1.0 Executive Summary

The High Level Waste (HLW) Tank 48H Disposition Team (henceforth referred to as Team) was formed on December 13, 2001 under the sponsorship of the WSRC High Level Waste Vice President and General Manager. The Team was chartered to identify options, evaluate alternatives and recommend a selected alternative(s) for processing HLW Tank 48H contents to a waste form capable of being processed or stored by existing or planned facilities.

The Team was comprised of appropriately qualified experts from WSRC and its partners. Team membership is identified in Appendix 2, Team Membership. The overall methodology for achieving the Team's mission is described in the Systems Engineering Management Plan (SEMP)[1].

During Phase 1 multiple approaches were used to identify alternative processes to meet the production and safety requirements for tank disposition. Formal brainstorming sessions with a range of stakeholders were supplemented by historical reviews and literature surveys. In addition, a Briefing Package for soliciting site wide experience was distributed to SRS Operations, Engineering and DOE. All ideas were captured on information sheets included in this report as Attachment 2.

In 1996-1998, chemistry studies aimed at developing an understanding of the reaction mechanisms and kinetics associated with the ITP process were performed. These studies were intended to lead to closure of DNFSB Recommendation 96-1 and the results were an input to the process for evaluating alternatives.

The resulting list of 40 alternatives was screened against a set of minimum screening criteria, which included engineering maturity, safety, and permitting. Alternatives were either accepted as written, modified by combination or addition, or dropped. Ranking was performed within four (4) decomposition categories to focus on the alternatives with the highest potential for success. The result of the exercise was an "Initial List" of fifteen (15) alternatives selected as written or in part for further evaluation.

The main focus of the Team's work in Phase 2 was on the technical investigation of the initial alternatives, the identification of technical risk and the application of selection criteria for complexity, science maturity, interfaces and process rate to establish a short list for further evaluation. New thoughts on three "dropped" alternatives required the alternatives to be reconsidered. To evaluate these remaining options, more information was needed concerning these processes. As a result, SRTC performed simple, screening experiments designed to determine the feasibility of these 18 processing options. A Task Plan and a Technical Report[3] summarize the work performed to evaluate the potential of these processing options. Most of the processing focused on four possible decomposition schemes: namely use of catalysts, use of oxidants, use of acids and thermal.

Tank 48H and its chemistry have been well characterized as a result of the in-tank demonstration of the ITP process in 1983 and the startup of the ITP facility in 1995. However, no well-mixed samples have been analyzed since 1998. As a result, the simulants used in this testing were based on the well-mixed samples pulled in 1998. No attempt was made to correct the 1998 sample results for radiolysis of the nitrite and nitrate or absorption of carbon dioxide by the waste in Tank 48H. However, a 6.5% decomposition of the KTPB was assumed because of the consistent data since 1997. It was also assumed the solids that have settled in Tank 48H can be easily resuspended. A well-mixed Tank 48H sample needs to be obtained to confirm the Phase 2 testing. In addition, samples are needed to allow demonstration of the preferred treatment options with actual waste.

Sixty-nine scoping tests and six carbon balance experiments were performed using options associated with (1) acid hydrolysis, (2) thermal decomposition, (3) oxidation (4) catalytic destruction and combinations of these four methods. The catalyst test included catalyst composed of platinum, palladium, copper and iron at concentrations of 25 mg/L. The four oxidants chosen for these tests were sodium perborate, sodium potassium ferrate, sodium permanganate and hydrogen peroxide at 2 and 5 times the TPB stoichiometry. Acid solutions comprised of either formic, nitric, or 8 wt % oxalic acid were used for the acid hydrolysis test. Temperature was a variable applied to acid, oxidation and catalytic destruction. The details of these tests are included in references to this report. The overview of the tests is contained in section 7 of this report. A private company under contract to WSRC/SRTC is continuing investigation of a possible bioremediation solution. Their results should be available in October 2002.

The selection process used an analytical hierarchy process employing the ECPro software tool and a "pair-wise" comparison of criteria. The technical and science risks were considered the critical elements of the selection criteria and were therefore weighted accordingly.

The results of the process indicated the Salt Cell technology and Steam Reforming were the first and second choices. This is not surprising since both processes are well understood when compared to the limited knowledge gained from the scoping studies for catalyst, acid and oxidation.

Note: The term "in-tank" as used in the text of this report does not imply the process is limited Tank 48H. The use of Tank 48H as a reaction vessel will incur some risks. The intent of the research for "in-tank" solutions was to identify options with minimum risks and minimum infrastructure requirements, e.g., a reaction tank coupled to the actinide removal process.

If the weighting factors for the alternatives are set equal, the first and second choices are the two alternatives that could possibly use Tank 48H as a processing tank, permanganate and catalytic destruction. The third ranked option was the salt cell process. This indicates that further research in the areas suitable for in-tank processing, along with increasing the

technical maturity and science knowledge, has a high probability of indicating a change in treatment options.

Therefore the Team recommends the following work be accomplished in FY03:

1. Additional data on oxidation, catalyst and acidic processes and the use of sodium permanganate and Fenton's reagent to oxidize the TPB should be developed as possible in-tank alternatives.

2. The results of the bioremediation study should be reviewed by WSRC/SRTC.

3. WSRC/SRTC observe the progress and problems with Hanford's efforts to use steam reforming and fund Hanford to test simulates of Tank 48H and actual waste, the composition of Tank 48H with MST/TPB. In addition, simple lab testing with simulates started by SRTC should be completed (see 7.3.7.2 and Attachment 4).

4. Actual waste samples are needed to understand the current composition of Tank 48H contents and to support the real waste testing of the three most promising alternatives. This should be completed to demonstrate no unexpected issues exist for processing actual waste.

5. When these four items are complete the alternative selection process should be re-visited.

The Team believes that this work effort for technology development (excluding the Hanford Steam Reforming Process) could be accomplished in about 11 months (Attachment 4) after funding is available. The team was unable to determine the Hanford testing dates.

2.0 Purpose

The purpose of this report is to document the progress and process used by the Team to systematically develop alternative methods or technologies for final disposition of HLW Tank 48H contents. This report will document the process utilized to reduce the total list of identified alternatives through the down select phases.

Revision 0 of this report meets the milestone Deliverable for the Phase 1 report specified in the Team Milestones, Appendix 3. Revision 1 of this report meets the milestone Deliverable for the Phase 2 Report specified in Appendix 3.

3.0 Introduction

The HLW System is a set of six different interconnected processes (Figure 3.1) operated by WSRC. These processes function as one large treatment plant that received, stored, and treated high-level wastes at SRS and convert these wastes into forms suitable for final disposal. The three major permitted disposal forms are borosilicate glass, planned for disposal at a Federal repository; saltstone grout, disposed in vaults on the SRS site; and treated water effluent, released to the environment.

These processes currently include:

1) High-Level Waste Storage and Evaporation (F and H Area Tank Farms)
2) Salt Processing (not yet functional)
3) Sludge Processing (Extended Sludge Processing Facility)
4) HLW Processing and Vitrification (Defense Waste Processing Facility)
5) Wastewater Treatment (Effluent Treatment Facility)
6) Solidification (Saltstone Facility)

F and H Tank Farm, Extended Sludge Processing, Defense Waste Processing Facility, Effluent Treatment Facility, and Saltstone Facility are all operational. Salt processing operations are limited to safe storage and direct transfer of low-cesium waste to the Saltstone Facility. The Late Wash Facility (Building 512-S) has been tested and is in the process of being brought out of a dry lay-up status to support a planned actinide removal process. The In-Tank Precipitation Facility (ITP) initiated radioactive operation in Tank 48H in September of 1995. During pump operation in December of 1995, benzene evolved from Tank 48H at higher rates than expected; though the operational safety limit was never approached. The benzene formede as a byproduct of the process from the catalytic decomposition of sodium tetraphenylborate (NaTPB) and consequently made the contents of Tank 48H incompatible with the current facilities to treat waste.

In August 1996, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1. The DNFSB recommended that operating and testing in the ITP Facility not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In response to Recommendation 96-1 efforts to explain, through chemistry research, benzene generation, retention and release were conducted from August 1996 through the present. To date a definitive explanation of the mechanism for the decomposition has not been determined. In 1998, following evaluation of technical and safety issues, DOE abandoned the project and researched new technologies for cesium removal. However the selected new technology – solvent extraction – cannot readily treat the waste in Tank 48H, which contains significant quantities of TPB from the ITP operation.

As a result of work completed under Recommendation 96-1, controls are in place to maintain Tank 48H in a safe interim condition. Only the disposition of the waste in Tank 48H remains a safety issue. Recovery of Tank 48H was addressed in the Board's Recommendation 2001-1, High-Level Waste Management at the Savannah River Site. As discussed in the implementation plan for that Recommendation, the Board expects the DOE to evaluate the options for Tank 48H recovery. The evaluation should consider the technical and regulatory risks and identify any research and development work that must be accomplished.

The site desires to return High Level Waste (HLW) Tank 48H to routine service to provide more space in the HLW System. Tank 48H currently contains 250,000 gallons of a salt solution, which contains potassium and cesium tetraphenylborate (KTPB and CsTPB) slurry. To return this tank to service, the TPB must be destroyed or removed. This TPB solution was designed to be processed in the In Tank Precipitation (ITP) Facility, the Late Wash Facility, and the Defense Waste Processing Facility (DWPF) Salt Cell. These facilities were designed to concentrate the TPB, wash out the non-radioactive salts and reduce the nitrite concentration, decompose the TPB to benzene and separate the benzene from the aqueous waste. However, operation of these facilities stopped due to high benzene generation during startup of the ITP Facility.

A team has been established to evaluate processing options, which would return Tank 48H to routine HLW service. The team is using a Systems Engineering approach[1] to evaluate the alternatives and make a recommendation to HLW management. The group evaluated a total of 40 options. As noted in section 1, these options were in part historical efforts and therefore refer to CIF, the Salt Cell at DWPF, etc. The Team recognized these facilities were no longer available but parts of the processes could be viable. The team narrowed these to 18 options using the Team's screening criteria.

To evaluate these remaining options, more information was needed concerning these processes. As a result, SRTC was tasked to perform simple, screening experiments designed to determine the feasibility of these 18 processing options. This report summarizes the work completed and the work necessary to evaluate the success of potential processing options. Most of the processing focuses on four possible decomposition schemes: namely use of catalysts, use of oxidants, use of acids and thermal.

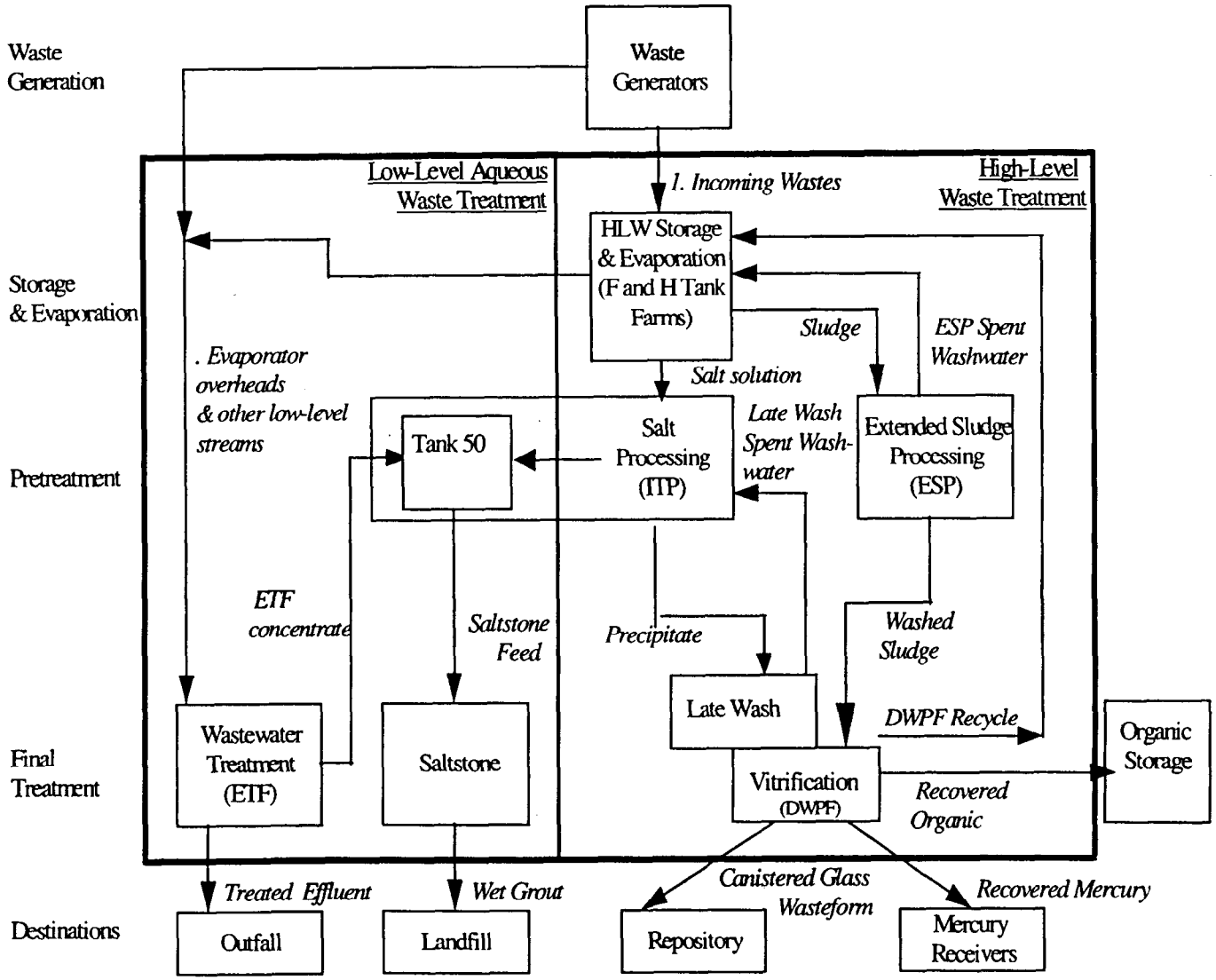


Figure 3.1 – HLW System Process

4.0 Tank 48 Disposition Team

A Tank 48H Team was proposed to systematically develop and recommend technologies for the disposition of Tank 48H contents. A Team Charter (Appendix 1) was developed to establish an overview of method and direction and the team membership (Appendix 2) was staffed to ensure required areas of expertise were available.

As a starting point the Team used the DNFSB Recommendation 2001-1, High Level Waste Management at the Savannah River Site, Commitment 3.5. This Commitment required an evaluation, focusing the technical options to disposition the material in Tank 48H, discussing the confidence level of success based on technical and regulatory risks and identify any research and development work that must be accomplished.

The Team recognized that two categories of options would emerge: (1) options where the technology is understood and (2) where a process would need development. The Team also recognized that any comparison with respect to confidence of success would by default lean toward the more understood technology.

