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Vitrification as a Complex-Wide Management Practice for High-Level Waste

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EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

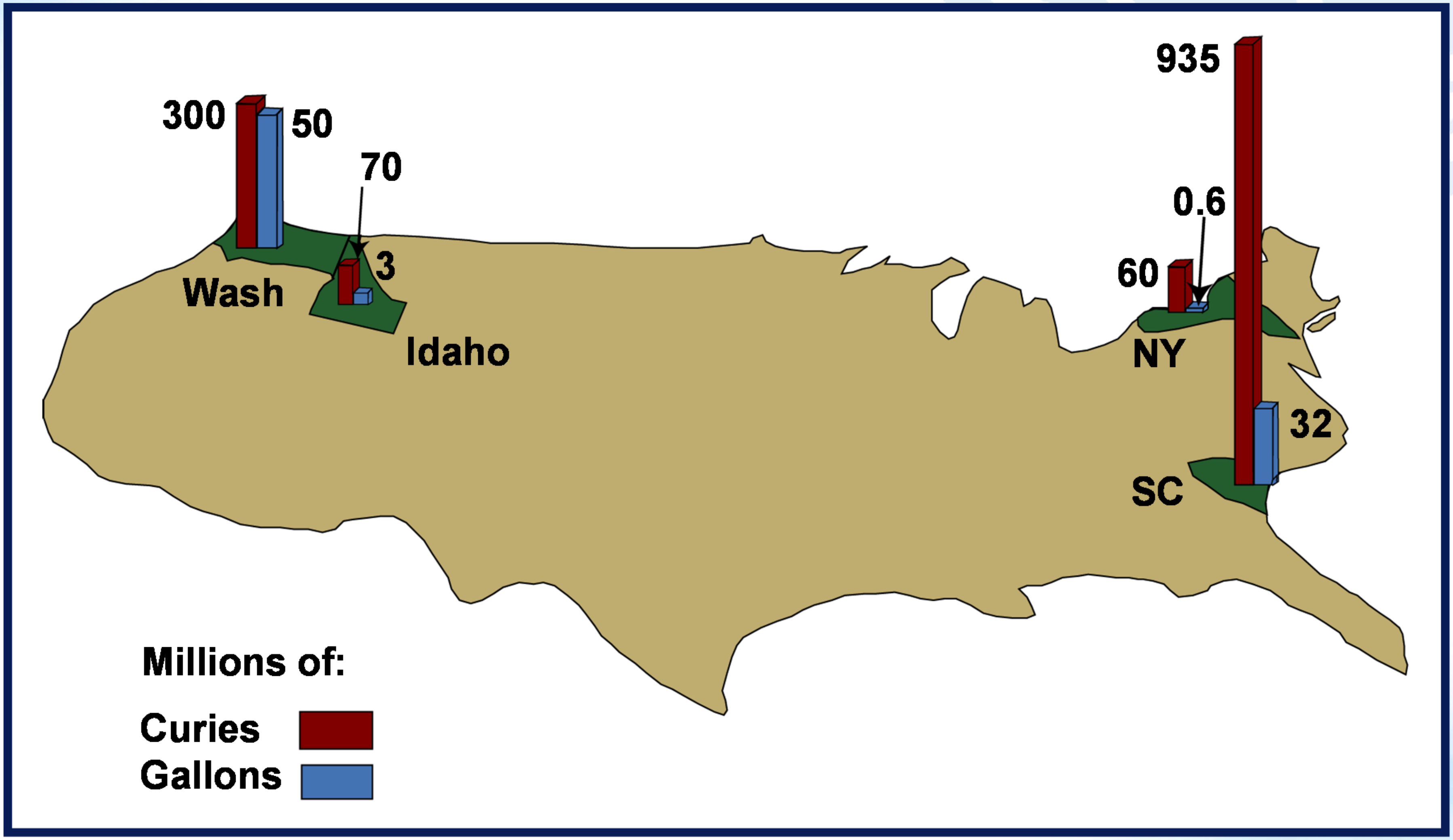
SRNL-STI-2013-00197

Summary of Talking Points

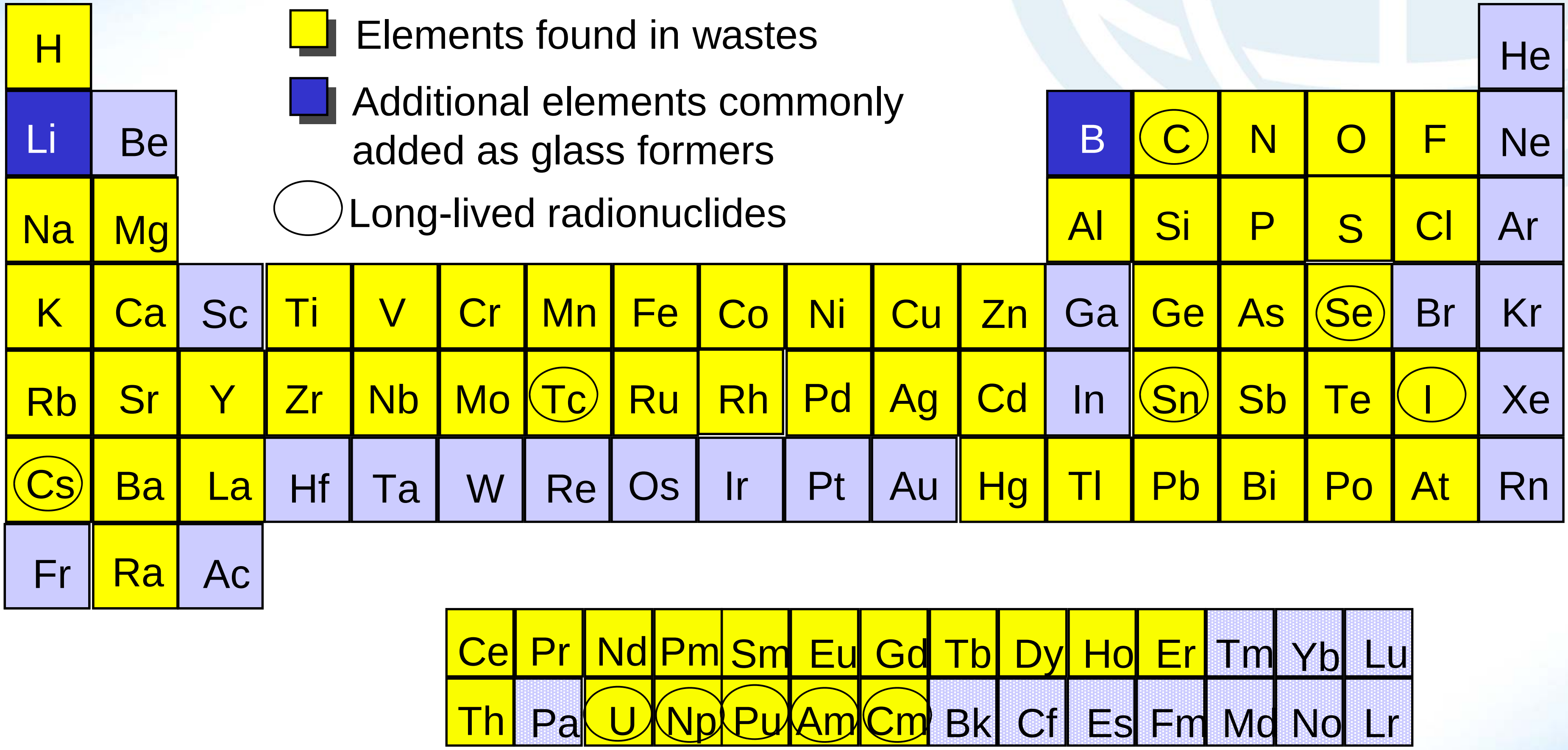
STATUS REPORT ON THE COMPLEX-WIDE EFFORT TO VITRIFY HLW

- Timeline of HLW glass and glass-ceramics development
- What types of glass will be produced?
  - How much of each type and how many waste canisters?
- How are the strategies at the different EM sites similar or different?
- What are the technical and performance standards for glass as a waste form
  - tests for the determination of the long-term performance of glass with respect to disposal in different geologic environments (salt, granite, clay, and tuff)

HLW Distribution in the US



Elements in US HLW Defense Glass



🟨 Elements found in wastes

🟦 Additional elements commonly added as glass formers

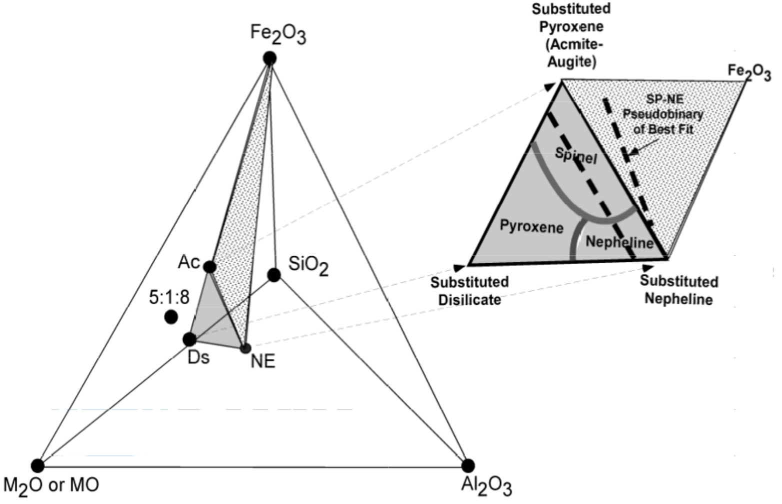
○ Long-lived radionuclides

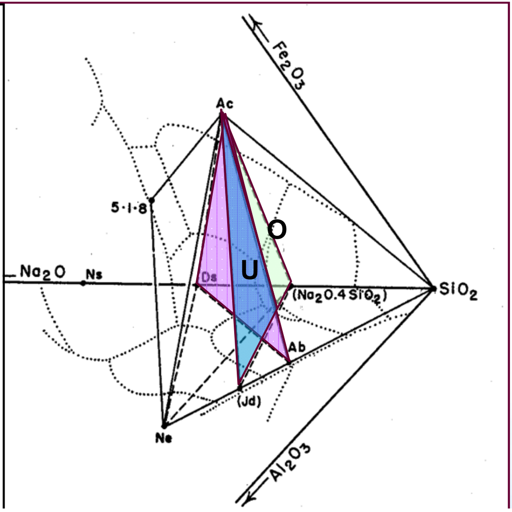
🟨 H																	He
🟦 Li	Be											🟦 B	🟨 C ○	🟨 N	🟨 O	🟨 F	Ne
🟨 Na	🟨 Mg											🟨 Al	🟨 Si	🟨 P	🟨 S	🟨 Cl	Ar
🟨 K	🟨 Ca	Sc	🟨 Ti	🟨 V	🟨 Cr	🟨 Mn	🟨 Fe	🟨 Co	🟨 Ni	🟨 Cu	🟨 Zn	Ga	🟨 Ge	🟨 As	🟨 Se ○	Br	Kr
🟨 Rb	🟨 Sr	🟨 Y	🟨 Zr	🟨 Nb	🟨 Mo	🟨 Tc ○	🟨 Ru	🟨 Rh	🟨 Pd	🟨 Ag	🟨 Cd	In	🟨 Sn ○	🟨 Sb	🟨 Te	🟨 I ○	Xe
🟨 Cs ○	🟨 Ba	🟨 La	Hf	Ta	W	Re	Os	Ir	Pt	Au	🟨 Hg	🟨 Tl	🟨 Pb	🟨 Bi	🟨 Po	🟨 At	Rn
Fr	🟨 Ra	Ac															

🟨 Ce	🟨 Pr	🟨 Nd	🟨 Pm	🟨 Sm	🟨 Eu	🟨 Gd	🟨 Tb	🟨 Dy	🟨 Ho	🟨 Er	Tm	Yb	Lu
🟨 Th	Pa	🟨 U ○	🟨 Np ○	🟨 Pu ○	🟨 Am ○	🟨 Cm ○	Bk	Cf	Es	Fm	Md	No	Lr

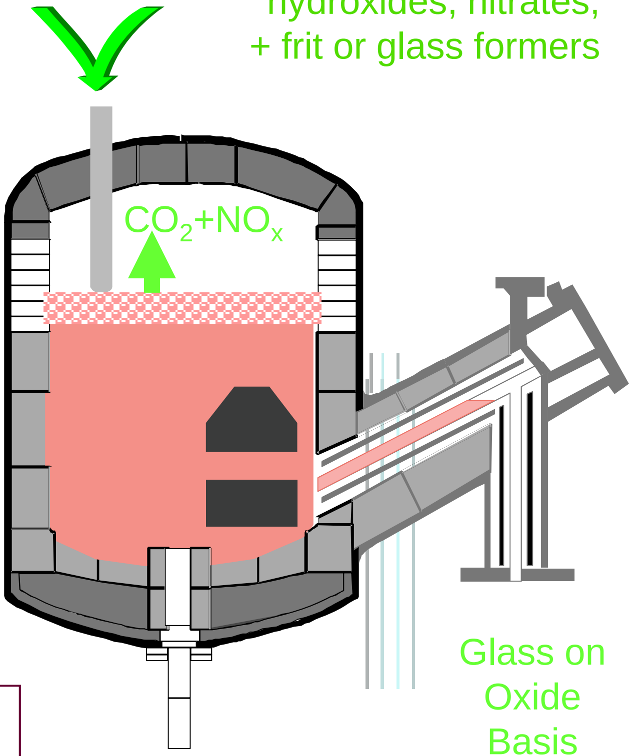
Similarity of HLW Glass to Basalt Magma

Oxide	165 Avg	131 HM	131 Purex	Tholeiite	Ijolite
				(Barth, Theoretical Petrology)	
Al_2O_3	6.5	13.1	3.8	14.4	20.0
CaO + MgO	3.2	3.7	4.0	17.5	16.3
Fe_2O_3	14.4	14.2	16.8	12.4	4.3
K_2O + Na_2O + (Li_2O)	14.5	15.0	19.6	3.3	13.2
SiO_2	61.4	54.0	55.9	52.4	46.1





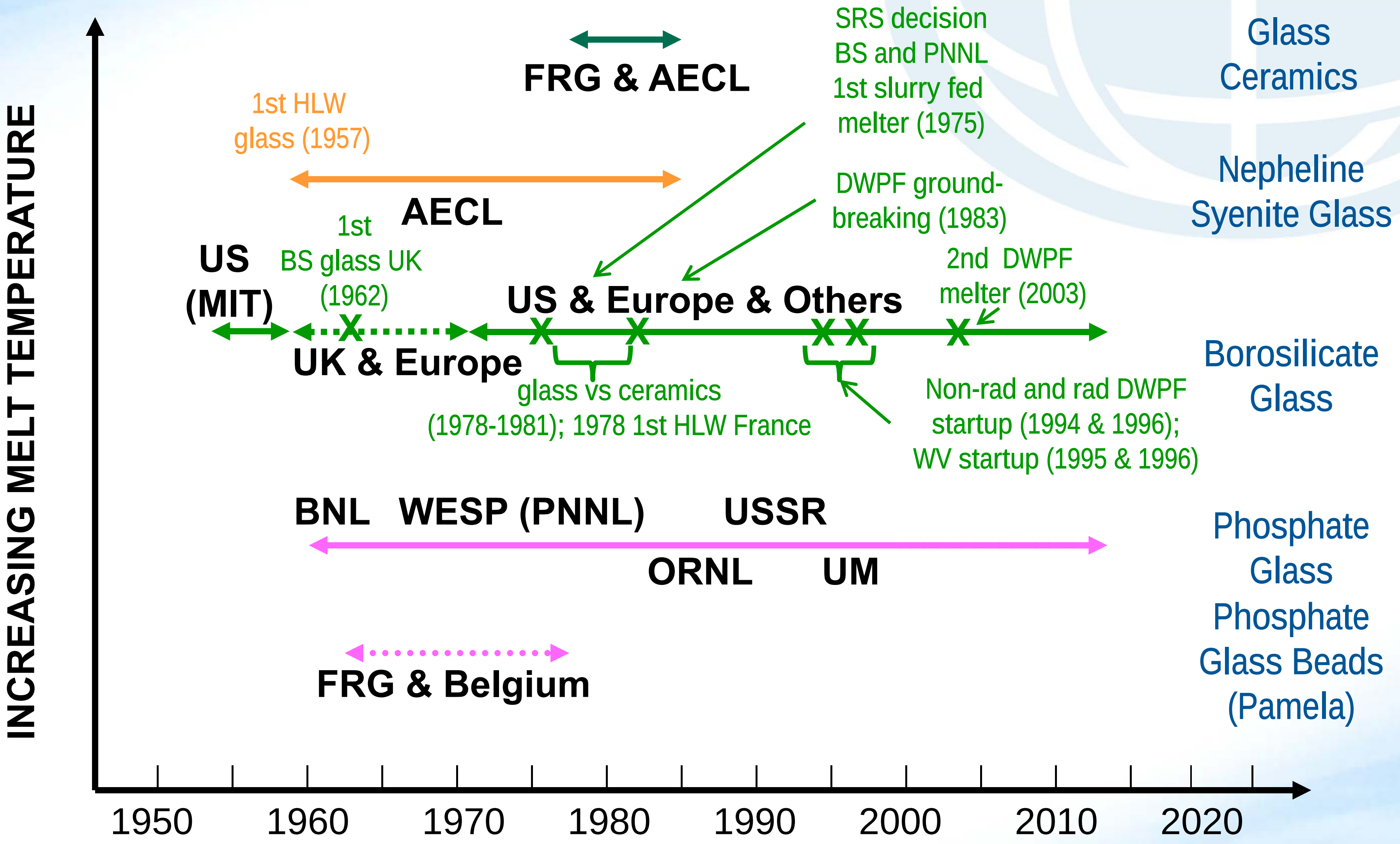
$NaNO_3$, $NaCOOH$, NaC_2O_4, Waste hydroxides, nitrates, + frit or glass formers



Glass on Oxide Basis

D.K. Bailey and J.F. Schairer, J. of Petrology, 7[1], 114-170 (1966); J. Nolan, Q. J. Geol. Soc. London, 122, 119–57 (1966); Jantzen, C.M., and Brown, K.G. J. Am. Ceram. Soc., 90 [6], 1866-1879 and 1880-1891 (2007).

