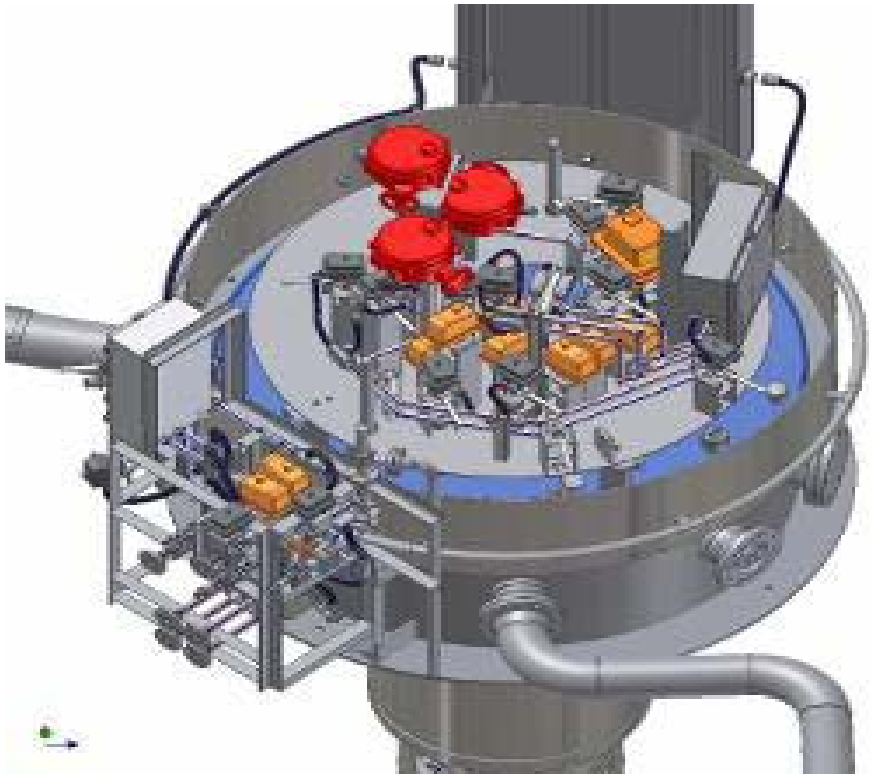
Overview: What is Secondary Waste



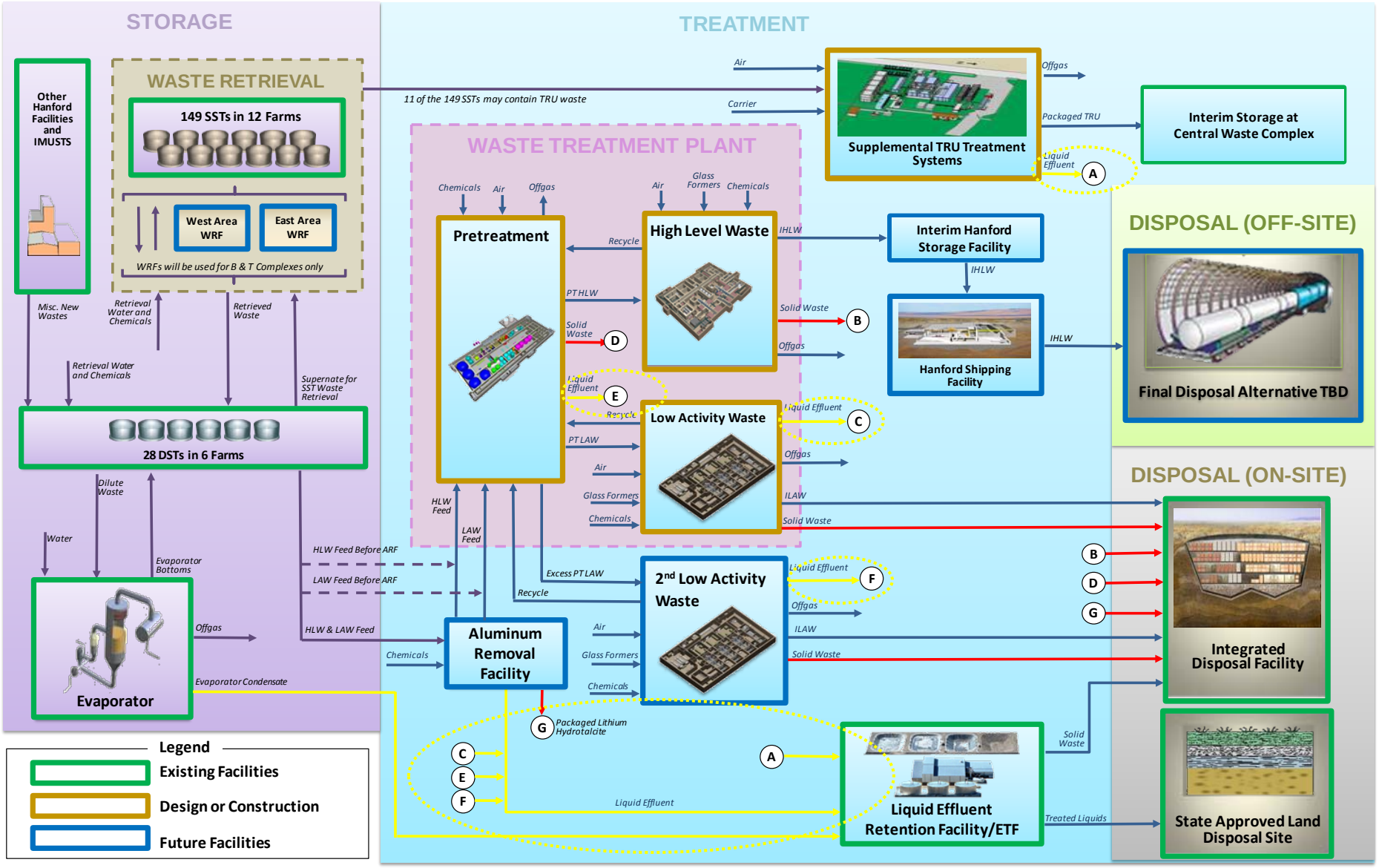
Tom Crawford
Paul Certa

June 14, 2010

Hanford Tank Wastes – 56M gallons (February 2010)

- Supernate (salt solutions)
  - Contain soluble radionuclides (e.g. cesium-137, iodine-129, technetium-99, etc.)
- Saltcake (crystalline salts)
  - When retrieved, produce supernatant solutions
  - Often comingled with sludge
- Sludge (metal compounds)
  - Insoluble metal compounds (aluminum, chromium, iron, uranium, etc.)
  - Insoluble radionuclides (strontium-90, plutonium-239, americium-241, etc.)

River Protection Project
Simplified Process Flow Diagram



Secondary Process-Related Liquid Waste

Secondary Process-Related Solid Waste

Many Sources of Secondary Waste

- Common sources
  - Failed or replaced equipment
  - Decontamination
  - Protective clothing
  - High Efficiency Particulate Air (HEPA) filters
- Tank Farms
  - Evaporator condensate
- Waste treatment facilities
  - Routine solid waste
    - Carbon absorption beds
    - Silver mordenite reactors
    - Spent Ion Exchange resin
  - Special case solid wastes
    - Spent or failed Low Activity Waste melters
    - Spent or failed HLW melters
    - Lithium Hydrotalcite
  - Liquid wastes
    - Process condensates
    - Scrubber/off gas treatment liquids from thermal treatment (usually caustic scrubbers)

Liquid Effluent Retention Facility & Effluent Treatment Facility

Sources of Liquid Secondary Waste

- Current Sources – 6 million gal/year
  - 242-A Evaporator
  - Leachate
    - Mixed Waste Burial Trench
    - Environmental Restoration Disposal Facility Leachate
  - Groundwater treatment projects
  - Decontamination and decommissioning projects

- Future Sources – 11 million gal/year
  - Potential Transuranic Tank Waste Treatment
  - Waste Treatment Plant
    - Pretreatment
    - HLW Vitrification
    - LAW Vitrification
  - 2nd LAW Vitrification Plant
  - IDF leachate

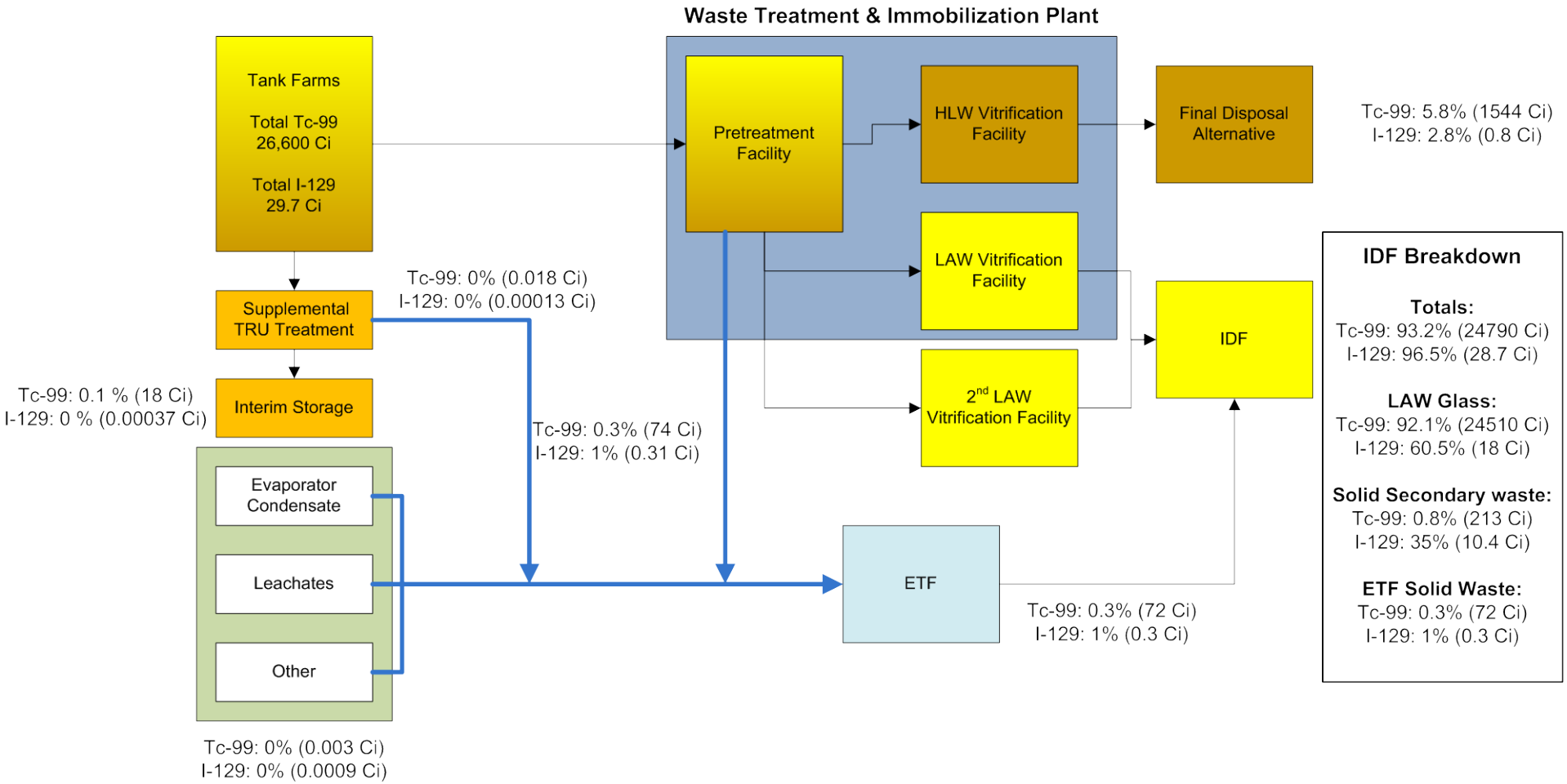
- Total Future Capacity – 17 million gal/year

Constituents of Concern

- Primary constituents of concern: Iodine-129 and Technetium-99
  - Studies show these constituents to be highly mobile in the vadose zone and ground water
  - Volatilize in glass melters and end up in secondary liquid waste
  - Long radioactive half lives
    - 213,000 years for ^{99}Tc
    - 15.7 million years for ^{129}I

- Potential constituents of concern from tank waste treatment may include, but are not limited to: uranium, chromium, mercury and nitrate

Liquid Secondary Wastes



Percentages are of the initial tank inventory.

Integrated Disposal Facility

Treatment Path Considerations for Liquid Secondary Waste

- Treatment capacity:
  - Volumetric throughput
  - Dissolved materials
  - Radionuclides
- Waste form acceptability to Integrated Disposal Facility
- Waste loading:
  - Waste concentration in the waste form
  - Final waste volume versus disposal capacity
- Cost effective treatment process

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CH2MHILL
Plateau Remediation Company

Integrated Disposal Facility (IDF) Performance Assessment & Secondary Waste Streams Context

Presented to: U.S. Department of Energy (DOE), Office of River Protection (ORP) Educational Forum

Presented by: Linda Lehman

Location :EMSL Auditorium**, PNNL Campus**

Date: June 14, 2010

One Team. One Culture.

Integrated Disposal Facility (IDF)

- DOE-Richland Operations Office (RL) Responsibilities for IDF
  - Performance Assessment (PA)
  - Composite Analysis (CA)
  - Operations
- DOE-ORP Responsibilities for IDF
  - Secondary waste and glass inventory and treatment
  - Waste Incidental to Reprocessing (WIR) determination
  - Dissolution rates for glass and secondary waste
- Because of the distribution of work scope, close coordination of schedule by the two offices of DOE is important and has been initiated.

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Need for the IDF PA

PA supports

- Immobilize Low-Activity Waste Waste Incidental to Reprocessing (ILAW WIR) decision.
  - Needed by ORP in order to dispose of the new ILAW glass within IDF
- Comply with DOE 435.1.
  - Reviews by DOE HQ, and the Low-level Waste Federal Review Group (LFRG)
  - Disposal Authorization Statement
  - Development of the revised IDF Waste Acceptance Criteria
- Assist in the waste form release rate and selection decisions.

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IDF Planning

- Started planning to develop a budget and schedule to support the startup of IDF in 2018.
  - Funding in FY-2010 to prepare a project execution plan
  - Funding requested in FY-2011 to start risk based budget tool

- Discussed preliminary schedule with ORP, Washington River Protection Solutions, LLC (WRPS), CHPRC and RL.

- Removed July 2010 date in the IDF RCRA Permit for a Risk Budget Tool (RBT).
  - Still tied to Tank Closure and Waste Management Environment Impact Statement (EIS) and Startup of IDF

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Plans for Developing the IDF PA

- We have an existing PA (2001 ILAW PA).
  - PA has been through Ecology and DOE HQ/LFRG reviews and accepted.

- Path forward
  - Utilize the 2001 ILAW PA as a starting point.
  - Incorporate information from draft 2005 IDF PA.
  - Evaluate what needs to be added or changed from the 2001 PA moving forward into the next revision.
  - NRC Consultative Review

Scoping

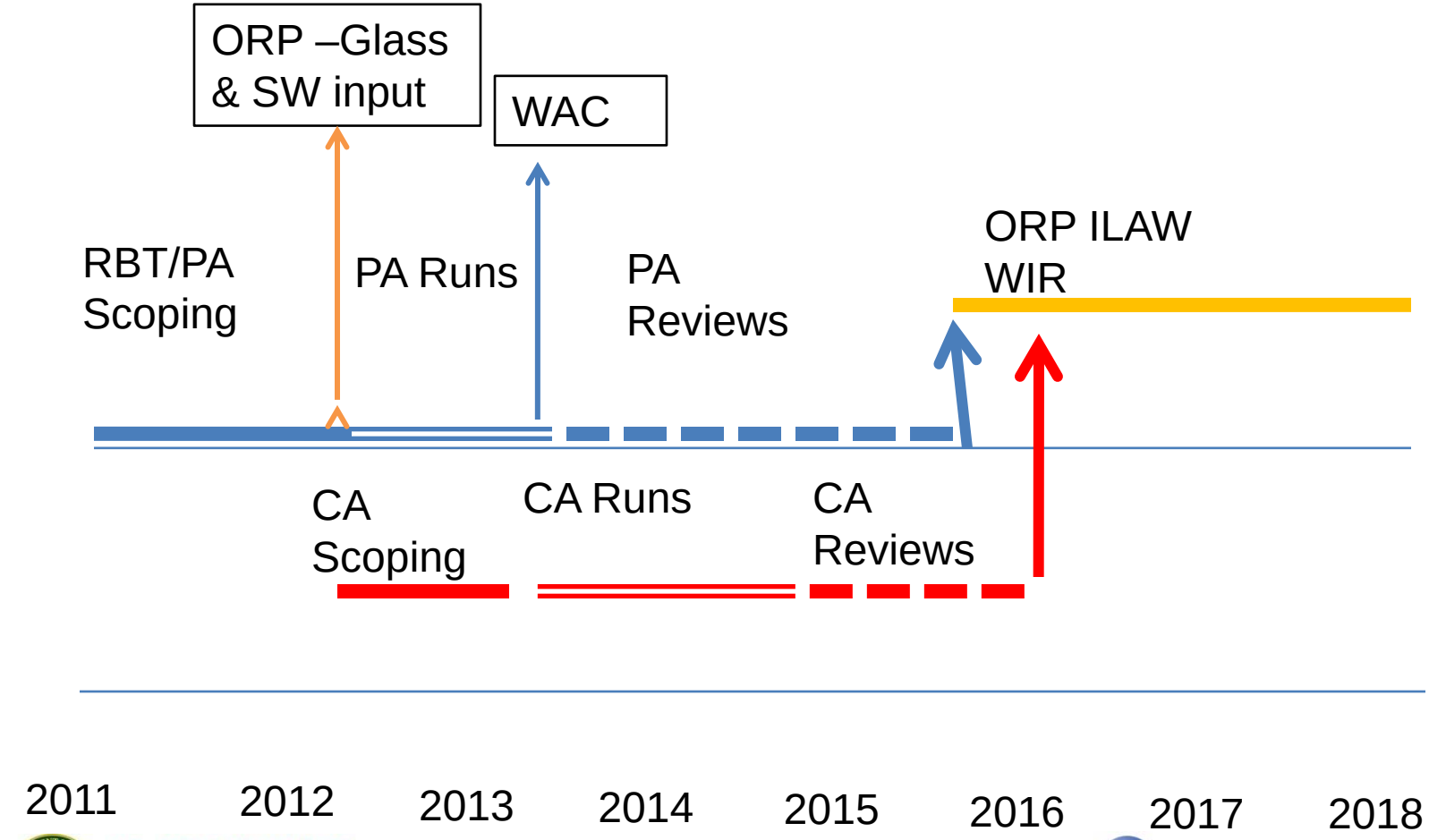
- Begin IDF PA Scoping with the Risk Budget Tool (RBT).
  - RCRA Permit condition (Ecology)

- Utilize the RBT as a learning tool during the IDF PA scoping to examine sensitivities to parameter distributions and potential outcomes based on the 2001 and 2005 PA model output.

