SRR-CES-2011-00069
Revision 0

October 31, 2011

TO: Clifford Winkler, 766-H

FROM: 10/31/2011
Karthik H. Subramanian, SRR

CC: David Little, SRR
Richard Edwards, SRR
Doug Bumgardner, SRR
John Contardi, SRR
John Occhipinti, SRR
Bill Van-Pelt, SRR
John Dickenson, SRR
Lyden D. Olson, SRR
Ian Pegg, Vitreous State Laboratory
Brad Bowan, EnergySolutions
Sam Fink, SRNL
Sharon Marra, SRNL

SUBJECT: RESULTS OF TANK 48 ALTERNATIVES TABLE-TOP ENGINEERING EVALUATION

Introduction

Tank 48, a new-style type IIIA waste tank at the Savannah River Site (SRS), currently contains legacy organics which potentially challenges the flammability envelope requiring specific Documented Safety Analysis (DSA) controls and the isolation of the tank. As a result of these specific controls the tank is currently unavailable for use within the liquid waste system. Fluidized bed steam reforming (FBSR) is currently being developed to destroy the organics and prepare the waste for permanent disposition. However, due to budget constraints, it was recommended the FBSR project be suspended/layed-up pending evaluation of cost-effective alternate technologies evaluations that have become viable due to liquid waste program process and system planning enhancements.

A review of the series of options that have been previously considered concluded small-tank chemical destruction and direct vitrification were promising in light of advancements in the liquid waste systems/processes. The chemical destruction option became viable when experimentation using copper catalyzed peroxide destruction chemistry revealed near-complete tetraphenylborate (TPB) oxidation in alkaline conditions. In addition, the availability of the stainless steel tanks in the current Actinide Removal Process (ARP), contained in 241-96H, may be used as small-tank reactors that will be resistant to corrosion. The direct vitrification option became viable due to the DWPF process enhancements including the bubblers and the flowsheet enhancements that will minimize hydrogen generation and open the flammability envelope within DWPF. A table-top engineering evaluation of these options was completed as a "zero-step" to further technology maturation. The output of the evaluation was used to provide direction on technology maturation.

Table-Top Engineering Evaluation

The engineering evaluation considered direct vitrification and chemical destruction in line with the team charter. The table-top engineering evaluation was conducted via a series of presentations (as shown in Appendix 1) describing:

1. Previous system engineering evaluations;
2. Current System Plan needs for Tank 48;
3. Direct Vitrification: Technology Maturation Testing; Deployment Needs, Authorization Basis Strategy, Transfer Path
4. Chemical Destruction: Technology Maturation Testing; Deployment Needs, Authorization Basis Strategy, Transfer Path

The criteria considered by the evaluation team were:

1. **Use of Existing Infrastructure**: Deployment of an alternate technology will not require construction of capital assets.

2. **Minimal Facility Modifications**: Deployment of an alternate technology will leverage the current planned enhancements to the liquid waste system, however, may require support system changes, e.g. electrical, steam, ventilation, etc; as defined by the safety envelope.

3. **No Impact to Life-Cycle**: Deployment of an alternate technology will support life-cycle completion in alignment with optimal system planning considerations.

4. **Deployment ROM Estimate**: Selection of initial sequencing of the technology maturation will require a preliminary rough-order-magnitude deployment estimate.

Evaluation Team

The evaluation consisted of a team of subject matter experts (SMEs) to provide review of the technologies and intended maturation and deployment as shown Table 1.

Table 1: Engineering Evaluation Team

Member	Organization
Mr. Cliff Winkler	Chief Engineer, Savannah River Remediation
Mr. Karthik Subramanian	Chief Technology Officer, Savannah River Remediation
Dr. Ian Pegg	Director, Vitreous State Laboratory
Mr. Brad Bowan	Senior Vice President, EnergySolutions
Ms. Sharon Marra	Savannah River National Laboratory
Mr. David Little	Deputy Chief Engineer, Savannah River Remediation
Mr. Richard Edwards	Project Engineering Manager, Savannah River Remediation

Lines of Inquiry

The following lines of inquiry (LOI) served as the framework for the engineering evaluation:

1) Assess the validity of the preliminary Tank 48 alternatives evaluation that led to two technologies for reconsideration:
   a) Do the two alternatives adequately represent potentially viable technologies given the changes to the liquid waste system?
2) Assess the potential viability of the selected technologies and current path forward:
   a) Is the current path forward for the Tank 48 project clearly defined?
   b) Is the preliminary technical maturation plan adequate to support process interface and performance needs? What changes to the preliminary plan are recommended?
   c) Has the range of potential impacts on downstream facilities been adequately considered?
   d) Is the ROM cost projection adequately bounded?
3) Identify risks and assess adequacy of risk management actions in context of technology maturation:
   a) Have the technical risks associated with the current path forward been adequately identified?
   b) Do the technology maturation strategies adequately address the identified risks?
4) Evaluate plans and practices for benzene management
   a) Are current practices and future plans for handling benzene generated in the course of Tank 48 processing and material transfer appropriate and consistent with the hazard?

The information for the evaluation was provided by key SMEs. The key SMEs and respective area of focus are shown in Table 2.

Table 2: SMEs

SME	Focus
Mr. Doug Bumgardner (SRR) Manager, System Planning	Tank 48 need within system planning and life-cycle and cost impacts from alternative technology deployment
Mr. John Contardi (SRR) Project Engineering Manager, Tank 48 Project	Relevant accomplishment of the Tank 48 FBSR project • Waste Characterization • Tank 48 Infrastructure • Safety Analysis • Permitting Documentation
Dr. Ian Pegg (VSL)	Technology development necessary for direct vitrification and destruction of the organics through the DWPF melter: • Bench Scale Simulant Testing • Viable Glass Frit Formulation • Small-Scale Melter Testing
Mr. John Occhipinti (SRR) Waste Solidification Engineering Manager	Description of the technology deployment needs: • DWPF/Melter Delivery including Transfer Paths • Liquid/Separation methods for volume reduction
Dr. Samuel Fink (SRNL) Separations and Actinide Science Programs	Description of the copper catalyzed peroxide oxidation chemical destruction process • Define Process Conditions • Conceptual Flowsheet • Flowsheet Integration Studies

SME	Focus
Mr. Bill Van-Pelt (SRR) Tank Farm Engineering Manager	Description of the technology deployment needs: • Transfer Routes to 241-96H and/or DWPF • Support Systems Evaluation • Safety Envelope Definition

Direct Vitrification

A summary of direct vitrification is shown in Figure 1. The bulk of the material will be sent to the Defense Waste Processing Facility (DWPF) for vitrification. The remaining heel will be disposed through aggregation at the Saltstone Production Facility (SPF) or grouted in-tank in compliance with closure documentation. The technology maturation for the direct vitrification will be performed in light of the intended DWPF process enhancements.

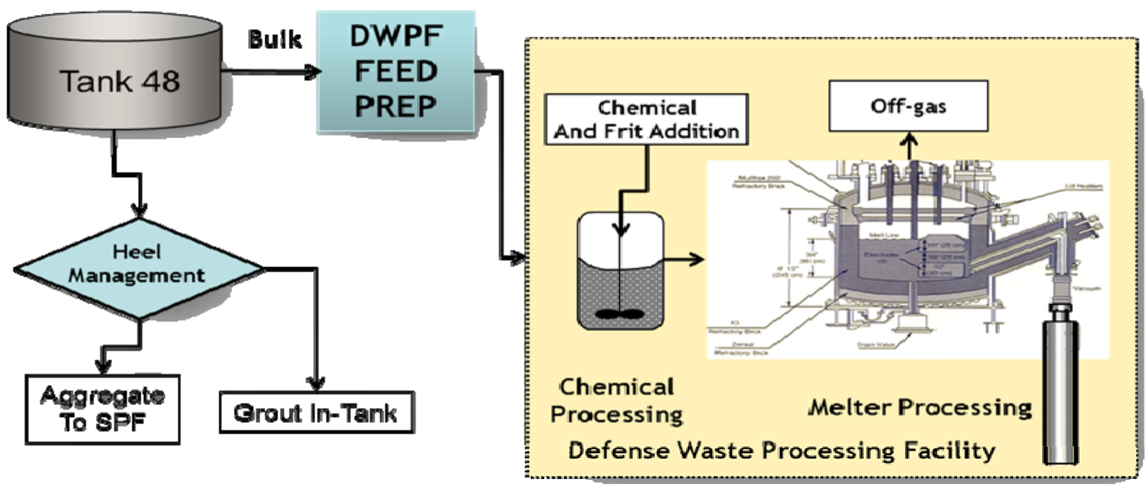

Figure 1: Direct Vitrification of Tank 48 Waste

A summary of the needed technology maturation for direct vitrification of Tank 48 materials is shown in Figure 2. The technology maturation will have to include a detailed analysis of the off-gas impacts from vitrification of the Tank 48 materials. The current TRL is estimated at 2, however, it is recognized that the DWPF has significant experience in sludge batch qualification and execution.

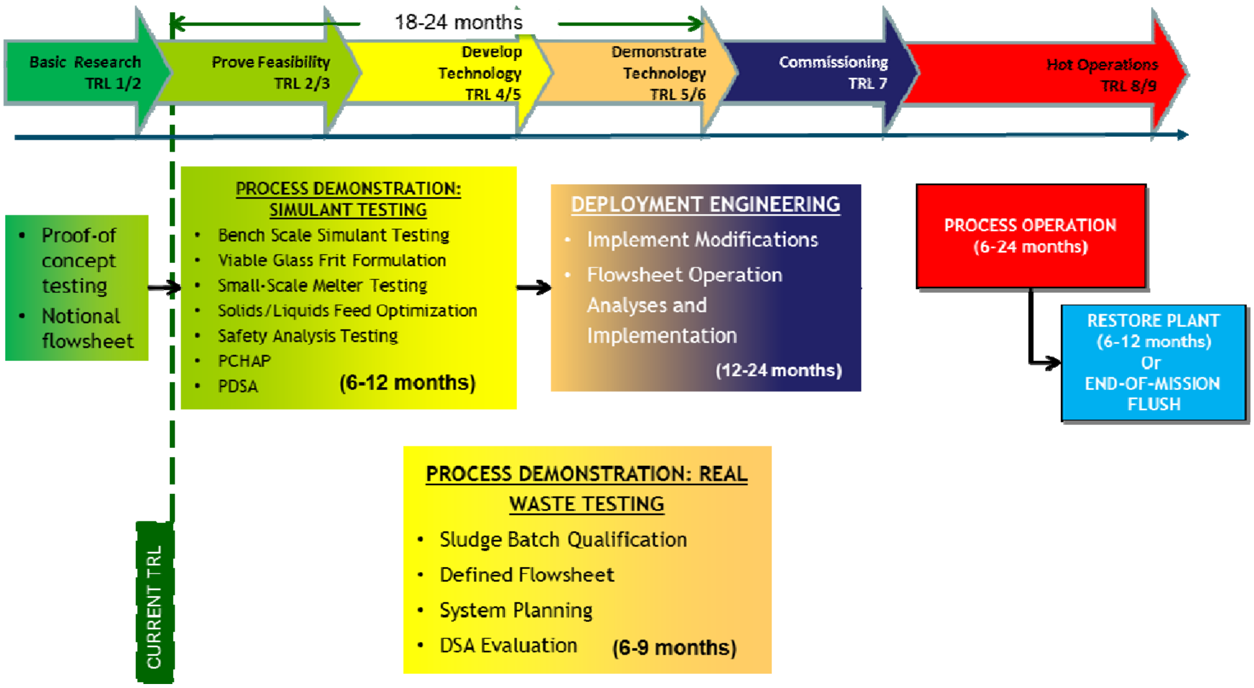

Figure 2: Technology Maturation for Direct Vitrification of Tank 48 Materials

Chemical Destruction

A summary of chemical destruction is shown in Figure 3. The proposed chemical destruction flowsheet for decomposition of the organics in Tank 48 is a copper catalyzed peroxide oxidation reaction, with the TPB oxidized to carbon dioxide. The proposed treatment chemistry is the combination of hydrolysis with Fenton's chemistry which involves the addition of hydrogen peroxide (oxidizer) and a metal catalyst, usually iron or copper in this case, to create hydroxyl free radicals ($^{\bullet}OH$) and hydroxide ions (OH^-). The free radicals are consequently responsible for the destruction of the organics. While the Fenton's chemistry typically proceeds at a pH of 3-5, the copper enhancement allows the reaction to proceed with reasonable kinetics at higher pH, conducive to corrosion control on the carbon steel wall of the tank. The copper may also play a role in catalyzing the solution phase hydrolysis reaction. In addition, review of the chemical destruction technology will consider the feasibility of an uncatalyzed hydrolysis reaction, if there is a surface (solid-liquid) interaction.

