# Glass formulation and challenges for vitrification of high level waste

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# Sea Glass

Glass Beach, located in MacKerricher State Park near Fort Bragg, California, is famous for its shoreline covered in colorful, smoothed sea glass, which was formed from decades of garbage dumped there between 1906 and 1967.

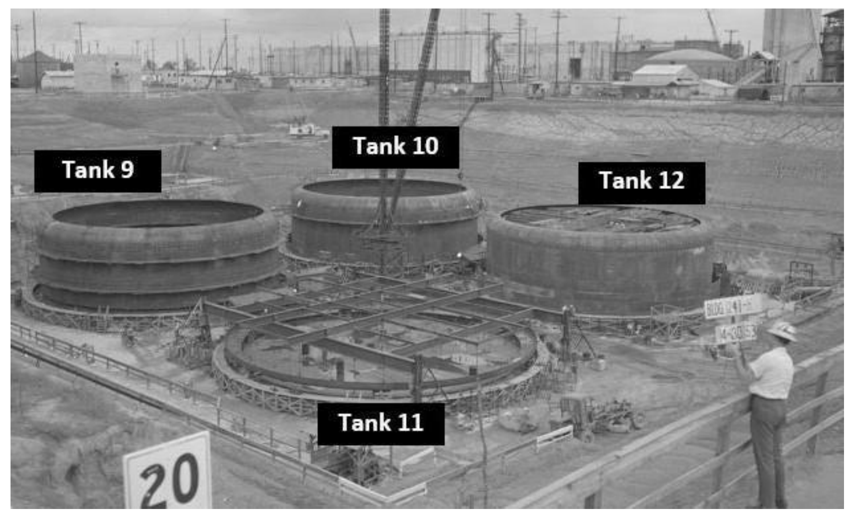
International Sea Glass Association photo

# Outline

- Why glass for high level waste vitrification
- Glass Fabrication at crucible-scale
- HLW Glass Product/Property Constraints
- Waste Loading Impacts and Factors
- Melting Rate Considerations
- Glass Formulation and Processing Strategies
- Examples for Defense Waste Processing Facility (DWPF)

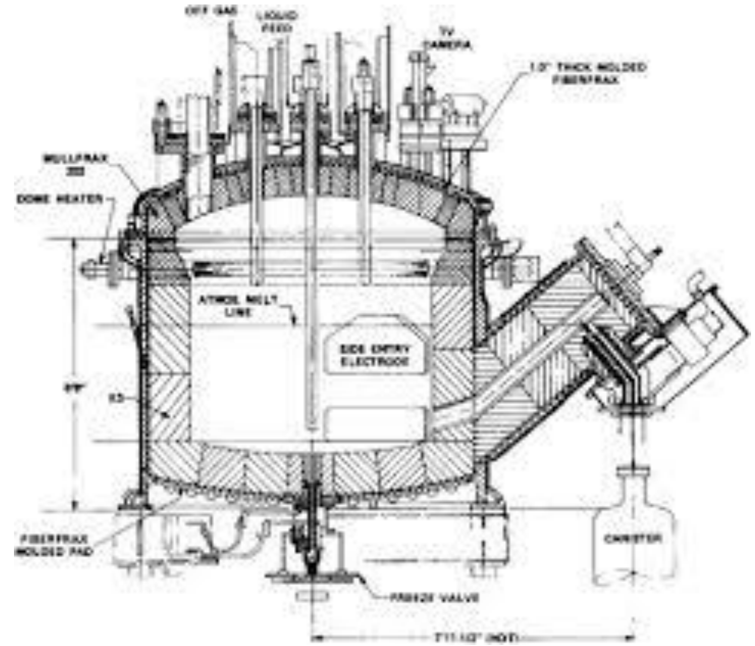
# Why Glass?

- **What is High-Level Waste (HLW)?**
  - By-product of nuclear fuel reprocessing
  - Highly radioactive and heat-generating
  - Contains long-lived radionuclides
  - Requires **immobilization** for thousands of years



# Why Glass?

- **What is Vitrification?**
  - Vitrification = converting waste into glass
  - Liquid HLW is mixed with glass-forming materials
  - Melted at ~1100–1200 °C
  - Poured into stainless steel canisters
  - Glass solidifies, trapping radionuclides in its structure



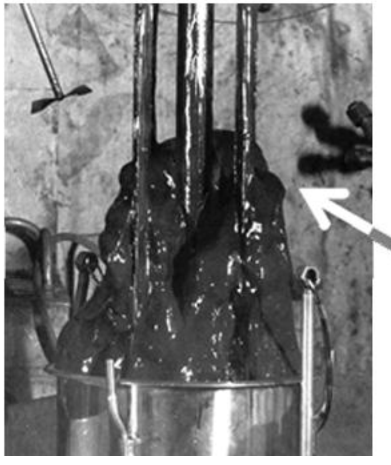

**Goal:** lock radioactive elements into a stable, durable form that won't easily escape into the environment.

# Why Glass?

- Glass is used because it offers an **ideal combination** of:
  - Chemical durability
  - Structural flexibility
  - Radiation resistance
  - Long-term stability
  - Proven industrial experience
  - No other material balances all these as well.

# Why Glass?

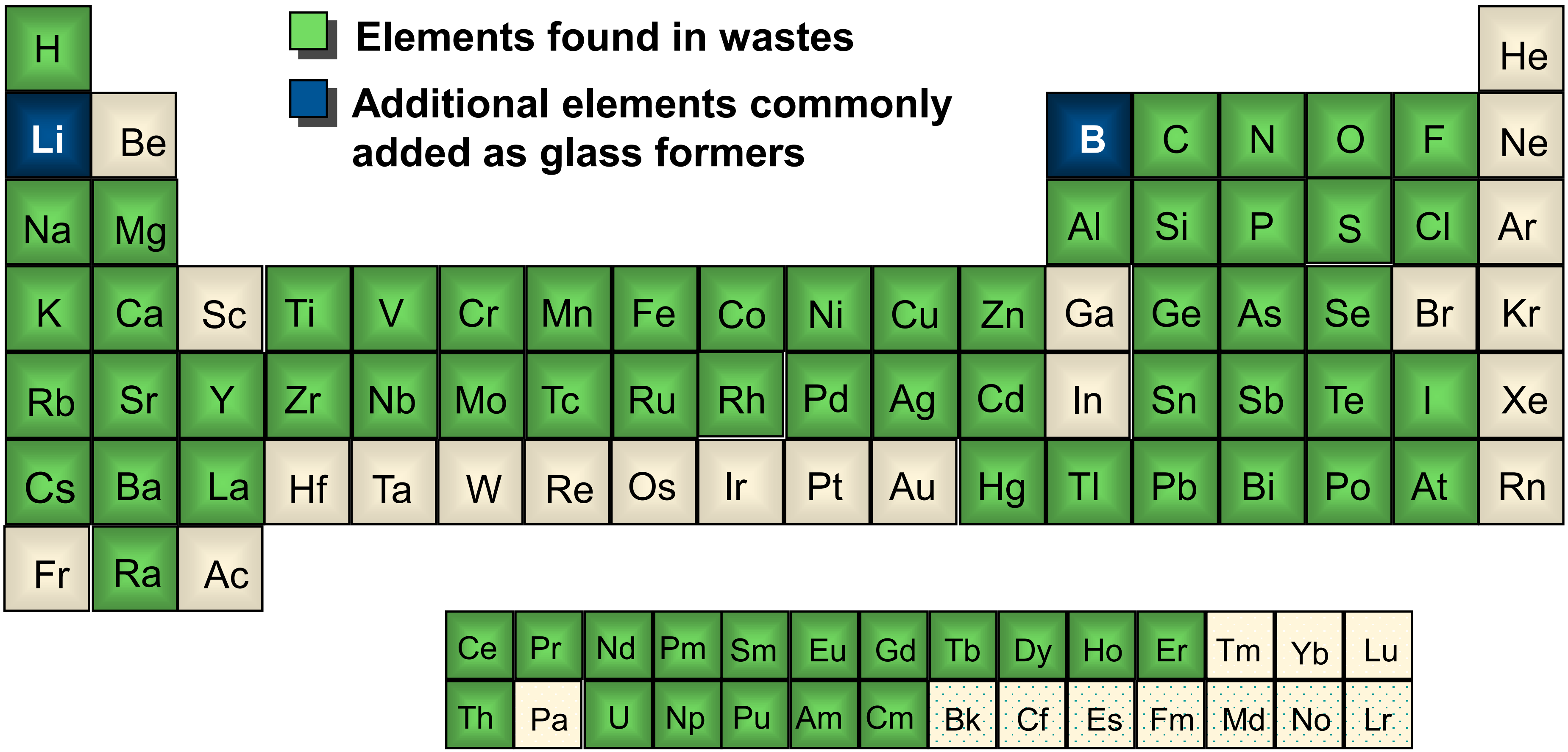
- **Ability to Incorporate Many Elements**
  - HLW contains dozens of different elements
- Glass can dissolve:
  - Actinides (e.g. plutonium)
  - Fission products (e.g. cesium, strontium)
  - Transition metals