Process Timeline

- The process timeline can be summarized as follows:
  - 3 years for PA completion, including scoping
  - 2 years for the review cycles for IDF PA
  - 2 1/2 years for CA completion, including scoping
  - 1 year for review cycle for the CA
  - 3 years for the ORP ILAW WIR and Disposal Authorizations.
- Schedule supports a 2018 startup of IDF.

Process Timeline



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Other Interactions

- Begin discussions with Ecology on the IDF Risk Budget tool and the PA in October 2010.
- Incorporate Ecology's review schedules into our schedules.
- Identify a Bechtel National, Inc. representative to participate in the planning.
- Review IDF EIS data package from ORP.

Fluidized Bed Steam Reforming Technology for Treatment of WTP Secondary Wastes

Brad Mason

June 14, 2010

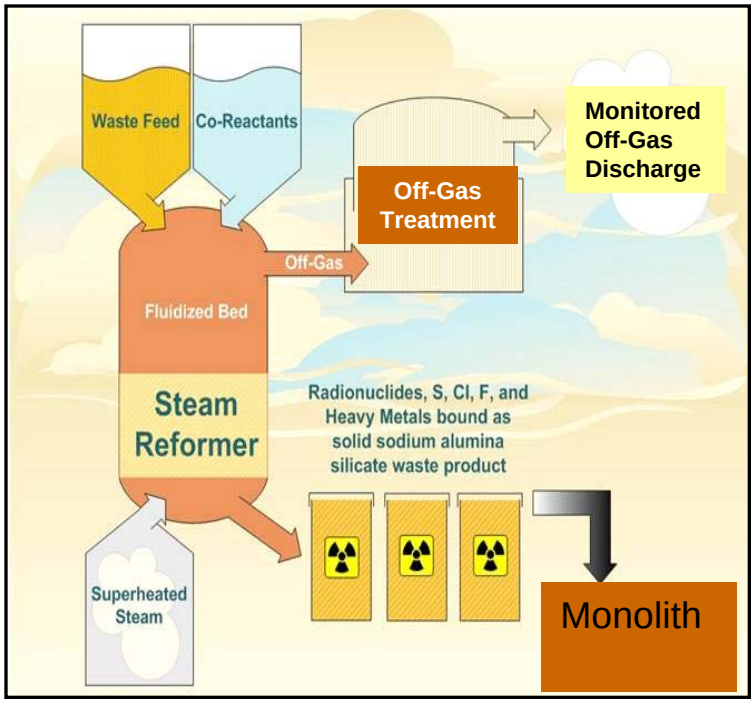
THOR Treatment Technologies

Discussion Outline

- ***What is steam reforming?***
- ***How does it work?***
- ***Background and process applications***
- ***Secondary waste application***
- ***Solid and monolith product characteristics***

What is Fluidized Bed Steam Reforming?

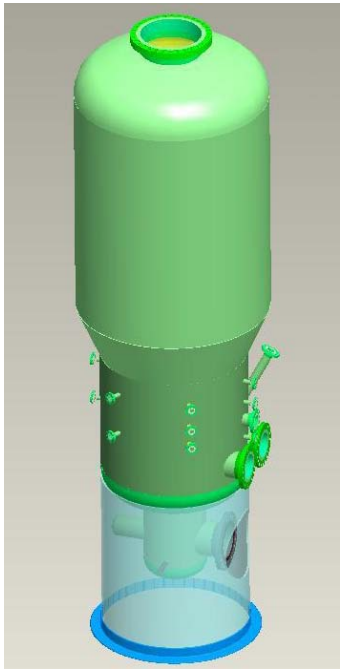
- ***Thermal process***
  - ***Fluidized bed of granular solids***
  - ***Fluidized with low pressure, hot steam***
  - ***Operates at 620-750°C***
  - ***Operates at near-ambient pressure***
- ***Waste preparation and inputs***
  - ***Secondary waste mixed with clay***
  - ***SW/clay slurry air atomized into bed***
  - ***Coal added as reductant and for energy***
- ***What happens inside the FBSR?***
  - ***Water evaporates***
  - ***Nitrates reduced to nitrogen gas***
  - ***Waste reacts with clay to form water insoluble mineral***
  - ***Radionuclides and heavy metals converted to water insoluble minerals***



- ***Fluidized bed agitated by low pressure steam***
- ***Energy produced by carbon reductant and oxygen (autothermal steam reforming)***

Why Use Fluidized Bed Steam Reforming?

- ***Accommodates widely varying wastes***
  - ***High or low pH (no adjustment required)***
  - ***Radionuclides (Cs, Re/Tc, some I) and heavy metals converted to water insoluble minerals***
  - ***High Cl, F, P, SO_4 –converted to water insoluble mineral, no off-gas scrubber required***
  - ***Nitrates converted to nitrogen inside FBSR, no off-gas NOx abatement required***
  - ***Organic and inorganic materials***
- ***Moderate temperature (620-750°C)***
  - ***Does not volatize Cs, Tc (Re)***
  - ***Simple off-gas treatment system***
  - ***No wet scrubber, so no liquid effluents***
- ***Non-Incineration***
  - ***Operates below flammability limits***



Idaho National Laboratory

Integrated Waste Treatment Unit FBSR - CRR

How Does Steam Reforming Work?

- ***Gas phase reactions, partial list:***
  - $C + O_2 \leftrightarrow CO_2$ — *Oxidation of carbon (energy)*
  - $C_xH_yO_z \leftrightarrow C + CH_4 + CO + H_2$, etc. — *Decomposition of organics*
  - $H_2O + C \leftrightarrow H_2 + CO$ — *Water gas reaction*
  - $CO + H_2O \leftrightarrow CO_2 + H_2$ — *Water gas shift reaction*
  - $2NO_3 + 3C \leftrightarrow N_2 + 3CO_2$ — *Conversion of nitrates to nitrogen gas*
  - $2NO_3 + 6H_2 \leftrightarrow N_2 + 6H_2O$

- ***Waste constituent reactions:***

Waste Constituent or Characteristic	No Solid Additive (Carbon Dioxide)	Clay Additive (Alumino-silicate)
Organics	Destroyed	Destroyed
Alkali Metals	Carbonate	Alkali alumino-silicate mineral (NAS)
Inorganic Metals	Oxides, Spinels	Spinels and Oxides bound in NAS matrix
Cl, S, F, P, I, B	Alkali Salt	Bound in NAS matrix
Radionuclides	Oxides or Carbonates	Spinels and Oxides bound in NAS matrix
Resulting Waste Form	Mostly water soluble carbonate	Leach resistant mineral - Maximum immobilization - Maximum leach resistance

Steam Reforming – Pilot Plant Experience

- ***Pilot plant testing with multiple surrogate wastes to qualify process***
- ***17 pilot plants test programs performed*** ***(6", 15" and 24" diameter FBSRs)***
- ***Scale up from pilot plant to radioactive waste treatment plants:***
  - ***Studsvik Processing Facility*** ***(45" diameter FBSR)***
  - ***DOE Idaho Integrated Waste Treatment Unit*** ***(48" diameter FBSR)***
  - ***DOE Savannah River: Tank 48 Treatment*** ***(23" diameter FBSR)***

SAIC STAR Center

Hazen Research

Steam Reforming – Pilot Plant Experience

Test No.	Year	Pilot Plant / Location	Surrogate Nitrate Wastes	Product
1	1997	Hazen 6" FBSR and 15" ESTD, Colorado	Hanford, LAW, 5.2 M $NaNO_3$	Carbonate
2	2000	SAIC STAR Center, 3" FBSR, Idaho	INL, Sodium Bearing Waste	Carbonate
3	2001	Hazen 6" FBSR, Colorado	Hanford, LAW, AN-107	Carbonate and Aluminosilicate
4	2003	SAIC STAR Center, 6" FBSR, Idaho	INL, Sodium Bearing Waste	Carbonate
5	2003	SAIC STAR Center, 6" FBSR, Idaho	SRS, Tank 48H	Carbonate
6	2003	SAIC STAR Center, 6" FBSR, Idaho	INL, Sodium Bearing Waste	Carbonate and Aluminosilicate
7	2004	SAIC STAR Center, 6" FBSR, Idaho	INL, Sodium Bearing Waste	Aluminosilicate
8	2004	SAIC STAR Center, 6" FBSR, Idaho	Hanford, LAW, Envelope A	Aluminosilicate
9	2005	Hazen 15" ESTD, Colorado	INL, Sodium Bearing Waste (CP1)	Carbonate
10	2006	Hazen 15" ESTD, Colorado	INL, Sodium Bearing Waste (CP2)	Carbonate
11	2006	Hazen 15" ESTD, Colorado	INL, Sodium Bearing Waste (MP1)	Aluminosilicate
12	2006	Hazen 15" ESTD, Colorado	SRS, Tank 48H	Carbonate
13	2008	Hazen 15" ESTD, Colorado	SRS, Tank 48H (P1)	Carbonate
14	2008	Hazen 15" ESTD, Colorado	ART, Hanford LAW	Aluminosilicate
15	2008	Hazen 15" ESTD, Colorado	ART, WTP Secondary Waste (SW)	Aluminosilicate
16	2008	Hazen 24" ESTD, Colorado	AML, Lagoon Nitrate	Aluminosilicate
17	2009	Hazen 15" ESTD, Colorado	SRS, Tank 48H (P2/3)	Carbonate

THOR® Process – Studsvik Processing Facility

- ***Treats wide range of radioactive wastes (>380,000 cu ft):***
  - ***Ion exchange resins (up to 600R/hr)***
  - ***Organic or inorganic sludges***
  - ***Filters***
  - ***Oils***
  - ***Aqueous wastes***
  - ***Dry active wastes (paper, plastics, rubber, wood)***
- ***No liquid waste effluents***
- ***Over 10 years successful LLRW operations***
- ***High Cs and Tc retention (>99.9999%)***

Studsvik's THOR® facility Meets All Air Permit and Emissions Limits

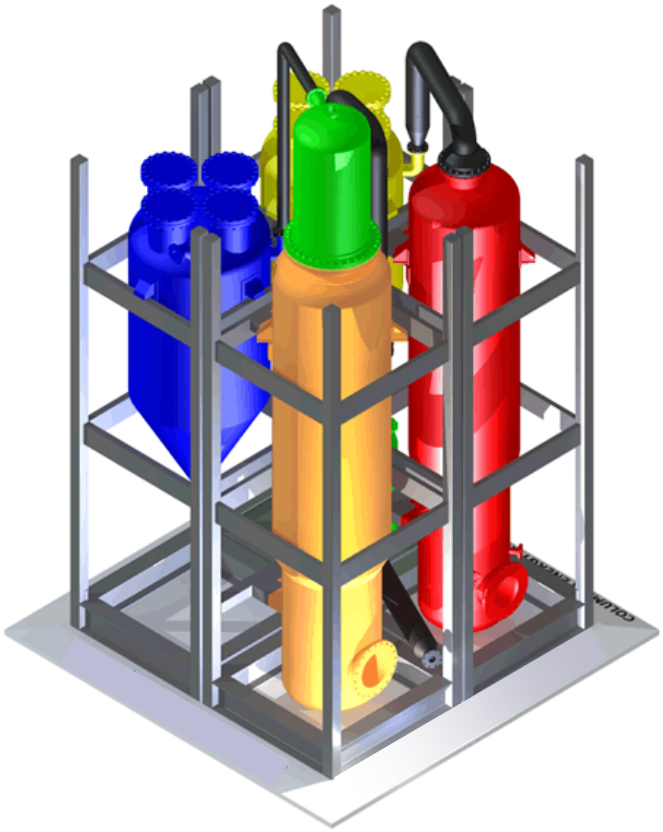
DOE Idaho Cleanup Project
THOR® Integrated Waste Treatment Unit

- ***THOR® treatment of ~3.8 million liters of Sodium Bearing Waste (SBW): sodium nitrate with nitric acid, ~100 R/hr)***
- ***SBW generated from spent nuclear fuel process systems decontamination and deactivation***
- ***Carbonate product to be packaged into RH-72B canisters and stored; alternative for future mineral product flowsheet***
- ***THOR® plant construction underway***
- ***Treatment to start 2011-2012***