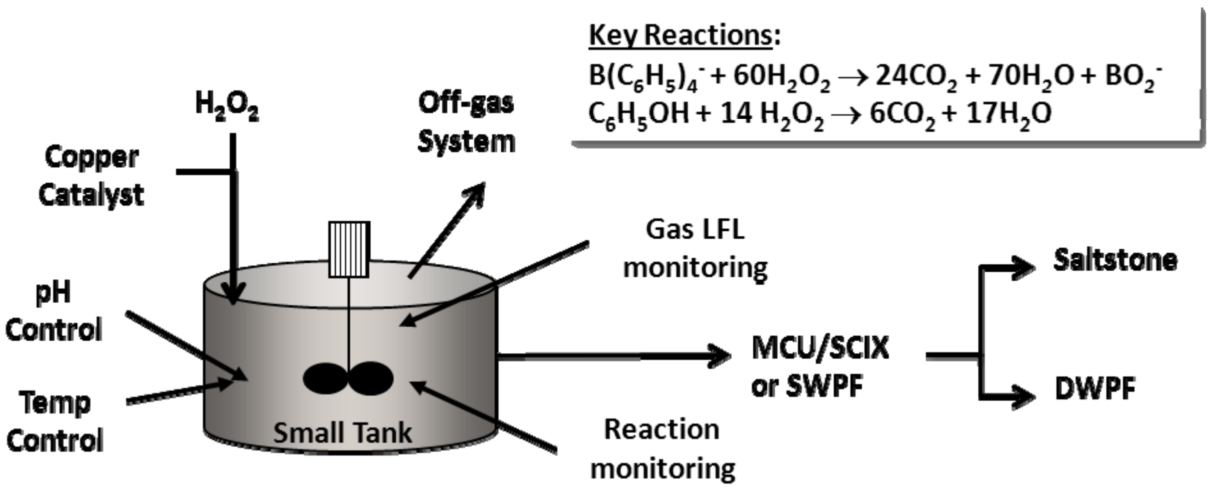

Figure 3: Conceptual Small-Tank Copper Catalyzed Peroxide Oxidation

A summary of the needed technology maturation for chemical destruction is shown in Figure 2. The current TRL is estimated at 3, since simulant testing has been performed.

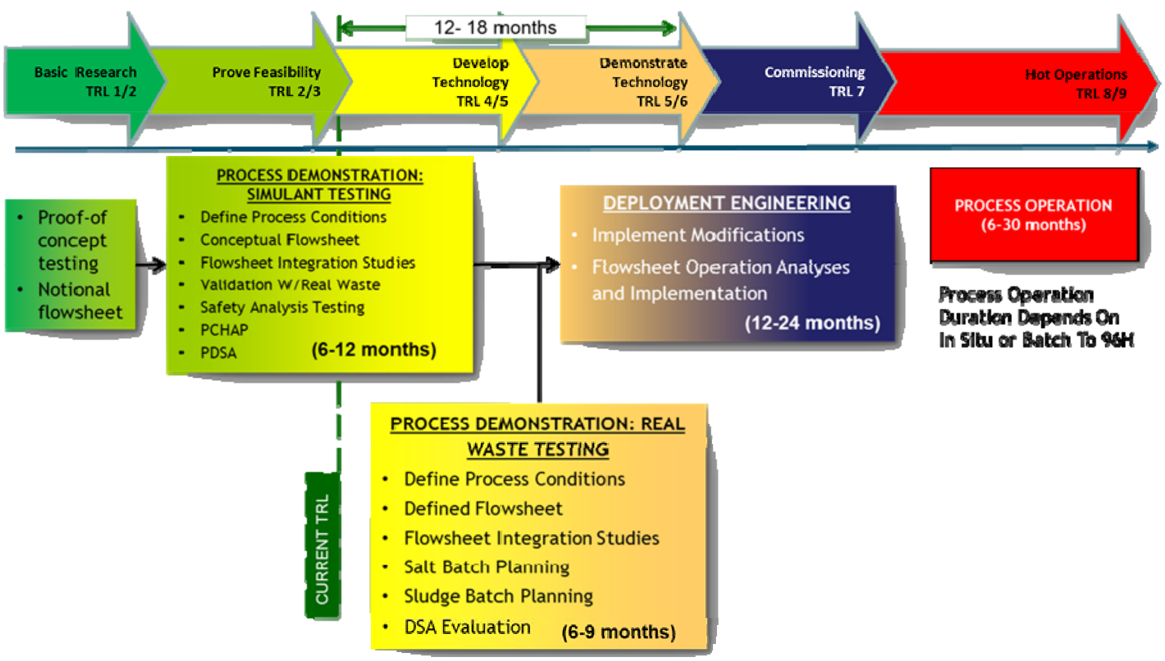

Figure 4: Technology Maturation for Chemical Destruction of Tank 48 Organics

Cost Comparison

A summary of the rough order magnitude (ROM) cost estimates are shown in Table 3. The chemical destruction option leverages current operational facilities and does not impact the liquid waste program life-cycle since the destruction will be carried out in concert with current salt and sludge processing campaigns. The direct vitrification of the Tank 48 materials would require the continued operations extension of the DWPF facility along with all of the support facilities, e.g. tank farms and saltstone, beyond the current life-cycle estimates

Table 3: Comparison of ROM estimate

Technology	Testing Cost	TPC	Operations	Liquid Waste Program Life-Cycle Impact
FBSR	N/A	$122M (to-go)	$35.8M	N/A
Chemical Destruction	$7-10M	$25-35M	$13-15M	$0M
Direct Vitrification	$7-10M	$10-30M	Included in life-cycle impact	$550 - $800M

Conclusions and Recommendation

The team provided preliminary assessment of process and downstream implications, safety, equipment availability and ROM cost estimates. The evaluation team concluded the following:

- Both chemical destruction and direct vitrification are technically viable given the parameters/assumptions presented, including the transfer strategy and overview of safety strategy. The preliminary technology development presented identified the necessary parameters to be addressed.
- Both options have a safety envelope that can be defined with some cost of implementation within existing infrastructure.
- The life-cycle cost impact of direct vitrification (given the known parameters) didn't yield cost savings over FBSR.
- The high-end cost ROM estimate for chemical destruction, even given a conservative safety envelope in 241-96H, yields potentially significant cost savings over FBSR.

As a result of the engineering evaluation and the potential for significant cost savings utilizing chemical destruction, it was recommended that the FBSR project be suspended/layed-up pending further technology maturation of the chemical destruction process. Initial technology maturation should include waste simulant and targeted real waste testing along with engineering analyses to determine the safety envelope definition. Results of the initial testing should be used to re-assess the feasibility of chemical destruction versus the same criteria and recommend whether further technology maturation is warranted. The chemical destruction technology maturation process in Bldg. 241-96H should leverage the significant effort of the FBSR project, which was intended to be deployed in 241-96H. These information include, for example: (1) Waste characterization and Tank 48 infrastructure; (2) safety analyses; (3) permitting documentation; (4) shielding calculations; and (5) civil/structural evaluation of 241-96H.

Given the change in need for Tank 48 within the system plan, this initial alternate technology evaluation is well within the time-frame to meet life-cycle completion dates including permanent disposition and closure of Tank 48.

APPENDIX

AGENDA

Tank 48 Alternate Technology Table Top Engineering Evaluation

5/25/2011 Savannah River Site, 766-H, Rm. 1026

Time	Topic	Presenter
7:30 – 8:00am	Introductory Remarks and Framework	Cliff Winkler, Karthik Subramanian (SRR)
8:00 – 8:30am	Review of previous SEEs	Karthik Subramanian (SRR)
8:30 – 9:00am	Current System Plan needs for Tank 48	Doug Bumgardner (SRR)
9:00 – 9:45am	Direct Vitrification: Technology Maturation Testing	Ian Pegg (VSL) Brad Bowan (Energy Solutions)
9:45 – 10:30am	Direct Vitrification: Deployment Needs, AB Strategy, Transfer Path	John Occhipinti (SRR)
10:30 – 11:15am	Chemical Destruction: Technology Maturation Testing	Sam Fink (SRNL)
11:15 – 12:00am	Chemical Destruction: Deployment Needs, AB Strategy, Transfer Path	Bill Van-Pelt, David Martin (SRR)
12:00 – 1:00	Lunch	
1:00 – 2:00	Review of Direct Vitrification	EE Team
2:00 – 3:00 pm	Review of Chemical Destruction	EE-Team
3:00 – 4:00 pm	Follow-up Q/A	All
4:00 – 5:00 pm	Develop Recommendation	EE Team

5:00 – 5:30	Outbrief	All

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Tank 48 Treatment Project Table-Top Engineering Evaluation Review and Charter

Karthik Subramanian
Chief Technology Officer

May 25, 2011
SRR-STI-2011-00319

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Background

- Tank 48 is a 1,300,000 gallon new style HLW tank
  - 22,000 kg Tetraphenylborate (TPB) solids from the ITP process, 1.7 Ci/gal Cs-137
- Physical
  - 250,000 gallons
  - Specific Gravity – 1.165
  - Insoluble solids – 3 wt%
- Chemical
  - 21,800 kg Potassium Tetraphenylborate (KTPB)
  - 0.15 wt% Monosodium Titanate (MST)
  - > 1M OH
  - ~ 1,350 curies alpha
  - 400,000 curies Cs-137
  - 3.8M Na
- The organic presents a unique Tank Farm hazard that must be dealt with and the waste permanently dispositioned

