Enhanced Chemical Cleaning

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U.S. Department of Energy
Office of Waste Processing Technical Exchange
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Overview

- SRS has taken a pro-active approach to meeting regulatory guidelines for tank closure by developing & implementing innovative technologies
- Based on an exhaustive search for an alternatives to bulk oxalic acid (OA), and a switch to a TRIZ type contradiction trading effort, the Enhanced Chemical Cleaning (ECC) concept was developed
- ECC uses dilute OA as the cleaning agent, ozone/UV to photolytically destroy the oxalate, evaporation for solid/liquid separation, & acid regeneration to recycle the spent cleaning solution

Overview (Continued)

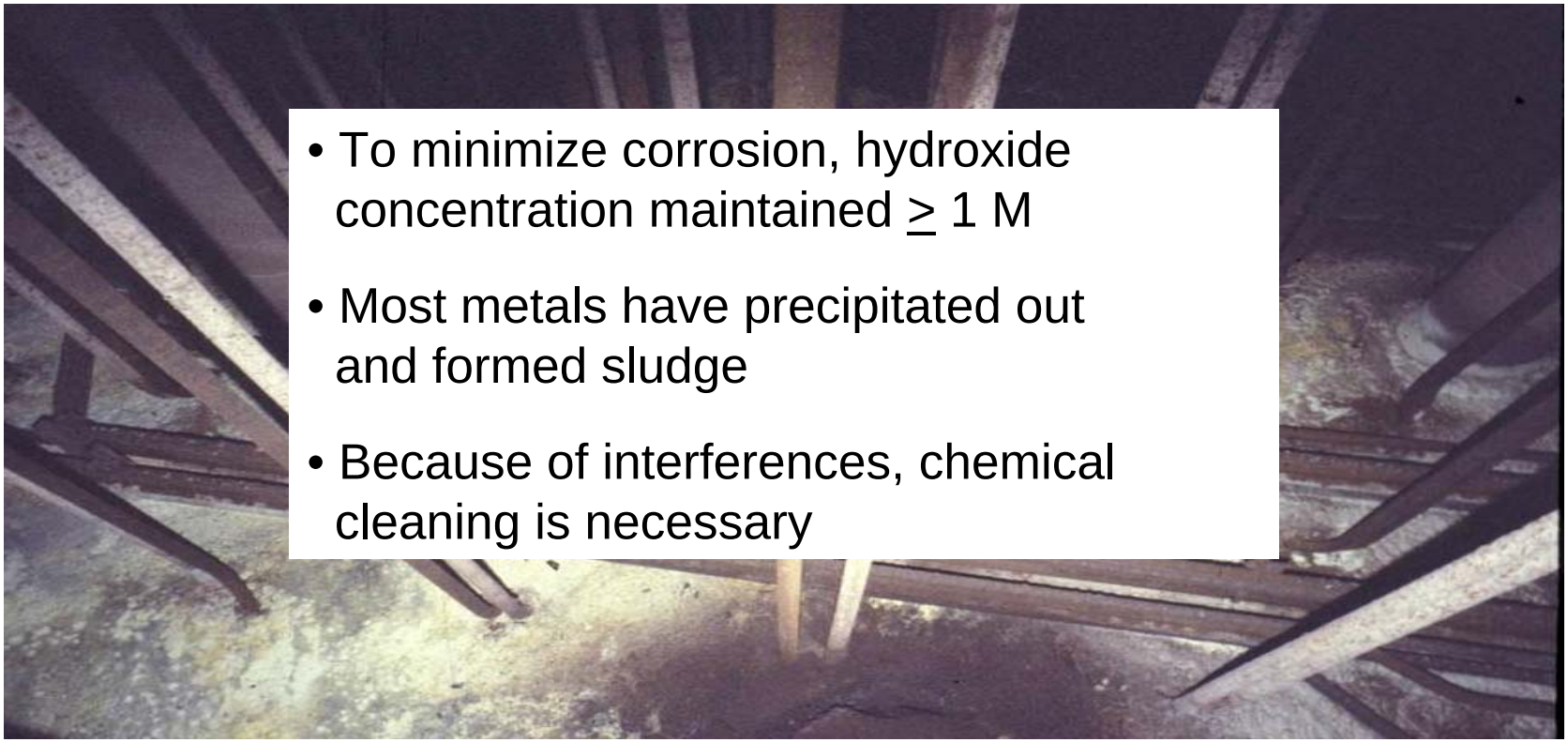
- Oxalate photolysis coupled with acid regeneration minimizes downstream impacts and amount of liquid added
- Proof of principle testing using sludge simulant and salt simulant has successfully demonstrated the viability of the concept
- Hazardous Simulant Testing & Real Waste Testing will close the technology gaps/advance Technical Readiness Level
- By the end of 2011, design will be finalized, the ECC process will be constructed and deployed in the SRS F-Tank Farm

Waste Tanks

- Located below grade/subsurface
- Shell constructed from mild-carbon steel
- Each has ~ a 1 million gallon capacity
- About half were built in the 1950's
- SRS currently has 49 non-decommissioned tanks