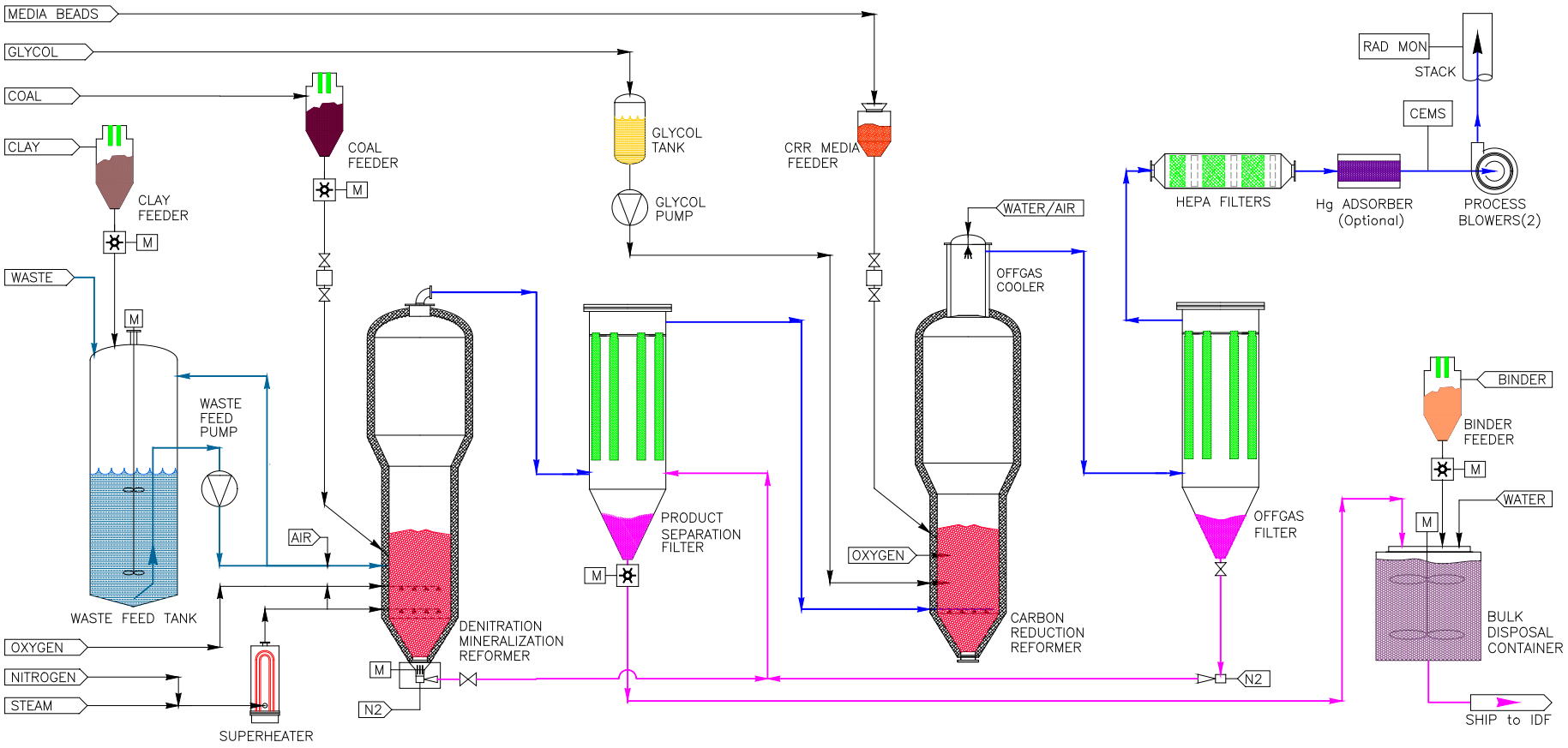
THOR Treatment Technologies

DOE Savannah River Remediation
Tank 48H – THOR® Process

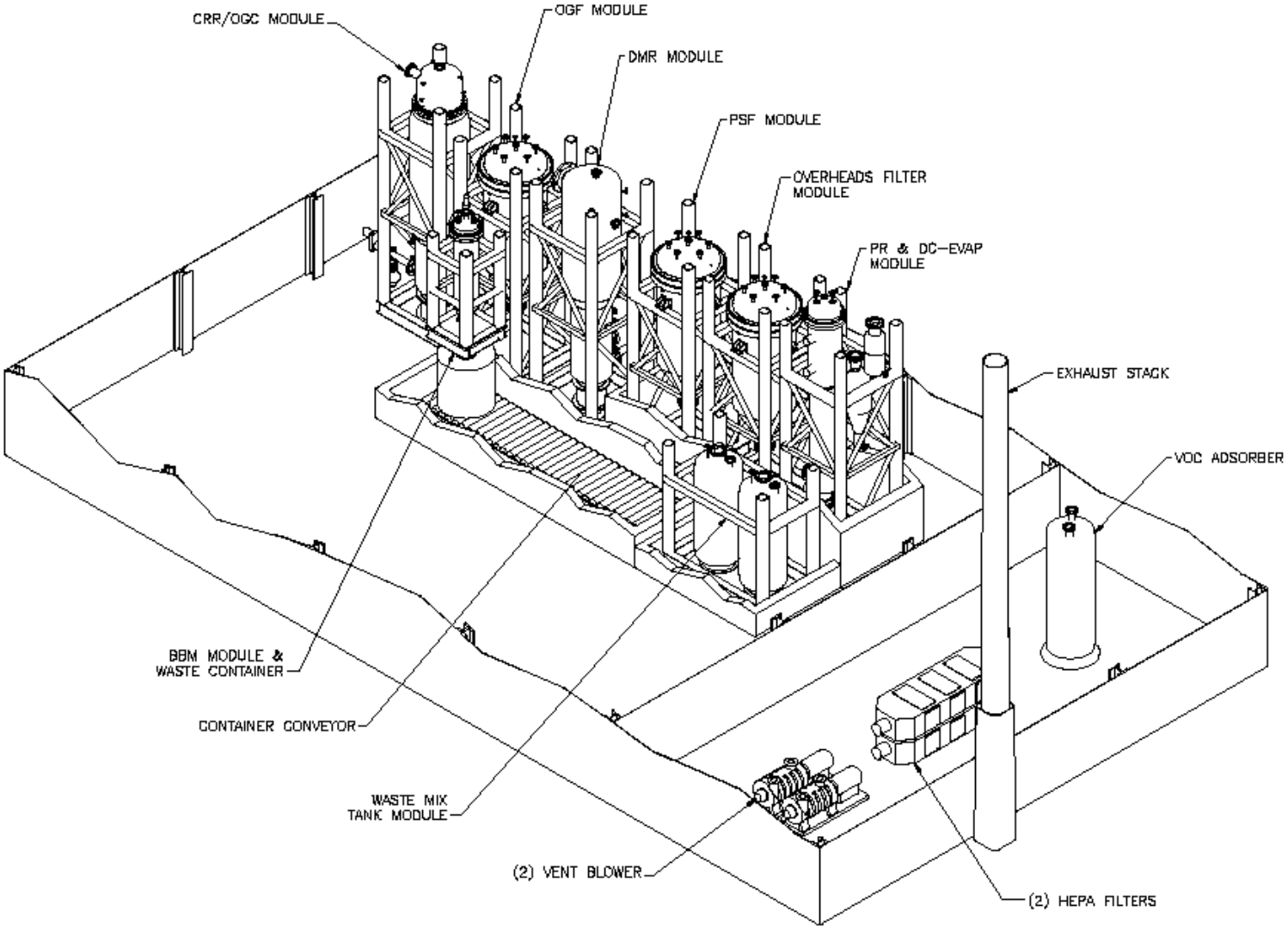
- ***THOR® treatment of ~1 million liters of radioactive high-level liquid waste in Tank 48H (sodium nitrate, >100 R/hr)***
- ***Complex nitrate mixture with ~ 21,800 kg organic tetraphenylborate***
- ***Two separate independent technical review teams selected THOR®***
- ***Integrated pilot plant tests complete***
- ***Detailed design for full-scale plant underway***



Steam Reforming Process – Flow Diagram for SW



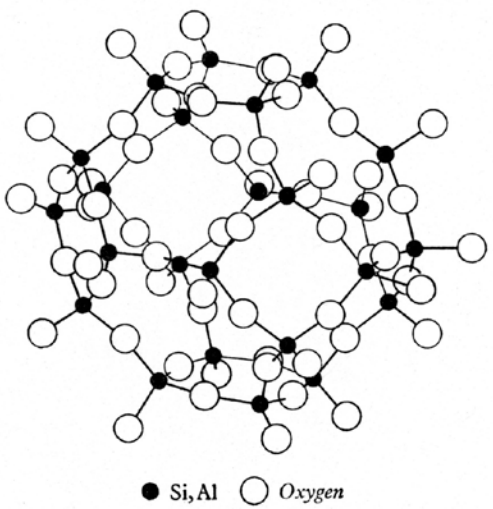
Steam Reforming Process – Secondary Waste



Steam Reforming – Mineral Product Form

Ceramic mineral waste form:

- ***Clay additive is mixed with waste***
- ***Waste/clay slurry is injected into FBSR***
- ***Alumino-silicate minerals form that incorporate:***
  - ***Radioactive materials (Tc, Cs, some I)***
  - ***Sodium and potassium (alkali metals)***
  - ***Sulfur***
  - ***Chlorides***
  - ***Fluorides***
- ***Spinel minerals form that incorporate***
  - ***Metals (Cr, Ni, Fe, etc.)***



Na_2O-Al_2O_3-$2SiO_2$
(Nepheline)

Na_2SO_4 or NaCl
Plus 6 Nephelines
(Nosean or Sodalite)

Source: SRNL Reports

Mineralized Product – Simple Formulation

Simple formulation to determine waste-clay mixture:

1. **Determine Na, Al and Si content of waste**
2. **Select type and quantity of clay**

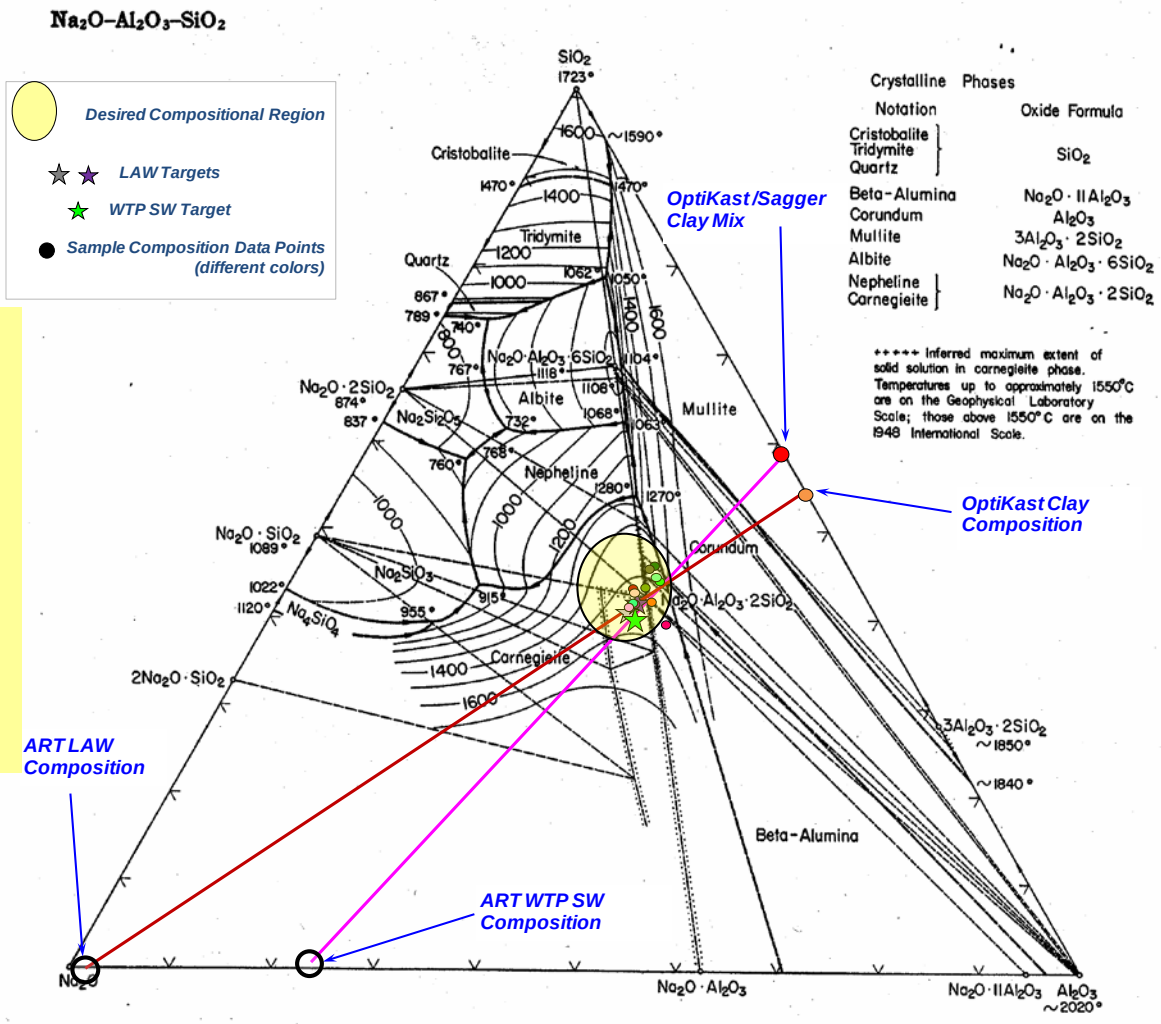


FIG. 501.—System Na_2O–Al_2O_3–SiO_2: composite.

Source: Test Report, TR-21-002, Rev 1

Thor Treatment Technologies

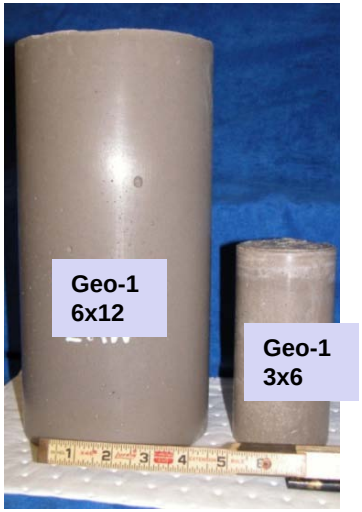
SW Mineral Waste Form Properties

- ***Granular mineral products are mixed with binder to make monolithic final waste form***
- ***Geopolymer binder has chemical properties similar to mineral product***
- ***Monolithic final waste form properties:***
  - ***Compressive strength of >1,500 psi***
  - ***Passes PCT test***
  - ***Passes TCLP test***
  - ***PNNL currently testing monoliths using EPA and ANSI methods***

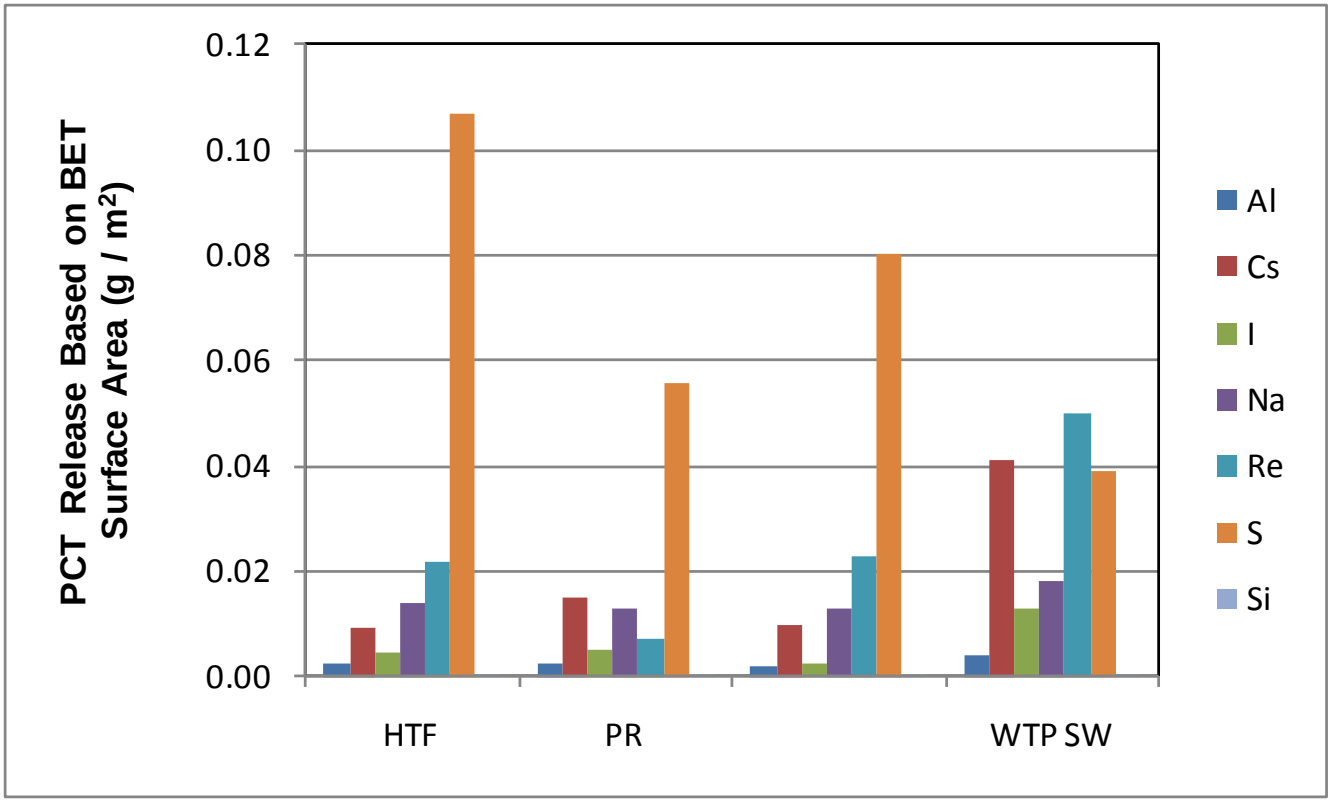
Monolith needed to pass IDF requirements for:

- ***Compressibility (>500 psi)***
- ***Intruder scenarios***

Binder



Granular SW Mineral Product Durability



- ***WTP SW is weight based proportioned mixtures of the PR and HTF granular products.***
- ***Various researchers have suggested that BET is a more appropriate surface area characterization for mineral and ceramic waste forms, which have much different porosities than glass waste forms. Geometric surface areas, as defined by ASTM 1285, are used for the less porous glass waste forms.****

LAW glass standard: <2.0 grams/m^2 for Na, Si, and B per DOE/ORP-2000-24

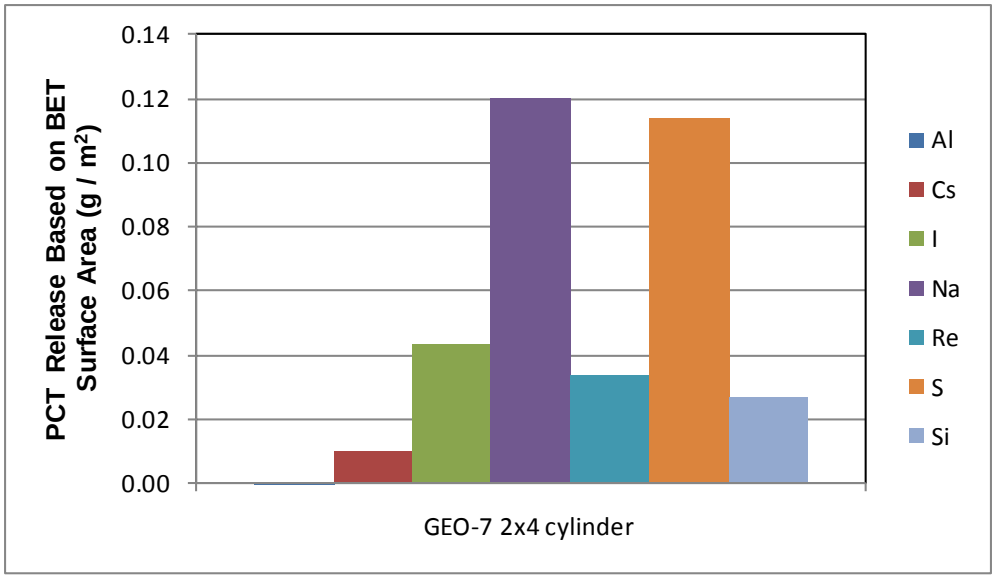
*Jantzen, C. M., *Mineralization Of Radioactive Wastes By Fluidized Bed Steam Reforming (FBSR): Comparisons To Vitreous Waste Forms, And Pertinent Durability Testing*, WSRC-STI-2008-00268, Rev. 0, January 2009.

