



Department of Energy

Washington, DC 20585

APR 04 2006

The Honorable A. J. Eggenberger
Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue, NW, Suite 700
Washington, DC 20004-2901

Dear Mr. Chairman:

I am forwarding you the enclosed Department of Energy's (DOE) plan for returning the Savannah River Site's (SRS) Tank 48 to active waste service and a technical report on the proposed allowable organic residuals in the tank. These documents complete commitments 3.8 and 3.9 of the DOE's Implementation Plan for Recommendation 2001-1 for *High-Level Waste Management at the Savannah River Site* to complete a technical evaluation of acceptable Tank 48 residual levels and to develop a plan and schedule for Tank 48, respectively.

The plan outlines that the intended Tank 48 recovery methodology will be aggregation of the current Tank 48 waste and disposal of the material in the Saltstone Disposal Facility consistent with the Secretarial approved 3116 Determination. In parallel, DOE plans to continue research and development activities for alternative treatment technologies, such as wet-air oxidation and steam reforming, for the treatment and destruction of the organic material in the Tank 48 waste and the associated rinse solutions to a level that the waste can be reintroduced into the general Tank Farm system. DOE is committed to having Tank 48 returned to active service by January 2010.

The technical report on residual organics outlines that the current limit for organics in a nominal waste tank can be significantly increased for Tank 48 provided some limitations are imposed on its utilization. These limitations are consistent with the planned utilization in salt waste processing for Tank 48.

If you have any further questions, please call me at (202) 586-0738 or Mr. Dae Y. Chung, Acting Deputy Assistant Secretary for Integrated Safety Management and Operations Oversight, at (202) 586-5151.

Sincerely,

A handwritten signature in cursive script that reads "Inés R. Triay".

Dr. Inés R. Triay
Chief Operating Officer for
Environmental Management

Enclosures

cc: Mark B. Whitaker, Jr., DR-1
Jeffrey Allison, SR




**Plan and Schedule for Tank 48H Disposition by
Aggregation**

CBU-SPT-2006-00064
Revision 2

April 4, 2006

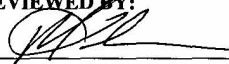
PREPARED BY:



R. H. Spires, Tank 48 Project Owner

4-4-06
Date

REVIEWED BY:



M. A. Lindholm, Manager, Salt Integrated Projects

4/4/06
Date

Plan and Schedule for Tank 48H Disposition by Aggregation

Tank 48H currently contains approximately 240,000 gallons of salt solution containing about 19,000 kg of tetraphenylborate (TPB) salts generated during the 1983 In-Tank Precipitation (ITP) Process demonstration and subsequent operation of the ITP facility in 1995 and 1996. TPB bearing material has the potential to decompose to benzene under certain conditions resulting in a flammability concern. Successful disposition of the material in Tank 48H and return of the tank to tank farm service is essential for having Tank 48H available to feed the future Salt Waste Processing Facility (SWPF). The need date for Tank 48H to be returned to service is January, 2010 to avoid impacts to the waste processing plan currently being finalized.

Several evaluations of methods to disposition Tank 48H TPB over the last several years have continued to show that aggregation is a preferred option. The evaluations considered attributes such as technical maturity and impact to system in addition to cost and schedule. Using aggregation, the waste in Tank 48H will be processed without further removal of radionuclides by combining the Tank 48H stream with another salt waste stream, currently planned to be the low-activity liquid recycle waste stream from DWPF. The two waste streams will be aggregated to ensure the processing limits for allowable organic content at Saltstone are not exceeded. The aggregated low-activity waste stream will then be transferred to the Saltstone facility feed tank.