Inside the Tanks

Type I, II, & III tanks contain miles of carbon steel cooling coils

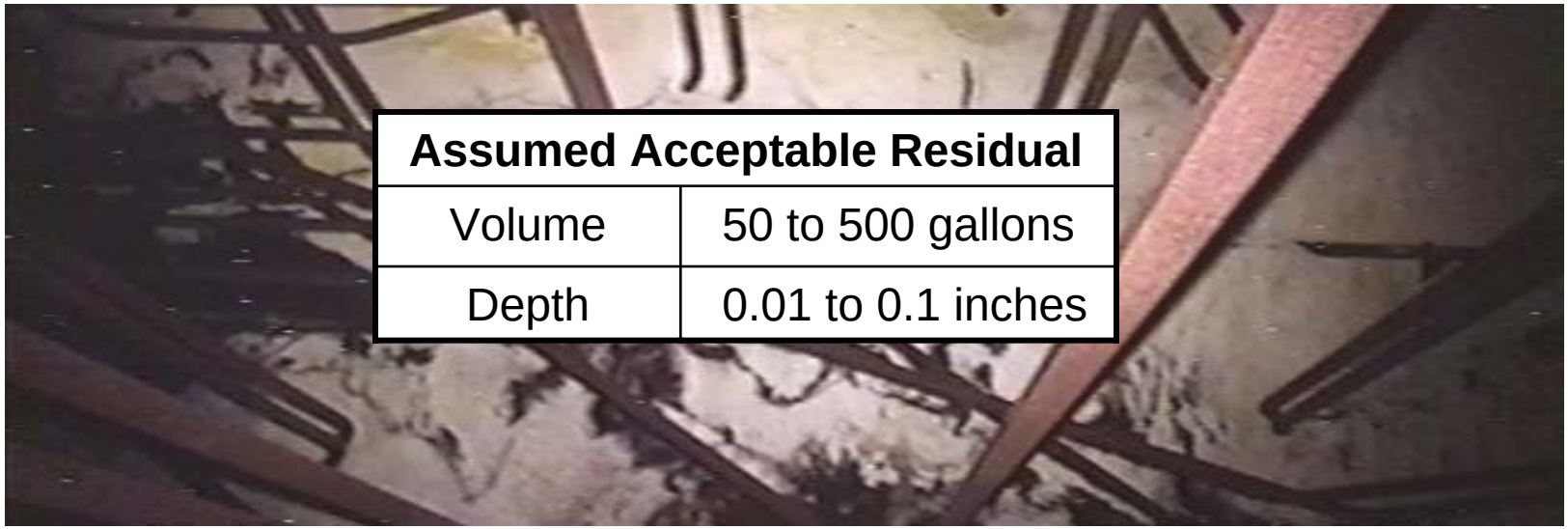


- To minimize corrosion, hydroxide concentration maintained $\geq$ 1 M
- Most metals have precipitated out and formed sludge
- Because of interferences, chemical cleaning is necessary

Cleaning Requirements

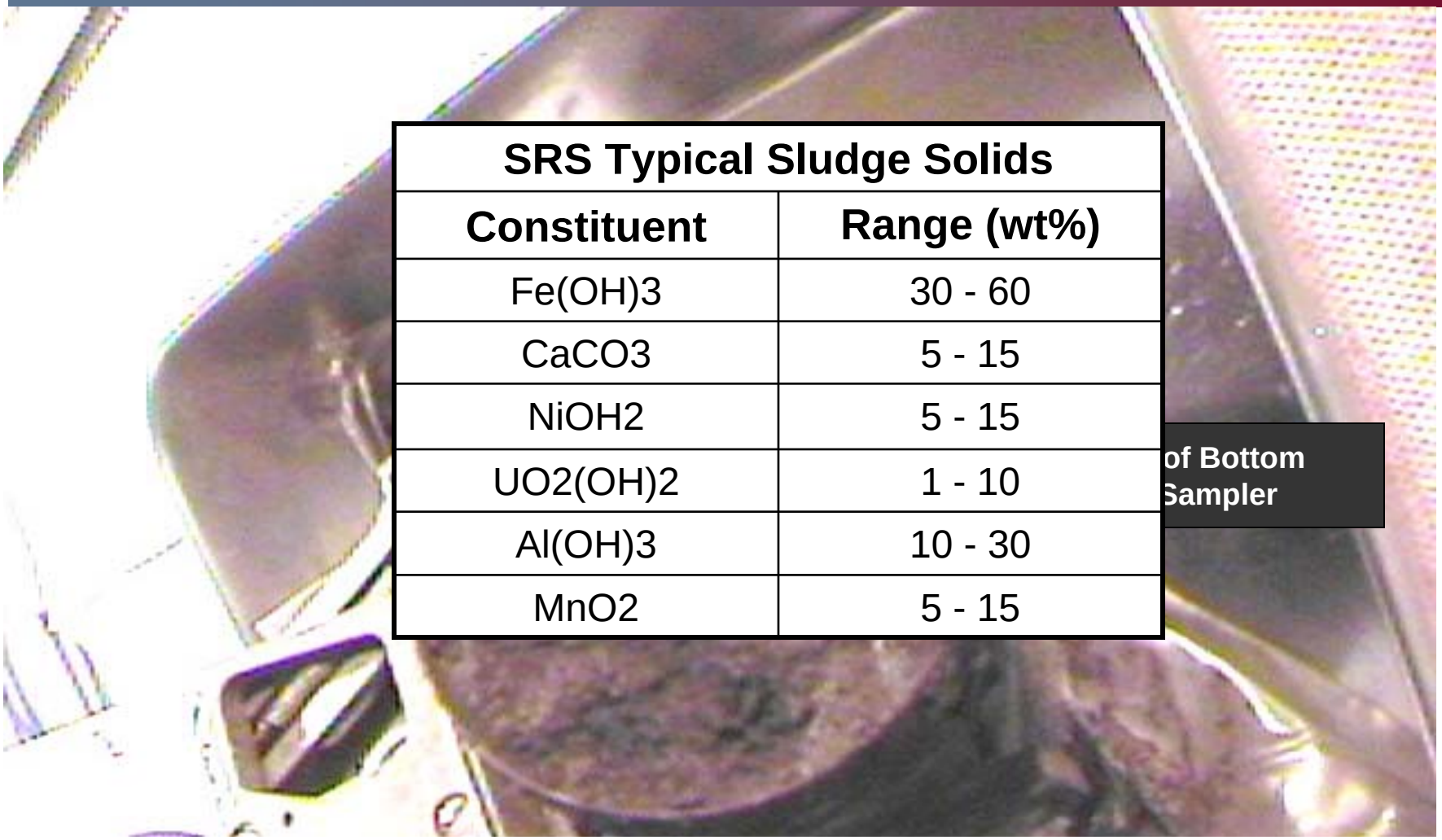
HLW tanks must be very clean in order to support closure

- High specific activity of the residual waste
- Close proximity to the water table
- Requirements currently being worked out with regulators
- Maximum extent practical (MEP) always the goal



