GEN IV International Forum℠

OVERVIEW OF WASTE TREATMENT PLANT, HANFORD SITE

Dr. David Peeler
Pacific Northwest National Laboratory, USA

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Meet the Presenter

Dr. David Peeler received his Ph.D. in Ceramic Engineering from Clemson University. Over the past 25 years, Dr. Peeler has focused on glass formulation development and developing alternative processing strategies to improve operational flexibility and waste throughput for the Defense Waste Processing Facility in Aiken, South Carolina, and for the Waste Treatment Plant in Hanford, Washington.

He currently serves as the Environmental Management Deputy Sector Manager at Pacific Northwest National Laboratory (PNNL), in which over $45M of R&D is annually performed focused on waste processing and environmental remediation.

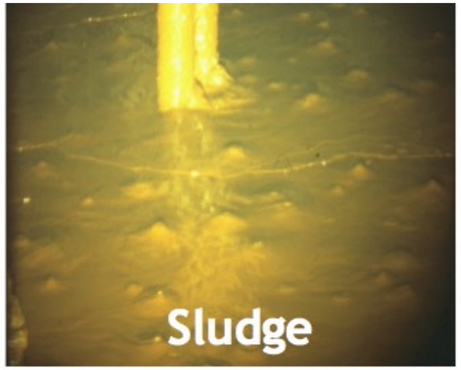
Dr. Peeler serves on the External Advisory Board for Clemson University's Material Science and Engineering Department and is an Adjunct Professor at Clemson. He is a Fellow of the American Ceramic Society and has over 85 external peer reviewed publications, over 300 internal technical reports, and has issued three patent disclosures with one international patent awarded.

David.Peeler@pnnl.gov

Email: David.Peeler@pnnl.gov

“The Challenge”

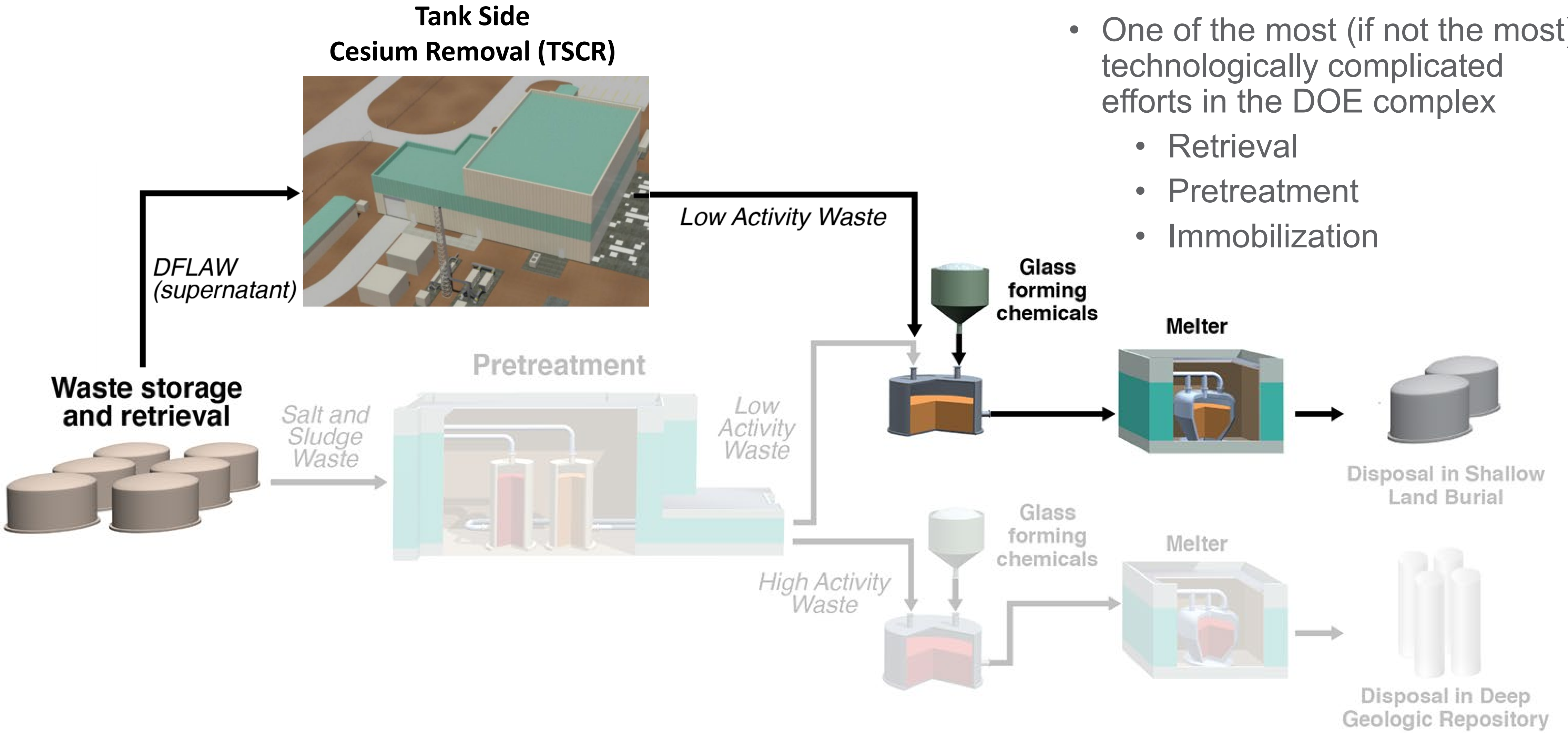
- Approximately 90 million gallons of radioactive liquid waste currently being stored across DOE complex
  - Stored in tanks (~1 million gallon capacity)
  - Stored primarily as a liquid waste
- Legacy waste presents a significant environmental risk
- Fundamental and applied research
  - Develop, mature, and deploy innovative solutions
- Mission
  - Retrieve, pretreat, immobilize and dispose



Outline

- High-level overview of integrated flowsheet
- Waste generation/troublesome components
- Immobilization unit operation
  - Batch to glass conversion process
  - Critical process/product properties
    - Why they are needed
    - How they relate to operations
  - Models and algorithms
  - Operating windows and operational flexibility
  - Operational considerations
    - Examples: “seeing the entire landscape”
- ORP Enhanced Waste Glass Program

Hanford Flowsheet



- One of the most (if not the most) technologically complicated efforts in the DOE complex
  - Retrieval
  - Pretreatment
  - Immobilization

Integrated Flowsheet

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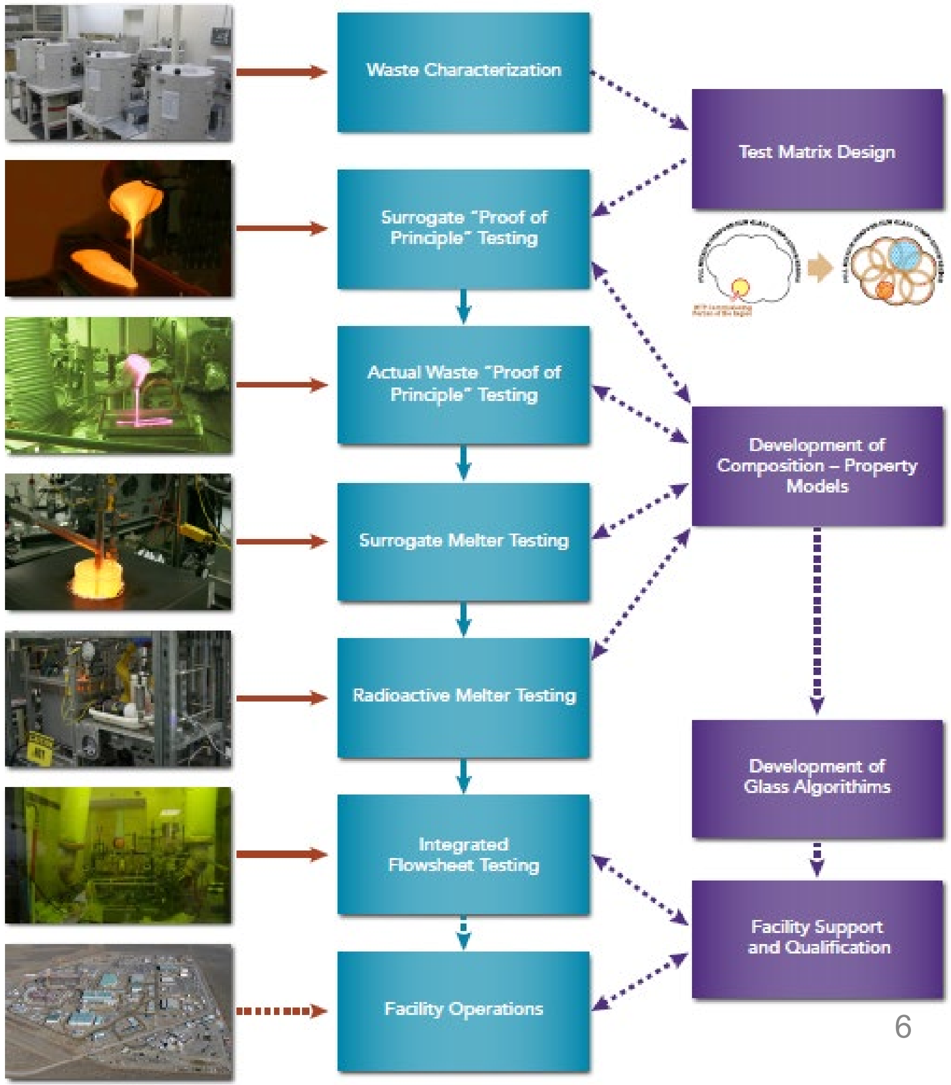
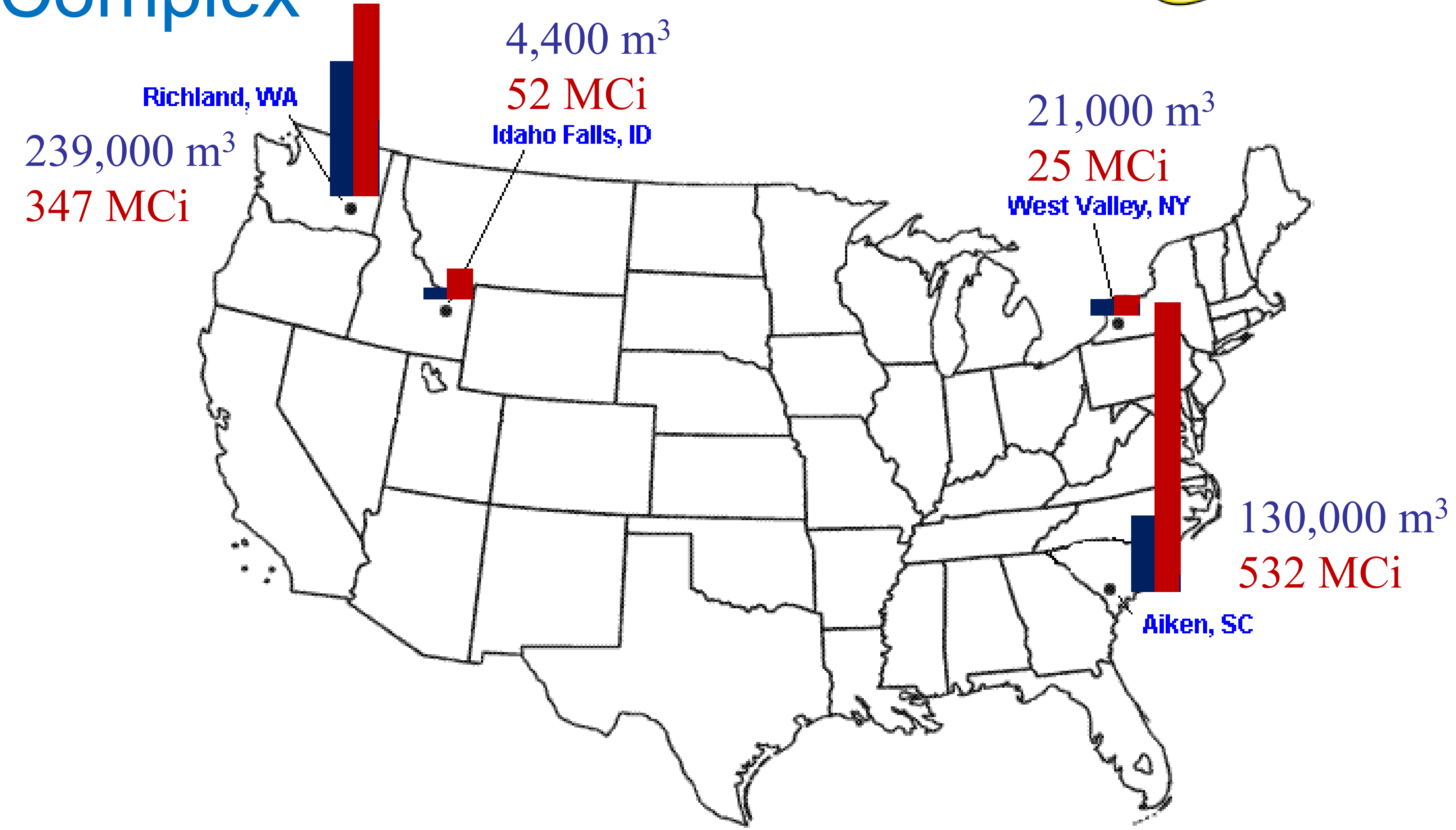
- Major flowsheet unit operations
  - Tank farms – retrieval/blending/washing strategies
  - Pretreatment – dissolution, IX, filtration
  - Vitrification – waste loading, melting rate, waste throughput, operational flexibility
  - **Integration is key**
- Technical challenges/issues (examples):
  - **What are the compositions of these wastes? Problematic components?**
    - **Mitigate by retrieval or blending? Impact on pretreatment decisions?**
    - **Transfer of material between facilities and process vessels – rheology, gel, precipitation issues**
  - What are the related process and product performance requirements? Melter constraints? Performance constraints?
  - How is the process controlled? Impact of process control models on acceptable glass compositional region?