Source: Draft SRNL Test Report, Data

Monolith SW Mineral Properties

- ***PCT: passes with 0.12 g/m² Na compared with LAW glass standard of <2 g/m² Na***
- ***TCLP: passes for all heavy metals***
- ***Geopolymer binder with waste loading of ~65% (dry basis)***
- ***Compressive strength of 2,300 psi at 33 days cure time***
- ***Density of 1.78 g/cc***

PCT Response – SW Monolith



TCLP Response-SW Monolith

Element	Value (mg/L)	UTS ** (mg/L)
Sb	1.10	1.15
As	0.30	5
Ba	1.47	21
Cd	<0.05 (U)	0.11
Cr	0.25	0.6
Pb	0.15	0.75
Se	1.70	5.7
Ag	<0.10 (U)	0.14
Hg	<0.002 (U)	0.025
Ni	0.21	11
Tl	0.15	0.2
Zn	0.51	4.3

Source: Draft SRNL Test Report, WTP-SW Geo-7
Data: PCT =#9, Fig 34; TCLP =#5 Table 44.
LAW glass standard: <2.0 grams/m² for Na, Si, and B per DOE/ORP-2000-24

**40 CFR 268.48 – "Universal Treatment Standards (UTS)"
U = results less than detection limit

Thor Treatment Technologies

Summary – THOR® Steam Reforming of SW

Benefits and features:

- ***Accommodates widely varying wastes***
  - ***Treats solids, liquids, or sludges with high or low pH (no adjustment required)***
  - ***Provides high organic destruction***
  - ***Does not volatize SW radionuclides***
    - ***Re (Tc): >99.998% retention in mineral , no Re detected in off-gas system***
    - ***Iodine: ~19% retention in mineral (detection limited, higher for other wastes, more testing needed with higher iodine input, no iodine detected in off-gas system)***
    - ***Cs: >99.9999% retention in mineral***
  - ***Uses single-component mineralizing additive, low cost clay***
- ***Mineral final waste form – monolith***
  - ***Qualifications to date validate highly leach resistant granular and monolith waste forms***
  - ***Radioactive materials (Cs, Tc, some I) converted into water insoluble mineral waste form that passes PCT and TCLP tests***

Summary – THOR® Steam Reforming of SW

Benefits and features:

- ***Safe, robust process operations***
  - ***Operates below flammability limits, non-Incineration***
  - ***Reviewed by DNFSB for IWTU (RH-TRU) and Tank 48 (HLW) systems***
  - ***Process shutdown capable in <15 minutes***
- ***No off-gas scrubber system required***
  - ***Mineralizes Cl, F, P, and SO_4 into leach resistant mineral solid***
  - ***Less complex off-gas system as no wet scrubber is required***
  - ***No liquid effluents***
  - ***Meets MACT gaseous emissions limit***

Summary – THOR® Steam Reforming of SW

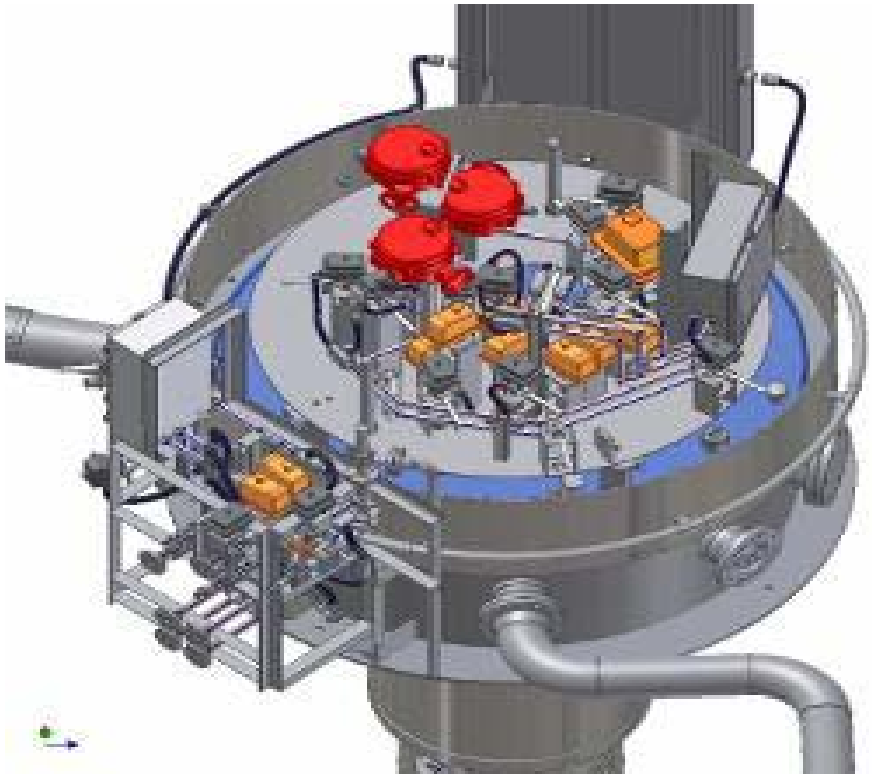
Ongoing work:

- **PNNL surrogate SW analyses**
  - Performing ASTM and EPA method testing of SW granular and monolithic products
  - Performing performance assessment comparison of SW technology waste forms
- **SRNL radioactive SW simulant testing**
  - Performing FBSR testing of radioactive DWPF SW solution spiked with radioactive Tc, Iodine, and Cs
  - Verify radioactive Cs, Tc, and I retention in mineral form and mass balance closure

Recommended future work to close data gaps:

- Perform more pilot plant testing with variable surrogate waste compositions
- Perform more testing of monolithic final waste form to validate compliance with Washington disposal requirements
- Perform full-scale monolith tests

Secondary Waste Treatment Project Baseline



Tom May

June 14, 2010

Secondary Waste Treatment

- Problem statement
- Solutions
- Status

Problem Statement

- No current facility has capacity to treat all secondary waste from Hanford's Waste Treatment Plant (WTP)
  - Effluent Treatment Facility (ETF) Capacity 2-3X too small
- Waste form must prove acceptable to Integrated Disposal Facility (IDF)
  - ETF Currently sends drums of dry powder to Environmental Restoration Disposal Facility (ERDF)
  - Plans are to send solidified Product to IDF
    - Linda Lehman – IDF Performance Assessment
    - Felix Miera – IDF Regulatory
    - Joe Westsik – Waste Form Testing

Solutions

- Upgrade existing facility or build new facility
  - ETF
  - FBSR
  - Other new facility
- Other
  - Tighter controls on Waste Treatment Plant (WTP) secondary liquid waste
  - Concentrate and return to Tank Farms

Effluent Treatment Facility

- RCRA permitted multi-waste treatment, storage and disposal (TSD) unit
- Dangerous, low-level, and mixed wastewater
- 150 gallons per minute influent (varies with composition)
- Primary treatment train – removes solids
- Clean water to state-approved liquid disposal site (SALDS)
- Secondary treatment train – dries solids
- Solids drummed and sent to ERDF
- Started up 1995 – 30 year design life

200 Area LERF and ETF

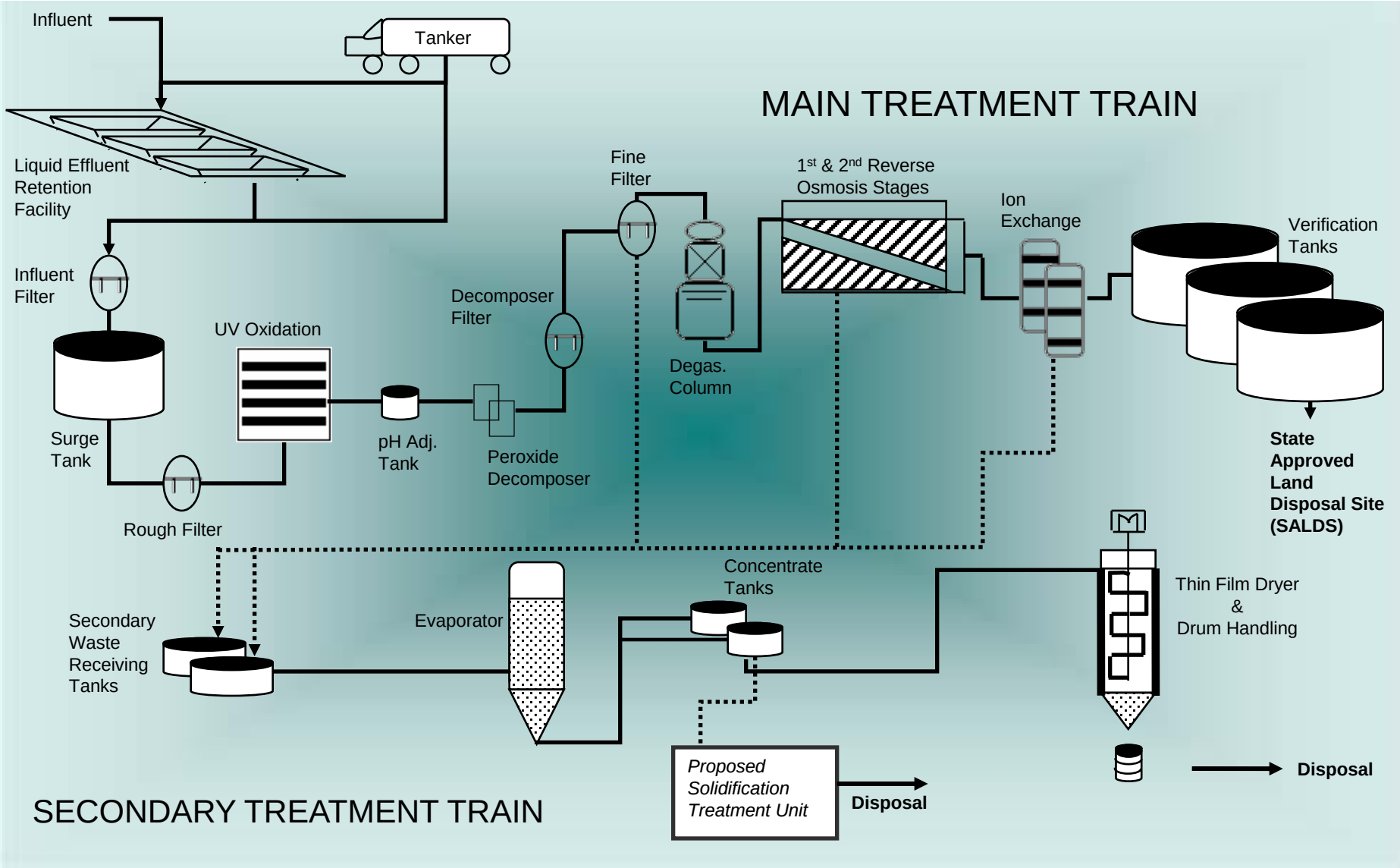
Liquid Effluent Retention Facility Basins

Effluent Treatment Facility

Liquid Effluent Retention Facility (LERF)

- 3 covered basins, 7.8 M gallons permitted capacity each
- Less than Category 3 Nuclear Facility
- Final status RCRA permitted facility

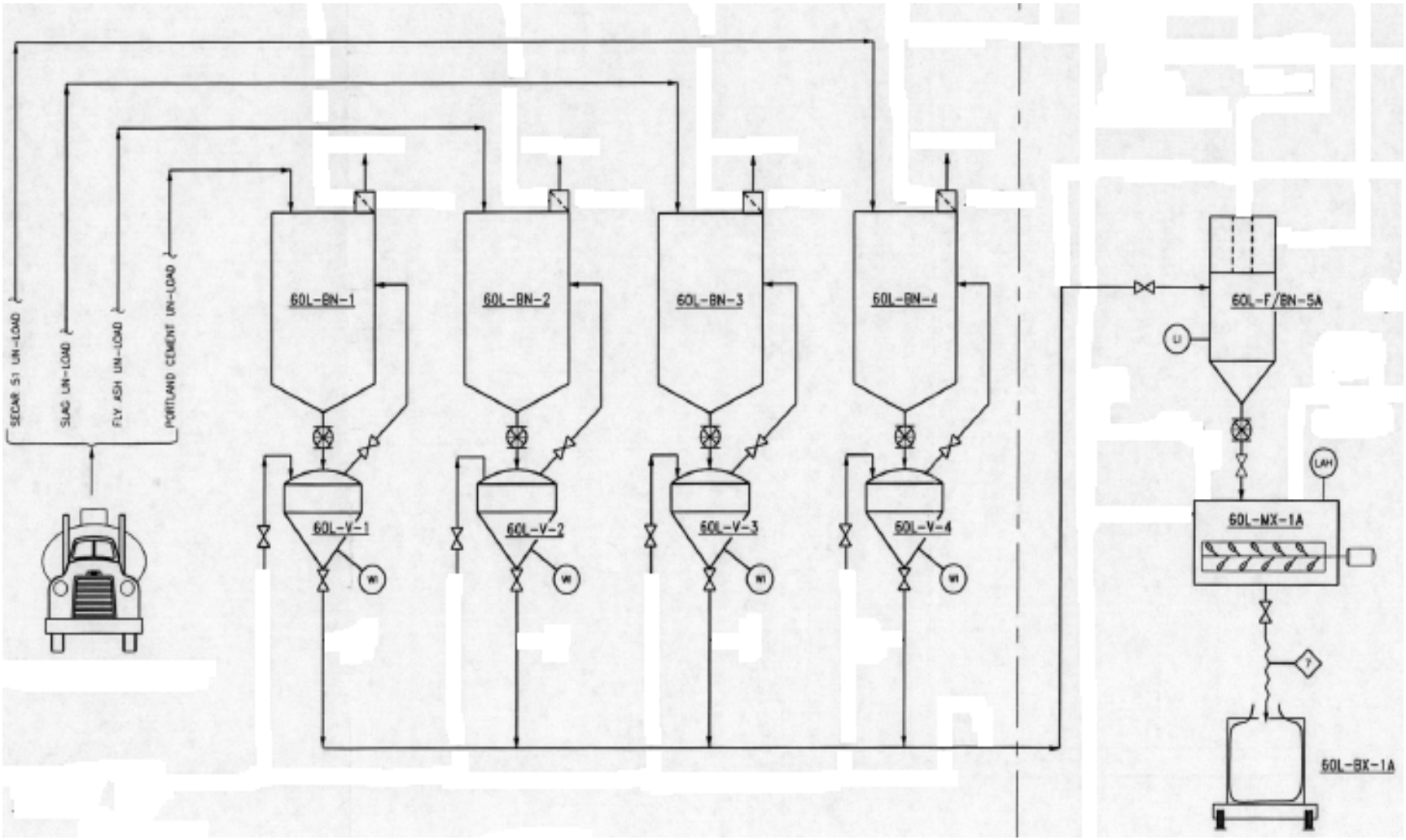
ETF Process Flow



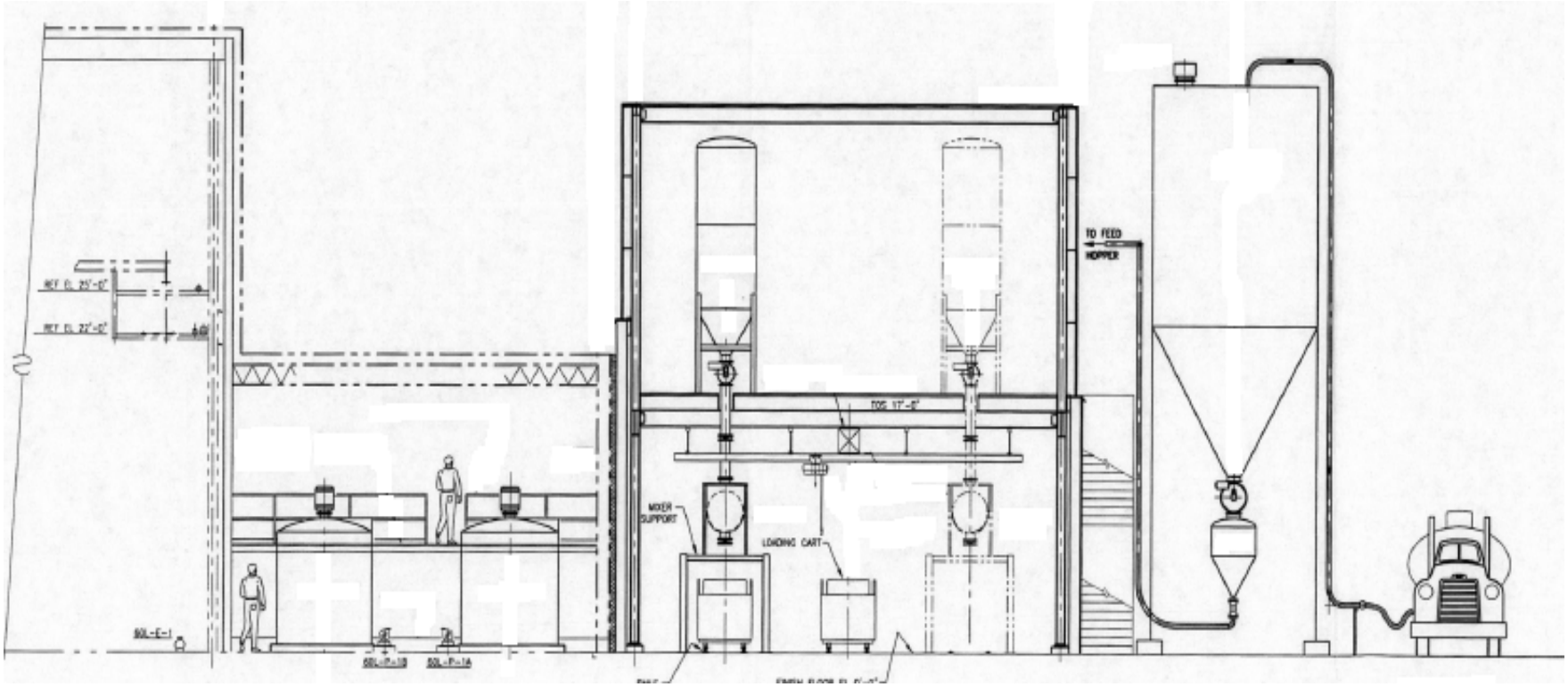
ETF – Unit Operations

- Filtration – removal of suspended solids
- Ultraviolet Light /Oxidation (UV/OX) – destruction of organics
- Reverse Osmosis (RO) – removal of dissolved solids and radionuclides
- Ion Exchange (IX) – removal of dissolved solids and radionuclides
- Evaporator – reduction of waste volume
- Thin-Film Dryer – waste dried to powder