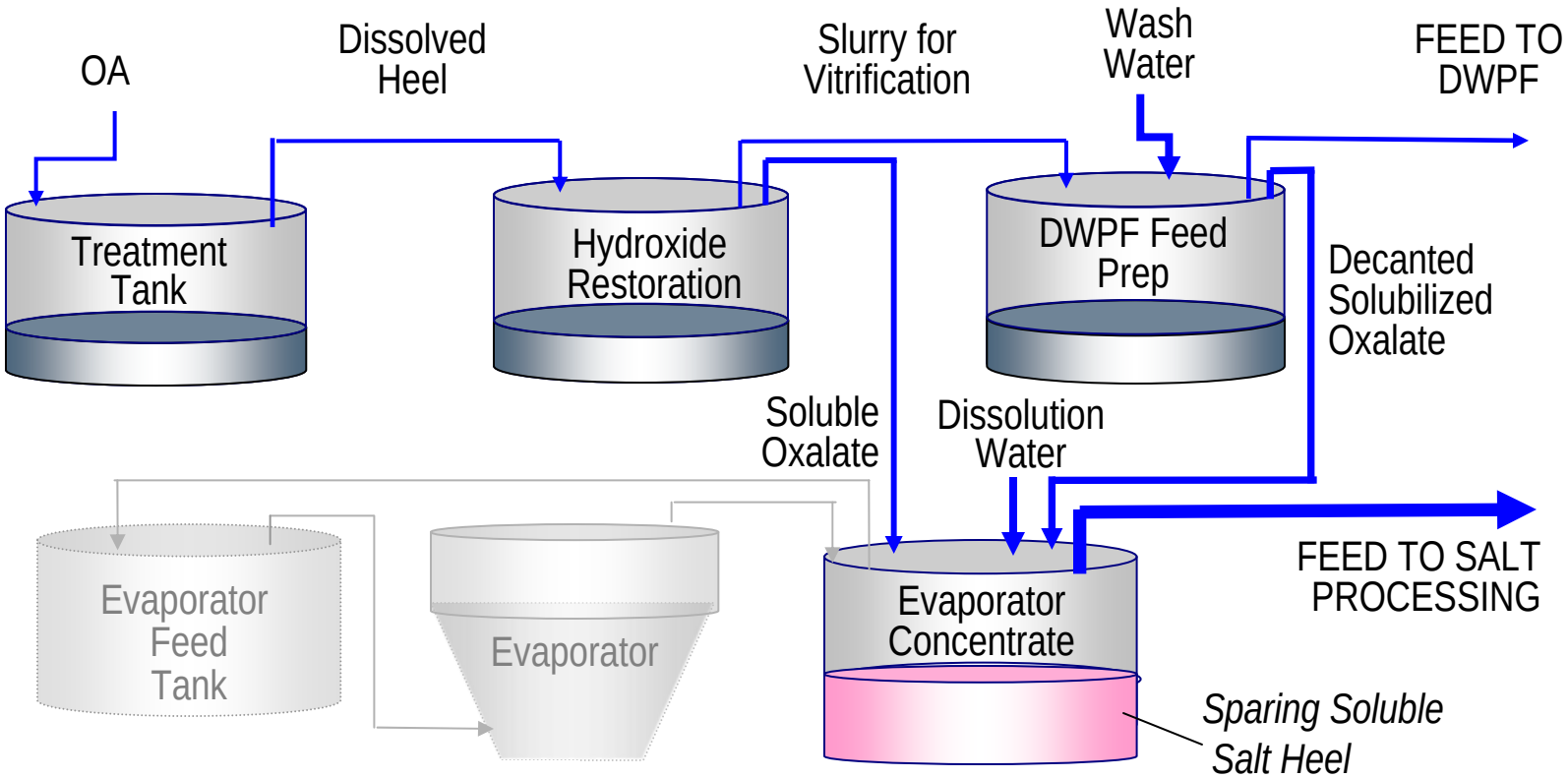
Assumed Acceptable Residual	
Volume	50 to 500 gallons
Depth	0.01 to 0.1 inches

Sludge Solids



SRS Typical Sludge Solids	
Constituent	**Range (wt%)**
Fe(OH)3	30 - 60
CaCO3	5 - 15
NiOH2	5 - 15
UO2(OH)2	1 - 10
Al(OH)3	10 - 30
MnO2	5 - 15