Nuclear Waste Across DOE Complex

- Approximately 90 million gallons of radioactive liquid waste
  - Stored primarily as a liquid waste
    - Sludge, salt cake, and supernate
- ~230 tanks at three primary sites
  - Hanford, Savannah River Site, and Idaho (calcine/SBW)
- Legacy waste presents a significant environmental risk
- Fundamental and applied research required to
  - Develop, mature, and deploy innovative solutions
  - Retrieve, pretreat, immobilize and dispose
- R&D with "eye toward implementation"
  - Define baseline, reduce risk/uncertainty, opportunity for improvement

Nuclear Waste Across DOE Complex



Question

How was it generated?
(compositional complexity)

Generation of Hanford Tank Waste

9 Reactors; 4 Fuel Reprocessing Flowsheets; 100,000 MT Fuel Processed

DOE/RL-2000-43

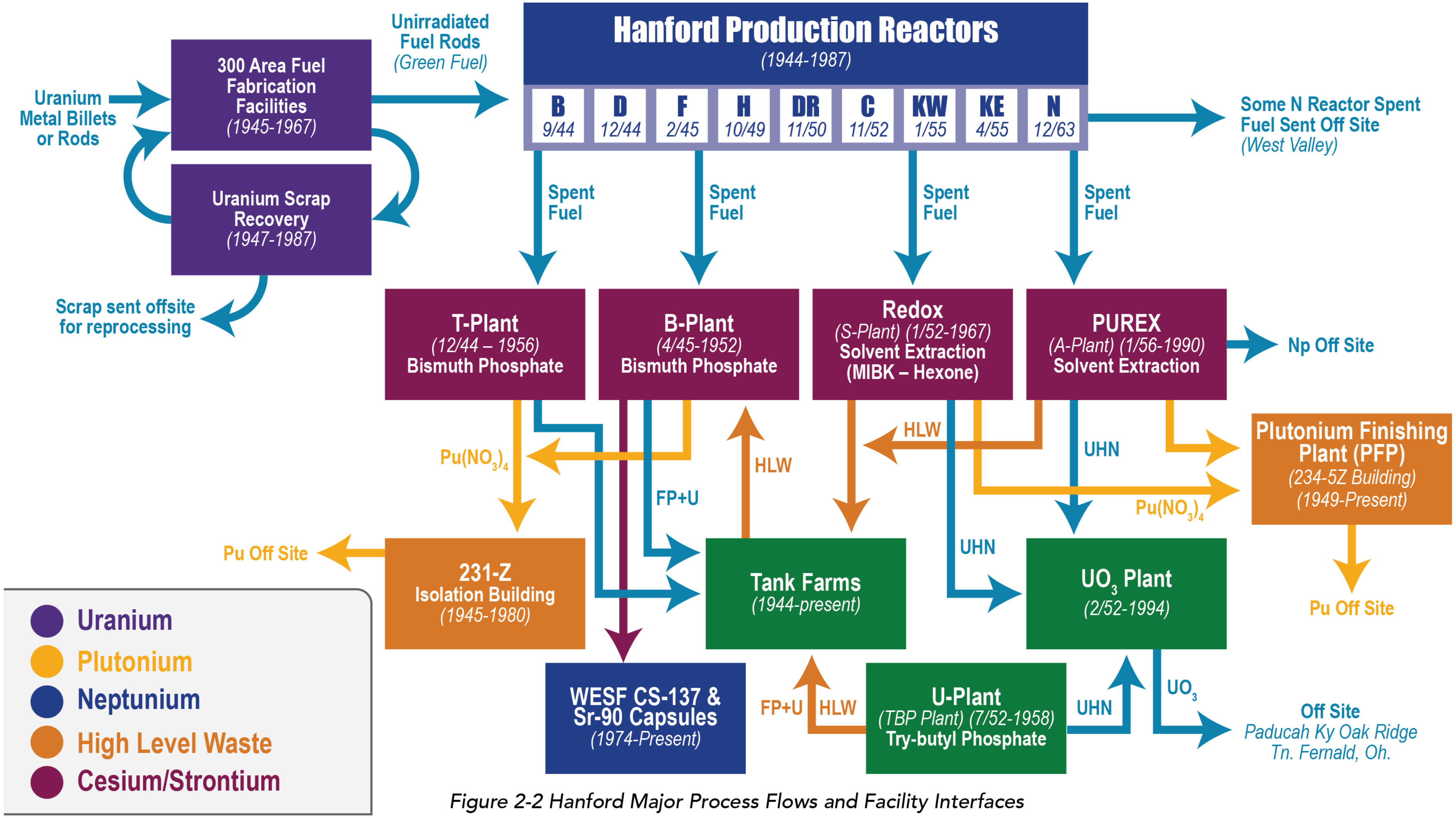
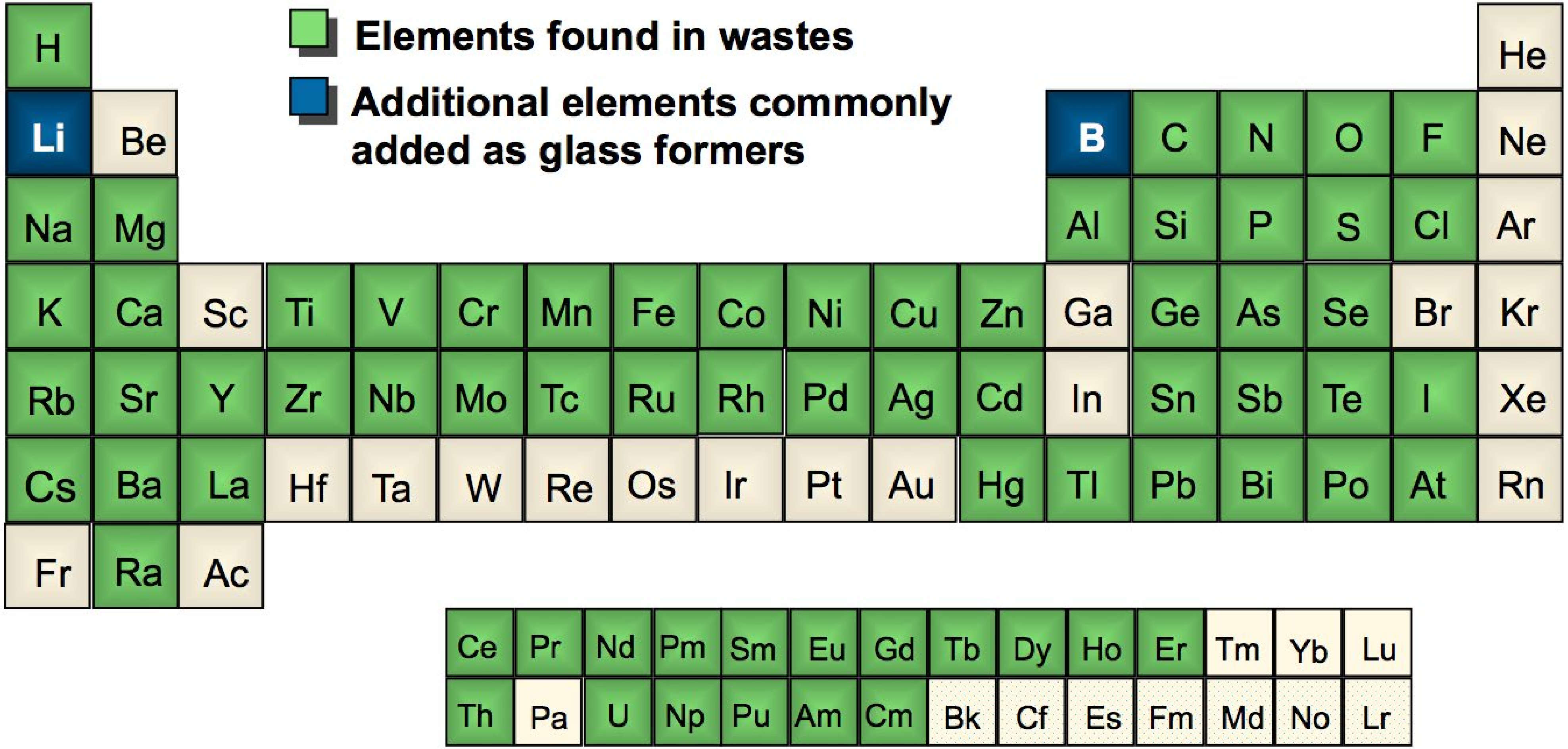


Figure 2-2 Hanford Major Process Flows and Facility Interfaces

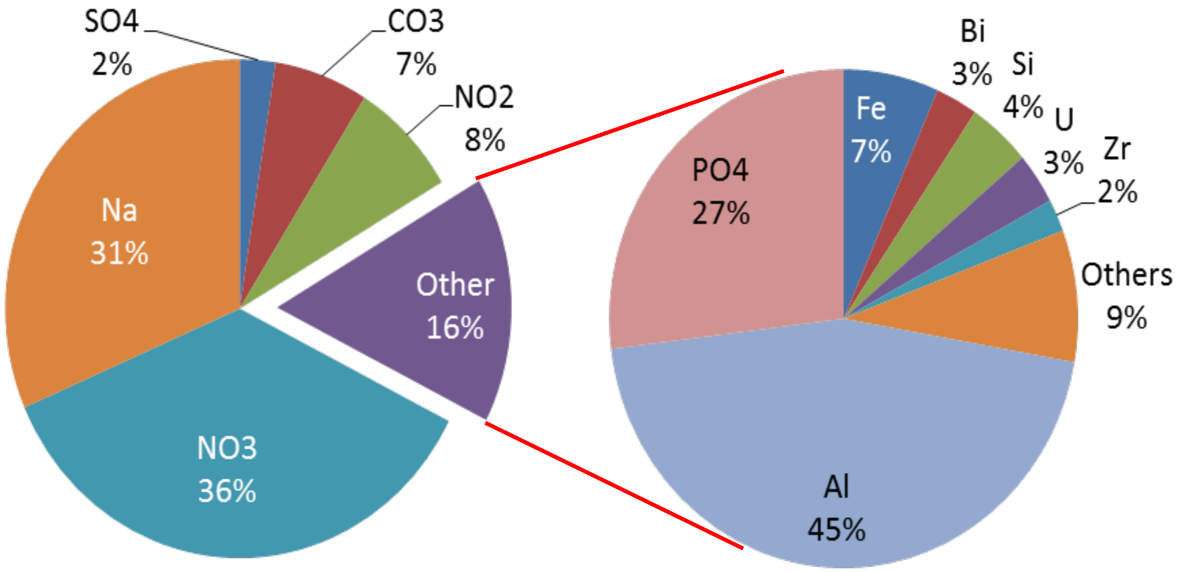
Complexity of Waste



- SRS wastes are a “compositional sub-set” of the diverse waste streams that WTP will have to process
- Not shown: difference in concentration or mass% between Hanford and SRS → e.g., Al, P, Bi, Cr

