Waste Vitrification - Overview of Current Practice

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Washington, DC

ICTP-IAEA Workshop
November 6 – 10, 2017
Overview

- VSL background
- Vitrification – what and why?
- Vitrification constraints
- Glass formulation and process optimization
  - Defense legacy wastes vs. modern reprocessing wastes
- Vitrification processes
- Off-gas treatment
Glass Formulation and Process Development at VSL

- Developed the glass formulations used at WVDP and SRS M-Area
- Support to Hanford WTP since 1996
- Support to Rokkasho since 2005
- Support to DWPF since 2009
- VSL Joule Heated Ceramic Melter (JHCM) Systems:
  - The largest array of JHCM test systems in the US
  - The largest JHCM test platform in the US

3 scales, 60X scale-up across VSL test melters
Vitrification

• Immobilization of waste by conversion into a glass
  • Internationally accepted treatment for HLW
  • Can also have advantages for other waste streams

• Why glass?
  • Amorphous material – able to incorporate a wide spectrum of elements over wide ranges of composition; resistant to radiation and transmutation damage
  • Waste elements become part of the glass structure
  • Long-term durability – natural analogs
  • Relatively simple process – amenable to nuclearization at large scale

• There are numerous glass-forming systems – why borosilicate glass?
  • Relatively low-melting temperature
    • Materials of construction, component lifetimes
  • Potential for high chemical durability
Vitrification...

- Waste and additives are heated and react to form molten glass
  - Additives can be separate chemicals or a glass frit
  - Can be pre-mixed or fed separately
  - Additives are formulated to optimize the process
- Molten glass is typically poured into containers where it solidifies; container is sealed and decontaminated
- Alternatively, melting can be done in the disposal container
- Major systems:

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Waste and Additives → Feed System / Pretreatment → Melter → Off-Gas Treatment System → Exhaust
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Glass Product Handling
During Vitrification...

- Water is evaporated
- Salts melt and decompose
  - $\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2$; $\text{Al(NO}_3)_3 \rightarrow \text{Al}_2\text{O}_3 + \text{NO}_x$, $2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$; etc.
- Oxides react and melt to form molten glass
- Organics are pyrolyzed and oxidized
- Most metals, if present, are oxidized if sufficiently small amounts and particle size
- Most species are incorporated into silicate glasses as their oxides; exceptions include Cl, F, I
- Volatile species (such as $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{NO}_x$, etc.) are completely lost to the off-gas stream
  - Typically contributes to significant volume reduction
- Other species are retained in the glass melt to varying extents
- Additional losses due to physical entrainment (dust)
JHCM – Principle of Operation

- Reaction at an interface so *melt rate* scales as the melt surface area, other things equal
- Melt rate also depends on temperature, mixing, feed and glass composition, etc.
- PAMELA, WVDP, DWPF, WTP, Mayak, VEK, Rokkasho, Tokai, Lanzhou, etc.

![Diagram of JHCM process]

- Input: Waste + glass forming additives (chemicals or frit)
- Output: Glass Product
VSL DM1200 HLW Pilot Melter System

About 400,000 kg glass made from about 1 million kg feed
DM1200 Cold Cap Samples
Spinels and Noble Metals Phases
Inside the VSL DM1200 HLW Pilot Melter: **Start of Feeding**
Inside the VSL DM1200 HLW Pilot Melter: Partial Cold Cap
Inside the VSL DM1200 HLW Pilot Melter: Steady State
Process Optimization

- Higher waste treatment rate capability translates into cost savings through small plant size and/or reduced operating time

\[
\text{Waste Treatment Rate} = \text{Glass Production Rate} \times \text{Waste Loading in Glass}
\]

- Increased *waste loading* increases waste treatment rate and reduces volume for disposal
- Increased *glass production rate* increases waste treatment rate
- Both factors depend on waste composition and *glass composition*
- Optimization of glass composition can have drastic effects on overall process economics
  - Such changes are easy to implement since they do not require hardware changes
  - Complicated by numerous components present in typical wastes
  - Problem in constrained optimization of multiple properties with respect to numerous composition variables
  - Typically requires large data sets and development of glass property-composition models
Typical Vitrification Constraints