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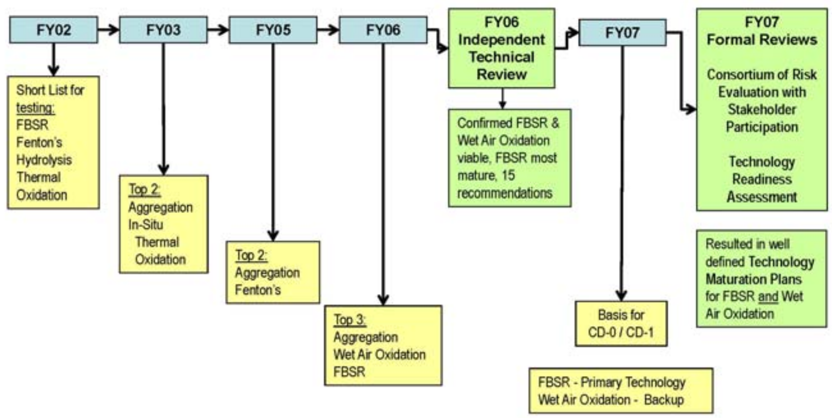
Treatment Alternative Analyses



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Current Status

- FBSR
  - Current technical maturity of TRL 6
  - On schedule for CD-3B due September 2011
  - Ahead of schedule for next DNFSB milestone due December 2011

- Since the last in-depth systems engineering evaluation of Tank 48 waste treatment alternatives, the following factors have resulted in revised weighting for cost, schedule, and maturity evaluation criteria:
  - Significant program progress has eliminated dependency on Tank 48 return to service and reduced weight of schedule criteria
  - Reduced schedule weighting opens a window for further maturation of closely competing technologies
  - Advent of DWPF enhancements provides previously unavailable capacity
  - Technology maturation of copper catalyzed process that was not considered in the previous evaluations

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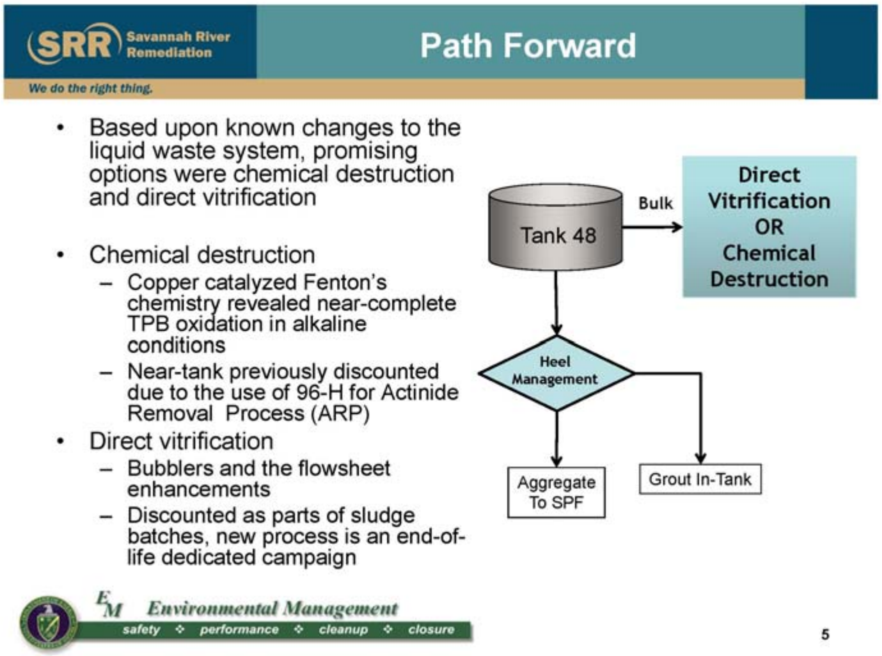
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Path Forward
• Based upon known changes to the liquid waste system, promising options were chemical destruction and direct vitrification
• Chemical destruction
– Copper catalyzed Fenton's chemistry revealed near-complete TPB oxidation in alkaline conditions
– Near-tank previously discounted due to the use of 96-H for Actinide Removal Process (ARP)
• Direct vitrification
– Bubblers and the flowsheet enhancements
– Discounted as parts of sludge batches, new process is an end-of-life dedicated campaign
Tank 48
Bulk
Direct Vitrification OR Chemical Destruction
Heel Management
Aggregate To SPF
Grout In-Tank
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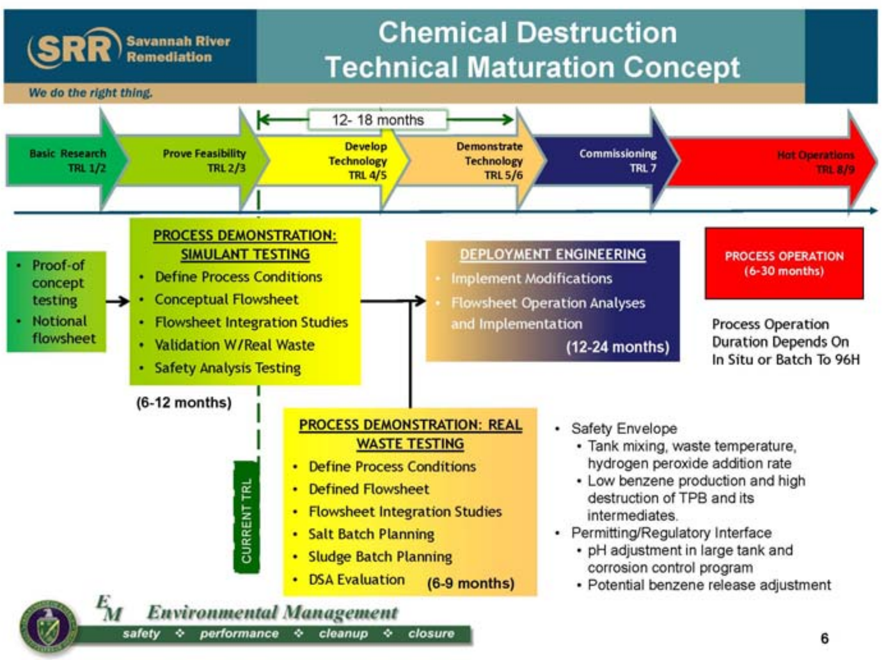
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Chemical Destruction Technical Maturation Concept
12- 18 months
Basic Research TRL 1/2
Prove Feasibility TRL 2/3
Develop Technology TRL 4/5
Demonstrate Technology TRL 5/6
Commissioning TRL 7
Hot Operations TRL 8/9
• Proof-of concept testing
• Notional flowsheet
PROCESS DEMONSTRATION: SIMULANT TESTING
• Define Process Conditions
• Conceptual Flowsheet
• Flowsheet Integration Studies
• Validation W/Real Waste
• Safety Analysis Testing
(6-12 months)
DEPLOYMENT ENGINEERING
• Implement Modifications
• Flowsheet Operation Analyses and Implementation
(12-24 months)
PROCESS OPERATION (6-30 months)
Process Operation Duration Depends On In Situ or Batch To 96H
CURRENT TRL
PROCESS DEMONSTRATION: REAL WASTE TESTING
• Define Process Conditions
• Defined Flowsheet
• Flowsheet Integration Studies
• Salt Batch Planning
• Sludge Batch Planning
• DSA Evaluation
(6-9 months)
• Safety Envelope
• Tank mixing, waste temperature, hydrogen peroxide addition rate
• Low benzene production and high destruction of TPB and its intermediates.
• Permitting/Regulatory Interface
• pH adjustment in large tank and corrosion control program
• Potential benzene release adjustment
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Direct-to-Vitrification Technical Maturation Concept

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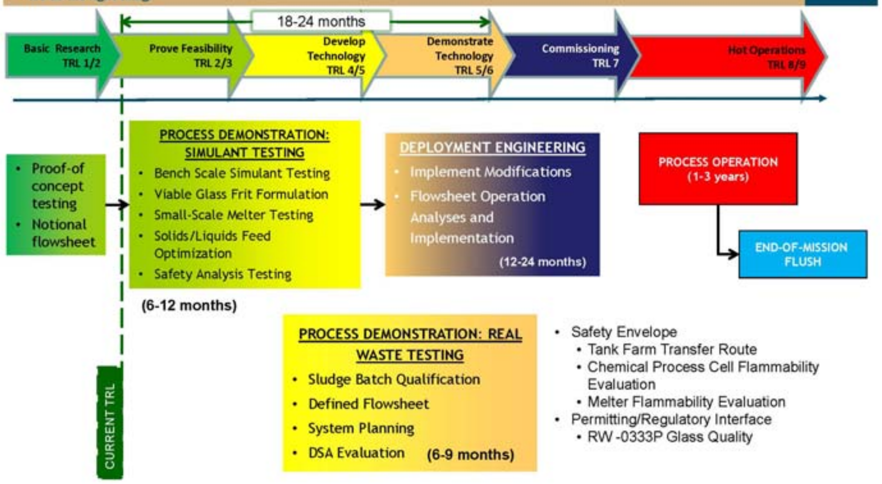

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Heel Management

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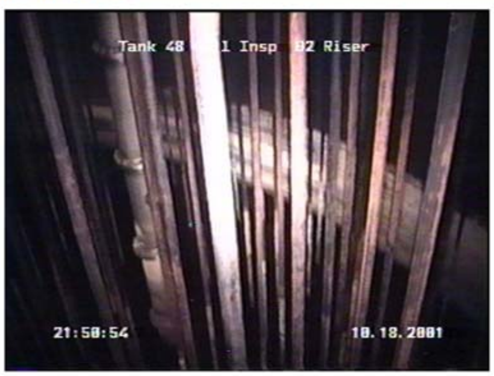

Tank Level on 10/18/01 – 69.5 inches
Pump Column Supports – 5 foot sections
Bath tub ring height estimate – 6.5 feet above liquid level
Total height of bath tub ring – 69.5 + 78 = 147.5 inches (517,725 gallons)

Any technology selected will leave residual organics and radionuclides after treatment.

- material adhering to internals (estimated as 33 kg TPB)
- slurry not removed by bulk suspension (pump efficiency losses begin at 38 inches in current configuration)
- bounding estimate of heel losses set as high as 3-5 vol %

Treat by grouting either in tank or by washing and transfer to Saltstone. New pump configurations may be required to mitigate heel.