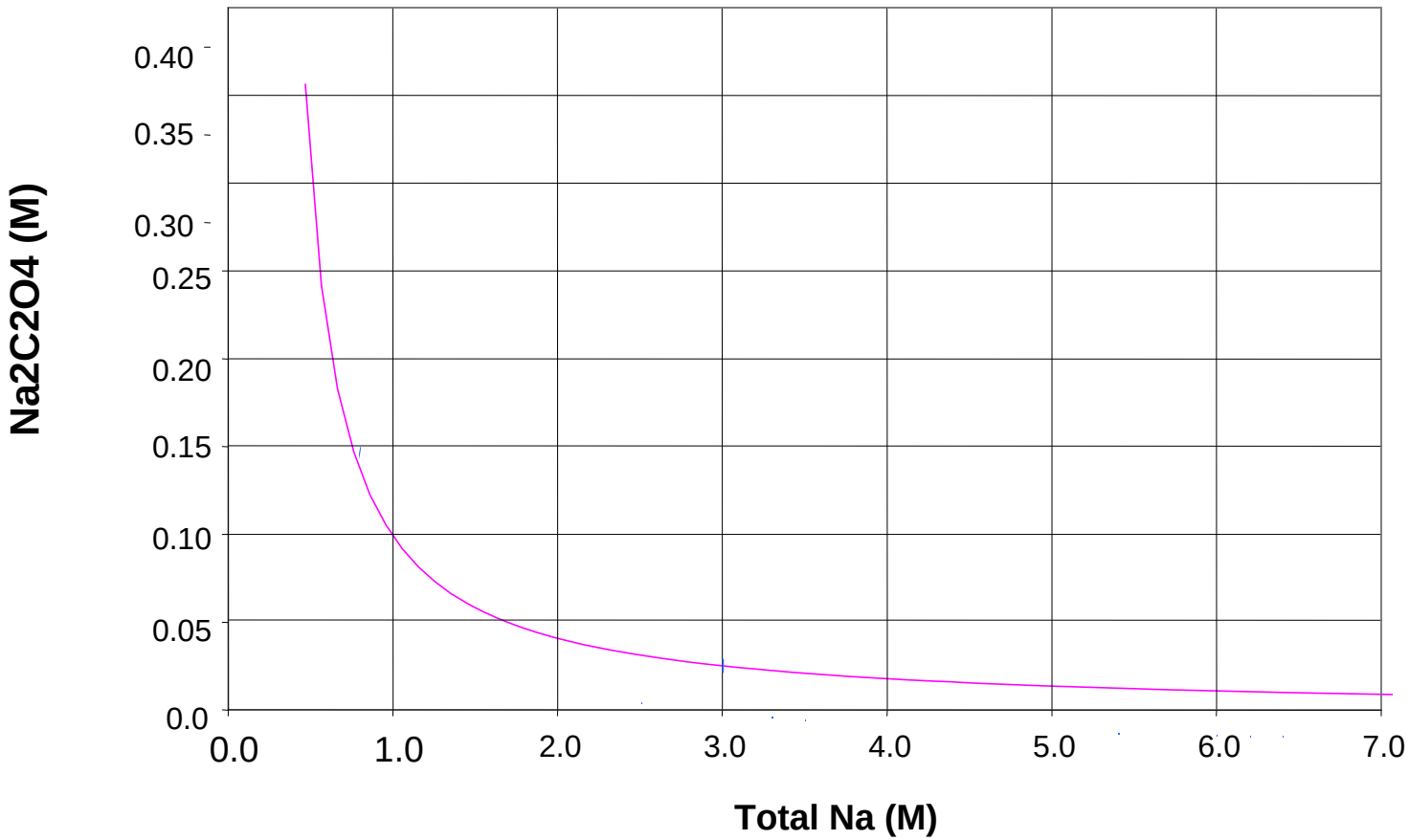
Current - Tank 5 & 6 OA Cleaning



For 5,000 kg of sludge solids

- Form about 50,000 kg of additional sodium oxalate solids
- ~20% of the solids will go to DWPF
- ~80% go to evaporator system, representing
- ~500,000 gallons of feed to salt processing

Effect of Oxalate Solubility



As part of sludge batch preparation for DWPF, washing the sludge to a sodium concentration of < 1M will solubilize a large fraction of the oxalate

Search for An Alternative Begins

- Comprehensive review of national & international cleaning technologies concluded oxalic acid to be the preferred cleaning solution
  - preferred over nitric acid
    - considered more compatible with carbon steel
  - preferred over oxalic/citric acid mixes
    - shown to be equally effective
  - demonstrated digestion & chelating effect
- Use of oxalic acid successfully demonstrated in the 1980's
  - removed 99.9% of initial activity from SRS Tank 16

Ref. WSRC-TR-2003-00401

Wish List for a New Process

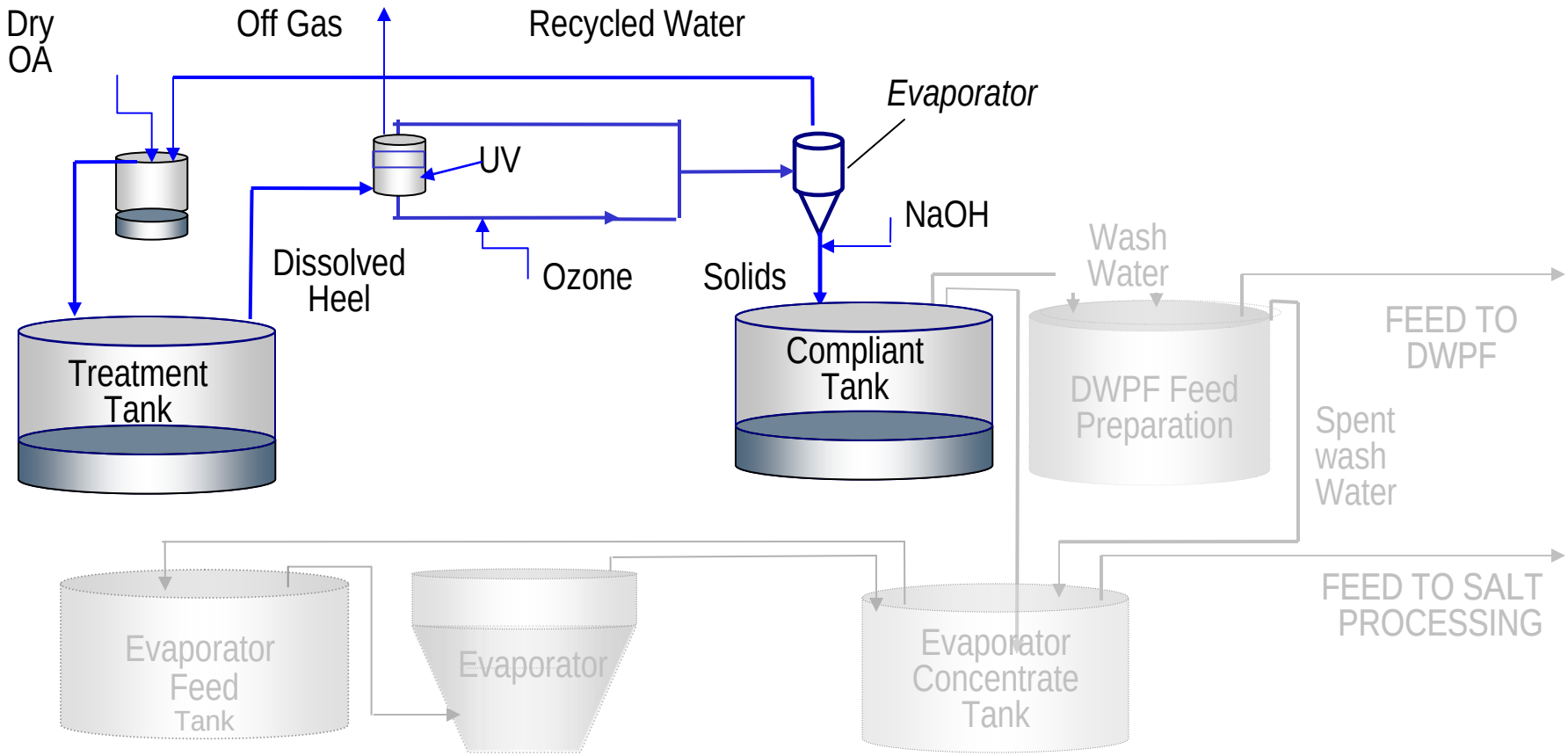
- Shown in similar applications to be successful
- Does not create new radioactive waste streams (e.g., use ion exchange)
- Minimize the creation of excessive ferrous oxalate in the treatment tank
- Eliminate the downstream impacts to the Tank Farm from spent oxalic acid
- Use small dilute acid to minimize MAR & ALARA concerns
- Use portable, modular, temporary equipment
- Leverage commercial industry processes
  - Adapt to our needs
  - Quickly became focused on Nuclear Power Dilute Decontamination Technologies (DDTs)