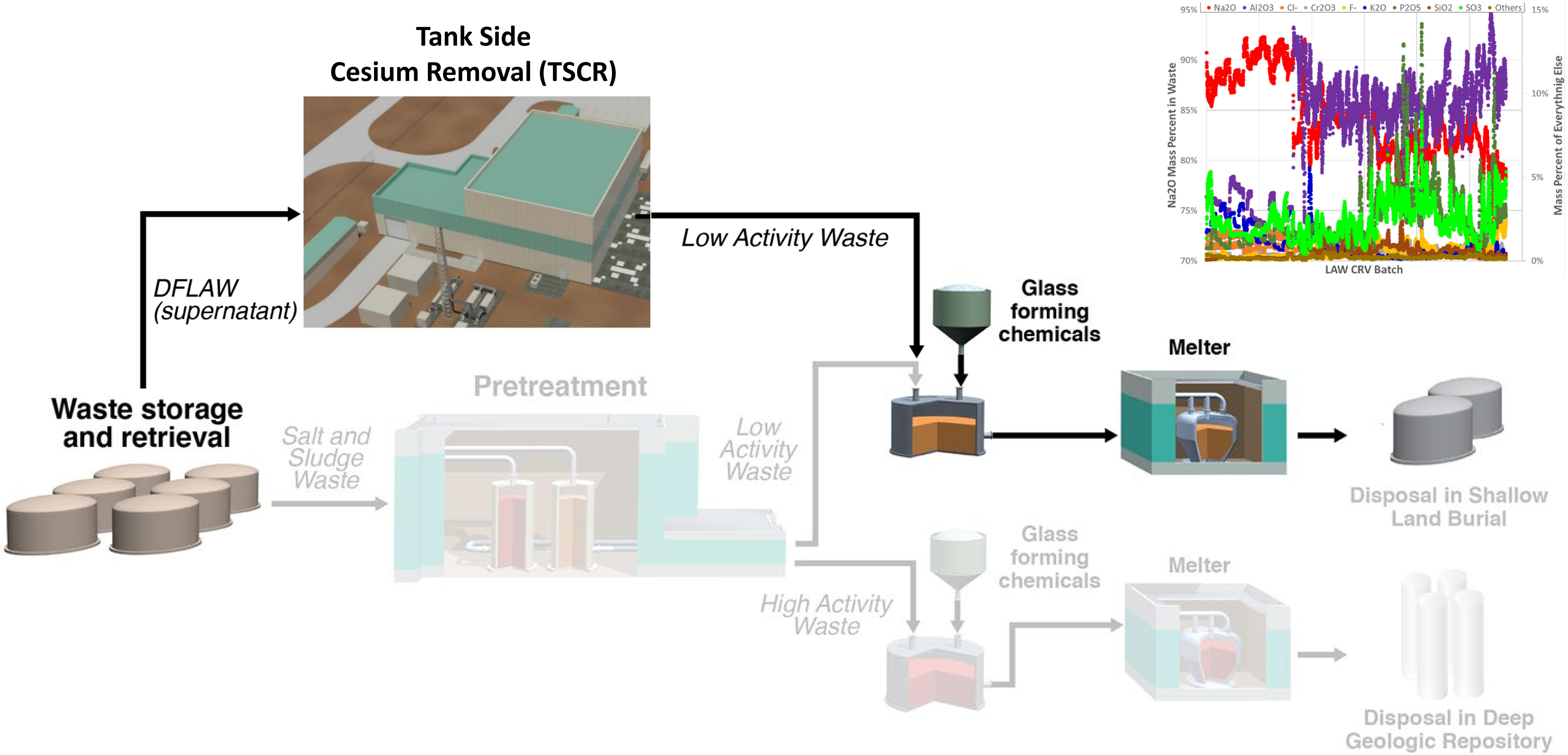
Waste Compositions

- Distinct compositions driven by multiple reprocessing operations

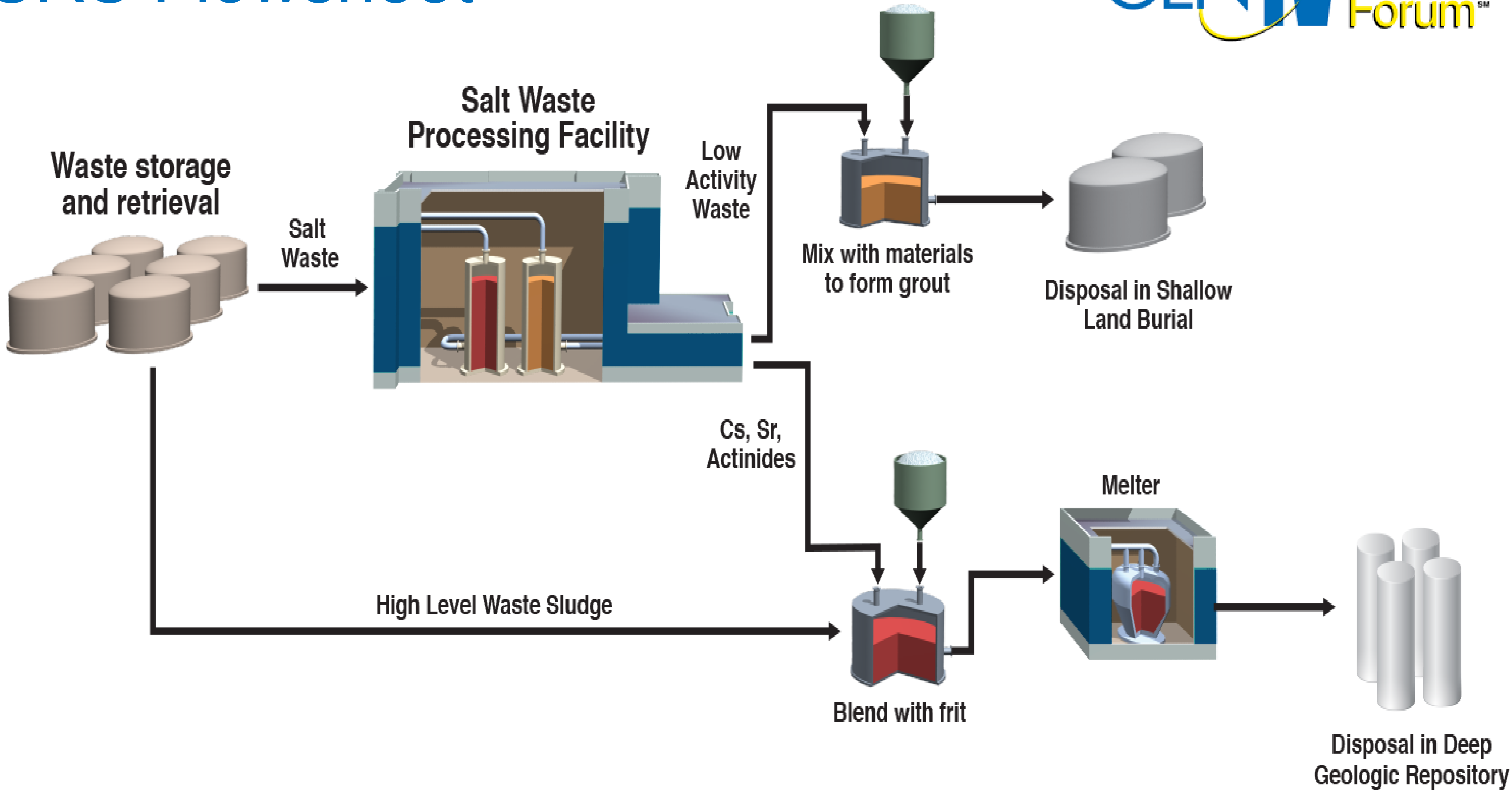


Estimates of Hanford Tank Waste

Hanford Flowsheet



SRS Flowsheet



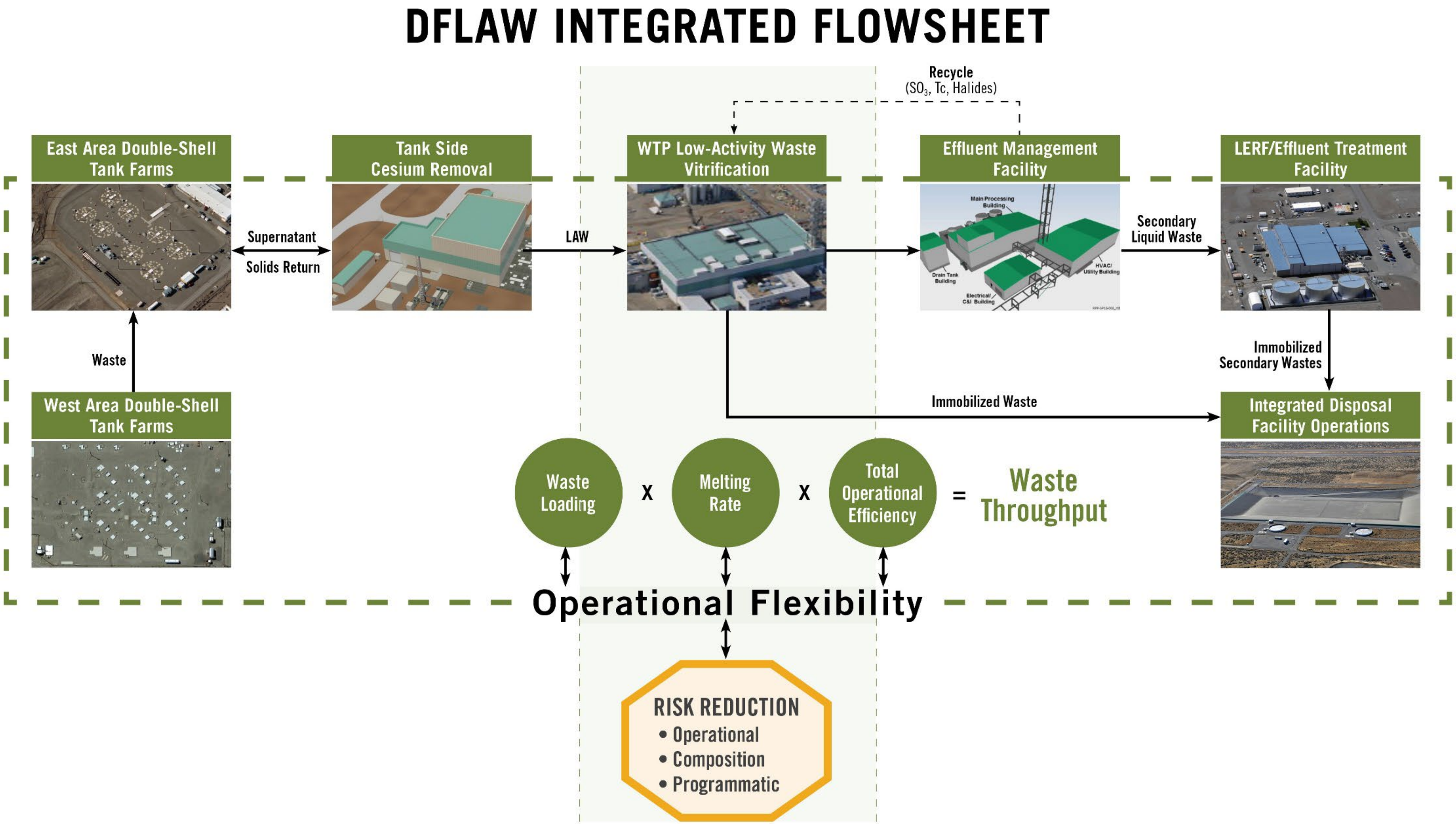
Key Terms

- Waste loading
  - Amount of waste (calcined) contained in each canister
  - Higher waste loading → fewer canisters produced
- Melting rate
  - Conversion rate of incoming liquid feed to molten liquid state
  - Higher melting rate → faster canisters can be produced
- Waste throughput
  - Amount of waste being processed per unit time
  - Key factor in determining overall WTP mission life and cost
- Operational flexibility

Waste Throughput = **Melting Rate** × **Waste Loading** × **Operational Efficiency**

(Assumes waste feed delivery, pretreatment, and other upstream processes are not rate limiting)

Integration of Unit Operations: Operational Flexibility and Risk Reduction



Questions?

"Early Example: Integrated Flowsheet"

What is pretreatment?

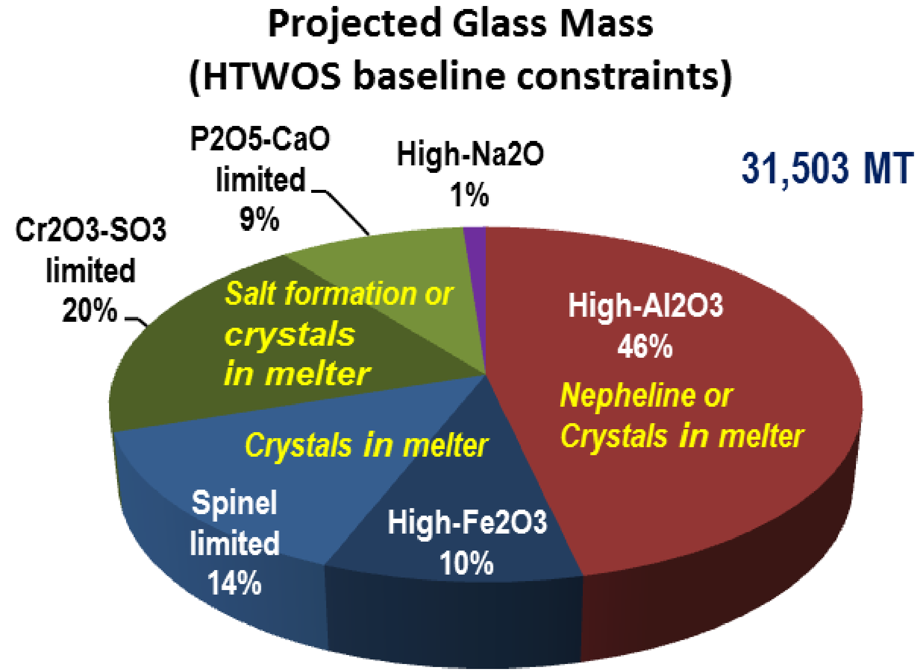
Why would you perform pretreatment?