• Product Quality – Depends on requirements
  • Chemical durability – per specific short-term test and long-term performance assessment
  • Thermal and radiation stability
  • Phase composition
  • Heat load

• Processability – Depends on melter technology
  • Melt viscosity
  • Melt electrical conductivity
  • Crystallinity
  • Salt formation – e.g., sulfate, molybdate, etc.
  • Processing rate

• Economic
  • Processing rate
  • Waste loading
  • Volume reduction
  • Materials compatibility (melter lifetime)

• Other
  • Typically also require information on properties such as density, thermal conductivity, heat capacity, etc.
Salt Formation

- **Sulfate**
  - High-sulfate feeds increase the tendency for sulfate salt formation
  - Sulfate salt formation in the melter is deleterious:
    - Salt is very corrosive, low melting, very fluid, highly electrically conductive, and incorporates toxic elements (e.g., Cr) and radionuclides (e.g., Tc, Cs, Sr) into the water-soluble salt
  - Additives such as Li, V, Ca significantly increase sulfate tolerance
  - Cl, Cr, Mo, Re reduce sulfate tolerance

- **Molybdate**
  - Na/Li/Cs Molybdate
  - Ca/Ba Molybdate
Yellow Phase Evolution

Phase stability of yellow phase varies with temperature

Migration of yellow phase depends on salt composition $\rightarrow$ Density ($f(C_i, T)$)

YP Sinks (lower $T \rightarrow$ Ca-Mo separate)

YP Floats

HLW glass melts
Structural Characteristics of Mo in HLW Glass

Molybdenum species in HLW glass:
$\text{Mo}^{6+}\text{O}_4^{2-}$ by XAS (Mo XANES)

Molybdenum species in HLW Glass:
$\text{R}_2\text{Mo}^{6+}\text{O}_4^{2-}$ by Raman
XAS (XANES, EXAFS) Studies on Silicate Glasses

- Na: Na\(^{+}\)O\(_{3-7}\) : Na-O = 2.30 -2.60 Å
- Mn: Mn\(^{2+}\)O\(_{4-5}\) : Mn-O = 2.07 Å, Mn-Mn = 3.48 Å
- Cu: Cu\(^{2+}\)O\(_{4}\) : Cu-O = 1.96 Å, Cu-Cu = 2.98 Å
- Sr: Sr\(^{2+}\)O\(_{4-5}\) : Sr-O = 2.53 Å
- Zr: Zr\(^{4+}\)O\(_{6-7}\) : Zr-O = 2.08 Å
- Mo: Mo\(^{6+}\)O\(_{4}\) : Mo-O = 1.75 Å
- Ag: Ag\(^{+}\)O\(_{2}\) : Ag-O = 2.10 – 2.20 Å
- I: I\((Na,I)_{4}\) : I-Li = 2.80 Å, I-Na = 3.04 Å
- Re: Re\(^{7+}\)O\(_{4}\) : Re-O = 1.74 Å
- Bi: Bi\(^{3+}\)O\(_{3}\) : Bi-O = 2.13 Å
- S: S\(^{6+}\)O\(_{4}\) surrounded by network modifiers; S\(^{2-}\); S-S
- Cl: Cl-O = 2.70 Å; Cl-Cl = 2.44 Å; Cl-Na; Cl-Ca
- V: V\(^{5+}\)O\(_{4}\); minor V\(^{4+}\)O\(_{5}\) under reducing conditions
- Cr: redox sensitive: Cr\(^{6+}\)O\(_{4}\) Cr-O = 1.64 Å; Cr\(^{3+}\)O\(_{6}\) Cr-O = 2.00 Å; Cr\(^{2+}\)O\(_{4}\) Cr-O ~ 2.02 Å
- Tc: redox sensitive, Tc\(^{4+}\)O\(_{6}\) Tc-O = 2.00Å; Tc\(^{7+}\)O\(_{4}\) Tc-O = 1.75 Å; evidence of Tc-Tc = 2.56 Å in hydrated, altered glass
- Sn: Sn\(^{4+}\)O\(_{6}\) (minor Sn\(^{2+}\)O\(_{4}\)) Sn-O = 2.03 Å; Sn-Sn = 3.50 Å
- Al: Al\(^{3+}\)O\(_{4}\) : Al-O: 1.77 Å
- Si: Si\(^{4+}\)O\(_{4}\) : various polymerizations
- Zn: Zn\(^{2+}\)O\(_{4}\) : Zr-O: 1.96 Å, Zn-Si \(2^{nd}\) nearest-neighbor evidence
Standard Glass Leach Tests - Examples