Solidification Treatment Unit



Solidification Treatment Unit



Types of Wastewaters Treated at ETF

- **Wastewaters processed within an acidic pH range with primary constituents being ammonia, sodium, sulfate, nitrate, and organics.**
  - ***Example:*** *242-A Evaporator process condensate.*

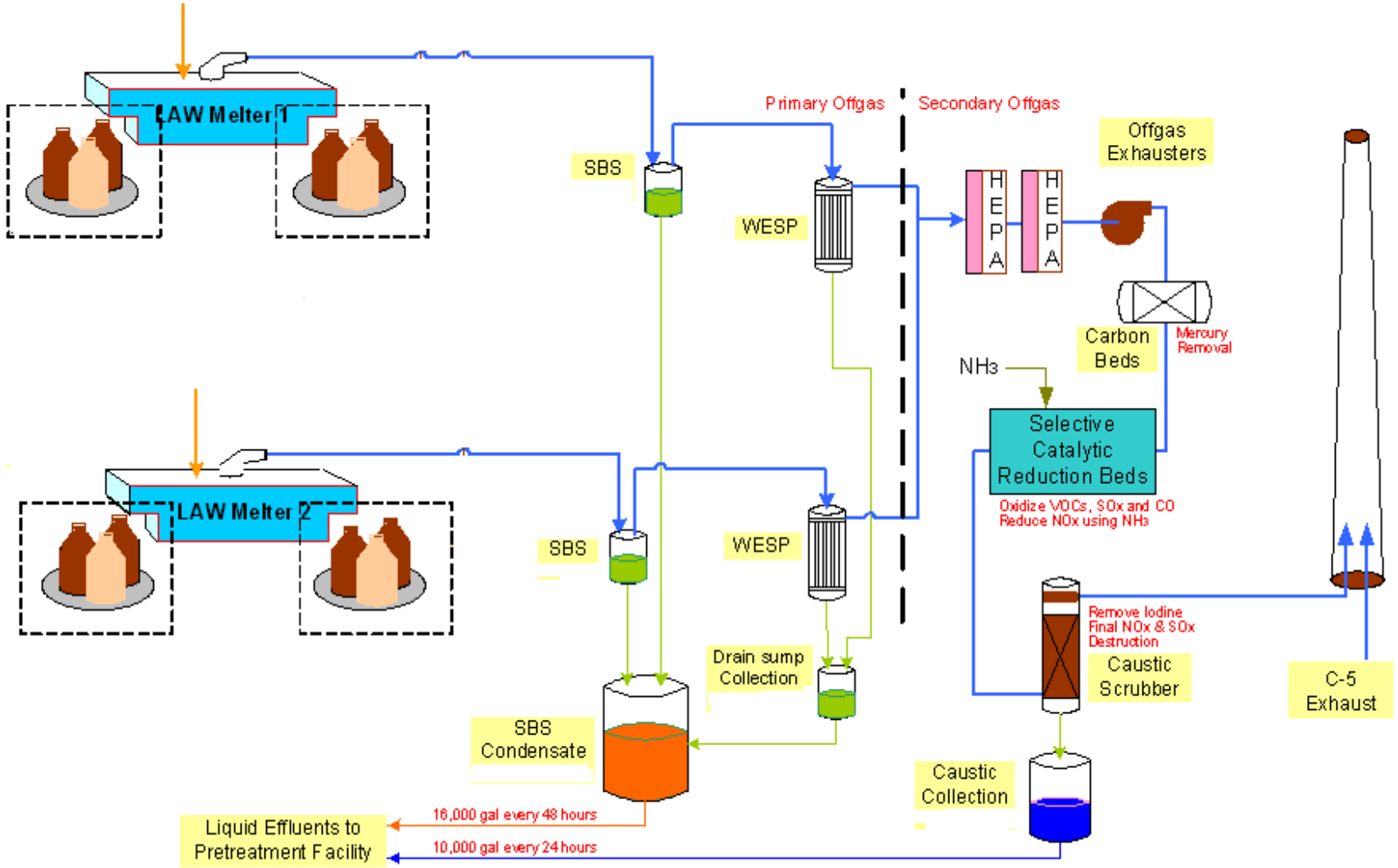
- **Wastewater processed within a caustic pH range with primary constituents being calcium, silica, magnesium, sodium, sulfate, nitrate, and chloride.**
  - ***Examples*** *: groundwater from pump-and-treats, leachates, purgewater, fuel storage basin waste, CERCLA wastewaters generated from deactivation and decommissioning activities.*

- **Wastewater processed through the secondary treatment train first with high total dissolved solids and primary constituents being sodium, sulfate, nitrate, chloride, and heavy metals.**
  - ***Example:*** *laboratory wastewater.*

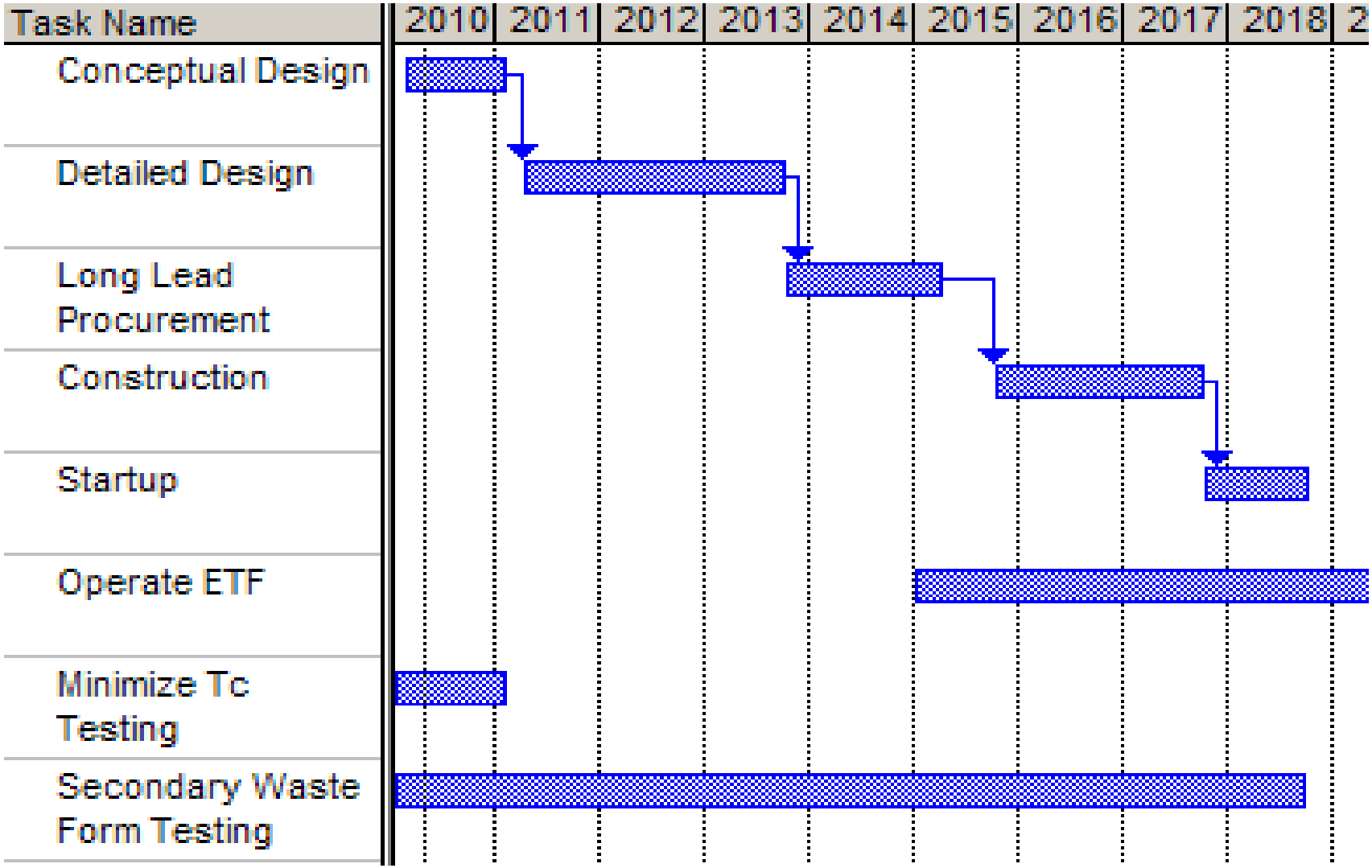
ETF Projected Waste Volumes

Wastewater Source	Annual Volume (Millions of Gallons)	FY Start and/or duration
ERDF Leachate	1	On-going
Purge Water	0.3	On-going
Mixed Waste Burial Trenches Leachate	0.4	On-going
Ground Water Ion-exchange Regeneration	0.2	On-going
FFTF Sodium Cleanout	1	FY2016
242-A process Condensate	3.5	On-going
Integrated Disposal Facility	1	
Tank Farm Contact Handled Waste System	0.66	FY2018
Waste Immobilization and Treatment Plant (WTP)	9.7	FY2018

WTP LAW Secondary Liquid Waste



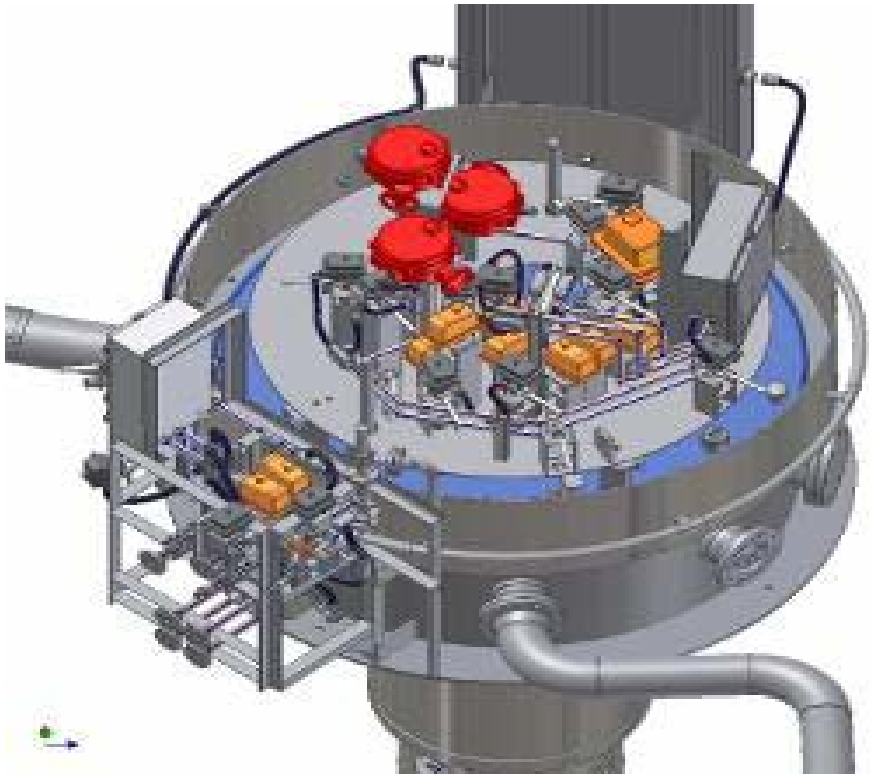
Secondary Waste Treatment Project Status



Contact information

- Thomas H May
- 372-2493
- Thomas_H_Tom_May@rl.gov

Technetium & Iodine Management



Tom May

June 14, 2010

Technetium (TC-99) and Iodine (I-129) Management

- Problem statement
- Solutions
- Status

Problem Statement

- ^{99}Tc and ^{129}I releases in Integrated Disposal Facility (IDF) are of concern in the Performance Assessment
  - ^{99}Tc and ^{129}I are soluble and much ends up in low activity waste (LAW).
  - ^{99}Tc and ^{129}I volatilize in the LAW melter and may end up in secondary liquid waste.
  - Non-glass waste form not as completely characterized for release in IDF

Solutions

- Improve retention of ^{99}Tc and ^{129}I in LAW glass
- Remove ^{99}Tc in LAW melter off-gas stream and divert to high level waste (HLW)
- Improve retention of ^{99}Tc and ^{129}I in solidified LAW secondary liquid wastes

Tc and I Retention in LAW Glass Testing

- Crucible melts – 236 Tc/14 U/14 Hg
- DM10 – 48 feeding tests and 7 idling tests to date
- DM100
  - Total of four fifty-hour tests using two LAW compositions.
- DM1200
- Single pass results – no recycle

DM-10

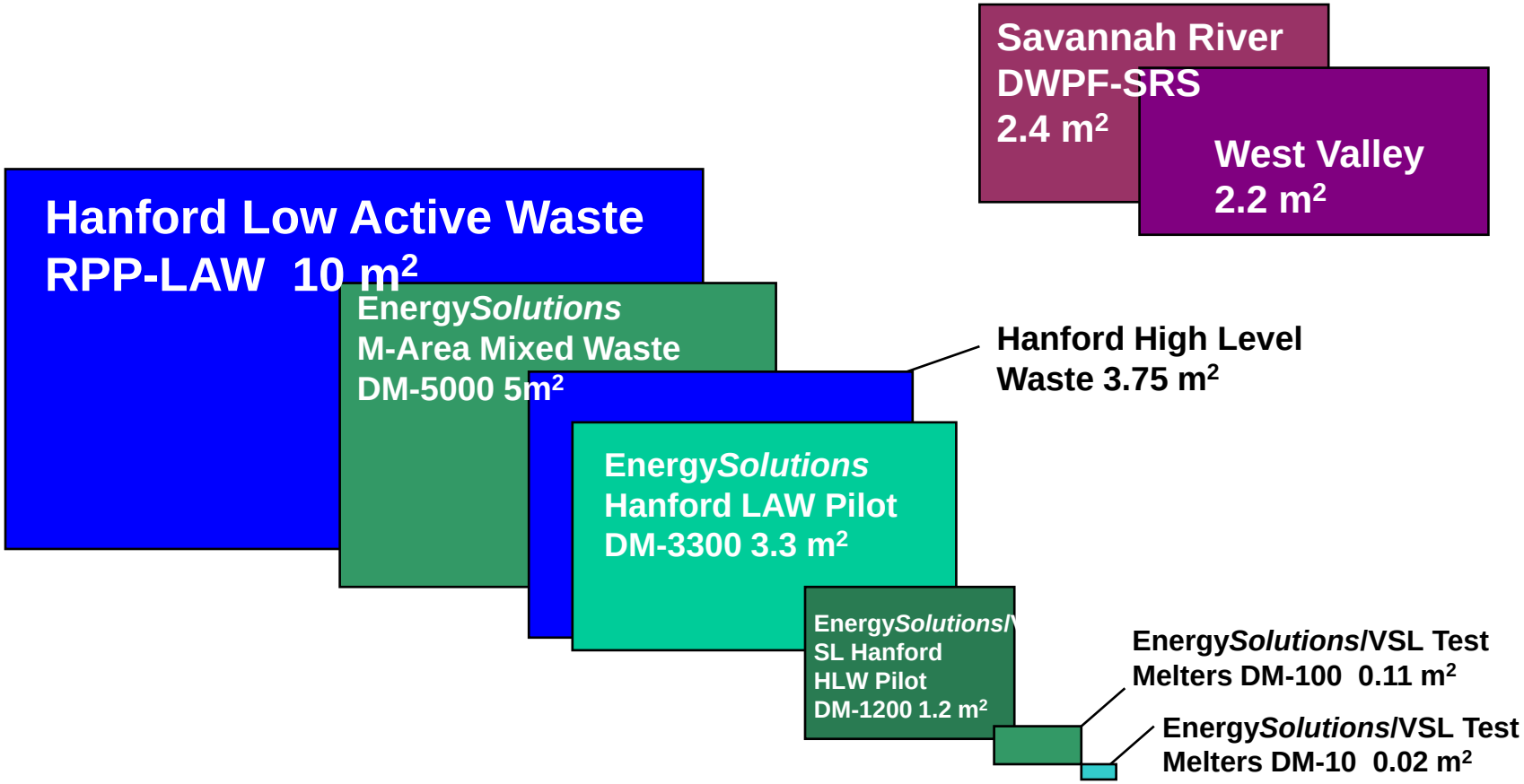
washington river protection solutions

DM-100

DM1200

- DM1200, Washington, DC
- One-third scale, 1.2 m^2
- Commissioned January 2001; over 650,000 lbs of glass made
- Prototypical HLW/LAW off-gas train:
  - Film-cooler/ SBS/ WESP/ HEME/ HEPA/ TCO/SCR/ AgM/SAC/PBS