Can pretreatment have negative impacts?

Integrated Flowsheet

- HLW Glass Mass / Canister Counts
  - Troublesome components have limited solubility in borosilicate glasses
  - Limits waste loading; Increases canister counts
- "Solution" → Balanced Approach
  - Pretreatment
    - Caustic dissolution (Al)
    - Oxidative leaching (Cr)
    - Sludge mass reduction for HLW
  - Enhanced glasses
    - Increase solubility limits for troublesome components
      - Al_2O_3: 16 wt% → >25 wt%
      - Cr_2O_3: 0.5 wt% → 1.5 wt%

Distribution of HLW Glass by Limiting Factors

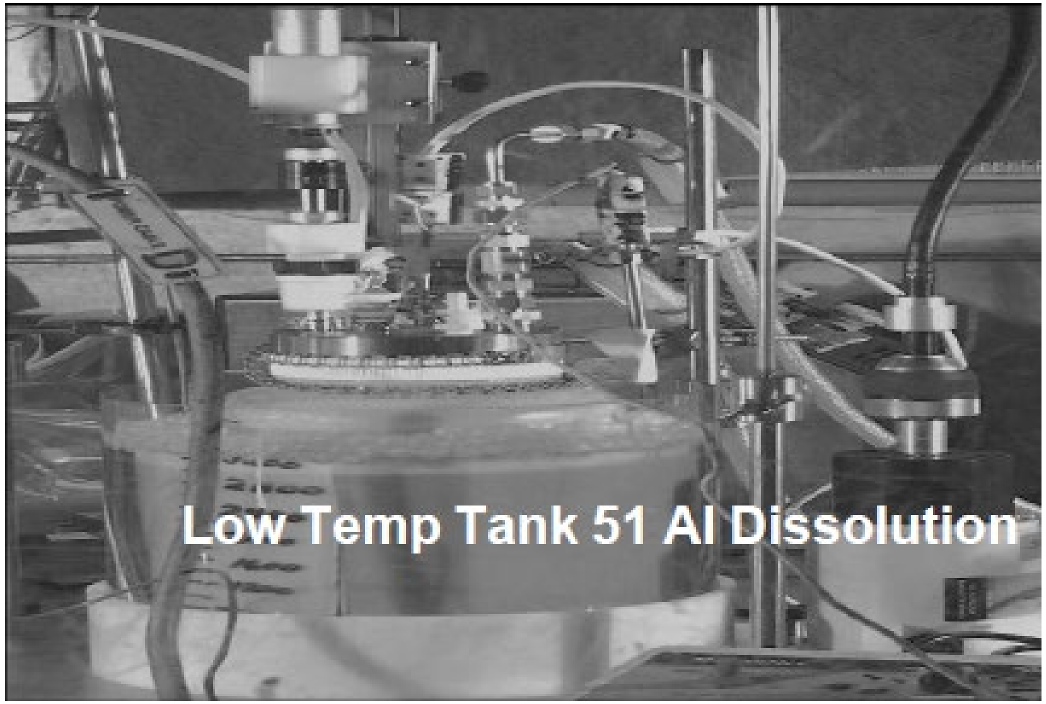


Kim DS, et al. 2011. *Formulation and Characterization of Waste Glasses with Varying Processing Temperature*. PNNL-20774, Pacific Northwest National Laboratory, Richland, WA.

Caustic addition to flowsheet?

Example of Flowsheet Integration

- Al-dissolution implemented for "high Al_2O_3" sludge at Savannah River Site
  - Caustic added to feed/prep tank to reduce aluminum content
- During planning phase, initial projections of sludge batch composition showed extremely low concentrations of Al_2O_3
- TOC did not know about lower limit of Al_2O_3 in glass for durability specifications
- Ultimately resulted in targeting Al_2O_3 content in sludge that would not require Al_2O_3 addition in frit (balanced approach)



What are technical challenges associated with vitrification?

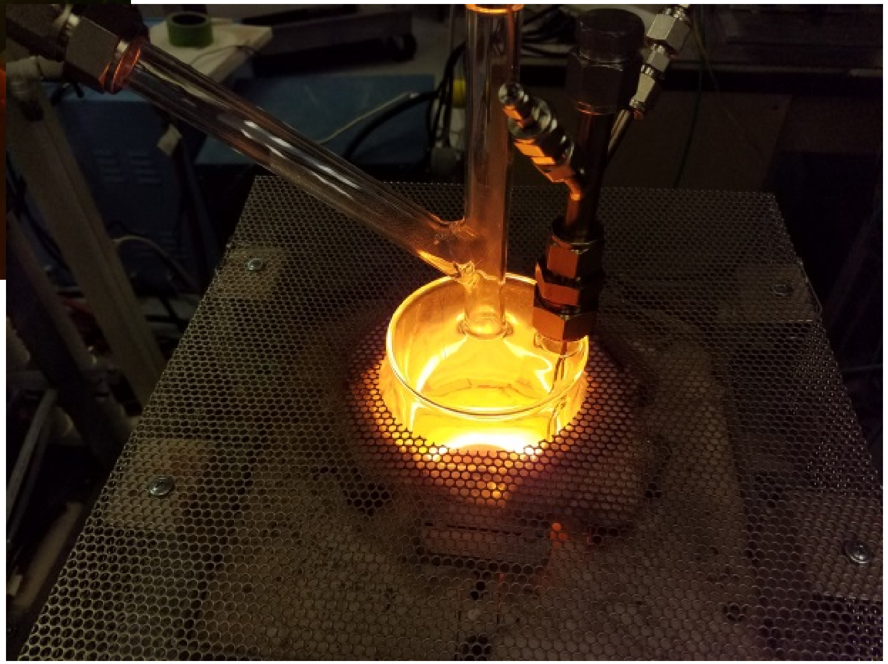
Conceptual Flowsheet:
Converting Waste → Glass

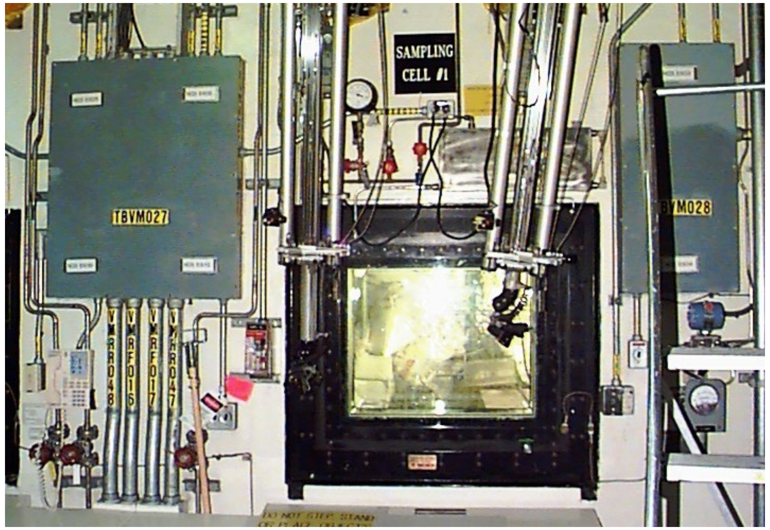
Sludge + Glass Forming Chemicals = Glass

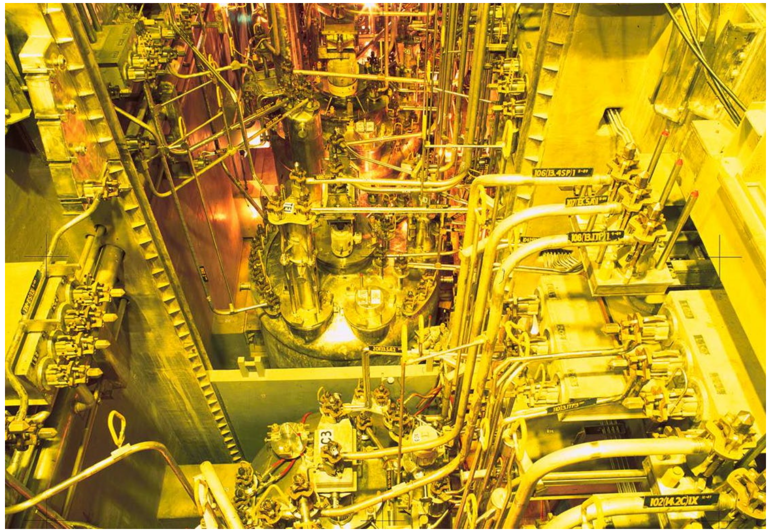
- Specific sludge/supernatant retrieved
- Pretreatment of sludge/supernatant (dissolution, IX, filtration, washing, etc.)
- Sludge (HLW) or decontaminated supernatant (LAW) transferred to vitrification facility
- Additions of glass forming chemicals (GFCs) mixed with HLW/LAW to produce melter feed
  - Process control strategies; models/algorithms
- Melter feed introduced to melter (cold cap dynamics)
  - Melter feed rheology; REDOX adjustments; volatility/off-gas
- Melter feed converted into glass product