- **Product Consistency Test (PCT)**
  - Glass powder (75 – 150 um), deionized water, 90°C, 7 days, S/V = 2000 m⁻¹
- **Toxicity Characteristic Leaching Procedure (TCLP)**
  - Glass pieces (<1 cm), sodium acetate buffer (~pH 5), 23°C, 18 hrs, constant end-over-end rotation at 30 rpm
- **MCC-1**
  - Glass monolith, deionized water, typically 90°C and 28 days, S/V = 10 m⁻¹
- **Vapor Hydration Test**
  - Glass monolith, steam in pressure vessel at 200°C, typically 24 days; measure altered layer thickness
- **Single-Pass Flow Through**
  - Glass powder in flow cell; various leachants, temperatures, and flow rates; run to steady state concentrations in leachate
- **Soxhlet Test**
  - Glass monolith, refluxing water (100°C); variable durations
- **IAEA Test**
  - Glass monolith, 25°C, deionized water, periodic total replacement
- **ANS/ANSI 16.1**
  - Diffusion-based - primarily intended for cementious waste forms; cylinder, deionized water, 25°C, periodic total replacement
- **Many Others**
Schematic Overview of Water-Glass Reaction

Stages

I

Initial rate $r_0$

Rate drop

Residual rate $r_r$

II

Possible Resumption

III

Time

Amount of altered glass

Hydrolysis

Protective layer & solution saturation

Interdiffusion

Water diffusion & Secondary phases precipitation

Large precipitation of silicate minerals
Long-Term Glass Leaching Tests
Thousands of tests, up to 39 years

Zeolite-type aluminosilicate phases, identified as phillipsite

Slow growth of a phyllosilicate (smectite-type identified as a nontronite)
Example: Glasses Characterized to Support Hanford WTP LAW Operating Envelope

- 538 LAW glasses, designed, fabricated and characterized
- Combination of statistical and active design
- Multiple properties relating to product quality and processability
- Data set used to develop glass property-composition models for those properties
Example LAW Glass Property Models
HLW Glass Property Models

- PCT B, Li, Na
- TCLP Cd
- Spinel T$_{1\%}$
- Melt viscosity
- Melt electrical conductivity
- Nepheline formation

- Model development supported by statistically-designed test matrices
Melter Technologies - Examples

- Hot wall induction melters
  - La Hague, Sellafield, India (several)
- Cold wall induction melters (“cold crucible” CCIM)
  - Radon, Ulchin, La Hague
- Joule-heated ceramic melters (JHCM)
  - PAMELA, WVDP, DWPF, WTP, Mayak, VEK, Rokkasho, Tokai, Lanzhou
- Others
  - Plasma
  - Microwave
  - Cyclone combustion
  - Submerged combustion
  - In-can
  - Stirred
Hot Wall Induction Melting

French Two-Stage Continuous Vitrification Process

Diagram showing the process with various steps such as:
- Additives
- Flow rate measurement
- Dust recycling
- Condensation
- Final gas treatment
- Gaseous release
- Dust removal
- Liquid waste treatment
- Air cooling
- Glass frit
- Calcination
- PF concentrates
- Sampling
- Supply
- Glass melting
- Glass pouring
- Cooling
- Decontamination
- Interim storage
- Control
- Lid welding
- Heat and activity will decrease naturally over time
Cold Crucible Induction Melting