Waste Glass Vitrification Timeline

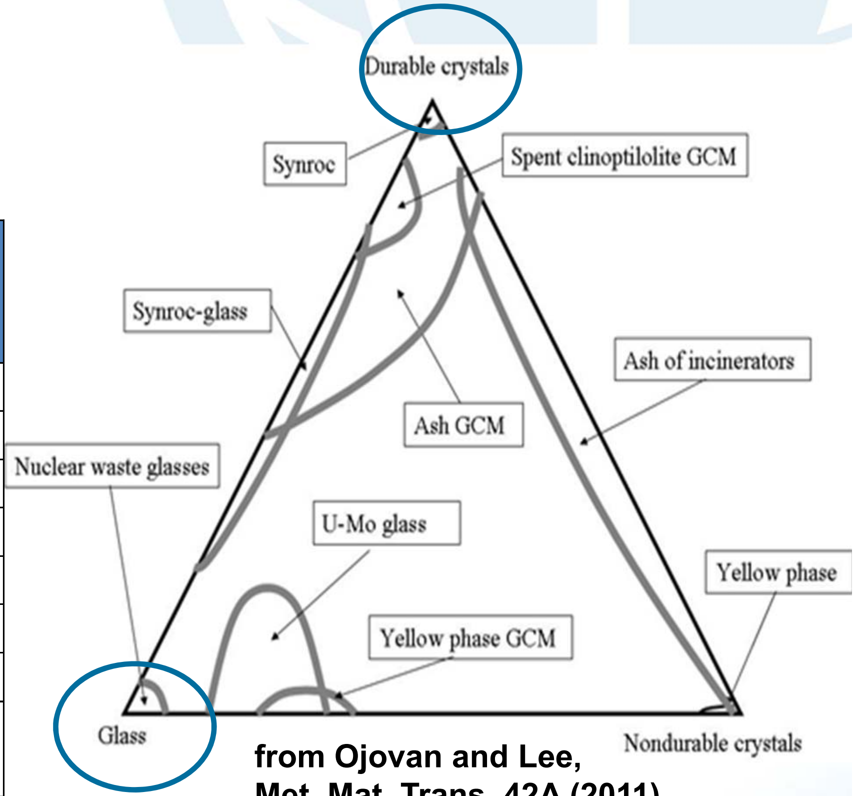


Glass vs. Ceramics (1978-1982)

DOE's "Hench" Panel

- 3 year study comparing simulated HLW glasses and ceramics

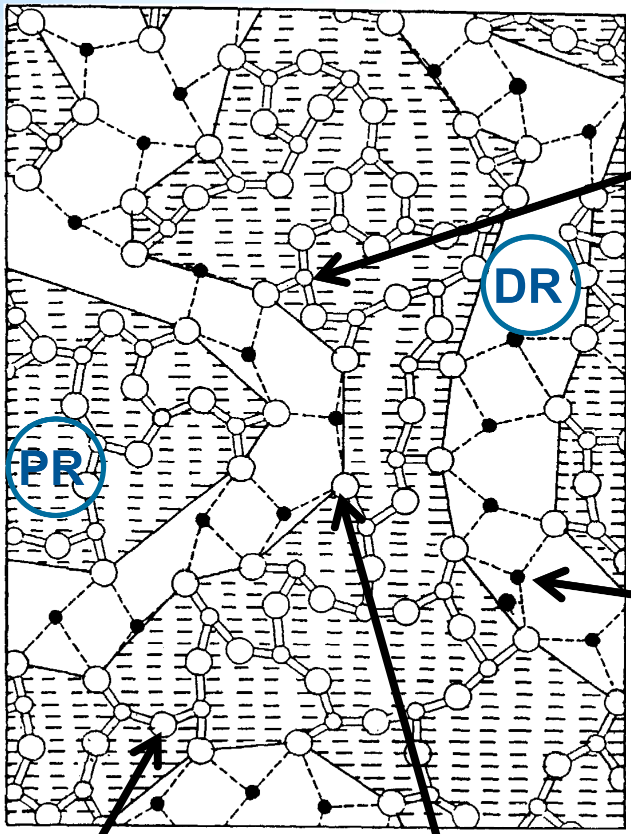
Waste Form	Product Score	Process Score	Combined Figure-of-Merit
Borosilicate Glass	67	83	75
SYNROC	95	42	63
Tailored Ceramic	93	42	62
High-Silica Glass	64	51	57
FUETAP Concrete	39	77	55
Coated Particles	87	32	53
Glass Marbles in a Lead Matrix	40	58	48



from Ojovan and Lee, Met. Mat. Trans. 42A (2011)

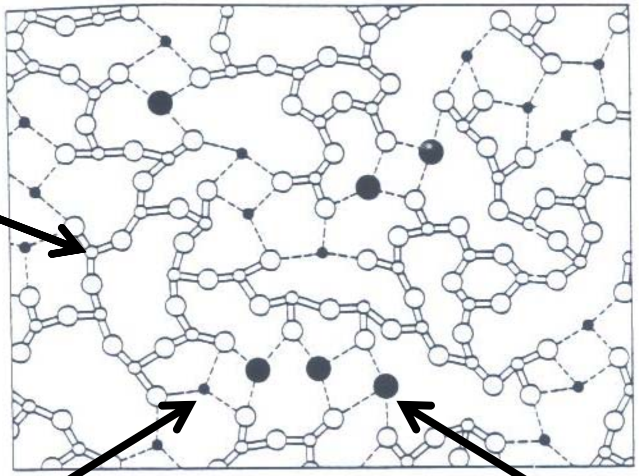
- **recommended borosilicate glass for SRS and WV**
- **recommended that ceramics continue to be studied**

Short-Range Order (SRO) and Medium-Range Order (MRO) in Alkali Borosilicate Glasses



Greaves, 1985, EXAFS

Polymerizing cations like Al, Si



Greaves, et al 1989, XAS

Clustered U Cations

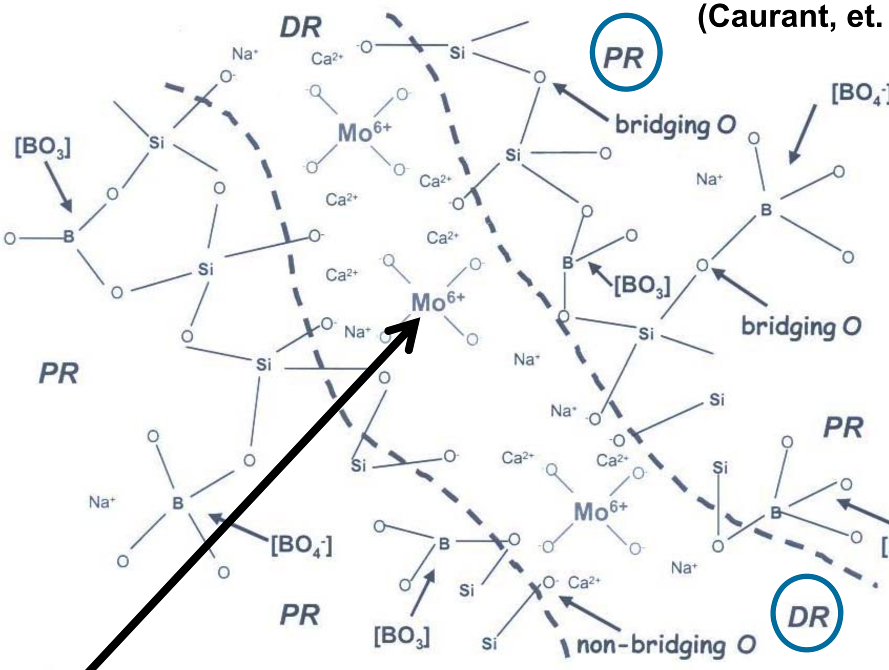
Modifying Cations like Na, Ca, Cs

Bridging Oxygens

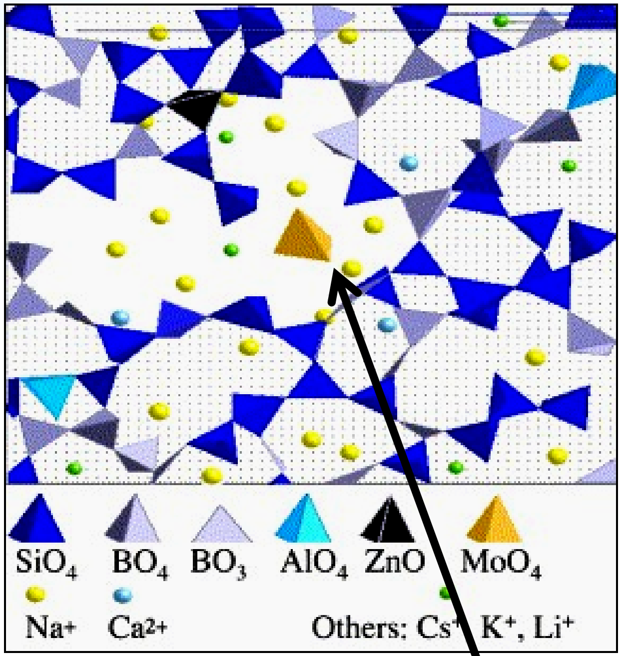
Non-Bridging Oxygen (NBO)

- SRO/MRO structure (the polymerized regions vs. de-polymerized regions) controls the waste form durability by
  - establishing the distribution of ion exchange sites and hydrolysis sites
  - the access of water to those sites
- MRO clustering impacts solubility of species

Short-Range Order (SRO) and Medium-Range Order (MRO) in Alkali Borosilicate Glasses



(Caurant, et. al. 2009)



(Calas, et.al. 2003) French nuclear waste glass

Clustered Mo cations as Na_2MoO_4

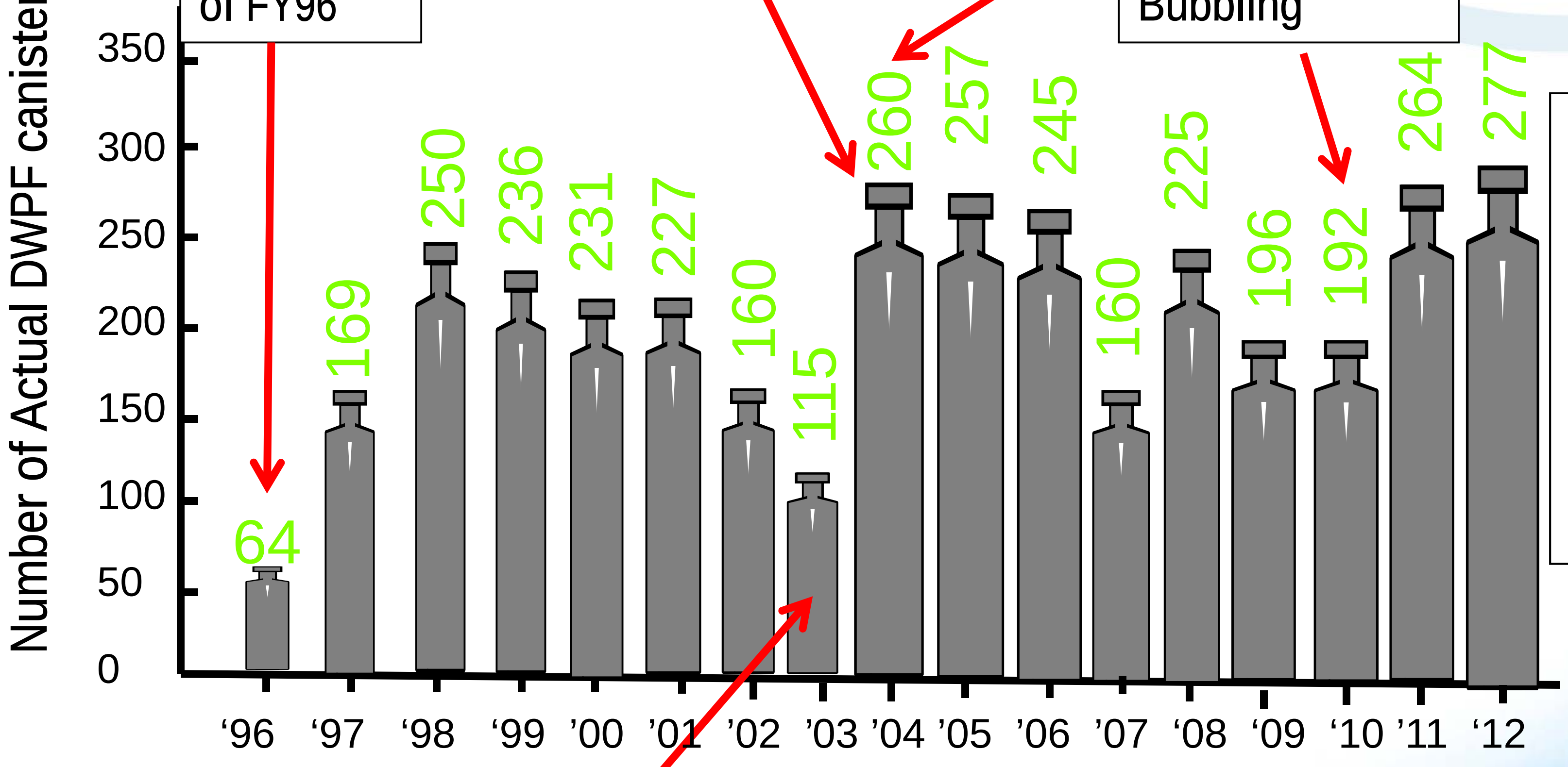
- SRO/MRO structure impacts ion exchange sites, hydrolysis sites, and the access of water to those sites
- MRO clustering impacts solubility of species
  - SO_4 and MoO_4 have poor solubility due to MRO clustering

HLW Vitrified in the US as of March 2013

Vitrification Plant	Borosilicate Waste Glass Produced (metric tons)	Waste Loading Range (wt%)	Size of Canisters (meters)	Number of Canisters	TBq[‡] Stabilized
DWPF Savannah River Site	6350 (1996-2013)	28-40	0.61 x 3.05	3,603 made	1.85 x 10^{6}
				7,580 proj.	3.46 x 10^{7}
West Valley Demonstration Project (WVDP)	~500 (1996-2002)	~20.4-23.5	0.61 x 3.05	275 made	8.9 x 10^{5}
				275 proj.	
Hanford Waste Treatment Plant HLW	32,000 (projected)	~35-38	0.61 x 4.57	0	0
				10,600 (2011) 120 Cs/Sr capsules	1.11 x 10^{7}