The mission was established as "Evaluate processing technologies to return Tank 48H to Service by making the contents compatible with current or planned High Level Waste Facilities."

The goal was to determine, through a selection process, the technology(s) with the highest potential to meet the mission and recommend a path forward.

The problem was approached in two phases and sets of milestones (Appendix 3) and the solution(s) where constrained to the critical needs, boundary conditions and constraints listed in section 4.1.

4.1 Critical Needs, Boundary Conditions and Constraints

Critical Needs

- Shall meet all applicable safety criteria
- Shall meet all applicable environmental regulations
- All waste must go to final disposal forms
- Shall meet FFA and Site Treatment Plan Regulatory commitments
- Shall accommodate other SRS missions and associated schedules
- Shall meet all applicable final disposal product quality requirements
- Shall meet all applicable waste acceptance criteria

Boundary/Constraints

- Safety of the process
- Impact to HLW final waste form disposition
- Programmatic/technical risk
- Relative cost/schedule
- Regulatory/safety/permit acceptability
- Operational complexity

- Ability to support currently planned future SRS missions and schedules
- Maximum tank farm space kept available
- Use of existing or planned facilities
- Constructability
- Reliability, Availability, Maintainability, and Inspectability (RAMI)

5.0 Background

The objective of the ITP process was to chemically treat radioactive salt solution such that the bulk of the radionuclides could be separated into a low volume, high activity stream that could be vitrified with radioactive sludge; and a high volume, low activity stream that could be solidifed as grout, and disposed of as low level waste.

In the ITP process, monosodium titanate (MST), and sodium tetraphenylborate (NaTPB) are added to salt solution to adsorb Sr-90/Pu-238 and precipitate Cs-137, respectively. The chemical addition and subsequent reaction form precipitate slurry that is then filtered. The filtrate is decontaminated salt solution that is stripped of benzene, sampled and then pumped to a separate facility, Saltstone, where it is mixed with cement, slag and fly ash to form a grout and disposed of as low level waste. The precipitate remaining after filtration is washed with water to reduce the Na concentration, sampled and transferred to the DWPF to be combined with radioactive sludge and vitrified.

The ITP process was demonstrated at Savannah River in 1983. The demonstration facility consisted of a 1.3 million gallon HLW tank (the current ITP processing tank – Tank 48H) retrofitted with chemical addition facilities, slurry pumps, process feed pumps, filters, filtrate hold tanks, and process monitoring instrumentation. The actual demonstration was considered to be "full scale" in the 500K gallon batch of radioactive salt solution that was chemically treated and filtered producing 450K gallons of decontaminated filtrate and 53K gallons of 2.5 wt % precipitate. The precipitate was then washed to reduce the sodium concentration. The demonstration was considered a success and design of the permanent ITP facility started in 1985.

During the demonstration, the amount of benzene released during the precipitate washing step was greater than anticipated. This was the subject of further study at Savannah River and at the University of Florida from 1983 to 1986. The conclusion of the studies was that benzene generated by radiolytic decay of the TPB was retained within the TPB crystal until the addition of water during the precipitate washing step. It was believed that the TPB crystal was dissolved during water addition thus rapidly releasing "trapped" benzene present within the crystal lattice. The permanent ITP facility was designed on this basis.

The ITP facility initiated radioactive operation in September 1995 with the addition of 130K gallons of salt solution and 37.3K gallons of NaTPB to the heel of precipitate in Tank 48 that remained from the 1983 demonstration. Initial operations were conducted under the guidance of a test plan that specified controlled evolutions and additional sampling and monitoring requirements. During October, the first of three pump tests was conducted in

which the effect of tank mixing was determined. This test was characterized by a nearly constant benzene release from the liquid phase to the vapor phase that maintained the vapor space concentration at nearly 60 ppm during pump operations.

Following the completion of the first pump run on October 12,1995, the tank remained quiescent until October 20, 1995.

Filtration began on October 20, 1995 and continued until October 25 producing 140K gallons of filtrate. Filtration was conducted at a nearly constant temperature of 39°C. Filtration was followed by the second pump run starting October 26. The benzene concentration in the vapor space was higher than expected, but well below the Operational Safety Requirements (OSR). A water addition was made without an expected increase in benzene concentration. A second filtration step was conducted producing 160K gallons of filtrate and bringing the liquid level in Tank 48H to 160K gallons. The third pump run, which was designed to be conducted at higher temperatures to support oxygen control testing, resulted in heating the tank to 52°C. Again, the benzene concentration was higher than expected but still below the OSR. The tank was quiescent during ventilation tests and had cooled to 30°C by December 1, 1995.

On December 1, 1995, all four slurry pumps were operated for about 3.5 hours to prepare the tank for sampling. Pump operation was then halted due to the observed high benzene readings (2,000 ppm) in the tank vapor space (well before the operational safety requirement was approached). Data from Tank 48H instrumentation and tank sample analyses indicated that NaTPB decomposition had occurred. Efforts began to remove the benzene that had accumulated. A Justification for Continued Operation (JCO) was written to incorporate additional fuel controls on the rate of benzene release that would be allowed during pump operation. A series of single pump runs were conducted under the JCO to deplete the benzene from the tank between December 8, 1995 and January 3, 1996. From January 3 to March 5, 1996, the tank was quiescent. During this period, an alternate nitrogen system was installed and the Justification for Continued Operation was revised to credit nitrogen inerting and to provide restrictive pump operating limits.

On March 5, 1996, one slurry pump was operated at low (600 rpm) speed. A large quantity of benzene was immediately seen in the tank vapor space and pump operation was terminated after 14 minutes. This data indicates periods of non-uniform distribution of benzene in the tank vapor space. Starting on March 8, periodic pump operations were resumed in a conservative, controlled manner in continued efforts to deplete benzene from the tank. Initial operations employed only one slurry pump. As benzene release rates decreased, additional pumps were started. By April 25, 1996, all four pumps were operating at the maximum speed of 1,180 rpm. From November 5, 1995 to April 22, 1996, an estimated 8,500 kg of benzene was removed from Tank 48H. Since April 1996, Tank 48 has essentially been depleted of benzene as indicated by the very small releases observed even with operation of all four pumps since that time.

Savannah River had planned to proceed with a series of Process Verification Tests (PVTs) in Tank 48H designed to increase the level of understanding of NaTPB chemistry and release mechanisms. The tests were to proceed after installation of a backup nitrogen supply as part of a program to transition from fuel control to oxygen control as the primary means of assuring safe operation of the ITP Facility. The first such test, PVT-1, required the addition of a small amount of NaTPB to reprecipitate soluble cesium before filter operation and filter-cleaning operations. Key objectives of this test included: determination of the effectiveness of cesium recovery, validation of benzene generation in Tank 48H, validation of the benzene generation rate in Tank 50H, and to determine the impact of oxalic acid addition to Tank 48H. The next test, PVT-2, included significant quantities of new waste and NaTPB to be added to Tank 48H. The Department of Energy deferred the conduct of PVT-2 until such time as an improved understanding of NaTPB chemistry is achieved and the appropriate modifications to facility hardware engineered controls and administrative controls have been completed.

6.0 Phase 1

The SRS High Level Waste Tank 48H Disposition Team ("Team") was chartered to systematically develop and recommend alternative methods, and/or technologies for disposition of High Level Waste Tank 48H by the end of FY2002. Major milestones (Appendix 3) were established to accomplish the task. One of these major milestones is a report summarizing the activities leading to an initial list of alternatives and screening criteria for the short list. This section provides the details pertaining to the evaluation methods and criteria used to create the "initial list," the alternatives considered in the process and the disposition of the considered alternatives in support of the required report.

6.1 Alternative Identification Process Overview

Two aspects of the Team Charter had to be accommodated in the final process - the need to comprehensively consider all available alternatives and the goal of recommending a preferred alternative(s) within a six-month time frame. The process also had to document the technical concerns of non-viable alternatives with the potential to be modified or combined to create a new alternative.

Figure 6.1 is a representation of the selection process for the initial list. The selection methodology has explicit steps to require full consideration of potentially favorable fragments of dropped alternatives (such as choices among possible reagents and/or engineering implementations).

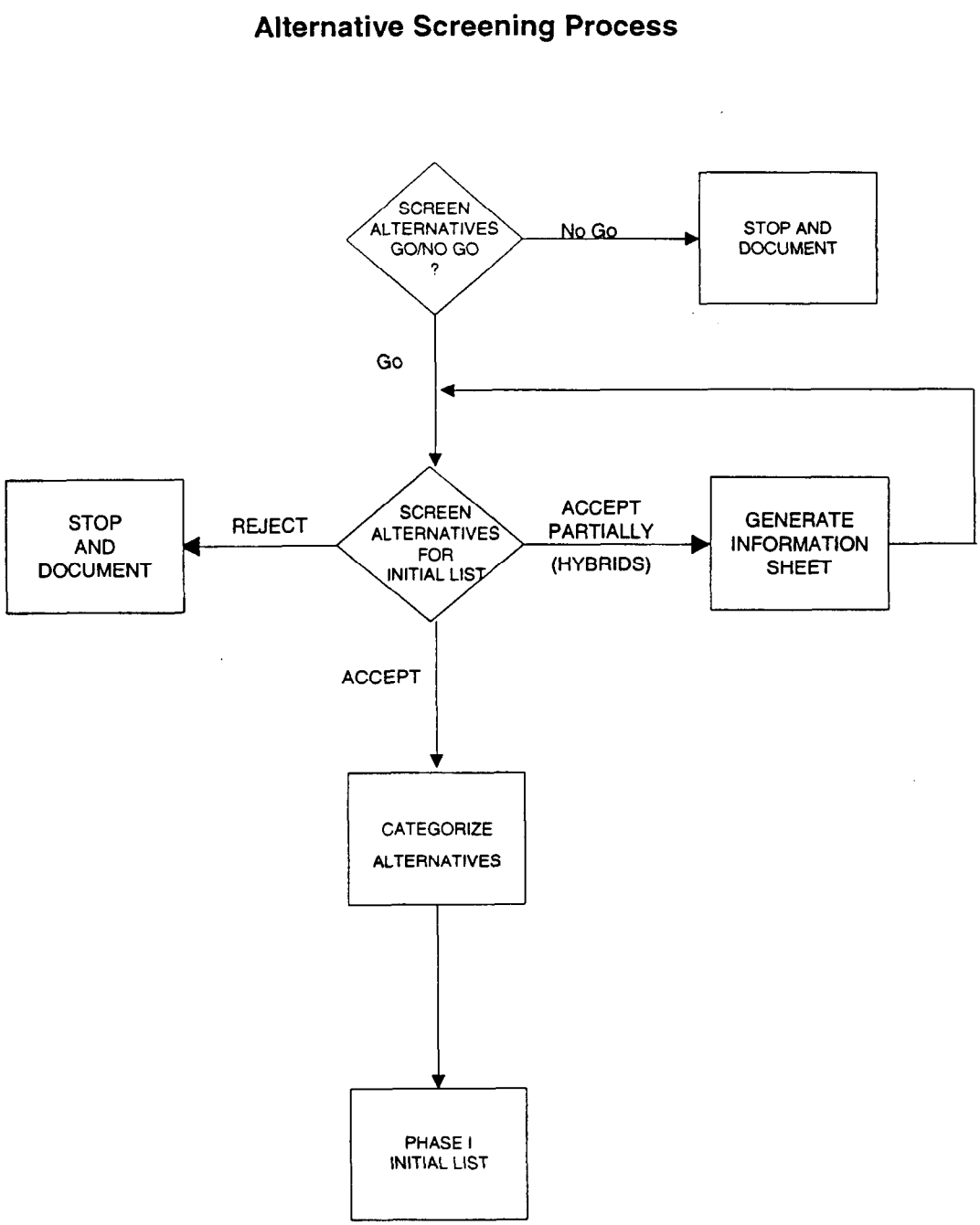


Figure 6.1 – Logic Diagram for Screening Process

6.2 Generation and Organization of Alternatives

As described in SEMP (Ref 1), the input for the selection of the initial list was generated from a number of sources, including SRS employee input, historical reviews, formal brainstorming and early, informal, results from independent subject matter experts. This input was documented on information sheets. These information sheets were used to assure an adequate description of the proposed method or technology, to support screening, and to capture the originators' views on safety aspects, permitting, facility interfaces, strengths and weaknesses of the proposal. The Team then grouped these alternatives into the following decomposition categories:

- Catalyst
- Oxidation
- Thermal
- Acidic

The information sheets were numbered. Additional information sheets were later created by the Team based on subsequent input and Team discussions and were also grouped into the categories. All of the information sheets generated during the creation of the initial list are in Attachment 2.

6.3 Go/No Go Screening of Alternatives

The first step of the screening process was to assure that the alternatives were viable for continued consideration (Per Figure 6.1). In the case of go/no-go screening, it was necessary to simplify the evaluation criteria due to the lack of specificity inherent in a technology category and a requirement that the screening be sufficiently conservative so alternatives were not discarded if there was any potential that they could ultimately emerge as the preferred alternative. These considerations resulted in the Team choosing to apply two evaluation criteria and two rules for this screening:

Evaluation Criteria:

1. Technical Maturity – Does this category reflect concepts, which have never been tested, or, at the other extreme, are they fully proven in nuclear/chemical applications?
2. Reasonable Chance of Deployment – Given the technical maturity, degree of complexity of the technology and infrastructure requirements, does it have a reasonable chance of deployment on the time line needed?

Rules:

1. In the event that insufficient expertise existed for the Team to determine in this screening that an alternative clearly failed to meet one or both of the criteria, the alternative passed this screening and went on to the next level of review. Thus, insufficient knowledge to reject the alternative resulted in initial acceptance.

2. If an alternative meets the two criteria, the alternative is accepted.

   Note that cost was not explicitly used as a criterion for alternative screening due to the lack of implementation detail for the individual alternatives to support an evaluation against such a criterion.

   Any alternative screened out at this level would have the causative failure documented and the alternative would be dropped from further consideration and documented in Table 1A.

6.4 Screening of Alternatives

The next step of screening used the following criteria extracted from Section 4.3 and Level 1 mission requirements of Reference 1.

1. Safety

   Does the process have inherent hazards that preclude it from being made safe?

2. Permits

   Can permits be approved for the process?

   (a) Is the process covered under existing permits?

   (b) Can existing permits be modified?

   (c) Can new permits be approved?

3. Interfaces

   Can interfaces be established/maintained?

   (a) Does expected waste produced meet the Waste Acceptance Criteria of receiving facilities?

4. Maturity

   Will the process be sufficiently matured for successful near term deployment?

   (a) Is there evidence the process has or will have sufficient R&D to support successful near term deployment?

   (b) Is there likelihood for successful field application?