The existing flammability controls for Tank 48H will remain in place including a minimum free hydroxide limit, a liquid level control and requirements for nitrogen inerting. A dedicated transfer path will be installed to reduce the potential for spreading TPB to other tanks through common piping and to minimize the impact to Tank Farm operations. Modifications will be installed on Tank 50H to safely manage the TPB. Tank 50H will be modified to include a vapor space mixing capability to prevent localized accumulation of flammable vapor. Interlocks will be installed to stop slurry pump operation on high temperature and high flammable concentration. While the Documented Safety Analysis will be modified to extend controls for TPB salt decomposition to Tank 50H, no new accidents have been identified to date. The flammability controls proposed for Tank 50H are similar to the controls currently implemented within the Liquid Waste Disposition Area Project. To ensure that the Saltstone Disposal Facility can also safely handle the TPB, inerting of the vaults is being explored. The baseline schedule for these projects and the subsequent Tank 48H waste disposition meet the need for tank space and SWPF feed preparation.

Although aggregation is the baselined option to disposition the TPB, the plan is to continue to develop alternative technologies in parallel. Research and development is ongoing for alternative treatment technologies, such as Steam Reforming and Wet Air Oxidation (WAO), for the treatment and destruction of the organic material in the Tank 48H waste and the associated rinse solutions to a level that the waste can be reintroduced into the general tank farm system. While research and development continues, the Savannah River Site will continue to move forward with the aggregation approach, described in the 3116 Determination, to dispose of Tank 48H organic-laden waste

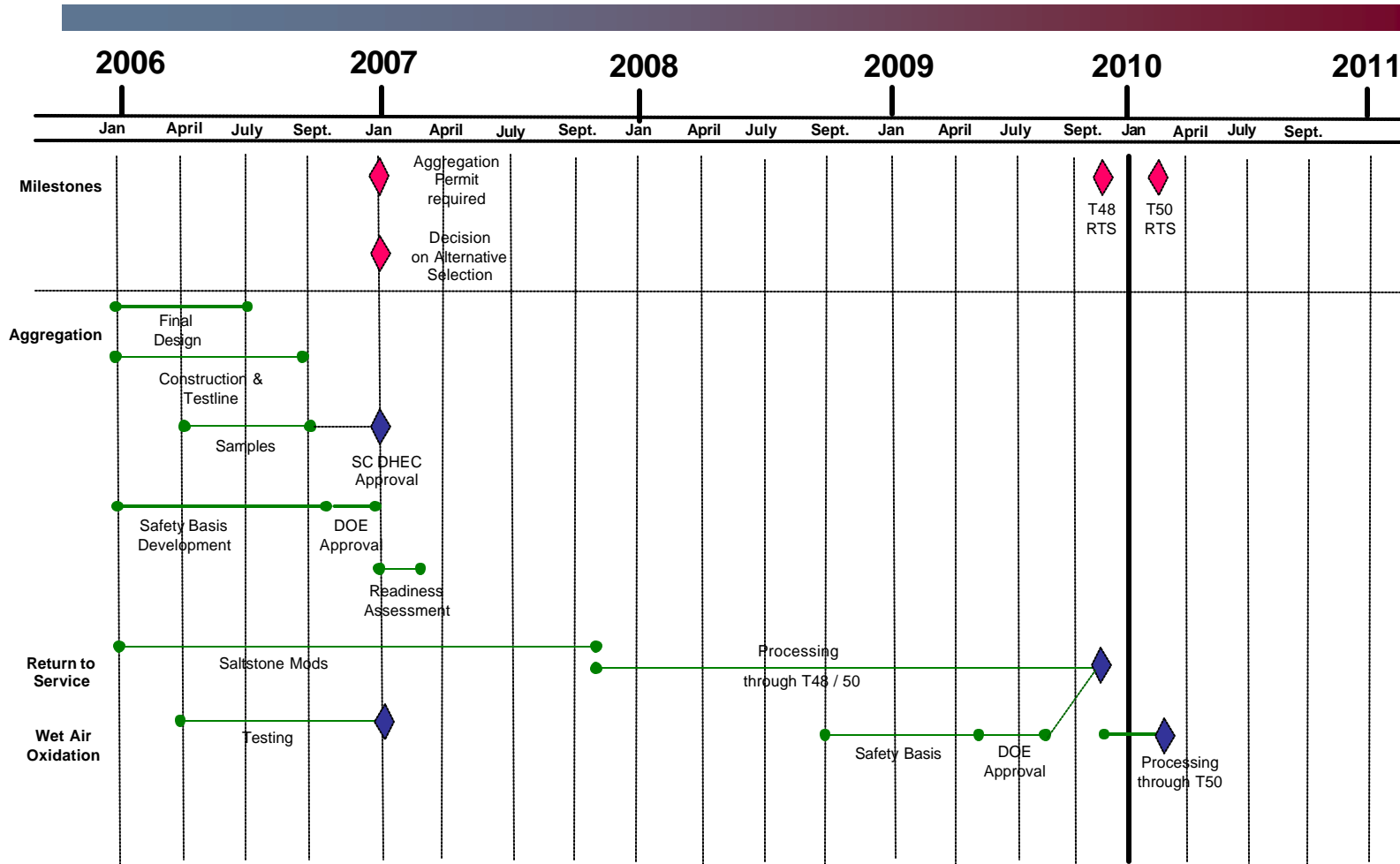
through aggregation of Tank 48H material with other low-level waste streams (as part of the DDA processing) and disposal in the Saltstone Disposal Facility.