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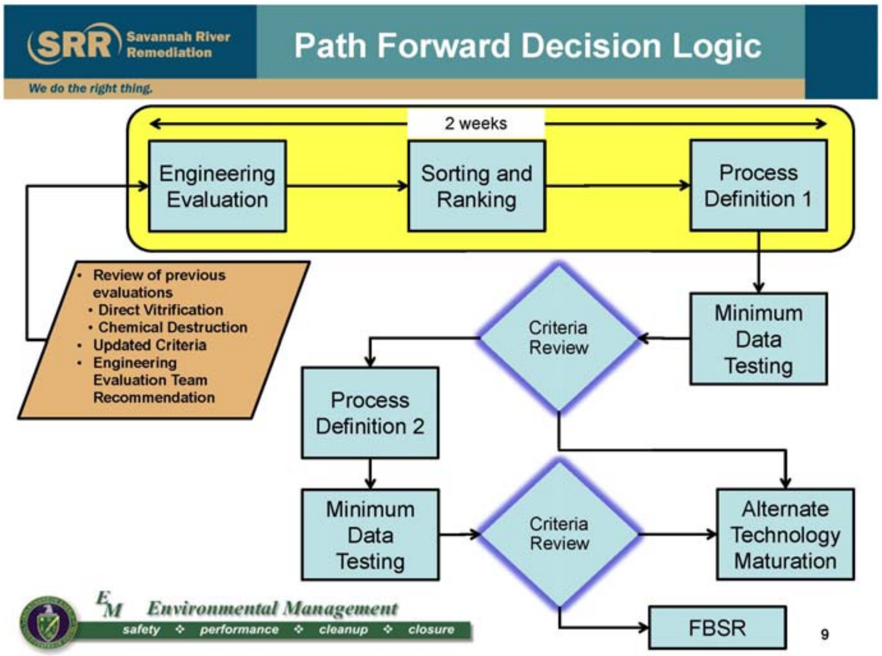

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Table-Top Engineering Evaluation

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- "Zero-step" to further technology maturation
- Review of technology development and deployment needs
- Provide recommendation on the sequence of technology maturation to SRR Chief Engineer

Member	Organization
Mr. Cliff Winkler	Chief Engineer, Savannah River Remediation
Mr. Karthik Subramanian	Chief Technology Officer, Savannah River Remediation
Dr. Ian Pegg	Director, Vitreous State Laboratory
Mr. Brad Bowan	Senior Vice President, EnergySolutions
Ms. Sharon Marra	Savannah River National Laboratory
Mr. David Little	Deputy Chief Engineer, Savannah River Remediation
Mr. Richard Edwards	Project Engineering Manager, Savannah River Remediation

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Evaluation Criteria

- Use of Existing Infrastructure: Deployment of an alternate technology will not require construction of capital assets.
- Minimal Facility Modifications: Deployment of an alternate technology will leverage the current planned enhancements to the liquid waste system, however, may require support system changes, e.g. electrical, steam, ventilation, etc; as defined by the safety envelope.
- No Impact to Life-Cycle: Deployment of an alternate technology will support life-cycle completion in alignment with the Enhanced Tank Waste Strategy (ETWS)
- Deployment ROM Estimate: Selection of initial sequencing of the technology maturation will require a preliminary rough-order-magnitude deployment estimate.

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BACKUP

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Tank 48H Characterization

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CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL
	Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	(kg)
Ag	1.88E-02	2.12E-03	1.67E-02	1.72E-02
Pd	9.28E-02	7.37E-02	1.91E-02	8.50E-02
Cu	4.0E+00	1.01E+00	2.99E+00	3.66E+00
Cd	2.16E-02	1.57E-02	5.90E-03	1.98E-02
Hg	2.20E+01	6.73E-02	2.19E+01	2.02E+01
Rh	2.30E-01	1.09E-01	1.21E-01	2.11E-01
Ru	3.80E-01	2.93E-01	8.70E-02	3.48E-01
B	1.03E+03	4.60E+02	5.70E+02	9.43E+02
Fe	1.69E+02	<2.14E-01	1.69E+02	1.55E+02
K	2.65E+03	2.55E+02	2.40E+03	2.43E+03
Na	8.80E+04	8.80E+04	~0	8.06E+04
Al	2.31E+03	2.31E+03	~0	2.12E+03
Ca	4.30E+01	6.42E-01	4.24E+01	3.94E+01
Cr	7.0E+01	4.75E+01	2.25E+01	6.41E+01
Mn	7.82E+00	3.60E-02	7.78E+00	7.16E+00
Mg	2.02E+01	<0.058	2.02E+01	1.85E+01
Ba	3.47E+00	<0.117	3.47E+00	3.18E+00

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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Tank 48H Characterization

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CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL
	Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	
As	<4.6	NM	NM	<4.21E+00
Pb	<2.83E-01	<2.83E-01	NM	<2.59E-01
Se	<4.8	NM	NM	<4.40E+00
Co	NM	NM	NM	NM
Li	9.9E-01	9.9E-01	NM	9.07E-01
Mo	1.33E+01	9.94E+00	3.36E+00	1.22E+01
Ni	<1.5E-02	<1.5E-02	NM	<1.37E-02
P	2.41E+02	2.41E+02	~0	2.21E+02
S	3.78E+02	3.2E+02	5.8E+01	3.46E+02
Sb	1.15E+01	6.87E+00	4.63E+00	1.05E+01
Si	1.25E+02	6.67E+00	1.18E+02	1.15E+02
Sn	2.21E+01	4.92E+00	1.72E+01	2.02E+01
Sr	9E+00	<3.12E-01	9E+00	8.24E+00
Ti	8.40E+02	<1	8.40E+02	7.69E+02
U	5.31E+00	1.1E+00	4.21E+00	4.86E+00
V	8.89E-01	8.89E-01	~0	8.14E-01

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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Tank 48H Characterization

CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL
	Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	
Zn	1.19E+01	5.41E+00	6.63E+00	1.09E+01
Zr	1.47E+00	1.47E+00	NM	1.35E+00
Gd	<0.01	<0.01	NM	<9.16E-03
La	<0.032	<0.032	NM	<2.93E-02
Total Organic Carbon	2.14E+04	3.01E+03	1.84E+04	1.96E+04
NO_2^-		2.14E+04		1.96E+04
NO_3^-		1.34E+04		1.23E+04
PO_4^{3-}		9.16E+02		8.39E+02
SO_4^{2-}		5.28E+02		4.84E+02
NH_4^+		NM		NM
CO_3^{2-}		4.92E-01 M		2.70E+04
OH^-		1.34E+00 M		2.09E+04
Total Base		2.49E+00 M		n/a
Other Base (excluding CO_3^{2-})		2.67E-01 M		n/a
Density, g/mL	1.165 g/mL	1.164 g/mL	n/a	n/a
Total Solids, wt %	20.19 wt %	17.68 wt %	n/a	n/a
MST solids, wt %	0.15 wt %	<0.0024 wt %	n/a	n/a
Total Insolubles, wt. %	3.05 wt %	NM	n/a	n/a
KTPB wt. %	2.01 wt %	<0.001 wt %	n/a	n/a

Note: "<" [illegible] based on detection limit. NM refers to "not measured"

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System Planning Needs for Tank 48

Doug Bumgardner
Manager, System Planning

May 25, 2011
SRR-STI-2011-00320

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Initial System Plan Tank 48 Needs

- System Plans Rev. 13, 14
  - FY06 for potential waste concentrate storage
  - FY12 as a salt blend tank for SWPF
- System Plan Rev. 15
  - FY14 as a salt blend tank for SWPF
- System Plan Rev. 16
  - Tank 48 RTS in October 2016
  - Beginning in Nov 2016 Tank 48 is used for SCIX Batch 11 preparation
  - Tank 48 is used for Salt Batch preparation until FY23
  - Tank 48 RTS enables earlier closure of Tank 21 in June 2017 vs. FFA Commitment of September 2022

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Tank Space Recovered (1000s gallons)

	FY07	FY08	FY09	Total
Evaporator Operations	1,908	2,348	3,827	8,083
DWPF Vitrification	169	280	227	676
ISDP Treatment	N/A	144	560	704
Saltstone Disposal	253	1,289	1,556	3,098
Total	**2,330**	**4,061**	**6,170**	**12,561**

- Remove waste from and clean old-style tanks
- Prepare, qualify, and treat sludge waste for disposal
- Prepare, qualify, treat, and dispose of salt waste
- Support continued nuclear materials disposal through H-Canyon

EM Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

3

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System Plan Impact from Tank 48 Delay

- No impact to waste processing or FFA Commitment if Tank 48 RTS is completed by October 2021
- Between October 2016 and October 2021 multiple Type III/IIIA Tanks are made available:
  - Tank 27 (BWR Complete June 2021)
  - Tank 30 (Closed December 2020)
  - Tank 31 (Closed June 2021)
  - Tank 33 (Closed June 2021)
  - Tank 34 (Chemical Cleaning Complete July 2021)
  - Tank 39 (BWR Complete September 2019 – H-Canyon dependent)
  - Tank 44 (Chemical Cleaning Complete November 2020)
  - Tank 45 (Heel Removal Complete July 2021)
  - Tank 47 (Chemical Cleaning Complete March 2021)
- Replace Tank 48 as a salt blend tank with one of the above tanks would allow Tank 21 to be closed by the FFA Commitment date and would not impact feeding SWPF or SCIX
  - Tank 39 is 1st preference (located on East Hill of H-Tank Farm)
  - Tank 30 or 31 are next most preferred (located on West Hill of H-Tank Farm)
  - Remaining tanks are less desirable because they are located in F-Tank Farm
- Last Sludge Batch Prep begins in FY22, Last Salt Batch Prep begins in FY23

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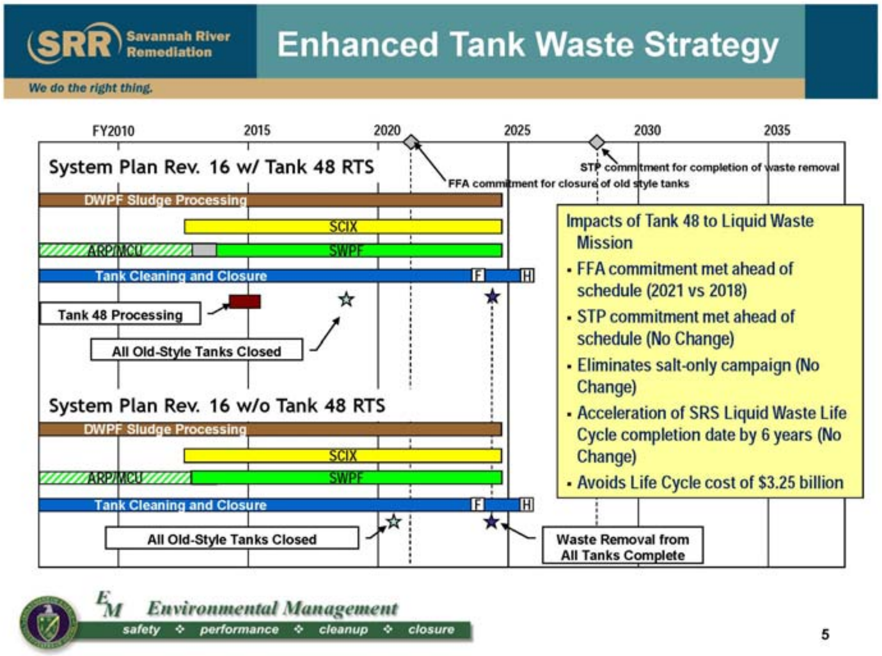
4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Enhanced Tank Waste Strategy
FY2010
2015
2020
2025
2030
2035
System Plan Rev. 16 w/ Tank 48 RTS
FFA commitment for closure of old style tanks
STP commitment for completion of waste removal
DWPF Sludge Processing
SCIX
ARP/MCU
SWPF
Tank Cleaning and Closure
Tank 48 Processing
All Old-Style Tanks Closed
System Plan Rev. 16 w/o Tank 48 RTS
Waste Removal from All Tanks Complete
Impacts of Tank 48 to Liquid Waste Mission
• FFA commitment met ahead of schedule (2021 vs 2018)
• STP commitment met ahead of schedule (No Change)
• Eliminates salt-only campaign (No Change)
• Acceleration of SRS Liquid Waste Life Cycle completion date by 6 years (No Change)
• Avoids Life Cycle cost of $3.25 billion
Environmental Management
safety performance cleanup closure
5