   After review against the criteria above, each alternative received one of three dispositions:

   - Reject (The failure to meet a specific criterion was documented, the alternative was not carried forward for further review)
   - Included / Accept (Carried on to the next level of review)
   - Hybrid (The alternative appeared to have merit when used in combination with other alternatives and/or hybrids and would be further considered in that context)

Table 1B is a list of alternatives that failed one or more criteria and were not carried forward. A brief statement of criteria that was not met is given in the "Disposition" column and the "Comment" column briefly states the reasons. Table 1C is a list of alternatives that, while not accepted as stand–alone alternatives, contain attributes for hybrid consideration. The "Disposition" column briefly addresses criteria not met. Table 1D is a list of the alternatives that were accepted for ranking.

6.5 Selected Alternatives

It is important to note that the initial list generated by the process described in Phase 1 of this report was not "frozen" at the 15 alternatives. As information from literature searches, professional and commercial inquiries, and other submitted information becomes available, new alternatives were screened by the process already described for addition to the list. Both the initial list and short list could be added to at any time up to completion of the final Team deliverable of the recommendation of the preferred alternative(s).

The following alternatives were accepted onto the Phase 1 "Initial List:"

Alternative	Alternative Description
3 *	Feed KTPB Slurry To DWPF Salt Cell For Catalytic Decomposition
5	Catalytic Decomposition Of TPB Directly In Tank 48
6	Catalytic Decomposition Of TPB In A New Or Existing Facility.
7	Catalytic Decomposition Of TPB Directly In Tank By Lowering pH (Acid Addition)
33	Catalytically Decompose TPB Using Tank 49 as a Reaction Vessel
38	Volume-Reduce By Filtration, Sending Filtrate To Tk 49/50, Catalytic Decomposition of Residual In-Tank
8	Oxidation Of TPB Using UV Catalyzed TiO_2
9	Oxidation Of TPB Using Water Soluble Mild Oxidant
10	Oxidation Of TPB Using Permanganate
35	Hybrid - Actinide Removal Process (ARP) Oxidation of TPB Using Permanganate
11	Thermal Decomposition Of TPB
37	Hybrid - Microwave Destruction Of Organics
39	Steam Reforming / Fluidized Bed Destruction Of Organics
26	Hybrid - Metathesize With Cold Cesium
36	Hybrid - Tank In Tank

* Considered for the process/technology

7.0 Phase 2

Phase 2 of the effort to select an alternative(s) to process the contents of Tank 48H, was divided into four steps.

Step 1 divided the 15 alternatives from Phase 1 into three groupings for technical investigation. The first line of inquiry combined acidic, oxidation, catalyst and thermal. The second was microwave decomposition and the third was ultraviolet (UV) decomposition. The options to metathesize with cold cesium and tank-in-tank processing were not in the grouping since they only provide partial solutions to the problem.

Step 2 of the down select process was the development of selection criteria. The criteria had to contribute to the effort to differentiate between the alternatives and be independent enough to allow the criteria to be weighted with regard to relative importance.

Step 3 was to compare the selection criteria to the studies in the lines of inquiries to ensure the lab studies provided the information to address the questions required for the evaluation.

Step 4 combines the previous steps and essentially results in a de-selection process by comparing the data for each alternative, by criterion, to each other. This process results in alternatives with strong to weak attributes that when weighted and compared results in the alternatives best suited for the processing of Tank 48H contents. This list is recommended for further evaluation.

7.1 Organization of Alternatives

The Tank 48H Team identified 18 alternatives that should be investigated to determine if any of these are feasible for returning Tank 48H to HLW service. The 18 alternatives differed in chemical reaction requirements as indicated by the "How" column in Table 7.1.

All but two these ideas contain at least one of four destruction mechanisms, namely (1) catalyzed destruction, (2) oxidation, (3) thermal and (4) acidic hydrolysis. The two exceptions are metathesize with cold cesium and Tank-in-Tank options, which are really partial solutions that might be used in combination with other destruction options to return Tank 48H to service. Alternatives 17, 18 and 23, from the initial "Rejected" list were added for further consideration. Alternative 17 is the idea of transferring the waste to many waste tanks in the Tank Farm and alternative 18, Direct Grout disposal as part of tank closure, were grouped together as dilution and were considered a paper study. Alternative 23, Bioremediation, was reconsidered due to the industrial success of PMC Technology, Inc. in this field, bringing the total number of alternatives to 18 and the groupings for technical inquiry to five.

To determine whether any of these options is feasible, scoping tests were completed during Phase 2 using a Tank 48H simulant. The testing investigated (1) catalysts, (2) oxidants, (3) acids, and (4) thermal destruction methods. The reaction components and products helped determine the environment required for the process, i.e. "Where". The bioremediation process is being pursued by PMC under contract to WSRC/SRTC[2].

Alternative #	Alternative Description	How?
3*	Feed KTPB Slurry to DWPF Salt Cell for Catalytic Decomposition	Thermal + Catalytic + Acidic
6	Catalytic Decomposition of TPB in a New or Existing Facility	Thermal + Catalytic + Acidic
5	Catalytic Decomposition of TPB Directly in Tank 48	Catalytic
7	Catalytic Decomposition of TPB Directly in Tank by Lowering pH (Acid Addition)	Acidic
11	Thermal Decomposition of TPB	Thermal
37	Hybrid – Microwave Destruction of Organics	Thermal
39	Steam Reforming/Fluidized bed Destruction of Organics	Thermal
38	Volume-Reduce by Filtration, Sending Filtrate to Tk 50, Catalytic Decomposition of Residual In-Tank	Catalytic
33	Catalytically Decompose TPB Using Tank 49 as a Reaction Vessel	Catalytic
35	Hybrid – Actinide Removal Process (ARP) Oxidation of TPB Using Permanganate	Oxidation
36	Hybrid – Tank In Tank	
8	Oxidation of TPB Using UV Catalyzed TiO_2	Catalyzed Oxidation
17	Distribute Among Other Tank	Data Study
18	Direct Grout	Data Study
9	Oxidation of TPB Using Water Soluble Mild Oxidant	Oxidation
10	Oxidation of TPB Using Permanganate	Oxidation
23	In-Tank (or a coupled tank) Bioremediation	Bioremediation/ Contract
26	Hybrid – Metathesize with Cold Cesium	

* Considered for the process/technology

Table 7.1 – Phase 2 Alternatives List

7.2 Selection Criteria

NOTE: No programmatic risks have been identified that discriminate between the options at this time. The Team recognized that some of the process options may require the use of selected facilities (e.g., the ITP filter/stripper building) and may conflict with other program activities from the accelerated mission.

Similarly, the selection criteria does not include cost or schedule. The Team understood the System Plan requires return of Tank 48H to routine service in FY06 (i.e., Cases 2 & 3 of Revision 13. However, development of the best processes does not depend upon cost or schedule. The application of the selected process will effect cost and schedule and should be considered in the final selection phase.

7.2.1 Criteria Development

During Phase 2, the Team developed criteria to evaluate the Initial List options. The goal of the Team was to develop criteria that would:

Differentiate between options
Relate to goals, objectives and values of stakeholders
Be reasonably measurable or estimable
Be independent of each other
Be well understood by all team members

It would not serve the alternative selection process to select criteria, which when applied to each option results in an approximately equal score. Therefore, the team developed criteria that could clearly be used to differentiate between the Initial List options.

The mission, goal, (as identified in Section 4.0) and values of the stakeholders were used to guide the team in developing criteria. The criteria were developed to facilitate the evaluation of those risks threatening the successful achievement of stakeholder interest.

As performance must be capable of being measured or estimated for each of the criterion applied, the team developed criteria applicable to all of the Initial List options.

Another major factor that was considered by the team was to develop criteria that are independent of each other. If the criterion were not to be independent it could skew the results of the evaluation by amplifying the positive or negative aspects of an option by counting the same criterion multiple times.

It was very important for all the team members to fully understand the criteria. This was accomplished by obtaining the consensus of the entire team for each selection criterion and by, when necessary, adding clarifying notes to help "focus" the reader.

During the investigation of alternatives (subsequent to initial screening), the potential could exist to identify a previously unknown safety risk. Therefore, as part of the evaluation process each alternative was screened one final time to ensure no alternatives were carried forward that had a newly identified safety risk.

The team approved selection criteria is shown in Table 7.2.1

Table 7.2.1 – Phase 2 – Selection Criteria

1. Safety
   How difficult is it to control the hazards in the process?

2. Technical Risk
   How mature is the process with respect to a radioactive environment. This question is to differentiate between a process that can treat radioactive material from those that would require extensive design changes or re-design. For example, the portable equipment used to decompose organics in the soil does a great job of destroying PCBs but would be almost impossible to use if the soil was radioactive.

3. Science
   Is the process supported by experimental and other data where the outcome is understood and the results are acceptable?

   This question looks at the chemical process, intermediate and final products in terms of how well the basic science is understood.

4. Design Complexity

   Are the parameters that must be controlled (temperature, pH, pressure, etc.) so sensitive that the process design could be complicated?

   The purpose of this question is to highlight an alternative that, based on what we know now, will require a tightly controlled chemical process.

5. Operation Complexity
   Is operation made more difficult by the complexity or instability of the process (upsets, control, sampling, etc.)?
   The purpose of this question is to highlight an alternative that, based on what we know now, will require many controls and/or many operators.

6. Infrastructure

   Does the process have the potential to use existing Systems, Structures and Components (SSC) as opposed to new SSC?

   It is more desirable to use existing infrastructure.

7. Process Rate

   Does the process support maximum net space gain versus time? This question deals only with the process rate exclusive of design, construction, etc.

8. Regulatory Risk

   Does the process and products fall within the current regulatory envelope and if not, how difficult is it to modify the regulatory envelope?

   The purpose of this question is to ensure that any required changes to permits are considered.

7.2.2 Weighting of Criteria

The selection criteria identified in Table 7.2-1 was weighted by the team. The weighting of criteria was necessary to ensure the correct measure of relative importance was placed on each of the selection criterion. The Team employed an analytical hierarchy process by using the ECPro software tool and a "pair-wise" comparison of criteria. The results of the process weighted technical risk and science heavier than the other criterion as the Team consistently judged them to pose the greatest risk to the successful deployment of any option. Safety, although the most important of all aspects, was weighted above the remaining criteria but below technical risk and science as no unsafe options will be allowed to be deployed and all options which are deployed will have the necessary controls in place to maintain safe operation. The discriminating factor of safety is not how safe the option is but how difficult it will be to make the option safe. The remaining criteria of design complexity, operational complexity, infrastructure, process rate and regulatory risk were not considered by the team to involve risks that would severely jeopardize the deployment of a selected option and therefore were not weighted as heavy as technical maturity, science or safety.

The criteria weights developed by the Team are shown in Table 7.2.2

No.	Criterion	Weight
1	Science	0.329
2	Technical Risk	0.245
3	Safety	0.152
4	Regulatory Risk	0.092
5	Operational Complexity	0.076
6	Design Complexity	0.045
7	Infrastructure	0.037
8	Process Rate	0.024

Table 7.2.2 – Criteria Weights

The ECPro software performs a data check of the pair-wise comparisons to ensure that the comparisons are logical and consistent. This calculation produces an "inconsistency ratio." For this type of analytical hierarchy process (AHP) an inconsistency ration of less than 0.1 would be preferred. The data produced an inconsistency ratio of 0.07 that was within the desired range.

7.3 Screening Experiments

SRTC researchers completed a series of tests to evaluate the Team's alternatives and to develop additional alternatives for consideration. The experimental design allowed direct comparison of the various chemical treatment options under comparable conditions. The bulk of the tests examined the destruction efficiency at 7 days for different chemical recipes with a subset of the tests aimed at determining the influence of temperature and the stoichiometry of the reactions (i.e., amount destroyed as a function of the amount of reagent added). A final set of experiments collected and analyzed samples of the slurry and the offgas as a function of time in an attempt to complete a carbon balance for several of the most promising decomposition options.

Analyzing the filtrate for soluble potassium and boron provided indirect measure of the degree of TPB decomposition. As the TPB decomposes, the byproducts become soluble and the soluble potassium and boron increase. In comparing the alternatives, we present graphs showing the percent TPB destruction based on the increase in soluble potassium and boron concentration. The soluble potassium is more accurate than soluble boron for the prediction of TPB decomposition since insoluble boron compounds form during decomposition, especially under acidic conditions.

Testing used either unwashed or washed precipitate. It would be preferable for the process to treat unwashed precipitate as this would simplify processing and minimize additional waste generation through processing. The current Tank 48H contents are unwashed and contain a high concentration of sodium hydroxide, sodium nitrate and sodium nitrite. Historical processing required washing of the precipitate slurry to remove the nonradioactive salts which would have been processed by the Saltstone Facility. This washing reduced the concentration of sodium to 0.13 M and the nitrite from 0.47 M to 0.01 M. This degree of washing assumes pretreatment of the contents of Tank 48H by addition of 2 million gallons of inhibited water (i.e., 0.01 M NaOH) and filtration to remove the excess volume (1.75 million gallons). Washing would most likely need to occur in Tank 48H using the Building 241-96H filters. The wash water will require evaporation or disposal through the Saltstone facility.

It should be noted that percent destruction means that the cesium and potassium are being released into solution although the decomposition of the TPB to benzene or CO_2 may not be complete. As a result, additional analysis of the organic present for the options with high destruction rates determined the degree of decomposition for the organic.

In addition, personnel measured the solution pH after each 7-day test and twice per day in the final set of tests. The solution pH is especially important in the tests that may be processed in-tank. Attempts were made to complete some of the tests at pH 9.5. However, due to the over addition of acid in the experiments, the final solution pH was lower than planned.

7.3.1 Catalytic Options

A number of catalytic options were proposed to destroy the TPB in Tank 48H. This is because of the success of the copper catalyzed acid hydrolysis process used in DWPF cold chemical runs and the successful use of the copper catalyst to destroy TPB in Tank 49H[3]. However, the destruction of the TPB in Tank 48H is expected to be much more difficult than Tank 49H due to the higher concentration of TPB and the insolubility of the KTPB and CsTPB. (Tank 49H contained primarily soluble NaTPB.)

Catalyst testing considered four catalysts based on previous catalyst testing: copper, palladium, platinum and iron. Copper and palladium have been used at SRS to decompose TPB. Platinum was chosen due to its good catalytic activity in similar chemistry. Iron was chosen due to its ability to catalyze peroxide through Fenton's chemistry. The catalysts were tested at 25 °C and 40 °C.

