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Revision 0

Liquid Waste System

Mercury Removal Study

Savannah River Remediation
A URS COMPANY TEAMED
WITH BECHTEL | CH2M HILL | B&W | AREVA

Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under
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List of Acronyms and Abbreviations

APC	Air Pollution Control
BPHC	Bicarbonate-treated Peanut Hull Carbon
CHAP	Consolidated Hazards Analysis Process
DNAPL	Dense Nonaqueous Phase Liquid
DOE	Department of Energy
DSA	Documented Safety Analysis
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
ETP	Effluent Treatment Plant
GAC	Granular Activated Carbon
HLW	High Level Waste
IX	Ion Exchange
LWO	Liquid Waste Organization
LWS	Liquid Waste System
MCU	Modular Caustic Side Solvent Extraction Unit
MHBD	Modified Hardwickia Binata Bark
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
psi	Pounds per square inch
PVV	Process Vessel Vent
RCRA	Resource Conservation and Recovery Act
RCT	Recycle Collection Tank
RWT	Recycle Waste Tank
SAMMS	Self-Assembled Monolayers on Mesoporous Supports
SCIX	Small Column Ion Exchange
SDF	Saltstone Disposal Facility
SEE	Systems Engineering Evaluation
SME	Subject Matter Expert
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratories
SRR	Savannah River Remediation (LLC)
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TCLP	Toxicity Characteristic Leaching Procedure

TRL	Technology Readiness Level
UF	Ultrafiltration
UV	Ultraviolet

Summary of Revision

Revision Number	Date	Description of Change
0	11/18/15	Initial Issue

EXECUTIVE SUMMARY

The mercury levels within the Liquid Waste System (LWS) being encountered are higher than previously predicted. This may be attributed to ineffective removal of mercury from the sludge feed to the Defense Waste Processing Facility (DWPF). The original flowsheet design had DWPF as the major purge point for mercury in its elemental form. It is possible that removal of mercury in DWPF may not be sufficient to meet system removal requirements and also prevent significant recycling of mercury (Hg) to the Tank Farm. Therefore as part of an overall strategy to reduce the Liquid Waste System mercury level, a team was chartered to identify and examine options to determine the best possible alternative means to remove mercury from the LWS (excluding DWPF) and provide a recommendation for implementation of a preferred option(s).

The SEE team deliberations underscored the emerging significance of mercury speciation in various parts of the liquid waste system. Recent data highlight the dominant impacts of speciation on mercury behaviors, including mercury separation/removal and mercury leachability from saltstone. In particular, the presence and predominance of organic mercury species, such as methyl mercury cation, in the liquid waste system represent a significant challenge. Technology solutions that address the organic mercury are crucial to the long term success of liquid waste processing success at the Savannah River Site. Thus, mercury speciation was considered in developing and evaluating the SEE team recommendations. The final recommendations include relatively low-cost opportunistic methods that provide significant near-term removal of elemental and inorganic-ionic mercury, along with medium term actions to address organic mercury.

From the documents provided to the SEE team, the following purge and collection points for mercury were identified: 1) Elemental mercury removed at DWPF (outside the scope of this evaluation); 2) Elemental mercury collected at the bottom of process vessels; 3) Elemental mercury collected at the H-area evaporators; 4) organic mercury cation (HgR+) sent to Saltstone (Toxicity Characteristic Leaching Procedure [TCLP] tests have shown that the organic mercury cation is the major mercury soluble leachate). This could be a potential concern in Saltstone if the concentration of soluble mercury in the LWS increases over time.

The SEE process used for this evaluation was a structured alternative analysis with weighted evaluation criteria. 20 potential options were initially identified to remove mercury from the Liquid Waste System. The 20 options were subsequently reduced to 13 options through a screening process. The evaluation of the 13 final options resulted in three recommendations by the team because of the different forms of mercury in the LWS:

(A) Deploy Option 8: Target process vessels (e.g. overheads tank) for mechanical removal of elemental mercury observed to collect at the bottom of process tanks (opportunistic)

(B) Deploy Option 5a: Enhanced removal of ionic mercury at the H-area Evaporators using chemical addition of a reducing agent to enhance the reduction of ionic mercury to elemental mercury for collection (minimal chemical addition option)

(C) Pursue the conversion of the organic mercury cation (HgR+) in Tank 50 (feed to Saltstone) to ionic and elemental mercury using ultraviolet (UV) light by testing the photo reactor **Option 10** (Photoreactor on Tank 50), **and maturing the technology for deployment**. In parallel, test to **mature Option 7** (Enhanced retention of mercury in Saltstone). Important in this development are robust techniques that are compatible with LWS operations to convert organic mercury to either ionic or elemental state. This initiative would potentially allow Saltstone to incorporate higher mercury levels and still pass the mercury TCLP even if the UV treatment is not successful.

This report documents in detail the activities and recommendations of the team.

1.0 Background

Mercury continues to be a difficult constituent in the LWS flowsheet and has led to facility issues [e.g. Process Vessel Vent (PVV) system performance] as well as other issues (e.g., increased saltstone Hg inventory). Mercury levels within the LWS are being encountered which are higher than previously predicted. This may be attributed to ineffective removal of mercury from the waste streams being processed.

It is possible that removal of mercury in DWPF may not be sufficient to meet system removal requirements. As one part of an overall strategy to reduce the High Level Waste (HLW) System mercury level, an alternate method(s) of removing mercury from the LWS, excluding DWPF, must be established.

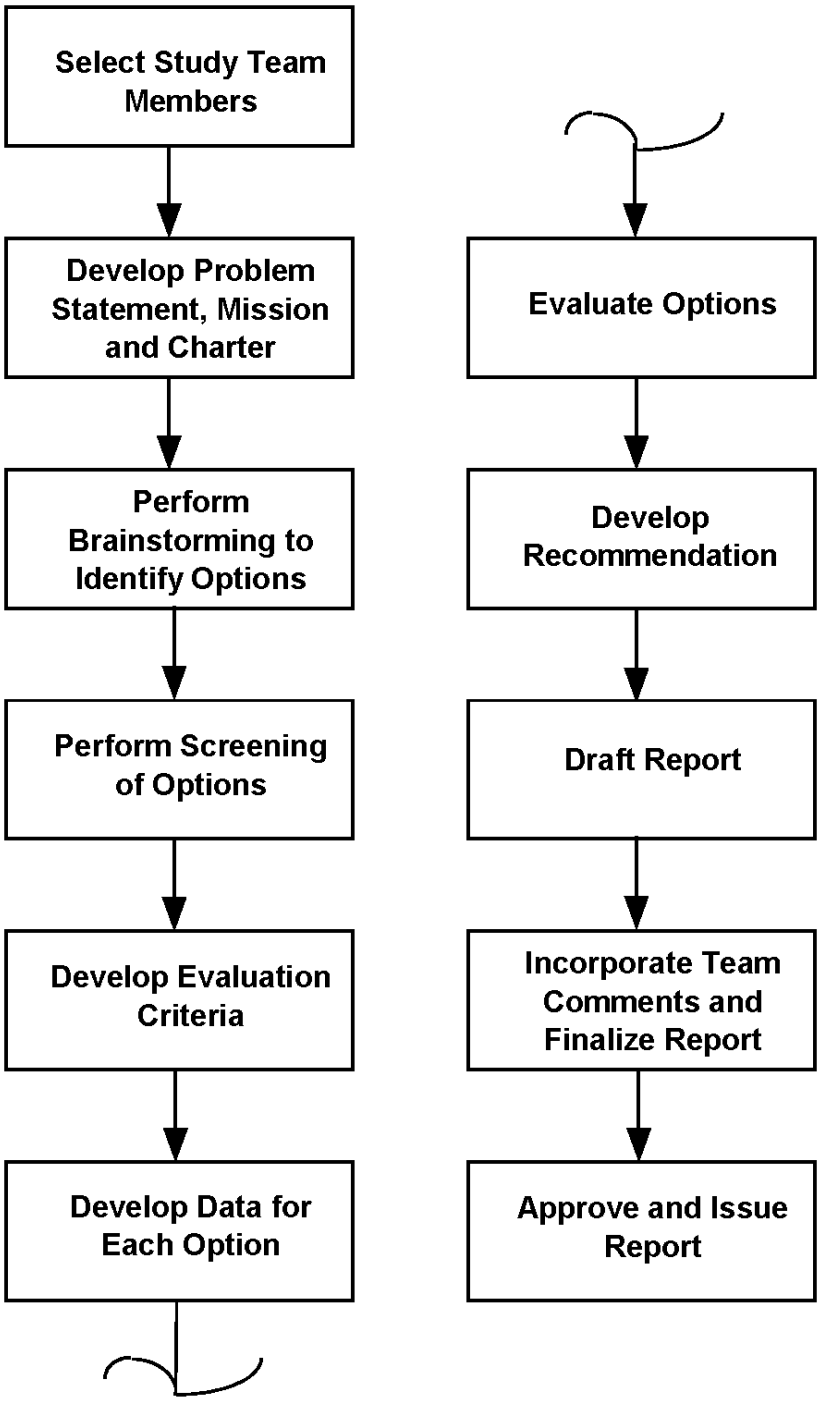
A team was subsequently chartered to identify and examine options to determine the best possible alternative means to remove mercury from the LWS (excluding DWPF) and provide a recommendation for implementation of a preferred option(s). This report documents the activities and recommendations of the team.

2.0 Process

The process used for this evaluation was a structured alternative analysis with weighted evaluation criteria. The team used alternative study methods defined in E7 Manual procedure 2.15 (Reference 5.2) and Alternative Studies and System Engineering Methodology Guidance Manual, WSRC-IM-98-000033, Appendix A (Reference 5.3). This methodology is commonly used to select an alternative from two or more options which would be available to meet specific functions, selection criteria, and requirements.

The SEE process is shown in Figure 2-1 and is described in detail within the following sections.

Figure 2-1: Study Process



2.1 Selection of Study Team Members

The Team was managed by the Chief Technology Officer. The initial activity of the study was to identify SEE team members and resources. The Team consisted of subject matter experts (SMEs) selected for their specific knowledge relating to the LWS (Tank Farms) and mercury removal. The Team comprised of core members who, in addition to participating in team activities will be responsible for screening and evaluating options, and supplemental SMEs who will be participants as needed by the SEE process. The following functional areas were be represented within the Team:

- Operations
- Engineering
- Savannah River National Laboratory (SRNL)
- Nuclear Safety
- Flowsheet
- System Planning
- External SMEs

The list of SEE team members is shown in Table 2.1-1:

Table 2.1-1: Team Members

Name	Organization
Richard Edwards	Engineering
Vijay Jain	Chief Technology Officer
Brian Looney	SRNL
Dennis Jackson	SRNL
Eric Harrison	ETP Engineering
John Gregory	Ops & Facility Management
John Schwenker	Tank Farm Operations
Kent Gilbreath	Planning
Lou Papouchado	URS-PS
Bob Petras	Env. & Waste Characterization
Michael Smith	Flowsheet Engineering
Annah Garrison	Tank Farm Engineering
Scott Reboul	SRNL
Kishan Patel	Flowsheet Engineering
Azi Samadi-Dezfouli	DWPF Engineering
Don Blake	DOE
Joe Copeland	DOE
Gavin Winship	Risk Management (Facilitator)

2.2 Problem and Mission Statement

The initial step of this SEE was to identify and succinctly state the problem and define a mission and goal for the study. To ensure these prerequisites were accepted by the facilities, management and engineering, a Charter was developed and approval obtained (Reference 1). Within this Charter the problem statement was defined as:

> **"There is a risk that re-establishing DWPF Mercury removal and recovery may be insufficient and DWPF recycle will continue to contain high levels of mercury."**

From this the team developed the following mission statement:

> **"Recommend an option or options to reduce or sequester the level of mercury in the LWS (excluding DWPF)."**

2.3 Brainstorming

Using the Problem and Mission/Charter statements, the team performed brainstorming to identify potential options. 20 potential options were identified (see Table 2.4-1) to reduce or sequester mercury from the LWS.

2.4 Screening

Screening criteria were developed by the team based on the desired function to reduce or sequester mercury from the LWS and the constraints within which this must be performed. As with the Problem and Mission statements these screening criteria were included in the Charter (Reference 1) and approved by management, facilities and engineering. The following screening criteria were developed:

- All removed mercury shall be either disposed of through existing waste disposal paths or captured and held for further treatment prior to final disposal.
- Option shall not constrain planned LWS operations.

After applying the above screening criteria to the 20 options identified during brainstorming, 7 options were screened out. The results of initial brainstorming and screening are shown below in Table 2.4-1:

Table 2.4-1: Brainstorming and Screening Results

#	Option	Pass/Fail	Remarks
1	Electrode Based Separation	**FAIL**	• Low TRL in liquid waste scenario, • High maintenance needs, • Production of hydrogen, • Complex operations • Uncertain wasteform.
2a	Install Filtration – Recycle Stream	**PASS**	
2b	Install Filtration – DSS and 512-S Cleaning & Maintenance streams	**FAIL**	DSS, 512-S Cleaning, and Maintenance streams ultimately enter Tank 50 and feed to Salstone. With the increased flow to Saltstone after SWPF startup, implementation before, after, or within Tank 50 would create a bottleneck that would affect the production of Saltstone.
2c	In Tank Filtration	**PASS**	
3a	Sorption of Mercury – Recycle Stream	**PASS**	
3b	Sorption of Mercury – DSS and 512-S Cleaning & Maintenance streams	**FAIL**	See Option 2b remarks.
3c	In Tank Sorption	**PASS**	
4a	Install IX – Recycle Stream	**PASS**	
4b	Install IX - DSS and 512-S Cleaning & Maintenance streams	**FAIL**	See Option 2b remarks.
4c	In Tank IX	**PASS**	
5a	Enhance Evaporator Functionality: Minimal Chemical Option	**PASS**	
5b	Enhance Evaporator Functionality: Complete Chemical Option	**PASS**	
5c	Enhance Evaporator Functionality: Photoreactor Option	**PASS**	
5d	Enhance Evaporator Functionality:	**PASS**	

	Photoreactor Option (in-tank)		
5e	Enhance Evaporator Functionality: Electrochemical Option	**FAIL**	• Potential for high maintenance needs • Hydrogen production • Impacts to flowsheet. low TRL for liquid waste application
6	Install Evaporator between DWPF and Tank Farm	**FAIL**	Adding an Evaporator between the two facilities does not accomplish the goal of removal of the mercury from the system.
7	Mercury Retention in Saltstone Disposal Form	**PASS**	
8	Target tanks with high mercury Levels for mechanical removal	**PASS**	
9	Reduce Methylation Fraction by Chemical addition or changing conditions.	**FAIL**	• Lack of basic information • Low TRL in liquid waste scenario • Potential impact on flowsheet low probability of success.
10	Tank 50 Photoreactor	**PASS**	

Descriptions of failed options are presented in Appendix D. Descriptions of Passing options are presented in Appendix C along with the additional information developed on those options for the evaluation process.

2.5 Develop Evaluation Criteria

Evaluation criteria were developed based on those specific attributes that the team considered critical to mission success and of specific interest to stakeholders. The evaluation criteria were also considered to be discriminating between options in that each option would vary in how well they perform against each criterion. The evaluation criteria developed by the team and topics associated with the criterion were as follows:

Mercury Removal Capability
Options with greater mercury removal were considered more favorable than options with lesser mercury removal capability.

Impact to System Plan Execution
Impacts to the System Plan are those which impact the execution of the production of

Saltstone, canisters, closures etc., as defined in the system plan. The lower the impact to the execution of the System Plan, the more preferable the option.

Cost of Modifications
The cost of modifications to deploy the option in the Liquid Waste System. The lower the cost, the more preferable the option.

Schedule to Deploy
The shorter the duration from receiving notice to proceed to complete deployment, the more preferable the option.

Technology Readiness Level
The higher the Technology Readiness Level (TRL), the more preferable the option.

Ease of Disposal
The easier the form of mercury removed is to dispose of, the more preferable the option.

Operability
The easier the option is to operate (e.g. fewer/simpler operational steps, replenishment of consumables), the more preferable the option.

Impact to liquid Waste Flowsheet
Impact to the Liquid Waste Flowsheet are those changes which modify the chemistry and rheology of the flowsheet. The smaller the impact, the more preferable the option.

Life Cycle Cost
The cost of operation within the Liquid Waste System. The lower the cost, the more preferable the option.

2.6 Data Development

After the development of evaluation criteria, the final options that passed screening were investigated further and matured to provide an understanding of how they would perform for each of the evaluation criteria. The final options and developed data are presented in Appendix C.

2.7 Evaluation

A software package specifically designed for alternative analyses was used to perform the evaluation. The software, Expert Choice Pro© provides an analytical platform capable of recording data in the form of weighted criteria and scoring and performing a synthesis of these data to arrive at rankings. Secondary features are the ability to modify criteria weights and show in real time, ranking changes. Using the data developed for each option and weighted criterion, the options were scored, ranked, and a sensitivity analysis

performed. After interpreting the results, options were determined not to be mutually exclusive, so a grid was prepared to optimize the solution. Risks were assessed for top option(s) as discussed below.

2.7.1 Criteria Weighting

The analysis hierarchy was developed using Expert Choice Pro© and a pair-wise comparison of criteria performed to establish weights based on preference judgements. The resulting hierarchy and criteria weights are shown in Figure 2.7.1-1:

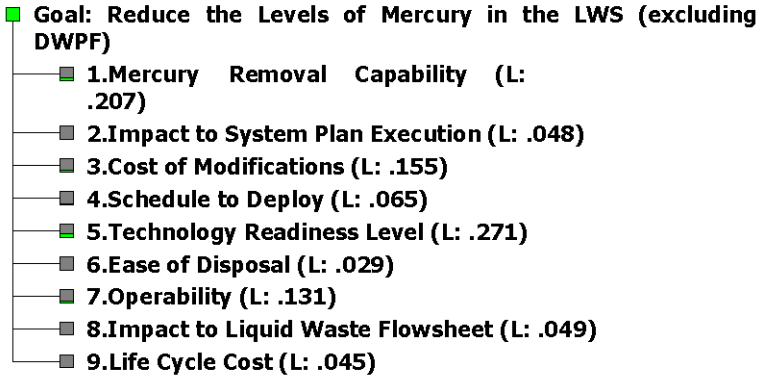


Figure 2.7.1-1: Analytical Hierarchy and Criteria Weights

As expected the highest weighted criteria were Technology Readiness Level and the capability to remove mercury. Technology Readiness Level was weighted high as it is essential to have mature option to assure mission success. Mercury removal capability was weighted high as is essentially the mission of the preferred option. Cost of modification was the third highest weighted criteria as typically a higher cost deployment option is less likely to be funded in the current environment. Operability, was the next heavily weighted criteria, as the team considered once the capability was deployed, it would be a long term burden on the program if the option were difficult to operate. Of the remaining criteria, schedule to deploy was weighted higher as an early deployment would ensure mercury issues were resolved quickly, which is a stakeholder concern. All other criteria were considered discriminators but not as significant as the five discussed above.