[‡] 1 Tera-Becquerel (TBq) = 10^{12} atoms decaying per second or transmutations per second

17 Years of Continuous Radioactive Operation at DWPF



Operated
5 months
of FY96

New
Liquidus
Model
2002-3

Added
Glass
Pump
2004

Removed
Glass Pump:
Added Ar
Bubbling

1st melter
= 8.5 years;
2nd melter
= 10 years;
melter
change
scheduled
FY14

Changed
Melter 2003

Fiscal year

DWPF ↔ WVDP ↔ WTP

Similarities

Differences

- Hardware
- Flowsheet Design
- Process Control Strategy

Similarities/Differences

SIMILARITIES

- Joule heated (electrically heated)
- Use Monofrax K-3 Refractory
- Use Inconel® 690 electrodes
- All slurry fed
- Canisters all 304L stainless steel
- Nominal Melt Temperature ~1150°C

DIFFERENCES: Melter Size, Shape, and Primary Type of Melt Pool Convection

Hanford HLW
AJHM Melter
3.75 m^2

Air Bubbled-6

SRS HLW
JHM Melter
2.6 m^2

1996-2004 (Natural Convection)
2004-2010 (Glass Airlift Pump)
2010-current (Ar Bubbled-4)

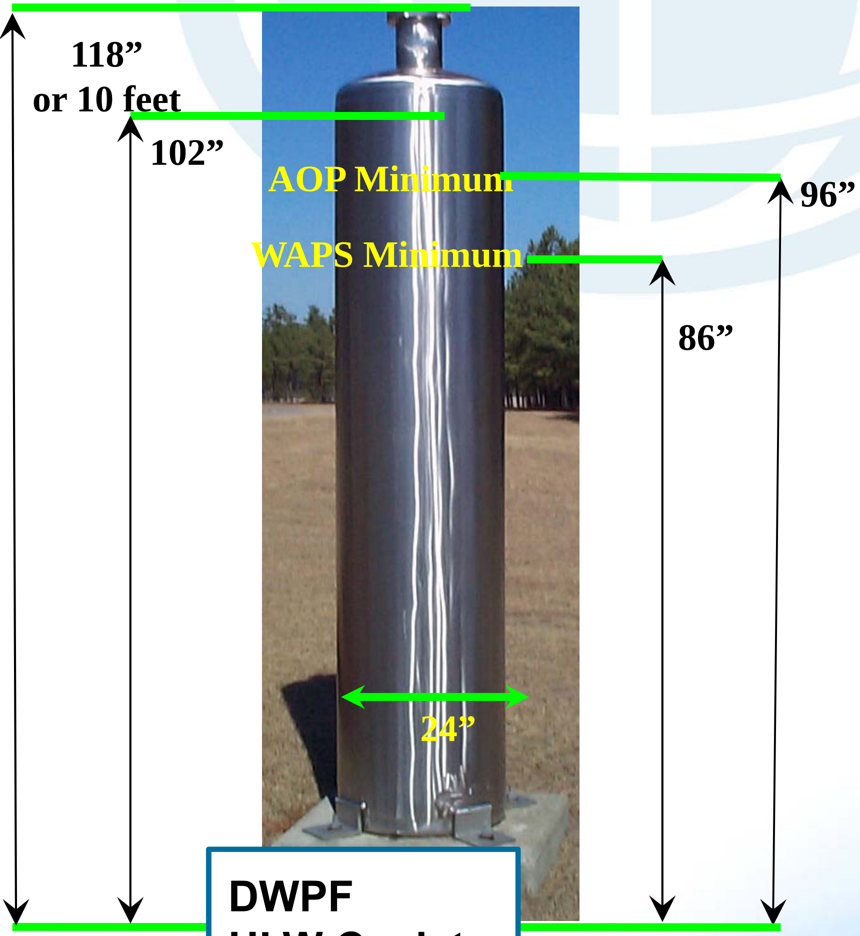
West Valley HLW
JHM Melter
2.2 m^2

Natural
Convection

Differences: Variation of Canister Size and Neck

WTP
HLW Canister
15’ x 2’
LAW Canister
7’ x 4’

WVDP
HLW Canister
10’ x 2’



DWPF
HLW Canister
10’ x 2’

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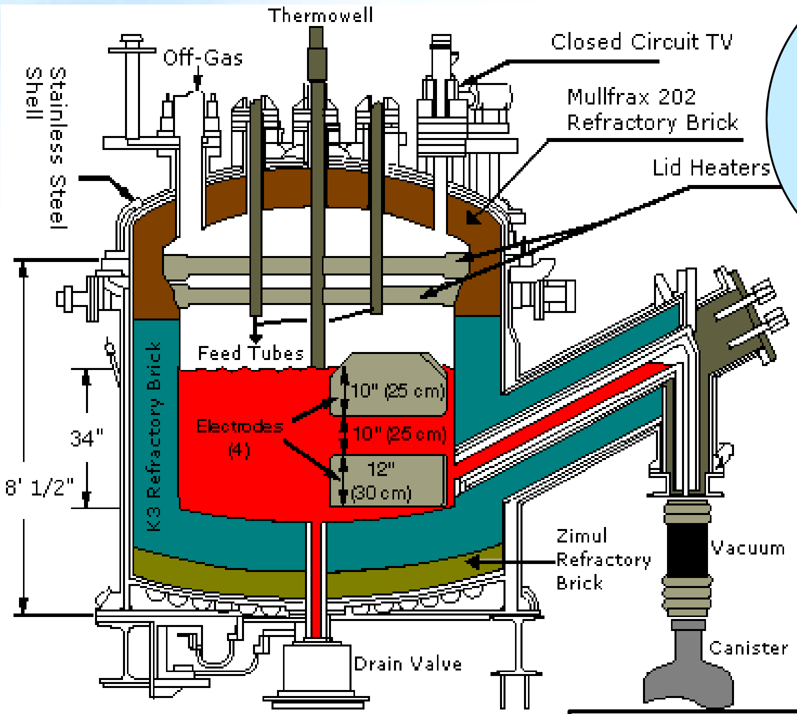
DWPF - Joule Heated Melter (JHM)



SRS HLW
JHM Melter
2.6 m^2

DIFFERENCES

- Differential pressure pour (semi-continuous)
- Emergency bottom drain with canister
- Slightly sloped floor and pour spout offset (for noble metal/crystal accumulation)
- Lid heaters
- Complete dual jumpered off-gas system(s) for cleaning
- Size (65 ton) limited by crane - holds ~9 metric tons of glass
- Designed for 238 lbs/hr glass pour = 2.6 metric tons/day
- Off-gas line made of Hastelloy® for resistance to acid gases

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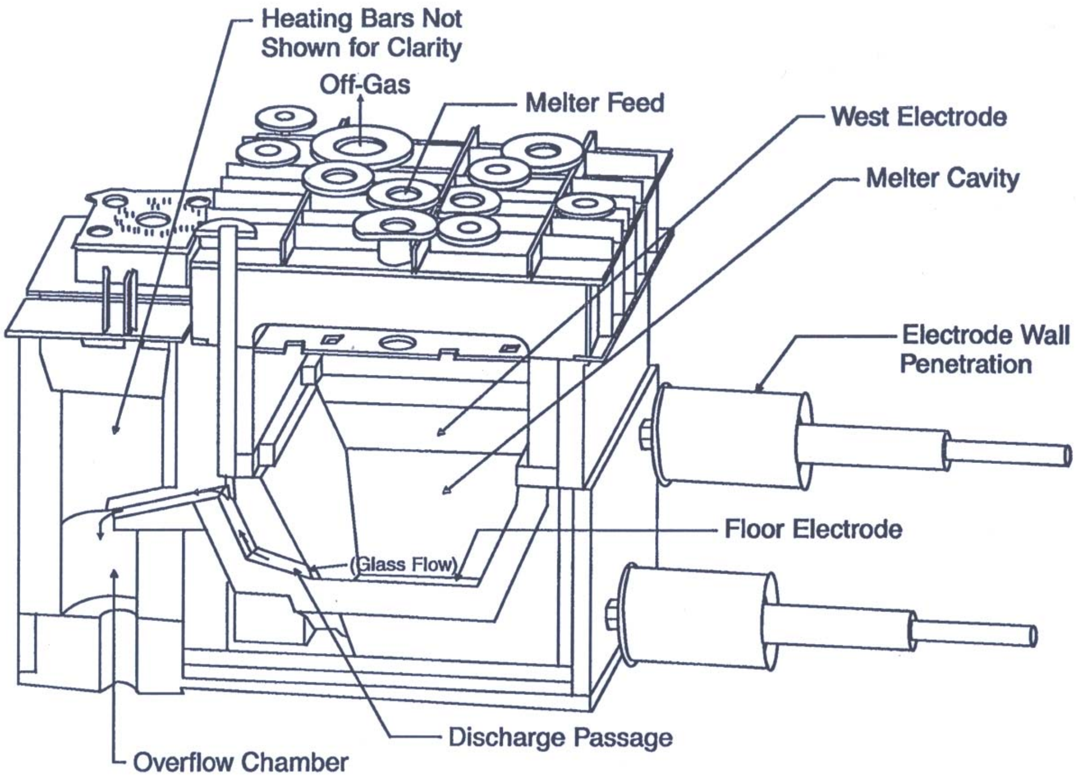
WVDP - Joule Heated Melting (JHM)



DIFFERENCES

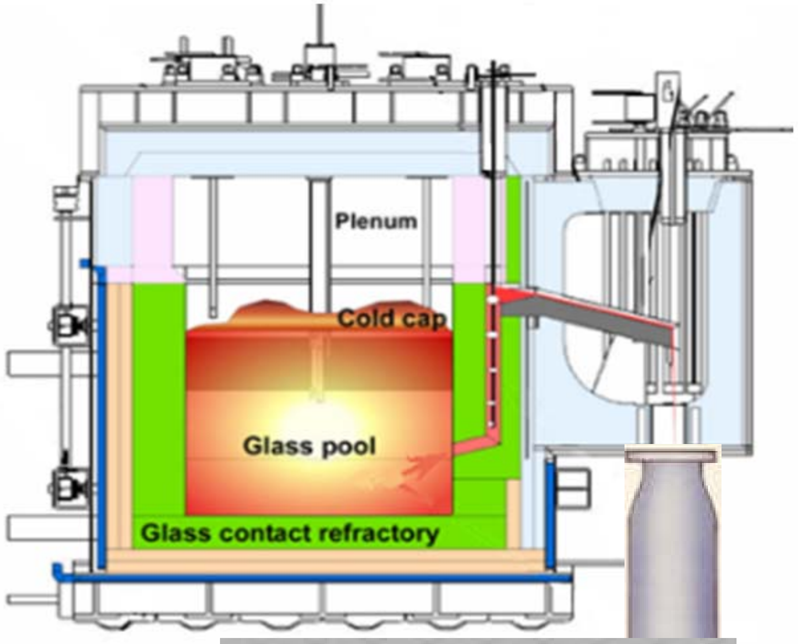
- Air lift pour (batch pour)
- Vacuum lift from top of melter for emergency drain
- Sloped floor (inverted prism) and pour spout offset (for noble metal/crystal accumulation)
- No lid heaters
- Single off-gas system with certain spare components
- design pour 455kg/hr glass =1 metric ton/day
- Size ~50 metric tons moved by rail - melter held ~2.5 metric tons of glass
- 2 discharge chambers for redundancy
- Off-gas line of Hastelloy ® and Inconel ® for resistance to acid gases

West Valley HLW
JHM Melter
2.2 m^2

WTP - Advanced Joule Heated Melting (AJHM)

DIFFERENCES

- 2 melters
- Bubble rise overflow (normal and emergency pours)
- Flat floor (pour spout offset allows for noble metal/crystal accumulation)
- No lid heaters
- Single off-gas system for each melter with some spare components
- 79-90 metric tons - holds 11 metric tons glass - replacement by rail
- design for 3-3.75 metric tons/day/melter
- Off-gas line of Hastelloy ® and Inconel ® for resistance to acid gases



Hanford HLW
AJHM Melter
3.75 m^2

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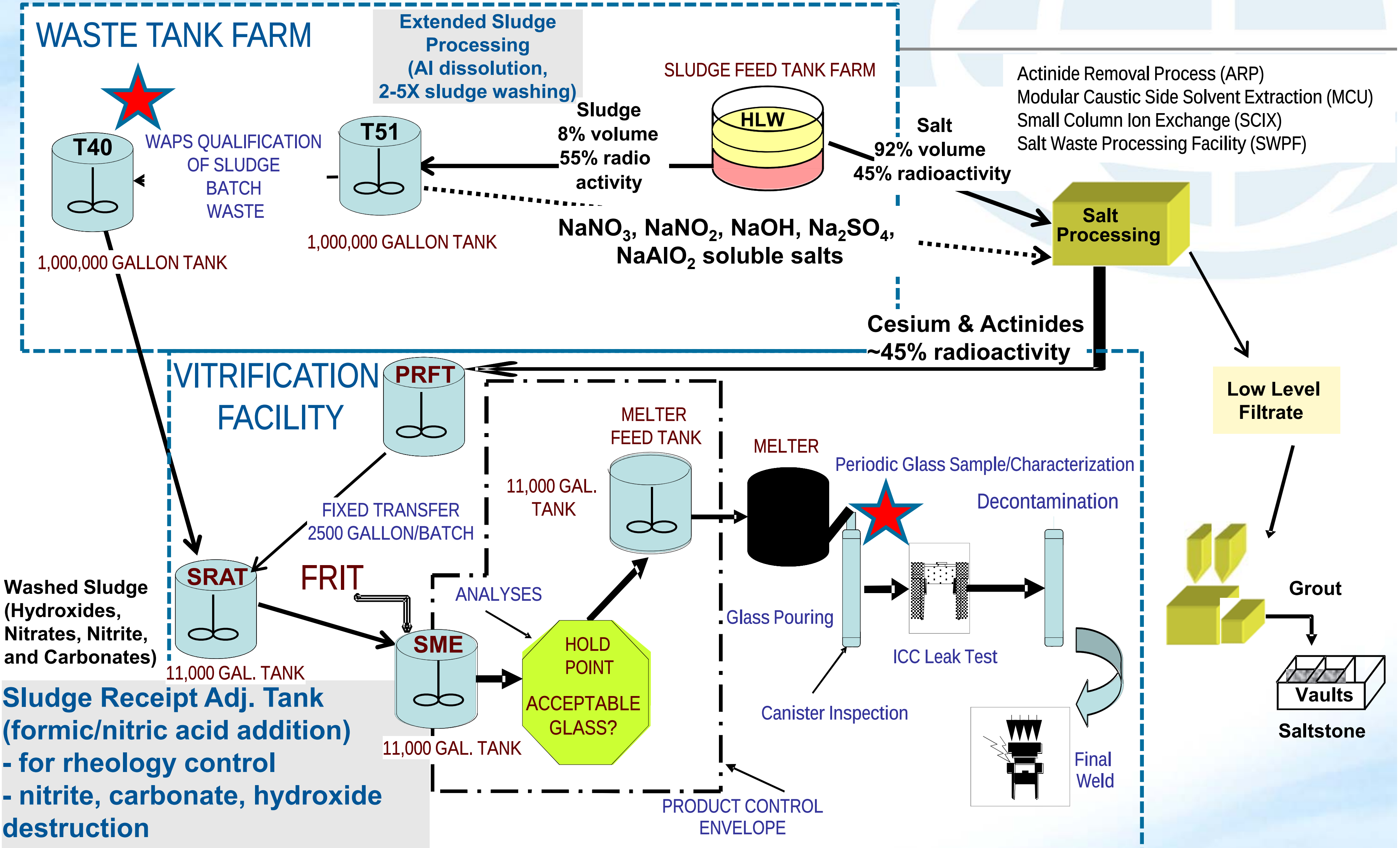
DWPF - Flowsheet



WASTE TANK FARM

Extended Sludge Processing (Al dissolution, 2-5X sludge washing)

SLUDGE FEED TANK FARM

HLW

Sludge
8% volume
55% radio activity

Salt
92% volume
45% radioactivity

Actinide Removal Process (ARP)
Modular Caustic Side Solvent Extraction (MCU)
Small Column Ion Exchange (SCIX)
Salt Waste Processing Facility (SWPF)

T40

WAPS QUALIFICATION OF SLUDGE BATCH WASTE

1,000,000 GALLON TANK

T51

1,000,000 GALLON TANK

$NaNO_3$, $NaNO_2$, NaOH, Na_2SO_4, $NaAlO_2$ soluble salts

Salt Processing

Cesium & Actinides
~45% radioactivity

Low Level Filtrate

VITRIFICATION FACILITY

PRFT

FIXED TRANSFER 2500 GALLON/BATCH

MELTER FEED TANK

11,000 GAL. TANK

MELTER

Periodic Glass Sample/Characterization

Decontamination

Washed Sludge (Hydroxides, Nitrates, Nitrite, and Carbonates)

SRAT

11,000 GAL. TANK

FRIT

SME

11,000 GAL. TANK

ANALYSES

HOLD POINT

ACCEPTABLE GLASS?