a PUREX sludge sample being extruded from a collection vessel at the SRNL

Crystalline materials struggle with this level of chemical complexity

# Challenge: Complexity of HLW Compositions



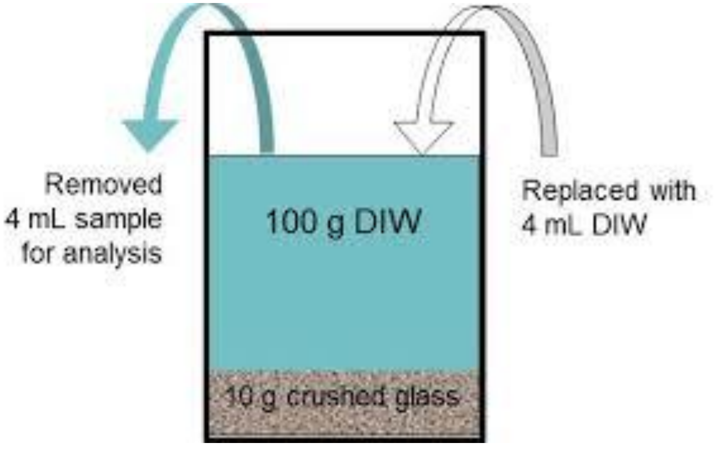
# Why Glass?

- **Excellent Chemical Durability**
  - Glass resists corrosion and dissolution
  - Very low leaching rates in groundwater
  - Radionuclides are **chemically bonded** within the glass network
  - Even if cracked, release is extremely slow

These attributes makes glass ideal for **geological disposal**

# Why Glass?

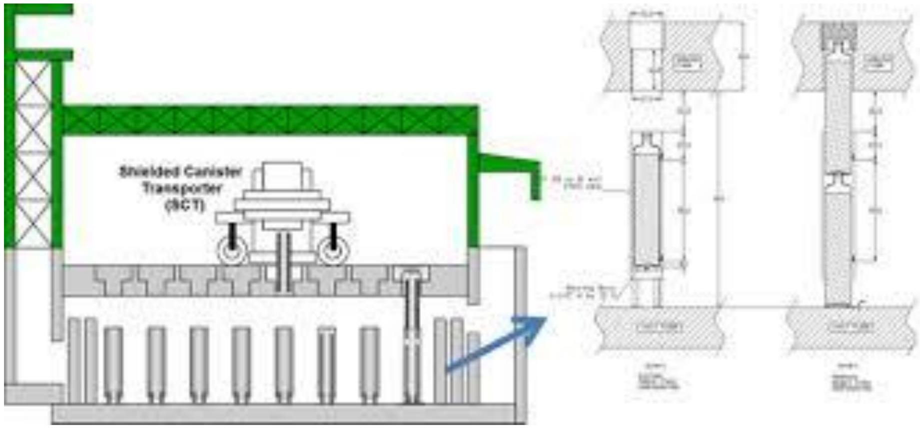
- **Long-Term Predictability**
  - Natural volcanic glasses (e.g. obsidian) have survived **millions of years**
  - Glass corrosion behavior is well-studied and modelled
  - Performance over geological timescales can be reliably predicted




Long-term behavior understanding is critical for safety assessments

# Why Glass?

- **Engineering and Handling Advantages**
- Can be poured, shaped, and sealed easily
- Compatible with stainless steel canisters
- Strong, compact waste form
- Suitable for transport, storage, and disposal
- Also scalable for industrial-level waste processing.



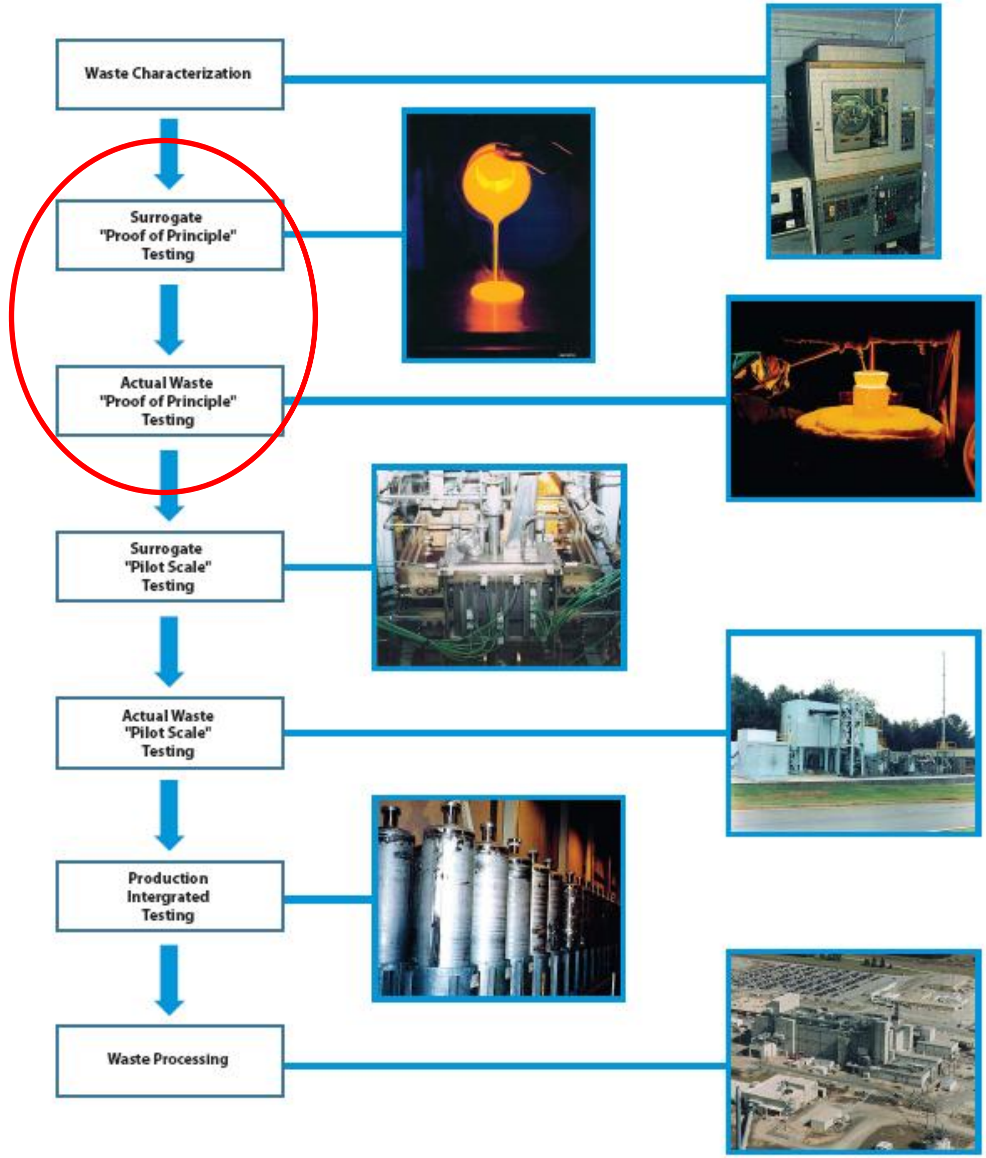
# Why Glass?