Feed KTPB Slurry to DWPF Salt Cell for Catalytic Decomposition
Catalytic Decomposition of TPB in a New or Existing Facility

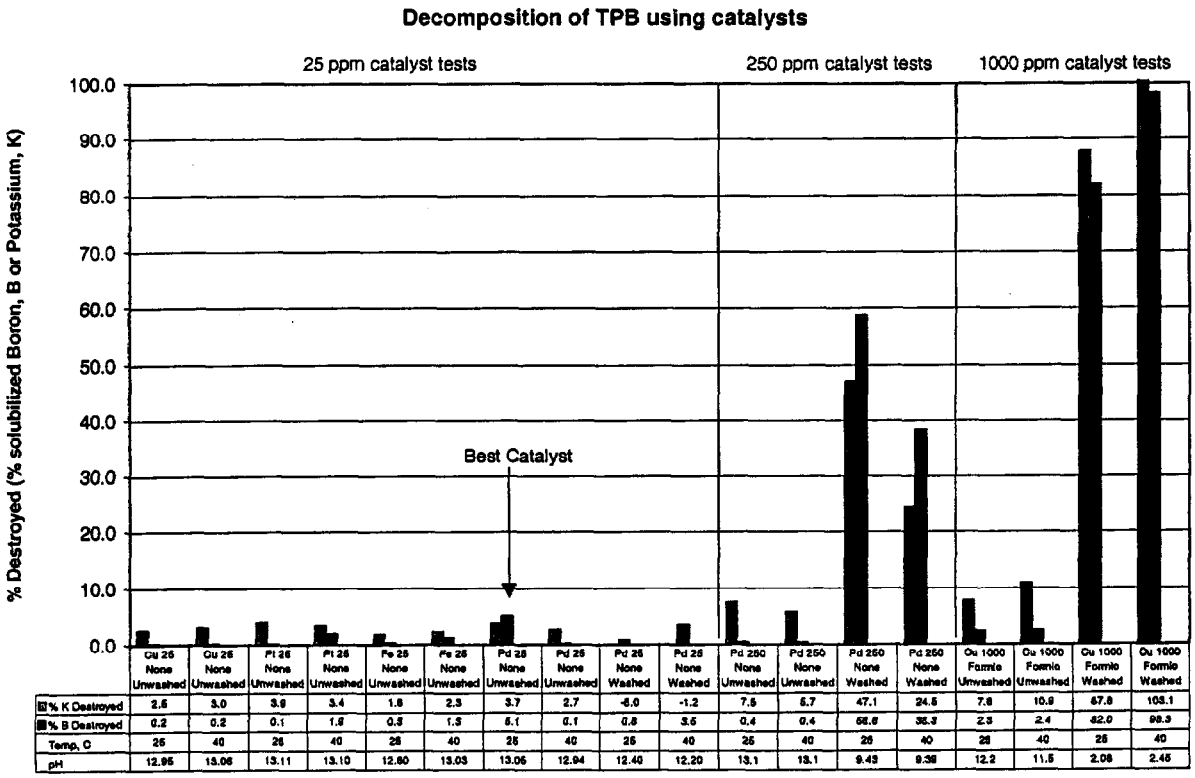
Both of the above processes use a copper catalyzed, formic acid hydrolysis reaction to destroy the TPB. This process was used in DWPF during cold, chemical startup. No testing was completed to duplicate this processing, as this is a very mature technology[4]. However, several tests were completed at similar processing conditions. These tests used 1000 ppm Cu with added formic acid using a washed precipitate. These tests resulted in 80% and 100% destruction of the TPB at 25 °C and 40 °C, respectively.

Catalytic Decomposition of TPB Directly in Tank 48H

Several of the experiments examined whether it would be feasible to add a catalyst to Tank 48H to complete the destruction of TPB in the tank. Catalytic decomposition is likely to lead to a large production of benzene. Figure 7.3.1.1 shows that the catalysts tested had low TPB destruction rates at 25 mg/kg.

Because of the low TPB destruction during the seven days of testing at 25 mg/kg, personnel conducted additional tests at higher catalyst concentrations. The testing conditions chosen were 250 mg/kg palladium and 1000 mg/kg copper. These concentrations were chosen, as these were the maximum concentrations tested by other researchers. In testing at higher catalyst concentrations, the catalysts were most effective in the washed simulate. The destruction rate increased approximately six-fold with the Palladium catalyst and roughly ten-fold with the copper catalyst.

The TPB destruction rate of the catalysts in the unwashed precipitate was much less effective than in the washed precipitate. In testing with the washed precipitate, increasing the palladium concentration ten-fold led to a ten-fold increase in TPB destruction. However, in testing the unwashed precipitate, increasing the palladium concentration ten-fold led to just a two-fold increase in TPB destruction. The use of a catalyst in-tank (unwashed precipitate) might be effective, but would have a slower destruction rate than many of the other alternatives. If the development of an in-tank alternative is desirable, consideration should be given to testing the Pd catalyst at 250 – 1000 ppm in experiments with unwashed precipitate for longer time periods (continue testing for several months) to determine the time necessary to completely destroy the TPB.



	Cu 25 None Unwashed	Cu 25 None Unwashed	Pt 25 None Unwashed	Pt 25 None Unwashed	Fe 25 None Unwashed	Fe 25 None Unwashed	Pd 25 None Unwashed	Pd 25 None Unwashed	Pd 25 None Washed	Pd 25 None Washed	Pd 250 None Unwashed	Pd 250 None Unwashed	Pd 250 None Washed	Pd 250 None Washed	Cu 1000 Formic Unwashed	Cu 1000 Formic Unwashed	Cu 1000 Formic Washed	Cu 1000 Formic Washed
% K Destroyed	2.6	3.0	3.9	3.4	1.6	2.3	3.7	2.7	-6.0	-1.2	7.5	5.7	47.1	24.5	7.8	10.9	87.8	103.1
% B Destroyed	0.2	0.2	0.1	1.8	0.3	1.3	5.1	0.1	0.8	3.5	0.4	0.4	58.6	36.3	2.3	2.4	82.0	99.3
Temp, C	25	40	25	40	25	40	25	40	25	40	25	40	25	40	25	40	25	40
pH	12.95	13.06	13.11	13.10	12.80	13.03	13.06	12.94	12.40	12.20	13.1	13.1	9.43	9.38	12.2	11.5	2.08	2.45

Figure 7.3.1.1 - Comparison of Catalysts for TPB Destruction

Catalytic Decomposition of TPB Directly in Tank by Lowering pH (Acid Addition)

We examined whether the combination of catalyst and acid would lead to rapid TPB decomposition. In these experiments, formic acid and 1000 ppm of copper catalyst were added. The results are summarized in the last four columns of Figure 7.3.1.1. Copper was much less effective in destroying TPB in unwashed precipitate. However, the TPB rapidly decomposed in experiments with washed precipitate. This is not a viable in-tank process due to the pH being too low.

Catalytically Decompose TPB Using Tank 49H as a Reaction Vessel

This option would feed the contents of Tank 48H to Tank 49H where the decomposition would take place. A catalyst would be present in Tank 49H to decompose the TPB. Tank 49H would be suitable for this service since it was modified to allow the use of nitrogen to inert the tank and prevent a flammable mixture from forming during processing. This has some advantages over catalytic destruction in Tank 48H as the precipitate volume can be controlled.

There are some disadvantages to this option including it would tie up an additional HLW tank throughout the duration of the processing. Tank 49H has been returned to service as a high level waste tank and is not currently available for this service. This is a more controlled reaction than completing the decomposition in Tank 48H because it would be possible to control the slurry volume fed to the reaction vessel. However, it requires an additional waste tank and is impractical at this time.

This was considered as one of several options for catalytic destruction of the TPB. This could be accomplished for catalytic destruction of the TPB in a new tank, in an existing tank or in a processing vessel inside the tank.

Volume-Reduce by Filtration, Sending Filtrate to Tank 50H, Catalytic Decomposition of Residual In-Tank

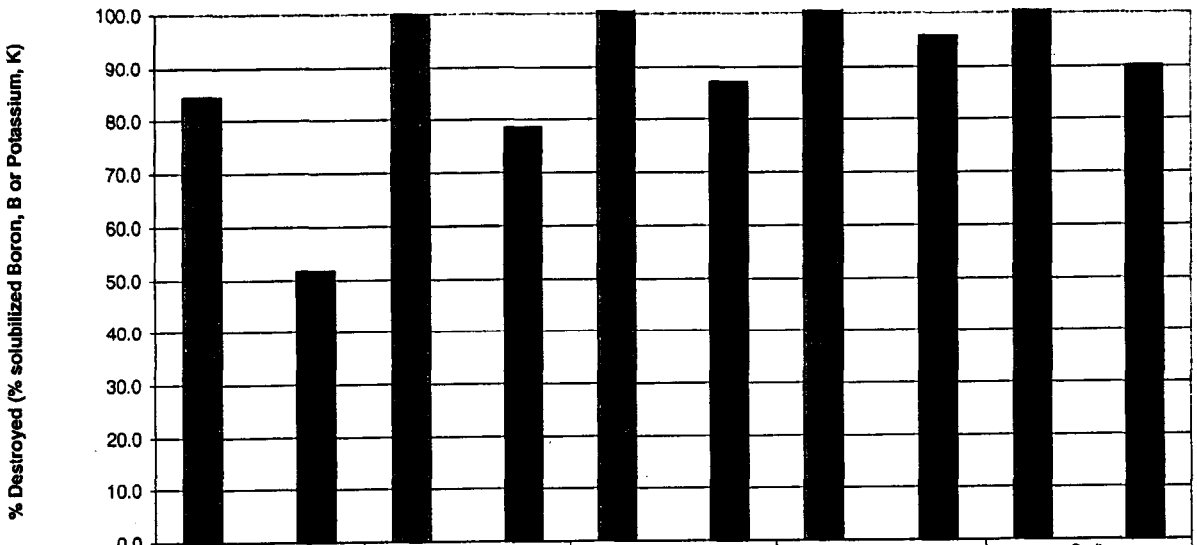
This option is similar to the above option but also requires the startup and operation of the ITP filters to concentrate the waste. Current HLW plans call for this equipment to be used as part of the Actinide Removal Process. As was noted previously, the use of a catalyst by itself is unlikely to be effective. This option was not evaluated independent of catalytic destruction inside Tank 48H by the Team.

7.3.2 Thermal Options

A number of thermal conditions were explored to determine the impact of temperature on TPB decomposition. Based on previous experience with TPB, higher temperature was expected to have a strong impact on TPB decomposition. The Salt Cell Process destroys the TPB by hydrolyzing the TPB to benzene at 90 °C. Testing was planned at 25 °C and 40 °C, as these are the typical ranges for in-tank processes, and at 90 °C as this temperature exceeds benzene's boiling point. Other thermal options such as steam reforming would be processed at much higher temperatures.

Testing was performed at room temperature (~25 °C), 40 °C, and 90 °C. For most of the testing with catalyst, acids and oxidants, higher temperatures led to more complete destruction of TPB. The exception was that the palladium catalyst led to lower destruction at higher temperatures, which defies expectations from prior studies. Most likely, the difference either reflects a variance in the inducting period for the Pd between the two experiments or some other uncontrolled variable that altered the activity of the added Pd.

Below is an evaluation of the thermal treatment options. Figure 7.3.2.1 is a comparison of TPB destruction at various temperatures.



	High Formic Unwashed B8	High Formic Unwashed C6	High Formic Unwashed D2	High Nitric Unwashed D4	Oxalic Unwashed D6
% K Destroyed	84.4	99.9	119.9	113.9	105.8
Temp, C	25	40	90	90	90
pH	4.77	4.18	5.80	3.74	4.61
% B Destroyed	51.7	78.5	87.1	95.6	90.2

Figure 7.3.2.1 - Comparison of Catalysts for TPB Destruction

Thermal Decomposition of TPB

The TPB will decompose under extreme conditions of temperature and pressure. Previous thermogravimetric testing measured the TPB auto-ignition temperature of ~325 °C[5]. For that reason, thermal (i.e., high temperature) and steam reforming (600-800 °C) processes are very likely to result in TPB decomposition. However, these processes would not be deployable as in-tank processes. Steam reforming has the added advantage that control of the oxidizing conditions in the column would lead to conversion of nitrite and nitrate to nitrogen and conversion of TPB to carbon dioxide.

Personnel began a series of 8 Thermogravimetric Analyses (TGA) to understand the decomposition of TPB using both thermal and steam reforming. Half of the experiments used sugar, a reductant that might be used in steam reforming to reduce nitrite and nitrate to nitrogen. Experiments were completed using both an inert off-gas and air as the dilution gas. The thermal testing was not completed by July 15, 2002.

Steam Reforming/Fluidized bed Destruction of Organics

In the steam reforming process, the Tank 48H slurry, superheated steam, and co-reactants (reductant such as coal or sugar) are introduced into the steam reformer vessel where liquids are evaporated, organics are destroyed, nitrite and nitrate are reduced to nitrogen and reactive chemicals are converted to a stable waste product or liquid that incorporates almost all of the radionuclides. For the waste to fully and quickly react, the steam reformer vessel should provide a large surface area as in a fluidized bed. Off-gases from the steam reformer vessel are treated to neutralize corrosive acids or bases so that the only emissions released to the atmosphere from the process ideally are carbon dioxide and water vapor.

In the steam reformer, the Tank 48H slurry is combined with superheated steam and co-reactants. In tests with other alkaline wastes, greater than 99% of S, Cl, and F stayed in the solid product with less than 1% of the incoming S, Cl, and F in the waste going to the off-gas. Additionally, waste feed nitrates and nitrites are converted into nitrogen gas. Organics are initially converted into carbon monoxide, hydrogen, carbon dioxide, and water in the lower part of the fluidized bed. In the upper part of the bed, oxygen is injected to oxidize the gases. Off-gas from the reformer consists of water vapor, carbon dioxide, and nitrogen with less than 1% of the acid gases and less than 300 ppm NO_x.

The steam reformer is operated at 650°C to 800°C and can be electrically heated or operated in an auto thermal mode, whereby the energy needs are supplied by the incoming superheated steam and by the oxidation of organics in the waste and co-reactants.

Microwave Destruction of Organics

A series of five experiments were performed to evaluate the use of microwave radiation to destroy TPB. The results are summarized in the Figure 7.3.2.2. The five experiments all led to approximately 10% destruction of the TPB. The last experiment, MW100-1, microwaved the sample to dryness (approximately 180 °C). Use of microwave energy may be a quick way to heat and decompose the organic slurry but does not seem to have an advantage over other, simpler chemical methods.