ENERGYSOLUTIONS

SRS – Tank 48 Alternative Treatment:
Direct Vitrification Through DWPF
Concept and Technical Maturation

Bradley W. Bowan

CUA

May 25, 2011

SRS Tank 48

- Tank 48
  - 1.3 million gal tank
  - ~240,000 gal salt solution
  - ~22,000 kg potassium tetraphenylborate (TPB)
- Organic content and flammability management issues prevent disposition through SRS Saltstone facility
- Steam Reforming technology selected to destroy organics
- Steam reformer products (sodium carbonate and coal) would be added to DWPF sludge treatment flow-sheet

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Summary

- Direct vitrification provides an alternative disposition path that has several potential advantages:

- **Avoids new capital construction project**
- **Avoids new technology risk**
- **Leverages newly available surplus DWPF melter capacity from installation of bubblers**
- **Avoids TBD risk of impact of FBSR product on DWPF flow-sheet**

CUA ENERGYSOLUTIONS

Summary

- Leverage newly available surplus DWPF melter capacity resulting from deployment of bubblers
- Process Tank 48 waste through DWPF in a dedicated campaign
  - Tank 48 waste is fed to DWPF feed make-up system and combined with glass frit that is tailored to produce a fully compliant glass product
  - No addition of sludge, so DWPF chemical processing cycle (SRAT/SME) is avoided; simple use of existing tankage
  - DWPF melter naturally oxidizes TPB with high-nitrate waste
  - Processing duration estimated at ~6 months
  - Total canisters produced estimated at ~220
    - Potentially off-set with higher waste loadings in subsequent sludge batches
  - Possible without impact to overall mission completion because sludge processing is not the critical path (salt is the bottleneck) or can be processed at the end of DWPF mission

CUA ENERGYSOLUTIONS

Initial Assessment of Concept

- Based on presently available information, initial assessment of concept viability with respect to:
  - Inorganic chemistry and waste loading in glass
  - Melter feed properties
  - Melting rate
  - Organics
  - Glass redox
  - Glass formulation
- Information used to outline data gaps and technology maturation needs
- Step-wise testing program recommended

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Initial Assessment: Inorganic Chemistry and Loading in Glass

- Total waste oxides: ~88,000 kg
- Waste loading limiting oxide: Na_2O
  - Assume 20 wt% in glass based on Hanford LAW
  - At this loading, incorporation of other oxides would not be a concern
    - e.g., SO_3 ~ 0.12 wt%, K_2O ~ 0.8 wt%
- Total mass of glass: ~ 440 MT
  - Approx. 220 canisters
  - ~ 6 months at 400 cans per year

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Initial Assessment: Melter Feed

- Total frit addition: ~ 350 MT
- Total melter feed: ~ 1420 MT
- Glass yield: ~ 0.31 kg glass per kg feed
  - Comparable to typical DWPF feed
    - Therefore expect comparable or faster melt rates
  - Does not account for any added water, e.g., for frit addition (assumes dry frit process implemented)
    - Under this assumption, viable melter feed is possible without evaporation

Potential Issues

- Frit suspension, rheology, mixing/transport, abrasion
- If evaporation is required, potential for TPB decomposition and limits imposed by off-gas composition in CPC

CUA ENERGYSOLUTIONS

Initial Assessment: Organics

- TOC in melter feed: ~ 14,000 ppm
  - Based on projected mass of melter feed and Tank 48 organics inventory
- TSR for Sludge Batch 6: 18,900 ppm

Potential Issues

- Detailed safety/flammability assessment for this specific chemistry could lead to a lower limit
- Current bubbler gas is argon; air bubbling would be preferred to maximize organic destruction

CUA ENERGYSOLUTIONS

Initial Assessment: Glass Redox

- Excess of TOC over nitrates
  - Melt may be too reducing
- Mitigate by supplementing nitrates via nitric acid addition in CPC using existing equipment

Potential Issues

- Possible TPB decomposition and increased off-gas generation in CPC

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Initial Assessment: Glass Formulation

- Design frit to produce a product glass that falls within DWPF PCCS system requirements
- At the projected waste loadings, existing glass data indicate that formulation of a processable and compliant glass product is practical
- Based on Hanford high-Na glasses and projected glass yield, melt rates are expected to be high

Potential Issues

- Frit will need to be low in alkali to maximize waste loading; could present fabrication issues

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Recommended Path Forward

- Initiate testing to collect supporting data to validate the viability of this strategy
  - Develop melter feed, glass frit, and glass product chemistry
  - Characterize off-gas in CPC
  - Melter testing to demonstrate throughput, product quality, and characterization of off-gas for input to safety assessment
  - Required test platforms are available
- Complete concept technical maturation in 3 phases
  - TRL 2 to 4: Confirm fundamentals of concept - months 0 to 4
  - TRL 4 to 5: Collect data to support process modeling - months 4 to10
  - TRL 5 to 6: Large-scale process demonstration - months 4 to 10
    Active waste testing - months10 to 24

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Crucible and Bench-Scale Tests

Develop Viable Glass Frit and Product Glass Composition

- Demonstrate glass product quality
- Demonstrate acceptable glass melt properties for DWPF processing
- Optimize waste loading
  - Prepare and characterize glass frit to demonstrate acceptable properties for processing at DWPF
  - Prepare glasses with Tank 48 simulant and glass frit
    - PCT on as-melted glass sample
    - PCT on glass sample subjected to CCC heat treatment
    - Melt viscosity
    - Melt electrical conductivity
    - Liquidus temperature
    - Assess feed processing rate

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Crucible and Bench-Scale Tests (cont'd)

Collect CPC Processing Data and Off-Gas Composition

- Demonstrate that dewatering in DWPF CPC is not required
  - Determine effects of dewatering as back-up
- Demonstrate acceptable rheology, mixing and transport properties
- Characterize off-gas composition to support safety assessment
  - Characterize feed prepared by blending Tank 48 simulant with glass frit
    - Measure settling characteristics
    - Measure rheological properties
    - Measure the effect of feed solids content on rheological properties and settling
    - Identify additives to maintain acceptable rheological properties, if necessary
    - Identify additives to mitigate foaming, if necessary
    - Measure off-gas composition as a function of temperature based on maximum expected temperature in the tank, including effects of agitation
    - Identify any corrosion/erosion issues
    - Measure redox of glass samples prepared from melter feed and adjust additive concentrations for desired redox state

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Small-Scale Melter Testing

- Conduct small-scale melter tests using feed prepared by blending Tank 48 simulant with glass frit
  - Demonstrate processing rate and processing characteristics
    - Measure steady-state glass production rate
    - Assess cold-cap behavior
    - Demonstrate steady-state melter operation
    - Demonstrate acceptable feed system performance
  - Identify any operational issues
    - No feed settling or inability to transport
    - No off-gas issues
    - No pressure excursions or unacceptable cold-cap characteristics
  - Characterize melter off-gas to support flammability analysis
    - Measure organic off-gas composition
    - Measure inorganic off-gas composition and carry-over, including Cs
  - Characterize discharge glass to demonstrate product quality
    - Conduct PCT on discharge glass
    - Measure redox of discharge glass

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Develop Flow-Sheet

- Define glass frit composition
- Define glass composition (including waste loading)
- Define expected glass composition region for processing
  - Assess whether additional data are needed to qualify the composition region for PCCS
- Define range of feed solids contents for viable melter feeds
- Define preferred glass redox state range
- Define type and amount of additives to control glass redox state
- Define nominal and range of feed processing rates to comply with safety analysis

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Large-Scale Melter Testing

- **Demonstrate Flow-Sheet at Pilot Scale**

  Larger-scale validation of small-scale tests
  - Demonstrate processing rate and processing characteristics
    - Measure steady-state glass production rate
    - Assess cold-cap behavior
    - Demonstrate steady-state melter operation
    - Demonstrate acceptable feed system performance
  - Identify any operational issues
    - No feed settling or inability to transport
    - No off-gas issues
    - No pressure excursions or unacceptable cold-cap characteristics
  - Characterize melter off-gas to support flammability analysis
    - Measure organic off-gas composition
    - Measure inorganic off-gas composition and carry-over, including Cs
  - Characterize discharge glass to demonstrate product quality
    - Conduct PCT on discharge glass
    - Measure redox of discharge glass

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Actual Waste Testing

- General approach would parallel that used to support typical DWPF sludge batches
- Actual waste run through proposed CPC melter feed preparation process
- Resulting melter feed vitrified
- Glass product tested to demonstrate product quality

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Tank 48 Direct Vitrification – TRL 2 to 4
Months 0 to 4 (~ $300k - $400k)

- Crucible and Bench-Scale Tests
  - Develop Viable Glass Frit and Product Composition
  - Collect CPC Processing Data and Off-Gas Composition

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Tank 48 Direct Vitrification – TRL 4 to 5

Months 4 to 10 (~ $1M)

- Small Scale Melter Testing
- Develop Flow-sheet

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Tank 48 Direct Vitrification – TRL 5 to 6

Months 4 to 10 (~ $1.0M)

- Large Scale Testing
  - Demonstrate flow-sheet at pilot scale
  - Identify any scale-up issues

Months 10 to 24 (~ $1.5M)

- Active Waste Testing
  - Vitrify actual Tank 48 sample with new frit
  - Test sample for DWPF product compliance

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Tank 48 – Direct Vitrification

Questions?