Simple Concept → Complex to Implement

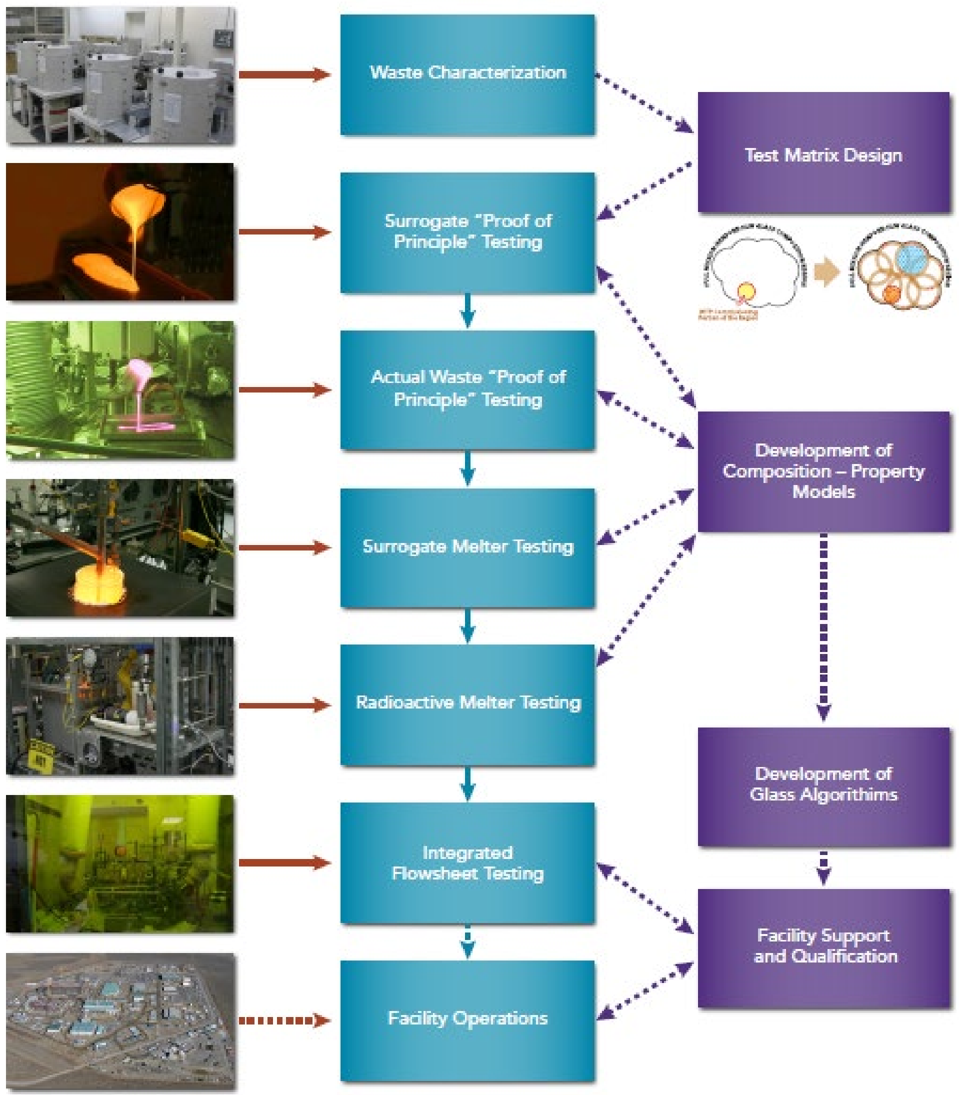
Complexity of Facility Operations







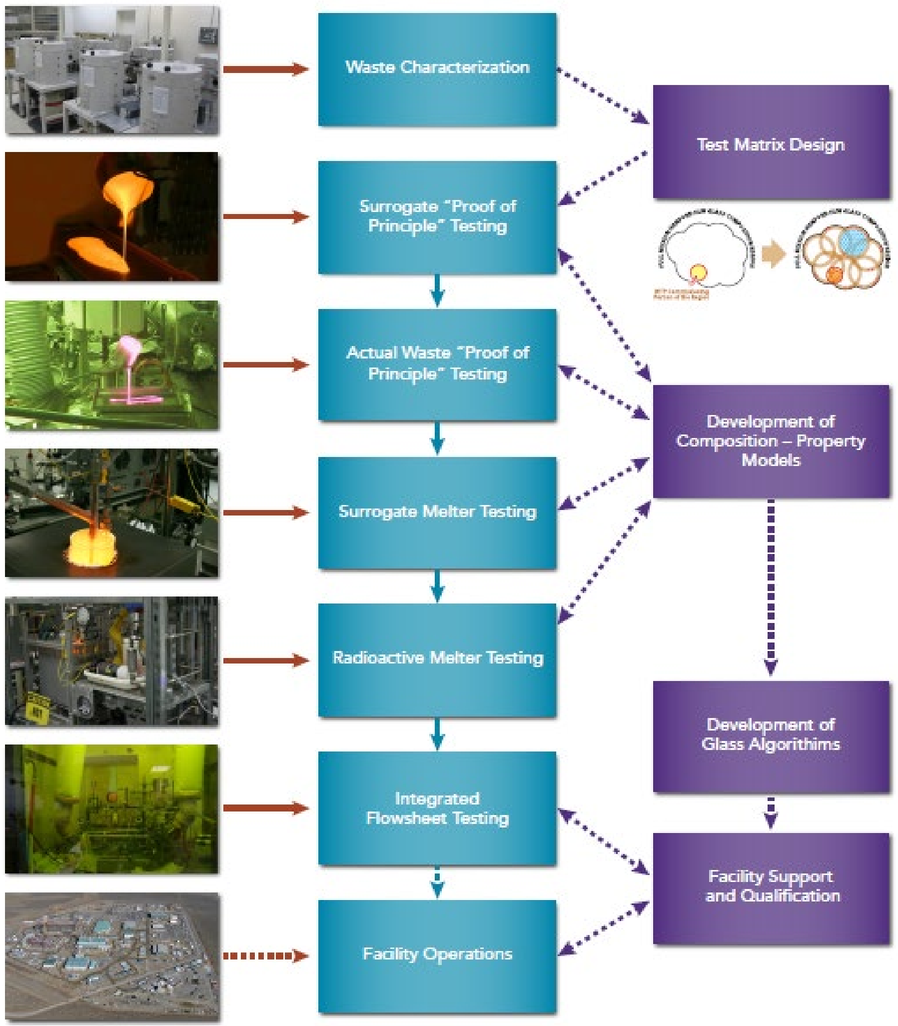
Vitrification Development Stages



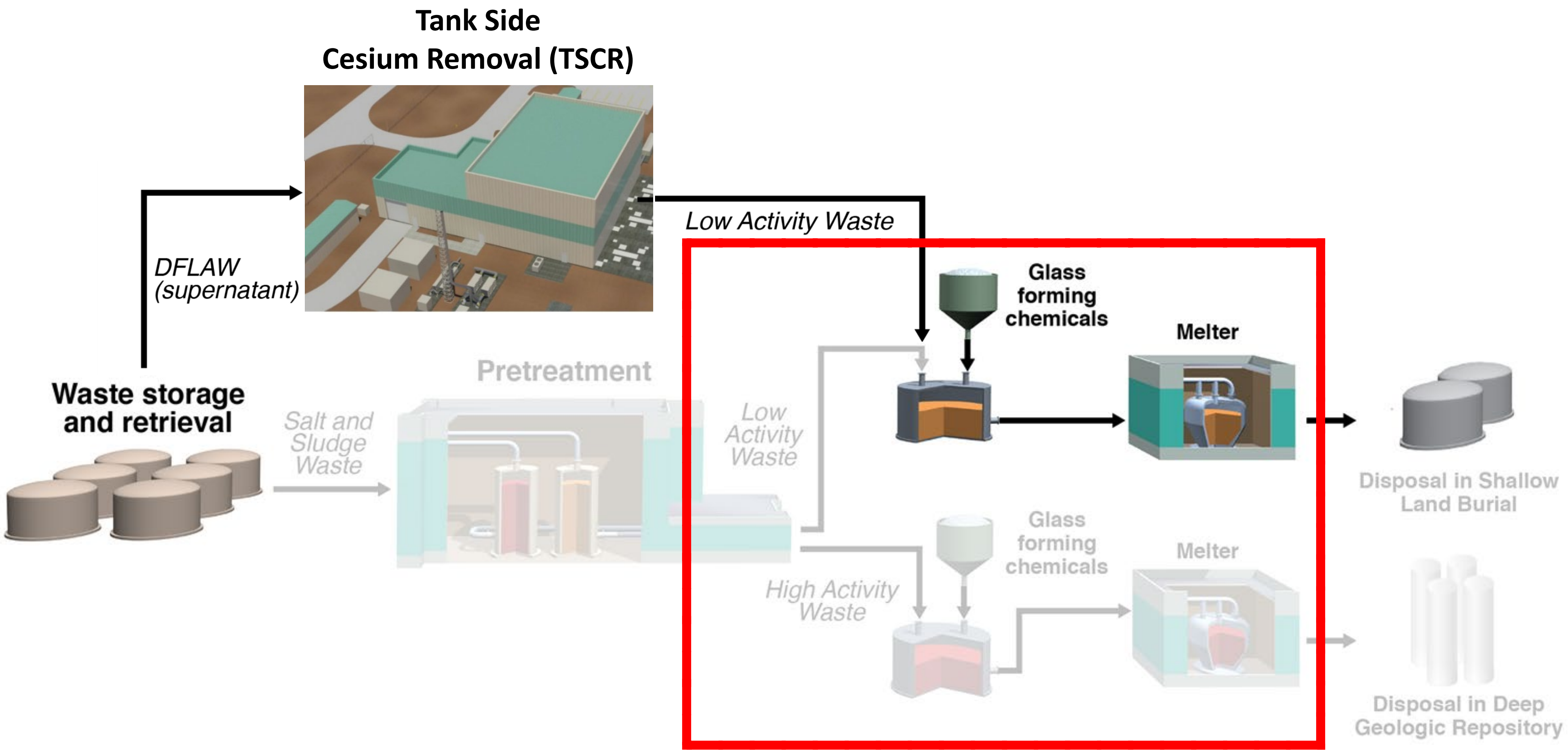
Integrated Flowsheet

- What are the flowsheet unit operations?
  - Tank farms – blending strategies
  - Pretreatment – washing strategies
  - Vitrification – waste loading, melting rate, waste throughput, operation flexibility

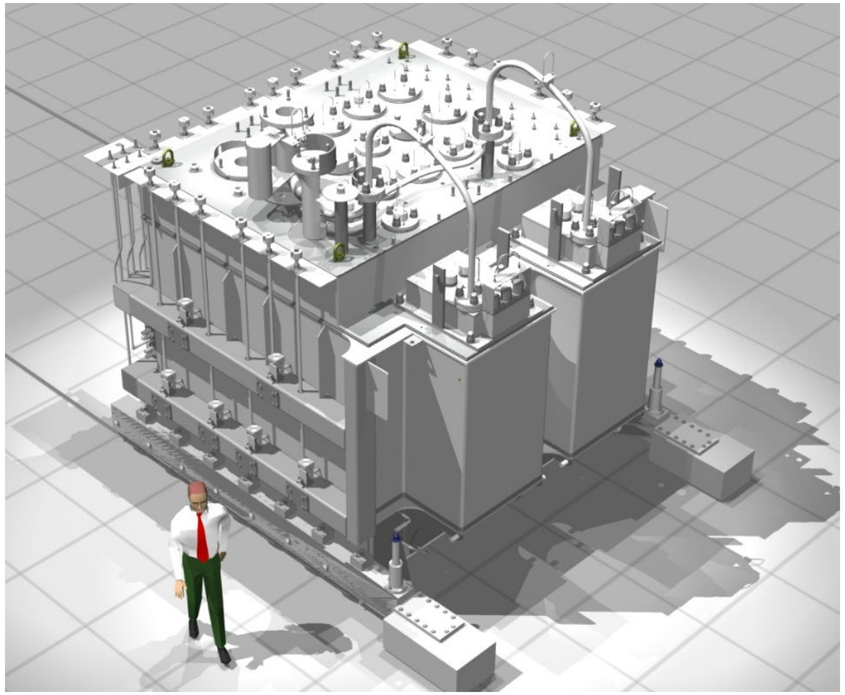
- Technical Challenges/Issues (examples):
  - Radioactive material (manipulator controlled)
    - Transfer of material between facilities and process vessels – rheology issues
    - What are the compositions of these wastes? Problematic components? Pretreatment requirements?
  - **What are the related process and product performance requirements?**
  - **How is the process controlled?**
  - **Impact of process control models on acceptable glass compositional region?**

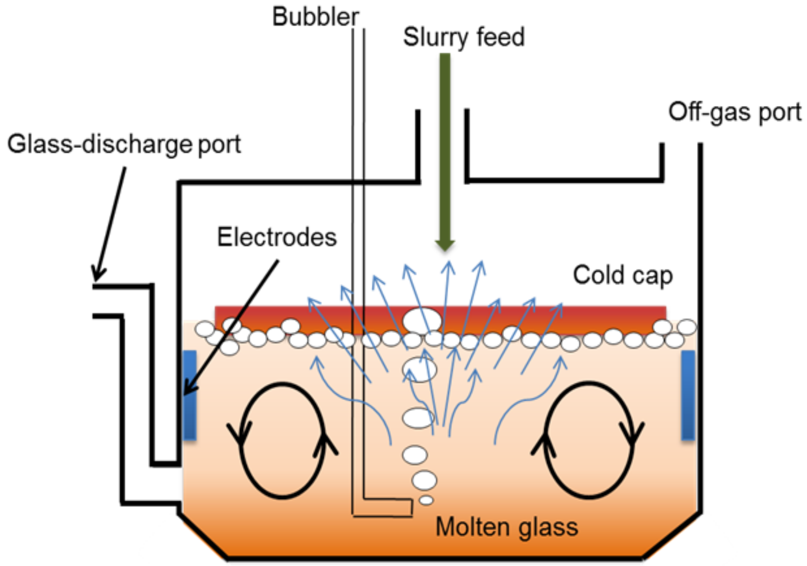


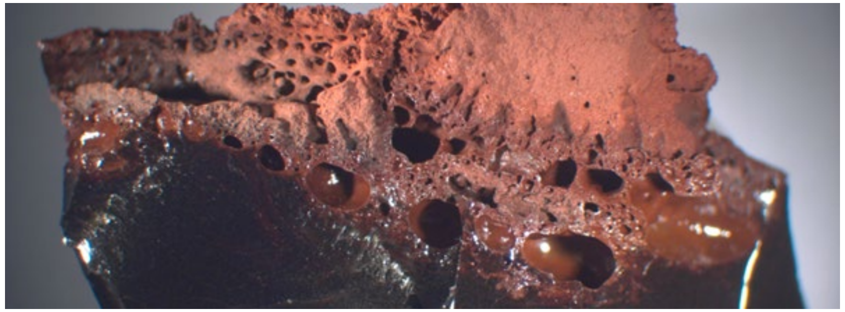
Hanford Flowsheet

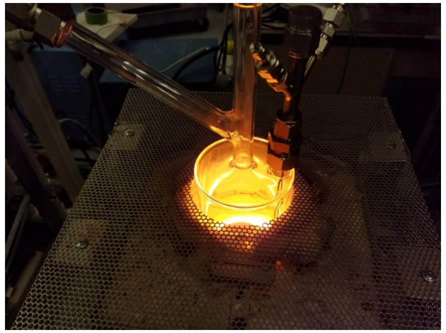


What goes in→ Must come out→ Must be durable









Balancing Key Glass Properties

- Glass formulation efforts must balance key processing and product performance-related constraints
  - Processing constraints (not inclusive)
    - Viscosity, liquidus temperature, electrical conductivity
  - Product performance constraints
    - Durability
      - PCT-A (HLW)
      - PCT-A and VHT (LAW)
- Process control models
  - Models that related composition to properties