- **Why Borosilicate Glass Specifically?**
- Most commonly used vitrification glass
- Benefits:
  - High chemical durability
  - Lower melting temperature
  - High waste loading capacity
  - Resistant to phase separation

Borosilicate glass used worldwide for high level waste vitrification

# Glass Formulation Development – Crucible Scale

- Glass composition development to optimize formulation and determine properties is conducted at lab-scale
  - Testing and analyses have demonstrated that crucible tests directly relate to large-scale



# How do you make glass?

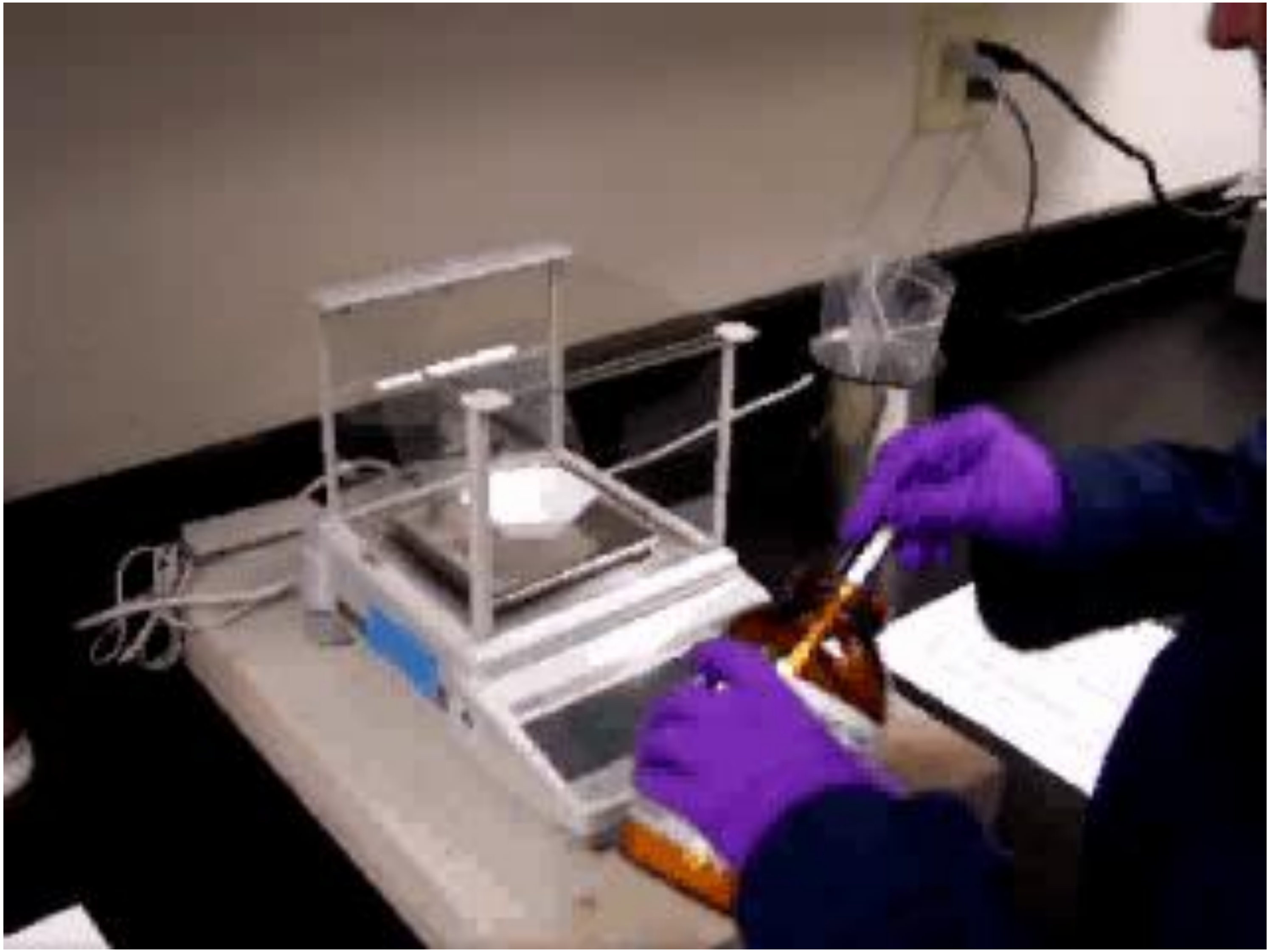
- Batching:
  - Use of batch chemicals
    - Reagent grade oxides, carbonates, sulfates, etc…
    - Batch sheets developed to target a specific glass composition
      - Frit, sludge composition and waste loading
  - Use of waste feed product and frit at a fixed waste loading
    - Blend waste feed product with pre-fabricated frit at a targeted WL
- Melting:
  - HLW glasses typically melted at 1050-1150°C for 1 – 2 hours
    - Poured on stainless steel plate or quenched in water
    - Subjected to cooling profile to represent pouring in large canister

# Sample Batch Sheet

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Glass ID: | SB4-Neph-1 | | | Batched by: | | | Date: | | |
| | | | | | | | | | |
| | Frit 320-1100 can Max Al, 40% WL | | | | | | | | |
| | SB4 Nepheline Formation Study | | | | | | | | |
| | see WSRC-NB-2004-00134, pp. 112 - 115 | | | | | | | | |
| | | | | | | | | | |
| Component | MF Oxide | wt% oxide | | Source | Wt% of chemical after LOD | 100 g | 150 g | Amount added | |
| Al2O3 | 0.00000 | 12.612 | | Al2O3 | 100.00% | 12.612 | 18.918 | | g |
| B2O3 | 0.00000 | 4.800 | | H3BO3 | 100.00% | 8.526 | 12.789 | | g |
| Bi2O3 | 0.00000 | 0.000 | | Bi2O3 | 100.00% | 0.000 | 0.000 | | g |
| CaO | 0.00000 | 0.884 | | CaCO3 | 100.00% | 1.578 | 2.367 | | g |
| CdO | 0.00000 | 0.000 | | CdO | 100.00% | 0.000 | 0.000 | | g |
| Cr2O3 | 0.00000 | 0.092 | | Cr2O3 | 100.00% | 0.092 | 0.138 | | g |
| F | 0.00000 | 0.000 | | NaF | 100.00% | 0.000 | 0.000 | | g |
| Fe2O3 | 0.00000 | 9.087 | | Fe2O3 | 100.00% | 9.087 | 13.631 | | g |
| K2O | 0.00000 | 0.682 | | K2CO3 | 100.00% | 1.001 | 1.501 | | g |
| Li2O | 0.00000 | 4.800 | | Li2CO3 | 100.00% | 11.870 | 17.805 | | g |
| MnO | 0.00000 | 1.913 | | MnO | 100.00% | 1.913 | 2.870 | | g |
| Na2O | 0.00000 | 16.348 | ** | Na2CO3 | 100.00% | 27.468 | 41.203 | | g |
| NiO | 0.00000 | 0.583 | | NiO | 100.00% | 0.583 | 0.875 | | g |
| P2O5 | 0.00000 | 0.000 | | NaPO3 | 100.00% | 0.000 | 0.000 | | g |
| SiO2 | 0.00000 | 44.482 | | SiO2 | 100.00% | 44.482 | 66.723 | | g |
| SrO | 0.00000 | 0.000 | | SrCO3 | 100.00% | 0.000 | 0.000 | | g |
| ThO2 | 0.00000 | 0.020 | | ThO2 | 100.00% | 0.020 | 0.030 | | g |
| TiO2 | 0.00000 | 0.010 | | TiO2 | 100.00% | 0.010 | 0.015 | | g |
| U3O8 | 0.00000 | 2.111 | | U3O8 | 100.00% | 2.111 | 3.167 | | g |
| ZnO | 0.00000 | 0.040 | | ZnO | 100.00% | 0.040 | 0.060 | | g |
| ZrO2 | 0.00000 | 0.095 | | ZrO2 | 100.00% | 0.095 | 0.143 | | g |