WAO is an aqueous process in which soluble or suspended waste components are oxidized using oxygen contained in air. The process operates at elevated temperatures and pressures typically ranging from 100-320°C and 1500 -2000 psi. The products of the reaction are CO₂ and H₂O. Steam Reforming uses a fluidized bed to pyrolyze organics in the presence of carbon which forms an intermediate carbon rich material which is then treated with superheated steam to convert carbon from all sources to CO₂. One or both of these options will continue to be pursued.

To manage aggregation and its alternatives, decision points have been added at key steps in the aggregation schedule (attached). One decision point in the aggregation project highlights the permit need date. Another decision point is the down-selection between WAO and Steam Reforming after completion of some testing of WAO. If a replacement alternative is decided upon, the project will proceed through change control to re-scope and re-baseline as appropriate.

In summary, the project to disposition Tank 48H TPB by aggregation is the current WSRC baseline and it is an active project. The need date for Tank 48H to be returned to service is January, 2010. The aggregation project currently meets that target. In parallel with aggregation implementation activities, alternative processes are being developed.

Tank 48 Disposition Schedule



CBU-SPT-2005-00177
REVISION: 2
April 4, 2006

KEYWORDS:
Tank 48H, Salt Program

RETENTION: PERMANENT
CLASSIFICATION: N/A

Tank 48H

Analysis of the Allowable KTPB Residual Quantity

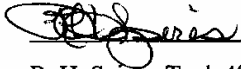
R. H. Spires

R. E. Edwards


Westinghouse Savannah River Company
Closure Business Unit
Aiken, SC 29808

Prepared for U.S. Department of Energy Under Contract No. DE-AC09-96S

Authors:

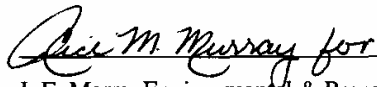


R. H. Spires, Tank 48H Project Owner
4-4-06
Date

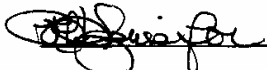


R. E. Edwards, Residual Team Lead, SRNL
4-4-06
Date

APPROVED BY:



J. E. Marra, Environmental & Process Technology
April 4, 2006
Date



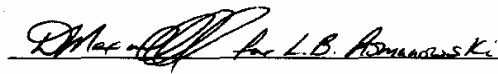
M. S. Miller, Manager, Waste Solidification Engineering
4-4-06
Date



D. B. Little, Liquid Waste Engineering
4-4-06
Date



N. R. Davis, Salt Programs
4-4-06
Date



L. B. Romanowski, PIT, Salt Disposition Planning
4/4/2006
Date

Table of Contents

- 1. Executive Summary.....4
- 2. Purpose.....4
- 3. Discussion.....5
 - a. Parametric study.....5
 - b. Potassium Tetraphenylborate Degradation Rate8
 - c. Downstream Process Impacts Review9
- 4. Conclusions 11
- 5. Attachment 1.....12
- 6. References..... 13

1. Executive Summary

The removal and disposition of Tank 48H material, consisting primarily of potassium and radioactive cesium tetraphenylborate solids, presents some unique challenges for formulating a safety control strategy. This document summarizes the work performed to establish the foundation for determining an overall strategy for Tank 48H with respect to two major issues:

- 1) The residual quantity of tetraphenylborate solids that can remain in Tank 48H following bulk removal, and
- 2) The means to predict with a high degree of confidence the possible degradation rate of tetraphenylborate solids, and subsequent generation rate of benzene, for various processing conditions with these residual solids.