Dilute Decontamination Technologies

Six DDTs with potential applicability

TECH	DISSOLUTION	SECONDARY RAD WASTE	DOWNSTREAM IMPACTS	THROUGHPUT
CORD-UV	Proven	None	Minimized- via photolysis	Proven
Can-Decon	Proven	Contradiction- ion exchange resin	Contradiction- EDTA impacts	Proven
CITROX	Proven	Contradiction- ion exchange resin	May be acceptable	Proven
DfD	Proven	Contradiction- ion exchange resin	Contradiction- Fluoroboric impacts	Proven
DfDx	Proven	Contradiction– carbon collection media	Contradiction- Fluoroboric impacts	Contradiction– not well proven
LOMI	Contradiction– not in air	Contradiction- ion exchange resin	May be acceptable	Proven

ENVISIONED ECC PROCESS



For 5,000 kg of sludge solids

- Minimal additional solids added
- Minimal impact on process, including DWPF and salt processing

Primary Reactions

Dissolution

- Metal (hydro)oxide + oxalic acid = metal oxalate + water
  - $Fe_2O_3 + H_2C_2O_4 = Fe_2(C_2O_4)_3 + H_2O$

Hydroxyl Radical Formation

- Example in water
  - Ozone + water + UV = oxygen + hydroxyl radicals
  - $O_3 + H_2O + uv = O_2 + 2HO\bullet$

Photolytic Destruction

- Metal oxalate+ radical = carbon dioxide + metal (hydro)oxide
  - $Fe_2(C_2O_4)_3 + 6HO\bullet = 6CO_2 + Fe_2O_3 + 3H_2O$

Balance

- Oxalic acid + ozone and UV + carbon dioxide and water
  - $H_2C_2O_4 + O_3 + UV = CO_2 + H_2O$

In a seeming peculiar twist to the classic textbook definition, using photolysis makes acid cleaning the tanks a “Green” process

ECC Technology Gaps and Testing

Table 1. Identified Testing Needed for ECC

1	Dissolution
2	Oxalate Destruction
3	Corrosion
4	Temperature
5	Gas Generation
6	Fate on multi-valence hazardous metals
7	Evaporation and Solid/Liquid Separation
8	Actinide Solubility: Criticality & Material and Risk
9	Mixing
10	Integrated Testing
11	Scaled Testing

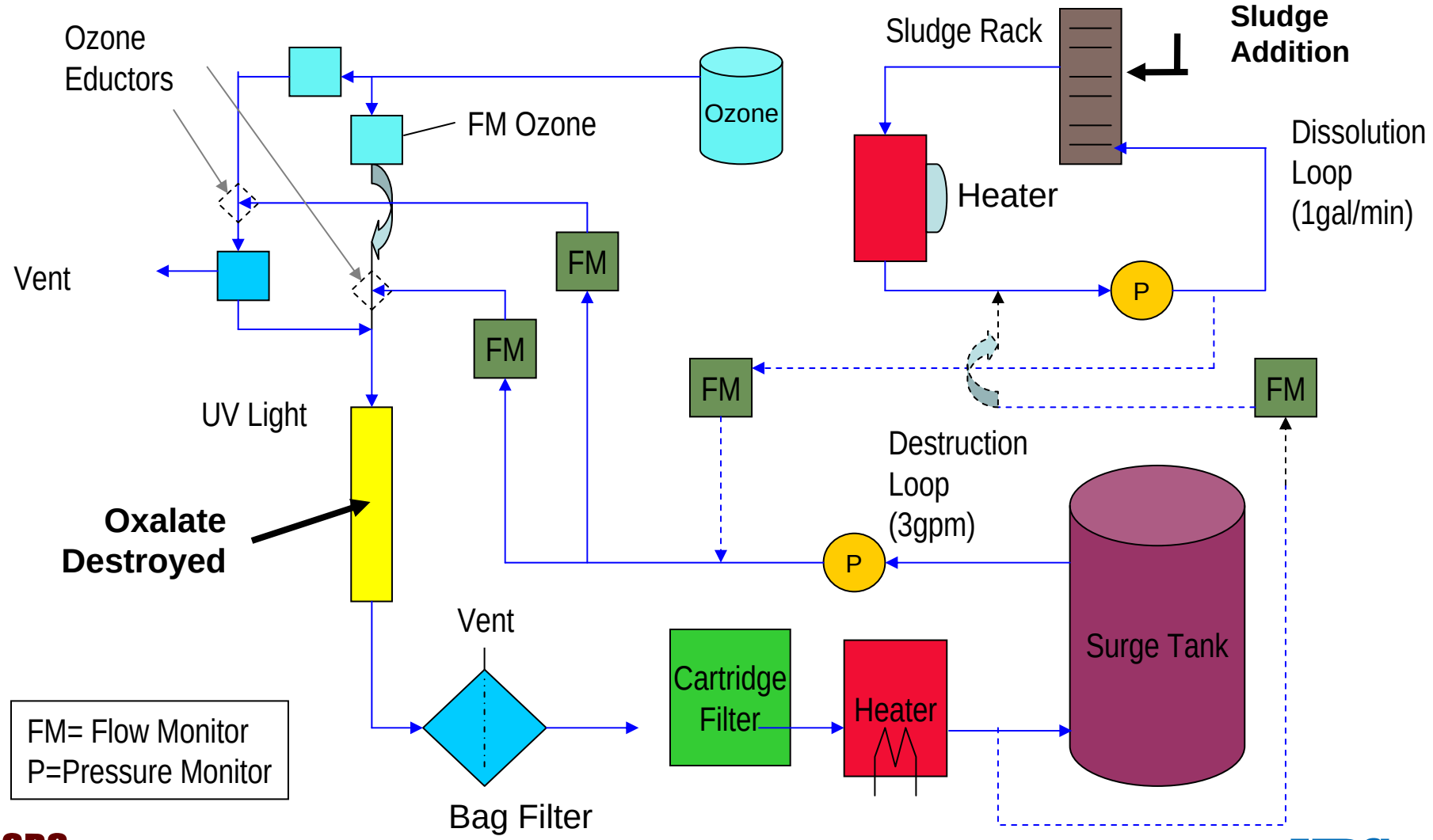
Groups of Testing

- Proof of Principle Tests
  - Sludge simulant demonstration (complete)
  - Insoluble salt simulant demonstration (complete)
- Technical Maturation Tests
  - Hazardous simulant testing
  - Real waste testing
- Equipment Demonstration Tests
  - Mixing testing
  - Full scale testing