Cold Crucible Melting Principle

- Cold crucible
- Cold cap
- Solidified glass
- Molten glass
- Coil

Korean, Ulchin

Russian, Radon

French
DWPF and WTP HLW Melters

- 2.6 m² melt surface area
- Vacuum discharge
- Lid heaters
- Glass frit
- Bottom drain

- 3.75 m² melt surface area
- Air-lift discharge
- Bubblers
- Glass forming chemicals
- WTP has two HLW melters
Other JHCMs
West Valley Demonstration Project

- Only US commercial reprocessing facility
- VSL Support 1985 – 1993
  - Glass formulations developed at VSL
  - Melter testing
- ~660,000 gal HLW containing 24 million curies converted to 275 canisters of glass (~550 MT) using VSL glass formulation
- Vitrification facility decommissioned
WVDP Vitrification Process
Defense Waste Processing Facility (DWPF)

Facility has been operating on DOE site in South Carolina since 1996. Since 2009, VSL has been providing R&D support to enhance its performance to expedite completion of waste treatment

~Doubled melter throughput with retro-fit of bubblers
Melt Rate Enhancement

- Conventional JHCMs rely on natural convection in a viscous melt
- Melt rate is limited by heat and mass transport at the cold cap
- VSL developed active melt pool mixing using bubbler arrays
- Provides drastic increases in melt rates (up to 5X)
  - Used successfully at SRS M-Area
  - Incorporated into Hanford WTP LAW and HLW melters
  - Retro-fitted into Savannah River DWPF melter
DWPF Melter Off Gas Treatment System
The Hanford Waste Treatment Plant

HLW Melter

LAW Melter
WTP LAW Melters

- LAW Production = 30 MT glass/day with ES-VSL bubbler technology
- Weight: 330 tons
- Exterior Dimensions: 29’-6” (L) x 21’-6” (W) x 15’-9” (H)
- 10 m² glass pool surface area
- 7630 L molten glass pool
- Design production rate 15 MT glass/day each

LAW Melter During Installation
Hanford WTP HLW Vitrification

WTP HLW Flow Diagram

C5

Glass Formers

Pretreated HLW Concentrate

HLW Melter 1 Feed 5500 gal

Hold Point

HLW Melter 2 Feed 5500 gal

HLW Melter 2 Feed 5500 gal

HLW Melter 1 Feed 5500 gal

Submerged Bed Scrubber SBS

Offgas cooling Particulate Removal

Wet filter for aerosol removal

High Efficiency Mist Eliminator HEME

Wet Electrostatic Precipitator WESP Particulate Removal

Particulate removal

High Efficiency Particulate Air Filter HEPA

Primary Offgas (HOP)

C5 Exhaust Fans

C5

Secondary Offgas

Booster Extraction Fan

Activated Carbon Column ADSR Mercury removal

NH3 supply

Silver Mordenite Column ADSR

Remove gaseous halides such as I-129

Selective Catalytic Oxidizer & Reducer SO2 & SCR

Oxidize VOCs Reduce NOx using NH3

Slack Extraction Fan

Provide Offgas motive force

C5

Condensate (SBS) 5,300 gal

Sumps/Washings

Plant Wash and Drains 6,400 gal

CS condensate, HEME/WESP drains

Condensate (SBS) 5,950 gal

Primary Offgas Identical to Melter 1 Offgas

C5

Primary Offgas

Condensate (SBS) 5,950 gal

SBS condensate, HEME/WESP drains

Secondary Offgas

Canister Decon

Waste Neutralization 4,076 gal

Acid Waste 11,000 gal

Liquid Effluent to Pretreatment Facility

Liquid Effluent to Pretreatment Facility

HDH - 4 560 gal per canister

HDH - 2 560 gal per canister

C5

C5

CUA
Foaming During *Cooling* of High Bi-P HLW Glass Melts

Hanford WTP
HLW Melter

Risk of overflow of HLW glass during canister cooling
Foaming During **Cooling** of High Bi-P HLW Glass Melts