There are a number of placement strategies for Tank 48H that accommodate a greater residual potassium tetraphenylborate (KTPB) than previously analyzed. The evaluations conducted in this study resulted in an allowable residual for Tank 48H of 35 kg of KTPB if Tank 48H was the feed tank to ARP/MCU. If Tank 48H is fed to SWPF, then the residual quantity allowed is smaller. For any processing strategy, the key points for handling this residual quantity after disposition of the bulk of the material from Tank 48H are as follows:

- 1) The quantity of KTPB is limited such that 100% of the Composite Lower Flammability Limit (CLFL) is not reached upon loss of ventilation in Tank 48H. The analysis uses the thermodynamic properties of benzene solubility determined from lab tests and Henry's law to determine the equilibrium benzene vapor phase concentration. Controls to protect the assumptions in the analysis must be implemented.
- 2) The quantity of KTPB is limited so that concentrations and quantities can be handled in the downstream facilities without causing flammability concerns.
- 3) A KTPB degradation model is used as defense-in-depth to show that the degradation rate is slow enough that non-equilibrium conditions do not present a flammability concern.

2. Purpose

Tank 48H currently contains ~240,000 gallons of salt solution containing 19,000 kg of KTPB salts generated during the 1983 In-Tank Precipitation (ITP) Process demonstration and subsequent operation of the ITP facility in 1995 and 1996.¹ Successful disposition of the material in Tank 48H and return of the tank to service is required to feed the future Salt Waste Processing Facility (SWPF).² For Tank 48H to meet the requirements of the current Concentration, Storage and Transfer (CST) Documented Safety Analysis (DSA) for a non-organic containing tank, bulk disposition resulting in no more than 378 grams of TPB (424 grams of KTPB) left in Tank 48H is allowed.³

The Residual Task Team was chartered to define an achievable and measurable end state for the Tank 48H project. The team divided this major activity into three tasks:

- 1) Identify a reasonable range of KTPB residual quantities to be left in Tank 48H at the end of the project along with the technical basis and assumptions through a parametric evaluation,
- 2) Identify a reasonably conservative KTPB degradation rate based on Savannah River National Laboratory (SRNL) studies, and
- 3) Determine the impact of various residual amounts of KTPB on the downstream processes after Tank 48H is returned to service.

This study does not address the controls required for bulk removal of the KTPB through aggregation. This work only applies to the residual quantity remaining after bulk KTPB disposition is complete.

3. Discussion

Several studies have been completed to identify and evaluate processes to disposition the TPB in Tank 48H.^{4,5} These studies included both in-tank and out-of-tank options. While the current strategy for Tank 48H bulk disposition is the out-of-tank option of aggregation, determining an allowable, achievable residual for the KTPB is necessary for all tank options. The residual must also be compatible with any downstream processes.

The Residual Task Team was chartered from PIT (Planning, Integration and Technology) and lead by R. E. Edwards of SRNL. Other team members included R. H. Spires, J. T. Carter, D. C. Bumgardner, J. C. Griffin and R. M. Mobley. Others contributing to the team included S. L. Marra, T. E. Britt, E. W. Harrison, S. G. Campbell, M. A. Norato, T. A. Le, W. R. Wilmarth, D. D. Walker, T.B. Edwards, C. L. Crawford, and R. E. Eibling.