Glass Pouring

ICC Leak Test

Canister Inspection

Final Weld

PRODUCT CONTROL ENVELOPE

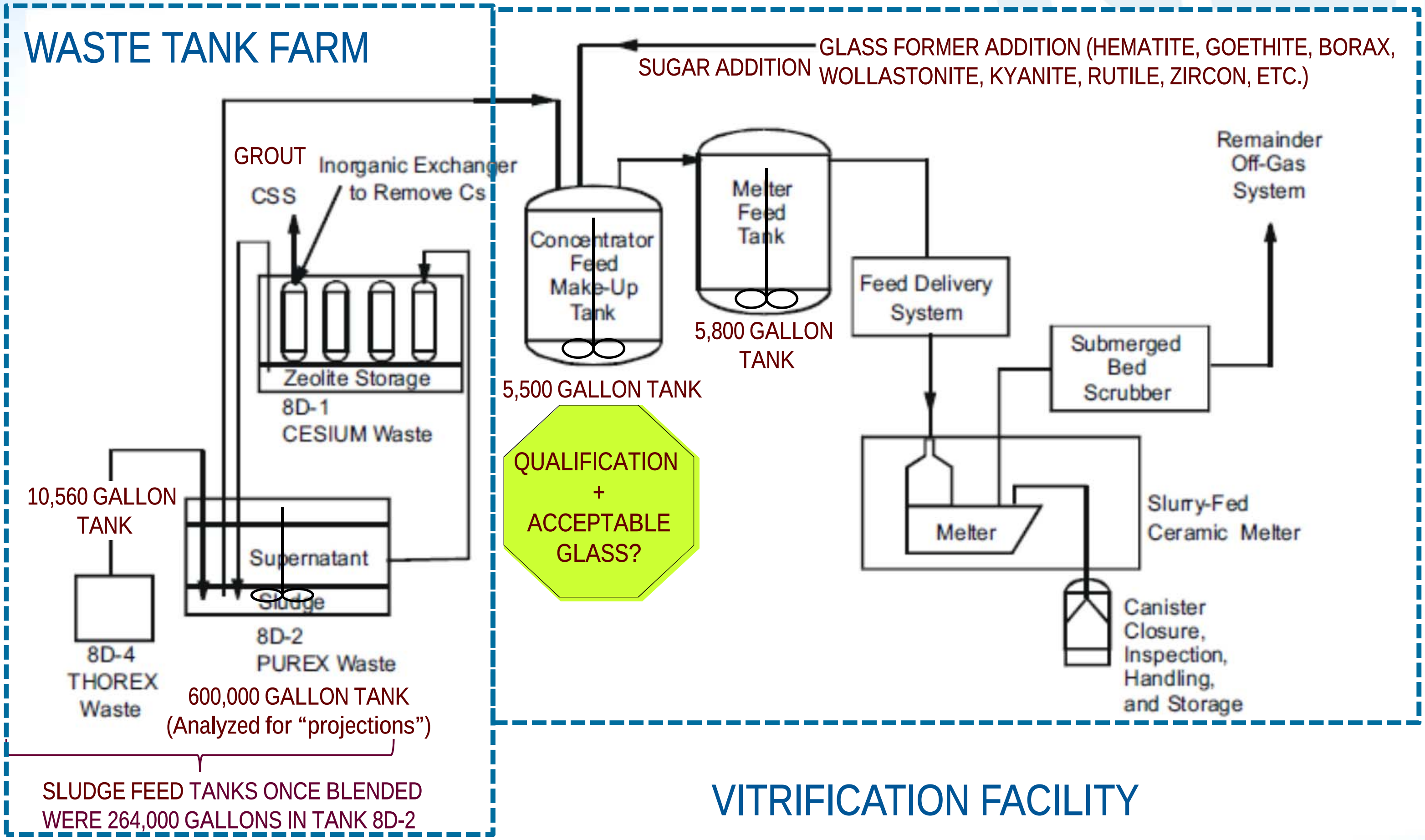
Grout

Vaults

Saltstone

Sludge Receipt Adj. Tank (formic/nitric acid addition)
- for rheology control
- nitrite, carbonate, hydroxide destruction
- for REDOX control, Hg° removal, Mn reduction to control melter foaming

WVDP Flowsheet



WASTE TANK FARM

10,560 GALLON TANK

600,000 GALLON TANK
(Analyzed for "projections")

SLUDGE FEED TANKS ONCE BLENDED WERE 264,000 GALLONS IN TANK 8D-2

SUGAR ADDITION

GLASS FORMER ADDITION (HEMATITE, GOETHITE, BORAX, WOLLASTONITE, KYANITE, RUTILE, ZIRCON, ETC.)

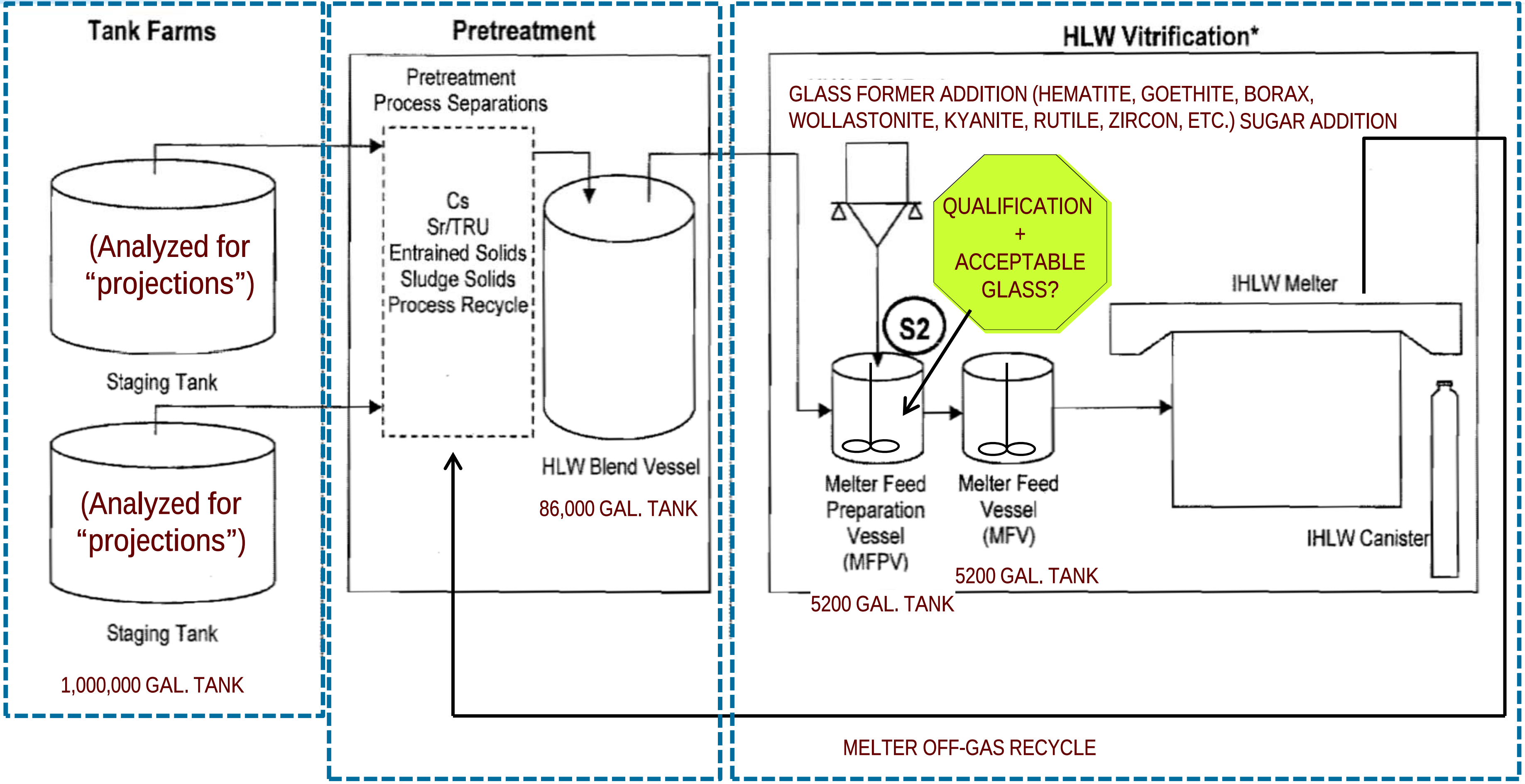
5,500 GALLON TANK

5,800 GALLON TANK

QUALIFICATION
+
ACCEPTABLE GLASS?

VITRIFICATION FACILITY

WTP Flowsheet



Tank Farms

(Analyzed for "projections")

Staging Tank

(Analyzed for "projections")

Staging Tank

1,000,000 GAL. TANK

Pretreatment

Pretreatment
Process Separations

Cs
Sr/TRU
Entrained Solids
Sludge Solids
Process Recycle

HLW Blend Vessel

86,000 GAL. TANK

HLW Vitrification*

GLASS FORMER ADDITION (HEMATITE, GOETHITE, BORAX, WOLLASTONITE, KYANITE, RUTILE, ZIRCON, ETC.) SUGAR ADDITION

QUALIFICATION
+
ACCEPTABLE
GLASS?

S2

Melter Feed
Preparation
Vessel
(MFPV)

5200 GAL. TANK

Melter Feed
Vessel
(MFV)

5200 GAL. TANK

IHLW Melter

IHLW Canister

MELTER OFF-GAS RECYCLE

Summary of Flowsheet Differences

- Blend sludge in Tank Farm to dampen composition variation, perform pretreatment in Tank Farm, and Qualify Sludge in Million Gallon Tank in Tank Farm
  - DWPF - Yes - 300,000-800,000 gallon batches (analytic need minimized)
  - WV and WTP - No - 4,000 gallon batches (analytic need maximized)
- REDOX Control (Reducing Melter Flowsheet) for Retention of ^{99}Tc,^{104}Ru, others
  - DWPF - REDOX control with formic acid, other reductants, and Ar bubbling
  - WV - REDOX control with sugar and no bubbling of air
  - WTP - No REDOX control - sugar reduces nitrates to N_2 but bubbling air re-equilibrates the melt pool to oxidizing conditions (~30% retention of ^{99}Tc in single pass)
    - requires extensive recycle loops back to melter
- All mix/blend/transfer tanks accessible due to concerns about sludge viscosity and erosion/corrosion from crystalline sludge particulates and all stirred mechanically
  - DWPF and WV - Yes
  - WTP - Some accessible and stirred tanks rest are pulse-jet mixers in “black cells”
- Frit (a melted mixture of glass formers) chosen on makeup of large Sludge Batches - leads to only one transfer error and one analytic error during batching
  - DWPF - Yes
  - WV and WTP - No

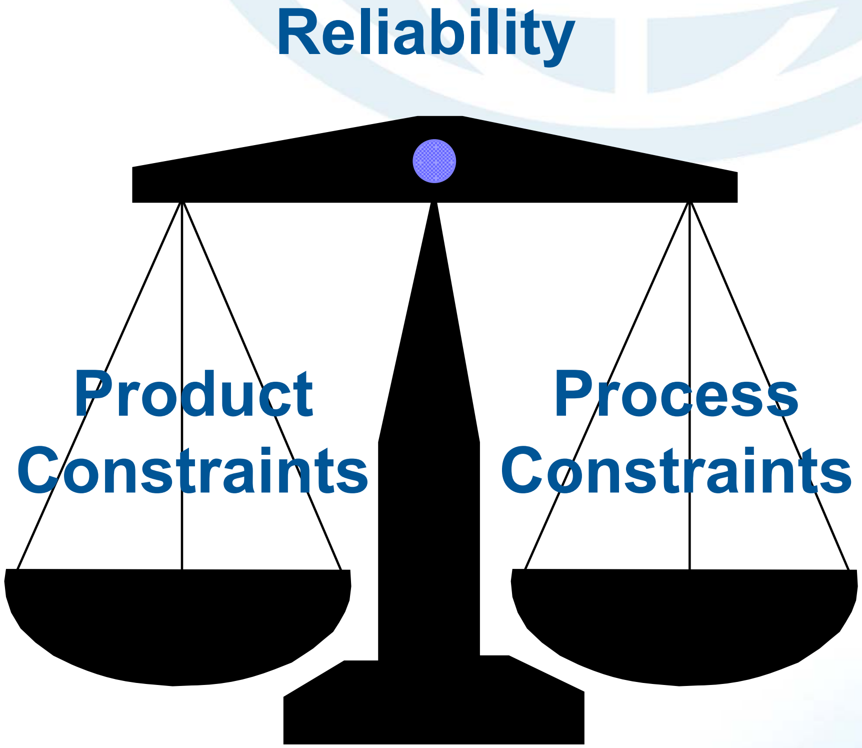
DWPF/WVDP/WTP Similarities: System's Approach

Product

- Chemical Durability (model)
  - Homogeneity (composition limit)
- Regulatory (test range or model)
- Thermal Stability (test range)
- Mechanical Stability (test range)

Process

- Viscosity (model)
- Liquidus (model)
- Waste Solubility (test range)
- Melt Temperature (set range)
- Volatility (test range and REDOX*)
- Melt Corrosivity (test range)

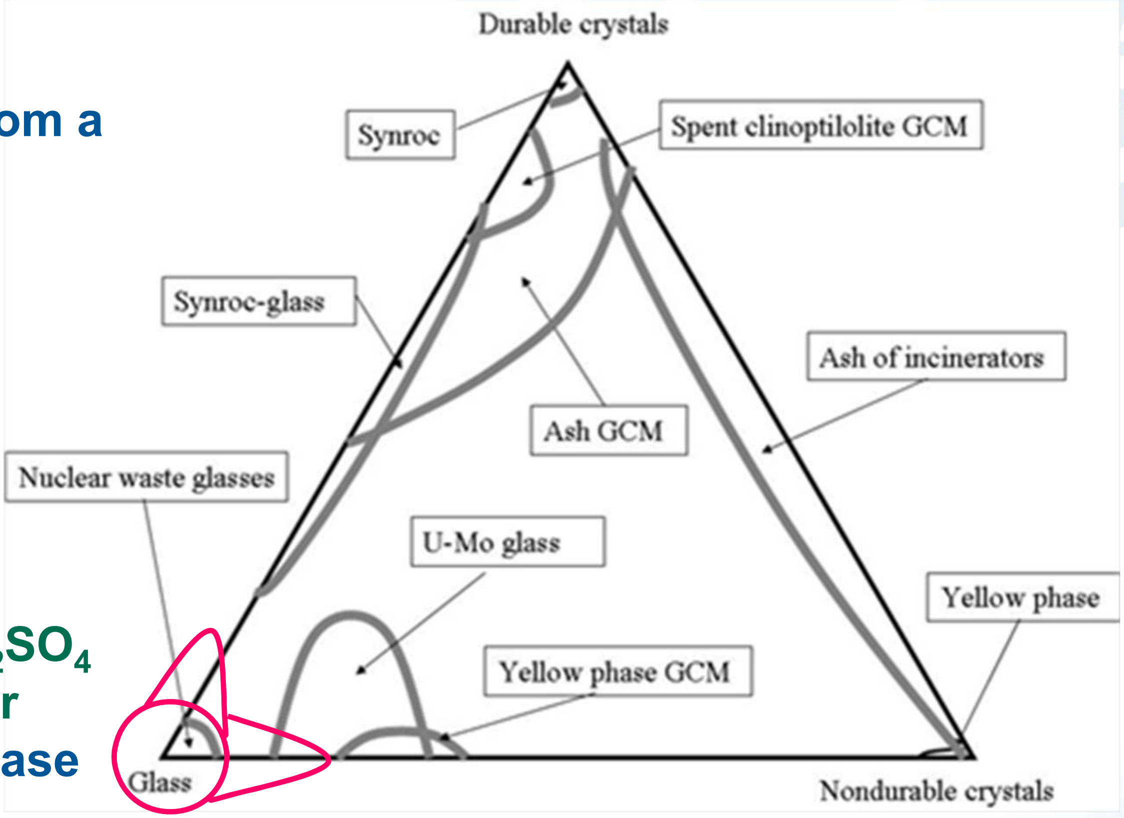


* controls foaming and melt rate

Solidification by Chemical Incorporation in Glass Wasteforms

- **Homogeneous Glass**
  - easier to model durability/ release of radionuclides from a single source