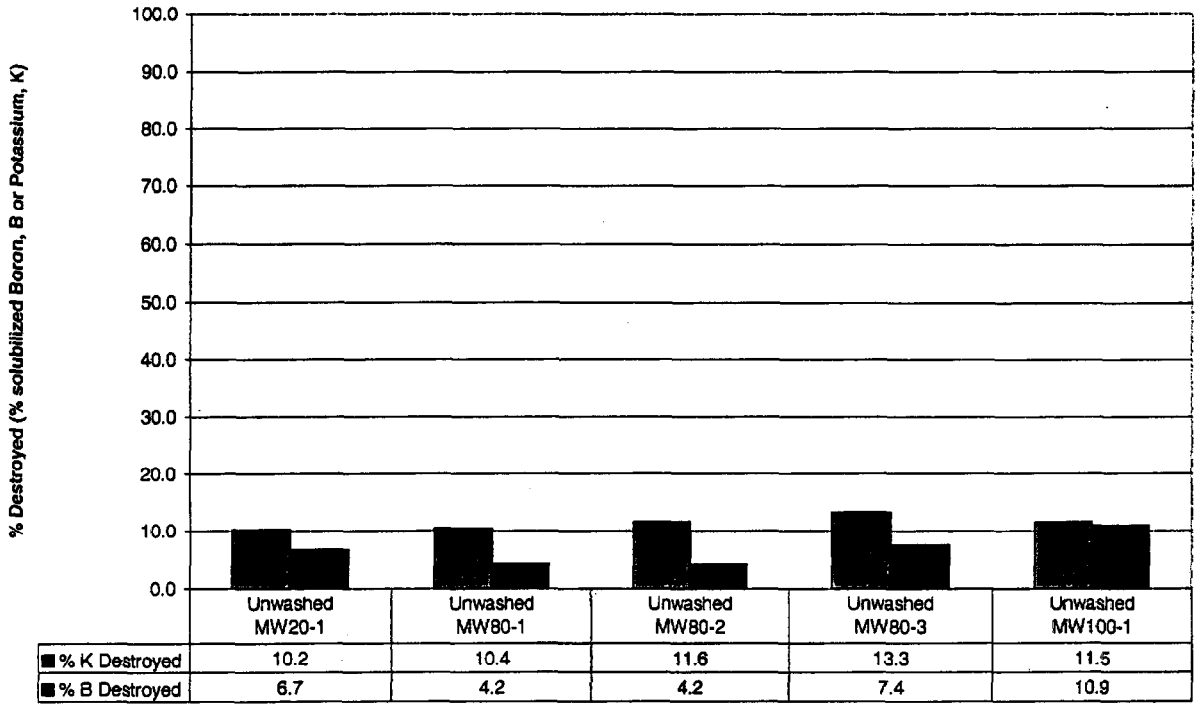
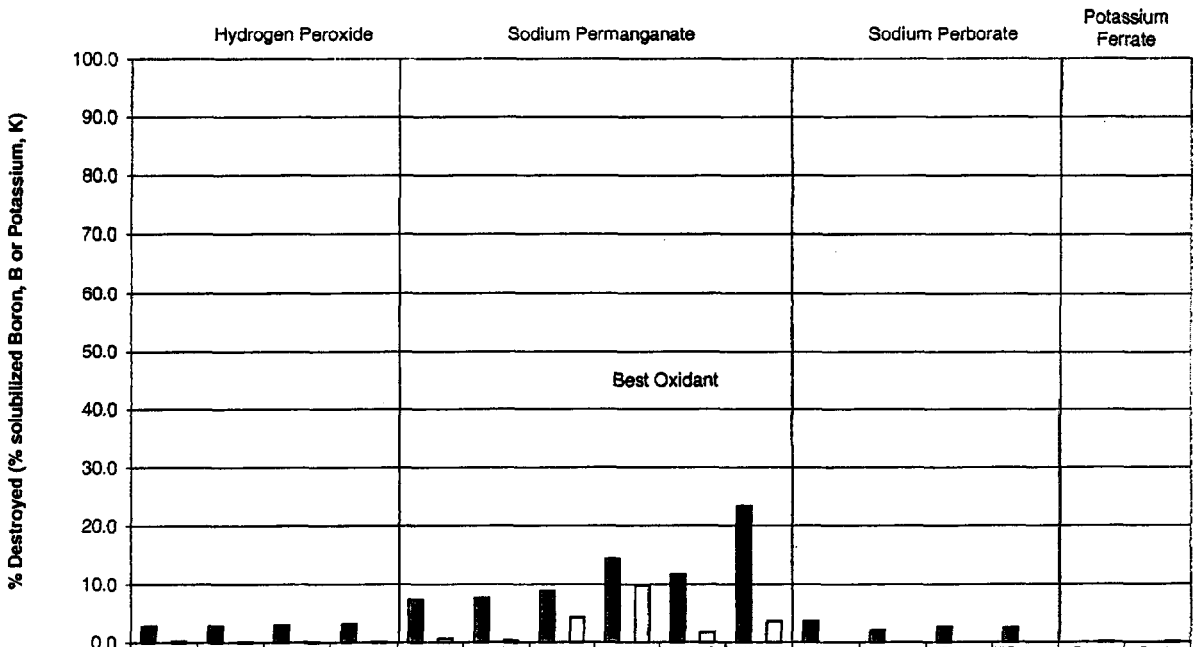


Figure 7.3.2.2 - Comparison of Microwave for TPB Destruction at 20%, 80% and 100% Power

7.3.3 Oxidation Options

Four oxidants – sodium permanganate ($NaMnO_4$), hydrogen peroxide (H_2O_2), sodium perborate ($NaBO_3$) and potassium ferrate (K_2FeO_4) – were tested to determine the best oxidant for destruction of TPB. Because of difficulty finding a commercial source of potassium ferrate, only two ferrate experiments were performed using an old and suspect sample of the reagent.

The use of an oxidant may lead to lower benzene production and high generation of carbon dioxide and other decomposition products that are less flammable than benzene. Sodium permanganate was the best oxidant in our testing. Testing was completed at oxidant levels of two (i.e., low) and five (i.e., high) moles of oxidant per mole of TPB. The most complete destruction of TPB (25%) occurred at 40 °C, so there is a definite advantage at this higher temperature. The TPB decomposition was more complete with washed precipitate, but that may be due to the lower pH of the washed precipitate as testing of permanganate plus formic acid also led to a higher TPB destruction. The results of these experiments are summarized in Figure 7.3.3.1



	Low H2O2 Unwashed B3	Low H2O2 Unwashed C3	High H2O2 Unwashed B4	High H2O2 Unwashed C4	Lo NaMnO4 Unwashed B5	Lo NaMnO4 Unwashed C5	Lo NaMnO4 Washed B22	Lo NaMnO4 Washed C22	Hi NaMnO4 Unwashed B6	Hi NaMnO4 Unwashed C6	Lo Perborate Unwashed	Lo Perborate Unwashed	Hi Perborate Unwashed B18	Hi Perborate Unwashed C18	Ferrate Unwashed B17	Ferrate Washed B17W
% K Destroyed	2.8	2.5	2.9	3.1	7.4	7.7	8.6	14.3	11.7	23.4	3.6	2.0	2.7	2.6	874.5	839.0
Temp, C	25	40	25	40	25	40	25	40	25	40	25	40	25	40	25	25
% B Destroyed	0.2	0.2	0.1	0.2	0.6	0.3	4.1	9.8	1.8	3.6	76.7	83.2	154.8	132.9	0.1	0.1

Figure 7.3.3.1 -- Comparison of Oxidants for Destruction of TPB

Actinide Removal Process (ARP) Oxidation of TPB Using Permanganate Oxidation of TPB Using Permanganate

These two options used permanganate as an oxidant to destroy TPB. The first option above, the oxidation of TPB in the Actinide Removal Facility, is an out of tank alternative to the second option, the Oxidation of TPB In-tank.

The experiments using sodium permanganate led to the destruction of 7% to 23% of the TPB as measured by the increase in soluble potassium. Figure 7.3.3.1 summarizes the results of the various oxidants tested. As can be seen from Figure 7.3.3.1, sodium permanganate was the best oxidant tested. It should also be noted that the TPB destruction was more complete at 40 °C than at 25 °C. The last fact to be noted from this testing is that the higher addition of sodium permanganate (5 moles of oxidant per mole of TPB) led to a significantly higher TPB destruction than the lower addition of sodium permanganate (2 moles of oxidant per mole of TPB).

A carbon mass balance was performed to understand the degree of TPB decomposition and the byproducts that formed during decomposition. The simple TPB decomposition products for hydrolysis are (oxidation and other competing reactions are more complex):

$Na(C_6H_5)_4$ (TPB or 4PM) → 3PB + Benzene [1]

3PB → 2PB + Benzene [2]

2PB → 1PB + Benzene [3]

1PB → Boric Acid + Benzene [4]

Analysis of the decomposition products from the experiment using 5 moles permanganate per mole of TPB based on HPLC analysis showed that 11.7% of the TPB decomposed, primarily to 3PB and 2PB. Based on the carbon balance, 4.8% of the original organic carbon was present as 3PB and 4.2% of the original organic carbon was present as 2PB. Phenol, 1PB and other decomposition products accounted for <1% of the decomposition products. If the TPB decomposed to form benzene along with the 2PB and 3PB, it was calculated that 3.7% of the original organic carbon would be present as benzene. Summing these 3 decomposition products (3PB + 2PB + benzene) should equal the amount of TPB decomposed. This sum is 12.7%, which agrees well with the 11.7% decomposition predicted by the HPLC analyses. Note that this is a much lower decomposition than was predicted by the soluble potassium analysis (23% decomposition predicted by soluble K. The agreement between soluble K and TPB destruction by HPLC was excellent in the other experiments where both analyses were performed.

The disadvantage of using $NaMnO_4$ is that it will result in the addition of MnO_2, an insoluble oxide in HLW. The quantity of MnO_2 that would result from the addition of five moles of $NaMnO_4$ per mole of TPB (127,000 lb) would lead to the addition of 70,500 lb of MnO_2 to the HLW. This is equivalent to the Mn present in 600,000 gallons of Batch 2 sludge. Linear extrapolation of the data suggests that Iit doesn't seem feasible to destroy the TPB with permanganate by itself without the addition of a huge quantity of $NaMnO_4$ such as 21.7 moles of $NaMnO_4$ per mole of TPB (560,000 lb. of $NaMnO_4$).

Oxidation of TPB Using UV Catalyzed TiO2

This is an option that we planned to test using a vendor. In our discussions with vendors, it was decided that this is not a workable process for an opaque liquid, such as a TPB slurry. Because of this discovery, a decision was made not to establish a contract with Calgon Carbon.

Oxidation of TPB Using Water Soluble Mild Oxidant

Testing with water-soluble mild oxidants (sodium perborate and hydrogen peroxide) was much less effective than testing with sodium permanganate. These tests led to high foam generation, which would make the mild oxidant hard to process in Tank 48H. The picture below (Figure 7.3.3.2) shows the foaming during testing with hydrogen peroxide. In addition, these tests resulted in much lower TPB decomposition than sodium permanganate (see Figure 7.3.3.1). The decomposition rate of these oxidants was approximately equal to that of the blanks, experiments conducted without the addition of extra chemicals (i.e., no oxidants, no acid, and no catalyst). There was virtually no difference between the low peroxide addition and the high peroxide addition. This suggests that the peroxide must have reacted with the sodium hydroxide instead of the TPB leading to little decomposition. However testing with Fenton's Reagent (hydrogen peroxide with iron catalyst) was very successful in destroying TPB with the addition of sufficient acid to reduce the solution pH to 9.5 (see Figure 7.3.10.1).

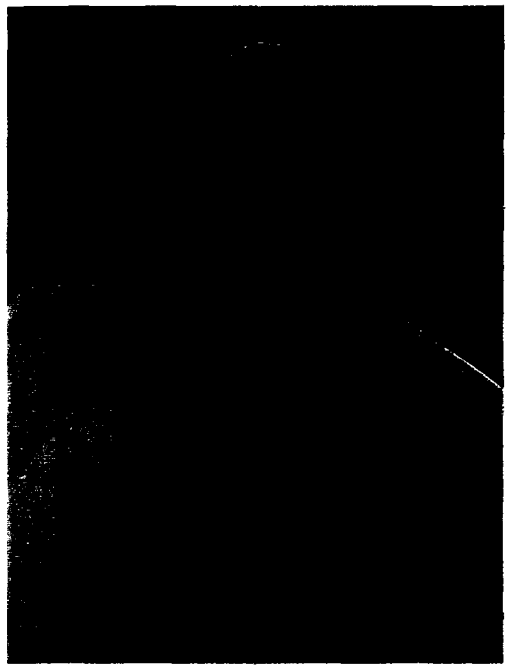


Figure 7.3.3.2 - Foaming produced during peroxide addition to Unwashed Precipitate

7.3.4 Acid Hydrolysis Options

The reference flowsheet for the destruction of TPB uses formic acid as the acid source for acidic hydrolysis of TPB. Several acids were investigated to determine whether formic acid is the best acid for this process. Oxalic and nitric acid were tested in addition to formic acid. The advantage to these acids is that they all will decompose in the melter/offgas system and will not produce more glass in DWPF. In addition, they are not particularly corrosive to the DWPF process (although any acid will be corrosive in the carbon steel waste tanks if the solution pH is low enough). Oxalic acid has a low solubility in water (~8 wt %) so it would not be practical to bring the pH down below 9.5 through the addition of >750,000 gallons of water. Many strong acids – including HCl, HF, and H_2SO_4 – were rejected as they would be too corrosive or cause other problems such as glass solubility in the downstream processing. However, the decomposition of TPB through acid hydrolysis is likely to produce benzene, which may lead to flammability issues.

Nitric Acid

Nitric Acid was the most effective of the three acids tested, leading to complete destruction of the TPB via the addition of 4.1 moles of acid per mole of TPB. Formic acid was nearly as effective and produced fewer tar-like organics as judged by visual inspection. Based on the semi-volative organic analysis, twice as many aromatic compounds, 16 in total, were detected in the experiment with nitric acid than were detected in the nitricformic acid run. Many of these additional compounds were nitrated organics. Oxalic acid was not as effective as nitric or formic acid in our testing at 25 °C or 40 °C but was equally effective at 90 °C. Acids were very effective in destroying TPB but are not deployable as in-tank solutions as they would likely lead to excessive tank corrosion. Figures 7.3.4.1 and 7.3.3.1 summarize the results of this testing.

An organic carbon mass balance was performed to understand the degree of TPB decomposition and the byproducts that are formed during decomposition. The HPLC analysis of the decomposition products showed that all of the TPB decomposed, primarily to 1PB. Based on the carbon balance, 8.2% of the original organic carbon was present as 1PB from the experiment using 4.1 moles of nitric acid per mole of TPB. If all of the TPB had decomposed to 1PB and stopped, there would be 25% of original carbon still present. This means that roughly two-thirds of the 1PB decomposed to benzene or another decomposition product. The data is summarized later in the report in Table 7.3.4.