2.7.2 Scoring

A guide scale (Table 2.7.2-1) was developed to help assign a numerical performance value when evaluating options against a specific criterion:

Table 2.7.2-1: Scoring Guide Scale

Excellent	1
Very Good	
	0.75
Good	
Acceptable	0.5
Marginal	
	0.25
Poor	
Very poor	0

The team then proceeded to apply a score to each criterion for each option. The results of the scoring are shown in Appendix A.

2.7.3 Ranking

After the scoring had been completed the software program synthesized the results by multiplying the score by the weighting factor for each criterion and totaling the score for each option to arrive at a ranking. Figure 2.7.3-1 shows the ranking score results for all options.

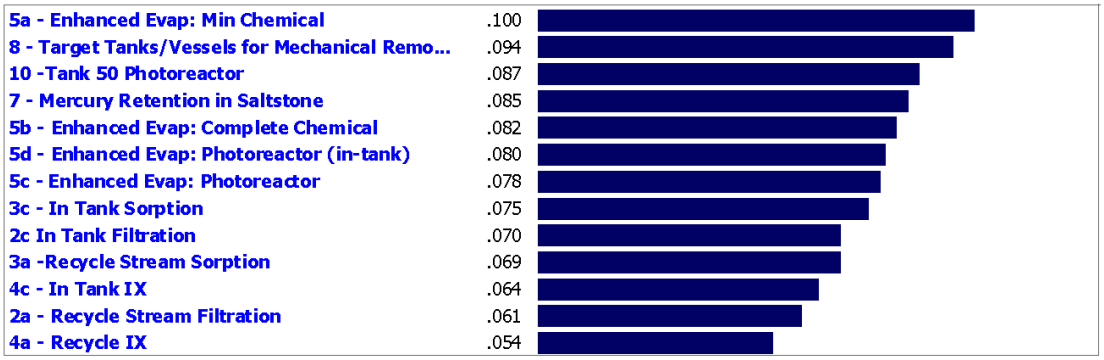


Figure 2.7.3-1: Results

As can be seen from Figure 2.7.3-1, Option 5a (Enhanced evaporator operation with minimal chemical addition), and Option 8 (Target tanks/vessels for mechanical removal) were the highest ranking options.

2.7.4 Sensitivity Analysis

A model's results are considered robust if evaluation criteria weights can be altered by ± 10% and the top ranking option is not displaced. A sensitivity analysis was performed by increasing and decreasing the weight of a particular criterion, resulting in the increase or decrease being proportionally distributed to the other criteria. This changed the scores of the options. It was observed that in no case did this degree of change displace the top two options. The criteria generally had to be changed upwards of 30% to change position and in many cases drastic decreases or increases in selected criteria did not displace the top two options. This model and result were therefore considered robust and valid.

2.7.5 Solution Optimization

Unlike most evaluations of this type, the two top ranking options (Option 8, targeting process vessels for mercury removal and Option 5a, enhanced evaporator operation with minimal chemical addition) were not mutually exclusive, i.e. if one were deployed the other could not. This gave the team the opportunity to select the top two ranking options for deployment. While these options did remove mercury, they may not be effective in the removal of organic mercury. To further optimize the solution, a further means to remove organic mercury was identified by selecting an organic mercury removal option from the remaining organic mercury removal options:

- Option10: Photoreactor on Tank 50 – 8.7%
- Option 7: Mercury retention in Saltstone – 8.5%
- Option 5b: Complete chemical evaporator option – 8.0%
- Option 5d: Enhanced Evaporator Photoreactor (in tank, Tank 22 or 43) – 8.0%
- Option 3c: In Tank Sorption of mercury (Tank 22) – 7.4%

Again, the top two organic mercury removal options (Option 10, Tank 50 photoreactor and Option 7, enhanced retention in saltstone) were not mutually exclusive.

2.7.6 Risk Assessment

Two risk identification processes (premortem and brainstorming) were used to identify risks and opportunities associated with the top two mercury removal options and the top two organic mercury removal options from the SEE. The risks/opportunities identified and their associated handling strategies are presented in Appendix B. The risks associated with Options 5a and 8 were low and manageable and risk handling strategies were developed. There were a greater number of potentially higher risks associated with Options 7 and 10 and these generally were relating to maturation of the processes. Risk handling strategies were identified for each.

3.0 Discussion of Results

The evaluation results show that Option 8 (Target process vessels (e.g. overheads tank) for mechanical removal of elemental mercury), and Option 5a (Removal of ionic mercury using the enhanced Evaporator minimal chemical addition) were the highest ranking

options that could be deployed in concert. The sensitivity analysis demonstrated this to be a robust model and ranking. The high rankings of these two options were driven by the low cost and ease of deployment and operation; thus they represent opportunistic technologies. Neither of these high ranked options, however, address the important long term challenge of organic mercury in the liquid waste system.

The solution was further optimized with the inclusion of two techniques that address organic mercury in the liquid waste system. The SEE team recommends including technologies that target organic mercury in the final decision. Throughout the brainstorming process the significance of mercury speciation in various parts of the liquid waste system was emphasized. The presence of organic mercury, such as methyl mercury cation, represents a significant challenge for processing the liquid waste. The team recognizes that neither Option 8 nor Option 5a address the organic component. Options that scored high that would address the organic component were Option 10 (ranked third), Option 7 (ranked fourth), and Option 5b (ranked fifth). These rankings were strongly influenced by technology readiness level. The logic of Option 10 is that converting organic mercury to inorganic mercury will increase the adsorption of mercury within saltstone. Option 10 initially considered a photoreactor to promote the conversion process. Through the brainstorming processes other options were identified that could also convert the organic mercury to inorganic mercury at Tank 50, specifically enhanced oxidation of organic mercury using ozone. This embodiment was identified as a component of Option 5b, complete chemical removal using the evaporator. This option was ranked fifth. Narrative of ozone oxidation and applicability to organic mercury is provided in Section 5b in Appendix B. Solutions(s) that address the organic mercury are crucial to the long term success of liquid waste processing success at the Savannah River Site. Independent of the conversion of organic mercury, Option 7 considers modification of saltstone to enhance the retention of the methyl mercury cation.

The risk assessment identified risks that existed with each of these options and generally risk handling strategies were considered effective to minimize the risk during the path to deployment. The final recommendations include relatively low-cost opportunistic methods that provide significant near-term removal of elemental and inorganic-ionic mercury, along with medium term actions to address organic mercury.

4.0 Recommendation

It is the recommendation of the team to:

(A) Deploy Option 8: Target process vessels (e.g. overheads tank) for mechanical removal of elemental mercury (opportunistic)

(B) Deploy Option 5a: Removal of ionic mercury using the enhanced Evaporator minimal chemical addition

(C) Pursue the removal of organic mercury by testing the photo reactor Option 10 (Photoreactor on Tank 50), and maturing the technology for deployment, in parallel with testing to mature Option 7 (Enhanced retention of mercury in saltstone). Important in this development are robust techniques that are compatible with LWS operations to convert organic mercury to either the ionic or elemental state.

5.0 References

5.1 SRR-LWE-2015-00086, Alternate Method for Mercury Removal from the Liquid Waste System – Evaluation Team Charter, Revision 0, October 6, 2015.

5.2 Manual E7, Procedure 2.15, Alternative Studies.

5.3 Systems Engineering Methodology Guidance Manual, WSRC-IM-98-00033, Appendix A.

6.0 Appendices

Appendix A – Option Scoring
Appendix B – Premortem Results
Appendix C – Passing Options Descriptions and Data
Appendix D – Failed Options

Appendix A – Option Scoring

		DIRECT	DIRECT	DIRECT	DIRECT	DIRECT	DIRECT	DIRECT	DIRECT	DIRECT
Alternative	**Total**	**1.Mercury Removal Capability (L: .207)**	**2.Impact to System Plan Execution (L: .048)**	**3.Cost of Modifications (L: .155)**	**4.Schedule to Deploy (L: .065)**	**5.Technology Readiness Level (L: .271)**	**6.Ease of Disposal (L: .029)**	**7.Operability (L: .131)**	**8.Impact to Liquid Waste Flowsheet (L: .049)**	**9.Life Cycle Cost (L: .045)**
2a - Recycle Stream Filtration	.067	.028	.200	.400	.200	.850	.400	.200	.900	.500
3a -Recycle Stream Sorption	.055	.111	.200	.100	.200	.800	.200	.100	.900	.200
4a - Recycle IX	.048	.069	.200	.100	.200	.700	.200	.100	.700	.200
5a - Enhanced Evap: Min Chemical	.105	.069	.700	.900	1.000	.800	.900	.800	.500	.900
5b - Enhanced Evap: Complete	.072	.111	.400	.600	.400	.600	.900	.600	.200	.400
5c - Enhanced Evap: Photoreactor	.075	.083	.600	.400	.200	.700	.900	.600	.500	.700
5d - Enhanced Evap: Photoreactor	.080	.069	.600	.700	.500	.600	.900	.600	.500	.700
7 - Mercury Retention in Saltstone	.083	.083	1.000	.700	.500	.400	1.000	.900	.900	.400
8 - Target Tanks/Vessels for	.109	.028	1.000	1.000	.800	1.000	.800	.500	.900	.500
10 -Tank 50 Photoreactor	.086	.083	.400	.700	.500	.700	.900	.600	.800	.700
2c In Tank Filtration	.083	.014	.700	.600	.500	.850	.400	.400	.900	.500
3c - In Tank Sorption	.071	.083	.700	.400	.500	.800	.200	.200	.900	.200
4c - In Tank IX	.064	.056	.700	.400	.500	.700	.200	.200	.700	.200

Appendix B – Premortem Results

Option 8: Target Process Vessels for Mechanical Removal of elemental mercury-Risk Identification

ID	Risk	Handling
1	Identifying targets (mercury at the bottom of tanks) is ineffective	• Further R&D on ultrasonic or electrochemical probes and sensors etc., to refine the process of detection
2	Additional safety controls are required for vapor generated by use of pneumatic pumps	• Design measures to modify pump • Investigate other types of pump
3	Disposal is made more difficult due to removal of "dirty" mercury	• Investigate purification options • Investigate disposal as amalgam

Option 5a: Enhanced Evaporator - Minimum Chemical addition for enhanced mercury recovery - Risk Identification

ID	Risk	Handling
1	Tin/boron mercury reductants impact glass quality	• Perform additional glass qualification • Investigate downstream impacts
2	Chemical handling of reductant is more difficult than anticipated	• Develop an optimized plan for storage and handling • R&D to define process parameters • Evaluate tank corrosion control
3	Safety basis changed based on mercury removal quantity. Requires new/additional controls	• Perform analysis • Identify and deploy controls

Option 7: Mercury Retention in Saltstone - Premortem Results

ID	Risk	Handling
1	TCLP Fails with new mercury binder	• Perform R&D • Perform testing
2	Amount of binder impacts quality of product/processability (e.g. set time, slump, pumpability, air entrainment etc.)	• Perform R&D • Perform testing
3	Binding agent does not mix well	• Perform R&D • Perform testing
4	Cost of binder is prohibitive	• Identify alternatives
5	Binder is not available (cannot be successfully formulated)	• Perform R&D early
6	Binder causes other metals to fail TCLP	• Perform R&D • Perform testing
7	Binder causes flammability issues	• Perform R&D • Perform testing
8	Binder is not commercially available in the quantities required	• Investigate the feasibility of SRR producing binder
9	Regulators do not approve of approach or regulations tighten up	• Introduce approach ahead of time to Stakeholders and Regulators
10	DSA/CHAP identifies additional safety controls required	• Develop Safety Strategy early
11	IH concerns with handling binder	• Perform R&D • Perform testing
12	Long term viability challenges PA	• Perform UWMQE • Perform SA if needed
13	Form of Mercury Changes in LWS flowsheet	• Perform periodic characterization and trending
14	Leachate results are inconsistent (not predictable)	• Perform R&D • Perform testing • Develop a more stable form

Option 10: Tank 50 Photoreactor - Premortem Results

ID	Risk	Handling
1	DSA/CHAP identifies additional controls	• Develop safety strategy early
2	SWPF flowrate is too high to allow sufficient photolytic reaction time	• Evaluate flow rates and capacity • Identify the need for multiple units
3	Maintenance greater than expected (e.g. difficult/more frequent change out of diodes or lamps)	• Perform a RAMI analysis • Design modification
4	Photoreactor introduces an ignition source to Tank 50	• Early evaluation/safety strategy
5	Photoreactor materials are not compatible with radiation field	• Evaluate and include in design
6	High pH in Tank 50 is an issue as it is higher than what has been tested	• Early R&D (go/no go decision point) • Perform R&D • Perform testing
7	Commercial grade equipment does not have suitable containment for rad application	• Evaluate and include in design
8	Decomposition creates flammable products/deleterious effects	• Perform R&D • Design fix as needed • Pilot
9	Reactor surface fouls continuously	• Perform R&D • Design fix as needed • Pilot
10	Resultant mercury containing grout form fails TCLP	• Perform R&D • Pilot
11	Photo-intensity is insufficient	• Early R&D (go/no go decision point) • Perform R&D • Design fix as needed (e.g., add titanium reactive surfaces or ozone to increase reaction rate) • Examine chemical alternatives e.g., ozone) • Pilot

ID	Risk	Handling
12	Photoreactor equipment becomes obsolete	• Evaluate market conditions • Identify alternate components
13	Form of Mercury Changes in LWS flowsheet	• Perform periodic characterization and trending
14	Infrastructure will not allow for installation of photoreactor	• Modify design/infrastructure to accommodate constructability concerns

Appendix C – Passing Options Descriptions and Data

Option 2a: Install filtration in recycle stream

Recycle from DWPF to the tank farm should be one of the "cleaner" streams. Installation of a filtration skid or system along this line could provide a method to remove mercury. This filtration could also go into the DSS/512 system. Most mercury filtration systems are designed for Offgas situations however. The following method has been utilized to some degree in industry.

Proposed

Installation of a duplex or triplex filter system at either 511-S, HDB-8, or HDB-5. This filter system would be in the direct line of transfers from the RWT (at 511-S) to Tanks 22 and 43. The system would consist of filters that remove a mercury compound that likely require pretreatment for coagulation or absorption. The multi-filter arrangement would allow filter replacement without impacting the throughput. A simple version is shown in the following pictures.

An above ground enclosure area would be built adjacent to the associated diversion box or RWT cell. A jumper would exit the cell/box go to the filter unit and then return to the cell/box. A bypass jumper system would also be required for the unit. The enclosure would need to provide shielding to the passersby. A drain line would be required to be routed to sumps to allow for depressurization and draining of the filters for replacement. Remote access to the filter tops would be required to allow for replacement of cartridge type filters. This system could be built into a pit that would allow more accessible filter swaps. Leak detection could be provided by floor level monitoring by conductive probes.

Key assumptions:

- No enclosure ventilation is required.

- Filters could be replaced remotely.
- No active safety systems are required.
- Double wall piping system is not required.
- Hydrogen accumulation is not a safety concern.

Design, fabrication, and installation would be in the $ 5-10 Million range for such a system.

1. Mercury Removal Capability:	The insoluble fraction of the mercury would be removed by the filter. Also additional insoluble particles would also be removed from the flow stream. This would result in heavy fouling by non-mercury material.
2. Impact to System Plan Execution:	This modification should have little to no adverse impacts to the system plan.
3. Cost of Modifications:	The modification would be in the $5-10 million dollar range to design build. There would be ongoing lifecycle costs associated with filter replacement.
4. Schedule to Deploy:	Requires laboratory testing to show that the filter media will preferentially remove mercury without clogging with other contaminants. Could be deployed in 2-3 years.
5. Technology Readiness Level:	TRL 4/5. Filtration is a common commercial technology used in many different industries. The use for mercury removal is also common. Commercial nuclear plants use duplex filters in the Chemical and Volume Control system to clean the primary recirculation system and the reactor coolant pump seal injection water. This is a radioactive stream but is already a fairly pure stream. However the unique feedstream of the LWO waste poses a problem with claiming a higher TRL.
6. Ease of Disposal:	Filter media would need to be disposed of and should be a standard type disposal process.
7. Operability:	The filter system is a proven technology but the waste stream would cause the dose and shielding requirements to be quite high. Typical commercial usage is with long reach tools.
8. Impact to Liquid Waste Flowsheet:	This would produce an alternate waste stream from the filters. Over all, the impact to the flowsheet should improve the cleanliness of the recycle stream and reduce the amount of solids that would need to be sent back through DWPF.

Background

Most mercury filtration systems are designed for Offgas situations however. The following methods have been utilized to some degree in industry.

A) Coagulation/filtration is a common treatment which uses AlSO4 that reacts with the mercury to form a solid which can precipitate out of the water.

B) MEMBRANE FILTRATION

Summary

Membrane filtration can remove a wide range of contaminants from water. This technology has been used in a limited number of full-scale applications to treat wastewater contaminated with mercury. Before membrane filtration, a pretreatment step may be used to cause mercury to form precipitates or coprecipitates that can be more effectively removed by this technology. Membrane filtration can reduce concentrations of mercury to less than 2 µg/L.

Technology Description and Principles

Membrane filtration passes water through a semi-permeable, microporous membrane to concentrate contaminants into a smaller volume of water. This technology separates the influent into two effluent streams:

The permeate, or effluent stream, is the fluid that passes through the membrane. It usually contains reduced levels of contaminants. This stream may or may not contain contaminants at concentrations below the desired levels. If a reduction in concentration is still required, this stream may be sent to additional treatment units. In the case study described later, the permeate is neutralized and sent to an equalization and disposal unit.

2. The concentrate, or reject stream, contains water and contaminants that have not passed through the membrane. The reject may be recycled back through the membrane filtration system to further concentrate the contaminant and reduce the volume of reject. If the concentrate is not recycled, further treatment may include processing in a filter press, as in the case study described later (Ref. 9.5), or dewatering in solar evaporation ponds (Ref. 9.2).