- **Inhomogeneous Glass**
  - secondary phases should be durable
  - secondary phases that are soluble should be avoided
    - often incorporate radionuclides, e.g. Na_2SO_4 incorporates Cs and Sr
  - complicates durability/release modeling of radionuclides



from Ojovan and Lee, Met. Mat. Trans. 42A (2011)

Durability of Homogeneous vs. Inhomogeneous Glasses

Homogeneous Glass

$$\sum Durability = \underbrace{durability_{(homogeneous)}}_{1st\ term} + \cancel{\underbrace{durability_{(amorphous\ phase\ separation)}}_{2nd\ term}} + \cancel{\underbrace{durability_{(crystallization)}}_{3rd\ term}}$$

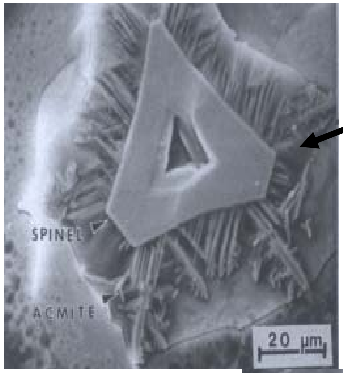
$$+ \cancel{\underbrace{durability_{(accelerated\ grain\ boundary)}}_{4th\ term}}$$

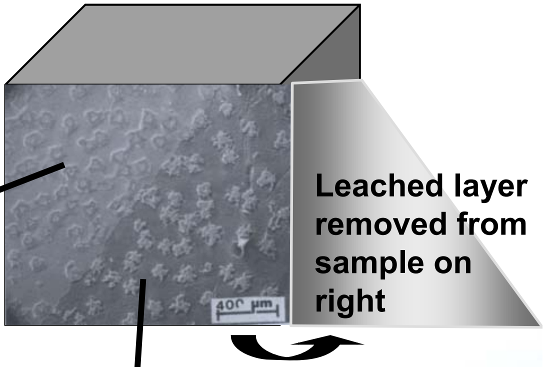
Phase Separated Glass and/or crystallized glass (requires that distribution of radionuclides amongst the phases be known)

$$\sum Durability = \underbrace{durability_{(homogeneous)}}_{1st\ term} + \underbrace{durability_{(amorphous\ phase\ separation)}}_{2nd\ term}$$

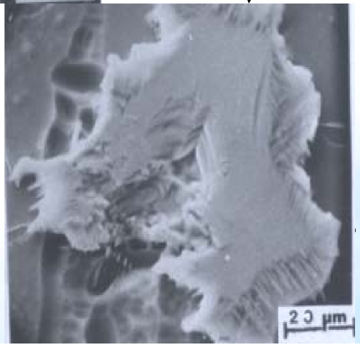
$$+ \underbrace{durability_{(crystallization)}}_{3rd\ term}$$

$$+ \underbrace{durability_{(accelerated\ grain\ boundary)}}_{4th\ term}$$





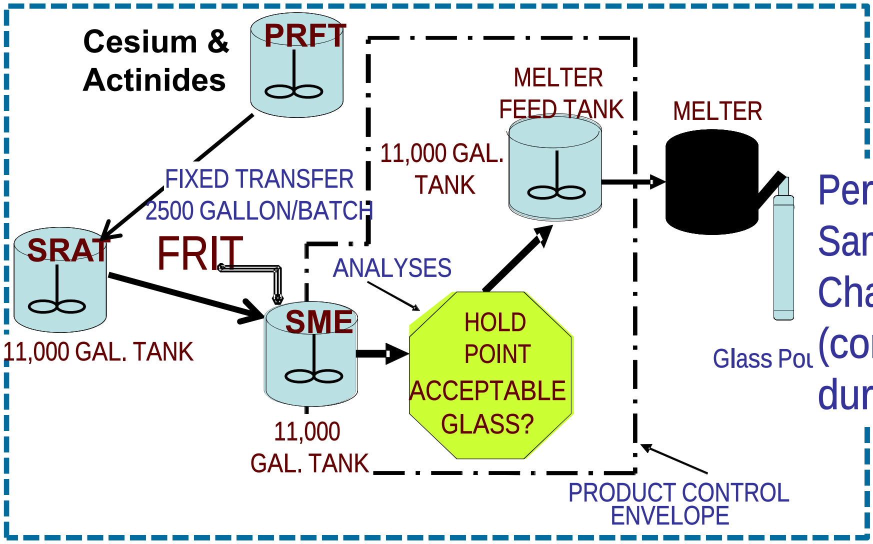
Leached layer removed from sample on right



Jantzen, C.M., Brown, K.G., and Pickett, J.B., International Journal of Applied Glass Science, 1 [1], 38-62 (2010).

Feed Forward Statistical Process Control (SPC): Canister Contents are Determined by Upstream Melter Feed Analysis

- **Multiple waste streams must be simultaneously blended**
- **Waste streams are highly variable and very difficult to characterize**
- **Rework of the product is impossible**
- **Constraints exist on multiple Processing/Product (P/P) properties**
- **P/P property constraints must be satisfied to a very high degree of certainty (> 95%)**
- **P/P properties cannot be measured directly**



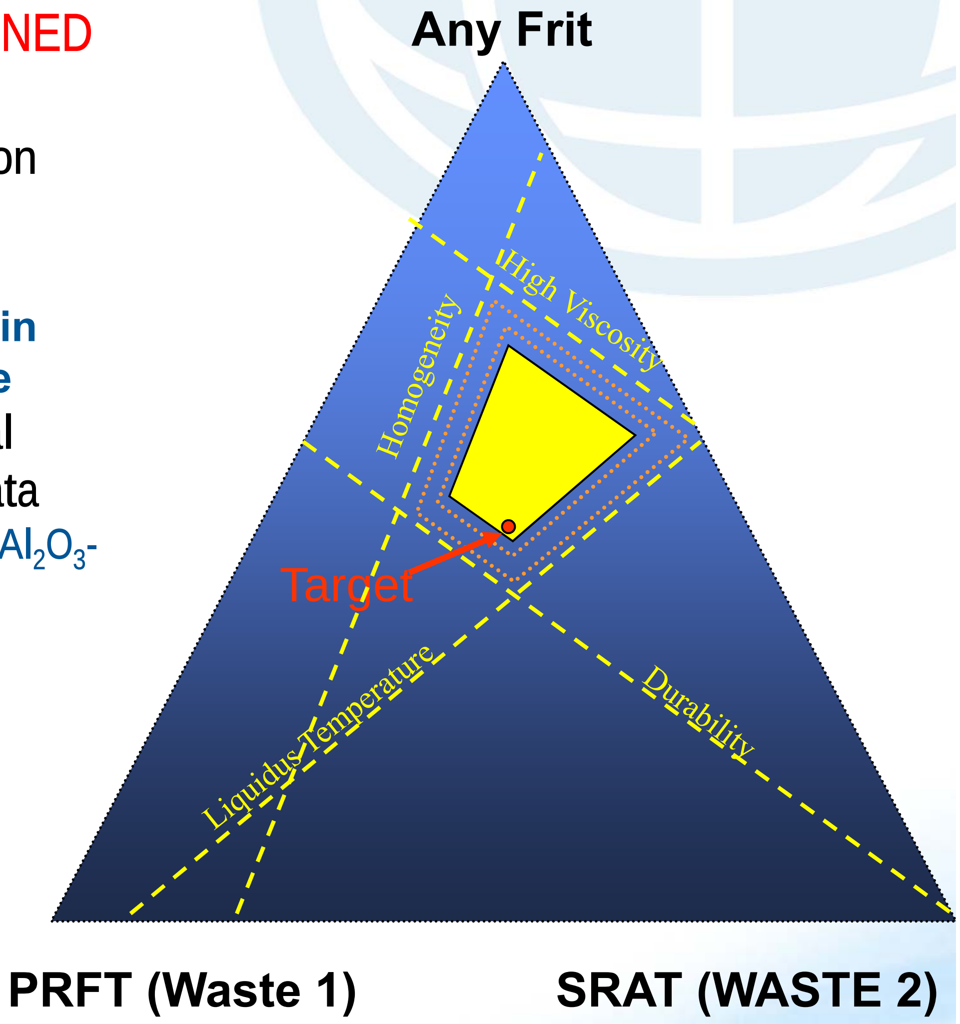
Periodic Glass Sample and Characterization (composition & durability testing)

1. **How SRNL defined the process control region for DWPF**
2. **How SRNL qualified DWPF's process control region during non-radioactive startup ("black box")**

DWPF Product Composition Control System (PCCS)

CONTROL IS ON GLASS COMPOSITION DEFINED BY GLASS PROPERTIES

- To be a compliant glass, the glass composition must have properties that fall within the solid quadrilateral shown
  - Multivariate **theory used to control within multi-dimensional composition space**
- Each process model is based on geochemical principles and/or glass structure models + data
  - Homogeneity: Nolan's (1966) basalt system (Al_2O_3-[Fe_2O_3-FeO]-Na_2O-SiO_2)
  - Liquidus: Nolan, Bailey & Schairer (1966) crystallization in same basalt system and Burnham's quasicrystalline theory
  - Viscosity: glass polymerization and XAS
  - Durability: glass polymerization and thermodynamics
- PCCS accounts for "model error", analytic error, tank transfer error, and heels
  - 95% confidence is obtained at max WL

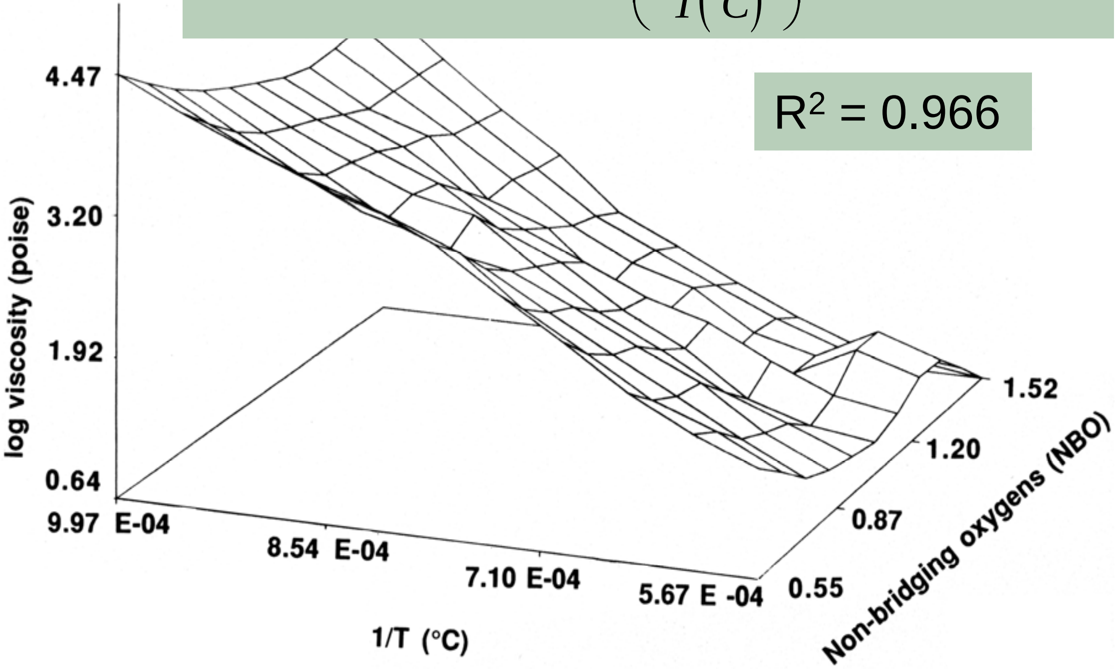


Example of a Mechanistic/Semi-Empirical Model (Viscosity 1991)

$$NBO \equiv \frac{2\,(Na_2O + K_2O + Cs_2O + Li_2O + Fe_2O_3 - Al_2O_3) + B_2O_3}{SiO_2}$$

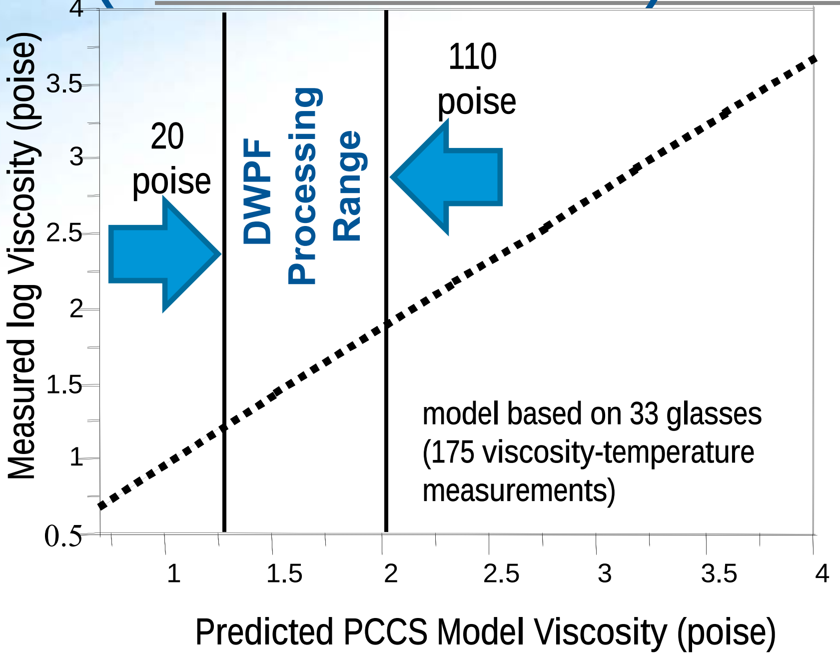
- **Viscosity model based on glass polymerization (8 terms)**
- **# of terms in each model minimized to reduce model, analytic, and measurement error**
  - **Problem species, PO_4, SO_4 taken care of by fixed limits**
- **For TiO_2, a limit of 2 wt% was set; FY13 will be adding a term to go to 5 wt%**
- **Parameter limits set on pilot scale melter experience**

$$\log \eta(poise) = -0.519571 + \left(\frac{445387}{T(^{\circ}C)}\right) - (1.690326 * NBO)$$

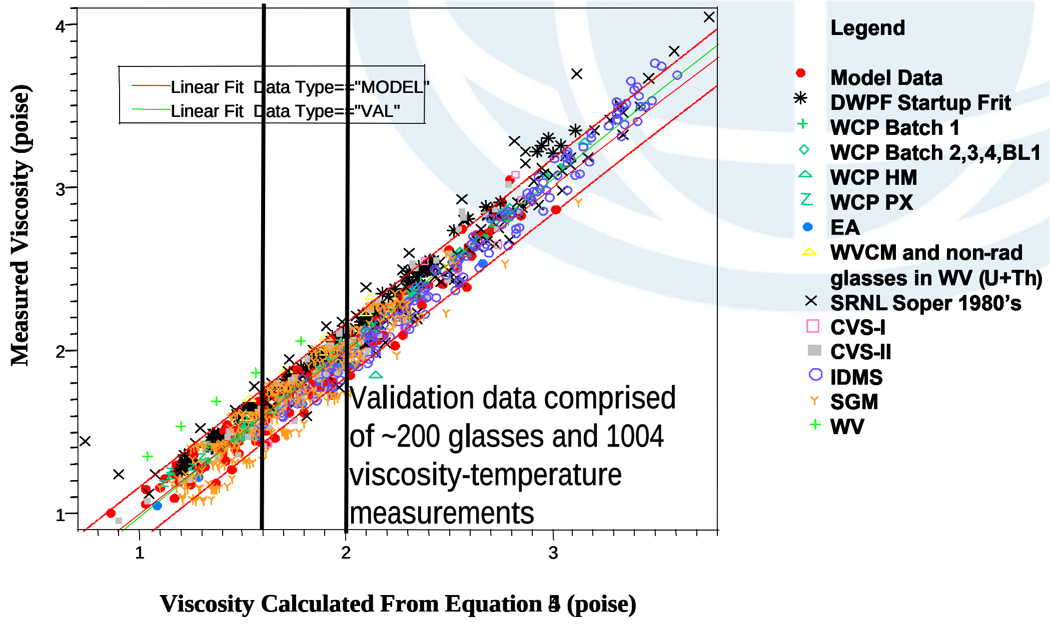


$R^2 = 0.966$

Example of a Mechanistic/Semi-Empirical Model (Newtonian Flow)



model based on 33 glasses (175 viscosity-temperature measurements)