Challenge is to design glasses that meet contractual obligations (waste loading, production rates, etc.) while simultaneously meeting both process and product performance constraints

Data Generation

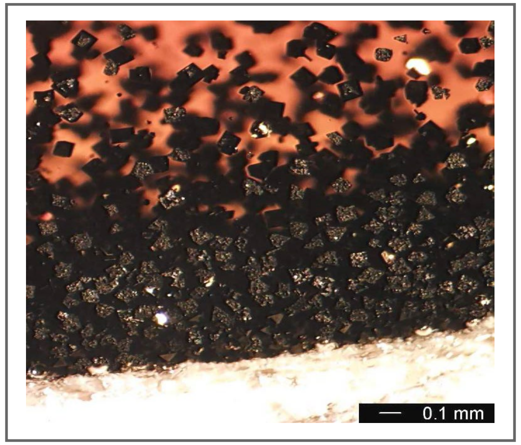
- Data needed to support model development
- Test matrix to cover compositional region
  - Statistically-designed studies, one-at-time component changes, two-at-a-time component changes...
- Targeted glass compositions are produced in laboratory
  - Batched
  - Melted
  - Properties measured
- Data then used to develop models
- Models used to support facility operations

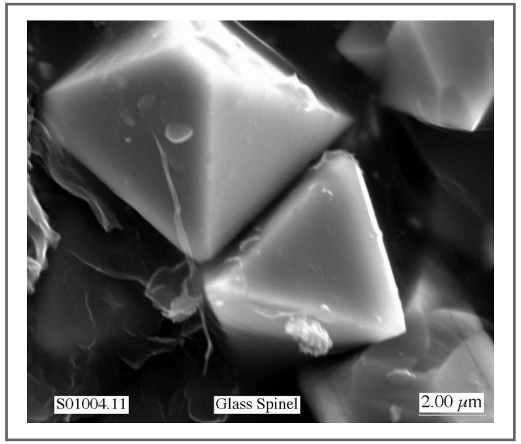
Batching

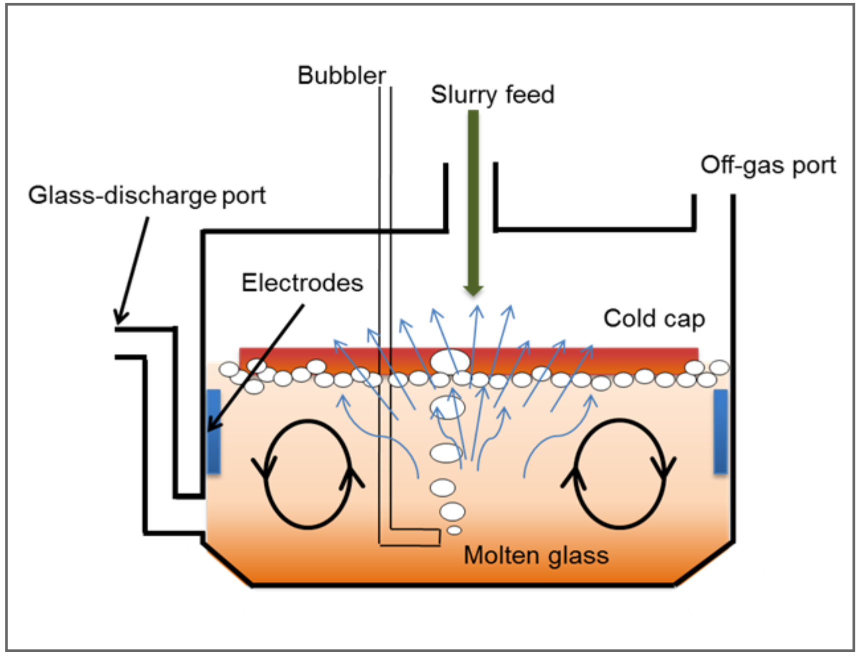
Melting

Crystallization

- Significance of T_L
  - If T_L is above melter operating temperature (T_M), crystals may form in melter
  - If crystals form, they can settle to melter bottom
    - ✓ Faster if they are large or form large agglomerates
    - ✓ Slower if they are small, but rate increases during melter idling when convective flow is slowed
  - Crystals can clog melter pour spout, short electrodes, and/or disrupt flow in melter

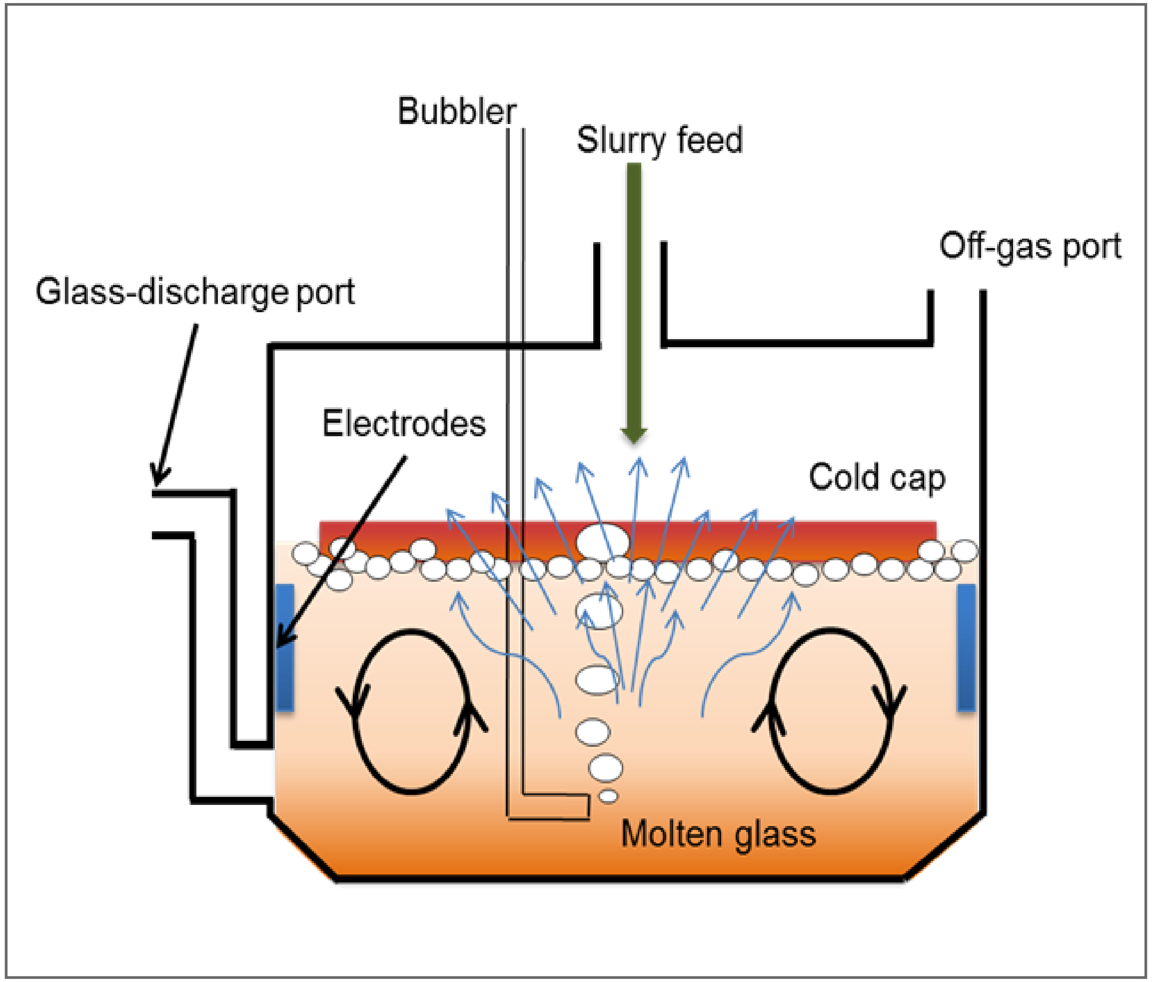






Viscosity (η)

- If η is too low:
  - Refractory, bubbler, and electrode corrosion rate can increase
  - Volatility rate can increase
- If η is too high:
  - Processing rate can lowered
    - Offset by bubblers
  - Incomplete melt homogenization
  - Pouring could be hindered
  - Glass may not adequately fill canister



Sulfate Salt

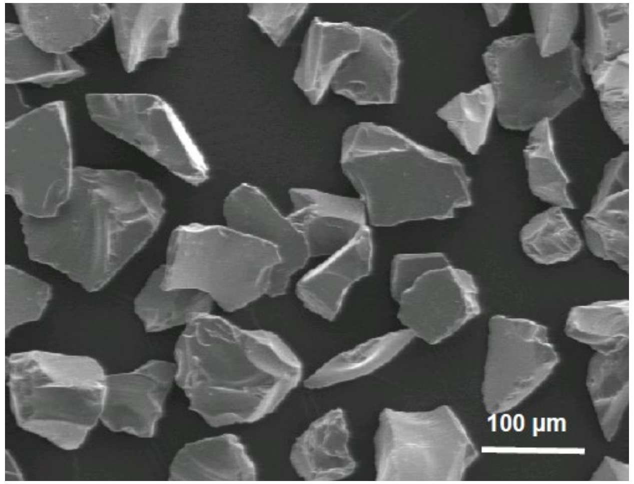
- Wastes high in SO_3, Cl, Cr_2O_3 may form sulfate-containing salt on melt surface
- Potential impacts
  - increased corrosion
  - increased volatility of Cs and Tc
- Avoiding salt formation is a primary issue for LAW glass
- Can limit waste loading of high SO_3 wastes (LAW or HLW)

K.S. Matlack, W. Gong, I.S. Muller, I. Joseph, and I.L. Pegg, 2006. LAW Envelopes A and B Glass Formulations Testing to Increase Waste Loading, VSL-06R6900-1, Vitreous State Laboratory, Washington, D.C.

Chemical Durability

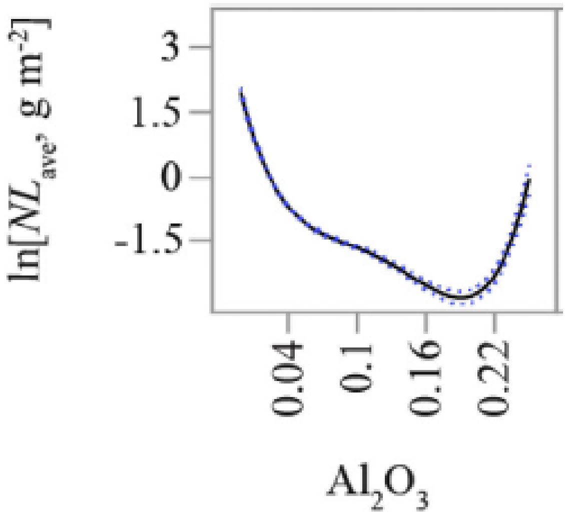
- Objective: immobilize radioactive and hazardous components of waste while meeting long-term performance metrics
- Durability requirements for LAW and HLW glass:
    - *HLW: Product Consistency Test (PCT)*
    - *LAW: PCT and Vapor Phase Hydration (VHT)*

- PCT: 75 to 150 mm crushed glass, 90°C, 7 d, DIW




General Composition – Property Relationships (specific composition space)

Oxide	Al_2O_3	B_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	ZnO	ZrO_2	Other
Viscosity	↑	↓	↓	↔	↔	↓	↓	↓	↓	↑	↔	↑	
EC	↔	↔	↔	↔	↔	↑	↑	↔	↑	↓	↔	↔	
T_L, C_T (sp)	↑	↓	↓	↑	↑	↓	↓	↔	↓	↓	↑	↑	NiO, MnO↑
PCT	↓↑	↓↑	↔	↔	↔	↑	↑	↑	↑	↓	↔	↓	
VHT	↓↑	↓↔	↔	↔	↔	↑	↑	↔↑	↑	↓	↔	↓	
Nepheline	↑	↓	↑	↔	↔	↑	↑	↔	↑	↓	↔	↔	
Salt	↑	↓	↓	↑	↔	↓	↓	↔	↓	↑	↔	↔	SO_3, Cl ↑, V_2O_5↓
TCLP	↓	↑	↔	↔	↔	↑	↑	↔	↑	↓	↑	↓	MnO↑
Corrosion	↓	↔	↔	↓	↓	↑	↑	↔	↑	↓	↓	↓	NiO↓



LAW Glass Property and Composition Constraints

Table 2. Summary of LAW Glass and Melt Constraints Used in ILAW Algorithm[a]