Technology Description: Membrane filtration separates contaminants from water by passing it through a semi-permeable barrier or membrane. The membrane allows some of the constituents to pass through while blocking others. Media Treated:

- Drinking water
- Groundwater
- Surface water
- Industrial wastewater

Types of Membrane Filtration Processes:

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse osmosis

Membrane filtration processes vary based on the pore size of the membrane. The pore size is selected based on the molecular weight or size of the target contaminant and the pressure required to move wastewater through the filter. The four types of membrane filtration processes, from largest to smallest filter pore size, are :

- Microfiltration

- Ultrafiltration (UF)
- Nanofiltration
- Reverse osmosis

UF has been used in a treatment train with precipitation/coprecipitation to treat wastewater that contains mercury. The sources used for this report did not contain information on the use of microfiltration, nanofiltration, or reverse osmosis to remove mercury. Therefore, these technologies are not discussed in this technology summary.
UF units are used to remove oils, suspended particles, and biological solids (Ref. 9.1). UF requires a pressure of 5 to 100 pounds per square inch (psi) to move the fluid through an ultrafiltration filter (Ref. 9.6). UF filters can filter out contaminants with a molecular weight greater than 1000 g/mole (Ref 9.3).
Applicability, Advantages and Limitations
UF is primarily used to remove high-molecular weight contaminants and solids. This technology is usually preceded by precipitation/coprecipitation to cause the mercury species to form or adsorb onto a suspended solid because dissolved mercury species are typically too small to be effectively removed by UF. The energy required to operate membrane filtration units is related to the pressure requirements (Ref. 9.3). This type of treatment may be run in either batch or continuous mode. This technology's effectiveness is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, colloids, and other contaminants can cause membrane fouling.

Case Study: Episode #4671, Hazardous Waste Combustor
Ultrafiltration was included as part of a treatment train used to treat a variety of contaminants in wastewater generated by the APC equipment of a hazardous waste combustor. The wastewater treatment system included a primary and secondary treatment loop. The secondary treatment loop contained a stage for precipitation with sodium hydroxide followed by sedimentation and ultrafiltration. Analysis of samples collected at the influent and effluent of this treatment loop showed that the mercury concentration was reduced from 0.4 µg/L to below the detection limit of 0.2 µg/L.

C) PECOFacet's Mercury Removal System utilizes SAMMS™ or Self Assembled Monolayers on Mesoporous Supports, a nano-porous sorbent with a very high internal surface area. This innovative filtration method combines two advanced frontiers of materials science to specifically remove mercury and other contaminants such as arsenic, and other heavy metals from produced waters and condensate liquids from natural gas. SAMMS™ can absorb as much as 2/3 of its weight in mercury and the sorption kinetics are extremely fast (within minutes) compared to traditional resin products on the market. In addition, the filtration media can be tailored for a specific application. The sorbent has a high specificity for the mercury being removed, such that the free end of the monolayer is designed to selectively bind targeted

molecules while the pore size, monolayer length, and density can be adjusted to give the material specific diffusive and kinetic properties

D) **Mercury in crude oil and condensate can be effectively reduced by up to 98%**

MERCAWAYSM process technology is a straightforward process for reducing mercury (Hg) content in crude oil and condensate using easily understood chemistry and well-proven unit operations. It is a semi-continuous operation with a single filter while continuous operation can be achieved by online switching between two filters. There are four key steps in the MERCAWAYSM processing scheme as follows:

- Desanding to remove sand and other particles
- Reaction to convert elemental mercury, Hg°, to particulate HgS
- Filtration to separate HgS particles from treated crude/condensate stream
- Polishing to adsorb most of the remaining mercury after the filtration step

Desanding Step

The Desanding Step is accomplished using a hydrocyclone to achieve removal of sand and other particulates. The Desanding Step reduces the filtration load and improves cycle length. Depending on the nature of the produced crude/condensate stream, this step may be omitted.

Reaction Step

The Reaction Step is conducted by introducing a treat chemical bearing at least one Hg reactive sulfur (S). The treat chemical dosage required can be readily determined using laboratory test methods for the crude or condensate to be treated. The reaction takes place in a stirred reactor at modest temperature and pressure. The key reaction is Hg° + S donating compound → HgS

Filtration Step

The Filtration Step uses a pressurized precoat filtration system with operating cycle expected to range from 12 - 48 hours depending on feed and other filtration variables. In the current application, diatomaceous earth, DE, is added first as a filter precoat and later a finer grain DE is added to the feed to achieve filtration to 0.7µ. DE addition rate is determined during laboratory testing phase. Filtration has proven to provide 98% removal of HgS. The Hg containing filter cake is discharged at the end of every cycle for environmentally acceptable disposal.

Polishing Step

The Polishing Step is conducted in a fixed absorbent bed for further reduction of Hg content of the crude. This step may be unnecessary if acceptable levels of Hg removal are achieved after the Filtration Step.

Option 2c: Install filtration in a tank

Installation of a filtration skid or system inside a tank could provide a method to remove mercury. Most mercury filtration systems are designed for Offgas situations however. The following method has been utilized to some degree in industry.

Proposed

The system as described in Option 2a would be optimal but the limitations of having to work inside a tank or tank riser does not provide adequate space for installation of a duplex or triplex filter system. The alternative is a filter that is located inside a tank riser. This filter system would be in the direct line of transfers from the tank or possibly as an in tank recirculation system. The system would consist of filters that remove a mercury compound that likely require pretreatment for coagulation or absorption. The single filter arrangement would not allow filter replacement without impacting the throughput. A filter mechanism that would fit within a tank riser is very limited in circumference.

The filter mechanism would require opening the tank boundary to change out filters unless the system could be designed to include a seal at the tank to filter interface point. An above ground enclosure area would be built above the tank to help mitigate the consequences of opening the tank vapor space.

Key assumptions:

- No enclosure ventilation is required.
- Filters could be replaced remotely.
- No active safety systems are required.
- Hydrogen accumulation is not a safety concern.

Design, fabrication, and installation would be in the $ 3-10 Million range for such a system.

The overall criteria would grade out similar to Option 2a.

9. Mercury Removal Capability:	The insoluble fraction of the mercury would be removed by the filter. Also additional insoluble particles would also be removed from the flow stream. This would result in heavy fouling by non-mercury material.
10. Impact to System Plan Execution:	This modification should have little to no adverse impacts to the system plan.
11. Cost of Modifications:	The modification would be in the $3-10 million dollar range to design build. There would be ongoing lifecycle costs associated with filter replacement.
12. Schedule to Deploy:	Requires laboratory testing to show that the filter media will preferentially remove mercury without clogging with other contaminants. Could be deployed in 2-3 years.
13. Technology Readiness Level:	TRL 4/5. Filtration is a common commercial technology used in many different industries. The use for mercury

	removal is also common. Commercial nuclear plants use filters in the Chemical and Volume Control system to clean the primary recirculation system and the reactor coolant pump seal injection water. This is a radioactive stream but is already a fairly pure stream. However the unique feedstream of the LWO waste poses a problem with claiming a higher TRL.
14. Ease of Disposal:	Filter media would need to be disposed of and should be a standard type disposal process.
15. Operability:	The filter system is a proven technology but the waste stream would cause the dose and shielding requirements to be quite high. Typical commercial usage is with long reach tools.
16. Impact to Liquid Waste Flowsheet:	This would produce an alternate waste stream from the filters. Over all, the impact to the flowsheet should improve the cleanliness of the recycle stream and reduce the amount of solids that would need to be sent back through DWPF.

Option 3A: Mercury Removal from Aqueous Solution by Adsorption

Assumption:

- All tests and data produced with adsorbents and adsorption systems were done using chlor-alkali and synthetic waste water. In this paper, it is assumed our system reflects that and all proposals are made based on that.

Adsorbent:

The best choice for adsorbent would be sulfur impregnated granular activated carbon (GAC). While a regular activated carbon would also work, it would not provide the specificity that the sulfur impregnated carbon would. There would not be as much competition for activate sites when the stream flows through the column due to the high affinity of mercury for sulfur. In addition to that, research has shown that speciation of mercury is not an issue and this adsorbent can remove all types of mercury effectively (98.64% removal efficiency at a pH of 10.0-11).

Other options for adsorbents

- PACs – PACs (powdered activated carbon) work as well as GACs in tests. Advantage of this technology is the high surface area due to small particle size. Tests have shown that it has near ~100% removal efficiency for all types of mercury. Should be looked as backup option because it has a high operating cost if used continuously, cannot be regenerated, and dust from PAC makes handling difficult and issues with flammability.
- Thiol SAMMs – has high functionality and extensive surface area that result in high loading capacity and selectivity. Has a high affinity for Hg as well as other organics. For example, tests have shown that it can reduce 25 ppb Hg to about ~5 ppt. This test was done with well water. Should be looked at as a backup option due to cost.
- BPHC, MHBB, Coal Fly Ash, Forager Sponge – These other materials have been used in the adsorption processes and have been found to be comparable in mercury treatment. They are still at the research level and would most likely not apply to our system.

Location and Configuration:

The increase in volume of streams after the implementation of SWPF and overall cost guided the decision on the location of the column. With the increase in volume, the streams going to Tank 50 would increase to the point that an adsorption column would create a bottleneck if placed before or after that tank. Therefore, the location chosen would be after the DWPF recycle stream before it reaches Tank 22. There would be three options on how to set up the system.

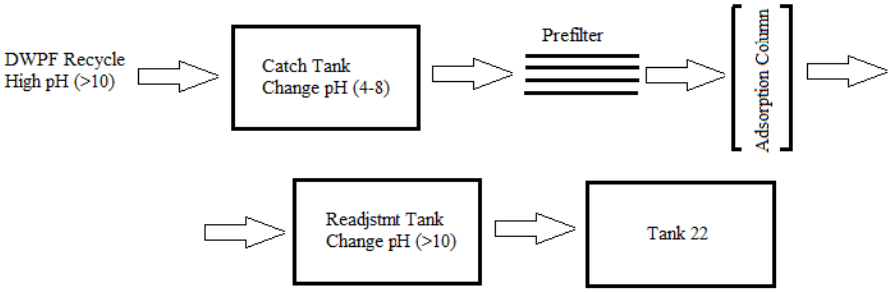
Each of the options will need to have

- A pre-filter to remove any organics and solids to prevent fouling of adsorbent column
- A spent adsorbent deposit tank

A: Recycle Stream (Out of Tank)

The best out of tank location to implement this system would be after the DWPF recycle stream before it reaches Tank 22. There would be three options on how to set up the system.

1. Since the DWPF recycle stream is at a high pH, a change in pH may be needed. Therefore, a tank would be needed to receive the stream, change the chemistry and lower the pH to neutral to basic



(~4-8). The stream would then enter a pre – filter, go through the column, and end at a tank were the chemistry can be changed back to >10. Then the stream can be sent to Tank 22.

Figure 1: Option 1

2. If DWPF can send the stream with a slightly lower pH, then the stream can do directly through the pre filter and into the adsorption column. Then it can be readjusted to a high pH before going to tank 22.

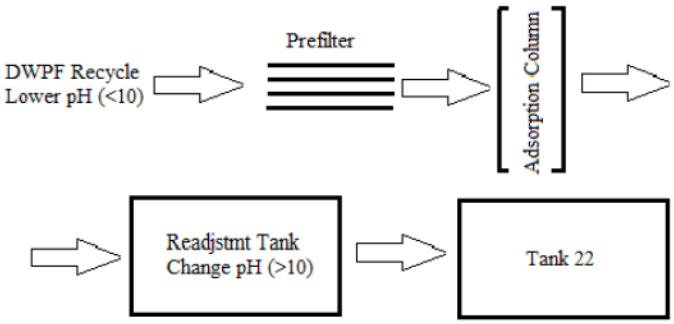


Figure 2: Option 2

3. If a pH change is not necessary the recycle stream can go directly to the pre filter and into the adsorption column. Then it can go directly to Tank 22.

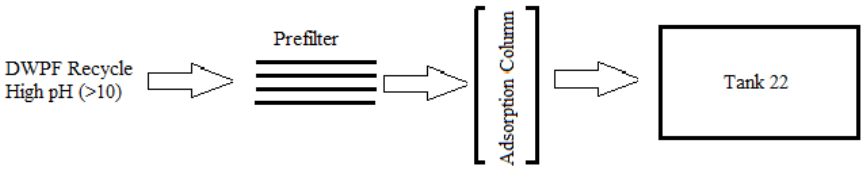


Figure 3: Option 3

Sizing for the column was done based off a scale up from a pilot test done with 4 columns (with a GAC – Mersorb) in series in 2003. The recycle stream would increase to 3.2 MGal/yr (7.42 gpm) after the startup of SWPF (System Plan). Therefore, based off a per volume basis, about a 260 gallon bed volume would be needed (concentration of stream was not taken into account). (The pilot had a pH stream of 10-11 and a mercury intlet concentration of 4.5-86 ppb which left the system at 25-413 ppt = 98.64% removal efficiency)

Disposal:

The pilot test showed that about 20-25 bed volumes can be processed before the adsorbent is spent. Therefore, after about 15 hours of flow, the adsorbent would have to be replaced.

If the adsorbent is bought as a cartridge, the column can be opened and the cartridge disposed of. This would help deal with microbial growth if it occurs. A cleaning of the column would not be necessary since the entire cartridge can be removed. Essentially, if the cartridge of spent adsorbent can pass TCLP and land disposal limits it can go to a burial site. However, since it is not yet known exactly how much mercury will be taken up by the adsorbent from our waste streams, a specific disposal path will have to be determined after further testing.

Evaluation Criteria of Option 3A (Recycle Stream Before Tank 22):

1. **Technology Readiness Level**
   The adsorbents and generally this adsorption technology are widely applied in water treatment technologies already. However, the adsorbents have not been tested with our wastewater yet.

2. **Mercury Removal Capability**
   High capacity to remove all types of mercury (elemental, ionic, and organic). All wastewater will contact the column so there will be a high removal efficiency.

3. **Cost of Modifications**
   With the addition of a spent adsorbent tank, pre – filter, adsorbents, and an adsorption column, the cost can be considered high. An entire new building would have to be made to house this system.

4. **Operability**
   The operability of this system is moderately easy with the exception of the filtration. The filtration aspect would have to be monitored constantly. In addition to that, the column may require some cleaning if fouling is expected.

5. **Schedule to Deploy**
   Major addition to the system therefore it will be a minimum of 3 years.

6. **Impact to System Plan Execution**
   Low to none. This system at most will change pH for the adsorption process and then return the pH to normal values before sending back to the system.

7. **Impact to Liquid Waste Flowsheet**
   Low to none. This system at most will change pH for the adsorption process and then return the pH to normal values before sending back to the system.

8. **Life Cycle Cost**
   Medium. Depending on the cost of adsorbent the constant removal/replacement of it and general operations costs can get moderately expensive.

9. **Ease of Disposal**
10. It is moderately easy if we fall under TCLP and land disposal limits. We can follow ETPs disposal path. However, if testing shows a high rate of removal, then another disposal path will have to be determined.

Kishan Patel

Option 3C: Mercury Removal from Aqueous Solution by Adsorption

Assumption:

- All tests and data produced with adsorbents and adsorption systems were done using chlor-alkali and synthetic waste water. In this paper, it is assumed our system reflects that and all proposals are made based on that.

Adsorbent:

The best choice for adsorbent would be sulfur impregnated granular activated carbon (GAC). While a regular activated carbon would also work, it would not provide the specificity that the sulfur impregnated carbon would. There would not be as much competition for activate sites when the stream flows through the column due to the high affinity of mercury for sulfur. In addition to that, research has shown that speciation of mercury is not an issue and this adsorbent can remove all types of mercury effectively (98.64% removal efficiency at a pH of 10.0-11).

Other options for adsorbents

- PACs – PACs (powdered activated carbon) work as well as GACs in tests. Advantage of this technology is the high surface area due to small particle size. Tests have shown that it has near ~100% removal efficiency for all types of mercury. Should be looked as backup option because it has a high operating cost if used continuously, cannot be regenerated, and dust from PAC makes handling difficult and issues with flammability.
- Thiol SAMMs – has high functionality and extensive surface area that result in high loading capacity and selectivity. Has a high affinity for Hg as well as other organics. For example, tests have shown that it can reduce 25 ppb Hg to about ~5 ppt. This test was done with well water. Should be looked at as a backup option due to cost.
- BPHC, MHBB, Coal Fly Ash, Forager Sponge – These other materials have been used in the adsorption processes and have been found to be comparable in mercury treatment. They are still at the research level and would most likely not apply to our system.

Location and Configuration:

The increase in volume of streams after the implementation of SWPF and overall cost guided the decision on the location of the column.

Assumption: A pH change will not be needed

This option will need to have

- A pre-filter to remove any organics and solids to prevent fouling of adsorbent column
- A spent adsorbent deposit tank

The in – tank location that would provide the greatest removal of mercury would be within Tank 22. The DWPF Recycle Receipt Tank (22) is a better choice since it will be more dilute than Tanks 43 and 38. In addition to that, Tank 50 would also not be a candidate for this option because of the increase in flow to the tank after SWPF startup. This increase in flow to tank 50 would not be able to be handled by the filter. However, after SWPF startup Tank 22 will receive ~7.42 gpm of feed. The in - tank rotary microfilter can handle up to 5-8 gpm so it would not create a bottleneck.

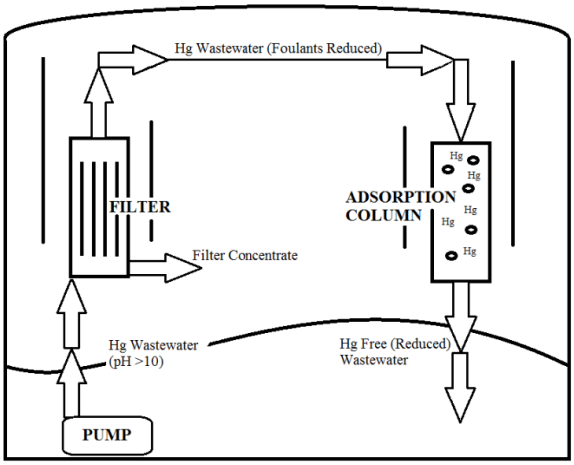


Figure 4: Option C

Within the tank, the filter and column would be set in risers. A pump would bring the wastewater up through the filter and through the column. The concentrate that builds up on the filter can be sent back to the tank. Similarly, the Hg free (reduced) wastewater would be sent back.