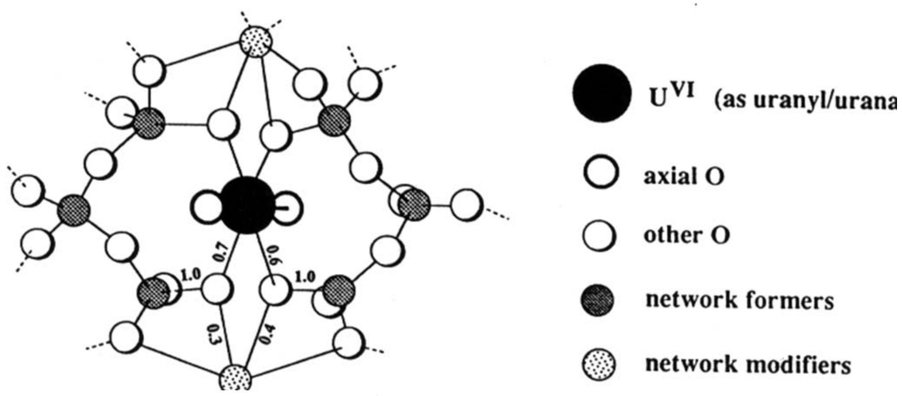


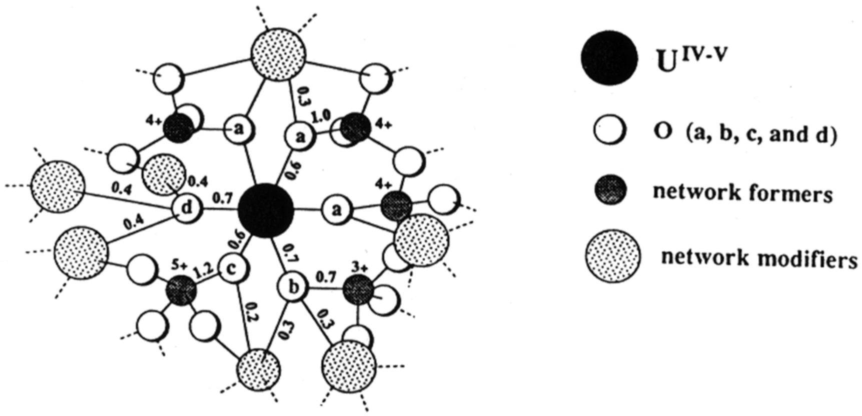
Validation data comprised of ~200 glasses and 1004 viscosity-temperature measurements

- melt too thin leads to refractory/electrode corrosion
- melt too thick leads to pouring problems and voids which can impact glass quality
- crystallized glass is non-Newtonian and more difficult to model

C.M. Jantzen, Ceramic Transactions, V.23 (1991).
C.M. Jantzen U.S. DOE Report WSRC-TR-2004-00311 (2005).

Example: Are Terms Needed for U^{+6}/U^{+4} and Th^{+4}

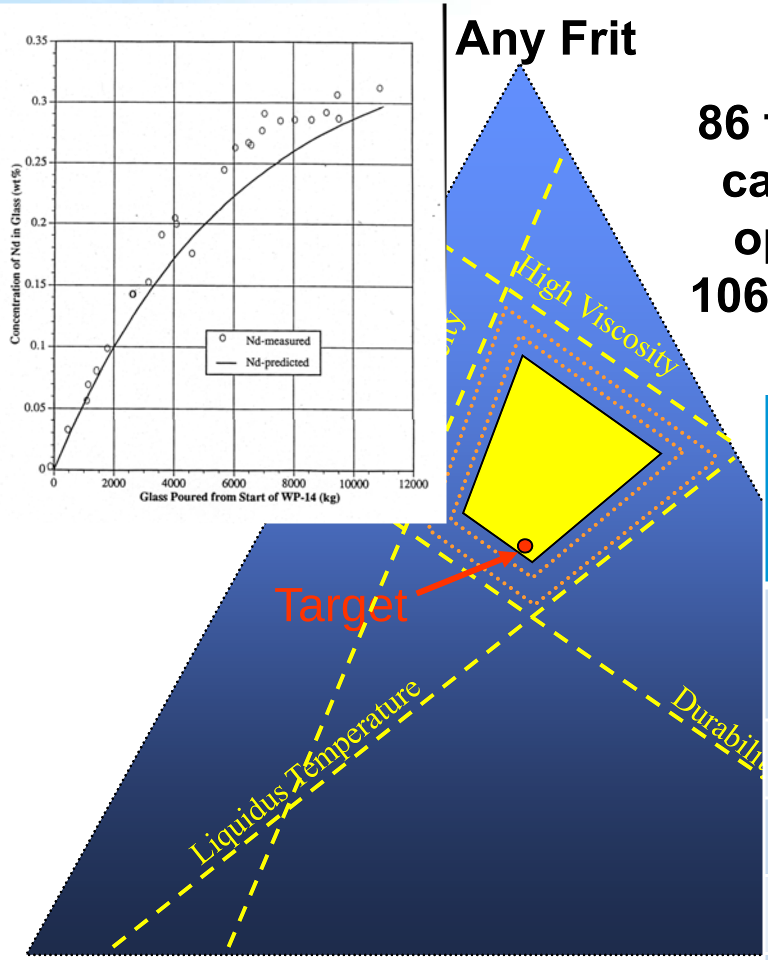




- **Go from simple to more complex**
- **1995,1992 literature indicates that U^{+6} and U^{+4} have 4 bridging and 2 NBO's so effects cancel out in model**
  - **Experiments verified this at U_3O_8 concentrations of up to 6 wt%**
- **1991 literature indicates that ThO_2 should lower viscosity (weak network modifier)**
  - **Consistent with SRNL testing**
  - **Inconsistent with high ThO_2 glass testing for WV**
  - **Th^{+4} term will be needed at ThO_2 ≥1wt%**

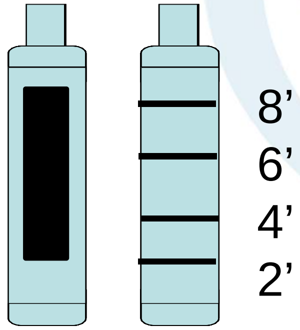
G.E. Brown, Jr., F. Farges, and G. Calas, Reviews in Mineralogy, V.32 (1995).
F. Farges, C.E. Ponader, G. Calas, G.E. Brown, Jr., Geochim Cosmochim Acta, v.56 (1992).
F. Farges, Geochimica et Cosmochimica Acta, v.55, (1991).

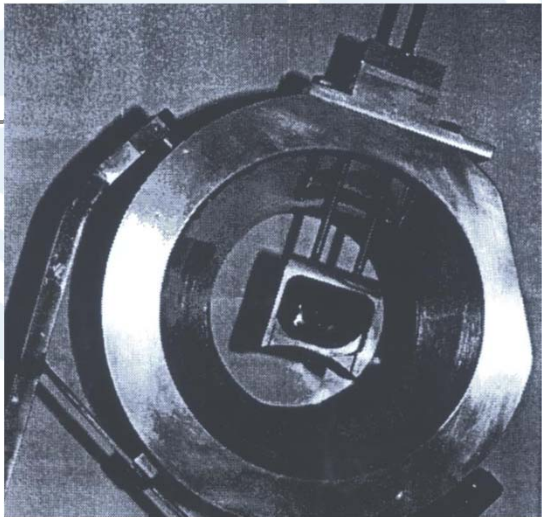
Validation of PCCS During DWPF Non-Radioactive Startup



PRFT (Waste 1)

86 full scale canisters opened; 106 sampled





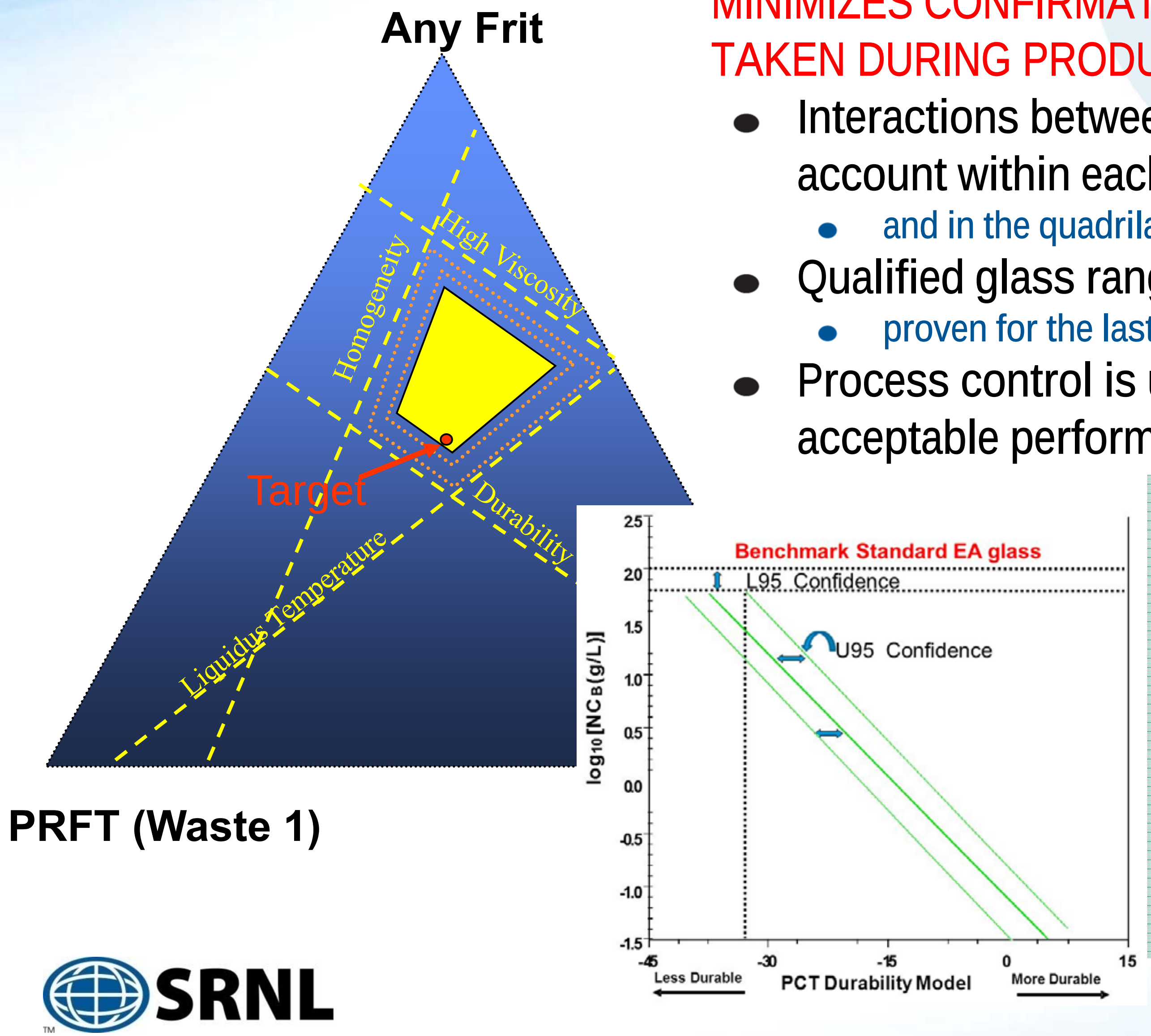
DWPF Non-rad	Canisters Sectioned	Canisters with walls Removed	Glass Sampler
Initial Conditions	3	3	24
Doped (Nd)	6	14	20
Low Vis.	7	13	21
High Vis.	7	13	21
Blend (Hg°)	7	13	20
Total	30	56	106

C.M. Jantzen, “Defense Waste Processing Facility (DWPF) Startup Test Program: Glass Characterization,” U.S. DOE Report WSRC-MS-92-015 (1992).

PCCS - Defines A Pre-qualified Glass Composition Range for Compliance

MINIMIZES CONFIRMATORY SAMPLES TO BE TAKEN DURING PRODUCTION

- Interactions between components is taken into account within each model
  - and in the quadrilateral space
- Qualified glass range is processable
  - proven for the last 19 years of DWPF operation
- Process control is used to demonstrate acceptable performance by linking relationships



process control
↓
composition control
↓
dissolution rate control
↓
performance control
↓
acceptable performance

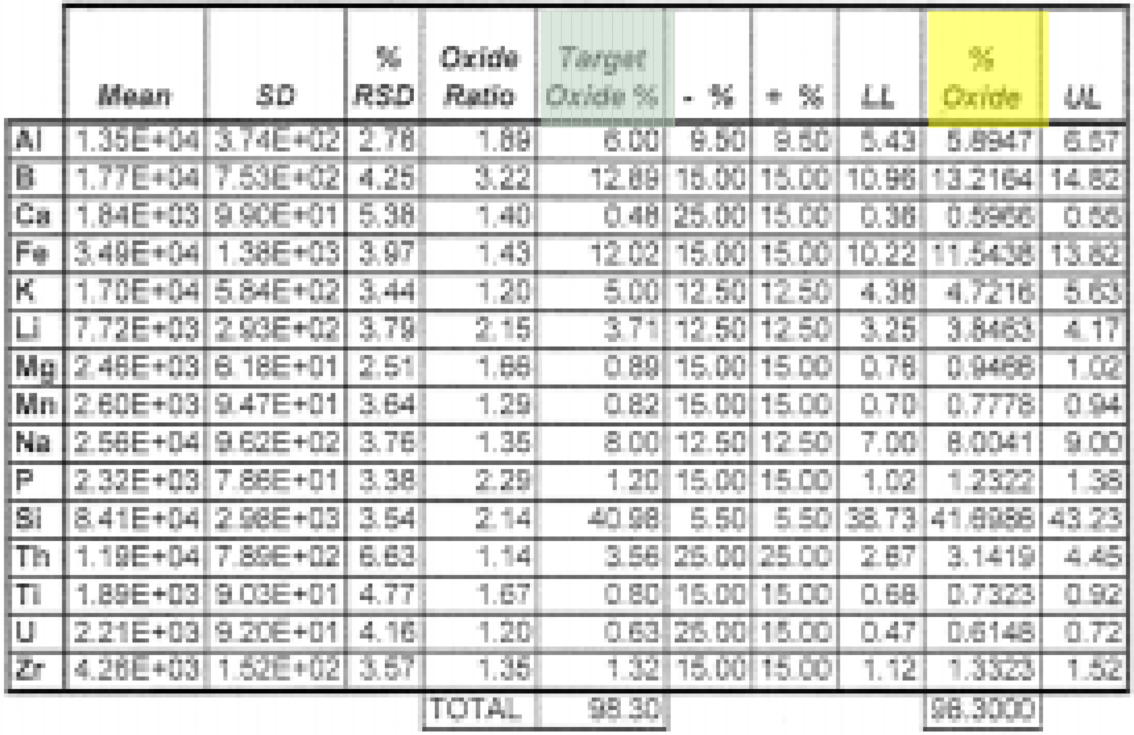
WV and WTP Statistical Process Control (Minimum Component Limits in WTP HLW Glass)