Melter Scale Comparisons



Tc and I Management Variables

- Variables
  - Additives
  - Reductants –type and concentration
  - Bubbler gas – rate and composition
  - Melt temperature
- ^{99m}Tc used as Tc source
- Rhenium to be used as Tc surrogate for DM1200 test

Tc and I Management Tests Variables

- Glass forming chemicals in reduced form
  - Magnetite or iron oxalate
  - Vanadyl oxalate
  - Tin(II) oxalate
  - Garnet
  - Chlorite
- Formic acid
- Cs (cesium) impact on Tc retention

Tc and I Management Results to Date

- Nominal retention with out modifications from these tests or recycle = 19% I/34% Tc
- Zr ~ 12% increase in Tc retention
- Sugar most effective for Tc and I retention. As sugar stoichiometry increased from 0.5 to 0.75:
  - ~ 24-40% increase in I retention
  - ~15-20% increase in Tc retention
  - Potential disadvantage – glass pool may become too reducing

Tc and I Management Results to Date

- Magnetite versus hematite as iron source ~ 7% increase in Tc retention (no change in I retention)
- Bubbler gas rate/composition – no effect on Tc or I retention
- Temperature –Tc retention increases as temperature is lowered (about 0.1 to 0.36% absolute with $1^{o}C$ decrease in temperature). I retention increases as temperature is lowered, but change is within the precision of the measurement

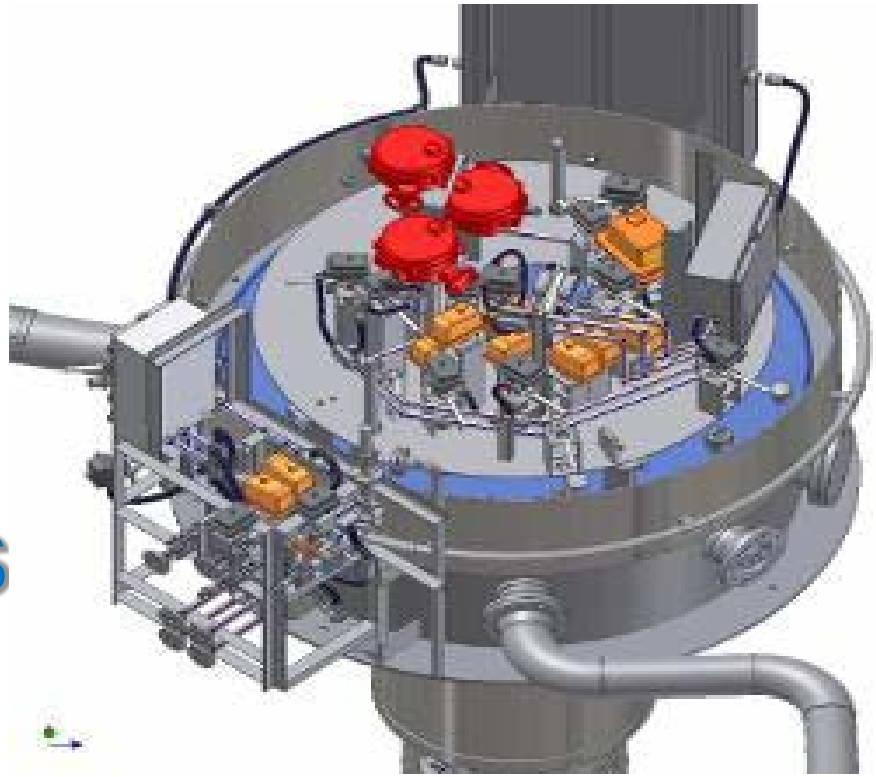
Tc and I Management Future Tests

- Complete analysis of DM10 tests
- Scale up to DM100 and DM1200 based on best results to date
- DM1200 off-gas treatment Tc/I balances
- DM1200 off-gas organic constituents

Contact information

- Thomas H May
- 372-2493
- Thomas_H_Tom_May@rl.gov

INTEGRATED DISPOSAL FACILITY REGULATORY REQUIREMENTS



Felix R. Miera
Manager, Environmental Projects -- WRPS

June 14, 2010

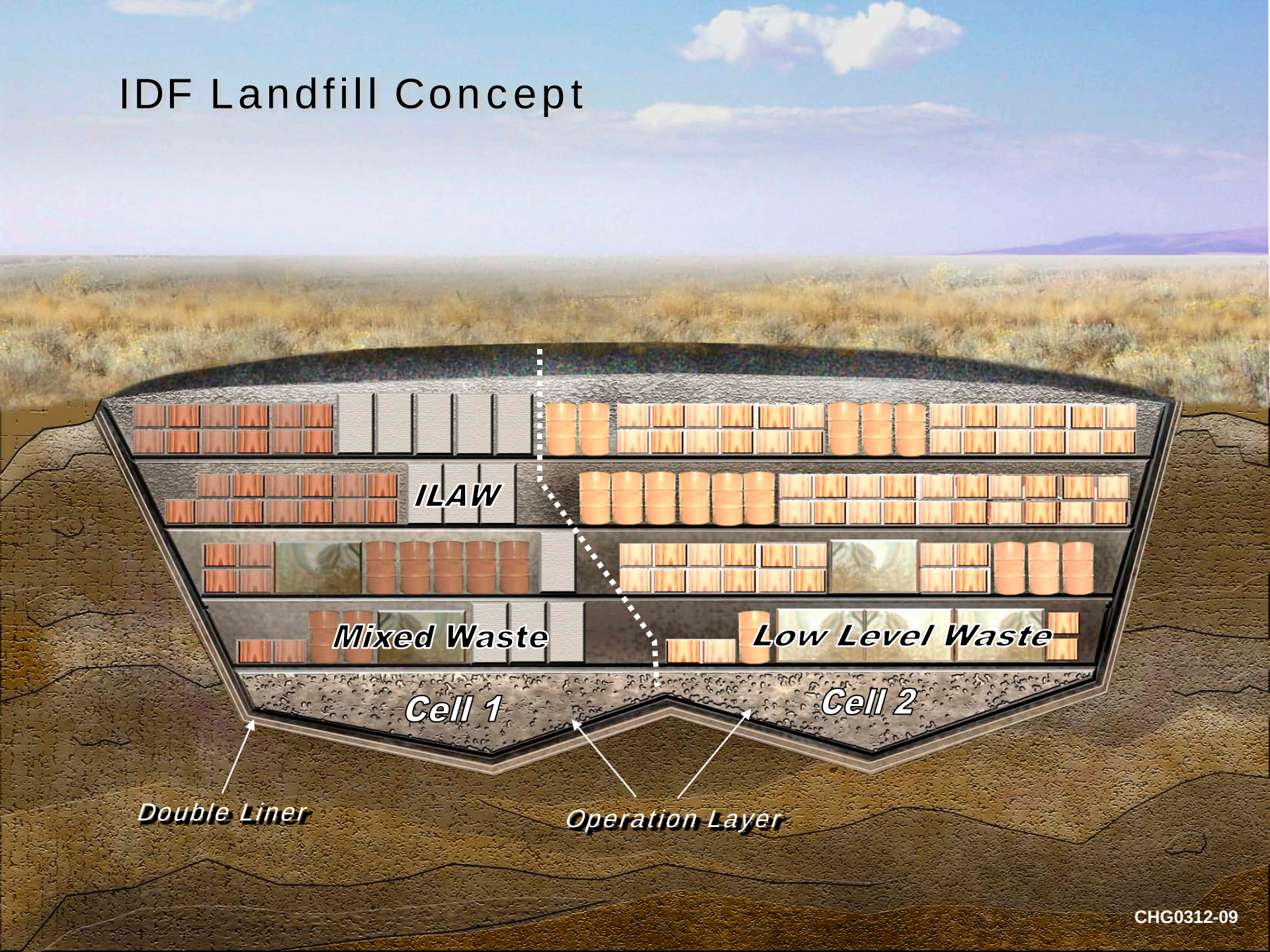
DESIGN OBJECTIVES

- Design, construct, and operate all DOE nuclear facilities to protect public health and the environment;
- Protect construction and operations personnel from occupational hazards and minimize occupational exposures to radioactive and chemical hazards;
- Install double liners with leachate collection systems and secondary leak detection technology;
- Transport waste and other materials in accordance with Department of Transportation and DOE requirements;
- Close the LLW and MMLW disposal facilities with engineered caps (barriers) designed and installed to meet regulatory requirements;
- Install environmental monitoring systems to detect potential releases to the environment;
- Dispose of LLW and MLLW containing more mobile contaminants in high-integrity containers or by encapsulating the waste in grout;
- Develop emergency response plans;
- Control dust emissions;
- Use pollution control or treatment to reduce or eliminate releases of contaminants to the environment.

IDF OVERVIEW

- IDF is an expandable double lined landfill including leachate collection and removal, with secondary containment and leak detection system
- Phase 1 lined area size overall is approximately 480 yd wide x 175 yd long x 16 yd deep
- Phase 1 will provide disposal capacity for approximately 216,000 yd^3..
- Cell 1 will be for disposal of mixed low-level waste containing Resource Conservation and Recovery Act (RCRA)/Hazardous Waste Management Act (HWMA) regulated components including Immobilized Low Activity Waste ILAW.
- Cell 2 will be for disposal of low-level waste with no RCRA/HWMA regulated components.

IDF Landfill Concept



IDF OVERVIEW (continued)

- In addition to the regulatory required barriers to protect the environment, the following enhancements are included in the IDF design
  - A Geosynthetic Clay Liner (GCL) layer has been added to the required primary liner to provide a composite barrier [High Density Poly Ethylene (HDPE) and bentonite clay] throughout the landfill cell floor
  - A second GCL layer has been added to the required secondary liner to enhance the effectiveness of the composite barrier under leak detection sump
  - A third HDPE geomembrane liner has been added beneath the liquid collection area to provide a secondary leak detection system.

AERIAL VIEW OF IDF CONSTRUCTION

IDF PERMITTING

- IDF Draft Permit issued for public review – May 6, 2005
- IDF Permit issued as final – March 10, 2006
- IDF Permit Effective – April 9, 2006
- The IDF Permit currently only allows for disposal of certain types of waste:
  - Low-activity glass from the Waste Treatment Plant
  - Glass waste from Bulk Vitrification
  - Dangerous waste resulting from IDF operations
- Other waste forms may be permitted after completion of the Tank Closure & Waste Management EIS
- IDF Permit was modified in November 2007 to place the facility in a stand-by mode until such time as waste is ready to be placed in the facility – Primarily driven by the delay in hot operation of the Waste Treatment Plant.

HAB ADVICE #175 (6/17/2005)

- "The IDF Permit should be modified to ensure subsequent Permit modifications require cumulative risk analysis of all wastes previously disposed in the IDF in addition to those proposed in future IDF Permit modifications."

  Ecology response to Advice (dated 8/16/2005): "We agree that a cumulative risk analysis of all wastes disposed in the IDF is needed. A condition has been added to the permit requiring the U.S. Department of Energy (USDOE) to conduct such an analysis each time new wastes are brought into the facility."

  - ✓ Added Permit Condition III.11.I.5.a, Modeling – Risk Budget Tool

- "Per the Board's prior advice, the Tri-Party Agreement should require cumulative risk analyses of all wastes disposed at Hanford."

✓ DOE is currently preparing a "Performance Assessment" required by DOE Orders that will evaluate cumulative risk of all wasted disposed at the IDF. The draft Performance Assessment will be issued after DOE-HQ review.

IDF PERMIT CONDITIONS OF INTEREST

- *Permit condition III.11.A.1.o.* Six months prior to IDF operations Permittees shall submit to Ecology for review, approval, and incorporation into the permit, all waste acceptance criteria (WAC) to address, at a minimum, the following: physical/chemical criteria, liquids and liquid containing waste, land disposal restriction treatment standards and prohibitions, compatibility of waste with liner, gas generation, packaging, handling of packages, minimization of subsidence.

- *Permit condition III.11.A.1.p*. ILAW Waste Acceptance Criteria -- The only ILAW forms acceptable for disposal at IDF are: (1) approved glass canisters that are produced in accordance with the terms, conditions, and requirements of the WTP portion of the Permit, and (2) the 50 bulk vitrification test boxes as specified in the DBVS test plans.

For any ILAW glass form(s) that DOE intends to dispose of in IDF, DOE will provide to Ecology for review, an ILAW Waste Form Technical Requirements Document (IWTRD).

IDF PERMIT CONDITIONS OF INTEREST (continued)

- *Permit condition III.11.A.1.p.* A performance assessment that provides a reasonable basis for assurance that each glass formulation will, once disposed of in IDF in combination with the other waste volumes and waste forms planned for disposal at the entire Integrated Disposal Facility, be adequately protective of human health and the environment; and will not violate or be projected to violate all applicable state and federal laws, regulations and environmental standards.

➢ Within 30 days of a request by Ecology, the Permittees shall provide a separate model run using Ecology's assumptions and model input.

- IDF Permit was modified for the performance assessment to be submitted for Ecology review as soon as possible after issuance of the Final Tank Closure and Waste Management EIS , and at least 180 days prior to the date DOE expects to receive waste at IDF.

IDF PERMIT CONDITIONS OF INTEREST (continued)

- *Permit condition III.11.A.I.s.i.* "The Permittees must create and maintain a **modeling - risk budget tool**, which models the future impacts of the planned IDF waste forms …and their impact to underlying vadose and ground water."

  - Modeling should represents a cumulative risk analysis of all waste previously disposed of in the entire IDF (both cell 1 and cell 2) and those wastes expected to be disposed of in the future for the entire IDF.

  - The groundwater impact should be modeled in a concentration basis and should be compared against various performance standards including but not limited to drinking water standards.

  - No waste shall be disposed of that will result ("through forward looking modeling or in real groundwater concentrations data") in a violation of any state or federal regulatory limit, specifically including but not limited to drinking water standards for any constituent as defined in 40 CFR 141 and 40 CFR 143.

IDF PERMIT CONDITIONS OF INTEREST (continued)

- Model is to be submitted for Ecology review at least 180 days prior to the date DOE expects to receive waste at IDF.

- Model is to be updated every 5 years.

- *Permit Condition III.11.A.I.5.* In accordance with DOE's authority under the Atomic Energy Act of 1954, as amended and other applicable law, prior to disposing of any mixed immobilized low-activity waste (ILAW) in the IDF, DOE will certify to the State of Washington that it has determined that such ILAW is not high-level waste and meets the criteria and requirements outlined in DOE's consultation with the U.S. Nuclear Regulatory Commission….