- Essential role of P & Cr but not Bi
- Stabilization of hexavalent Cr in phospho-chromate environments in the melt; auto-reduction to trivalent Cr on cooling as a result of its higher stability in spinels
- Results were used to modify glass formulations to mitigate melt foaming
- Confirmed in one-third scale DM1200 pilot melter tests
Effect of Form of Cr on Spinel Crystallization

- Cr tends to promote spinel formation
  - e.g., $\text{Cr}_2\text{O}_3 + \text{FeO} \rightarrow \text{Cr}_2\text{FeO}_4$
  - Redox conditions determine $\text{Cr}^{3+}/\text{Cr}^{6+}$
  - Form of Cr in the batch affects amount of crystallization in the glass product

Approach to Phase Equilibrium
XANES Analysis of Cr Redox

Cr XANES

Cr$^{3+}$/Cr$^{6+}$ (glass at 1150°C)

Approach to Redox Equilibrium

Cr$_2$O$_3$ as source material

Cr(NO$_3$)$_3$·9H$_2$O as source material

Cr XANES Fitting Results
Effect of Form of Cr on Spinel Crystallization – Melter Tests

- **Cr-nitrate** → less Cr$^{3+}$ → less spinel → more Cr dissolved in glass
  - $\text{Cr}^{3+}/\text{Cr}^{6+}$ increases as oxygen diffuses away
  - $2\text{Cr}^{6+}\text{O}_3 \rightarrow \text{Cr}_2\text{O}_3 + \frac{3}{2} \text{O}_2$
- **Cr-oxide** → more Cr$^{3+}$ → more spinel → less Cr dissolved in glass
  - $\text{Cr}^{3+}/\text{Cr}^{6+}$ decreases as oxygen diffuses in
  - $\text{Cr}_2\text{O}_3 + \frac{3}{2} \text{O}_2 \rightarrow 2 \text{Cr}^{6+}\text{O}_3$
- Very slow redox kinetics

Results can be used to reduce crystallization during processing of high-Cr HLW streams and thereby increase waste loadings
Reduction of $\text{Bi}_2\text{O}_3$ and Inconel 690 Metal Corrosion

- Effect of redox on high-Bi HW glasses
- Inconel 690 alloy (Ni-Cr-Fe) corrosion in Bi-rich HLW glasses

**Bi-rich HLW Glass**
- $\text{Bi}_2\text{O}_3 = 6.7$ wt%
- $\text{Fe}_2\text{O}_3 = 7$ wt%
- $\text{NiO} = 1.9$ wt%
- $\text{P}_2\text{O}_5 = 5$ wt%

**Inconel 690 Alloy**
- $\text{Ni} = 58$ wt%
- $\text{Cr} = 27-31$ wt%
- $\text{Fe} = 7-11$ wt%

CO+CO$_2$

1150°C
Reduction of $\text{Bi}_2\text{O}_3$ and Inconel 690 Metal Corrosion

- Inconel 690 Corrosion in Bi-rich and Bi-free HLW melts at 1150°C and $10^{-5.8}$ atm $\text{O}_2$
- Inconel 690 Corrosion in Bi-rich HLW melts at 1150°C and $10^{-5.8}$, $10^{-4}$ atm $\text{O}_2$, and ambient air
- Test metal coupon: 0.15x0.3x1 inch with S/V=0.15cm$^{-1}$ for 7 days under controlled atmosphere

**6.7 wt% $\text{Bi}_2\text{O}_3$**

**$10^{-5.8}$ atm $\text{O}_2$**

**Bi-free**

**$10^{-5.8}$ atm $\text{O}_2$**

**Redox**

**Inconel 690 Corrosion in Bi-rich HLW Glass**

$\text{Bi} + \text{reduction} \rightarrow \text{Ni/Bi alloying} \rightarrow \text{Catastrophic failure of Ni-Cr alloy at 1150°C}$