CONTROL IS ON OXIDE COMPONENTS at ±5%

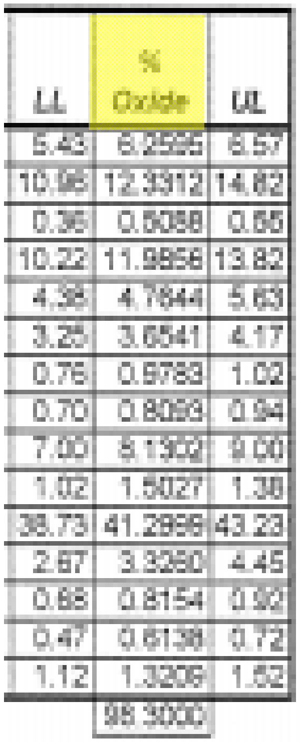
- To be a compliant glass, one constituent in the table shown must meet or exceed the corresponding wt% in HLW glass
- Computer routine estimates HLW glass volumes and uses these glass property models:
  - Nepheline
  - One-percent crystal temperature ($T_{1\%}$)
  - Viscosity
  - Durability based on ASTM C1285 (Product Consistency Test for B, Li, Na)
  - Liquidus Temperature (T_L)
- Other glass composition constraints and rules are then applied
- Models are empirical and have cross terms, square, and cubed terms
- Models have from 9-28 terms

Oxide	Wt%	Oxide	Wt%
Fe_2O_3	12.5	TiO_2	1.0
Al_2O_3	11.0	Bi_2O_3	2.0
Na_2O+ K_2O	15.0	P_2O_5	3.0
ZrO_2	10.0	F	1.7
U_3O_8	8.11	**Composite Limits**	
ThO_2	4.0	$Al_2O_3 + ZrO_2$	14.0
CaO	7.0	$Al_2O_3 + ZrO_2 + Fe_2O_3$	21.0
MgO	5.0	MgO + CaO	8.0
BaO	4.0	Cr_2O_3	0.50
CdO	3.0	SO_3	0.50
NiO	3.0	Ag_2O	0.25
PbO	1.0	$Rh_2O_3 + Ru_2O_3$ + PdO	0.25

Glass Product Control: Feed vs. Glass Shard Measurement from Canisters (~10% Sampled at WV)



	Mean	SD	% RSD	Oxide Ratio	Target Oxide %	- %	+ %	LL	% Oxide	UL
Al	1.35E+04	3.74E+02	2.78	1.89	6.00	9.50	9.50	5.43	5.8947	6.57
B	1.77E+04	7.53E+02	4.25	3.22	12.89	15.00	15.00	10.96	13.2164	14.82
Ca	1.84E+03	9.90E+01	5.38	1.40	0.48	25.00	15.00	0.36	0.5956	0.56
Fe	3.49E+04	1.38E+03	3.97	1.43	12.02	15.00	15.00	10.22	11.5438	13.82
K	1.70E+04	5.84E+02	3.44	1.20	5.00	12.50	12.50	4.38	4.7216	5.63
Li	7.72E+03	2.93E+02	3.79	2.15	3.71	12.50	12.50	3.25	3.8463	4.17
Mg	2.46E+03	6.18E+01	2.51	1.66	0.89	15.00	15.00	0.76	0.9468	1.02
Mn	2.60E+03	9.47E+01	3.64	1.29	0.82	15.00	15.00	0.70	0.7778	0.94
Na	2.56E+04	9.62E+02	3.76	1.35	8.00	12.50	12.50	7.00	8.0041	9.00
P	2.32E+03	7.86E+01	3.38	2.29	1.20	15.00	15.00	1.02	1.2322	1.38
Si	8.41E+04	2.98E+03	3.54	2.14	40.98	5.50	5.50	38.73	41.6986	43.23
Th	1.19E+04	7.89E+02	6.63	1.14	3.56	25.00	25.00	2.67	3.1419	4.45
Ti	1.89E+03	9.03E+01	4.77	1.67	0.80	15.00	15.00	0.68	0.7323	0.92
U	2.21E+03	9.20E+01	4.16	1.20	0.63	25.00	15.00	0.47	0.6148	0.72
Zr	4.28E+03	1.52E+02	3.57	1.35	1.32	15.00	15.00	1.12	1.3323	1.52
				TOTAL	98.30				98.3000	



LL	% Oxide	UL
5.43	6.2595	6.57
10.96	12.3312	14.82
0.36	0.5088	0.55
10.22	11.9856	13.82
4.38	4.7844	5.63
3.25	3.6541	4.17
0.76	0.9783	1.02
0.70	0.8093	0.94
7.00	8.1302	9.00
1.02	1.5027	1.38
38.73	41.2986	43.23
2.67	3.3280	4.45
0.68	0.8154	0.92
0.47	0.6138	0.72
1.12	1.3206	1.52
	98.3000	

Properties of canistered glass are predicted from composition using models; confirmatory test response is not measured

WV Batch #50 (%Oxide Target, Upper/Lower 95% Boundaries, and Measured %Oxide

Shards from Canister WV-279

SRNL

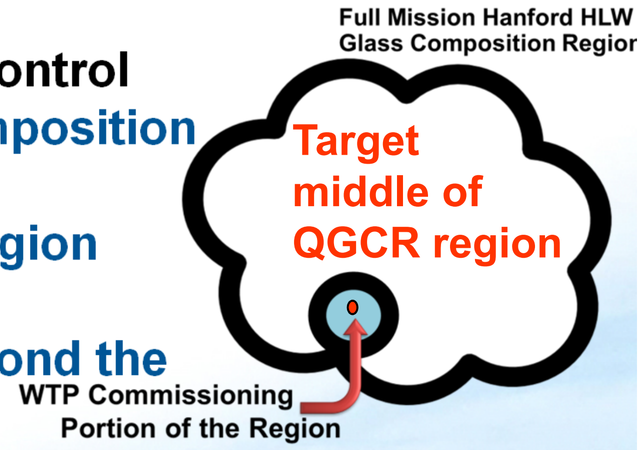
SRNL-STI-2013-00197

Differences in Performance Strategy

- **PROBLEM: A production facility cannot wait until the melt or waste glass has been made to assess its acceptability**

- **DWPF: Acceptability decision is made on the upstream process, rather than on the downstream *melt* or glass product**
  - **"feed forward" statistical *process* control**
  - **feed quality is controlled prior to vitrification**
  - **can operate at maximum waste loading at 95% confidence**
  - **minimal sampling of actual product during production**
  - ***mechanistic and semi-empirical models* can be validated beyond the qualified region**

- **WV/WTP: Alternate methods are statistical *quality* control**
  - **glass product is sampled *after* it is vitrified:composition compared to before vitrified composition**
  - **have to operate in the middle of the qualified region**
  - **sampling is analytic intensive**
  - ***empirical models* used cannot be validated beyond the qualified composition region**

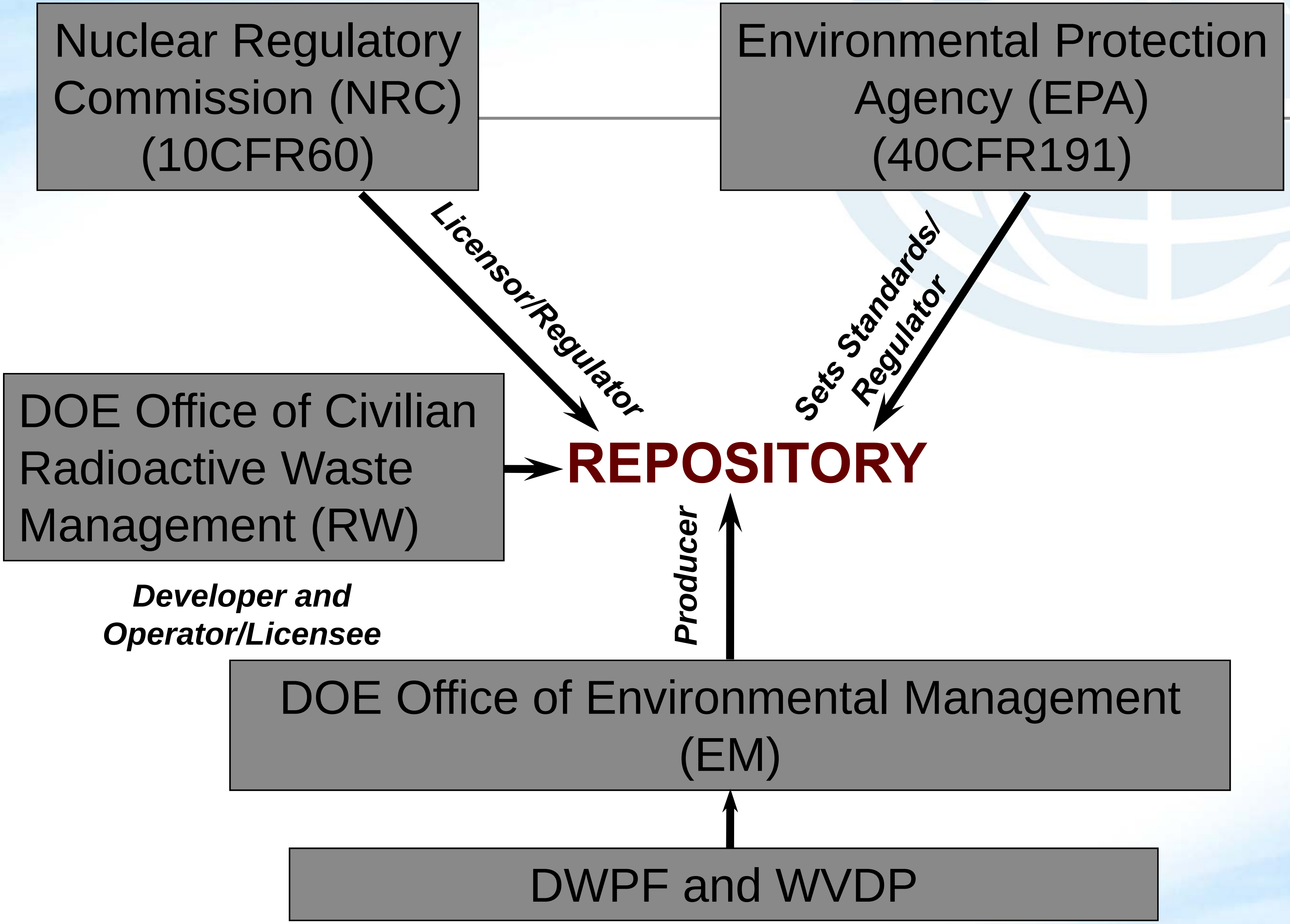


SRNL-STI-2013-00197

QGCR - Qualified Glass Composition Region

Development of Technical and Performance Standards for HLW Glass

- **Late 1970's DOE began evaluation of waste forms**
- **Dec 1982, ROD issued selecting borosilicate glass**
  - **Endorsed by EPA and several independent review groups**
  - **NRC had no objection**
- **1982 Nuclear Waste Policy Act (NWPA) mandated that HLW be sent to a federal repository**
  - **Actually a recommendation from the NAS in 1956-57 timeframe**
- **1985 President ratified the DOE decision to send defense HLW to a civilian repository (OCWRM)**
- **Early 1990's Waste Acceptance System Requirements Document generated requiring DOE-EM to develop Waste Acceptance Product Specifications (WAPS)**



Nuclear Regulatory Commission (NRC) (10CFR60)

Environmental Protection Agency (EPA) (40CFR191)

Licensor/Regulator

Sets Standards/ Regulator

DOE Office of Civilian Radioactive Waste Management (RW)

REPOSITORY

Developer and Operator/Licensee

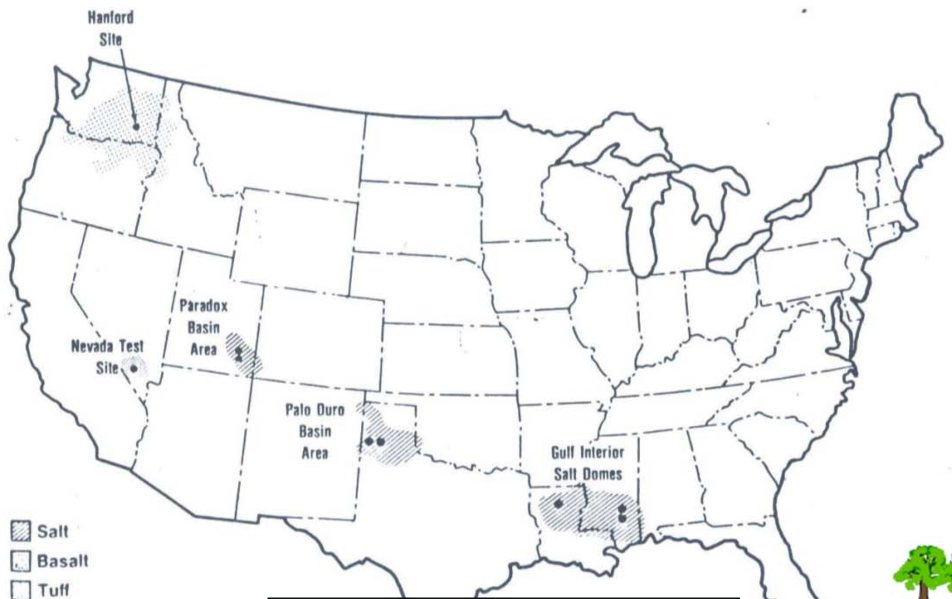
Producer

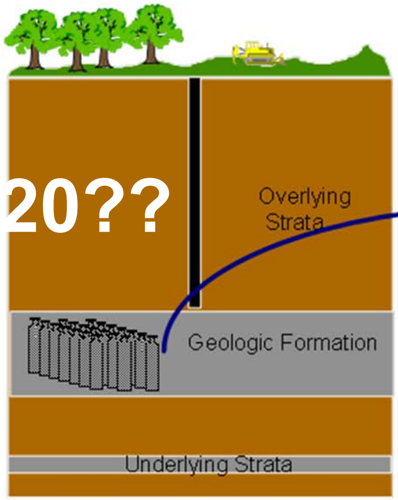
DOE Office of Environmental Management (EM)

DWPF and WVDP

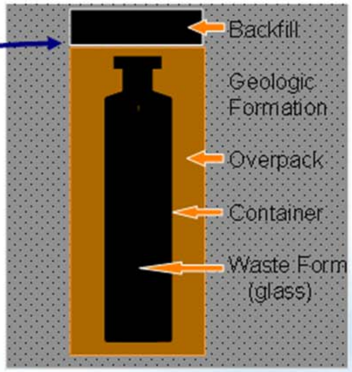
NUCLEAR WASTE POLICY DECISIONS 1982, 1987, 2009

ISSUE: Waste form must be acceptable to a repository yet to be sited and/or built





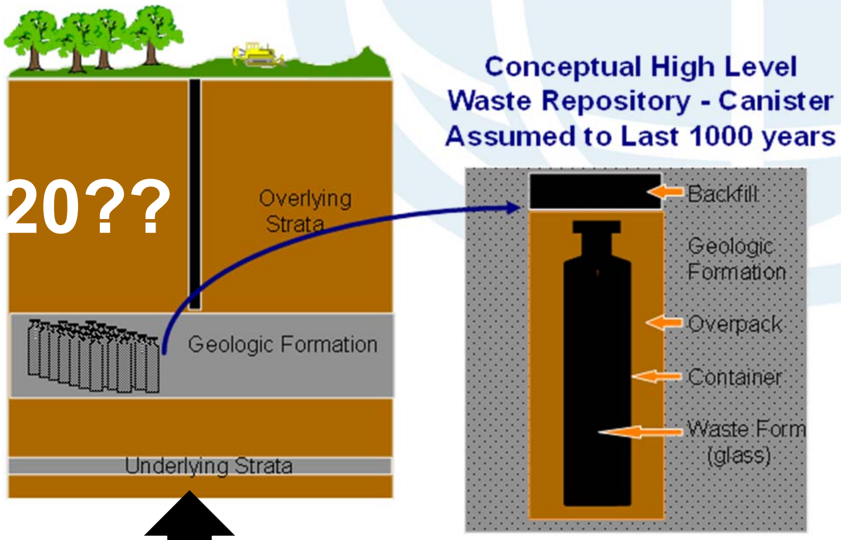
Conceptual High Level Waste Repository - Canister Assumed to Last 1000 years



How Can The Waste Form Producers Comply?