Immobilized Secondary Waste Form Options

Joe Westsik

Pacific Northwest National Laboratory

ORP Educational Forum

Secondary Waste Management

June 14, 2010

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Immobilization Methods

- Cast Stone
- Low-Temperature Immobilization Study
  - Ceramicrete phosphate bonded ceramic
  - Duralith alkali-aluminosilicate geopolymer
  - Alkali-aluminosilicate hydroceramic cement
- Encapsulated Fluidized-Bed Steam Reformer product
- Other waste forms

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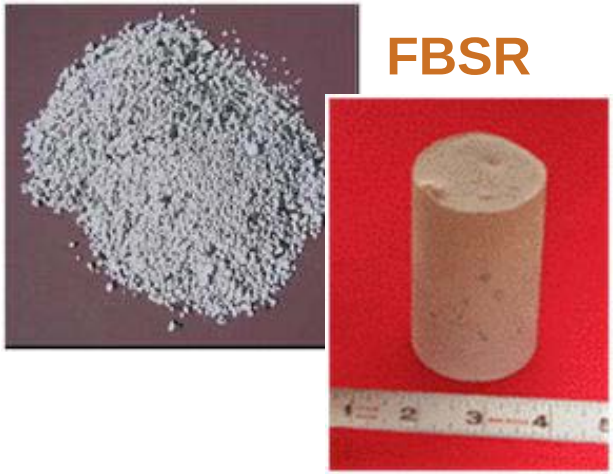
Waste Forms

Cast Stone

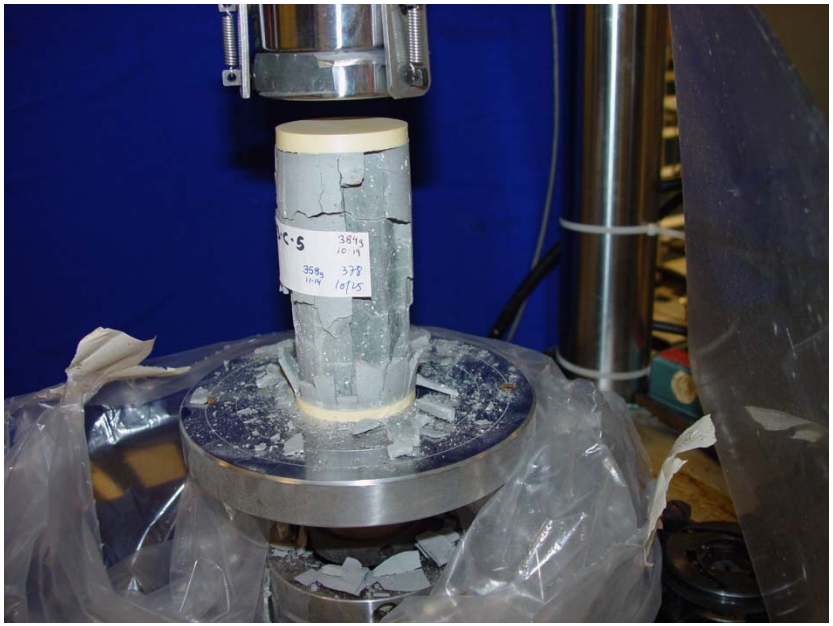
Ceramicrete
Side
Ceramicrete
Hanford Secondary Waste
HSN/NS/102005/7

Duralith
TB-9R3-Samples
VSL/CUA
Duralith
HW
5 cm


FBSR

Waste Form Characterization

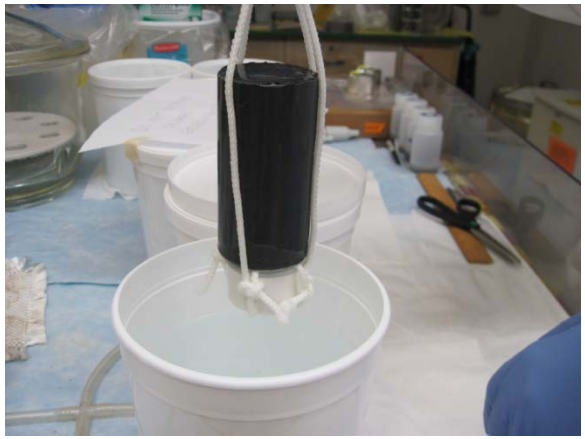
- Waste loading
- Compressive strength
- ANSI/ANS 16.1 Leachability

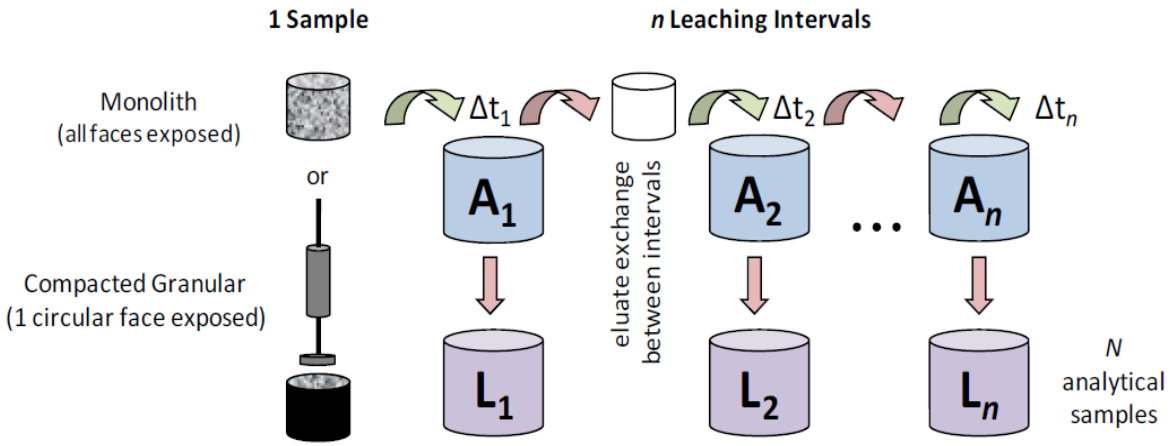


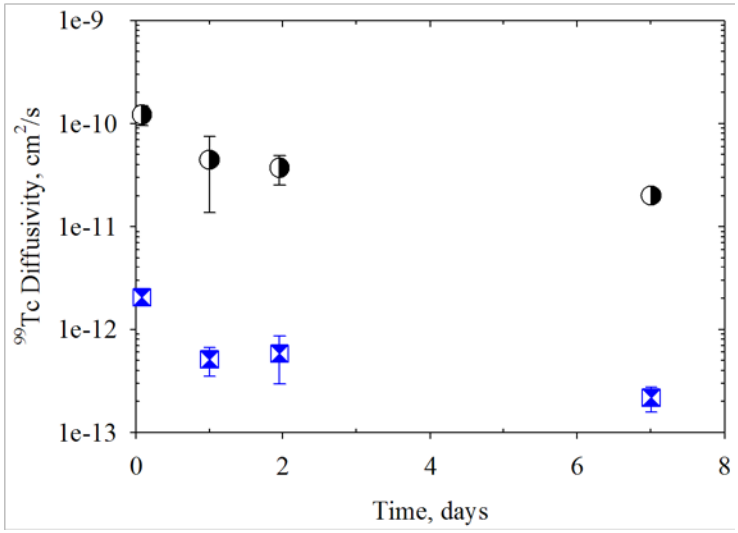
EPA Test Methods

- Toxicity Characteristic Leaching Procedure (TCLP) (Method 1311)
- Liquid-Solid Partitioning as a Function of Liquid to Solid Ratio (Draft Method 1313)
- Liquid-Solid Partitioning as a Function of pH (Draft Method 1316)
- Mass Transfer Rates of Constituents in Monolith (Draft Method 1315)
- Liquid-Solid Partitioning Using an Up-Flow Percolation Column (Draft Method 1314)

EPA Draft Method 1315







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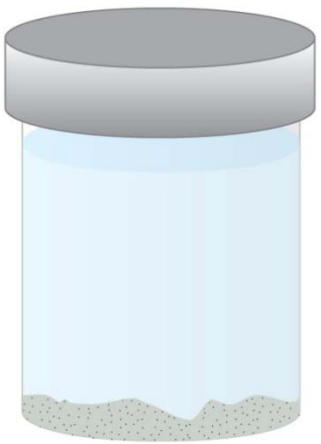
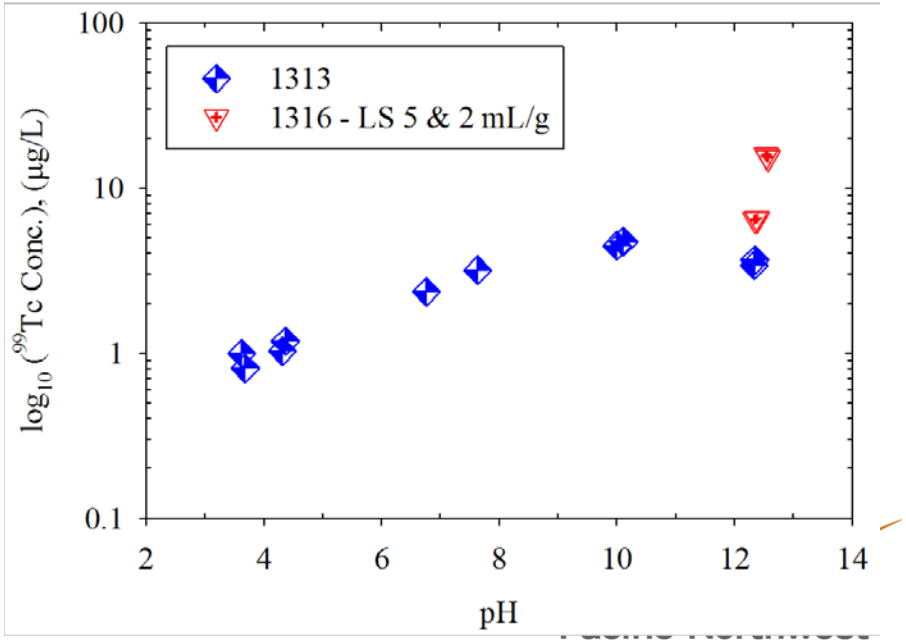
EPA Draft Methods 1313 and 1316



- Static leach test methods
- Crushed material
- Method 1313
  - Fixed pH by acid/base additions
    - HNO_3 (titration curve)
    - pH – 3.6, 4, 7, 10, and 12
- Method 1316
  - De-ionized water
  - Liquid to solid ratio
    - 10, 5, and 2 mL/g
    - 10 g of solid
  - 24 hr. contact time
  - Material controls pH



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Cast Stone

- CH2M Hill, Inc
- Ingredients
  - Portland Cement type I, II
  - Fly Ash Class F
  - Blast Furnace Slag
- Getters Tested
  - Bone char, bone ash, bone black, synthetic apatites, iron (Fe^0) powder, Fe- phosphate, silver (Ag)-zeolite, tin (Sn[II])-apatite
- Wastes
  - Basin 43 Waste – LERF
  - Low-Activity Waste (LAW) Simulant loading 8.2 – 24.2% wt
  - Iodine (I)-rich caustic waste - Hanford

Cast Stone

Parameter	Value	Acceptance Criteria	Test Method
Compressive Strength	8.0 – 16.3 MPa	>3.45 MPa	ASTM C39

- TCLP (EPA Method 1311) & WAC 183-303-140
  - Met Universal Treatment Standards (UTS) and WAC criteria
  - Cr failed UTS at highest waste loading (24.2% wt)

Cast Stone

- ANSI / ANS -16.1 Leachability Indices

Component	Leachability Index
^{99}Tc (techetium-99)	9.5 – 10.4
^{129}I (iodine-129)	>7.9
Cr (chromium)	~12.4 – 13.3
NO_3^- (nitrate)	7.5 – 8.5
NO_2^- (nitrite)	7.5 – 8.6

- The larger the LI value the less mass leaches
  - LI = -log of effective diffusion coefficient (e.g., $D_e = 10^{-9}$ equates to LI = 9; $D_e = 10^{-12}$ equates to LI = 12
- Getters reduce leachability
  - Sn-Apatite reduces ^{99}Tc leachability (LI ~12.7)
  - Ag mordenite reduces leachability : I >11, Ag 13.9 – 15.7

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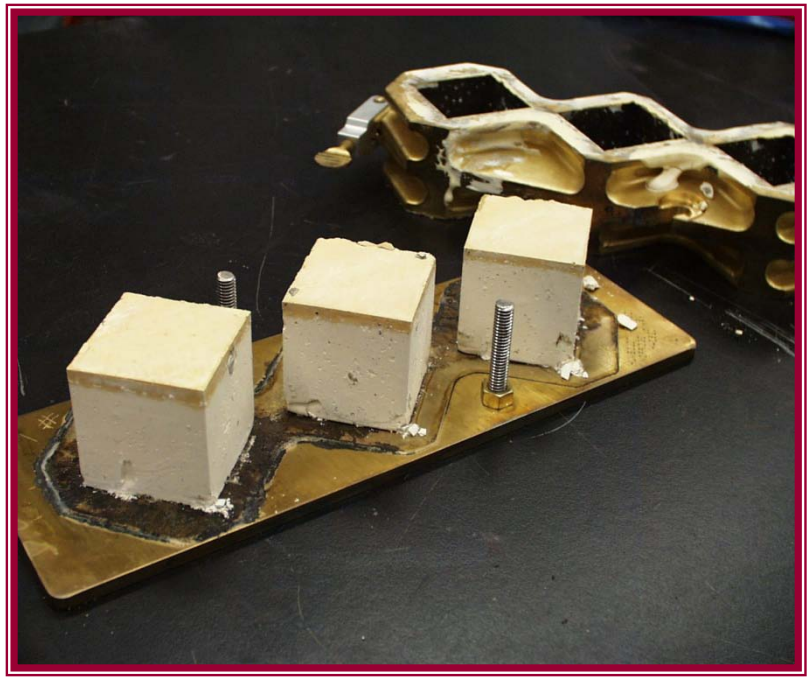
Low-Temperature Immobilization Study 2005 – 2006

- Seek solutions from private sector to demonstrate low-temperature immobilization technologies for mixed radioactive and hazardous waste
  - Low-temperature waste forms must contain volatile radionuclides including Tc and I
  - Only mature technologies with feasibility of deployment within 1 to 2 years were to be considered
- Conduct screening tests using low-temperature (<150° C) immobilization technologies on Hanford Tank Waste Treatment and Immobilization Plant (WTP) caustic scrubber and Idaho Sodium Bearing Waste (SBW) simulants

Alkali Aluminosilicate Hydroceramic Cement



- Mississippi State University
- Ingredients:
  - Sodium hydroxide
  - Metakaolin
  - Vermiculite
  - Silica
  - Sodium sulfide
  - Waste
- Developed as higher temperature process yielding insoluble sodalites and zeolites

Phosphate Bonded Ceramic

- CH2MHILL &
  Argonne National Laboratory (ANL)
- Ingredients:
  - Magnesium oxide
  - Potassium acid phosphate
  - Calcium silicate
  - Waste

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$$

Alkali Aluminosilicate Geopolymer

- Catholic University of America (Vitreous State Laboratory – VSL/CUA)
- Ingredients
  - Silica and alumina source
  - Alkaline solution
- Forms amorphous or partially microcrystalline geopolymer
- Three-dimensional matrix
  - poly sialate (-Si–O–Al–O-)
  - poly sialate-siloxo (-Si–O–Al–O–Si-)
  - sialate-disiloxo (-Si–Al–Si–O–Si–O-)

TB-9R3-Samples
VSL/CUA
Duralith
HW

5 cm

Hanford Secondary Waste Simulant

(caustic scrubber solution from LAW vitrification offgas treatment)

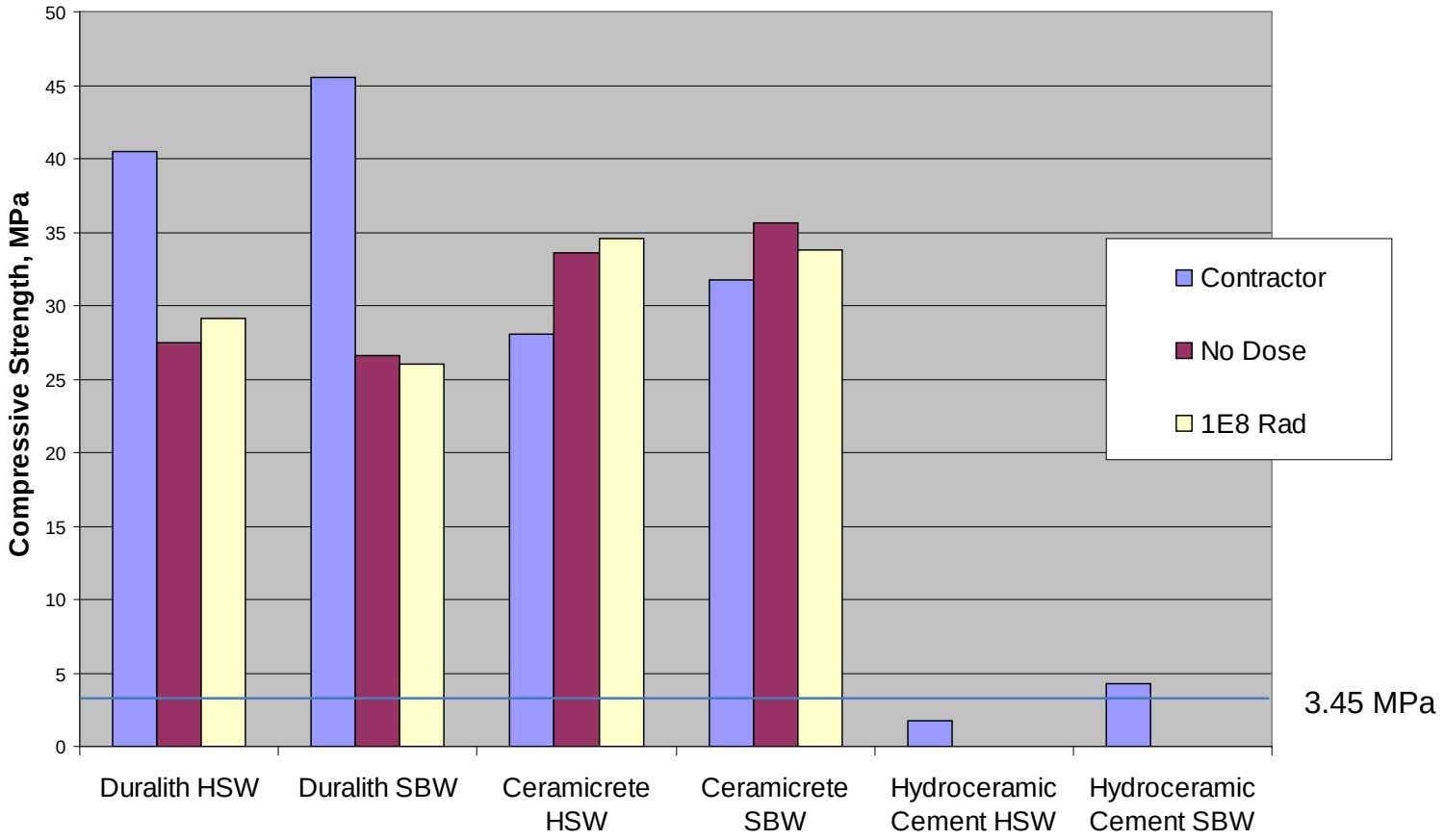
Element	Target (moles/L)	Target (g/L)
Na	2	46
Al	0.011	0.299
Cr	2.80E-04	0.0145
Ag	2.20E-04	0.0237
Cd	1.40E-05	0.00157
Re (analog for Tc)	6.00E-07	1.12E-04
I	2.90E-06	3.68E-04
Hg	2.40E-06	4.81E-04
Pb	1.50E-04	0.031
CO_3^-	0.96	57.6
NO_3^-	0.018	1.116
OH^-	0.094	1.598
TOC	0.18	13.86