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Direct Vitrification Option in DWPF for Tank 48

Tank 48 Alternate Technology Table Top Engineering Evaluation

May 25, 2011

John E. Occhipinti, SRR
Waste Solidification Chief Engineer

SRR-STI-2011-00317

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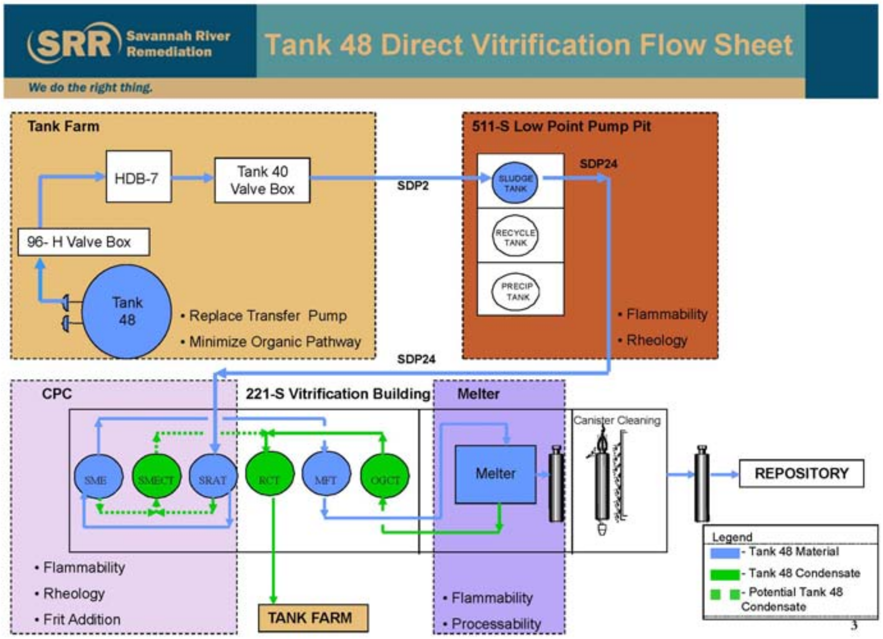
Outline

- Tank 48 Direct Vitrification Flow Sheet
- Integrated Assumptions with System Plan
- DWPF Assumptions
- Discussion – Potential Chemical Processing Cell (CPC) Flow Sheet Options
- Discussion – Melter Processing
- Anticipated Safety Controls and Permitting
- Conclusions
- Acronyms
- Contributors

2



Integrated Assumptions with System Plan

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- Tank 48 flow sheet is processed after the completion of the salt and sludge campaigns to ensure higher risk waste forms are stabilized as soon as practical
- Sludge/salt heels are flushed from existing vessels in 511-S Low Point Pump Pit (LPPP) Building and 221-S Vitrification Building prior to the start of the Tank 48 flow sheet to avoid potential chemical interactions
- The DWPF recycle stream and Decon stream generated from the Tank 48 flow sheet can be processed through Saltstone
- Radionuclides to Saltstone for the recycle streams are within the approved Performance Assessment (PA) and agreements with the state of S.C.
- The Tank 48 heel can be processed in Saltstone or grouted in place

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DWPF Assumptions

- Material of construction for major process equipment remains the same (e.g. tanks, agitators, coils)
- Minimal modifications will be required to support safety controls for process vessels and canyon areas
- Current flushing strategy is required to keep transfer path clear
- Frit is the only required chemical addition
- The glass product produced by the Tank 48 flowsheet meets current glass quality requirements
- The current Slurry Mix Evaporator (SME) sampling hold point will be used to show glass quality compliance
- Available space exists to store filled and decontaminated canisters
- A melter exists for DWPF

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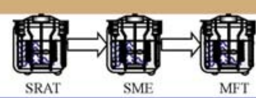
Discussion- Flow Sheet Options No Concentration Steps in the CPC



Description of Process

Tank 48 material would be received into the Sludge Receipt and Adjustment Tank (SRAT) and stored. Depending on waste loading target, a prescribed volume would be transferred from the SRAT to the Slurry Mix Evaporator (SME). The Tank 48 material would be blended with the remaining SME heel. A dry frit addition would be made and the resulting feed sampled. Upon complying with glass product requirements and melter off gas flammability requirements, the material is transferred to the Melter Feed Tank (MFT) and subsequently fed to the melter.

Assumptions:

- Dry Frit Addition System is installed & operational
- Water Separation for Canister Decon Frit is installed & operational
- Analytical techniques are developed to analyze samples

Questions:

- Are there any potential chemical interactions when the Tank 48 stream is subjected to an air purge or nitrogen purge under aggressive agitation?
- What is the minimum temperature required of the feed products?
- What are the physical & rheological properties of the Tank 48 stream and melter feed? Any increase in erosion rates anticipated for equipment?
- Do processing sump streams need to be pumped to process vessels?
- Over time the Tank 48 material will be diluted by line flushes and pump priming. Will this be a throughput concern?
- What CPC throughput (mass & cycle time) expected?

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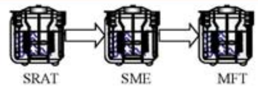
Discussion- Flow Sheet Options Concentration Steps in the CPC



Description of Process

Options exist to either boil in the SRAT and/or SME to concentrate the Tank 48 stream and/or melter feed. This would allow the removal of excess water that is added via line flushes and pump starts. Depending on waste loading target, a prescribed volume would be transferred from the SRAT to the SME. The Tank 48 material would be blended with the remaining SME heel. A dry frit addition would be made and the resulting feed sampled. Upon complying with glass product requirements and melter off gas flammability requirements, the material is transferred to the Melter Feed Tank (MFT) and subsequently feed to the melter.

Assumptions:

- Dry Frit Addition System is installed & operational
- Water Separation for Canister Decon Frit is installed & operational
- Analytical techniques are developed to analyze samples

Questions:

- Can the Tank 48 streams be boiled under an air atmosphere or is an inert atmosphere required?
- What are the by-products (i.e. feed and condensate) produced from boiling the Tank 48 stream and/or melter feed?
- Is an antifoam agent needed while boiling?
- What are the physical & rheological properties of the Tank 48 stream and melter feed? Any increase in erosion rates anticipated for equipment?
- Do processing sump streams need to be pumped to process vessels?
- What CPC throughput (mass & cycle time) expected?

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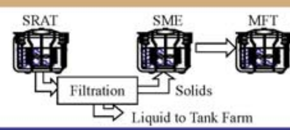
Discussion- Flow Sheet Options Filtration Step



Description of Process

Tank 48 material would be received into the Sludge Receipt and Adjustment Tank (SRAT) and stored. The material would be filtered and the solids would be sent to the SME and the resulting liquid stream would be sent to the Tank Farm. The Tank 48 material would be blended with the remaining SME heel. A dry frit addition would be made and the resulting feed sampled. Upon complying with glass product requirements and melter off gas flammability requirements, the material is transferred to the Melter Feed Tank (MFT) and subsequently fed to the melter.

Assumptions:

- Dry Frit Addition System is installed & operational
- Water Separation for Decon Frit is installed & operational
- Analytical techniques are developed to analyze samples
- A frit composition can be formulated to meet composition needs after filtration.

Questions:

- Similar questions for no boiling scenario.
- What is the current supernate and slurry composition of Tank 48?
- Is any pretreatment required to the filtrate prior to being processed at Saltstone?

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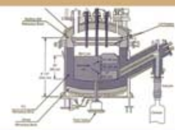
Discussion-Melter Processing



Description of Process

The melter feed product is fed to the melter at a rate that produces an acceptable glass product while meeting melter off gas flammability requirements.

Assumptions:

- Tank 48 melter feed meets melter off gas flammability controls

Questions:

- What will be the limiting factor with regard to feeding the melter? Flammable content? Liquid content?
- What will the REDOX state of the glass be?
- What will the radionuclide retention in the glass be?
- What are the by-products produced in the melter off gas condensate stream?
- What will be the canister throughput with melter off gas flammability controls?
- Can existing Product Composition Control System (PCCS) models be used?
- What will be the waste loading of Tank 48 material in the glass?

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Anticipated Safety Controls and Permitting

Transfer Path - Tank 48 to Low Point Pump Pit (LPPP)

- Utilize Existing Safety Strategy for Waste Transfers
  - Transfer Pipe as pressure boundary (i.e., contain the waste)
  - Leak Detection (i.e., detect leakage outside pipe)

LPPP – Interim Storage of Tank 48 Material

- Utilize Existing Safety Strategy for Storage Tank
  - Vessel Purge (air or nitrogen)
  - Temperature Monitoring and Chemistry Control
  - Process Vessel Ventilation

DWPF Process Vessels – No Boiling and Filtration Options

- Utilize Existing Safety Strategy for Process Vessels
  - Vessel Purge (air or nitrogen)
  - Temperature Monitoring
  - Building Ventilation

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Anticipated Safety Controls and Permitting

DWPF Process Vessels – Boiling Options

- Utilize Existing Safety Strategy for Process Vessels
  - Vessel Purge (air or nitrogen)
  - Temperature Monitoring
  - Steam Interlock (i.e., isolate steam to process vessels)
  - Building Ventilation
  - Primary Containment (Building)

Melter Processing

- Utilize Existing Safety Strategy for Melter
  - Melter Feed Flow Rate
  - Vapor Space Temperature Interlocks
  - Melter Air Flow (dilution and combustion air)

Permitting

- Impact of benzene and NOx emissions on existing air permits

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Conclusions

- Several options for Direct Vitrification of Tank 48 material have been presented and can be implemented.
- Processing of Tank 48 waste should follow completion of Salt and Sludge processing to ensure higher risk waste forms are stabilized as soon as practical.
- Direct Vitrification uses the same safety strategy currently deployed in DWPF
- In order to reduce the risk and answer technical questions, some research and development activities will have to be performed.

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Acronyms

CPC	Chemical Processing Cell of the DWPF
DWPF	Defense Waste Processing Facility
Frit	A vitrified crushed glass containing chemicals needed to form glass
LPPP	Low Point Pump Pit
LPPP-ST	Low Point Pump Pit – Sludge Tank
MFT	Melter Feed Tank
OGCT	Off Gas Condensate Tank
PA	Performance Assessment
PCCS	Product Composition Control System controls feed composition to ensure glass meets repository requirements and operating constraints
PRFT	Precipitate Reactor Feed Tank
RCT	Recycle Collection Tank
REDOX	REDuction-OXidation
SEFT	Strip Effluent Feed Tank
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank

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Contributors

- Terri Fellinger
- Bill Holtzscheiter
- Jonathan Bricker

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Tank 48 Tetraphenylborate Chemical Destruction




SRR-STI-2011-00318

Date: May 25, 2011

Presenters:
Bill Van Pelt, SRR

Dr. Sam Fink, SRNS, Savannah River National Laboratory

Event:
Presentation for Tank 48 Alternate Technology Evaluation

Savannah River Site, Building 766-H

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Summary

To deploy copper catalyzed peroxide destruction of Tank 48 tetraphenylborate:

- Use of Existing infrastructure
  - Utilize current strike tanks and infrastructure in 241-96H
  - Utilize existing transfer routes from 241-96H through HDB-7 to Tank 41(some modification)
  - Cesium and alpha removal through SCIX process in Tank 41
  - Decontaminated salt solution processed to Saltstone
  - High Level waste processed to DWPF
  - Tank 48 Heel Aggregated either via Saltstone or in-tank

- Modifications to existing facilities
  - Additional 241-96H strike tank cell piping (design available from FBSR)
  - 241-96H valve box re-piping (design available from FBSR)
  - Evaluate Tank 48 feed pumps and transfer lines to 241-96H - repair/replace as necessary
  - Cold chemical feed capability (e.g., peroxide, nitric acid, caustic, copper)
  - Process vessel ventilation upgrades
  - Nitrogen inerting/MOC controls for strike vessels
  - Heating and cooling capability for strike vessels
  - Gas Chromatographs for strike vessel off-gas
  - Liquid sampling system for product stream
  - Analytical equipment/instrumentation

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Summary (cont'd)

- Impacts to life cycle
  - Estimated time to process Tank 48 bulk contents ~ 24 months
  - Operating peroxide process concurrent with SCIX has no impact on system life cycle
- Fate of cesium and alpha
  - Bulk of Cs and alpha stabilized in DWPF
  - Residual heel treated at Saltstone or grouted in tank
  - Heel volume impacted by transfer pump configuration
    - Pump starts losing efficiency at 38 inches
  - Heel volume estimated as 3-5 vol % (e.g., undiluted heel of 7,000 – 12,000 gal)

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Tank 48 Rad Characterization

	Slurry	Supernate
	(dpm/ml)	(dpm/ml)
Cs-137	1.01E+09	3.0E+07
Gross Alpha	3.44E+06	NM
Sr-90	7.34E+05	NM
	(mg/L)	(mg/L)
Tc-99	2.26E+00**	2.26E+00
Th-232	NM	1.95E-02
Np-237	2.83E-01	5.39E-02
Pu-239	4.46E-02	2.80E-03
Pu-238	8.82E-02	1.77E-02
Pu-240*	5.67E-03*	NM
Pu-241*	9.36E-04*	NM
U-233	9.44E-02	4.94E-02
U-234	4.99E-01	3.58E-01
U-235	9.71E-01	5.74E-01
U-236	1.48E+00	1.41E+00
U-238	6.16E+00	3.62E+00
U Total	6.32E+00	6.01E+00
Total Pu	1.36E-01	2.05E-02

The current Tank 48 waste volume is approx. 238,000 gallons
** This value is for solids only.*
**The Tc-99 value for supernate will be used for slurry since measured slurry values are lower.