***Sample batch sheet – not complete***

# Batching

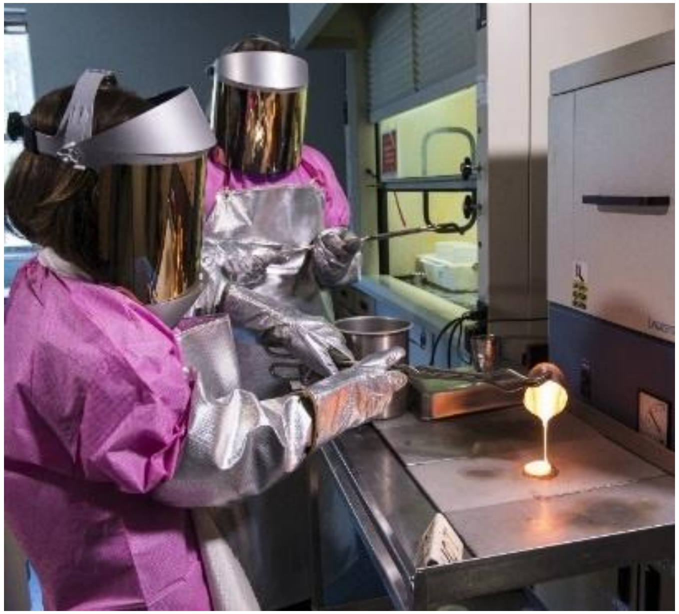


# Batching: Transfer to Pt Crucible

Note: Can also melt in alumina or quartz crucibles

# Melting

- HLW glasses typically melted at 1050-1150°C
- Poured onto stainless plate
  - Quenched glass
- Subjected to slow cooling profile
- Pour patty used as a sampling stock for physical and chemical property measurements
  - Physical: $T_L$, $\eta$, durability
  - Chemical: composition analysis



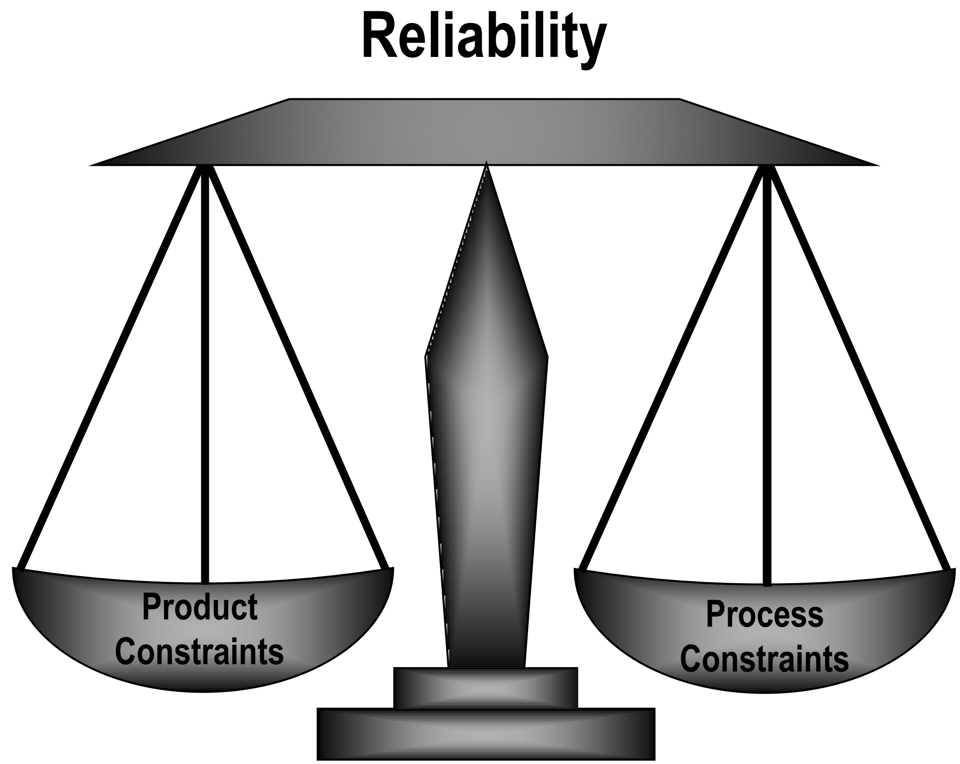
# Product/Property Constraints

## Product

- Chemical Durability
- Homogeneity
- Regulatory Compliance
- Thermal Stability
- Mechanical Stability

## Process

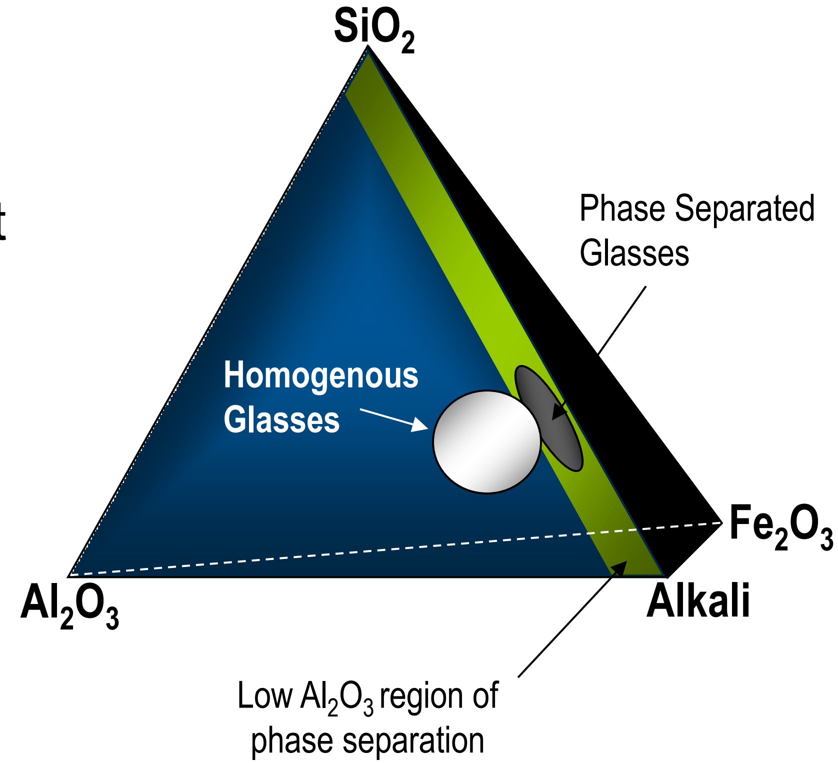
- Viscosity
- Liquidus
- Waste Solubility
- Melt Temperature
- Volatility
- Melt Rate

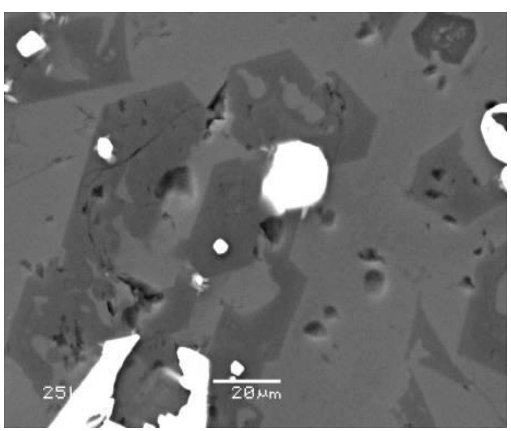



**Glasses must be formulated to balance product performance and processing properties to be acceptable**

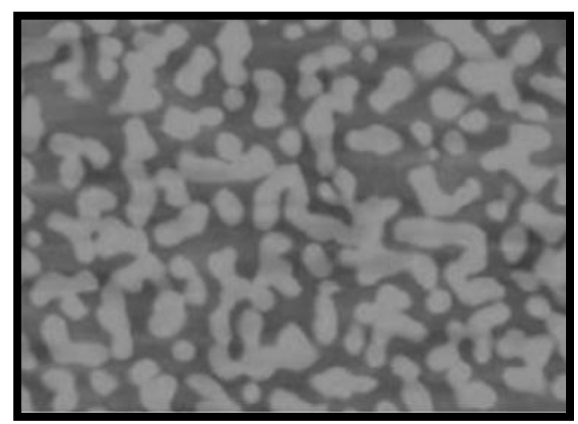
# Chemical Durability/Homogeneity

- Durability: resistance to aqueous corrosion
- Glass inhomogeneity can have significant negative impacts on glass durability
  - Crystallization (e.g. nepheline)
  - Phase separation
- ASTM C1285 developed by Jantzen et al.
  - Product Consistency Test (PCT)
  - U.S. HLW waste glass demonstrate lower release rates for specific glass elements