Constraint Description	Constraint	Source
Product consistency test (PCT) normalized releases of Na, B, and Si	< 2 (g/m^2) (for Na, B, and Si)	DOE 2000 (Spec. 2.2.2.17.2)
Vapor hydration test (VHT) 200°C alteration rate	< 50 (g/m^2/d)	DOE 2000 (Spec. 2.2.2.17.3)
Viscosity at 1100°C	≤ 150 (P)[b]	24590-LAW-3PS-AE00-T00001, Rev. 4
Viscosity at 1150°C	≥ 20 (P)	24590-HLW-RPT-RT-05-001, Rev. 0[c]
Viscosity at 1150°C	≤ 80 (P)	24590-HLW-RPT-RT-05-001, Rev. 0[c]
Electrical conductivity at 1100°C	≥ 0.1 (S/cm)	24590-LAW-3PS-AE00-T00001, Rev. 4
Electrical conductivity at 1200°C	≤ 0.7 (S/cm)	24590-LAW-3PS-AE00-T00001, Rev. 4
Waste loading (wt% waste Na_2O in glass)	$>$ 14, 3, and 10 (wt%) for envelopes A, B, and C LAW, respectively	DOE 2000 (Spec. 2.2.2.2)
Waste classification	$<$ Class C limits as defined in 10CFR61.55	DOE 2000 (Spec. 2.2.2.8)
^{90}Sr activity per unit volume of glass	< 20 (Ci/m^3)	DOE 2000 (Spec. 2.2.2.8)
^{137}Cs activity per unit volume of glass (waste form compliance)	< 3 (Ci/m^3)	DOE 2000 (Spec. 2.2.2.8)
^{137}Cs activity per unit volume of glass (system maintenance)	< 0.3 (Ci/m^3)	DOE 2000 [Section C.7 (d).(1).(iii)]
Canister surface dose rate	≤ 500 mrem/h	DOE 2000 (Spec. 2.2.2.9)

From 24590-LAW-RPT-RT-04-0003, Rev 1

ILAW Formulation Algorithm

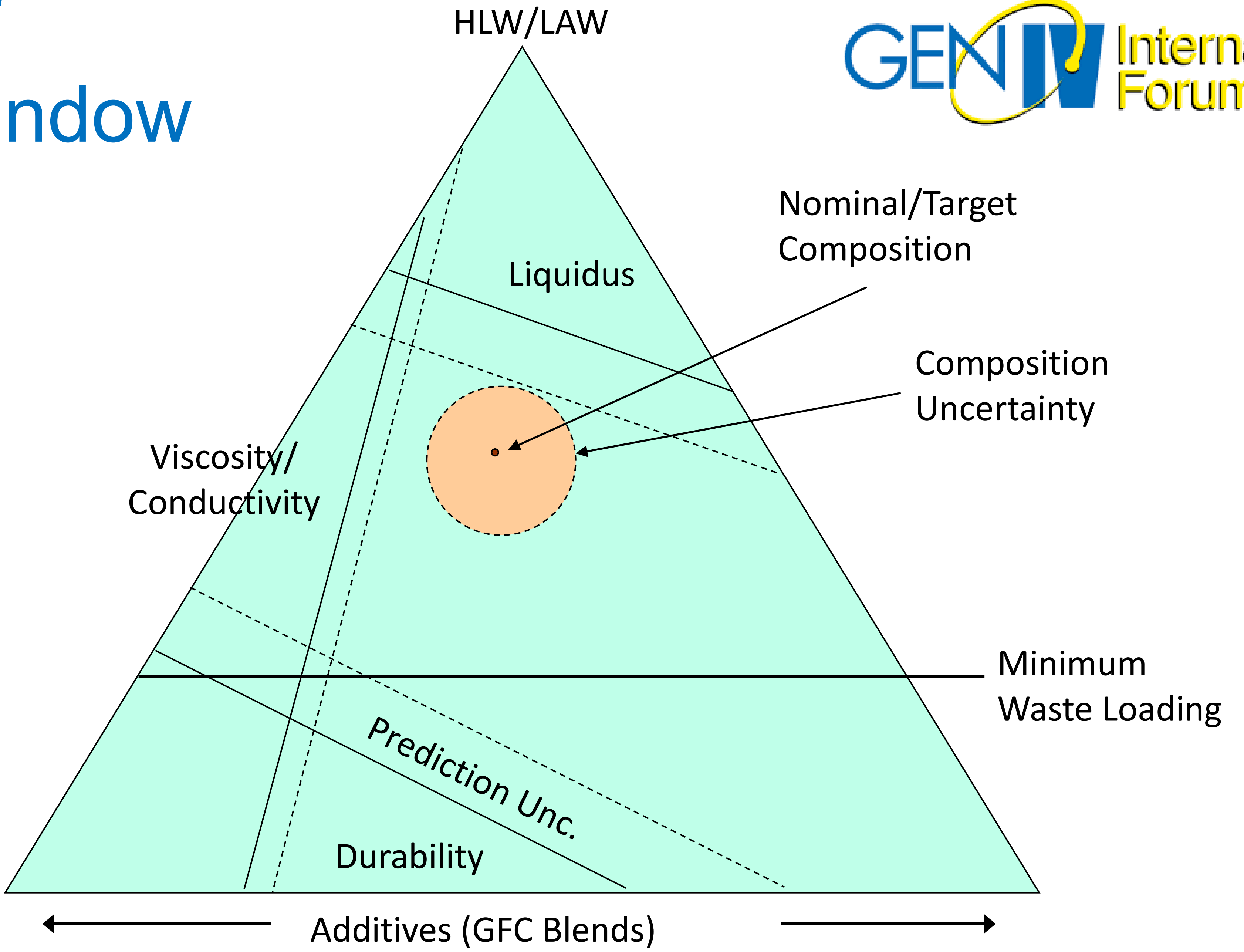
- Prescribe appropriate mix of LAW and GFCs to add to each LAW batch
- Ensure that glass property / composition constraints are all met by each batch

BECHTEL

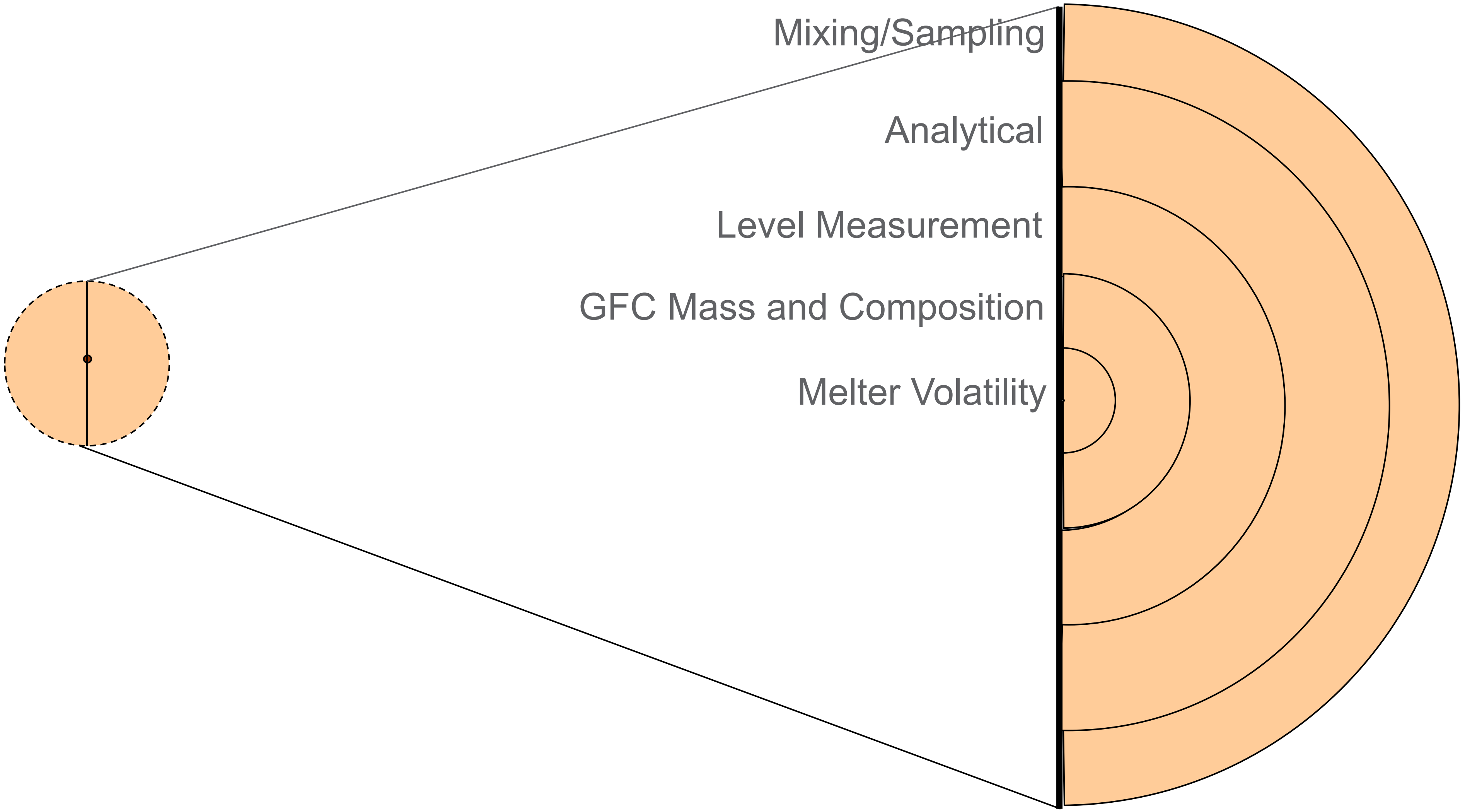
Document title:	**Preliminary ILAW Formulation Algorithm Description**
Document number:	24590-LAW-RPT-RT-04-0003, Rev 1
Contract number:	DE-AC27-01RV14136
Department:	Process Technology
Author(s):	D. Kim, J. D. Vienna
Checked by:	J. L. Nelson
Issue status:	Approved
Approved by:	S. M. Barnes
Approver's position:	Manager, Process Technology
Approver's signature:	Signature — 11/20/2012 Date

River Protection Project
Waste Treatment Plant
2435 Stevens Center Place
Richland, WA 99354
United States of America
Tel: 509 371 2000

Schematic of Operating Window

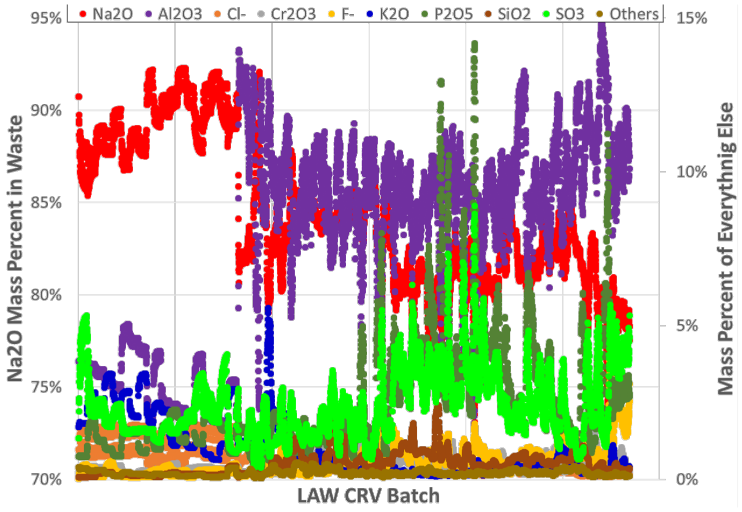


Composition Uncertainty



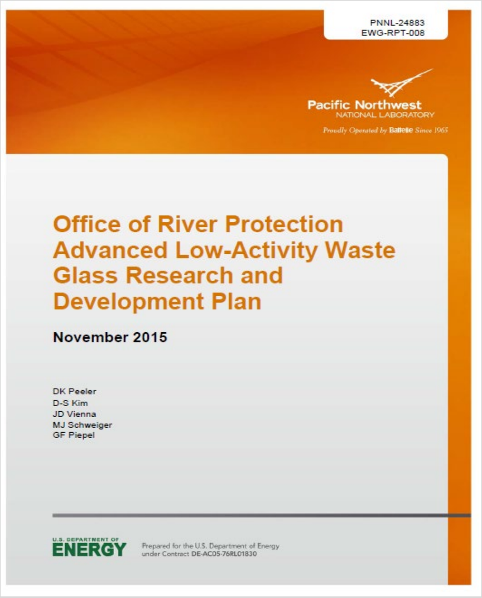
Why is an Algorithm Necessary?