Since wastewater is constantly entering and leaving the tank (to Tank 43 and the 2H Evaporator), not all liquid in the tank will contact the adsorption column during recirculation. Though this will reduce the amount of mercury removed, the cost will be significantly less since a structure will not need to be built to house this.

Sizing for the column was done based off a scale up from a pilot test done with 4 columns (with a GAC – Mersorb) in series in 2003. The recycle stream would increase to 3.2 MGal/yr (7.42 gpm) after the startup of SWPF (System Plan). Therefore, based off a per volume basis, about a 260 gallon bed volume would be needed (concentration of stream was not taken into account). (The pilot had a pH stream of 10-11 and a mercury intlet concentration of 4.5-86 ppb which left the system at 25-413 ppt = 98.64% removal efficiency)

Disposal:

The pilot test showed that about 20-25 bed volumes can be processed before the adsorbent is spent. Therefore, after about 15 hours of flow, the adsorbent would have to be replaced.

If the adsorbent is bought as a cartridge, the column can be opened and the cartridge disposed of. This would be slightly more difficult in - tank, but it would help deal with microbial growth if it occurs. A cleaning of the column would not be necessary since the entire cartridge can be removed. Essentially, if the cartridge and spent adsorbent can pass TCLP and land disposal limits it can go to a burial site. However, since it is not yet known exactly how much mercury will be taken up by the adsorbent from our waste streams, a specific disposal path will have to be determined after further testing.

Evaluation Criteria of Option C (In Tank Adsorption):

11. **Technology Readiness Level**
    The adsorbents and generally this adsorption technology are widely applied in water treatment technologies already. However, the adsorbents have not been tested with our wastewater yet.

12. **Mercury Removal Capability**
    High capacity to remove all types of mercury (elemental, ionic, and organic). Since this will run as a continuous recirculation, removal efficiency may go down since all wastewater will not be able to contact the column.

13. **Cost of Modifications**
    With the addition of a spent adsorbent tank, pre – filter, adsorbents, and an adsorption column, the cost can be considered medium to high. Since an entire new building will not be needed, costs will be saved there.

14. **Operability**
    The operability of this system is low to medium. The filtration aspect would have to be constantly monitored. Since this is an in – tank option, changing out filters would be more difficult. Similarly, when bacterial growth and plugging of the column occurs, cleaning becomes more difficult.

15. **Schedule to Deploy**
    Major addition to the system therefore it will be a minimum of 3 years.

16. **Impact to System Plan Execution**
    Low to none. This system will not affect the system plan execution in any major way.

17. **Impact to Liquid Waste Flowsheet**
    Low to none. This system will not affect Liquid Waste Flowsheet in any major way.

18. **Life Cycle Cost**
    Medium. Depending on the cost of adsorbent the constant removal/replacement of it and general operations costs can get moderately expensive.

19. **Ease of Disposal**
    It is moderately easy if we fall under TCLP and land disposal limits. We can follow ETPs disposal path. However, if testing shows a high rate of removal, then another disposal path will have to be determined.

Option 4a: Installation of IX System for Mercury removal from the DWPF Recycle Stream (Option C, side stream):

Ion Exchange (IX) is a mercury removal technology proven in the Liquid Waste System (LWS) at Effluent Treatment Project (ETP). IX removal would target ionic mercury, potentially methyl mercury, but not other organic mercury compounds. Placing IX mercury removal at the point of DWPF recycle influent to the tank farm (Tank 22) either in riser or directly adjacent to the tank is discussed.

Assumptions:

- System design would include adequate filtration/settling prior to the IX column(s),
- System design would include chemical cleaning/regeneration and adjustment
- Cleaning, regeneration and adjustment solutions could be disposed of directly into the waste tank
- IX resin would treat ionic mercury forms, methyl to a lesser degree, no effect on dimethyl/other organic mercury forms
- The system configuration would be that of a side stream tapping off of and recycling filter concentrate into the feed vessel (Tank 22).

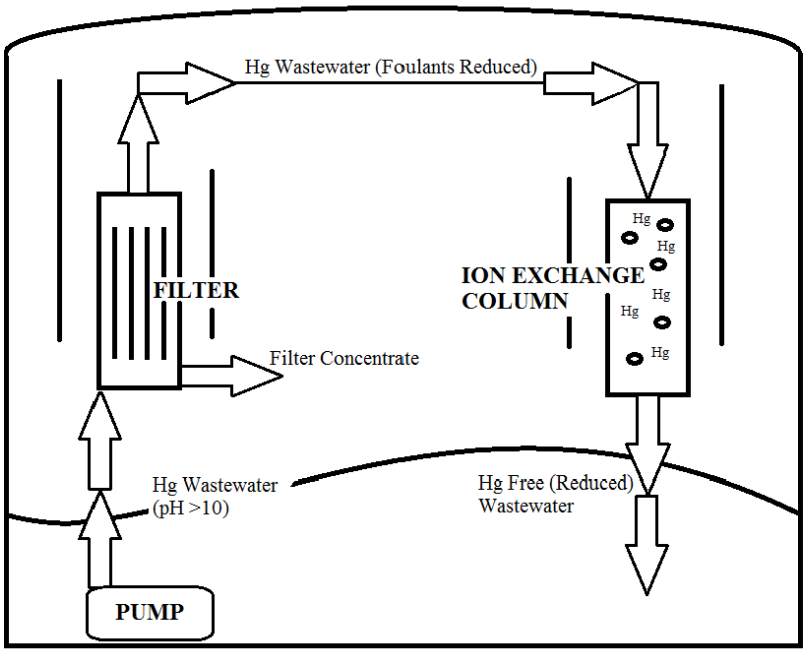
In the calendar year 2014 1.16 M gallons of recycle were transferred to the Tank Farm from DWPF, 2.2 gpm average for the year. However to match either the evaporator feed rate or the recycle transfer rate, the system would have to be sized for a considerably higher flow rate (~100 gpm for recycle, ~25 gpm for evaporator feed). A recirculating system built in riser or adjacent to the recycle receipt tank (22) would allow for a smaller, lower instantaneous flow rate unit.

The system would be a side stream recirculating off and back into the recycle receipt tank. There would be no direct impact on the feed of recycle forward to the evaporator system or salt batch preparation. However, in times of high throughput, residence time in the recycle receipt tank may be too low for the material to cycle through mercury removal so the system efficiency would drop and mercury would pass forward once again into the Liquid Waste System (Salt/Sludge Batch & eventually recycle).

A collection mechanism for spent resin would be required for the design.

Design, build, documentation and authorization time would, by estimation, exceed 2 years.

In comparison to placing IX on the recycle receipt location as opposed to the Decontaminated Salt Solution stream (DSS) at MCU, the recycle location is superior for better flexibility in location, size, and less interference system planning (example, maintenance on an IX system in MCU would potentially require an MCU outage and de-inventory).


Hg Wastewater (Foulants Reduced)
FILTER
Filter Concentrate
ION EXCHANGE
COLUMN
Hg
Hg
Hg
Hg
Hg
Hg Wastewater
(pH >10)
Hg Free (Reduced)
Wastewater
PUMP

Evaluation Criteria:

1. **Mercury Removal Capability**
   IX will target ionic forms, including methyl mercury. Other, nonionic, organic mercury compounds would not be removed.
2. **Impact to System Plan Execution**
   Placed as a side stream between the RCT (DWPF Recycle) and 2H Evaporator, impact on the system plan would be minimized.
3. **Cost of Modifications**
   Design and construction of infrastructure (tanks, filtration system, IX columns, mechanism for spent resin disposal) would set the costs high.
4. **Schedule to Deploy**
   Significant design and construction work, minimum 2 years, 3+ possible.
5. **Technology Readiness Level**
   Mercury removal resins are commercially available and in use on site for water treatment at ETP. TRL level 5. In design there are considerable overlaps with the SCIX project.
6. **Ease of Disposal**
   Hg laden IX resin has a history of disposal into the on-site burial ground (ETP's disposal path). The rad levels would be significantly greater for resin that processed recycle as opposed to filtered evaporator overheads.
7. **Operability**
   The filtration step would require cleaning and/or backflush capacity. The IX step would require backflush and cleaning capacity. Periodic fouling is expected.
8. **Impact to the Liquid Waste Flowsheet**
   Operated as a side stream, direct impact on the flowsheet would be minimized.
9. **Life Cycle Cost**
   This system is similar in function (filtration and IX) to the same systems at ETP, using those two as a baseline (40k and 90K respectively) an estimated 130k annual operating cost.

Option 4c Installation of IX System for Mercury removal from the DWPF Recycle Stream (Option A, in-line):

Ion Exchange (IX) is a mercury removal technology proven in the Liquid Waste System (LWS) at Effluent Treatment Project (ETP). IX removal would target ionic mercury, potentially methyl mercury, but not other organic mercury compounds. Placing IX mercury removal at the point of DWPF recycle influent to the tank farm (Tank 22) either in riser or directly adjacent to the tank is discussed.

Assumptions:

- System design would include adequate filtration/settling prior to the IX column(s),
- System design would include chemical cleaning/regeneration and adjustment
- Cleaning, regeneration and adjustment solutions could be disposed of directly into the waste tank
- IX resin would treat ionic mercury forms, methyl to a lesser degree, no effect on dimethyl/other organic mercury forms
- The system configuration would be that of a side stream tapping off of and recycling filter concentrate into the feed vessel (Tank 22).

In the calendar year 2014 1.16 M gallons of recycle were transferred to the Tank Farm from DWPF, 2.2 gpm average for the year. However to match either the evaporator feed rate or the recycle transfer rate, the system would have to be sized for a considerably higher flow rate (~100 gpm for recycle, ~25 gpm for evaporator feed). Placing the system on the receipt steam rather than the evaporator feed stream would require a higher capacity. It would reduce the potential impact on the evaporator system as volume in the receipt tank (22) would act as a buffer. In order to not impact DWPF operations a by-pass around the system may be included.

A collection mechanism for spent resin would be required for the design.

Design, build, documentation and authorization time would, by estimation, exceed 2 years.

In comparison to placing IX on the recycle receipt location as opposed to the Decontaminated Salt Solution stream (DSS) at MCU, the recycle location is superior for better flexibility in location, size, and less interference system planning (example, maintenance on an IX system in MCU would potentially require an MCU outage and de-inventory).

Evaluation Criteria:

10. **Mercury Removal Capability**
    IX will target ionic forms, including methyl mercury. Other, nonionic, organic mercury compounds would not be removed.
11. **Impact to System Plan Execution**
    Placed as an in line stream between the RCT (DWPF Recycle) and 2H Evaporator, impact on the system plan would require a by-pass line to minimize impact to other facility operations..
12. **Cost of Modifications**
    Design and construction of infrastructure (tanks, filtration system, IX columns, mechanism for spent resin disposal) would set the costs high.
13. **Schedule to Deploy**
    Significant design and construction work, minimum 2 years, 3+ possible.
14. **Technology Readiness Level**
    Mercury removal resins are commercially available and in use on site for water treatment at ETP. TRL level 5. In design there are considerable overlaps with the SCIX project.
15. **Ease of Disposal**
    Hg laden IX resin has a history of disposal into the on-site burial ground (ETP's disposal path). The rad levels would be significantly greater for resin that processed recycle as opposed to filtered evaporator overheads.
16. **Operability**
    The filtration step would require cleaning and/or backflush capacity. The IX step would require backflush and cleaning capacity. Periodic fouling is expected.
17. **Impact to the Liquid Waste Flowsheet**
    Operated as a side stream, direct impact on the flowsheet would be minimized.
18. **Life Cycle Cost**
    This system is similar in function (filtration and IX) to the same systems at ETP, using those two as a baseline (40k and 90K respectively) an estimated 130k annual operating cost.

Mercury in Liquid Waste Processing Facilities

Figure XX is a combined stacked bar and line graph that provides a graphical depiction of select mercury speciation data previously presented in Table 29 of SRR-CES-2015-00012. The representation is ordered (L-R) consist with flow diagrams of liquid waste through the process. This figure uses a stacked bar graph to depict speciation of elemental, ionic, organic, and particulate bound mercury within each tank. For simplification the organic mercury component is the sum of methyl, ethyl, and dimethyl data as reported in Table 29. For all species, values reported as Non-Detect are incorporated as zero and results reported as "less than" are interpreted at the reported value. The figure uses line graphs to portray the reported total mercury concentration and the total soluble mercury concentration within each tank. This allows readers to perform a mental mass balance of analytical results for each tack. Total soluble mercury should equal the sum of the elemental, ionic, and organic species; and the total mercury should equal the sum of the total soluble mercury and the particulate bound mercury. Readers can readily compare the data presented as line graphs with that presented in the stacked-bar to determine completeness of speciation data and if additional data is need to further understand mass-balance of mercury in the tanks.

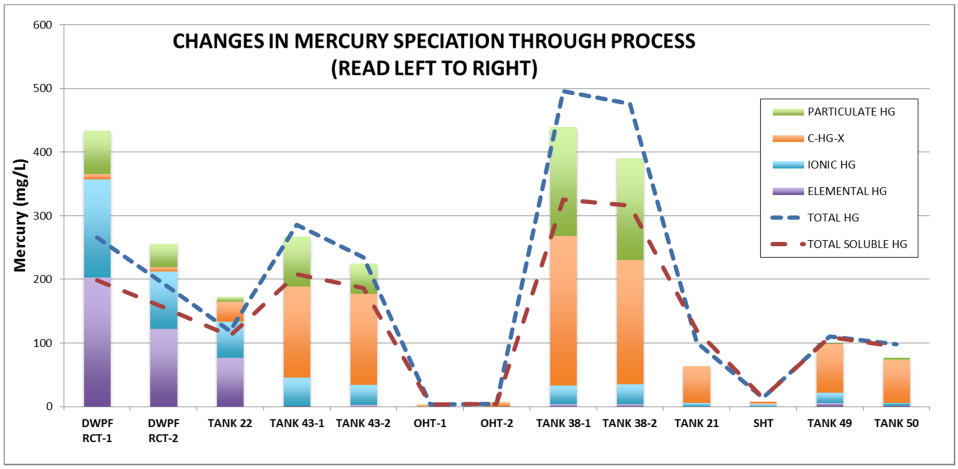


Figure XX: Combined stacked bar and line graph providing graphical depiction of select mercury speciation data (Ref: Table 29 of SRR-CES-2015-00012).

Option 5: Enhancing the Functionality of the Evaporator

Two evaporator systems are currently operating at SRS — the 2H and 3H systems. These systems are used to evaporate water from liquid waste to reduce volume, making better use of available tank storage capacity. Both of the evaporator systems have components that allows for the accumulation and removal of elemental mercury.

Identifying and developing an effective, reliable and robust mercury removal system for any wastewater system depends strongly on mercury speciation within the wastewater. The speciation of the mercury strongly effects distribution of mercury in various phases; i.e liquid, gas, or solid, and the transfer of mercury between phases. Important chemical properties such as boiling point, density, vapor pressure, and solubility are also species dependent. A firm understanding of speciation within the wastewater is critical for enhancing any mercury removal process. In most wastewater systems mercury can exist in three various states or conditions: 1) elemental, 2) ionic, and 3) organic, represented by at least one carbon-mercury covalent bond.

In the elemental state, key parameters that effect removal are a high specific gravity of the condensed liquid, a relatively low aqueous solubility and a modestly high vapor pressure. When present in abundance at temperatures below the boiling point (357°C) elemental mercury will accumulate as a separate phase liquid. Once present as a separate phase, the high specific gravity (SG = 13.6) strongly controls movement and allows liquid-liquid gravity separation of a significant fraction of the mass that is present in the elemental state.

In wastewater systems the ratio of the vapor pressure and aqueous solubility describe the air-water partitioning or Henry's Law Constant. The relatively low aqueous solubility and a modestly high vapor pressure indicate that elemental mercury will readily partition from the aqueous state to the vapor state. The figure to the right plots the dimensionless Henry's Law Volatility Constant (Vapor/Water) as function of temperature. As indicated by the increase in Henry's Constant the partitioning of elemental mercury in the air phase increases with increasing temperature. Highlighted in this figure are values for operating conditions at the M1 Air Stripper (as system discussed in subsequent section) and for the 2H and 3H evaporators.

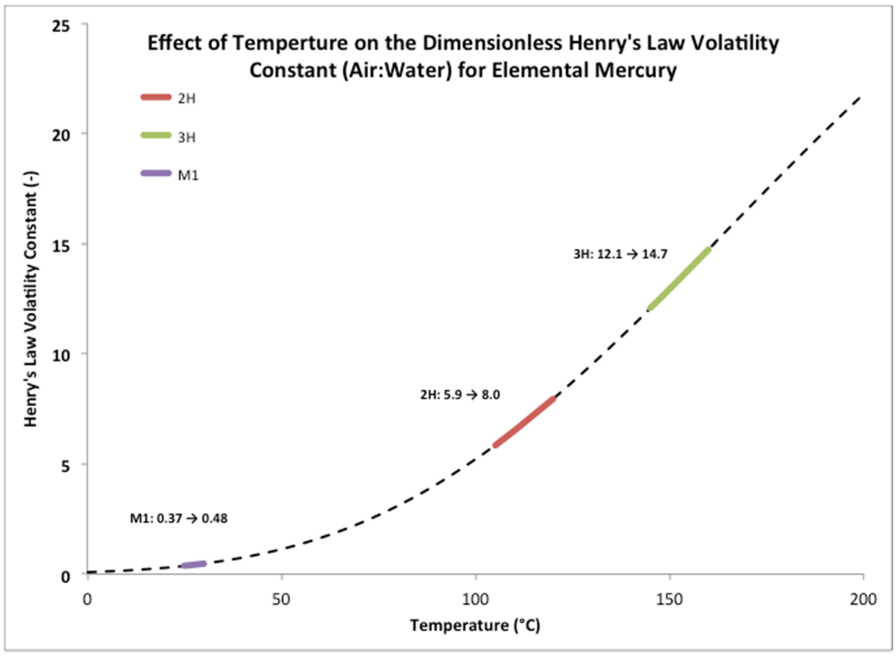


Figure YY: Effect of Temperature on the Air to Water Partitioning Coefficient for Elemental Mercury

The existing mercury removal components of the 2H and 3H evaporators are using vapor-liquid partitioning, liquid phase condensation, and gravity separation to remove the elemental mercury component present of these systems. Using only the elemental component of the speciation data from Tank 43 and operational parameters from 7-May-2015 (Q = 9.55 gpm) the 2H system should be removing 6 – 13 ml/day of elemental mercury. Between 4-May-2015 and 29-May-2015 approximately 400 ml of elemental mercury were recovered from the 2H evaporator, a rate of 8 ml/day. This reinforces the statement that in the current configuration the evaporator systems are only removing and capturing the elemental mercury component from the entering wastewater. It's noted that other volatile species, i.e. dimethylmercury, would also be removed. However, these species would not likely condense and be collected in the overhead collection system.