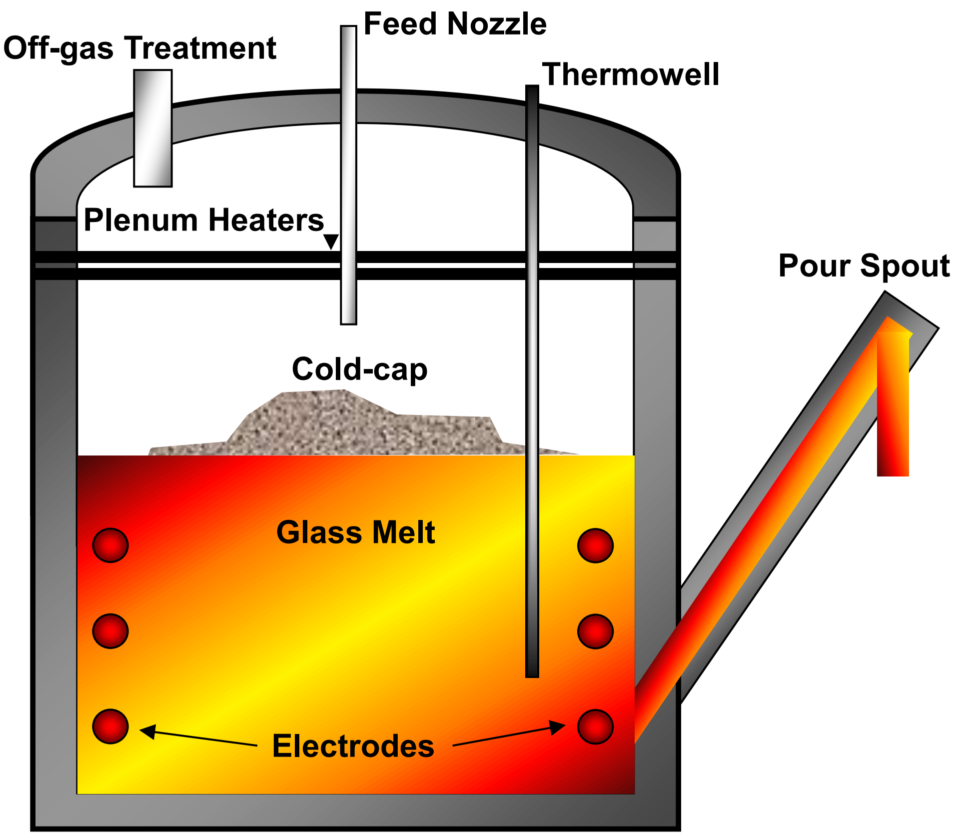




Dark gray: nepheline
White: spinel
Light gray: matrix glass



Glass-in-glass phase separation

# Viscosity (η)




- If η is too low:
  - Volatility rate can be too high
  - Refractory, bubbler and electrode corrosion rate can be too high
  - Risk of steam explosion increases
  - Settling of solid particles can be too fast
- If η is too high:
  - Process rate can be too low (delivery of heat to cold-cap)
  - Incomplete melt homogenization
  - Glass may freeze in the pour spout
  - Glass may not adequately fill canister
  - Thermal instability can cause melter "freezing"

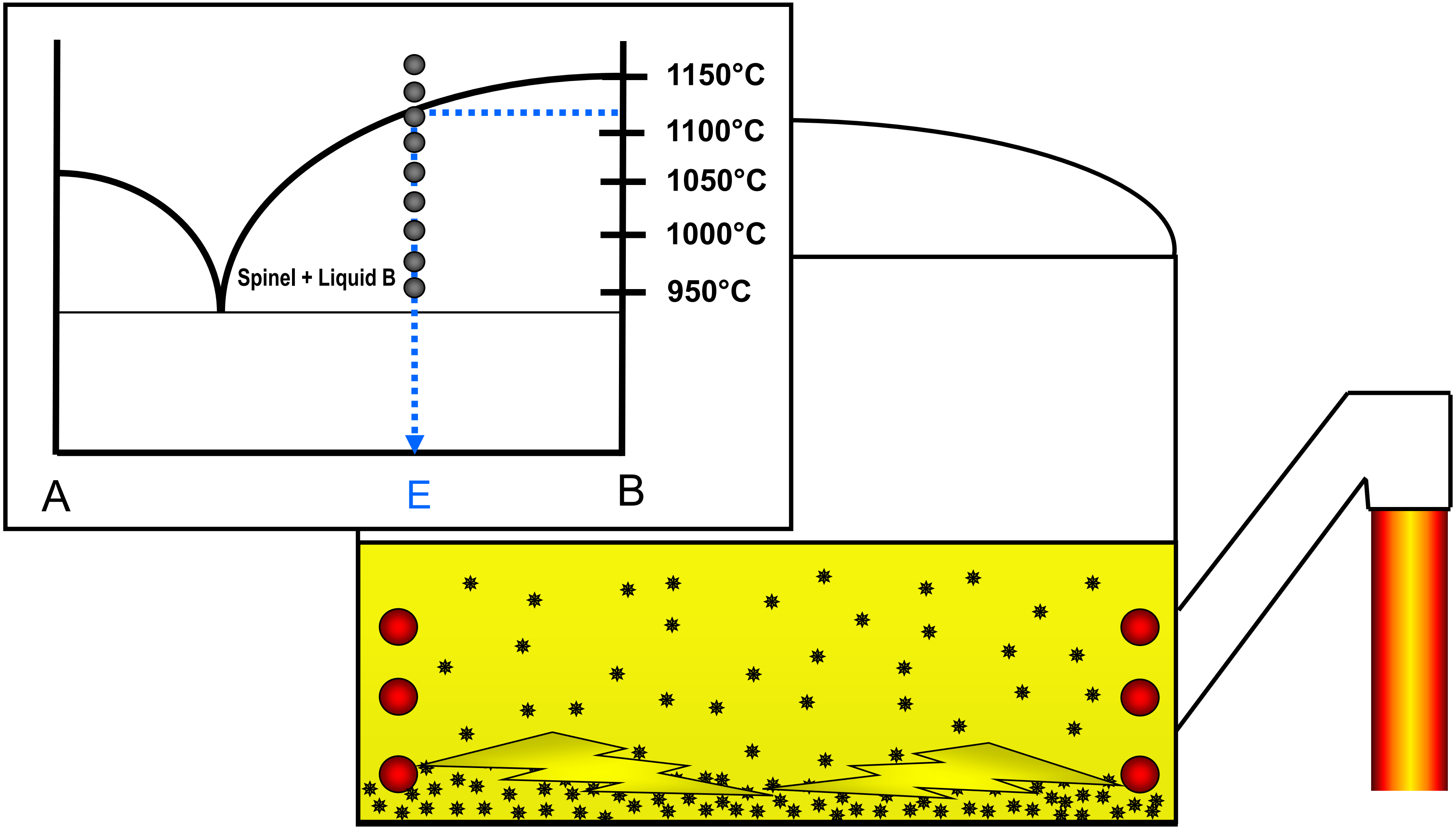
**DWPF Viscosity Constraint: 20 – 110 Poise at 1150°C**