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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Tank 48 Characterization

CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL
	Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	(kg)
TPB	2.12E+04	<10	2.12E+04	1.94E+04
Calculated KTPB	2.38E+04	NM	NM	2.18E+04
Phenol	9.73E+02	7.06E+02	2.67E+02	8.91E+02
BiPhenyl	6.32E+02	<10	6.32E+02	5.79E+02
Triphenylborate (3PB)	1.62E+02	<10	1.62E+02	1.48E+02
Biphenylborate (2PB)	1.42E+02	<10	1.42E+02	1.30E+02
Phenylborate (1PB)	1.51E+02	<10	1.51E+02	1.38E+02
Nitrobenzene	1.81E+02	<10	1.81E+02	1.66E+02
Nitrosobenzene	2.53E+01	<10	2.53E+01	2.32E+01
o-terphenyl	<50	<10	NM	<4.58E+01
m-terphenyl	<50	<10	NM	<4.58E+01
p-terphenyl	1.82E+02	<10	1.82E+02	1.67E+02
benzene	1.79E+01	<10	1.79E+01	1.64E+01
Ag	1.88E-02	2.12E-03	1.67E-02	1.72E-02
Pd	9.28E-02	7.37E-02	1.91E-02	8.50E-02
Cu	4.0E+00	1.01E+00	2.99E+00	3.66E+00
Hg	2.20E+01	6.73E-02	2.19E+01	2.02E+01

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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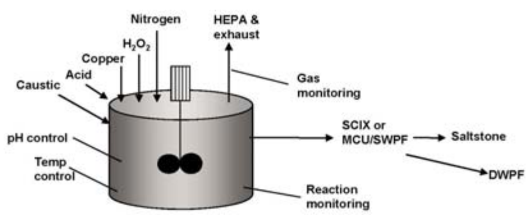
Flowsheet Schematic



- Conceptual Chemical Destruction In 96H Strike Tanks
- Organic Destroyed and Carbon Dioxide Exhausted
- Disposition as Salt Waste (SCIX, MCU/SWPF) Post Destruction
- Majority of Curies to Vitrification, Decontaminated Salt Solution to Saltstone

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Expected Reactions

- Peroxide Oxidation (desired reaction)
  $BC_{24}H_20 + 61H_2O_2 \rightarrow BO_3 + 71H_2O + 24CO_2$
  - Requires ~60 moles H_2O_2:mol TPB or ~2.4 moles H_2O_2:mol C

  5.593 g TPB- → 36.35 g H_2O_2

- Hydrolysis (minimize by temperature and pH control)
  $NaBC_{24}H_20 + 2H_2O \rightarrow NaBO_3 + 4C_6H_6$
  5.593 g TPB- → 5.475 g C_6H_6

- Peroxide Self Destruction (control addition sequence and rate to minimize reagent loss)
  $H_2O_2 \rightarrow H_2O + ½O_2$

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Typical Reaction Sequence

- **Adjust with nitric acid to pH 11**
- **Add copper catalyst**
  - **incremental Cu levels feasible**
- **Begin adding hydrogen peroxide (controlled rate)**
- **Controlled heating to operating temperature**

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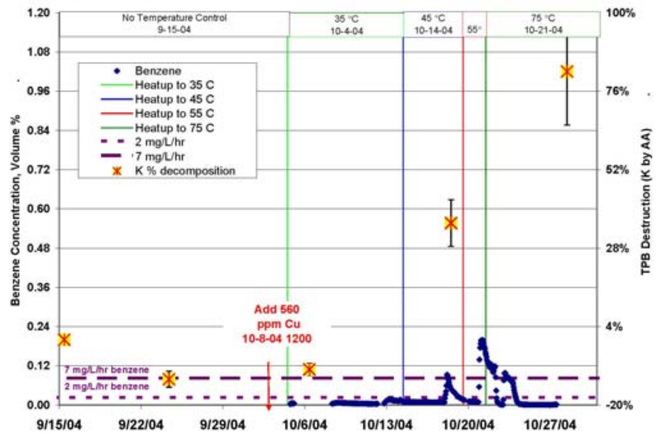
Benzene Concentration/Temperature Profile

EM Funded research documented in WSRC-TR-2005-0114

- Decomposition controlled to occur over three weeks
- 35 °C adequate for initial decomposition
- Low benzene Production



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Photograph of Product

Mixed Original Sample

Settled Final Sample

Residual solids include monosodium titanate

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Mass Balance

- Hydrogen Peroxide (20 day period)
  - Added 187% H_2O_2 of stoichiometric amount for oxidation of TPB
  - Average 54% efficiency
- >99.8% decomposition
- No measured decomposition products remaining
- No phenol or biphenyl

Species	Percent of Original C from TBP
Oxalate	17.7
Carbonate	8.4
Benzene	5.4
Formate	2.8
"tars"	0.3
CO_2 (not measured)	65.4 (balance)

Analyte	Actual	Predicted	Units
Nitrite	**0.236 0.024**	**0.465 0.093**	**M**
Oxalate	**0.0370 0.0037**	**0.0130 0.0026**	**M**

Benzene and NO_x emissions need assessed versus permits

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Confidence for Radioactive Waste Test

- Prior hydrolysis testing emphasized higher nitrite concentration for corrosion control in Tank 48H.
- Nitrite believes to interfere with catalytic cycle.
- Cu more effective than Fe in this application. (Cu known to catalyze final benzene ring cleavage.)
- Peroxide consumption by side reactions reduced at these pH values.
- Simulant used best available characterization data for Tank 48H waste.

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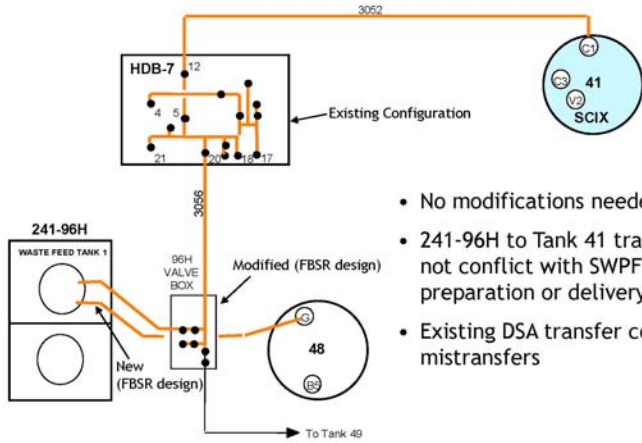
Transfer Paths and Interfaces



- No modifications needed in HDB-7
- 241-96H to Tank 41 transfer route does not conflict with SWPF/DWPF feed preparation or delivery
- Existing DSA transfer controls prevent mistransfers

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Anticipated Safety Controls and Permitting

- Modified Safety Strategy for Process Vessels (similar strategy used for Tank 48)
  - Vessel Purge (most likely nitrogen)
  - Gas Chromatographs with interlocks
  - Means to inhibit/quench reaction (e.g., caustic addition and temperature controls)
  - Robust process vessel and cell ventilation systems
  - Product analysis required prior to transfer to Tank 41 at least for initial processing (sample and hold approach)
  - Corrosion control strategy
- Regulatory Consideration
  - Impact of benzene and NOx emissions on existing air permits

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Support Systems

- Anticipated modifications
  - Additional 241-96H strike tank cell piping (design available from FBSR)
  - 241-96H valve box re-piping (design available from FBSR)
  - Evaluate Tank 48 feed pumps and transfer lines to 241-96H - repair/replace as necessary
  - Cold chemical feed capability (e.g., peroxide, nitric acid, caustic, copper)
  - Process vessel ventilation upgrades
  - Nitrogen inerting/MOC controls for strike vessels
  - Heating and cooling capability for strike vessels
  - Gas Chromatographs for strike vessel off-gas
  - Liquid sampling system for product stream

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Small Tank Benefits

- Tank is available in 241-96H; utilize portions of existing FBSR design
- Allows wider pH range to be considered for oxidation reaction
- Reaction more readily controlled in a smaller volume (e.g., caustic addition and temperature control)
- Safety controls more easily implemented
- Facilitates controlled, small additions to SCIX process

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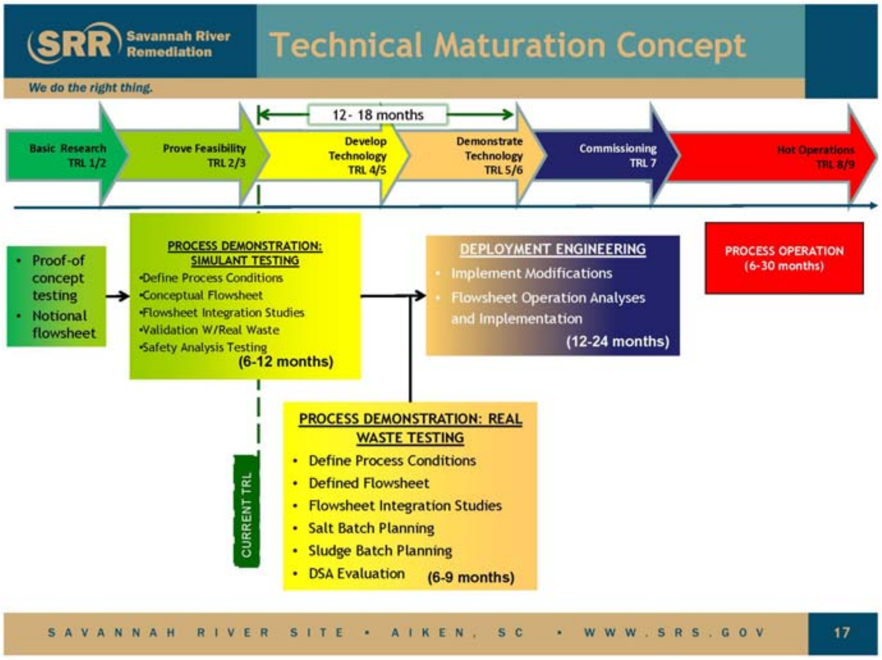

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Technology Needs - Flowsheet Development

- Optimize organic destruction and cycle time using simulated waste
  - pH,
  - temperature,
  - catalyst concentration,
  - peroxide addition rate
- Characterize reaction byproducts – both liquid product and offgas including formation of energetic compounds
  - Validate simulant results with actual waste
  - Identify safety control strategy
  - Identify corrosion control strategy
  - Validate measurements needed for environmental permit compliance (e.g., NOx, benzene)
- Understand impacts of oxidation product on downstream processes
  - SCIX
  - DWPF
  - Saltstone
  - MCU/SWPF (contingency if not processed through SCIX)
- Process scale-up (using simulant)
  - 1/10th scale assumed adequate

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Estimated Cost

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Conclusions

- Chemical Destruction can be implemented utilizing existing infrastructure with minimal modifications to support systems
- Processing of Tank 48 waste can occur concurrent with SCIX operations and as such will not extend the HLW System Life Cycle
- Chemical Destruction process will use a similar safety strategy in place on Tank 48 today.
- In order to reduce risk and validate the process flowsheet, real waste testing will have to be performed.