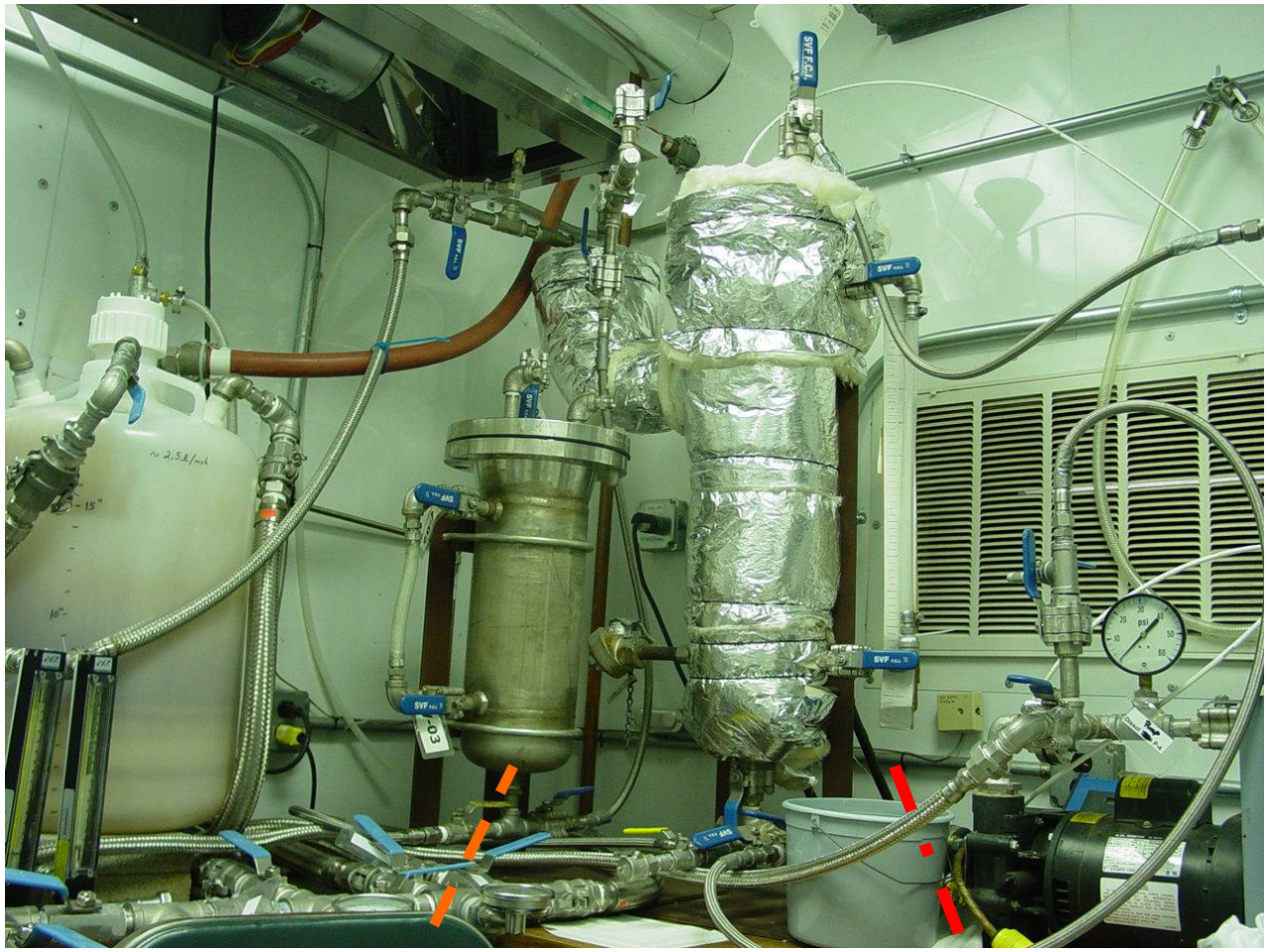
Proof of Principle Test Requirements

- 90% of the solids dissolved
- 90% destruction of oxalic acid used to dissolve tank deposits
- temperature in the tank can not exceed tank temperature limits
- particle reformation with delivery to target tank
- added net equivalent of $\leq$ 50,000 gallons additional liquid