# Liquidus Temperature ($T_L$)

- Significance of $T_L$
  - If $T_L$ is above the melter operating temperature ($T_M$), then crystals may form in the glass melter
  - If crystals form, they tend to settle in the melter bottom
    - Immediately - if they are large or form large agglomerates
    - Slower - if they are small, but the rate increases during melter idling when convective flow is slowed
  - The crystals can clog the melter pour spout, short electrodes, and/or disrupt flow in the melter
  - Typically, clogging in the pour spout is the most important concern
- DWPF $T_L$ constraint:
  - $T_L < T_M - k$, where k = 100°C
  - $T_L < 1050°C$ (without uncertainties)

**$T_L$ definition**: The lowest temperature at which the primary crystalline phase is in equilibrium with the glass

# Possible Impact of Crystallization on Melter Processing



# Waste Solubility

- Glass formulation must also meet individual component solubility constraints to prevent the formation of molten salts on the surface of the glass (cold cap), secondary phases in glass (crystalline species) and/or amorphous phase separation
  - $SO_4$: Solubility linked to acidity/basicity of glass, viscosity and salt phase formation
  - $Cr_2O_3$: Significant impact on $T_L$ and secondary phase formation
  - $TiO_2$: Impact on crystallization (nucleating agent)
  - $P_2O_5$: Secondary phase formation and amorphous phase separation
  - NaF and NaCl: Secondary phase formation and corrosion
  - $MoO_3$: Secondary phase formation and durability
  - Noble metals: Secondary phase formation and crystallization (nucleating agent)

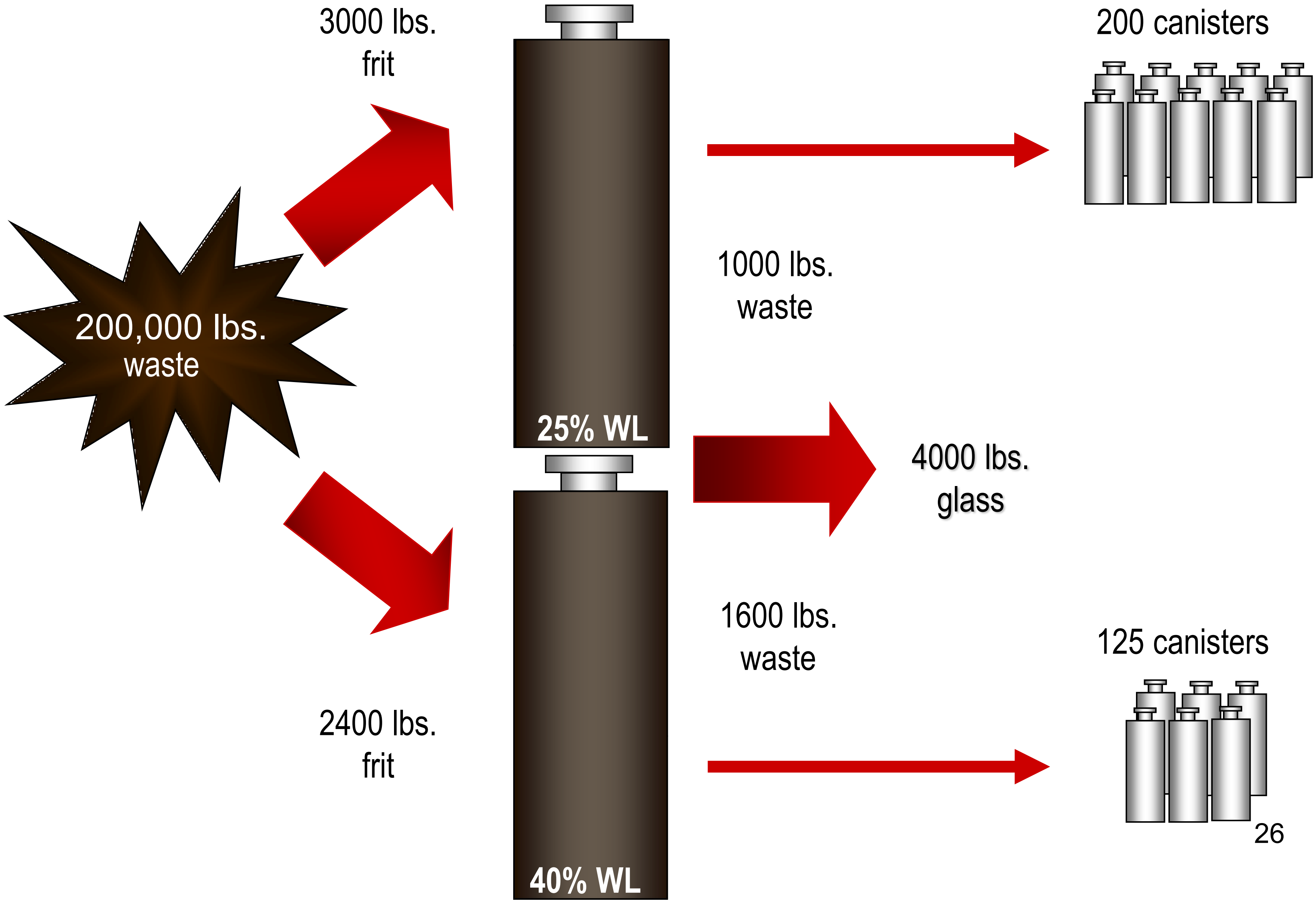
Solubility of $Cr_2O_3$ and $SO_4$ exceeded

Solubility of $MoO_3$ exceeded

# Terminology

- Waste Loading
  - kg of waste (calcined oxide basis) per 100 kg of glass
  - 35% WL: 35 kg of waste / 100 kg of glass
- Melting Rate
  - Time to convert incoming feed to a glass product
    - Complex series of reactions in which the frit/sludge mixture forms multiple intermediate phases along the pathway to forming a glass
- Melt rate and waste loading dictate waste throughput
  - Amount of waste processed per unit time
- Projected operating windows
  - Interval of waste loadings over which all glass system properties of importance are predicted to be acceptable