The strategy for defining the Tank 48H allowable residual was to first perform a parametric study varying process requirements and using thermodynamic and kinetic models in calculations to estimate potential tank vapor space flammability scenarios. A KTPB degradation rate was employed in the kinetic models based on an SRNL statistical analysis to develop a predictive model for degradation rate as a function of process conditions. This work provided a range of possibilities for the definition of an allowable residual quantity and a basis for a set of controls to address tank vapor space flammability scenarios. Future uses were defined for Tank 48H and the potential impacts on downstream processes were investigated.

a. Parametric study

The original TPB residual quantity calculation allowed no more than 378 grams (424 grams of KTPB) to remain in Tank 48H. This calculation was based on establishing Tank 48H under the current CST DSA requirement as a non-organic tank, thus requiring an organic contribution to the CLFL < 5%, a temperature of 100°C, and a minimum vapor space volume.⁶

To define the range of the residual allowance for Tank 48H, several process parameters important to the CLFL calculation were varied in this study.⁷

- The upper limit for temperature in Tank 48H was lowered below the boiling point of benzene. This allowed use of thermodynamic relationships such as Henry's Law to be applied to the benzene concentration in the vapor space.
- Vapor space volumes were varied.
- The benzene was allowed to contribute more than 5% to the CLFL.
- The allowable background CLFL was varied. This parameter is used in calculations to determine response times upon failure of safety equipment.

The quantity of KTPB was then limited such that 100% of the CLFL was not reached upon loss of ventilation in Tank 48H. The analysis uses the thermodynamic properties of benzene solubility determined from lab tests and Henry's law to determine the equilibrium benzene vapor phase concentration. Crediting some of these process parameters used as assumptions in the equilibrium analysis would result in changes to the CST DSA. However, the process of bulk removal also requires changes to the DSA. The limit and control selection for the residual allowance is expected to be a subset of the limits and controls selected for bulk removal.

After the benzene has established equilibrium, the time to CLFL calculations will be driven by the radiolytic destruction of hydrogen. Using a reasonably conservative hydrogen generation rate for salt solutions, the time to CLFL is greater than 30 days. Based on the time to CLFL, salt solution processing in Tank 48H after the residual is reached can be handled with the controls identified for the residual KTPB and normal flammability controls for hydrogen.

Using this strategy the residual for Tank 48H can range from 5 kg at 50° C with a CLFL of 25% to 63 kg at 30° C with a CLFL of 60% at a liquid level of 243 inches (current High Liquid Level Conductivity Probe (HLLCP) setting). A selection of the data from X-CLC-H-00561 is shown below. Current conditions in Tank 48H reflect trace hydrogen levels, but the current DSA requires a background of 20% hydrogen contribution when performing CLFL calculations. Results for both conditions are shown. The parameters for the original calculation for the allowable residual are also shown for comparison. This allows an increase in the allowed residual from 1 to 2 orders of magnitude above the original calculation, depending on the controls selected. The actual controls selected for processing after the residual quantity has been reached will be determined by the design authority. The data supports a number of viable control sets to achieve a larger residual quantity.

Table 1. Residual TPB allowed for Safe Staging of Salt Solutions

Temperature	% of CLFL	Liq Level, in.	Mass of KTPB, kg, with H ₂ Background – Trace	Mass of KTPB, kg, with H ₂ Background @ 20% of CLFL
Original Calc				
100° C	25%	367	N/A	0.42
50° C	60%	243	52.97	35.20
50° C	60%	367	15.61	10.38
45° C	60%	243	54.88	36.50
45° C	60%	367	16.85	11.21
30° C	60%	243	63.52	42.32
30° C	60%	367	23.58	15.71
30° C	60%	372	21.97	14.64
50° C	45%	243	39.57	21.8
50° C	45%	367	11.66	6.43
45° C	45%	243	41.02	22.64
45° C	45%	367	12.59	6.95
30° C	45%	243	47.54	26.34
30° C	45%	367	17.65	9.78
50° C	25%	243	21.71	3.94
45° C	25%	243	22.55	4.16
30° C	25%	243	26.23	5.03

b. Potassium Tetrphenylborate Degradation Rate

There have been numerous tests completed over the last ten to fifteen years with both simulants and real waste to analyze and understand the degradation rate of KTPB solids. These experiments have been over a broad range of conditions reflecting primarily changes in temperature, pH, KTPB concentration, catalyst presence and concentration, soluble TPB presence, and sodium concentration. All relevant data from these experiments was carefully interpreted in a conservative manner, converted to consistent units, collated into a single database, independently verified, and statistically analyzed to determine a realistically conservative degradation rate for KTPB for the conditions expected in Tank 48H. Statistically significant variables included TPB concentration, temperature, pH, sodium ion concentration, the presence or absence of soluble TPB precursors, and if the material was non-radioactive or either irradiated or radioactive.