Proof of Principle Test Rig



Dissolution Loop



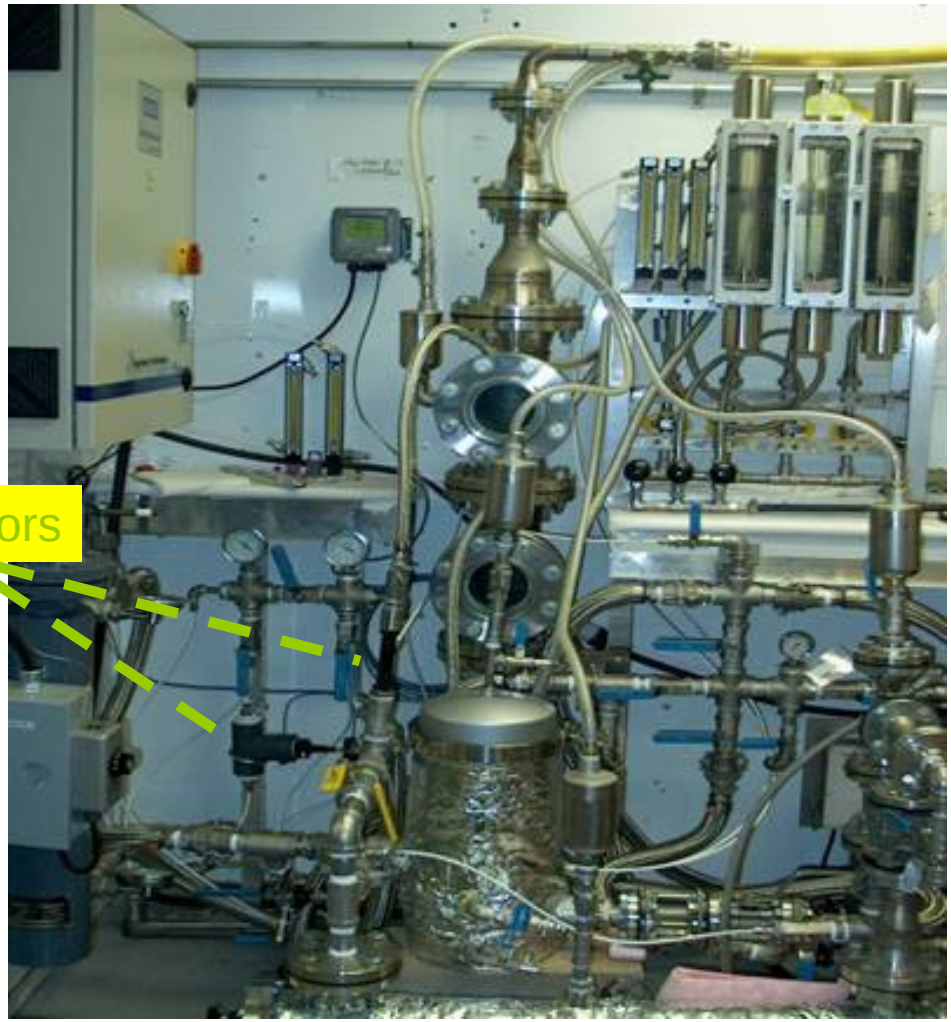
Sludge Rack

Heater

Destruction Loop

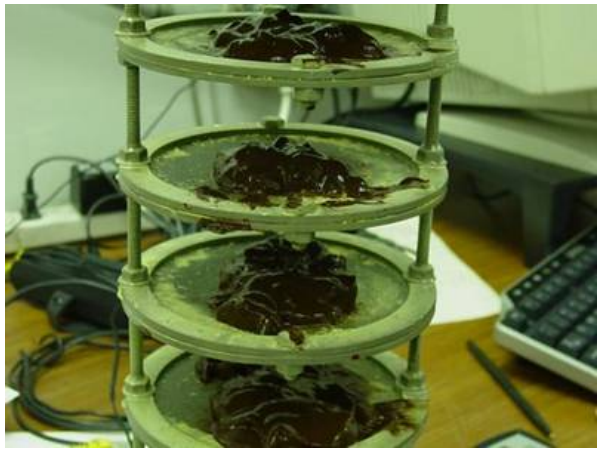
UV Light

Destruction Loop

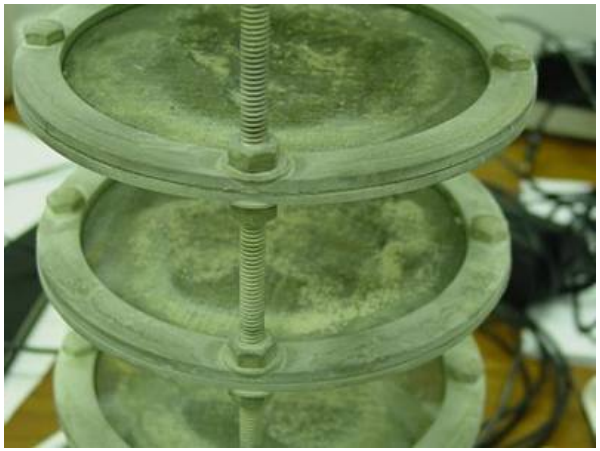


Completed Proof of Principle Sludge Simulant Test

- Proved dissolution of sludge simulant at a pH~2 (using 1 wt% oxalic acid)
- Proved oxalic acid destruction
- Developed first design concept



200 Grams of Sludge Simulant



6 Hours of Dissolution

- Confirmed >90% dissolution of the simulant
- Confirmed >90% of the oxalates were destroyed

Completed Proof of Principle Insoluble Salt Simulant Test

- Proved dissolution of salt simulant at a pH near 2 (using 1 wt% oxalic acid)
- Proved oxalic acid destruction
- Advanced the design concept

1200 Grams of Sludge Simulant

26 Hours of Dissolution

- Confirmed >90% dissolution of the simulant
- Confirmed >90% of the oxalates were destroyed

Technology Maturation

- We are currently at Technical Readiness Level (TRL) of 3
- The next step in project space is
  - Preliminary Design (30%)
  - Advance technology maturation to TRL5/6
- Technology gaps need to be addressed to advance from TRL 3 to 6
- Planned Hazardous Simulant Testing, Real Waste Testing, and Equipment Demonstration Tests to fill the gaps