In order to enhance the capability of the existing evaporators in removing mercury, the ionic and methyl mercury components need to be targeted. The accompanying table expands the previous analysis to include the ionic and methyl components of the entering wastewater (Note: Removal rates in this table are based upon design flow rates of the 2H Evaporator). This table indicates that if a technology can be implemented that converts the ionic and methyl mercury to elemental, over 135 gallons per year of

elemental mercury can be removed from the 2H evaporator using the existing mercury collection system.

Mercury Speciation data from Tank 43								
	Elemental (mg/L)			*Ionic (mg/L)*			*Methyl (mg/L)*	
	TK-43-1	TK-43-2		TK-43-1	TK-43-2		TK-43-1	TK-43-2
Flow (gpm)	1.44	3.46		44	30.5		135	134
15	9	21		266	184		816	810
25	14	35		443	307		1359	1349
	Hg Volume (ml/day)			Hg Volume (ml/day)			Hg Volume (ml/day)	
	1.90	gal/year		28.93	gal/year		104.47	gal/year
						Hg(0) + Hg(+2) + C-Hg =	135.30	gal/year

5a: Enhancing the Functionality of the Evaporator – Minimal Chemical Option.

A reasonable approach at enhancing the functionality of the existing evaporators in removing mercury is to take a step-wise approach at the two remaining mercury fractions – ionic and methyl. The removal rate of the existing Mercury Removal System has the potential to be increased above the baseline if the ionic mercury could be targeted. Speciation data indicates that the daily flux of ionic mercury entering the 2H evaporator is on the order of 266 – 307 ml/day, fifteen times the flux of the elemental mercury.

The ionic species of mercury generally exist in the +1 or +2 oxidation state and occurs when elemental mercury loses one or two electrons to another species in oxidation- reduction reactions. In wastewater systems the ionic (inorganic) species of mercury readily form chemical complexes with negatively charged ions that are also present in the solution. Each of the mercury complexes have their own unique chemical properties that are generally strongly pH dependent. Mercury in the ionic state will generally not volatilize, condense, and accumulate in the evaporator overheads like elemental mercury.

One consideration is the use of chemical reduction to convert the ionic mercury to elemental mercury. Under this process a reducing agent would be added to the evaporator system to chemically convert ionic mercury to elemental mercury. This would greatly enhance the removal rate of the existing mercury removal system. Chemical reduction and volatilization of mercury has been implemented to remove mercury from wastewater at the M1 Air Stripper in the A/M Area (Looney et al., 2003; Jackson et al., 2013). In this process stannous chloride, a reducing agent, is added to the entering wastewater. The reducing agent reacts instantaneously to convert the ionic mercury to elemental where it is removed by the existing air stripping technology. This system has been in continuous operation since December of 2007. Referring back to the figure of the dimensionless Henry's Law Volatility Constant as a function of temperature, the Henry's Law constant for this system is highlighted (Kh = 0.37 to 0.48).

Implementation of chemical reduction and air stripping removal process is viable using the existing 2H evaporator system. For this application a compatible reducing agent would be added to the 2H evaporator system. Reduction of mercury(II) to mercury (0) can be accomplished in aqueous solution

using various reducing agents. This includes stannous chloride, sodium tetraethylborate or terapropylborate, sodium cyanotrihydroborate(III), or sodium (or potassium) tetrahydroborate (NaBH4 or KBH4). Possible addition points include liquid phase addition using the abandoned chemical addition system (anti-foam) or via a modification to either the steam lift or steam lance.

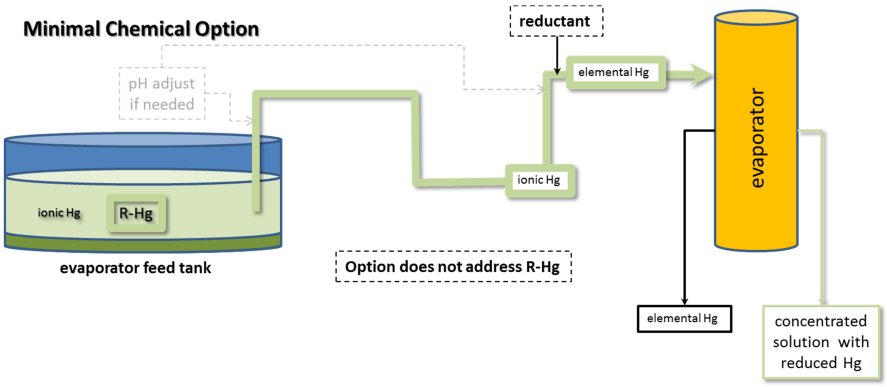


Table XYZ provides an order of magnitude estimate for two common, industrial reducing reagents – 1) stannous chloride dihydrate and 2) sodium borohydride. For stability considerations stannous chloride would likely be added as an acidic solution of HCl while sodium borohydride would be added as a caustic solution of NaOH. As indicated, approximately 200 gallons per week of a 50% stannous chloride solution is required, compared to 21 gallons per week of a 20% sodium borohydride solution. The difference in volume (essentially mass) originates in the stoichiometry of the redox-reactions and larger molar mass of stannous chloride. Laboratory and pilot scale testing of both reagents should be performed prior to full-scale implementation.

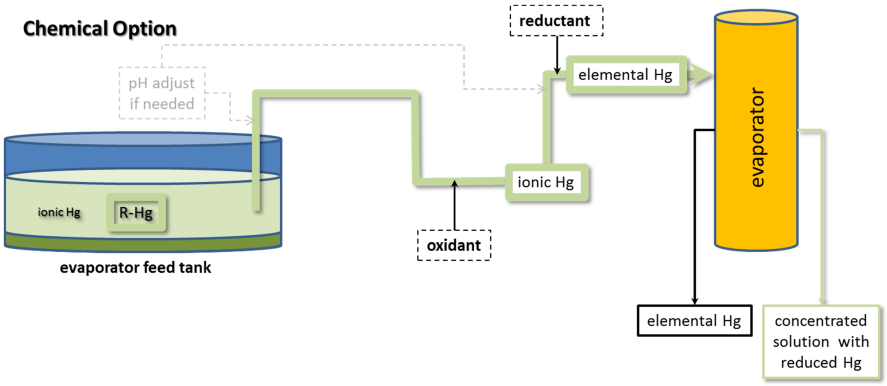
Evaluation Criteria: 5A - Enhancing the Functionality of the Evaporator – Minimal Chemical Option

1. Mercury Removal Capability:	Chemical reduction of the ionic mercury to elemental mercury will increase the mercury removal rate of the evaporator by a factor of 15X. The process has the capability to remove 23% of the total mercury in the entering wastewater.
2. Impact to System Plan Execution:	Minimal. The conversion of Ionic -> Elemental is rapid and should not reduce current evaporator operations.
3. Cost of Modifications:	Modifications include a small reagent storage tank and small injection pump. The specifications for these systems depend on the reducing agent selected (e.g. stannous or borohydride); See Table for preliminary reagent requirements.
4. Schedule to Deploy:	Requires limited laboratory testing, assume existing chemical addition system can be adapted/modified for

	reducing agent. Evaluation/adjustment of current mercury limits associated with evaporator.
5. Technology Readiness Level:	TRL 5/6. Chemical reduction and air stripping was implemented at the M1 Air stripper in A/M Area and has been in operation since in Dec-2007. Greatest uncertainty is potential for competing reactions in waste stream. Preliminary OLE simulations indicate ionic mercury is reduced to elemental. Limited laboratory scale testing is needed to verify chemical reduction of mercury of preferred reaction.
6. Ease of Disposal:	While volumes would increase, the accumulated mercury would be disposed of using existing disposal paths.
7. Operability:	Operation requires periodical replenishment of reagent. Schedule depends upon storage tank capacity and injection volume.
8. Impact to Liquid Waste Flowsheet:	Minimal - Require an evaluation of chemical impacts to process. Potential addition of Sn(IV) or Boron. Process could also add either chloride or sodium ions. Preliminary calculations indicate these components are minor compared to current levels.

5b: Enhancing the Functionality of the Evaporator – Complete Chemical Option.

Following along with the concept of step-wise conversion of mercury species to reach elemental, we now consider the conversion of methyl mercury. The monomethylmercury(II) cation is a unique species of mercury. This species is composed of a methyl group (CH3-) bonded to a mercury ion. As a positively charged ion it readily combines with other anions that may be present in the solution. When a second methyl group is present, the resulting compound dimethylmercury is a volatile liquid (BP = 156°C). Speciation data indicates that the majority (77%) of the mercury entering the 2H evaporator from Tank 43 is methyl mercury. For the evaporators to effectively remove methyl mercury, the species must be converted to elemental mercury. One approach would be chemical oxidation to remove the methyl group and produce ionic mercury. Once mercury is present in the ionic state, chemical reduction (Option 5a) would convert the ionic species to elemental by increasing the amount of reducing agent added to the system.



The challenge associated with a complete chemical option lies in a mechanism that will remove the methyl group (-CH4) from the monomethylmercury(II) cation. Common oxidation agents include hydrogen peroxide, sodium persulfate, potassium permanganate, sodium permanganate, sodium percarbonate, and ozone.

Hydrogen Peroxide	Colorless liquid, slightly more viscous than water, reaction are exothermic and generate gases. Hydrogen peroxide is thermodynamically unstable and decomposes to form water and oxygen. Reagent is short-lived, which limits ability to distribute via diffusion processes. The rate of decomposition increases with rising temperature, concentration and pH, with cool, dilute, acidic solutions showing the best stability. Natural organic matter (NOM) can increase oxidant demand. In basic solution, hydrogen peroxide can reduce a variety of inorganic ions. When it acts as a reducing agent, oxygen gas is also produced.
Persulfate	Highly corrosive. Compatibility of injection equipment with persulfate should be considered. May require injection and distribution of additional reagents to activate (strong bases, iron catalyst, chelating agent, hydrogen or calcium peroxide). The presence of naturally-occurring carbonate or bicarbonate has been noted to reduce oxidation rates, which could impact distribution Being the most recent of the oxidants to be applied, there is less of a knowledge-base of specific factors that may impact transport and distribution.
Permanganate	Permanganate(VII) ion is a strong, long-lasting oxidizing agent. Permanganate solutions stable in neutral or slightly alkaline solutions. In a strongly basic solution, permanganate(VII) is reduced to the green +6 oxidation state of the manganate ion, MnO42−. Manganese dioxide, an insoluble precipitate, is formed as a byproduct of the reaction.
Ozone	Gas phase amendment. An ozone process is always based on the effect of direct and indirect reaction mechanisms.

Table 1. Oxidant Form, Stability, Stage of Development and Oxidation Potential for Oxidants Used for In-Situ Chemical Oxidation

Oxidant	Reactive Species	Form	Persistence [1]	Stage of Development
Permanganate	MnO_4^-	powder/liquid	>3 months	developing
Fenton's	$\cdot OH$, $\cdot O_2^-$, $\cdot HO_2$, HO_2^-	liquid	minutes - hours	experimental/emerging
Ozone	O_3, $\cdot OH$	gas	minutes - hours	experimental/emerging
Persulfate	$\cdot SO_4^{2-}$	powder/liquid	hours - weeks	experimental/emerging

Oxidant and Reactions	Electrode Potential (E_h) [2]	
Permanganate		
$MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$	1.7 V (permanganate ion)	(1)
Fenton's (H_2O_2 Derived Reactants)		
$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	1.8 V (hydrogen peroxide)	(2)
$2\,\cdot OH + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	2.8 V (hydroxyl radical)	(3)
$\cdot HO_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	1.7 V (perhydroxyl radical)	(4)
$\cdot O_2^- + 4\,H^+ + 3\,e^- \longrightarrow 2\,H_2O$	-2.4 V (superoxide radical)	(5)
$HO_2^- + H_2O + 2\,e^- \longrightarrow 3\,OH^-$	-0.88 V (hydroperoxide anion)	(6)
Ozone		
$O_3 + 2\,H^+ + 2\,e^- \longrightarrow O_2 + H_2O$	2.1 V (ozone)	(7)
$2\,O_3 + 3\,H_2O_2 \longrightarrow 4\,O_2 + 2\,\cdot OH + 2\,H_2O$	2.8 V (hydroxyl radical, see rxn 3)	(8)
Persulfate		
$S_2O_8^{2-} + 2\,e^- \longrightarrow 2\,SO_4^{2-}$	2.1 V (persulfate)	(9)
$\cdot SO_4^- + e^- \longrightarrow SO_4^{2-}$	2.6 V (sulfate radical)	(10)

1 Persistence of the oxidant varies depending on site-specific conditions. Durations specified here are based on general observations.
2 Reactive species in parentheses; reduction potential is negative.

(Source: EPA Engineering Issue – In-Situ Chemical Oxidation, U.S. EPA/ORD/NRMRL/GWERD, P.O. Box 1198, Ada, OK 74820)

It has been shown that the hydroxyl radical (•OH) is effective in oxidizing the methyl mercury cation (Chen and Che-Jen, 2003). Two compounds of those identified that produce hydroxyl radical and have minimal residuals are Hydrogen Peroxide and Ozone.

Hydrogen Peroxide is one of the most powerful oxidizers known -- stronger than chlorine, chlorine dioxide, and potassium permanganate. And through catalysis, H2O2 can be converted into hydroxyl radicals (•OH). The decomposition products of H2O2 are oxygen and water. Consequently, H2O2 does not produce chemical residues that are associated with other chemical oxidants. And since H2O2 is totally miscible with water, the concentration of reagent is easily controlled. Industrial strength H2O2 is a strong oxidizer and as such requires special handling precautions. Most hydrogen peroxide applications involve its simple injection into the water stream with no requirement for additional

chemicals or equipment. The oxidizing properties are strongly dependent upon pH. Uncertainty of stability in high pH solution (pKa = 11.75) Uncertain on how elemental mercury will react with H2O2 – indication behave as a catalyst. Additional review of literature and possible laboratory studies needed to further evaluate hydrogen peroxide as a potential oxidizing agent.

Ozone is a powerful oxidant and has many industrial and consumer applications related to oxidation. Ozone is a highly reactive allotrope of oxygen that has a rate of decomposition dependent on the organic solutes and inorganic constituents present. Modem water and wastewater treatment systems often utilize the strong oxidizing potential associated with ozone at several points throughout the treatment process, including pre-oxidation, intermediate oxidation, and final disinfection. The advantage of ozone in water treatment applications is that it is effective at low concentrations. Common doses of ozone that are used in water treatment applications range between 1 - 5mg/l with contact times of around 10 min. The disadvantages of ozone disinfection includes the relatively high capital cost associated with ozone production6 as well as maintenance and operation costs of the generation equipment.2'8 Ozone can be present as a gas or dissolved in a liquid with the majority of water and wastewater applications relying exclusively on gas phase applications

Ozone can either react directly with a compound or it can react indirectly through decomposition to the hydroxyl radicals. Direct reactions are selective and occur almost quantitatively with organic compound. In the indirect reactions the hydroxyl radical promotes a chain reaction that oxidizes the desired compound and consumes ozone. Direct or indirect oxidation reactions are controlled by the presence of scavengers and promoters. The most significant promoter in aqueous solutions is the hydroxide ion that reacts with ozone to produce the hydroxyl radical. Direct oxidation processes are considered slow and selective compared to the corresponding indirect oxidation process. During indirect oxidation, the hydroxyl radicals formed by the initiators react with both the desired compound and the available ozone. The reaction proceeds until the source of the radicals, typically ozone, is depleted. Under acidic conditions (pH < 4) the direct pathway dominates, and above ph = 10 the reaction is primarily indirect. In aqueous solutions with an abundance of the hydroxide ion, these ions readily promote the decomposition of ozone into the reactive hydroxyl radicals. These radicals, being extremely electrophilic, continue to react with the ozone and other compounds that are present. This process can be divided into three different parts: 1) Initiation, 2) Radical Chain, and 3) Termination Step. Numerous investigators have presented rate constants for the reaction of ozone with the hydroxyl radical, most of these studies are not representative of conditions of interest. Additional laboratory testing is needed to evaluate rates under the conditions of interest.

Deployment Strategy – The implementation of a complete chemical removal process is inherently a two-stage batch treatment process. During the first-stage methyl mercury would first be converted to ionic mercury by adding a suitable oxidizing agent (likely ozone). The second stage involves the addition of a reducing agent to convert the ionic mercury to elemental, where it volatilizes and is captured in the existing mercury removal system. The process is characteristically sequential since the oxidizing agent will likely preferentially react (and consume) the reducing agent without effecting the speciation of mercury. Implementing a complete chemical option will likely reduce the throughput of the evaporator

to allow for an increased residence time associated with each chemical process (Methyl -> Ionic -> Elemental).

Table XYZ provides an order of magnitude estimate for two common, industrial reducing reagents – 1) stannous chloride dihydrate and 2) sodium borohydride. For stability considerations stannous chloride would likely be added as an acidic solution of HCl while sodium borohydride would be added as a caustic solution of NaOH. As indicated, approximately 820 gallons per week of a 50% stannous chloride solution is required, compared to 85 gallons per week of a 20% sodium borohydride solution. Note these estimates are a complete reagent dose (ionic + methyl mercury) that would be applied following the conversion of the methyl fraction to ionic. The difference in volume (essentially mass) originates in the stoichiometry of the redox-reactions and larger molar mass of stannous chloride. Laboratory and pilot scale testing of both reagents should be performed prior to full-scale implementation.