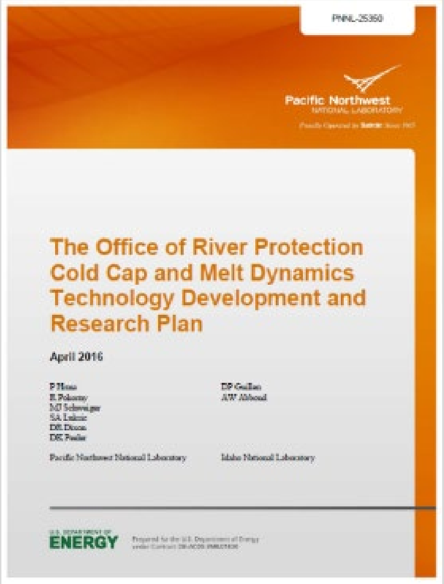
- Need for “real-time” formulation
  - Waste feed compositions change from batch-to-batch
  - Frequency of different compositional feed vectors requires changes to GFC additions to provide operational flexibility
    - Different strategy than DWPF where a fixed frit composition is used for a single sludge batch
- Production schedule is very aggressive
- There is no lag storage – glass formulations need to be adjusted and determined **within *minutes***



Enhanced Waste Glass Program

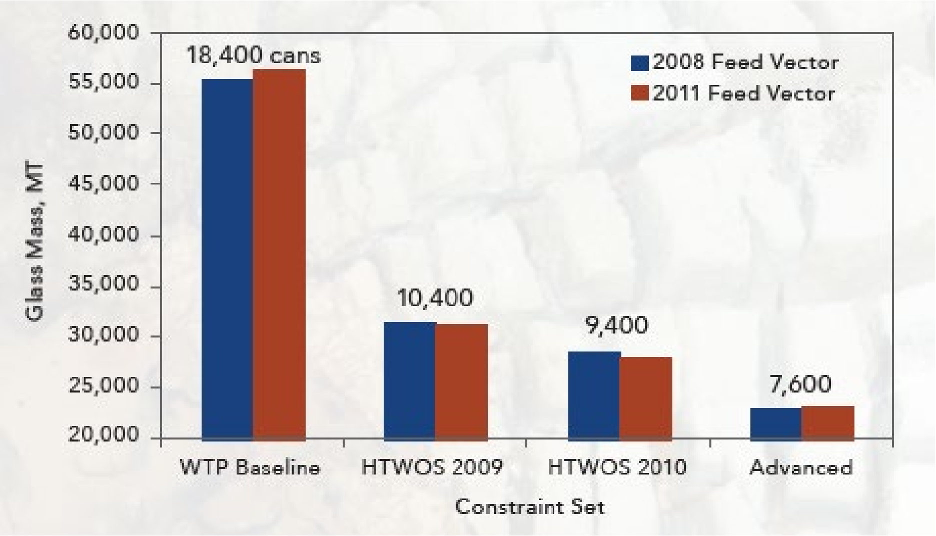
- Office of River Protection program under direction of Albert Kruger
  - Integrated program focused on technical areas of:
    - Enhanced waste glasses
      - Expanding compositional regions for both HLW and LAW
      - Developing models /algorithms for expanded compositional regions
    - Tc and halide retention
    - Crystal-tolerant glasses
    - Nepheline formation
    - Melting rate
    - Cold cap dynamics





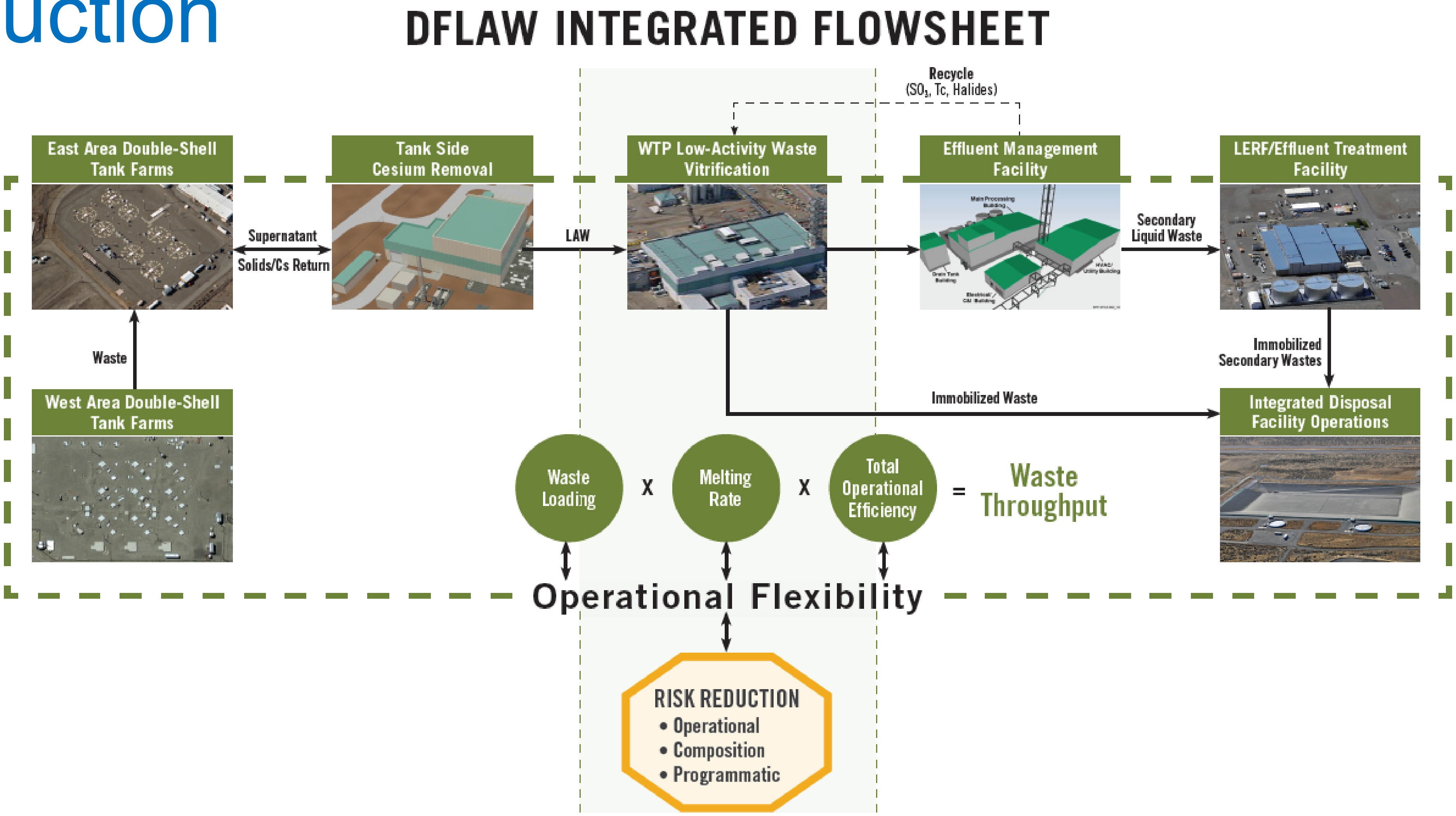
ORP EWG Program: Example Impacts

- Enhanced glass formulation work has demonstrated significant increases in waste loadings for key feed vectors or troublesome components
  - Al_2O_3 concentration
    - 16% (baseline) → >25% (enhanced)
    - Impact: reduce or eliminate need for Al-dissolution in pretreatment
  - Cr_2O_3 concentration
    - 0.3% (baseline) → 1.5% (enhanced)
    - Impact: reduce or eliminate need for oxidative leaching in pretreatment
  - Na_2O concentration
    - 20% (baseline) → ~24% (enhanced)
    - Impact: significant reduction in LAW glass mass
  - Increased operational flexibility
    - Greater tolerance for waste variation including recycle



Although significant advancements have been made within the ORP program, continuous improvement is a priority in support of operational readiness, commissioning, and operations.

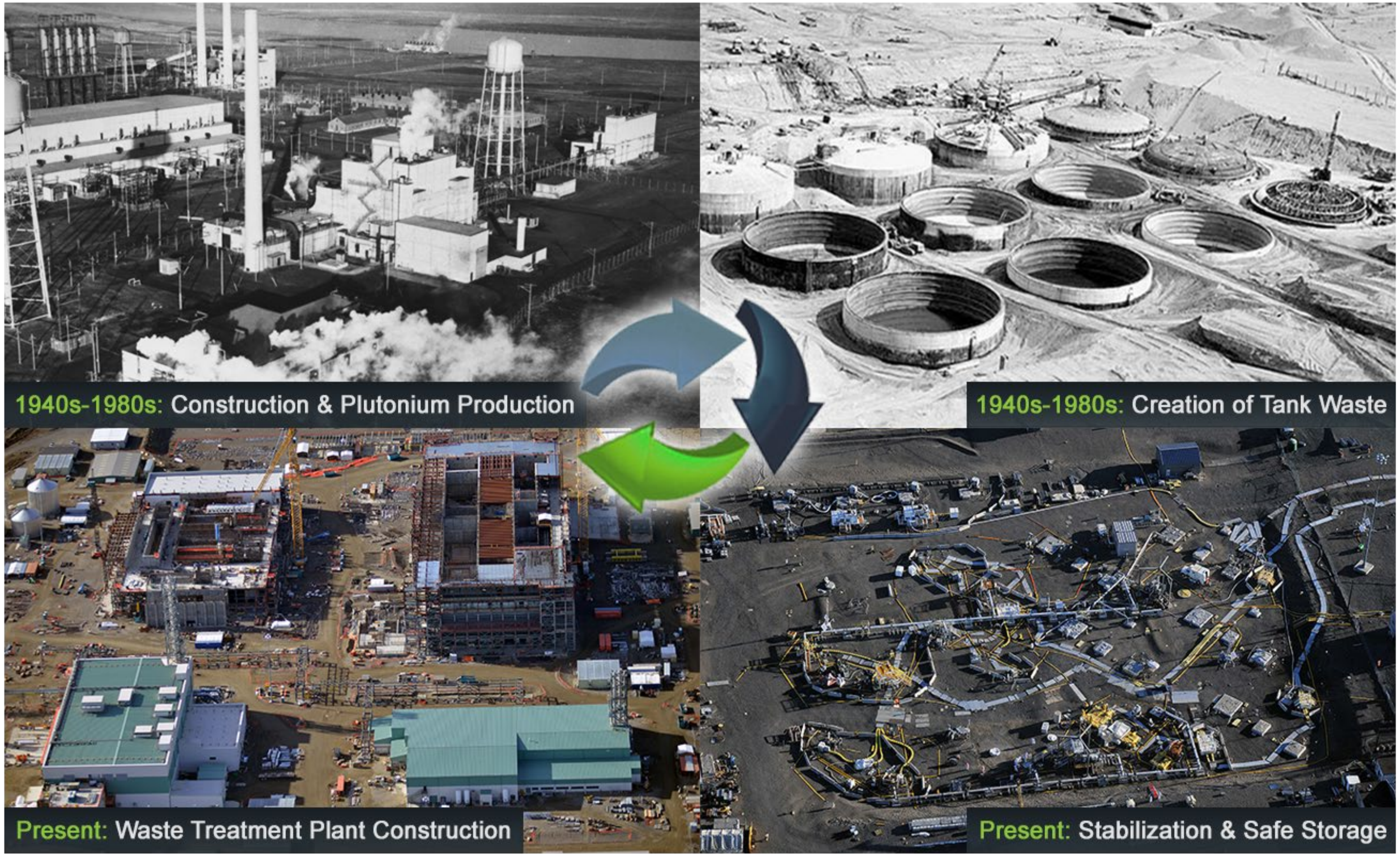
Integration of Unit Operations: Operational Flexibility and Risk Reduction



Operational Thoughts

- Integrated flowsheet
  - Define operating/process windows for unit operations; do not just focus on optimization
  - Provide operational flexibility for flowsheet and decision-makers
  - Systems approach versus optimization of unit operations
- Open lines of communication among unit operations
  - Acknowledge advances, limitations, concerns, and unknowns
  - Don't work in vacuum; avoid implementing processes that may cause downstream impacts
- Be vigilant of a changing flowsheet
  - The baseline flowsheet will likely change; stay focused and stay out front of changes to avoid system impacts or process delays
- "Stuff" happens
  - Reduce risk in advance; but can't predict everything (change is inevitable)
  - Establish/maintain critical platforms/capabilities to ensure response to emerging issue is effective and efficient, facility downtime is expensive

Historical Overview of the Hanford Site



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Upcoming Webinars

25 March 2021	Introducing New Plant Systems Design (PSD) Code	Prof. Nawal Prinja, Jacobs, UK
22 April 2021	Experience of HTTR Licensing for Japan's New Nuclear Regulation	Mr. Etsuo ISHITSUKA, JAEA, Japan
25 May 2021	Advanced Manufacturing for Gen IV Reactors	Dr. Isabella Van Rooyen, INL, USA