TCLP Results,
expressed in milligrams per liter (mg/L)

	Duralith		Ceramicrete		Hydroceramic Cement	
	HSW	SBW	HSW	SBW	SBW	UTS
Ag	<0.07	<0.07	0.008	0.003		0.14
Cd	<0.03	<0.03	<0.0003	<0.0003	0.6	0.11
Cr	0.015	0.04	0.05	<0.002	0.003	0.6
Hg	<0.01	<0.01	<0.008	<0.008	0.1	0.025
Pb	<0.1	<0.1	0.01	0.001		0.75

UTS = Universal Treatment Standards in 40 CFR 268.48

Compressive Strength
(Acceptable Target > 3.45 MPa (500 psi))



ANS-16.1 Leachability Index Results (Rhenium [Re] and Iodine)

- Duralith
  - Bettered Leachability Index (LI) target (Re/Tc LI > 9)
  - Did not meet LI target (iodine LI >11)
- Ceramicrete
  - Did not meet target for Re/Tc leachability
  - ANL work with Tc eluate and magnesium potassium phosphate ceramic (MKP)
    - Tc LI in the range of 11 to 14.5 for MKP with $SnCl_2$
    - Tc Li in the range of 8.5 – 9 for MKP without $SnCl_2$
  - No iodine detected in leachate so could only report less than values below target
- Testing with improved analytical sensitivity required to have confidence in Re and I results

Summary – Low Temperature Immobilization Study

- “Ceramicrete” phosphate bonded ceramic and “Duralith” alkali aluminosilicate geopolymer show potential based on TCLP, compressive strength and sodium (Na) leachability index requirements

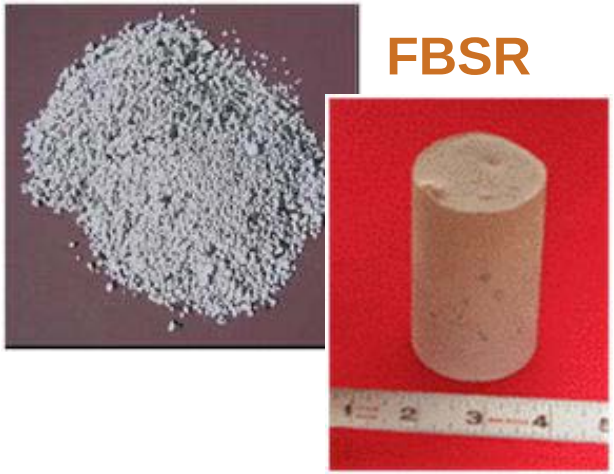
- Re (Tc) and iodine immobilization not easily demonstrated at expected low waste concentrations

Waste Forms

Cast Stone

Ceramicrete
Side
Ceramicrete
Hanford Secondary Waste
HSN/NS/102005/7

Duralith
TB-9R3-Samples
VSL/CUA
Duralith
HW
5 cm


FBSR

Compressive Strength
3.45 MPa (500 psi) Minimum

	Cast Stone	Ceramicrete	Duralith Geopolymer	FBSR / Geopolymer	Saltstone
Other Wastes	8.0 – 16.3			8.6 – 15.2	6.3 – 8.4
Secondary Waste		28.1 - 33.6	27.5 – 40.5		
Secondary Waste Irradiated		34.6	29.1		

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Leachability Index – Tc (ANSI/ANS 16.1 or EPA Draft Method 1315)

	Cast Stone	Ceramicrete	Duralith Geopolymer	FBSR / Geopolymer	Saltstone
Other Wastes – Tc	9.5 – 10.4	8.5 ---14.6			11.4
Secondary Waste – Tc	12.1		10.2		
Secondary Waste – Re		7.2	10.4		

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TCLP

	Cast Stone	Ceramicrete	Duralith Geopolymer	FBSR / Geopolymer	Saltstone
Other Wastes	Pass except for Cr at highest waste loading			Pass except for Se in highly spiked waste	Pass
Secondary Waste		Pass	Pass		

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Next Steps

- Waste form development and optimization
  - Optimize waste loading
  - Evaluate robustness of waste form to waste variability
  - Cast Stone, Ceramicrete, Duralith
- Fluidized Bed Steam Reformer product characterization
- Mechanisms of radionuclide retention to support waste form selection
- Demonstrate compliance with waste acceptance criteria
- Final waste form selection
- Testing to support design
- Testing to support Integrated Disposal Facility (IDF) performance assessment

Questions?

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Technetium Management

Joe Westsik
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ORP Educational Forum

Secondary Waste Management

June 14, 2010

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Objective

- Develop technologies and approaches to effectively manage technetium-99 (^{99}Tc) in low-activity waste (LAW), off-gas recycle streams, and secondary wastes
  - Reduce environmental impact of LAW and secondary waste disposal at Hanford Integrated Disposal Facility (IDF)
  - Provide for alternative disposal paths for liquid LAW off-gas recycle, thus reducing LAW glass production needs

Tc-99 Removal Using Goethite Precipitation

- Possible solution:
  - Remove Tc from LAW melter off-gas recycle stream and divert to high level waste (HLW) vitrification
- Scope
  - Test laboratory-scale fabrication and characterization of Tc goethite prepared from LAW off-gas recycle and secondary waste aqueous simulants
  - Demonstrate rhenium (Re, a surrogate for Tc) goethite fabrication on bench-scale
  - Evaluate impacts of additional iron on HLW glass
  - Conduct Re goethite melter test

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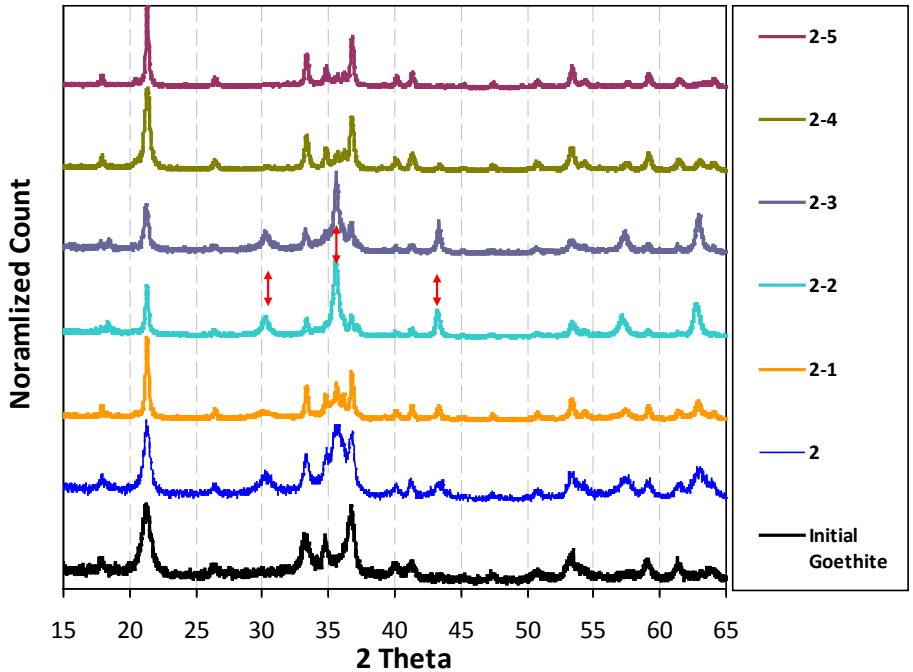
What is Goethite?

- Goethite [α-FeO(III)OH]
- Stable iron oxyhydroxide
- Similar bond length between Fe(III)—O and Tc(IV)—O (2.06 and 2.01 Å, respectively)
- Direct substitution of Tc(IV) for Fe(III) in the goethite mineral lattice possible

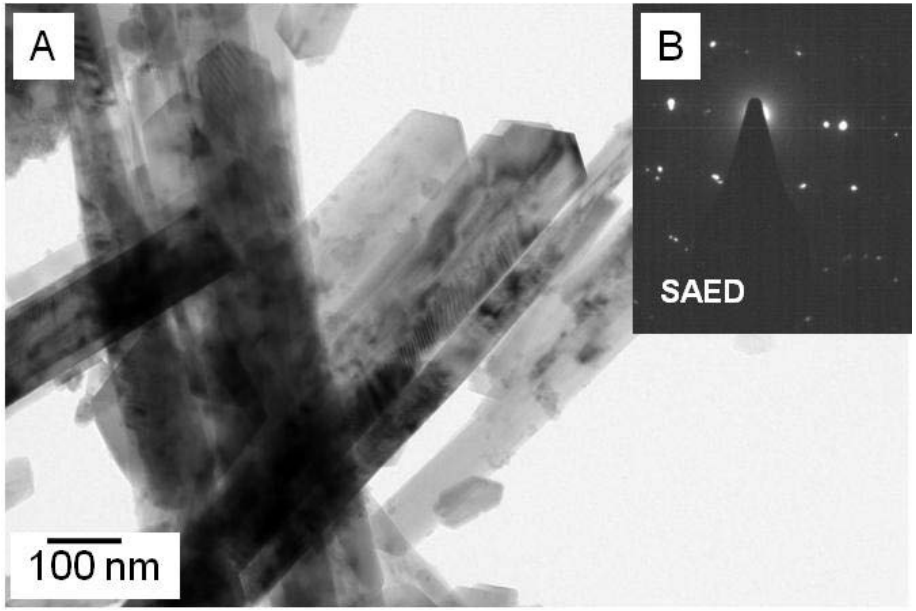
Tc Goethite



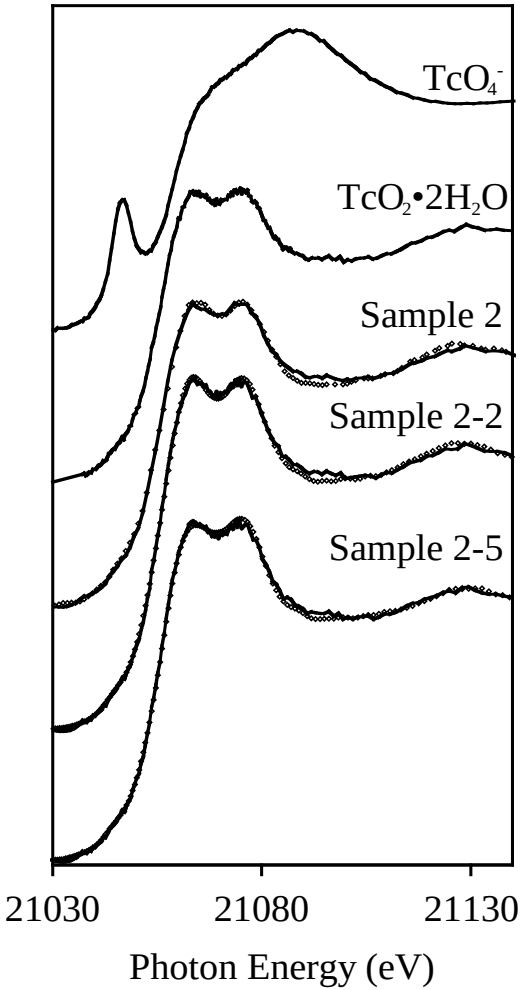
X-ray Diffraction

- Scoping tests with caustic scrubber secondary waste simulant show >90% capture of Tc into goethite mineral
- Final solid form is predominantly goethite with some magnetite

Tc Goethite (Cont.)

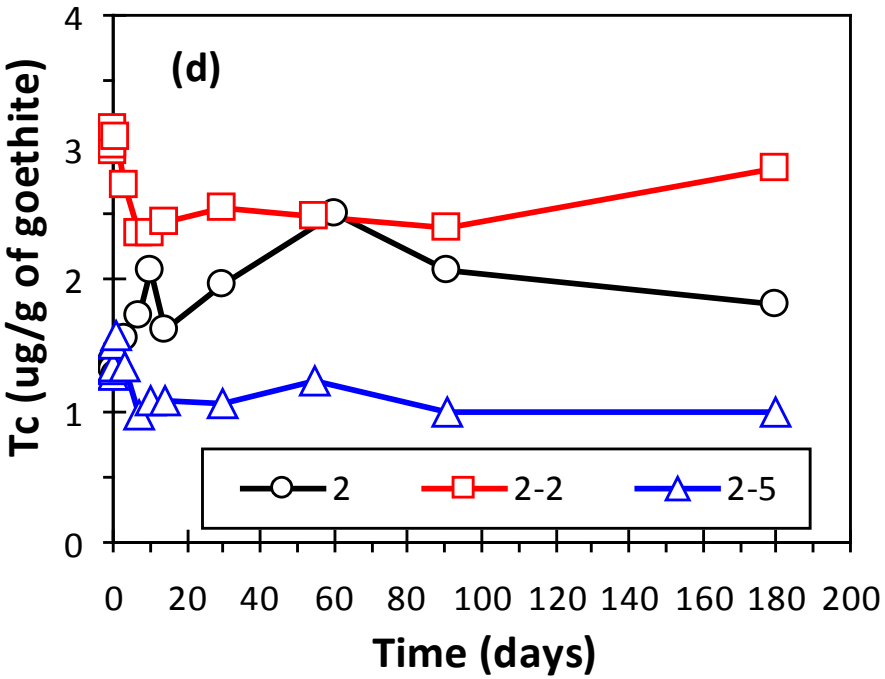


Typical acicular shape of goethite containing Tc incorporated within goethite lattice in transmission electron microscopy (TEM) with selected area electron diffraction (SAED)



Dominant oxidation state Tc (IV) by X-ray absorption near edge spectroscopy (XANES)

Tc Goethite (Cont.)

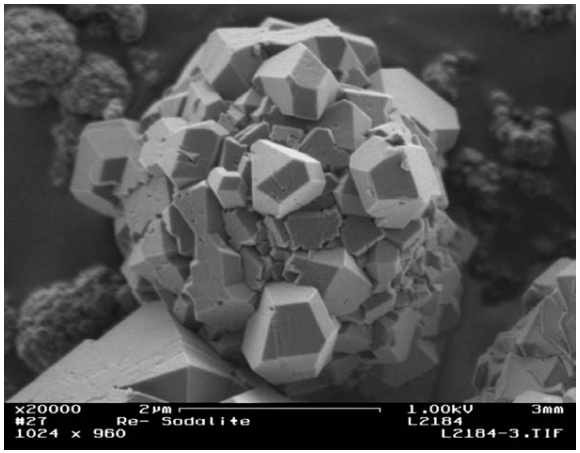


Tc-goethite leaching data for samples 2, 2-2 and 2-5 in the IDF pore water solution

- Armoring with additional goethite (samples 2 and 2-5) reduces Tc re-oxidation (compared with sample 2-2) prepared without additional goethite armoring process.

Improve Retention in Secondary Wastes

- Possible Solution:
  - Develop method to immobilize Tc within stable minerals or structures to reduce Tc release from cements and other low-temperature waste forms
- Scope
  - Characterize initial materials
    - Goethite
    - Functionalized flyash
    - Sodalite



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Technetium Management

- Next Steps
  - Continue work to improve Tc retention in glass during glass melting process
  - Demonstrate goethite precipitation process at bench scale and evaluate impacts to HLW vitrification
  - Evaluate methods to improve Tc immobilization in secondary waste forms.

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