Evaluation Criteria: 5B - Enhancing the Functionality of the Evaporator – Complete Chemical Option

17. Mercury Removal Capability:	Chemical Oxidation coupled with chemical reduction (5b) of all the mercury to elemental mercury will increase the mercury removal rate of the evaporator by a factor of 55X. If effective the process has the potential to remove 100% of the total mercury in the entering wastewater.
18. Impact to System Plan Execution:	Implementation in current evaporator configuration may reduce the overall throughput as additional residence time required for two independent chemical treatments.
19. Cost of Modifications:	In addition to the modifications identified in 5b, this option would require the addition of oxidant, either liquid (H2O2) or vapor (O3). Current consideration for sequential processing using existing chemical addition system.
20. Schedule to Deploy:	Requires laboratory testing, assume existing chemical addition system can be adapted/modified for reducing agent. Evaluation/adjustment of current mercury limits associated with evaporator.
21. Technology Readiness Level:	TRL 2/3. Literature indicates that hydroxyl radical results in MeHg oxidation in wastewater to ionic mercury. Implementation would add reagent that would result in 100% ionic species in evaporator. Based up waste pH, oxidation would be from hydroxyl radical. Additional laboratory testing needed to develop/evaluate chemistry.
22. Ease of Disposal:	While volumes would increase significantly over 5a, the accumulated mercury would be disposed of using existing disposal paths.
23. Operability:	In addition to Operation of 5a, add components for storage and addition of a second reagent. Also may require operation of system to generate ozone.
24. Impact to Liquid Waste Flowsheet:	Analogous to Minimal Option 5a.

Table XYZ: Preliminary Estimates for Quantities of Commercial Reducing Agents to Chemical Reduce Ionic Mercury to Elemental Mercury in the 2H Evaporator.

	M1 Stripper	(a) 2H Evaporator - Ionic	(b) 2H Evaporator - Ionic + Methyl	
Liquid Flowrate	250	20	20	***gpm***
Air/Steam Flowrate	2000	350 - 450	350 - 450	***cfm or #/hr***
Operating Temperature	20	105 - 120	105 - 120	***°C***
Mercury Concentration	0.00025	44	179	***mg/L***
Mercury Flux	1.18E-06	1.66E-02	6.75E-02	***moles/min***
Dose Rate of SnCl2-2H2O	Basis - 1 Mole SN Reacts with 1 Mole of Hg			
Stoiciometric (1:1)	2.66E-04	3.74E+00	1.52E+01	grams/min
Realistic (10X Stoiciometry)	2.66E-03	3.74E+01	1.52E+02	grams/min
Reagent Flow As 10% (w/v) in 20% (v/v) HCl (M1 Soln.)	2.66E-02	374.20	1,522.30	ml/min
Reagent Volume per Day	3.83E-02	538.84	2,192.12	L/day
Reagent Volume per Week	0.07	997.86	4,059.47	gallons/week
Reagent Flow As 20% (w/v) in 40% (v/v) HCl	1.33E-02	187.10	761.15	ml/min
Reagent Volume per Day	1.91E-02	269.42	1,096.06	L/day
Reagent Volume per Week	0.04	498.93	2,029.74	gallons/week
Reagent Flow As 50% (w/v) in HCl	5.32E-03	7.48E+01	3.04E+02	
Reagent Volume per Day	7.65E-03	107.77	438.42	L/day
Reagent Volume per Week	0.01	199.57	811.89	gallons/week
Dose Rate of NaBH4	Basis - 1 Mole NaBH4 Reacts with 4 Mole of Hg			
Stoiciometric (1:4)	---	1.57E-01	6.38E-01	grams/min
Realistic (10X Stoiciometry)	---	1.57E+00	6.38E+00	grams/min
Reagent as 12% (w/v) in 14M NaOH	---	13.07	53.17	ml/min
Reagent Volume per Day	---	18.82	76.56	L/day
Reagent Volume per Week	---	34.85	141.78	gallons/week
DOW VenMet at 20% (w/v) in 14M NaOH	---	7.84	31.90	ml/min
Reagent Volume per Day	---	11.29	45.94	L/day
Reagent Volume per Week	---	20.91	85.07	gallons/week

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OPTION 5c -- Enhance Evaporator Functionality: Photoreactor Option

Synopsis: Pass due to:

- availability of commercial equipment
- potential to transform mercury with minimal alterations to liquid waste chemistry
- TRL is medium in liquid waste scenario.

Deployment location – Feed to 2H or 3H evaporator (or associated tanks or recycle streams)

Objective – Use a photoreactor (followed by reductant addition if needed) to convert methyl mercury to elemental mercury to enhance the mercury removal in existing evaporator systems

Discussion: Photoreactions represent an innovative concept for breaking down methylmercury into ionic and elemental mercury using minimal chemical modifications. A photoreactor could be integrated into a pretreatment of the evaporator feed, maximizing the elemental mercury available for removal. There is robust technical literature related to methylmercury and ionic mercury photoreactions. In many natural systems, photoreaction by sunlight is the primary pathway for methylmercury loss/destruction (Black et al., 2012; Lehnherr and StLouis, 2009; Celo, et al., 2006; Hammerschmidt and Fitzgerald, 2006 & 2010; Chen and Lin, 2003; Krabbenhoft, et al., 2002; Gårdfeldt et al., 2001; Costa and Liss, 2000; Sellers et al., 1996 and 1997; Suda and Hirayama, 1993; Ahmed and Stoeppler, 1986; Inoko, 1981). In these systems the balance between the rates of mercury methylation and methylmercury photodegradation determine the ambient levels of methylmercury in the water. In general, the literature indicates that methylmercury breakdown rate is significantly faster for UV wavelengths than for visible light wavelengths (UVC > UVB > UVA > visible light). A number of the studies provide approximate rates of degradation as a function of the light energy exposure, wavelength, and methyl mercury concentration. The literature also documents that sunlight photoreactions in seawater reduce ionic mercury to elemental mercury (e.g., Celo, 2006); thus, there is a potential that a photoreactor could convert both ionic and methyl mercury to elemental mercury without additional chemical oxidants or reductants.

The scientific literature provides a theoretical basis to perform scoping calculations for a photoreactor system to pretreat evaporator feedwater as a part of an integrated mercury removal strategy. Such a system is depicted in Figure *k*. In this configuration, the methylmercury (and ionic mercury) in the evaporator feed would be exposed to high intensity UV light. The high intensity photons would result in breakdown of methyl mercury to ionic mercury and transformation of ionic mercury to elemental mercury. Note that the background scientific studies were generally conducted at significantly lower mercury concentrations, pH, ionic strength, and solution complexity relative to the conditions measured in the liquid waste system. These studies also focused on natural sunlight (containing minimal amounts of UVC). Thus, confirmation studies would be required to determine if the technique would provide reasonable performance in a pre-evaporator treatment scenario. The objectives of such studies would be to determine kinetics (is the transformation fast enough to support a reasonable size reactor design?)

and the form of mercury leaving the photoreactor (ionic inorganic or elemental?) as a function of the chemical conditions in the simulant or waste being tested..

Commercially available photoreactor systems provide a reasonable basis for confirmation studies in the laboratory and potential designs. Figure *m* depicts a commercial unit in the approximate flow rate range for evaporator feed. This unit is constructed using 316 stainless steel and quartz wetted parts and is based on relatively low cost replaceable photoreactor modules (see http://buyultraviolet.com/infinity-page.aspx). All of the construction materials are chemical and radiation resistant and the electronics module can be remotely located. Small modules are available that can be used without modification for studies of reaction kinetics in simulated waste containing methyl mercury. The nominal lamp life in the commercial photoreactor is greater than 10,000 hours.

There are a number of uncertainties and issues that would need to be examined and resolved to assess the viability and practicality of the concept. Laboratory tests would need to evaluate methylmercury and ionic mercury photoreaction rates and products: a) under a range of chemical conditions relevant to liquid waste (pH, temperature, ionic strength, etc.), b) as a function of light wavelength (e.g., lamps producing primarily 254 nm wavelength versus lamps that also produce 185 nm wavelength associated with ozone and free radicals), and c) as a function of light intensity and exposure time (total photons delivered). Testing would also need to assess the potential for adverse reactions (e.g., oxidation or reduction of other liquid waste constituents) and operating limitations (such as deposits forming on the quartz tubes). A relatively straightforward testing campaign could address these issues and determine the viability and potential performance/configuration of a photoreactor. If viable, the test results would elucidate if a photoreactor could be used alone, or if additional actions (such as pH adjustment or addition of a reductant) would be required (Figure *4*).

A test of UV oxidation (in combination with hydrogen peroxide) for SRS liquid waste sludges was performed in 2010 (Areva, 2010). The results provide valuable information and context. Notably, deposits formed relatively quickly (e.g., hours to days) on the quartz tubes (Figure *n*). While the scoping work was performed on sludge simulants rather than supernate liquids, the Areava results suggest that a standard commercial photoreactor system in which the waste is in continuous contact with the quartz tube may encounter operational challenges in the tank farm. Instead, a “sheet flow” photoreactor design (proposed by SRNL) could be deployed. This design eliminates contact of the waste fluids with the quartz tubes (Figure *o*). A sheet flow reactor would be relatively simple to design and implement (using industry standard photoreactor and decorative fountain components). The reactor size and wall angles are based on fluid properties (e.g., viscosity). The reactor is designed to provide sheet flow down walls; for supernate liquid waste fluids there would be no need to filter liquid wastes if not loaded with suspended solids The sheet flow reactor design would have the positive characteristics of the standard commercial reactor (e.g., long lamp life and chemical/radiation resistant materials) without the potential for deposits on the quartz tubes that protect the UVC lamps. The screening criteria are based on the sheet flow design scenario.

In terms of technology readiness, the photoreactor option has a mixed rating. The technology readiness level (TRL) for the required equipment is relatively high (approximately 7, because adaptable systems are readily available in related industries). The TRL for the unique liquid waste application is moderate (3-4, because of the unusual chemical conditions that are substantively different from the supporting scientific literature and the need to develop the sheet flow reactor configuration).

Screening Criteria

1. Mercury Removal Capability –System (with possible reductant addition) would convert methyl mercury to elemental mercury, a form that could be effectively removed by the existing evaporators.
2. Impact to System Plan Execution – Requires access to liquid waste and potential new structure to house photoreactor module – may require reductant addition system. Minimal impact on system plan except during tie-in of new photoreactor infrastructure.
3. Cost of Modifications – medium to high - Significant facility modification
4. Schedule to Deploy - 3+ years
5. Technology Readiness Level –TRL for this application is 5 (medium) – good basic information in the scientific literature to jump start design effort as well as easily adapted equipment for kinetic studies and to provide the basic components for the final photoreactor system. This approach would require texhnology testing and development efforts.
6. Ease of Disposal – When combined with existing evaporators, generates flasks of relatively clean elemental mercury similar to existing waste stream
7. Operability –straightforward, requires operators working near/in target tanks
8. Impact to Liquid Waste Flowsheet – low– minimal chemical alterations.

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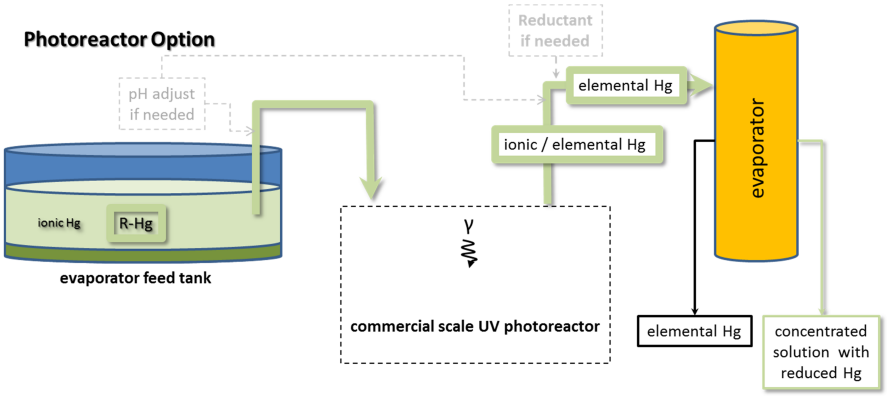


Figure *k*. Schematic diagram of a photoreactor to convert mercury into inorganic and ionic species and enhance evaporator removal

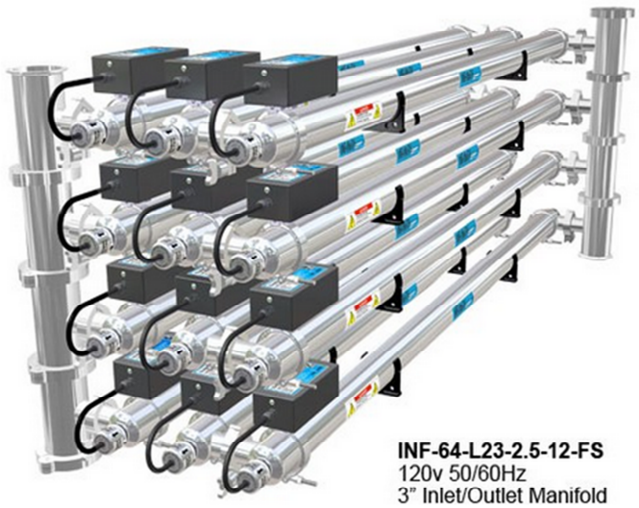
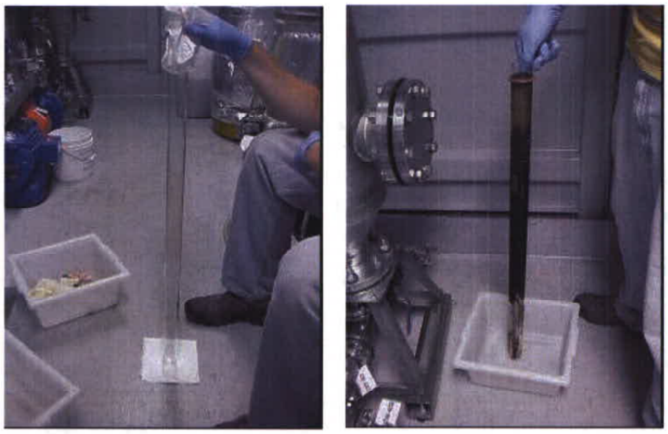


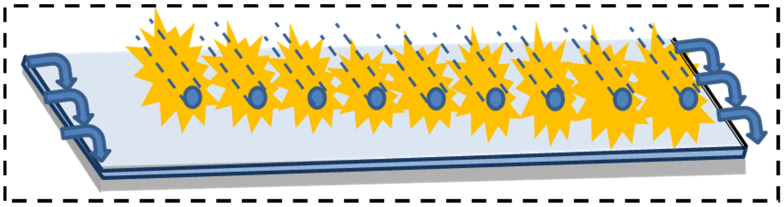
Figure *m*. Example commercial photoreactor constructed of stainless steel tubes and quartz

Results from previous testing of UV treatment for SRS liquid wastes/sludges



clean quartz tube post-test quartz tube

Figure *n*. Example photograph from a study of UV treatment for SRS liquid waste sludges showing the build-up of deposits on the quartz tube after a single campaign



Sheet flow Photoreactor

- eliminates liquid contact with quartz tubes
- Provides for explicit design control on light exposure intensity and time (based on flow rate, surface area, liquid depth/weir design, and the number/type of uvc lamps)
- Fairly compact reactor for moderate flow rates (e.g., <100 gpm)
    - For a 1 minute exposure time at 50 gpm, an example reactor geometry would be 13.5 ft long, 5 ft wide and a water depth of 0.1 ft.
- To maximize effectiveness, reactor top lined with UVC reflective material (e.g., ePTFE sheet with a 99% reflectance for UVC).

Figure *o* sheet flow reactor design concept

OPTION 5d -- Enhance Evaporator Functionality: Photoreactor Option (in-tank)

Synopsis: Pass due to:

- availability of commercial equipment and components
- potential to transform mercury with minimal alterations to liquid waste chemistry
- TRL is 3 to 4 (low to medium) in liquid waste scenario.

Deployment location – Tanks associated with 2H or 3H evaporator

Objective – Deploy a UV light source in the subject tanks or a riser to "continuously" convert methyl mercury to elemental mercury to enhance the mercury removal in existing evaporator systems (may require reductant addition in evaporator).

Discussion: See option 5c for summary of technical literature.

Deployment in a tank would require a system that could be inserted through available access ports or risers. Two deployment scenarios were sketched, a passive system (that does not require liquid pumping) and an active system (deployed in a riser with liquid pumping). In both configurations, the methylmercury (and ionic mercury) in the evaporator feed tank would be exposed to high intensity UVC light. The high intensity photons would result in breakdown of methyl mercury to ionic mercury and transformation of ionic mercury to elemental mercury. Confirmation studies would be required to determine if the technique would provide reasonable performance in the sketched scenario.

In a passive implementation, the access would limit the length of standard UVC lamp tubes that could be used. Because of this limitation and the potential for breaking tubes during deployment, a scenario based on UVC diodes was developed for screening. A schematic for deployment in tanks is depicted in Figure *q*. Factors that would influence effectiveness include: light intensity that can be generated with diodes, liquid area illuminated in the presence of cooling coils, etc. Individual UVC diodes (and similar UVC laser systems) have limited power (e.g., milliwatt), necessitating many laser or diode sources to provide relevant amounts of light and desired reactions. The sketched system (Figure *q* shows the diodes mounted on a hemisphere to maximize the light distribution into the tank from a deployment through the limited tank access point. Note that the documented longevity of the UVC diodes is significantly less than standard UVC lamps (3000 hours versus 10,000 hours, respectively) and the robustness of the diodes in a radiation environment is not known. Further, the cost of diodes is substantially higher (approximately $5 per milliwatt for diodes versus $0.1 per milliwatt for lamps). Therefore, this particular scenario has a number of added uncertainties and risks compared to the more conventional photoreactor.

In an active implementation, a spiral flow reactor could be constructed to fit in a riser. In this implementation, water would be pumped to the top of the riser and flow back into the tank through a shallow tray that spirals back to the bottom of the treatment system (providing time for the reaction). A

central uvc light system (using either lamps or diodes) would illuminate water as it traversed the reactor from top to bottom. (Figure *r*).

In either deployment scenario, this option would require studies similar to those outlined for Option 5c, with additional work to address the added uncertainties introduced by the unusual deployment requirements and use of UV diodes and/or the innovative design hydraulics.

Screening Criteria

1. Mercury Removal Capability –System (with possible reductant addition) would convert methyl mercury to elemental mercury, a form that could be effectively removed by the existing evaporators.
2. Impact to System Plan Execution –Requires waste tank or riser access – may require reductant addition system. Minimal impact on system plan.
3. Cost of Modifications – Medium to high – new system that would require engineering and development
4. Schedule to Deploy –3+ years
5. Technology Readiness Level – TRL is 3 to 4 (low to medium). Good basic information in the scientific literature to jump start design effort but substantial work needed to adapt technology to deployment in waste tank. This system would require significant testing and development efforts.
6. Ease of Disposal –When combined with existing evaporators, generates flasks of relatively clean elemental mercury similar to existing waste stream
7. Operability –Straightforward, requires operators working near/in target tanks, may require relatively frequent access to tank to change out diodes
8. Impact to Liquid Waste Flowsheet – Low– minimal chemical alterations.