Table 7.3.4 - Carbon Balance - %C based on HPLC analysis of selected samples

Description of Experiment	4PB	3PB	2PB	1PB	Others
5 moles NaMnO4 per mole TPB	88.28%	4.77%	4.23%	0.28%	52.00%
5 moles NaMn04 per mole TPB	5.28%	0.05%	0.19%	12.67%	8.08%
4.1 moles Formic Acid per mole TPB	0.04%	0.05%	0.04%	8.12%	1.59%
4.1 moles Nitric Acid per mole TPB	0.04%	0.05%	0.04%	14.06%	8.68%
1000 ppm Cu + 4.1 moles Formic Acid per mole TPB	0.04%	0.05%	0.04%	14.06%	8.68%

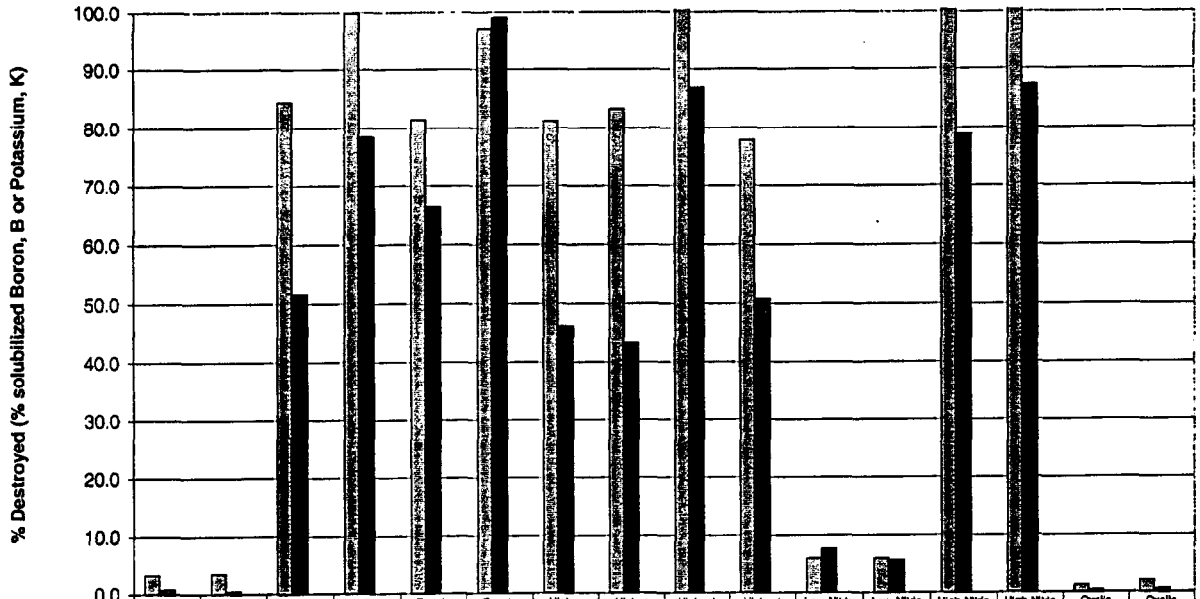
Nitric acid proved very effective in decomposing the TPB within the seven day testing period. Nitric acid led to 100% decomposition, as measured by soluble K, at both 25 °C and 40 °C. The disadvantage of this testing is that it led to a final pH of approximately 1, which would lead to increased tank corrosion. This alternative is viable, but is most likely to be successful in a separate processing tank rather than in Tank 48H.

Formic Acid

Formic acid was the second most effective of the three acids tested, leading to complete destruction of the TPB, as measured by soluble K, via the addition of 4.1 moles of acid per mole of TPB at 40 °C. As was mentioned above, formic acid produced fewer tar-like organics than nitric acid.

An organic carbon mass balance was performed to understand the degree of TPB decomposition and the byproducts that formed during decomposition. The HPLC analysis of the decomposition products showed that all of the TPB decomposed, primarily to 1PB. Based on the carbon balance, 14.1% of the original organic carbon was present as 1PB. If all of the TPB had decomposed to 1PB and stopped, there would be 25% of original carbon still present. This means that roughly 56% of the PBA decomposed to benzene or another decomposition product not measured by HPLC. The data is summarized in Table 7.3.4.

Formic acid was very effective in decomposing the TPB within the seven day testing period. Formic acid led to 84% decomposition at 25 °C and 100% decomposition at 40 °C. The disadvantage of this testing is that it led to a final pH of approximately 5, which may lead to increased tank corrosion. This alternative is viable, but is most likely to be successful in a separate processing tank rather than in Tank 48H.



	Low Formic Unwashed B7	Low Formic Unwashed C7	High Formic Unwashed B8	High Formic Unwashed C8	Formic Washed B21	Formic Washed C21	Higher Formic Unwashed	Higher Formic Unwashed	Highest Formic Unwashed	Highest Formic Unwashed	Low Nitric Unwashed B9	Low Nitric Unwashed C9	High Nitric Unwashed B10	High Nitric Unwashed C10	Oxalic Unwashed B19	Oxalic Unwashed C19
% K Destroyed	3.4	3.8	84.4	99.9	81.5	97.2	81.2	83.3	124.5	77.9	6.0	6.1	106.5	106.5	1.0	2.2
% B Destroyed	0.7	0.4	51.7	78.5	66.3	99.1	46.1	43.3	86.8	50.8	7.7	5.6	78.8	87.3	0.2	0.4
Temp, C	25	40	25	40	25	40	25	40	25	40	25	40	25	40	25	40

Figure 7.3.4.1 -- Comparison of Acids for TPB Destruction

7.3.5 Distribute Waste Among Other HLW Tanks

Calculations were completed which determined that it is not a feasible to distribute the Tank 48H waste to other HLW tanks. Transfer of the Tank 48H contents to four other waste tanks would provide sufficient dilution to meet the organic limit in the tanks. However, there would be a flammability issue in each of these tanks if the TPB decomposed to benzene. To prevent a flammable mixture from forming due to a transfer to another waste tank, small additions (as small as 625 gallons) would have to be made. If each mole of the TPB decomposed to four moles of benzene in a Tank with 250,000 gallons of liquid, the vapor space benzene concentration would exceed 25% of the Lower Explosion Limit with the addition of 625 gallons of Tank 48H slurry. In addition, any tank receiving greater than 625 gallons addition of the TPB containing waste would likely require benzene monitoring and nitrogen blanketing. However, even if controls and monitoring could lead to the safe deployment of this option, it may lead to future processing problems as this material is evaporated or fed to DWPF.

7.3.6 Direct Grout

The Team considered three possible methods for disposing the Tank 48H solution as grout. The first idea was to grout the waste in place in Tank 48H and later return the tank to service with a lower volume due to the loss of the grouted volume. This would lower the volume of the tank by at least 250,000 gallons unless the waste could be concentrated. This option was considered too risky as leaving grout in a HLW tank has not been demonstrated before and because it will take longer to receive regulatory approvals.

The second idea was to transfer the waste to another waste tank that will be closed and use it as the liquid necessary for grout. This is feasible, although this would be a radical departure

complexity of closing a waste tank and will take longer to receive regulatory approvals.

The third idea is to use the Tank 48H slurry as feed to the Saltstone Facility. If the proposed higher ^{137}Cs activity limit of 0.05 Ci/gal is adopted, it would take approximately 8-million gallons of waste free of ^{137}Cs to blend with Tank 48H to meet the ^{137}Cs limit. This is not a feasible option to quickly empty Tank 48H, as the feed to Saltstone will likely be approaching the ^{137}Cs limit. Calculations and information to support these conclusions are contained in a lab notebook[6].

7.3.7 In-Tank Bioremediation

This option has not been tested. A subcontract has been awarded to PMC, Inc. to complete testing to determine whether this option is practical. It will be approximately mid October before results will be available. It is recommended that this option be maintained as an acceptable option until the results of this testing is available.

7.3.8 Metathesize with Cold Cesium

Virtually all of the tetraphenylborate in Tank 48H is trapped as the cesium and potassium salt. This material is highly insoluble in the salt solution. It may be possible to remove the radiocesium from the K/CsTPB slurry, through a process known as isotopic dilution. Isotopic dilution is the process of adding one isotope (Cs-134) to lower the relative concentration of an existing isotope (Cs-137). If successful, isotopic dilution would exchange out most of the radiocesium with cold (Cs-134) cesium. The radiocesium would end up in the supernate, which could be pumped to other tanks. The resulting TPB slurry would possess a much lower activity and be much simpler to work with from a shielding perspective.

The researchers generated a small quantity of ^{137}CsTPB. This slurry was added to the Tank 48H salt simulant (unwashed), and the resulting slurry was well mixed. The slurry was aged for two days before a 1000 fold excess of $^{134}CsNO_3$ (i.e., non-radioactive or "cold" cesium) was added. The filtered supernate from this mixture was sampled over a period of one week and analyzed by gamma spectroscopycan.

If the isotopic dilution occurred as we predicted, the amount of radiocesium in the supernate should increase over time (up to a theoretical maximum of 5.9E+07 dpm/mL), to a point where 99.9% of the radiocesium should be in solution. What we observed was a decrease in radiocesium over time (see figure 7.3.8.1). By the end of the experiment, only 0.058% of the radiocesium remained in solution. The solution was not at equilibrium prior to the addition of the cold cesium despite waiting two days prior to adding the cold cesium. Due to the lower solubility constant (k_{sp}) of CsTPB vs KTPB, small quantities of free cesium in solution likely exchanged with the excess KTPB to form ^{137}CsTPB. That caused the cesium activity in solution to decrease. The addition of the cold cesium seemed to have little effect on the hot cesium in solution, possibly due to the slow exchange kinetics between the hot and cold cesium.

This scoping test does not show favorable enough results to pursue.

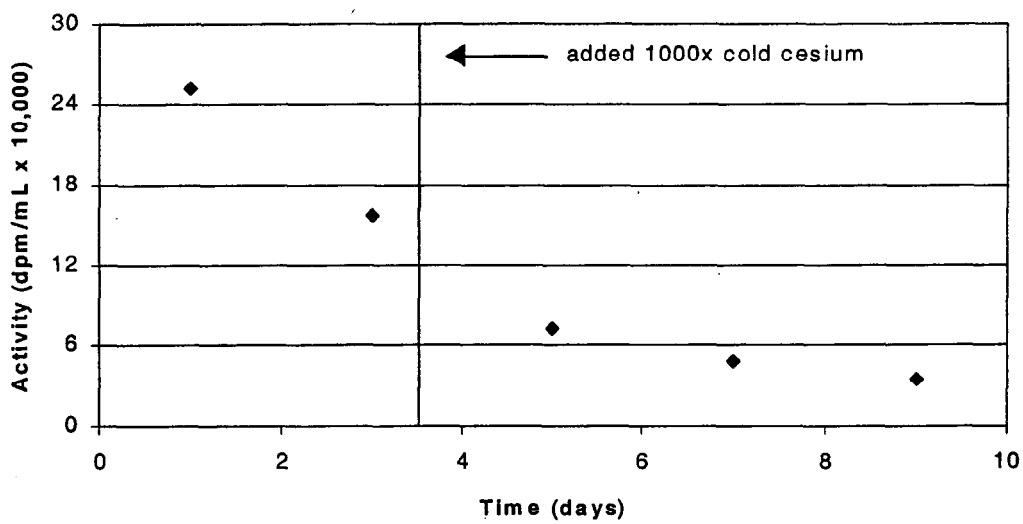


Figure 7.3.8.1 - Results of Metathesis Testing using Cold Cesium

7.3.9 Tank In Tank

The Tank-in-tank option involves to placing small and simple processing equipment into Tank 48H to eliminate the need for new equipment above the tank. Since Tank 48H is already shielded, this would lead to lower radiation exposure during processing. In-Tank filters were as used during the 1983 demonstration of the TPB precipitation and concentration. The type of equipment for the Tank-in-Tank processing has not been defined as it depends on the process chosen. As a result, this option was not studied. It is one of the hybrids that must be combined with other options to produce an acceptable solution.

7.3.10 New Options

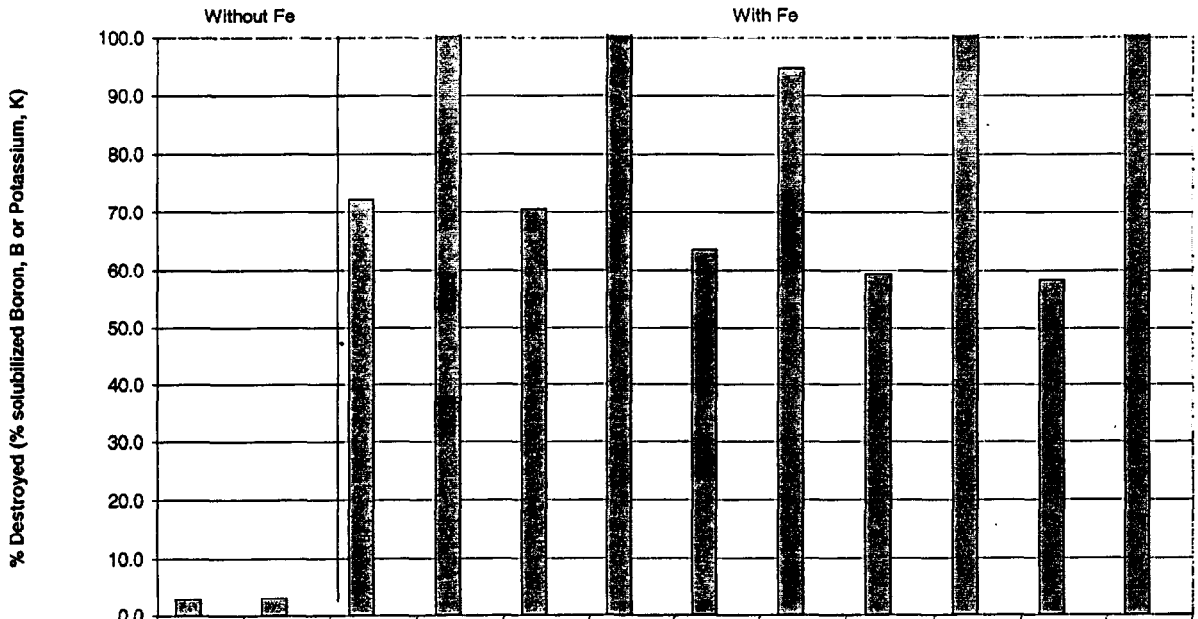
further testing be completed to determine whether these can be used to destroy the TPB in Tank 48H.

Fenton's Reagent

The addition of hydrogen peroxide with an iron catalyst (i.e., Fenton's reagent) was effective in destroying the TPB in all the experiments (see Figure 7.3.10.1). The experiments were tested at two levels of iron catalyst and the destruction was complete at both levels at 40 °C. Testing should be completed at lower concentrations so that the minimum amount of iron will be added. The testing was more effective at 40 °C but still destroyed 70% of the TPB at 25 °C in the seven days of testing. The final pH of all the solutions were much lower than planned. The final pH of the unwashed runs was approximately 5 (pH 9.5 was the target) due to over adding acid.

The recipe used in this experiment would result in the addition of 30,000 gallons of 90 wt % formic acid, 92,000 lb or 11,000 gallons of 30 wt % hydrogen peroxide, and 10,000 lb of ferric nitrate. The advantage of using Fenton's reagent is that it will result in the addition of iron hydroxide and water (i.e., the hydrogen peroxide will decompose to water) to the HLW. The quantity of Fe_2O_3 that would result from the addition of five moles of hydrogen peroxide per mole of TPB (127,000 lb) would lead to the addition of 2,000 lb of Fe_2O_3 to the HLW. This is equivalent to the Fe present in 2,500 gallons of Batch 2 sludge.