Four models were developed in successive fashion. These models involved the following data subset divisions: a) a model applicable to all the data, both non-radioactive simulants and radioactive and irradiated material, recognizing that non-radioactive simulants have statistically significant higher degradation rates; b) a model derived from the first but excluded the second order cross terms; c) a model applicable to radioactive or irradiated material; and d) a model applicable to radioactive or irradiated material with the absence of soluble TPB precursors and a measurable KTPB decomposition rate. The first and fourth models showed good agreement and correlation coefficients. SRNL selected Model 1 to use to predict a degradation rate for KTPB because it most accurately reflected the known relationships between the degradation rate and variables such as temperature and wt% KTPB. The results of these models with respect to predicting a degradation rate of KTPB for conditions similar to those expected for the Tank 48H residual material are shown in Table 2.⁸ Both the predicted degradation rate and the recommended 95% confidence value appropriate for the Tank 48H residual quantity are provided. Since Tank 48H will contain residual TPB solids as a result of the bulk KTPB removal process and thus will contain radioactive material with no TPB precursor material, the recommended rate for use is 2.0 and 11.0×10^{-6} mole KTPB/L/day for solution compositions of $3M$ Na^+ and $7M$ Na^+ respectively at $50C$, $pH = 14$, 0.003 wt% KTPB and no soluble TPB components.

**Table 2. Predicted KTPB Degradation Rate at Residual Concentrations
(10⁶ Moles KTPB/L/day)**

Model 1 All Data		
Sodium, Molarity	Predicted Rate	One sided 95% Confidence of the Average Value
3.0	1.0	2.0
7.0	3.4	11.0

Model 4 Rad Data Only/No NaTPB		
Sodium, Molarity	Predicted Rate	One sided 95% Confidence of the Average Value
3.0	1.7	3.2
7.0	7.0	22

c. Downstream Process Impacts Review

Aggregation through Saltstone is the current baseline process for Tank 48H. While Saltstone is the major downstream receipt facility, this study does not address the impacts to Saltstone. Safe acceptance of the TPB in Saltstone is being addressed by the Tank 48H project team and Waste Solidification.

The current interim salt processing strategy calls for Tank 48H to feed SWPF after bulk removal of the TPB.² However, several possible processing options were evaluated for the Tank 48H residual KTPB:

- Option A) as a feed tank for ARP/MCU processes
- Option B) as a feed tank for SWPF
- Option C) as an addition to a sludge batch
- Option D) as an addition to an evaporator feed tank

These were reviewed to identify the range of future processing options available for Tank 48H. See attachment 1 for the flowpaths of salt solutions through Tank 48H.

The analysis showed that the highest residual resulted from the use of Tank 48H after bulk removal of KTPB as a feed tank to ARP/MCU. The maximum allowable KTPB concentration in the Monosodium Titanate (MST)/sludge stream fed to the Sludge Receipt and Adjustment Tank (SRAT) was determined to be 250 ppm, assuming a 10 gpm feed rate. This is equivalent to 35 kg of residual KTPB remaining in Tank 48H assuming Tank 48H is filled to 1.0 million gallons prior to processing. This analysis assumes that the modifications required in DWPF for isopar carryover are installed and that the MST/sludge stream and strip effluent are processed sequentially through the SRAT.

Another option is to process the residual KTPB with SWPF. This option decreases the residual KTPB allowed because the MST/sludge stream may be contaminated with isopar from the strip effluent and processed together in the SRAT. If KTPB residual is processed with SWPF operation, the KTPB limit would be reduced below 35 kg.