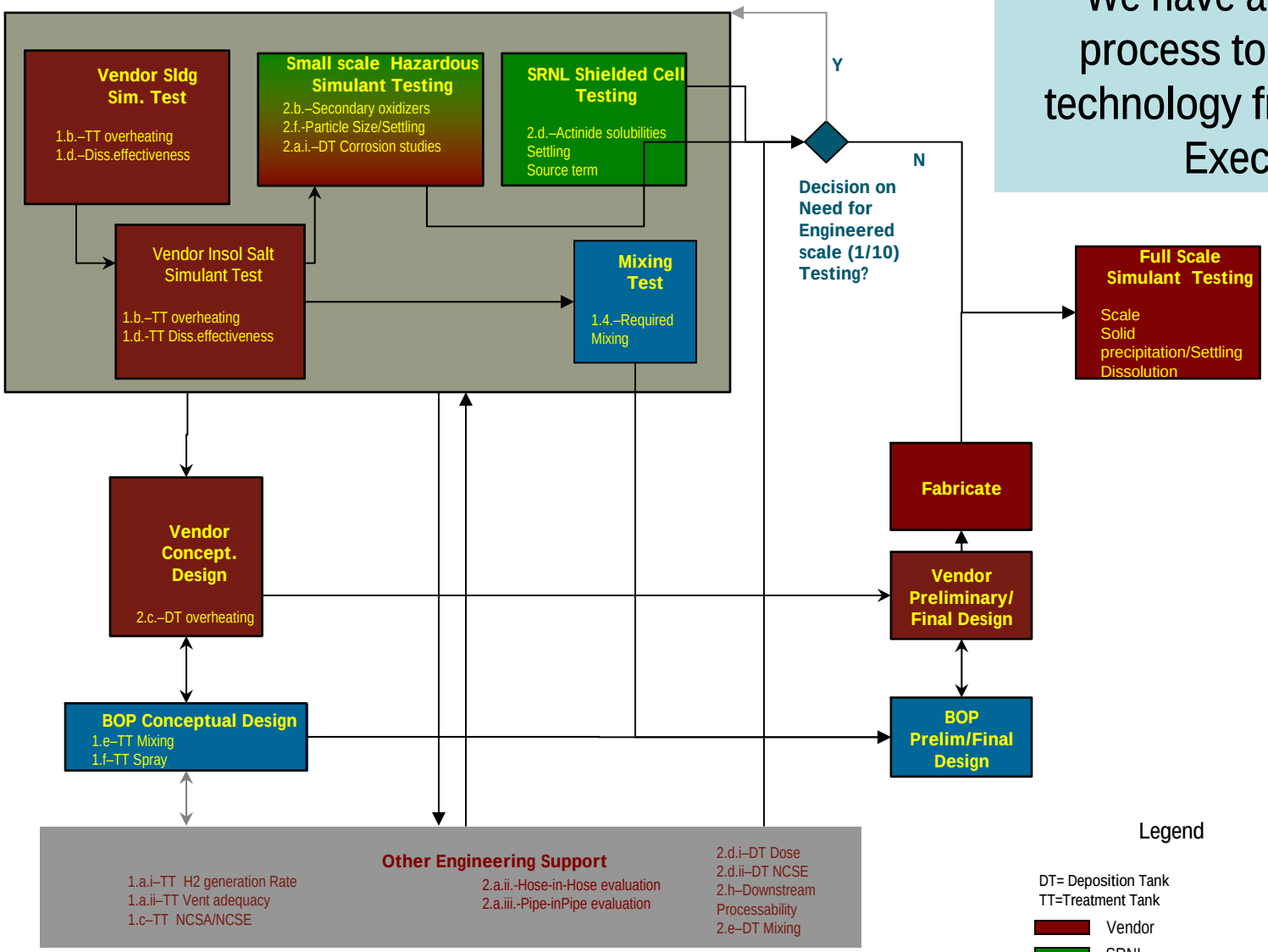
Testing Status

Table 2. ECC Testing Status

1	Dissolution - **Complete**
2	Oxalate Destruction - **Complete**
3	Corrosion - Hazardous Simulant Testing
4	Temperature-**Complete**
5	Gas Generation - Hazardous Simulant Testing & Real Waste
6	Fate on multi-valence hazardous metals – Hazardous Simulant Testing
7	Evaporation and Solid/Liquid Separation – Hazardous Simulant Testing & Real Waste
8	Actinide Solubility - Criticality & Material at Risk - Risk Real Waste
9	Mixing – Equipment Demonstration Test
10	Integrated Testing - Equipment Demonstration Test
11	Scaled Testing – Equipment Demonstration Test

ECC Technology Roadmap

We have a structured process to mature the technology from Vision to Execution



Legend

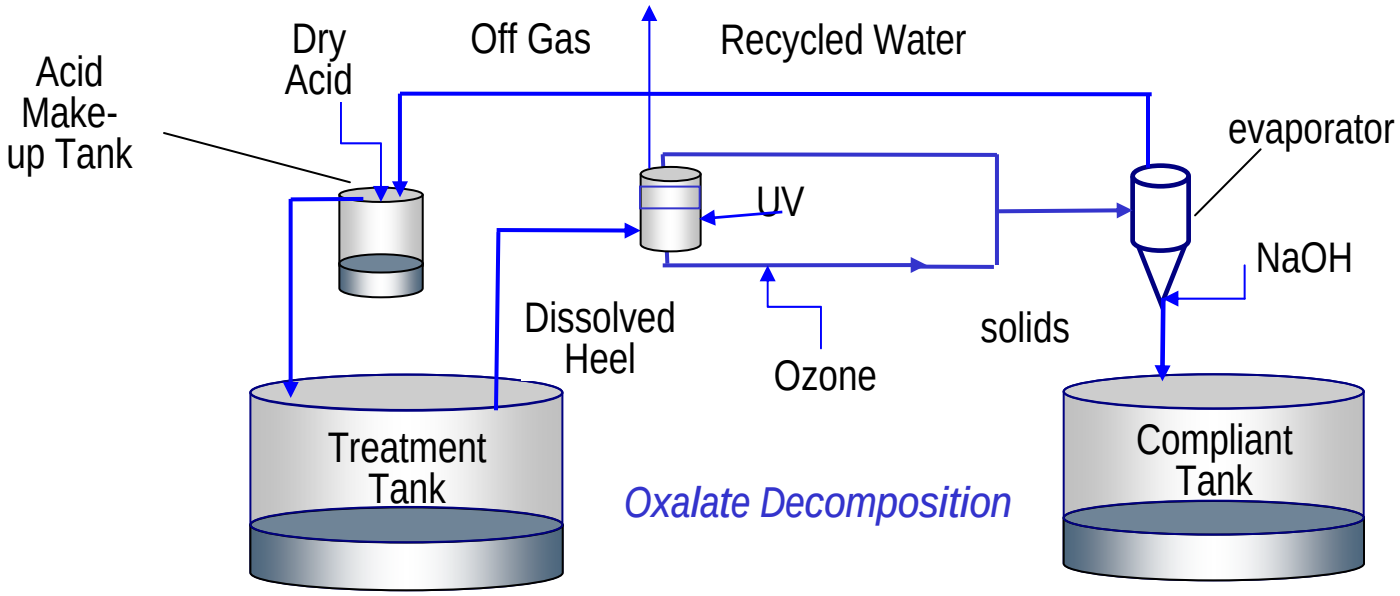
DT= Deposition Tank
TT=Treatment Tank

- Vendor
- SRNL
- SRS

Enhanced Chemical Cleaning

ECC SUMMARY

- Enhanced Chemical Cleaning is technically appealing
  - Achieves the regulatory requirements for tank closure
  - Minimizes creation of new waste streams & volumes
  - Does not impact the downstream process efficiency
- Need to complete testing, design, and construction
- Deployment planned for 2011



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Question and Answers

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