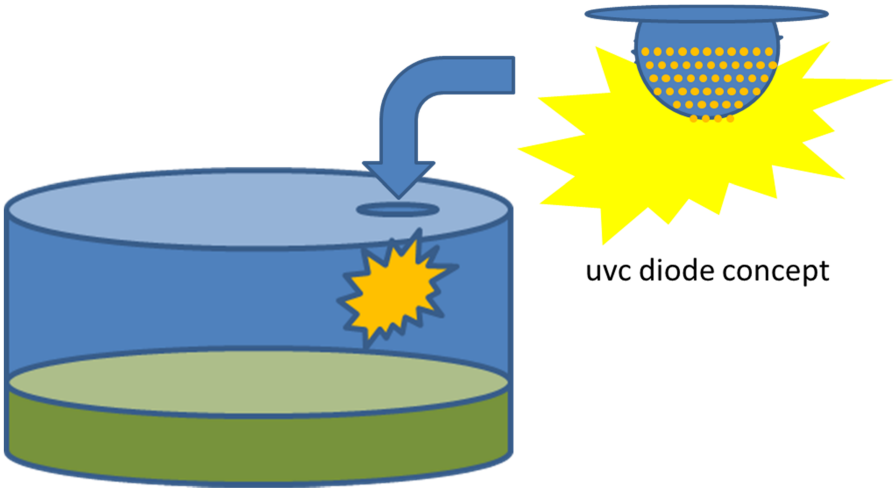
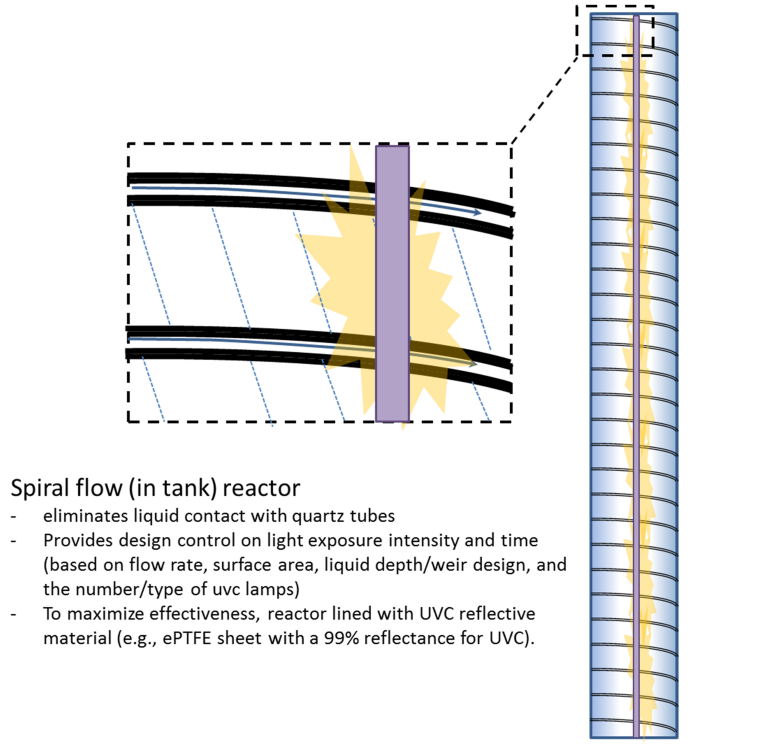


Figure *q*. Schematic diagram of diode-based hemisphere reactor. “Passive” in-tank photoreactor system to convert methyl-mercury into inorganic ionic species and elemental mercury to enhance evaporator removal



Figre *r*. Schematic diagram of spiral reactor for riser installation. "Active" in-tank photoreactor system to convert methyl-mercury into inorganic ionic species and elemental mercury to enhance evaporator removal

Systems Engineering Evaluation-Alternate Method for Removing Mercury from the Liquid Waste System

Option 7: Make Saltstone the Disposal Form – Modify the Speciation and/or Waste Form as Necessary to Ensure Adequate Retention of Mercury

Approximately 100 Mgal of dissolved salt waste will be processed and made into grout, for on-site disposition at the Saltstone Disposal Facility (SDF). Depending on the mercury concentration in the waste, the portion of mercury that goes to SDF could be moderate or high. For example, based on the average dissolved mercury concentration observed in SRS salt feed over the 2008 to 2014 timeframe, the expected mercury concentration would be on the order of 40-50 mg/L. At 50 mg/L, the total mass of mercury going to SDF would be ~19,000 kg. In contrast, if the content is dominated by a dissolved organic form such as monomethyl mercury, the mercury concentration could be on the order of 100-200 mg/L or more. At 200 mg/L, the total mass of mercury going to SDF would be ~76,000 kg. Clearly, 76,000 kg is high in the context of removing mercury from the liquid waste system.

As the concentration of dissolved organic mercury increases, additional measures may be necessary to assure compliance with RCRA land disposal limits, and to control potential leaching of mercury, to assure compliance with the Toxicity Characteristic Leaching Procedure (TCLP) limit. Measures to assure TCLP compliance could include: a) conversion of high leachability forms of mercury (such as monomethyl mercury) to low leachability forms (such as mercuric and/or elemental); b) addition of an appropriate mercury binding agent during the normal Saltstone grouting process; and/or c) re-formulation of the Saltstone grout recipe with the specific purpose of controlling mercury leaching . Each of these options would require testing and implementation. Note that there are multiple potential binding agents currently available for testing, including those utilizing sulfur compounds on their own, as well as sulfur compounds incorporated into particulate carbon sorbent materials, ion exchange materials, and other applicable solid phase media (including alternative concentrations of current waste form components such as slag).

Assuming an effective mercury leaching control strategy could be developed and implemented, there will be high confidence of meeting the TCLP limit, regardless of the mercury concentration and/or form in the feed stream. Such confidence will be increasingly important to assure regulators that the Saltstone waste form will effectively retain mercury over a long duration into the future, given the recent potential issues associated with understanding changes of mercury concentrations and forms. In the absence of an effective control strategy, failure of the waste form to comply with regulatory requirements is a real possibility.

Over the three year period between 4th quarter 2011 and 4th quarter 2014, the mercury concentration in the Tank 50 salt feed averaged at about 50 mg/L. However, in the most recent salt feeds (2015), the mercury concentrations have been in the 100-130 mg/L range. This suggests a potential upward trend, with possible cause associated with DWPF processing of the high mercury content H-modified waste. Although it is too early to tell how high the mercury concentration in salt feed will rise, there are indications suggesting that higher concentrations are certainly possible (480-500 mg/L was reported for Tank 38 supernatant and 230-290 mg/L was reported for Tank 43 supernatant). Such higher concentrations in salt feed would clearly facilitate increased removal of mercury from the liquid waste system.

The deployment time of this option is dependent on the extent of measures chosen to ensure retention of mercury within the waste form. If no additional measures are necessary to sufficiently retain mercury within the waste form, the deployment time is essentially zero. In contrast, if additional measures are necessary to retain mercury within the waste form, the deployment time would likely be extended to a minimum of a couple of years, between R&D testing, demonstration of effectiveness, obtaining DOE & regulator concurrence, and implementation.

The TRL for taking measures to ensure adequate retention of mercury within the waste form is in the 3-5 range. The lower end of the range is indicative of the R&D testing/demonstration work that would likely be required to assure adequate retention of all future potential high organic mercury feeds; and the higher end of the range is indicative of the laboratory scale validation work currently performed to show TCLP results comply with requirements. Note that the "approximate size" associated with this option is expected to be about the same as that associated with the existing Saltstone disposition process, assuming all operational changes can be accommodated within the existing facilities. Similarly, the physical location associated with this option is expected to be the same as that of the existing Saltstone process.

Evaluation discussion points:

1) Mercury Removal/Retention Capability – As identified above, the Saltstone path has the potential for removing a significant fraction of mercury from the liquid waste system. If mercury concentrations in the feed stream remain at the levels seen thus far or at near-term projected levels, a minimum of 20,000 to 30,000 kg of mercury is expected to be sent to Saltstone – more so if mercury concentrations in salt feed continue to rise in the future. Based on current knowledge, this option provides a practical means for removing 25-75% of the available mercury, assuming an effective mercury retention strategy is developed and implemented to assure that the waste form complies with mercury TCLP limits and other environmental requirements, and that DOE and regulatory representatives concur with the approach.

2) **Impact to System Plan Execution** – This depends somewhat on the level of mercury retention control that is targeted. With no changes to the current salt batch processing approach, approximately 25% of the existing mercury will be removed from the liquid waste system and there will be no impact on System Plan execution. However, in the absence of changes, the risk of being out of compliance from a TCLP perspective could increase in the future, unless a modification is made to assure increased retention in the waste form under conditions of higher mercury concentrations and/or higher organic mercury fractions. Although the goal is to develop and implement an effective mercury retention control strategy before problems occur, it is clear that an impact to the System Plan execution will occur if a point comes when Saltstone disposition is interrupted due to ineffective retention.

3) **Cost of Modifications** – This depends on whether the modification affects salt batch handling in Tank 50, waste form generation at the Saltstone Production Facility, or a part of the salt processing scheme elsewhere. Modifications impacting adjustment of the feed stream and/or generation of the waste form would have clear development and start-up costs. However, such modifications may fit within the existing window of waste form R&D demonstration testing and maintenance testing. From a program perspective, the overall additional costs would be expected to be modest.

4) **Schedule to Deploy** – The goal would be to integrate applicable changes into the existing schedule, such that current and future Saltstone disposition goals are met on schedule. However, the ability to do so depends on the mercury speciation characteristics and concentrations that arise in future salt batches. Between R&D testing, effectiveness demonstrations, DOE and regulator input, and implementation, the minimum time to deploy a mercury control strategy would likely be on the order of three years.

5) **Technology Readiness Level** – Changes associated with converting highly leachable mercury forms into minimally leachable mercury forms and/or incorporation of binding agents into the waste form will require effective R&D testing and demonstration.

6) **Ease of Disposal** – The disposal paths associated with this option are consistent with those of the existing Saltstone flowsheet. Changes to the processing strategy should have minimal impact on ease of disposal, assuming an effective mercury control strategy is developed and implemented. However, there are uncertainties associated with RCRA land disposal limits, TCLP limits, facility feed limits, and other potential limits that could require reconciliation.

7) **Operability** – Saltstone production operability could be slightly more complex, if addition of a mercury speciation control agent and/or a binding agent was incorporated into the process.

8) **Impact to Liquid Waste Flowsheet** – Minimal or none.

OPTION 8 Mechanical removal from tanks with high separate phase mercury Levels

Synopsis: Pass due to simplicity and low cost – potential opportunity for near term mercury removal and deployment in combination with other concepts.

Deployment location -- Overhead Collection Tanks at 2H and 3H evaporators

Objective -- Collect separate phase elemental mercury that has accumulated in these (and other) tanks

Discussion: This option would deploy a dense liquid collection pump placed in bottom of tank to collect "DNAPL" (dense nonaquaous phase) elemental mercury. There are a number of commercially available pumps that are constructed of materials that are compatible with SRS liquid waste and mercury -- consider modified versions of available environmental remediation equipment (pumps that use plant air and pneumatic lifting or mechanical pistons) – Figure *b*. The technique provides for removal of mercury that has been building up in tank locations for many years. Additional characterization to confirm the presence/quantity of target mercury would be needed (using existing sensors into the tank and/or ultrasonic measurements from outside single shell tanks). This approach could be modified to include an in tank sludge mercury separation step (with a second lift pump) if necessary. This approach is probably not feasible for collecting separate phase mercury accumulated beneath thick sludge layers at this time. This method would not remove organic merucy, ionic inorganic mercury or mercury oxide precipitates. An appropriate initial target to consider would be the overhead collection tanks at the 2H and 3H evaporators if characterization confirms the presence of significant separate phase mercury.

The technology readiness level (TRL) for this liquid waste application is medium high (7-8 because of the availability of appropriate commercial equipment). This strategy may provide near term ability to meet mercury removal targets while more complex options are being implemented

Screening Criteria

1. Mercury Removal Capability –medium - system would collect accumulated separate phase mercury from accessible tank locations (possible generation of 100s of gallons) but would not remove dissolved mercury or precipitated mercury.
2. Impact to System Plan Execution – 0low
3. Cost of Modifications – low
4. Schedule to Deploy –< 2 years
5. Technology Readiness Level –TRL is 7 to 8 (high). May require some testing/development/deployment of characterization tools to confirm and refine separate phase mercury accumulation zones to target.
6. Ease of Disposal – Generates flasks of elemental mercury similar to existing waste stream (some may be considered "dirty")
7. Operability –Straightforward, requires operators working near/in target tanks
8. Impact to Liquid Waste Flowsheet –low

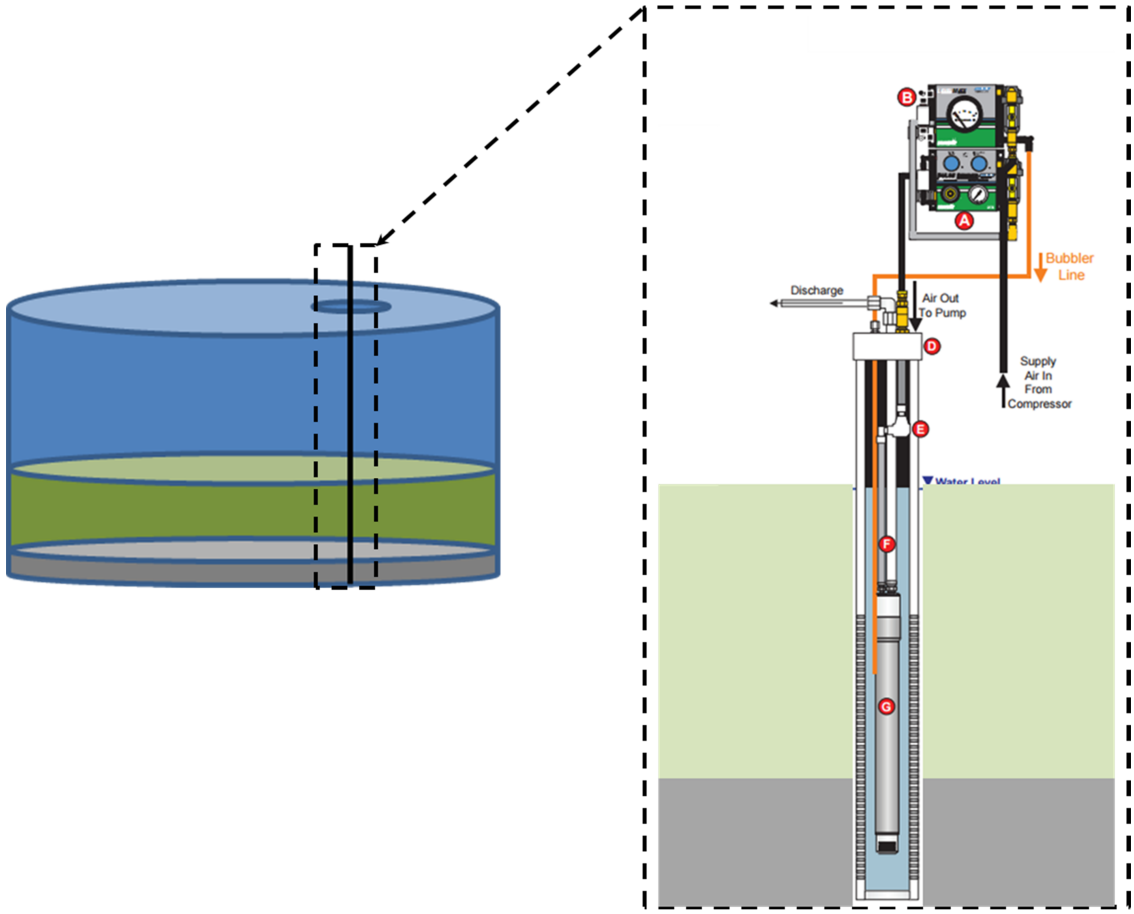


Figure *b*. Schematic diagram of the Mechanical Removal Option

OPTION 10 – Destroy methyl mercury in Tank 50 or saltstone feed material: Photoreactor Option

Synopsis: Pass due to:

- availability of commercial equipment
- potential to transform methyl mercury into less leachable ionic inorganic and elemental mercury with minimal alterations to liquid waste chemistry

But:

- TRL is low to medium for the salt waste and high flow scenario.

Deployment location – Tank 50 and/or salt waste feed stream

Objective – Use a photoreactor to destroy methyl mercury (converting it to ionic inorganic or elemental mercury) prior to making the wasteform – this has the potential to substantially reduce leaching of mercury from the wasteform.

Discussion: See option 5c for summary of technical literature and discussion of the sheet flow reactor option. This location would use a similar design (but would need to be sized for greater flow.

The higher flow rate might require additional development. However the target liquid waste (in and around Tank 50) is cleaner and clearer than most other areas of the tank farm / DWPF, maximizing the potential effectiveness of a photoreactor. Thus, the overall TRL for this option is similar to the option 5c evaporator enhancement scenario (TRL approximately 5). A number of deployment scenarios are possible including: a) a continuous cycling system through a standard above ground photoreactor, b) a spiral reactor deployed in a riser, and c) an in-tank hemisphere diode system (Figure *z*).