Sending the residual KTPB to a sludge batch was not deemed viable because of the large amount of water and decants required to transfer the residual KTPB. A detailed evaluation of sending material to the evaporator was not performed since the original residual allowance of 378 grams was based on the DSA assumption of 5% organic contribution, which is applicable to waste tanks and evaporators. In any event, Tank 48H serving as an evaporator feed or drop tank is not in any short or long term planning strategies, so this option can be dropped without consequence.

In summary, if Tank 48H is used as a feed tank to ARP/MCU, the allowable residual is 35 kgs of KTPB. If Tank 48H is used as a feed tank to SWPF, the allowable residual will be less. Although no immediate showstoppers were identified, the study does recommend additional work to ensure that the impacts are acceptable in either of these options. Specifically, the more significant potential process impacts needing confirmation include the following:

- Perform analysis to verify acceptability of current non-SC and non-SS systems at 96-H and 512-S actinide removal facilities (or at SWPF) due to the presence of organic KTPB solids.
- Perform experimentation to examine DWPF SRAT chemistry, especially KTPB behavior during acid additions and subsequent boiling operations, by performing SRAT experimental runs to evaluate process impacts, off-gas compositions, and confirm assumptions.

These issues represent risks that the residual amount of KTPB left in Tank 48H may have to be reduced.⁹