# Waste Loading: Impact on Canister Count

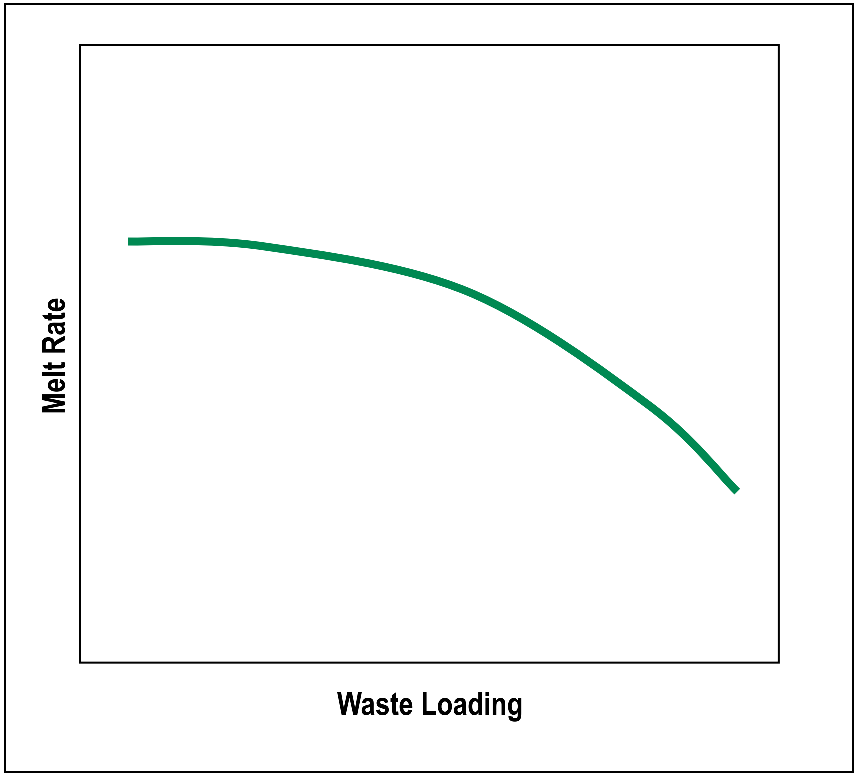


# Major Waste Loading Limiters

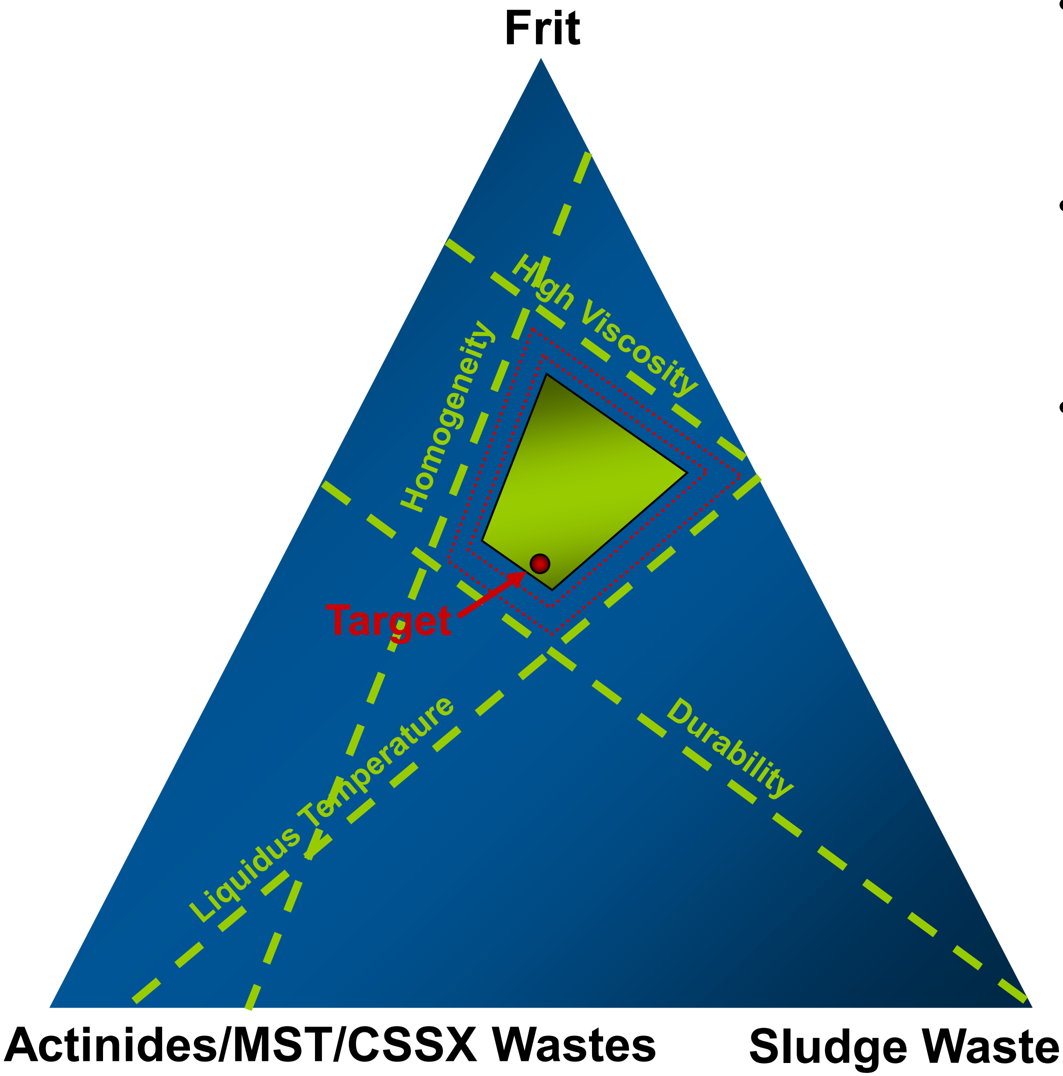
- Aluminum and sodium
  - Nepheline formation: corresponding decrease in durability (especially significant in glass that is slow cooled in canisters)
  - High aluminum content can increase viscosity
- Spinel formers (iron, nickel, chromium)
  - Increase $T_L$: potential impacts on glass pouring and electrical properties of melt due to crystal formation and/or settling
- Other low solubility waste components (Noble metals, molybdenum, sulfate, halides)
  - Secondary phase formation: corrosion, negative impacts to melter operations, safety

# Melting Rate

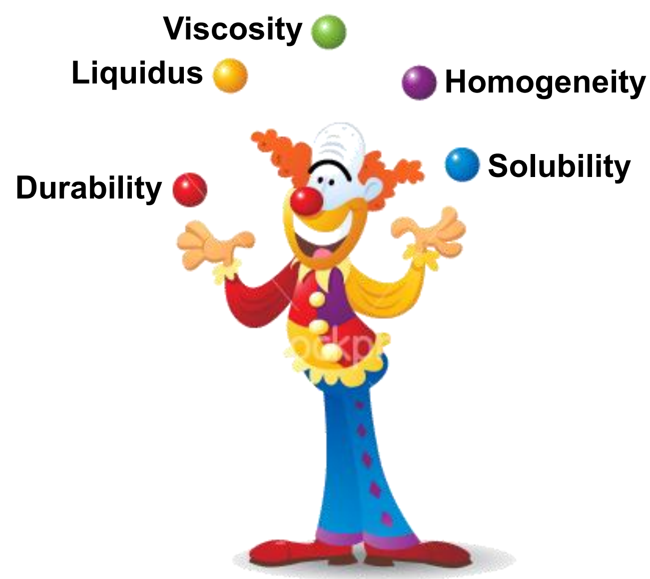
- Similar to waste loading, melting rate has impact on glass throughput
  - Melter feed preparation and canister closure and handling can be negatively impacted by melter “bottleneck” due to slow melting rate
- Melting rate is generally negatively correlated with waste loading
- Glass formulation changes shown to increase melting rate
  - Increase alkali (e.g. Li/Na)
  - Increase boron
- Melt rate measurement tools facilitate formulation optimization



# Product/Composition Models to Produce Acceptable Glass

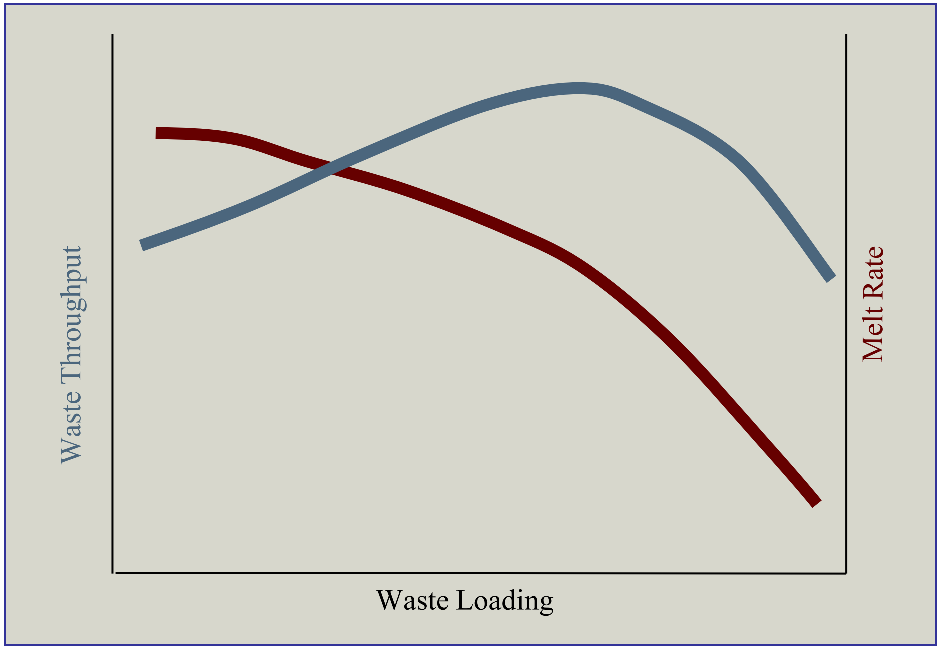



- Models can be based on fundamental glass chemistry relationships or empirical data
- Multivariate theory used to control within multi-dimensional composition space
- Parameter uncertainties incorporated into models



