicals added remain proportional to waste volume. On the other hand, there will be a bias in the radionuclide concentration through a campaign as a result of the waste rate trend. Radionuclides will be more dilute early in the campaign and more concentrated late in the campaign. Thus, there is an extra source of variability for radionuclides within each campaign that is tied to the waste rate trend parameter.

For example, the waste rate trend for R1 is ±73% of the mean over the campaign, which places an effective RSD for the radionuclides at ±50%. Thus, while the chemical composition variability for these tanks is within an RSD of ±12%, the radionuclides vary with an RSD of ±50%.

Quantification of Transaction Variability

There are three contributions to transaction variability; evaporator blending, concentrate carryover, and of course, inaccurate transaction information. As regards to inaccurate information, it is not possible to derive meaningful uncertainty estimates about what is not known. Therefore, variability estimates are only possible for the first two contributions.

Evaporator blending and concentrate carryover are now both approximations used within the HDW model. Evaporator blending assumes that all of the waste feed for a given time can be blended together and reduced in volume as a blend and then transferred to a bottoms receiver. In reality, this process was continuous feed and continuous volume reduction.

Concentrate carryover is an approximation within the HDW model whereby all liquids that are removed and recycled to the evaporator from a bottoms receiver are assumed to be homogeneous mixtures of the entire concentrate inventory of each tank. This approximation is valid for dilute wastes but increasingly invalid as wastes are concentrated. That is, waste concentrates are returned to the tanks from the evaporator and allowed to cool, sediment, and gel. Then, residual liquid is removed from these tanks and often reblended and further concentrated. The HDW model allows concentrated waste to be "carried over" into later receivers because of its assumptions and limitations. This represents a second major source of variability within the model, but it only affects concentrates.

Although these arguments provide a basis for transaction variability esimates, the task is not yet completed and therefore are not yet included in HDW Rev. 3 estimates.

VI. Summary

The HDW Rev. 3 estimates are the latest in a developing model of the tank waste inventories at Hanford. The HDW model variability estimates are not yet complete and the comparison of HDW estimates with analytical assays is also in progress. Both of these tasks are ongoing and represent the "bottom line" for the model validity.

Note, though, that comparison of HDW model results with assay data is more complex than just comparing one estimate with another. To derive a tank inventory from assay data for waste samples from within a tank is not a trivial task in and of itself. The extremely heterogeneous wastes within each tank make representative sampling problematic and this is compounded by limited access to the tank waste. Therefore, when comparing inventory estimates based on waste assays with the HDW model, one is actually comparing one model with another model and both models have significant uncertainties. Therefore, comparisons are often more effective if they are made among tank groups with similar process histories. Such grouping strategies can be very important in comparisons between assay data and HDW predictions.