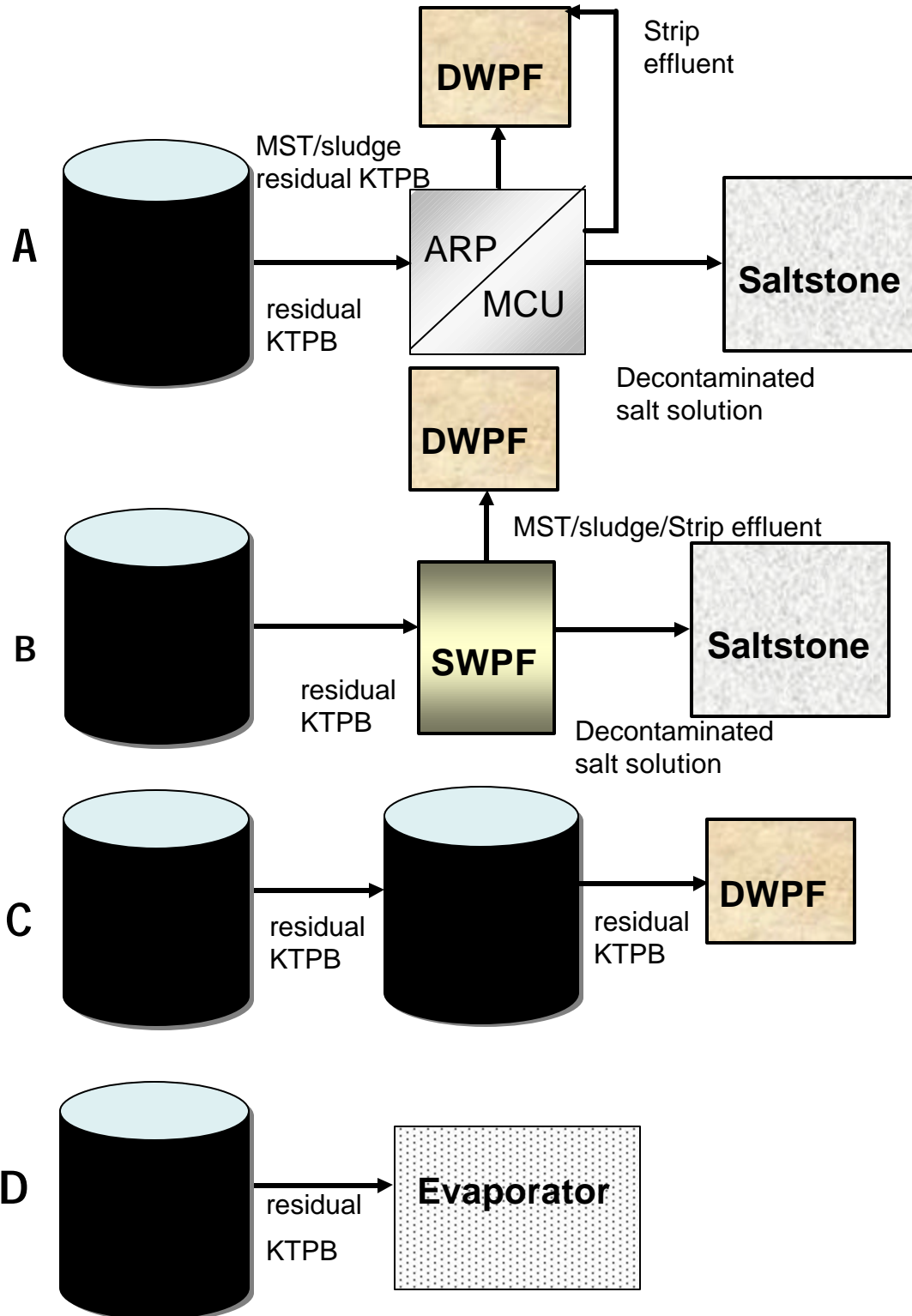
4. Conclusions

Based on using Tank 48H as a salt solution tank, the allowable residual for Tank 48H could be increased to 63 kg of KTPB or more by limiting temperature and maximizing vapor space, while applying reasonably conservative thermodynamic models. The limiting downstream facility that may receive the residual KTPB is DWPF. DWPF is the downstream facility if Tank 48H is used as a feed tank to either ARP/MCU or SWPF. The limit of KTPB to DWPF would be 35 kg of KTPB in a million gallons of salt solution if the residual is processed at the same time as ARP/MCU. It will be less if the first use of Tank 48H is as a feed tank to SWPF. This analysis assumes that the DWPF modifications required to take the Isopar solvent carryover are completed and no adverse impacts to SRAT processing are identified. An analysis of the current non-SC and non-SS controls at the actinide removal processes at 96H and 512-S (and potentially SWPF) is also required to verify acceptability.

Tank 48H would be returned to service at the point that the bulk of the material was removed. Using a reasonably conservative hydrogen generation rate from salt solutions, the allowable residual can be managed with some controls to protect process parameters and normal tank farm controls for hydrogen flammability.

In summary, Tank 48H can be returned to salt processing service with a higher allowable residual than 378 grams TPB. DSA changes would be required. Some downstream processing testing or analysis would also be needed.

5. Attachment 1 – Downstream Options



6. References

- ¹ CBU-PIT-2004-00034, Rev 0, Planning baseline for Tank 48H Aggregation to Saltstone @ 0.2 Ci/gal Cesium, D. Maxwell, January 12, 2005.
- ² CBU-PED-2005-00130, Rev 0, Interim Processing Plan, M. J. Mahoney, P. D. d'Entremont, June 17, 2005.
- ³ X-CLC-H-00495, Tank Farm Allowable TPB Heel Determination, J. M. Russell, March 18, 2004.
- ⁴ G-ADS-H-0007, Rev 0, Tank 48H Disposition Project Treatment Option Evaluation, W. B. Dean, February 4, 2004.
- ⁵ CBU-PIT-2005-00147, Re-Evaluation of Tank 48H Disposition Alternatives, D. Maxwell, July 20, 2005.
- ⁶ WSRC-SA-2002-00007, Rev 3, December, 2004 Concentration, Storage, And Transfer Facilities Documented Safety Analysis, Section 3.4.1.5.3.
- ⁷ X-CLC-H-00561, Rev 0, Allowable Mass of Residual KTPB in Tank 48H, T. E. Britt, July 31, 2005.
- ⁸ WSRC-TR-2005-00318, Potassium Tetrphenylborate Decomposition Rate Analysis, W. R. Wilmarth, et. al., September 2, 2005.
- ⁹ SRNL-ITS-2005-00154, Tank 48 Residual KTPB Impact Analysis Summary, S. L. Marra, July 7, 2005.