# Strategy for Glass Formulation

- Waste throughput is a function of melting rate and waste loading
  - Waste throughput is optimal amount of waste being processed through vitrification plant per unit time
  - Significant impact on life cycle costs of plant
- Objective: determine the "sweet spot" of waste loading and melting rate to maximize waste throughtput



# Increasing Waste Throughput

1) Process Faster → Increase Melt Rate

- More canisters per year
- Reduce production time and mission cost

2) Make Fewer canisters → Increase Waste Loading

- Less canisters containing more waste
- Reduce production time and mission cost
- Reduce canister storage and disposition cost

***Higher waste throughput ultimately reduces the total number of years the HLW system is operated (significant cost avoidance)***

# Approaches to Improve Waste Throughput

- Approaches to improve waste loading and/or melt rate
  - Reduce conservatism in process control models without compromising process or product performance issues
  - "Tailor" frits specifically to the waste composition
    - Higher waste loadings
    - Increased melt rates
  - Physical changes to the melter
    - Melt agitation (glass pump or agitators)
    - Advanced materials to increase melter temperatures
    - Advanced melters
  - Improving vitrification system attainment (time feeding melter)
    - Thorough understanding of processing steps and equipment to maximize facility operational time

# DWPF Example: Impact of new Frit Development

Implementation of “tailored” frits for SB2 and SB3 allowed significantly higher WLs to be targeted

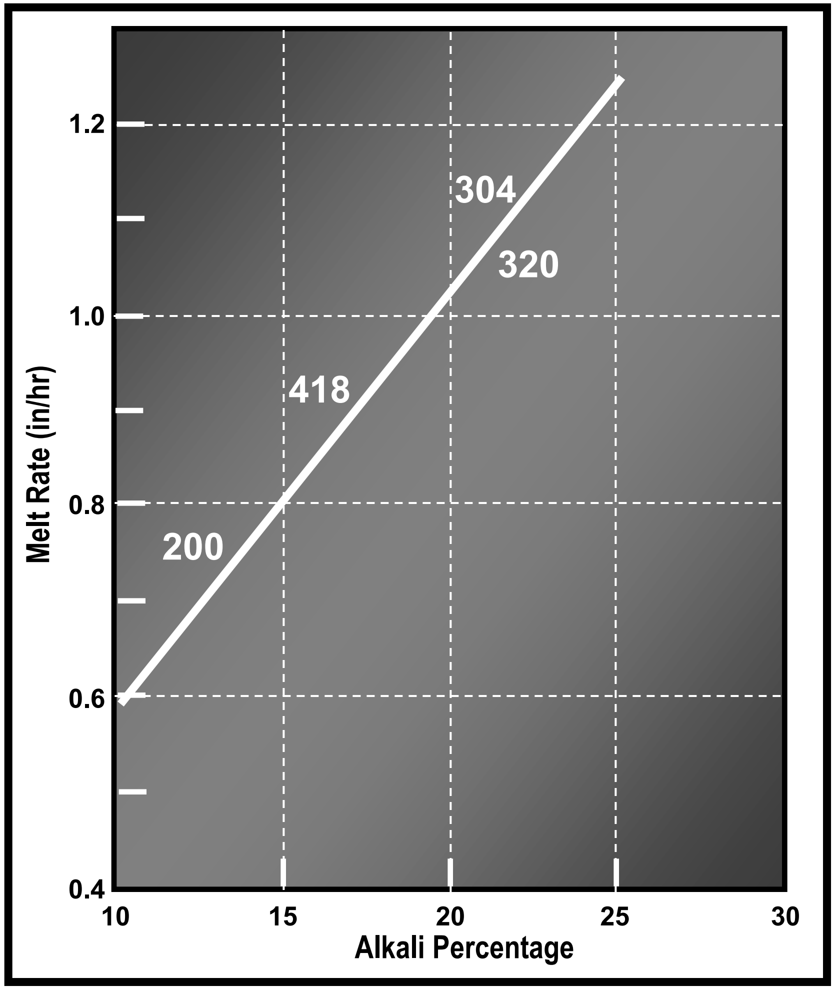
- Modeling to formulate new frits
- Testing with simulant compositions
- Testing with actual HLW waste

DWPF:
Frit 200 – SB2: nominal 28.1% WL
Frit 320 – SB2: nominal 33 – 34% WL
Frit 418 – SB3: nominal 38% WL

***Tailored frit development and implementation provided “step change” in WL potential***

# DWPF Example: Melt Rate - Impact of Alkali

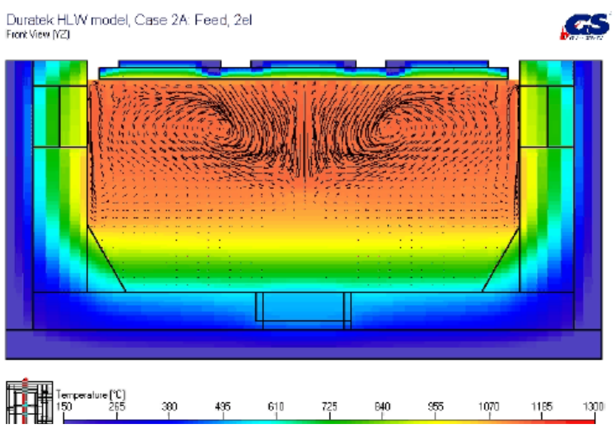
- Objective:
  - To improve melt rate without compromising processability or product quality
- Solutions:
  - Shift in frit development strategy
    - "Sliding $Na_2O$ scale" to balance durability requirements with amount of $Na_2O$ in waste
- Impacts:
  - Higher melting rates in DWPF
    - Trends between melt rate and total alkali in system
  - Improved rheological properties of sludge



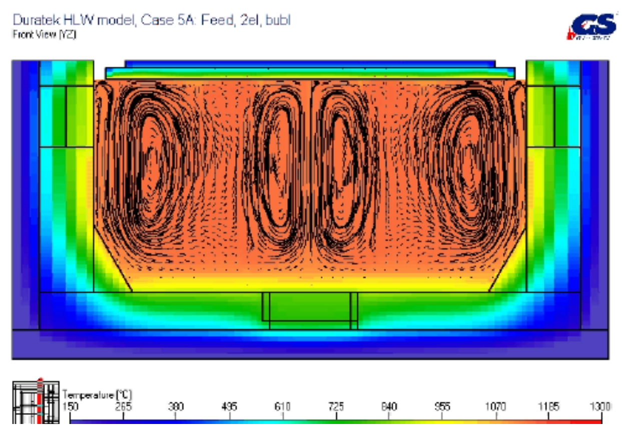
# DWPF Example: Melter Bubblers

- Objective:
  - Increase melt rate by delivering additional energy to agitate the melt to create forced convection and mixing
- Solution:
  - Install bubblers using existing penetrations in DWPF melter
- Impact:
  - By accelerating the melting process, bubblers have been shown to increase glass production rates by up to **66%**.
  - Coupled with a significant increase in waste loading; waste throughput significantly increased

**Unagitated Melter (natural convection)**




**Bubbled Melter (forced convection)**



# Summary

- Borosilicate glass provides the necessary properties to immobilize HLW
- HLW glass formulations must meet product quality and processing requirements
- Waste loading can be limited by formation of deleterious crystalline phases and insoluble species
- Melting rate impacts production rate and efficiency of other plant processes
  - Melting rate is generally negatively correlated with waste loading
- Glass formulation and melter improvements strategies are employed to increase waste throughput

Waste Throughput = Waste Loading × Melting Rate