Future testing should be completed with a decreasing acid addition to determine if the reaction is effective at a higher pH.



	High H2O2 Unwashed B4	High H2O2 Unwashed C4	Fenton Unwashed B25	Fenton Unwashed C25	Fenton Unwashed B26	Fenton Unwashed C26	Fenton Washed B27	Fenton Washed C27	Fenton Washed B28	Fenton Washed C28	Fenton Washed B29	Fenton Washed C29
% K Destroyed	2.9	3.1	72.3	107.3	70.6	131.0	63.5	94.8	59.4	101.3	58.3	101.9
Temp, C	25	40	25	40	25	40	25	40	25	40	25	40

Figure 7.3.10.1 - Comparison of Fenton's Reagent for TPB Destruction

Acid Plus Permanganate

The addition of sodium permanganate was effective in partially destroying the TPB. The combination of acid and permanganate is often used to destroy organics. (The combination of phosphoric acid and potassium permanganate is used in the Containment Facility in SRTC's Shielded Cell Facility to destroy TPB.) We examined whether TPB could be completely destroyed using a combination of sodium permanganate plus and acid (to lower the tank to 9.5). Two experiments used this combination. Figure 7.3.10.2 summarizes the results. The combination led to approximately a five-fold increase in TPB decomposition (100%) compared to experiments using only permanganate.

The recipe used in this experiment would result in the addition of 30,000 gallons of 90wt % formic acid and 127,000 lb of $NaMnO_4$. It is recommended that this combination be considered for treatment of the Tank 48H contents.

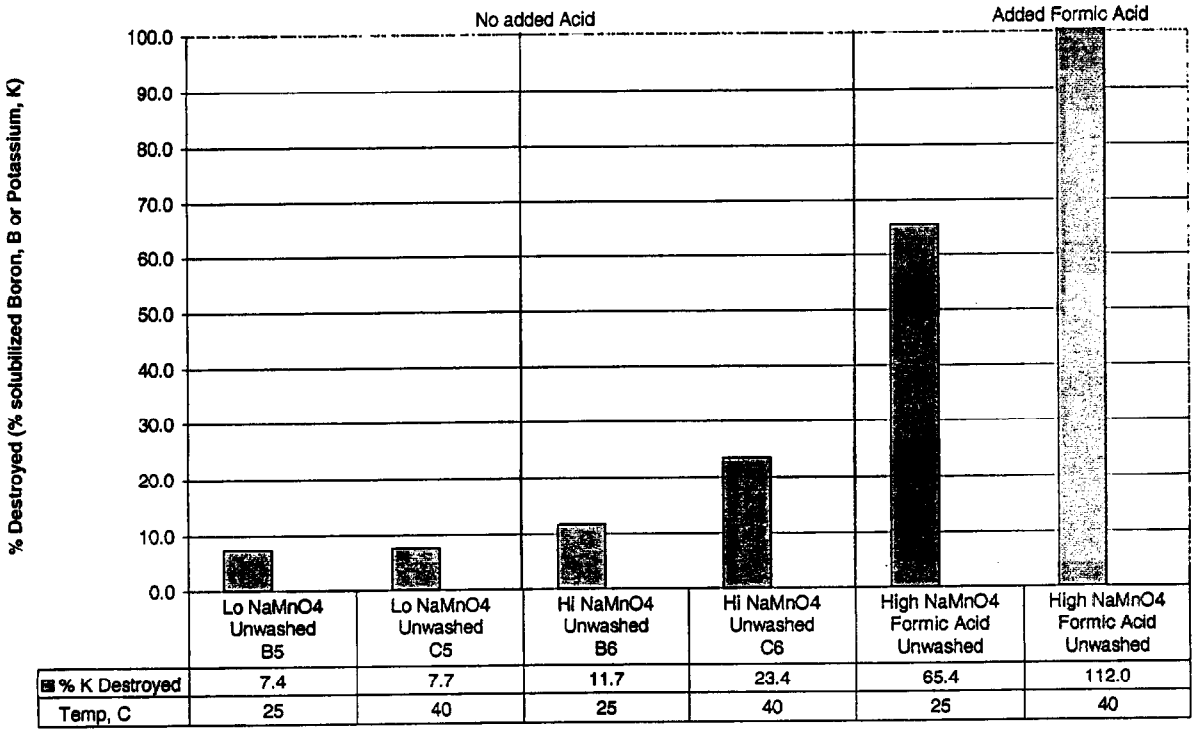


Figure 7.3.10.2 Comparison of Permanganate with and without Added Formic Acid for TPB Destruction

7.4 Risk Identification

As stated earlier, no programmatic risks could be identified that could be used to discriminate between the options at this stage of development. This does not mean to say that there are no programmatic risks associated with the options but merely that the programmatic risks are more or less equally applicable to all of the options. Technical risk however was judged significantly different between the options. There was enough difference in the regulatory risks to warrant using this area for comparison also. This approach required that technical and regulatory risk be employed as discriminating criteria during the evaluation. The technical and regulatory risks associated with each option were discussed in depth during the evaluation. The team employed subject matter experts during the evaluation to assist with risk identification and comparing the magnitude of risks between options during the pair-wise comparison.

7.4.1 Environmental Risks

Regulatory risks consist of both safety and environmental concerns. Safety risks are discussed in the appropriate Safety Analysis Report; therefore, this section will only discuss environmental concerns. These concerns include the generation of waste (including hazardous waste), waste minimization, and the impacts of air emissions and liquid effluents. For the reasons discussed below, the environmental risks for the removal of benzene from Tank 48H are believed to be known, and would have minimal impact to the alternatives as currently contemplated.

The South Carolina Department of Health and Environmental Control (DHEC) has issued an Industrial Wastewater Permit, # 17,424-IW, for the F/H Tank Farms (including Tank 48H). Tank 48H is also covered under a DHEC Bureau of Air Quality permit number 0080-0041-H. There are also radiological NESHAP limits for the tank farm. However for Tank 48H a special condition has been specified in the permit. That condition is for the emission of benzene and diphenyl mercury. The maximum permissible Benzene emission rate is 0.61pounds per hour (annual average) and 46.30 lbs./hr. instantaneous max. For diphenyl mercury, the maximum emission rate is 0.00055 pounds per hour (on an annual average). Currently, a new Part 70 Air Quality Permit application affecting Tank 48H and other HLW facilities is on file with DHEC. This application has been out for public comment, and is now awaiting a public hearing at a time and place to be determined by DHEC. Any changes to the Part 70 application on file arising from the public hearing and subsequent regulatory reviews will require a review of this section 7.4.1 for any impacts.

During this investigation to return Tank 48H to tank farm service, nine processes have been determined to be viable alternatives to eliminating the organics within the waste.

At the present time, no permit modifications or new permits are believed to be required for any of the processes which could be performed within the tank, so long as the tank temperatures and any required chemicals to be added to Tank 48H would not alter the composition of the tank farm effluent from that which was evaluated for the existing NPDES permits.

For the nine identified processes, any process which would require the contents of Tank 48H to be transferred to other existing facilities, such transfer(s) may require permit modifications to both the Industrial Wastewater and Air emissions permits. Regardless, a NEPA evaluation shall be performed for assessing the environmental impacts due to the selected process.

For the unlikely event of the construction of new facilities, a NEPA evaluation shall also be performed. New permits (or exemptions) for Industrial Wastewater effluents and Air emissions would be required from the regulators. Additionally, no new construction or modifications or the purchase of new equipment could begin until approval (or an exemption) has been received from DHEC's Bureau of Air Quality.

7.4.2 Safety

The current tank level in Tank 48H is approximately 70 inches and the evaluation results reported below are valid up to a tank level of 248 inches. It should be noted that no credit is taken for the fact that the increase in tank level would actually dilute the concentration of radionuclides in the tank. Therefore, the results are conservative. In addition, the inventory of radionuclides is limited to that which is currently in the tank because the Authorization Agreement (AA) only permits the storage of precipitate in Tank 48H and does not permit the transfer of waste into or out of Tank 48. In addition, the Authorization Basis (AB) does not permit the transfer of waste material into or out of Tank 48H. The current deflagration analysis for Tank 48 shows that the consequences of a deflagration event are well below Evaluation Guidelines for both onsite (TEDE is 58 mrem at 100 meters using ICRP-30 guidelines and 50th% quantile dose level) and offsite (TEDE is 28 mrem using ICRP-30 guidelines and 95th quantile dose level) receptors. These results support a likely determination that there will be no SAR controls required for any option from a radionuclide consequence standpoint. For this evaluation, it is assumed that this conclusion is unlikely to change during an in-tank detonation scenario.

For the in-tank catalytic disposition process, an evaluation (S-CLC-H-00757, Rev. 1) was performed for Tank 49H using a benzene release rate of 1000 g/min to determine the affects to the onsite worker. A 1000 g/minute release rate is expected to be a reasonable assumption, especially considering the experience on Tank 49H. Since it is a ground release, the difference in stack height between these tanks is inconsequential. The results showed that the concentrations at 100 meters was 1.3%, 0.03%, and 3.4% of ERPG-2 limits assuming a release form of benzene, CO2, and CO, respectively.

If higher benzene release rates were to occur, the consequence increase would be linear and thus, even if extreme rates are assumed, the consequences would still be a small percentage of ERPG-2 guidelines. This evaluation is reasonably expected to bound all other processes involving the production of benzene. For instance, batch processing will result in only a fraction of the consequence of the in-tank process. Based on the above, it is expected that no Safety Class or Safety Significant AB controls are warranted for any option involving benzene production.

Regardless of the option ultimately chosen, an evaluation would be included in the SAR that provides the basis for no AB controls. At this time, available documentation is indicating that no SAR controls are likely to be warranted. Other factors such as capital risk may affect the determination as to where the standard industrial type of controls would be captured and approved. In the most challenging circumstances of benzene release, the in-tank process, the ability to maintain the vapor space inerted for the duration of the activity has already been demonstrated in Tank 49H. In that case, the Tank 49H vapor space remained inerted for a few years with no process difficulties with respect to inerting. Knowing the above, the team chose to look at each process and provide a safety determination based on relative risk from a standard industrial hazard standpoint. For instance, even if benzene is produced in less quantity in one option (which involves an acid addition to lower the pH) than in another option, the lower benzene generation rate is likely to be offset by the need to have acid in a nearby storage tank. Another example involved the steam reforming/fluidized bed destruction of organics. In this option, the benzene generation was essentially eliminated and, relatively speaking, it was considered the safest option. However, the capability to maintain steam temperature at 600 degrees C presents its own safety challenges. As a result, the options did not vary significantly from a safety standpoint from one option to another and there was no substantive safety discriminator between each option.

7.4.3 Process Safety

Identifying the process risks is necessary in comparing the alternative processes. If any of the processing can be completed in Tank 48H, the processing must protect the integrity of the carbon steel tank. For processing in another facility, it is assumed that the materials of construction chosen are appropriate for the process chemistry.

There are risks that are common to each of the alternatives. The slurry in Tank 48H contains TPB, radioactive cesium, and radioactive sludge. As a result, these processes will all have similar radiological risks. In addition, the decomposition of TPB will produce some benzene, a potentially flammable and toxic gas and other TPB decomposition products. As a result, a flammability strategy involving dilution with air or nitrogen is expected. Unless the benzene production rate is small and constant, it is expected that a flammability strategy using nitrogen to minimize the oxygen concentration will be necessary in all options except the steam reforming.

All the options will produce a variety of TPB degradation products. For example, the Tank 49H decomposition produced considerable biphenyl. The biphenyl collected and solidified in the condenser and hindered heat transfer. Any of the processes could be designed to handle the production of biphenyl and other solid decomposition products.

Any of the processes below would need to be well mixed to control the reaction rate and maximize the TPB decomposition. Good mixing together with cooling is necessary to ensure the slurry temperature can be controlled. Any of the decomposition reactions will produce gaseous byproducts. The offgas system will need to handle this generation rate and prevent pressure excursions. This gas generation is also likely to produce foam which can be stable in this TPB matrix.

Below is a summary of the major process hazards expected for each of the process alternatives. This listing is based on studies to date and is not complete but will be developed as new risks are identified through the proposed follow-on studies, lessons learned findings, literature surveys and other testing designed to identify potential problems.

7.4.3.1 Salt Cell Process

The risks of the Salt Cell Process are well understood. The TPB is decomposed using acid hydrolysis, which requires concentrated formic acid (a reducing agent and organic acid), and copper catalyst at elevated temperature (90 °C) to decompose the TPB. The benzene produced is condensed and collected in a decanter. High boiling point organics are removed from remaining aqueous slurry via steam stripping. The resultant solution, approximately the same volume as the original solution, would be fed to the DWPF SRAT for processing. The other liquid product would be benzene and other organic decomposition products that are soluble in benzene. The organic decomposition products will have to be disposed of via an offsite vendor or a new processing facility.

7.4.3.2 Catalytic Process

A catalytic process, without the addition of additional reagents, could occur in Tank 48H or another facility. Although decomposition of TPB during processing generates mainly benzene, a number of other TPB decomposition byproducts, including biphenyl would be produced. The TPB is decomposed at ambient tank temperatures (25-40°C). The benzene from this process would be removed via natural evaporation to the atmosphere. The product from catalytic decomposition is a salt solution containing nonvolatile TPB decomposition products. This solution would likely be fed to the Salt Processing Facility. The solids from the Salt Processing Facility would be fed to DWPF for processing. The decontaminated supernate would be fed to

Saltstone. Testing would be needed to ensure that this slurry is compatible with the Salt Processing Facility, DWPF, and Saltstone.

7.4.3.3 Acid Only

The risks of the Acid Only Process are similar to the risks in the DWPF Salt Cell. The benzene produced could be condensed and collected in a decanter. This would produce more high boiling point organics and less benzene than the DWPF Salt Cell process. The resultant solution, approximately the same volume as the original solution, would be fed to the DWPF SRAT for ultimate processing. The other liquid product would be benzene and other organic decomposition products that are soluble in benzene. Testing would need to be completed to ensure that this slurry is compatible with DWPF.

7.4.3.4 Acid Plus Catalyst in a New Facility

The risks of the Acid Plus Catalyst Process are similar to the risks in the DWPF Salt Cell. This process would be similar in complexity to the DWPF Salt Cell process. This would produce more high boiling point organics and less benzene than the DWPF Salt Cell process. The resultant solution, approximately the same volume as the original solution, would be fed to the DWPF SRAT for ultimate processing. The other liquid product would be benzene and other organic decomposition products that are soluble in benzene. Testing would need to be completed to ensure that this slurry is compatible with DWPF.