Screening Criteria

1. Mercury Removal Capability - system does not remove mercury (only converts it to a more sable species for saltstone wasteform) but process would reduce the leachability of mercury from saltstone and provide increased confidence that mercury can enter the saltstone path with reduced risk to the environment.
2. Impact to System Plan Execution – low – requires tank 50 (tank or riser) or salt feed access and space for photoreactor module
3. Cost of Modifications – medium to high – facility modification
4. Schedule to Deploy – 3+ years
5. Technology Readiness Level – TRL for this application is medium (5) – good basic information in the scientific literature to jump start design effort as well as easily adapted equipment for kinetic studies. This system would require moderate testing and development efforts.
6. Ease of Disposal – Generates wastes that compatible with saltstone and mercury is disposed directly in a permitted wasteform
7. Operability – straightforward, requires operators working near/in target tanks
8. Impact to Liquid Waste Flowsheet – minimal to no impact on flowsheet

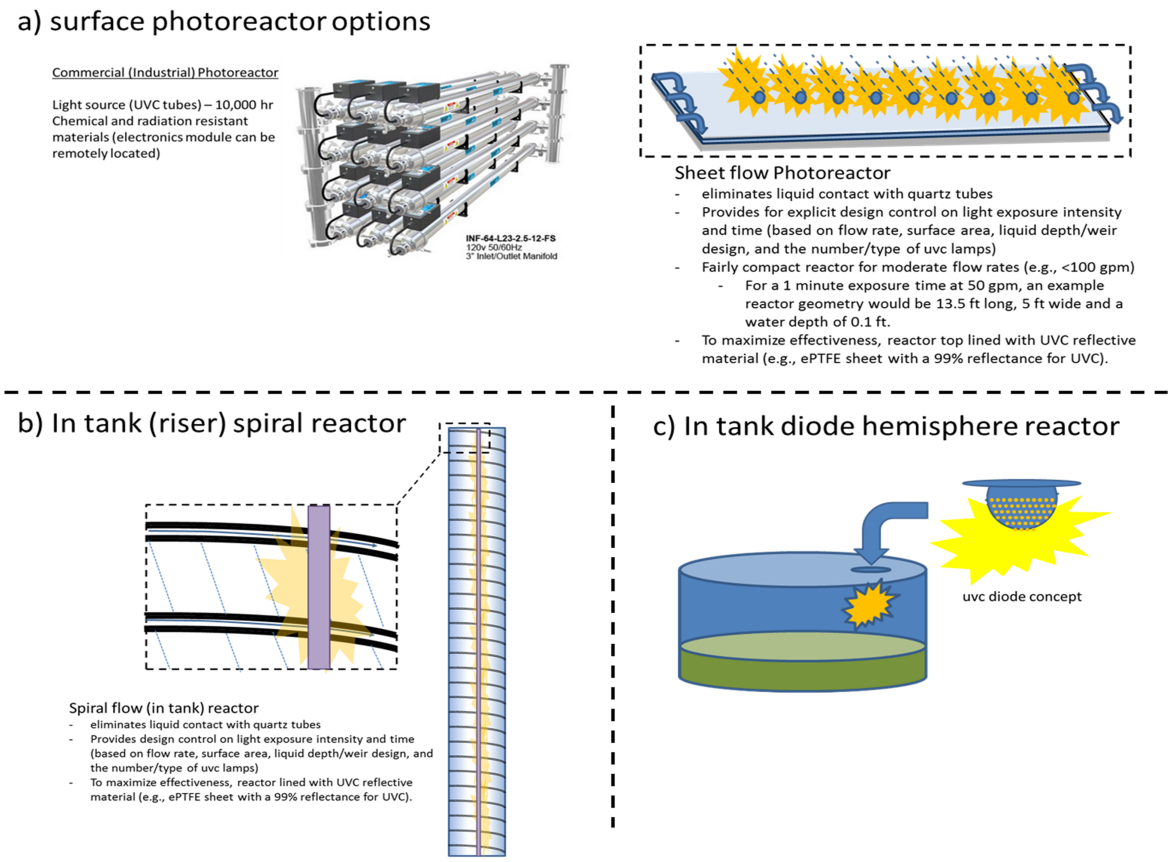


Figure *z* Schematic diagram os some of the options for implementing a photoreactor to convert methyl mercury in salt waste feed into less leachable species (ionic inorganic and elemental)

Project and Life Cycle Cost Data for Options

Option	R&D	Design & Construction	Total Project K$	Consumables & Maintenance [3]	Waste Disposal [1]	Operations [2]	Total Life Cycle Cost K$/Yr
2a	500	5,000	**5,500**	0+7	8.5	200	**215.5**
2c	500	2,500	**3,000**	0+7	8.5	200	**215.5**
3a	500	10,000	**10,500**	100+7	8.5	300	**415.5**
3c	500	5,000	**5,500**	100+7	8.5	300	**415.5**
4a	500	10,000	**10,500**	100+7	8.5	300	**415.5**
4c	500	5,000	**5,500**	100+7	8.5	300	**415.5**
5a	500	1,000	**1,500**	26+7	8.5	75	**116.5**
5b	750	2,000	**2,750**	150+14	8.5	150	**322.5**
5c	500	5,000	**5,500**	20+0	1	150	**171**
5d	500	2,000	**2,500**	20+0	1	150	**171**
7	2,000	500	**2,500**	200+0	0	50 [4]	**250**
8	500	750	**1,250**	0+50	10	150	**210**
10	500	2,000	**2,500**	0+20	1	150	**171**

[1] Used equipment disposal only, does not include the cost of mercury disposal
[2] Assumes one operator =$100,000 per year
[3] Consumable Materials + Equipment/Maintenance – Annual Cost
[4] This is in addition to the standard cost of operating SPF

Appendix D – Failed Options

OPTION 1 Electrode Based Separation – Stand Alone

Synopsis: Fail due to:

- low TRL in liquid waste scenario,
- high maintenance needs,
- production of hydrogen,
- complex operations
- uncertain wasteform.

Discussion: In order to stand-alone, electrochemical treatment needs to chemically transform and capture methyl mercury (or ionic mercury), and provide a viable mechanism to remove the mercury from the liquid waste system for disposal. Thus, stand-alone electrochemical treatment is distinct from an application where the technology precedes another process that can effectively remove a mercury species – such as an evaporator that removes elemental mercury. As described in the section discussing evaporator feed pretreatment options, an electrochemical cell delivers energy into the target solution. The major solution reactions that are induced by the electrical energy occur at or near the surfaces of the two electrodes (i.e., the cathode and the anode). The scientific literature suggests that the mercury electrochemistry is complicated, highly variable and dependent on pH and other ions in the solution (as well as electrode materials). The electrochemical configuration that is most applicable to stand-alone mercury capture would use an electrode that would capture or amalgamate mercury (e.g., gold, silver or carbon) and provide for periodic stripping/volatilization. This is somewhat equivalent to the laboratory use of gold and silver electrodes to monitor mercury species in solution by voltammetry under controlled conditions by alternating the polarity of the current to deposit and then strip off mercury while measuring the amperage plot (e.g., Schadewald, et al., 1984; Shay and Bruckenstein, 1989). For mercury treatment application, a system could capture mercury on a gold electrode and then release the mercury as ionic mercury into a low volume liquid wasteform by switching the polarity or (preferably) by draining/heating the electrode to release the elemental mercury for capture. Either application scenario is currently speculative and would require a customized electrode configuration and significant research studies.

The electrodes used in an electrochemical cell typically require a significant surface area in contact with the solution. The electrochemical reactions at the electrodes result in localized changes in pH, breakdown of water (forming hydrogen and oxygen gas) and strong gradients in redox conditions. Moreover, if operated at a consistent polarity, electrochemical cells are subject to the formation of mineral deposits requiring regular chemical.

A hypothetical electrochemical cell system for stand-alone mercury removal is depicted in Figure *a*. The process depicted shows the use of sequential electrodes (with a carbon electrode to oxidize R-Hg and a gold or silver electrode used to reduce and capture the mercury). After a period of mercury deposition and amalgamation, the gold would need to be regenerated by isolating the cell and reversing the polarity or by draining the cell and heating the electrode. If the heating method is used, both

electrodes might require chemical cleaning to remove mineral deposits. While a stand-alone electrochemical cell has the potential to capture mercury, the complexity and breadth of potential side-reactions are challenging. The potential operational issues and challenges are significant. The concept is speculative necessitating major campaigns of laboratory studies and with a high potential that a full scale process would not be viable or practical.

The technology readiness level (TRL) for this liquid waste application is low (1-2, because of the unique equipment, the potentially high costs and safety challenges, the unusual process conditions, and minimal supporting scientific literature).

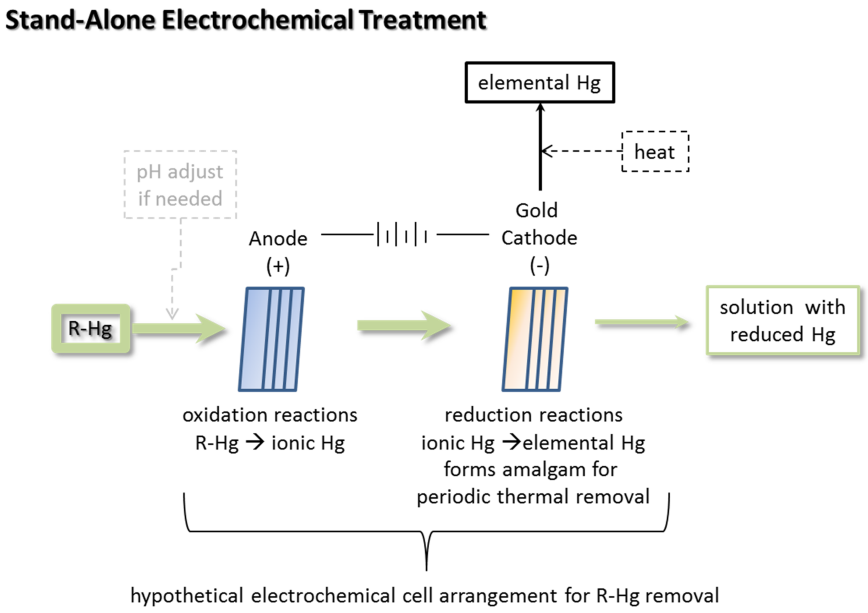


Figure *a*. Schematic diagram of a stand-alone electrochemical treatment option

References

Schadewald, L.A., Lindstrom, T.R., Hussein, W., Evenson, E.E., Johnson, D.C., 1984. Deposition and Stripping of Mercury at Gold Electrodes in Acidic Media I: Voltammetric Studies, *J. Electrochem. Soc.*, 131,1583-1587.

Shay, M. and Bruckenstein, S., 1989. Determination of Hg(I) Adsorption Accompanying the Coulostatic Underpotential Deposition of Mercury on Gold Using the Quartz Crystal Microbalance, *Langmuir*, 5, 280-282

Option 2d, 3d, and 4d, Install Filtration – DSS and 512-S Cleaning & Maintenance streams, Install Sorption – DSS and 512-S Cleaning & Maintenance streams and Install IX – DSS and 512-S Cleaning & Maintenance streams respectively, failed as: DSS, 512-S Cleaning, and Maintenance streams ultimately enter Tank 50 and feed to Salstone. With the increased flow to Saltstone after SWPF startup, the implementation of these options before, after, or within Tank 50 would create a bottleneck that would affect the production of Saltstone. Therefore, these options are not feasible.

OPTION 5e -- Enhance Evaporator Functionality: Electrochemical Option

Synopsis: Fail due to:

- potential for high maintenance needs
- hydrogen production
- impacts to flowsheet.
- low TRL for liquid waste application

Deployment location – Feed to 2H or 3H evaporator (or associated tanks or recycle streams)
Objective – Use a electrochemical cell followed by reductant addition to convert methyl mercury to ionic mercury and then elemental mercury to enhance the mercury removal in existing evaporator systems

Discussion: Similar to a photoreactor, an electrochemical cell delivers energy into the target solution. In an electrochemical cell, the energy and major solution reactions occur at or near the surfaces of the two electrodes (i.e., the cathode and the anode). There are a number of papers that study the behavior of mercury species at electrode surfaces in dilute solutions (primarily acids). The results of the various research studies suggest that the mercury electrochemistry is complicated, highly variable and dependent on pH and other ions in the solution (as well as electrode materials). Notably, elemental mercury is often used as a cathode in scientific experiments (e.g., Heyrovský, 1924) suggesting that elemental mercury is compatible with the cathode conditions. Also, gold and silver electrodes have been used to monitor mercury species in solution by voltammetry under controlled conditions by alternating the polarity of the current to deposit and then strip off mercury and then measuring the amperage plot (e.g., Schadewald, et al., 1984; Shay and Bruckenstein, 1989).

Electrochemical cells are commercially used to oxidize organic material. In aqueous solutions that contain chloride ions such as saltwater pools and sea-water aquariums, electrochemical cells generate hypochlorous acid that remains in the water for disinfection. The electrodes used in an electrochemical cell typically require a significant surface area in contact with the solution. The electrochemical reactions at the electrodes result in localized changes in pH, breakdown of water (forming hydrogen and oxygen gas), formation of free radicals, and strong gradients in redox conditions. Moreover, if operated at a consistent polarity, commercial electrochemical cells are subject to the formation of mineral deposits requiring regular cleaning using a strong acid (or alternatively, the use of a control system that provides frequent polarity reversal). Similar to voltammetry, a commercial polarity reversing system has the potential to convert mercury to an elemental form and then release the converted mercury into the water as ionic inorganic mercury when the polarity is reversed. Post-electrochemical cell addition of a reductant would be needed to complete the transformation of mercury into the elemental form for effective removal by the evaporator. There is little information on the behavior of methylmercury in an electrochemical cell under the chemical conditions of SRS liquid waste, necessitating significant laboratory study prior to final selection and implementation.

A hypothetical electrochemical cell system to pretreat evaporator feedwater as a part of an integrated mercury removal strategy is depicted in Figure *j*. The unit depicted is an example of a commercial polarity reversing system in the approximate flow rate range for evaporator feed. While an electrochemical cell has the potential to break down methylmercury, the complexity and breadth of potential side-reactions would be significantly greater than a photoreactor. The potential operational issues and challenges are also greater with an electrochemical cell, necessitating significantly more laboratory studies and entailing more risk related to viability.

As with a photoreactor, the electrochemical option has a mixed TRL rating. The technology readiness level (TRL) for the required equipment is moderately high (approximately 6-7; systems are available – but these systems would require substantive modifications). The TRL for the unique liquid waste application is low (1-2, because of the unusual conditions and minimal supporting scientific literature for relevant solution conditions). Thus the overall TRL for this application is low.

Screening Criteria

1. Mercury Removal Capability – low to medium - system to convert methyl mercury to ionic (or elemental) mercury. May require reductant addition system. Elemental mercury is effectively removed by the existing evaporators.
2. Impact to System Plan Execution – Requires waste access and potential new structure to house electrochemical module – may require reductant addition system. Minimal impact on system plan except during tie-in of new infrastructure.
3. Cost of Modifications – high – significant facility modification
4. Schedule to Deploy – 3+ years
5. Technology Readiness Level – Overall TRL for this application is 2 to 3 (low). System would require proof of concept and significant testing and development.
6. Ease of Disposal – When combined with existing evaporators, generates flasks of relatively clean elemental mercury similar to existing waste stream
7. Operability – Requires operators working near/in target tanks – may require cleaning and monitoring of electrode condition. Likely to require frequent manual electrode cleaning (even if operated in polarity reversing "self-cleaning" configuration) – increasing labor and operations costs and generating cleaning wastes.
8. Impact to Liquid Waste Flowsheet – moderate to high -- potential impacts to other elements in the area around the electrochemical cell, hydrogen generation, etc.

References

Heyrovský, J., 1924. The processes at the mercury dropping cathode. Part I. The deposition of metals, *Trans. Faraday Soc.*, 19, 692-702.

Schadewald, L.A., Lindstrom, T.R., Hussein, W., Evenson, E.E., Johnson, D.C., 1984. Deposition and Stripping of Mercury at Gold Electrodes in Acidic Media I: Voltammetric Studies, *J. Electrochem. Soc.*, 131,1583-1587.

Shay, M. and Bruckenstein, S., 1989. Determination of Hg(I) Adsorption Accompanying the Coulostatic Underpotential Deposition of Mercury on Gold Using the Quartz Crystal Microbalance, *Langmuir*, 5, 280-282

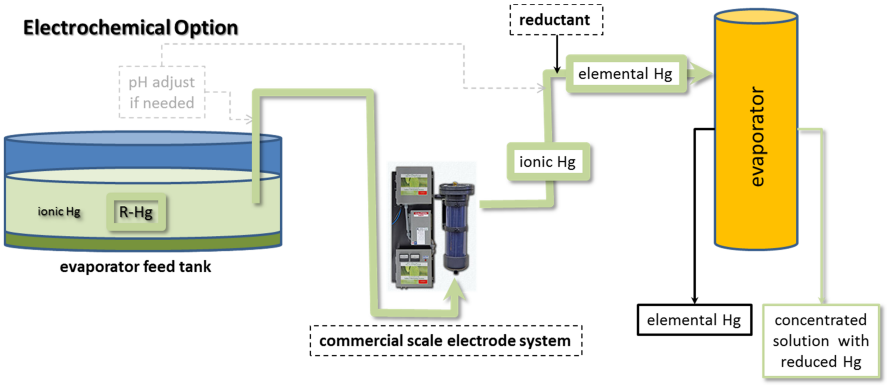


Figure *j*. Schematic diagram of a commercial electrochemical cell placed to enhance the evaporator removal

An Evaporator between DWPF and the Tank Farm would act similar to 16H Evaporator, since it is used primarily to evaporator DWPF Recycle material. The concentrated stream from the evaporator produce will be similar to the material sent to Tank 38 from the 16H Evaporator. Since this stream from the proposed evaporator would also be required to be sent to the Tank Farm, adding an Evaporator between the two facilities does not accomplish the goal of removal of the mercury from the system. In addition, this proposal has been evaluated by other SEE and has ended up being cost prohibited.

OPTION 9 -- Reduce methylation by modifying liquid waste chemistry

Synopsis: Fail due to:

- lack of basic information
- low TRL in liquid waste scenario
- potential impact on flowsheet
- low probability of success.

Discussion: This option would attempt to alter the liquid waste chemistry to minimize the formation of methyl mercury. Example modifications include addition of oxidants to remove organic precursors, changing chemical conditions or master variables (pH, orp, ionic strength), etc. Unfortunately, the basic science underpinning the formation of the methyl mercury in SRS liquid waste conditions is limited. Therefore the basis fo any chemical change would be somewhat speculative. A notable study (Bloom, 2003) on SRS liquid waste suggested that the presence of organics (particularly methylated antifoam agents) were a significant factor in the methylation of mercury in SRS tanks (under a range of chemical conditions, no significant formation of methyl mercury was observed in any experimental system that did not have the organics). This study reinforces the need to minimize the introduction of organics to the extent practicable, and suggests that the potential for minimizing mercury methylation by altering other aspects of waste chemistry is relatively low. The technology readiness level (TRL) for this liquid waste application is low (1-2).

Reference

Bloom, N., 2003. Formation of $(CH_3)_2Hg$ in Simulated Waste Tank Solutions. Subcontractor report AC3289N from SOW 5G2987Part2 to Frontier Geosciences, Westinghouse Savannah River Co, Aiken SC 29808.