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Contributors

- David Martin
- David Harris
- Barrick Blocker
- Mark Keefer
- Hal Hart

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Additional Supporting Information

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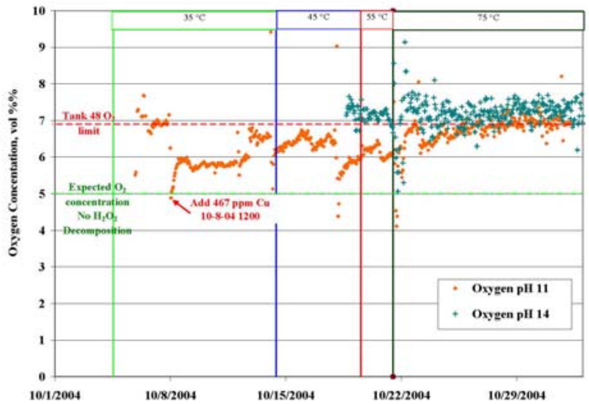
Oxygen Concentration

Data indicates MOC Control Strategy is Viable even with Peroxide Decomposition

- 560 ppm Cu added 10/8/2004
  - O_2 concentration dropped in pH 11 experiment
  - Reaction initiated at 35 °C
  - No change in pH 14 experiment



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Final HPLC Data

- >99.8% decomposition at pH 11
- No measured decomposition products remaining at pH 11
- No phenol or biphenyl in either test (pH 11 or 14)

Analyte	Units	pH 11	pH 14
TPB Anion	**mg/L**	**<10**	**1310**
3PB	**mg/L**	**<10**	**<10**
2PB	**mg/L**	**<10**	**<10**
PBA	**mg/L**	**<10**	**<10**
Phenol	**mg/L**	**<10**	**<10**
Nitrobenzene	**mg/L**	**<10**	**<10**
Nitrosobenzene	**mg/L**	**<10**	**<10**
4phenylphenol	**mg/L**	**<10**	**<10**
2phenylphenol	**mg/L**	**<10**	**<10**
Diphenylamine	**mg/L**	**<10**	**<10**
Biphenyl	**mg/L**	**<10**	**10**
o-terphenyl	**mg/L**	**<10**	**<10**
m-terphenyl	**mg/L**	**<10**	**<10**
p-terphenyl	**mg/L**	**<10**	**<10**

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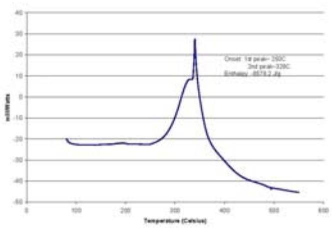
Thermal Analysis of Products

- Performed post mortem analyses on solid residues (up to 2 years later) revealing mildly energetic material.
- Used TGA rather than a technique such as Accelerating Rate Calorimetry to formally classify energetic rating of material.
- No controls were performed to remove the energies for the major inorganic species present in samples.



Note:
Sodium oxalate decomposes at 290 °C.
Sodium formate melts at 253 °C.
Sodium nitrite melts at 271 °C.
Sodium nitrate melts at 308 °C.
All these energies convoluted in the TGA scan.

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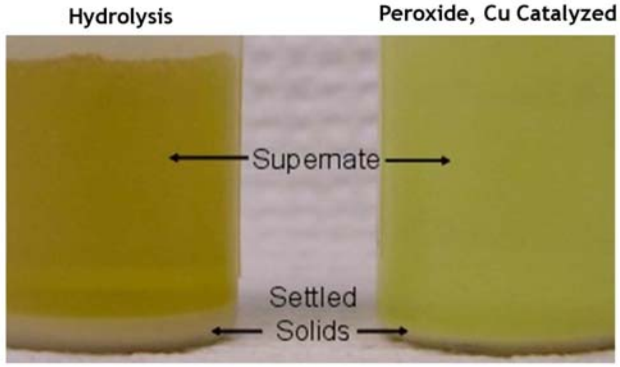
Residues at Completion

Hydrolysis **Peroxide, Cu Catalyzed**



Note the peroxide-assisted, Cu-catalyzed reaction produces less residual solids and the supernate is clearer (suggested less residual organic species)

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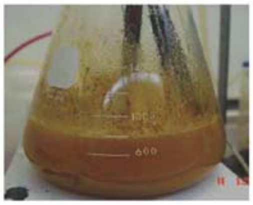
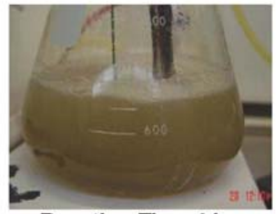
ORNL Fenton's Destruction of TPB


Acid added (Time 0)
pH = 7.5, boiling.


Reaction Time 2 hr
pH = 3.5, boiling.


Reaction Time 4 hr
pH = 3.5, boiling.


Samples throughout testing

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Typical AEA Reaction Sequence (100 mL Slurry)

- Add copper/iron catalyst
- Adjust with nitric acid to pH 7.5
- Heat to near boiling
- Begin adding hydrogen peroxide (low rate)
- Adjust with nitric acid to pH to 3.5
- Heat to boiling; increase peroxide addition rate


Beginning Slurry


H_2O_2 Addition


Reaction Products

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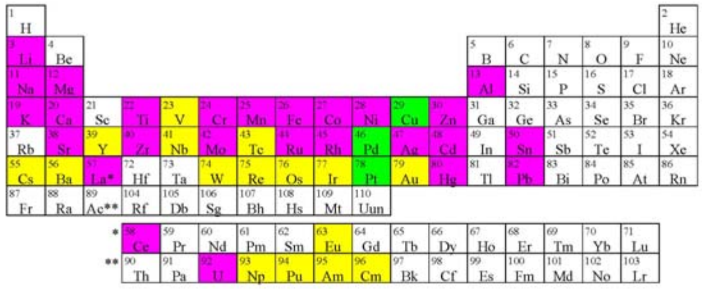
Catalysts for Tetraphenylborate Decomposition



- Present in SRS waste but not tested.
- Present in SRS waste. Tested and found inactive.
- Present in SRS waste and determined catalytically active. (Platinum determined by Y. Su at PNNL (EMSL).)

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Tank 48H Characterization

CONSTITUENT	CONCENTRATION ESTIMATE Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	TANK TOTAL (kg)
Ag	1.88E-02	2.12E-03	1.67E-02	1.72E-02
Pd	9.28E-02	7.37E-02	1.91E-02	8.50E-02
Cu	4.0E+00	1.01E+00	2.99E+00	3.66E+00
Cd	2.16E-02	1.57E-02	5.90E-03	1.98E-02
Hg	2.20E+01	6.73E-02	2.19E+01	2.02E+01
Rh	2.30E-01	1.09E-01	1.21E-01	2.11E-01
Ru	3.80E-01	2.93E-01	8.70E-02	3.48E-01
B	1.03E+03	4.60E+02	5.70E+02	9.43E+02
Fe	1.69E+02	<2.14E-01	1.69E+02	1.55E+02
K	2.65E+03	2.55E+02	2.40E+03	2.43E+03
Na	8.80E+04	8.80E+04	~0	8.06E+04
Al	2.31E+03	2.31E+03	~0	2.12E+03
Ca	4.30E+01	6.42E-01	4.24E+01	3.94E+01
Cr	7.0E+01	4.75E+01	2.25E+01	6.41E+01
Mn	7.82E+00	3.60E-02	7.78E+00	7.16E+00
Mg	2.02E+01	<0.058	2.02E+01	1.85E+01
Ba	3.47E+00	<0.117	3.47E+00	3.18E+00

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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Tank 48H Characterization

CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL
	Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	
As	<4.6	NM	NM	<4.21E+00
Pb	<2.83E-01	<2.83E-01	NM	<2.59E-01
Se	<4.8	NM	NM	<4.40E+00
Co	NM	NM	NM	NM
Li	9.9E-01	9.9E-01	NM	9.07E-01
Mo	1.33E+01	9.94E+00	3.36E+00	1.22E+01
Ni	<1.5E-02	<1.5E-02	NM	<1.37E-02
P	2.41E+02	2.41E+02	~0	2.21E+02
S	3.78E+02	3.2E+02	5.8E+01	3.46E+02
Sb	1.15E+01	6.87E+00	4.63E+00	1.05E+01
Si	1.25E+02	6.67E+00	1.18E+02	1.15E+02
Sn	2.21E+01	4.92E+00	1.72E+01	2.02E+01
Sr	9E+00	<3.12E-01	9E+00	8.24E+00
Ti	8.40E+02	<1	8.40E+02	7.69E+02
U	5.31E+00	1.1E+00	4.21E+00	4.86E+00
V	8.89E-01	8.89E-01	~0	8.14E-01

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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Tank 48H Characterization

CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL
	Slurry (mg/L)	Supernate (mg/L)	Calc Dry Solids (mg/L)	
Zn	1.19E+01	5.41E+00	6.63E+00	1.09E+01
Zr	1.47E+00	1.47E+00	NM	1.35E+00
Gd	<0.01	<0.01	NM	<9.16E-03
La	<0.032	<0.032	NM	<2.93E-02
Total Organic Carbon	2.14E+04	3.01E+03	1.84E+04	1.96E+04
NO_2^-		2.14E+04		1.96E+04
NO_3^-		1.34E+04		1.23E+04
PO_4^{3-}		9.16E+02		8.39E+02
SO_4^{2-}		5.28E+02		4.84E+02
NH_4^+		NM		NM
CO_3^{2-}		4.92E-01 M		2.70E+04
OH^-		1.34E+00 M		2.09E+04
Total Base		2.49E+00 M		n/a
Other Base (excluding CO_3^{2-})		2.67E-01 M		n/a
Density, g/mL	1.165 g/mL	1.164 g/mL	n/a	n/a
Total Solids, wt %	20.19 wt %	17.68 wt %	n/a	n/a
MST solids, wt %	0.15 wt %	<0.0024 wt %	n/a	n/a
Total Insolubles, wt. %	3.05 wt %	NM	n/a	n/a
KTPB wt. %	2.01 wt %	<0.001 wt %	n/a	n/a

Note: "<" indicates detection limit/based on detection limit. NM refers to "not measured"

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