7.4.3.5 Thermal Decomposition (Steam Reforming)

The risks of steam reforming are fairly well understood as steam reforming is used commercially. Decomposition of TPB during processing generates mainly CO_2 and Nitrogen, although incomplete reduction would lead to NO_x production and incomplete oxidation of benzene could lead to CO production. The TPB is decomposed using elevated temperatures (600-800°C), which requires superheated steam, a reductant such as coal or sugar, and a catalyst. The product from steam reforming would be a dehyrated solid. This solid would be combined with water and fed to the DWPF for ultimate processing. Testing would be required to ensure this slurry is compatible with DWPF.

7.4.3.6 Oxidant Process

An oxidation process may be possible in Tank 48H using sodium permanganate. Although decomposition of TPB during processing would produce relatively less benzene and more carbon dioxide, a number of other TPB decomposition byproducts, including benzene, phenol, and biphenyl would still be produced. The TPB is decomposed at ambient tank temperatures (25-40°C). However, oxidation of TPB leads to heat generation so higher temperatures can be reached if the oxidation reaction rate is not

properly controlled. The benzene from this process would be removed via natural evaporation to the atmosphere. The product from the oxidation of TPB is a salt solution containing nonvolatile TPB decomposition products. This solution would likely be fed to the Salt Processing Facility. The solids from the Salt Processing Facility containing a large concentration of MnO_2, would be fed to DWPF for ultimate processing. The decontaminated supernate would be fed to Saltstone. Testing would be needed to ensure that this slurry is compatible with the Salt Processing Facility, DWPF, and Saltstone.

7.4.3.7 Oxidant Plus Acid Process

The addition of sodium permanganate, an oxidant together with formic acid can be combined to increase the TPB decomposition. This process may be possible in Tank 48H or another facility. An acid addition leading to a final solution pH of 9.5 is possible in-tank while a lower solution pH of 4 or less would probably be performed in a new facility. The TPB is decomposed at ambient tank temperatures (25-40°C). However, oxidation of TPB leads to heat generation so higher temperatures can be reached if the oxidation reaction is not properly controlled. The benzene from this process would be removed via natural evaporation to the atmosphere. The product from the oxidation of TPB is a salt solution containing any nonvolatile TPB decomposition products. This solution would likely be fed to the Salt Processing Facility. The solids from the Salt processing facility containing a large concentration of $Mn0_2$, would be fed to DWPF for ultimate processing. The decontaminated supernate would be fed to Saltstone. Testing would be needed to ensure that this slurry is compatible with the Salt Processing Facility, DWPF, and Saltstone.

7.4.3.8 Fenton Process

The addition of sodium peroxide, an oxidant, iron, a catalyst together with formic acid can be combined to increase the TPB decomposition. The risks are very similar to the permanganate plus acid process. One additional risk is that hydrogen peroxide can react with itself andd decomposed to oxygen plus water. As a result, the process would have to be inerted and have oxygen monitoring to prevent a flammable mixture from forming. Although decomposition of TPB during processing would produce relatively less benzene and more carbon dioxide, a number of other TPB decomposition byproducts, including benzene, phenol, and biphenyl would be produced. The TPB is decomposed at ambient tank temperatures (25-40°C) but the tank contents could be cooled or diluted if the reaction rate is higher than expected. The benzene from this process would be removed via natural evaporation to the atmosphere. The product from the oxidation of TPB is a salt solution containing nonvolatile TPB decomposition products. This solution would probably be fed to the Salt Processing Facility.

The solids from the Salt Processing Facility containing iron, would be fed to DWPF for processing. The decontaminated supernate would be fed to Saltstone. Testing would be needed to ensure that this slurry is compatible with the Salt Processing Facility, DWPF and Saltstone.

7.4.3.9 Catalyst Plus Acid Process

A catalyst process may be possible in Tank 48H or another facility. An acid addition leading to a final solution pH of 9.5 is possible in-tank while a solution with a pH of 4 or less would probably be performed in a new facility. Formic acid plus a catalyst would be combined with the TPB slurry to decompose the TPB. The main risk of an acid hydrolysis process is the benzene generation during TPB decomposition. As a result, the process would have to be inerted to prevent flammability. Although decomposition of TPB during processing would produce less benzene and more carbon dioxide, a number o other TPB decomposition byproducts, including benzene, phenol, and biphenyl would be produced. The TPB is decomposed at ambient tank temperatures (25-40°C), but the tank contents could be cooled or diluted if the reaction rate is higher than expected. The benzene from this process would be removed via natural evaporation to the atmosphere. The product from the oxidation of TPB is a salt solution containing nonvolatile TPB decomposition products. This solution would likely be fed to the Salt Processing Facility. The solids from the Salt Processing Facility containing the catalyst, would be fed to DWPF for ultimate processing. The decontaminated supernate would be fed to Saltstone. Testing would be needed to ensure that this slurry is compatible with the Salt Processing Facility, DWPF, and Saltstone.

7.5 Selection Process

7.5.1 Re-Screening

In the initial screening (Phase 1), no option was rejected based upon lack of knowledge, however; several potentially fatal flaws were uncovered within some of the initial list options after reviewing the technical data obtained during Phase 2. If this knowledge had been available at the time of initial screening, it would have resulted in the exclusion of these options. As a result, the team decided to re-screen the all current options using the original Phase 1 screening criteria to reduce the number of alternatives for Phase 2 evaluation by eliminating those that are no longer viable.

The initial list was modified to add three new options:

- Permanganate + Acid
- Fenton's Reagent
- Acid Only

After screening the number of options was reduced down to nine see (Table 7.5-1).

Table 7.5.1 Options Carried Forward To Selection Process

Evaluation Code	Initial list Option upon which Selection option is based	Alternative Description	How?	Re-Screening Result
CDAT-D	3	DWPF Salt Cell Catalytic Decomposition Process (considered for technology/process)	Thermal + Catalytic + Acidic	Pass
CDAT-N	6	Catalytic Decomposition of TPB in a New Facility	Thermal + Catalytic + Acidic	Pass
CD	5	Catalytic Decomposition of TPB	Catalytic	Pass
CDA	7	Catalytic Decomposition of TPB by Lowering pH (Acid Addition)	Acidic + Catalytic	Pass
THERMAL	11	Thermal Decomposition of TPB	Thermal	Pass
	37	Hybrid – Microwave Destruction of Organics	Thermal	Testing showed tThis isto be another form of thermal and has been grouped with Alternative 11
	39	Steam Reforming/Fluidized bed Destruction of Organics	Thermal	Grouped with Alternative 11
	38	Volume-Reduce by Filtration, Sending Filtrate to Tk 50, Catalytic Decomposition of Residual In-Tank	Catalytic	Grouped with Alternative 5
	33	Catalytically Decompose TPB Using Tank 49 as a Reaction Vessel	Catalytic	Grouped with Alternative 5
	35	Actinide Removal Process (ARP) Oxidation of TPB Using Permanganate	Oxidation	Grouped with Alternative 10
	36	Hybrid – Tank In Tank		Considered for use with alternatives where applicable but not carried on as an option itself
	8	Oxidation of TPB Using UV Catalyzed TiO_2	Catalyzed Oxidation	Reject- vendor indicated technology will not work on opaque solutionsHas not been successfully proven

Evaluation Code	Initial list Option upon which Selection option is based	Alternative Description	How?	Re-Screening Result
	17	Distribute Among Other Tank	Data Study	Reject-Too great an impact on existing tanks and not allowed per current AB, 96-1 and regulatory restrictions
	18	Direct Grout	Data Study	Reject-Does not meet WAC without significant (approx ~32X) dilution which is not feasible for implementation
	9	Oxidation of TPB Using Water Soluble Mild Oxidant	Oxidation	Reject-Testing showed no favorable results
PERM	10	Oxidation of TPB Using Permanganate	Oxidation	Pass
	23	In-Tank (or coupled tank) Bioremediation	Contract	Investigation to be carried along in a parallel effort and re-introduced into the evaluation if favorable test results are achieved
	26	Hybrid – Metathesize with Cold Cesium		Considered for use with alternatives where applicable but not carried on as an option itself
PERM+ACID	New Option	Permanganate + Acid	Acid + Oxidation	Pass
FENTON	New Option	Fenton's Reagent (iron, acid and peroxide)	Acid + Catalyst + Oxidation	Pass
ACID	New Option	Acid Only	Acid	Pass

7.5.2 Methodology/Tool

The weighted selection criteria (Table 7.2-2) was used to evaluate the options listed in Table 7.5-1. The team employed an analytical hierarchy process by using the ECPro software tool and a "pair-wise" comparison of options. Each option was successively compared against each other for each of the selection the criteria. The ECPro software tool applied the selection criteria weights to the numerical values obtained from the comparisons to establish a score for each of the options.

To assist in the comparison of the options for process rate it was necessary to estimate additional data and assume the location (i.e. "in-tank" or "out-of-tank") for the option based on compatibility of the process chemistry with the tank. The process rates estimated and used in pair –wise comparison are shown in Table 7.5.2-1.

Table 7.5.2-1 Process Rates

Option	In Tank	gal/batch	Weeks to Process
Salt Cell Process	No	5,000	50
Catalytic Process	Yes	250,000	30
Acid Only	No	5,000	50
Acid + Cattiest New Facility	No	5,000	50
Thermal	No	5,000	50
Oxidant Only	Yes	250,000	20
Permanganate + Acid[1]	No	5,000	50
Catalyst + Acid[1]	No	5,000	50
Fenton[1]	No	5,000	50

[1]The team evaluated these processes as out of tank due to the lack of a complete data set at pH 9.5; however, the team expects that these processes will function at pH>9.5 and may be acceptable as in tank processes.

Although different hazards were associated with the options, the level of control necessary to make the hazards safe was relatively similar throughout. To assist in discriminating between the options Table 7.5.2-2 was developed.

Table 7.5.2-2 Process Hazards

Option	In Tank[1]	Benzene[2]	Chemical Interaction (CI) and Other
Salt Cell Process	No	100%	CI-Moderate
Catalytic Process	Yes	100%	CI-Low
Acid Only	No	100%	CI-Moderate
Acid + Catalyst New Facility	No	100%	CI-Moderate
Thermal	No	0%	CI-Low; Superheated Steam
Oxidant Only	Yes	50%	CI-High
Permanganate + Acid	No	50%	CI-High
Catalyst + Acid	No	100%	CI-Moderate
Fenton	No	50%	CI-High

[1] Easier to design controls for a well engineered out of tank process than to retrofit Tank 48 to accomplish the same process.

[2] Relative benzene production (a thermal method would destroy all of the benzene, while an oxidation reaction would destroy most of the benzene and the other reactions would produce virtually all benzene as the primary decomposition product).

After the pair-wise comparisons were completed the AHP determined the score of each option. The results are shown in Attachment 3-1.

7.6 Sensitivity Analysis

A sensitivity analysis was performed on the selected alternatives to see if change in the weighting of any Selection criterion would alter the final selection. The dynamic sensitivity analysis feature of the selection support software, ECPro, was used to perform this analysis. By increasing the weight of a selection criteria by 50%, the program proportionally adjusted the remaining criteria and recalculated the score for each option. This was done for each selection criteria and demonstrated that the rankings based on the obtained scores did not change for the firsttop and second ranked options. The leading two options were shown to be robust selections as the sensitivity analysis did not change their rankings. The third through fifth options remained relatively close during the analysis but did change in ranking order. (Refer to Attachments 3-2 through 3-9)

The team then adjusted the selection criteria weighting to equalize all weights. The resulting ranking (Attachment 3-1) shows Permanganate and Catalytic Decomposition ranked first and second with Salt Cell process and Thermal Decomposition ranked second and third. This demonstrates that if the technical risk and science issues could have been resolved with these in-tank options they would have been ranked first and second instead of the Salt Cell process and Thermal Decomposition.

7.7 Selection Conclusions

The first and second ranked options were Salt Cell Technology/Process and Thermal Decomposition.

The Team concluded that the first and second option should be carried forward to the final selection and recommendation phase where cost and schedule considerations will be investigated and considered in a final recommendation.

The research on the Bioremediation option should be allowed to continue to completion as this option, sufficiently matured and tested could provide the most favorable solution if the R&D results are acceptable.

The amount of research needed to complete development of the technical bases for the in-tank process options appears relatively modest versus the costs required to pursue the two leading candidates (see Attachment 4). Hence, continued research on the most promising of those options – i.e., use catalyst and permanganate – appears prudent. The Team recommends aggressive pursuit of these options.

If any of the remaining options are matured further before the final recommendation, the Team should perform a review as part of the final recommendation process to ensure that a desirable option has not been excluded.

8.0 References

1 WSRC-RP-2002-00131, HLW Tank 48 Disposition Systems Engineering Management Plan, Revision 0, February 5, 2002.
2 WSRC Purchase Order AC2607N to PMC Technologies, June 18, 2002.
3 WSRC-TR-2000-00253, Rev. 0, Tank 49 Disposition Plan, K.B. Martin, T.B. Peters, R.C. Fowler, R.J. Bentley, C.D. Banaszewski, M. R. Poirier, July 2, 2000.
4 WSRC-RP-93-527, Rev. 0, DWPF Coupled Feed Flowsheet Material Balance with Batch One Sludge and Copper Nitrate Catalyst, A.S. Choi, September 28, 1993.
5 WSRC-RP-94-149, Technical Investigation of the Aquafine Incident (U), M.J. Barnes, February 4, 1994.
6 WSRC-NB-2002-00031, Laboratory Notebook, "Tank 48 Decomposition Studies", pages 22-26.
7 HLW-SDT-99-0266, Salt Cell Equipment Relocation Study, Revision 0, August 31, 1999.

9.0 List of Abbreviations

The following abbreviations are used through the report and are listed for clarification.

1PB – phenylboronic acid – $C_6H_5B(OH)_2$
2PB – diphenylborinic – $(C_6H_5)_2BOH$
3PB – triphenylbor - $(C_6H_5)_3B$
4PB – tetraphenylborate or tetraphenyl boron, also TPB
CD - Critical Decision
CIF - Consolidated Incineration Facility

D&D - Decontamination and Decommission
DNFSB - Defense Nuclear Facility Safety Board
DOE - Department of Energy
DOE-SR - Department of Energy - Savannah River
DWPF - Defense Waste Processing Facility
e.g. - for example
EPA - Environmental Protection Agency
ESP - Extended Sludge Processing
ETF - Effluent Treatment Facility
FFA - Federal Facility Agreement
HLW - High Level Waste
ITP - In-Tank Precipitation
JCO – Justification for Continued Operations
MST – Monosodium Titanate
N/A - Not Applicable
NaTPB - Sodium Tetraphenylborate
RAMI – Reliability, Availability, Maintainability and Inspectability
R&D – Research and Development
SCDHEC - South Carolina Department of Health and Environmental Control
SE - Systems Engineering
SEMP - Systems Engineering Management Plan
SRS - Savannah River Site
SRTC – Savannah River Technology Center
SSC – Systems, Structures and Components
TBD - To Be Determined
TPB – Tetraphenylborate ($NaB(C_6H_5)_4$
WSMS - Westinghouse Safety Management Solutions, Inc.
WSRC - Westinghouse Savannah River Company