Relate short term test results to a “repository relevant” test when a repository is chosen

Develop a glass durability standard (EA glass) meets all the repository requirements because then all the other glasses will meet the requirements



- **Perform LT tests as possible (HLW glass and natural analogs)**
- **Perform repository relevant tests (rock cup tests in tuff, basalt, salt, with various groundwaters, low Eh, etc.)**
- **Perform in situ tests in a repositories (WIPP, STRIPA granite in Sweden, Ballidon clay in UK)**
- **Perform materials interactions tests (glass and metal, with and without rock present)**
- **Perform accelerated ST tests (without changing the durability mechanism) with HLW glass and analogs**
- **Relate LT and ST testing (rad and non-rad testing)**

Wasteform Qualification Strategy Used in US

Time Frame	Strategy
1982-1983	✓ develop acceptable waste form durability from geochemical modeling based on HLW performance modeling ✓ fractional dissolution rates between 10^{-4} to 10^{-6} parts per year ✓ a glass waste form would take 10,000 to 1,000,000 years to totally dissolve ✓ early versions of 10 CFR Part 60.113 specified fractional release rates of 10^{-5} parts per year ✓ which was in the middle of the range determined by HLW performance modeling ✓ this rate was adopted as the waste form specification.
	✓ if the long-term fractional dissolution rate of a waste form was $\leq 10^{-5}$ parts per year for the most soluble and long-lived radionuclides then borosilicate glass would provide acceptable performance for any repository site
1987-Present	✓ develop tests (MCC and ASTM) that would provide an under-standing of the glass durability mechanisms from a combination of the test protocols ✓ ASTM C1220, ASTM C1285 Product Consistency Test (PCT), ASTM C1662 SPFT and ASTM C1663 VHT, PUF

Wasteform Qualification Strategy Used in the US (Cont'd)

Time Frame	Strategy
1992	✓ develop a borosilicate glass standard ✓ Environmental Assessment (EA) glass (1981 DWPF EA; Jantzen, et.al. 1992) that bounded the upper release rate found to be acceptable from HLW performance modeling and 10 CFR Part 60.113
1987-present	✓ generate data for modeling the maximum radioactive release rate(s) in borosilicate glass by relating the release of soluble ^{99}Tc, ^{129}I, and ^{135}Cs to the release of soluble species such as Na, Li, and B, i.e. the DR vs PR ✓ all soluble species leach at the same rate (congruently) ✓ these references are part of the ASTM C1285 (PCT) test protocol
1987- present 1994-present	✓ develop a short term test and process control strategy for ensuring that every glass produced had a dissolution rate <EA glass at the L95% confidence level based on Na, Li, B ✓ this ensures acceptable performance control (part of the WAPS compliance strategy)
1996-present	✓ Continue to test (qualify) the radionuclide response of production glasses to verify that radionuclide release consistent with the releases predicted by Na, Li, B

Waste Acceptance Product Specifications (EM-WAPS-Rev. 3)

WAPS 1.0 Waste Form Specifications (Glass or RW Equivalent and complies with NWPAA)

WAPS 1.1 Chemical Composition (projections and during production)

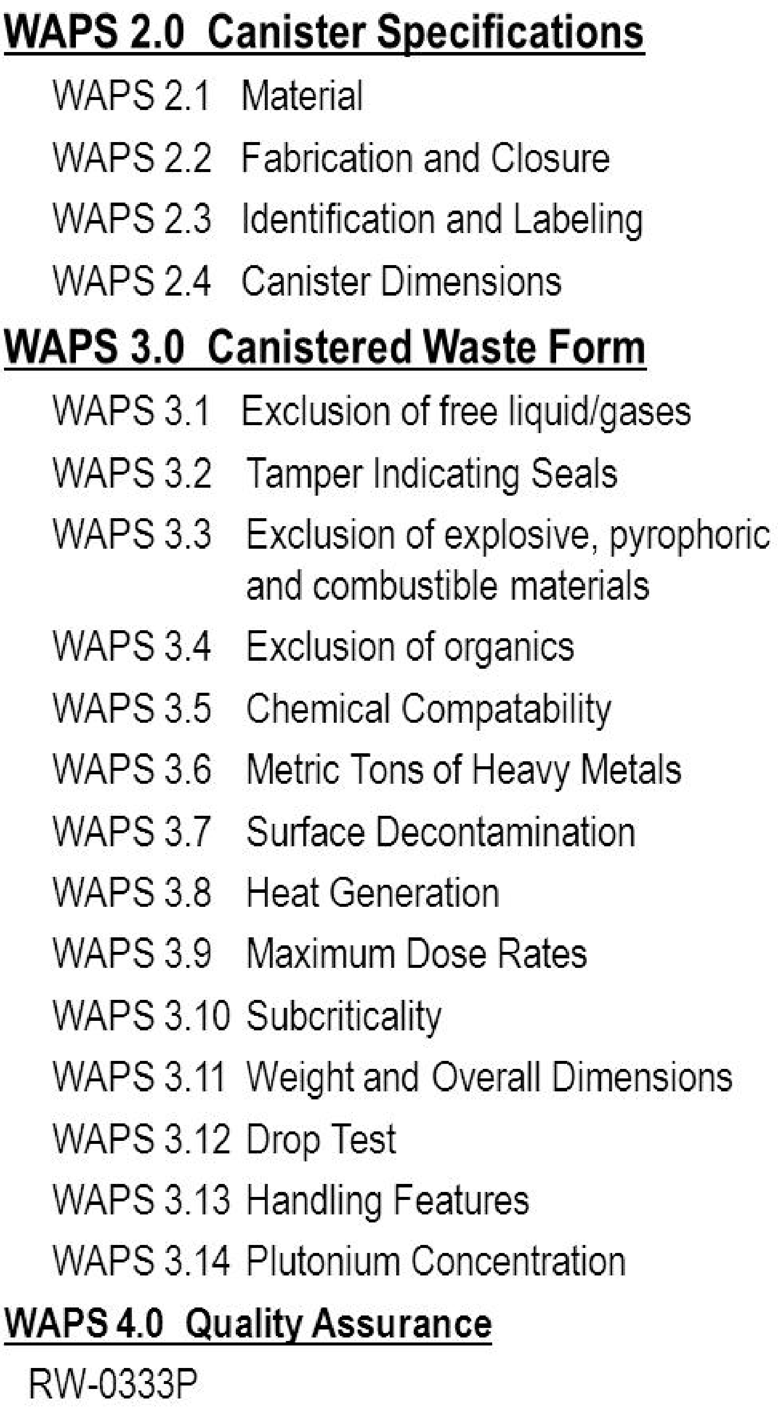
WAPS 1.2 Radionuclide Inventory (projections and during production)

WAPS 1.3 Product Consistency (more durable than the EA glass by two standard deviations; can project durability and/or meas. production glasses)

WAPS 1.4 Phase Stability

WAPS 1.5 Hazardous Waste

WAPS 1.6 IAEA Safeguards



WAPS 2.0 Canister Specifications

WAPS 2.1 Material

WAPS 2.2 Fabrication and Closure

WAPS 2.3 Identification and Labeling

WAPS 2.4 Canister Dimensions

WAPS 3.0 Canistered Waste Form

WAPS 3.1 Exclusion of free liquid/gases

WAPS 3.2 Tamper Indicating Seals

WAPS 3.3 Exclusion of explosive, pyrophoric and combustible materials

WAPS 3.4 Exclusion of organics

WAPS 3.5 Chemical Compatability

WAPS 3.6 Metric Tons of Heavy Metals

WAPS 3.7 Surface Decontamination

WAPS 3.8 Heat Generation

WAPS 3.9 Maximum Dose Rates

WAPS 3.10 Subcriticality

WAPS 3.11 Weight and Overall Dimensions

WAPS 3.12 Drop Test

WAPS 3.13 Handling Features

WAPS 3.14 Plutonium Concentration

WAPS 4.0 Quality Assurance

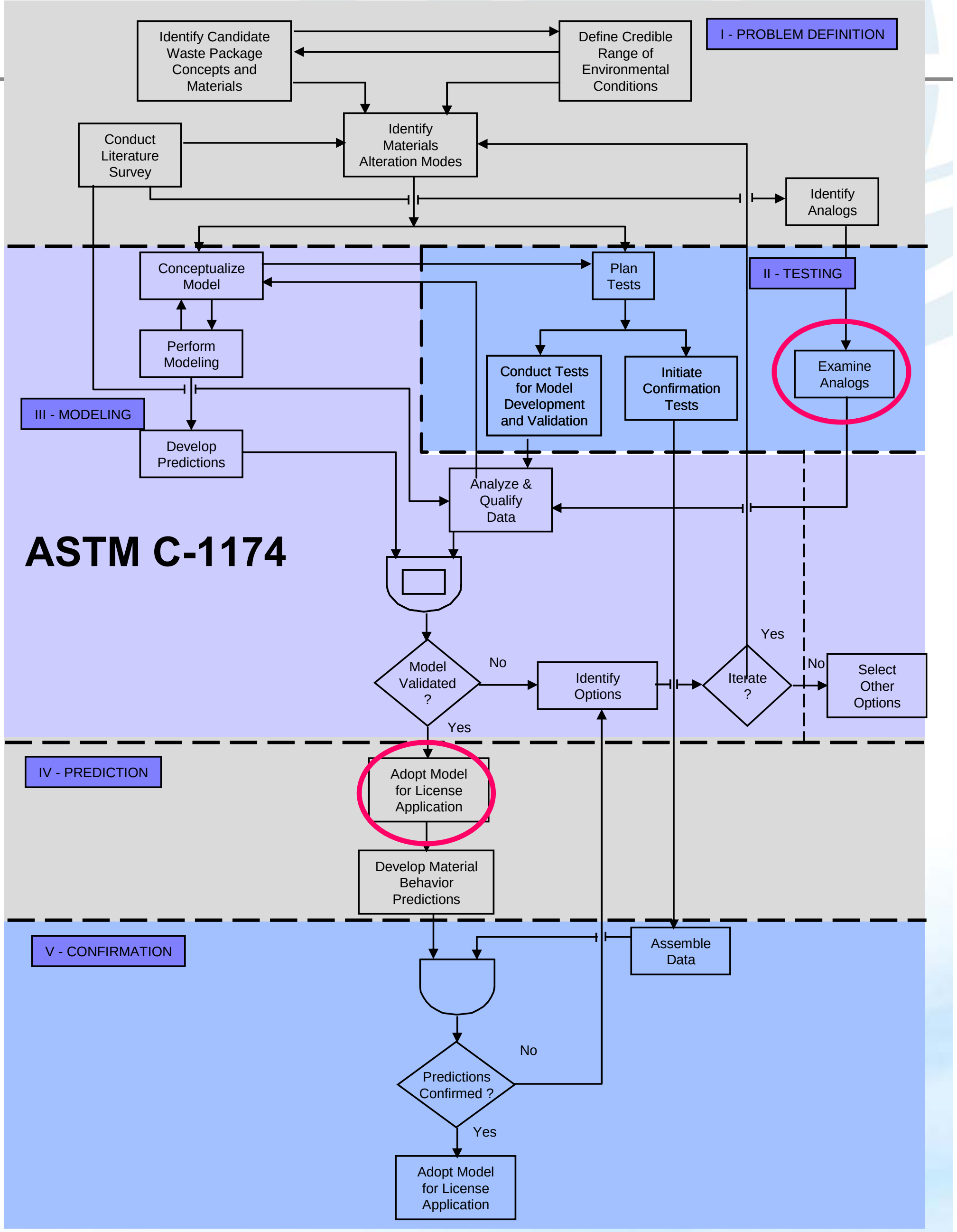
RW-0333P

ASTM C-1174 “The Roadmap to Predicting Long-term Behavior”

Title: “Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste”

A roadmap for the steps involved in predicting long-term behavior:
(1) problem definition
(2) testing
(3) modeling
(4) prediction
(5) model confirmation.

Many iterations between testing and modeling



I - PROBLEM DEFINITION

Identify Candidate Waste Package Concepts and Materials

Define Credible Range of Environmental Conditions

Conduct Literature Survey

Identify Materials Alteration Modes

Identify Analogs

II - TESTING

Plan Tests

Conduct Tests for Model Development and Validation

Initiate Confirmation Tests

Examine Analogs

III - MODELING

Conceptualize Model

Perform Modeling

Develop Predictions

Analyze & Qualify Data

ASTM C-1174

Model Validated ?

No

Yes

Identify Options

Iterate ?

Yes

No

Select Other Options

IV - PREDICTION

Adopt Model for License Application

Develop Material Behavior Predictions

V - CONFIRMATION

Assemble Data

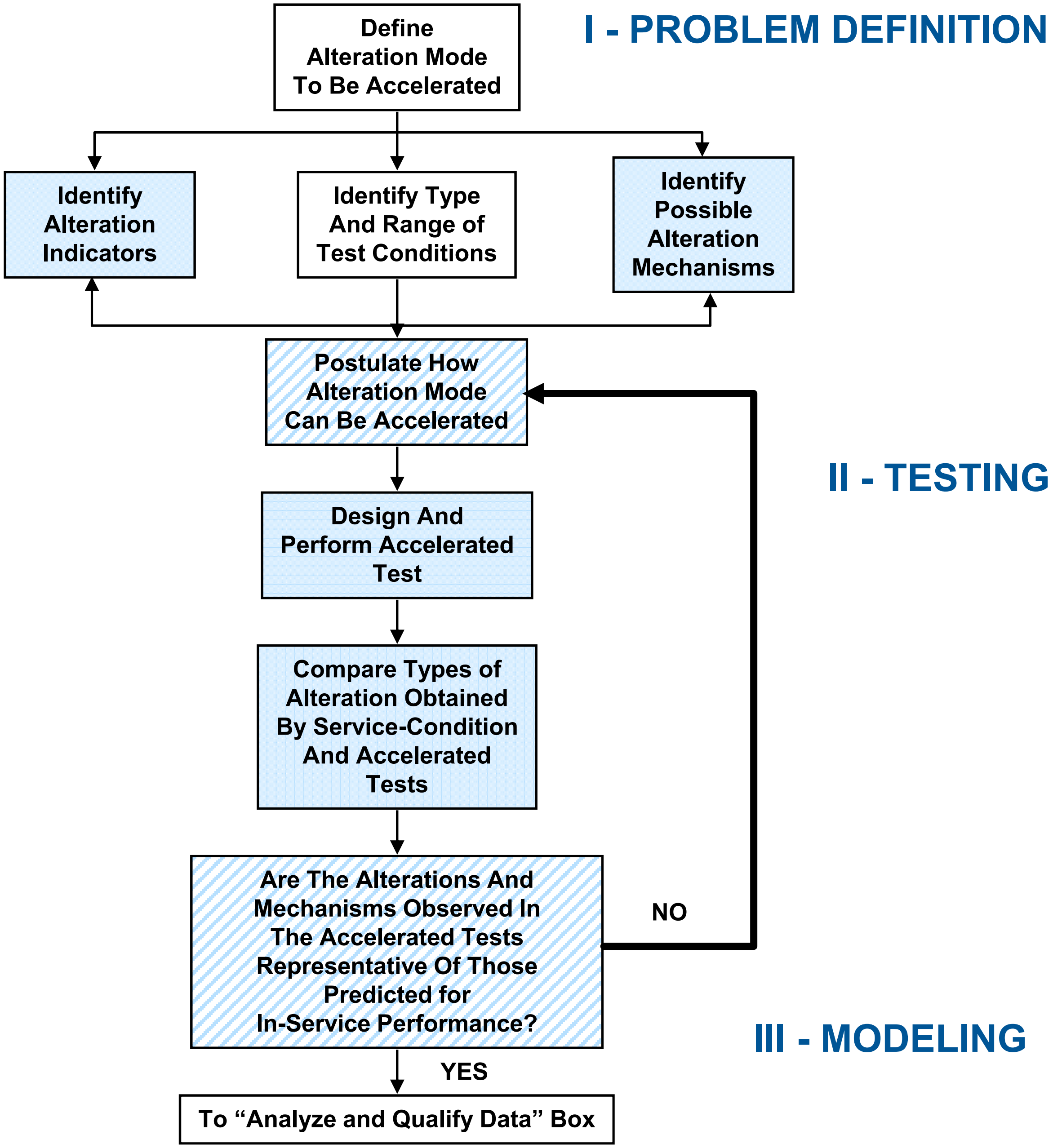
Predictions Confirmed ?

No

Yes

Adopt Model for License Application

ASTM C-1174 (Development of Accelerated Tests)



I - PROBLEM DEFINITION

Define Alteration Mode To Be Accelerated

Identify Alteration Indicators

Identify Type And Range of Test Conditions

Identify Possible Alteration Mechanisms

II - TESTING

Postulate How Alteration Mode Can Be Accelerated

Design And Perform Accelerated Test

Compare Types of Alteration Obtained By Service-Condition And Accelerated Tests

III - MODELING

Are The Alterations And Mechanisms Observed In The Accelerated Tests Representative Of Those Predicted for In-Service Performance?

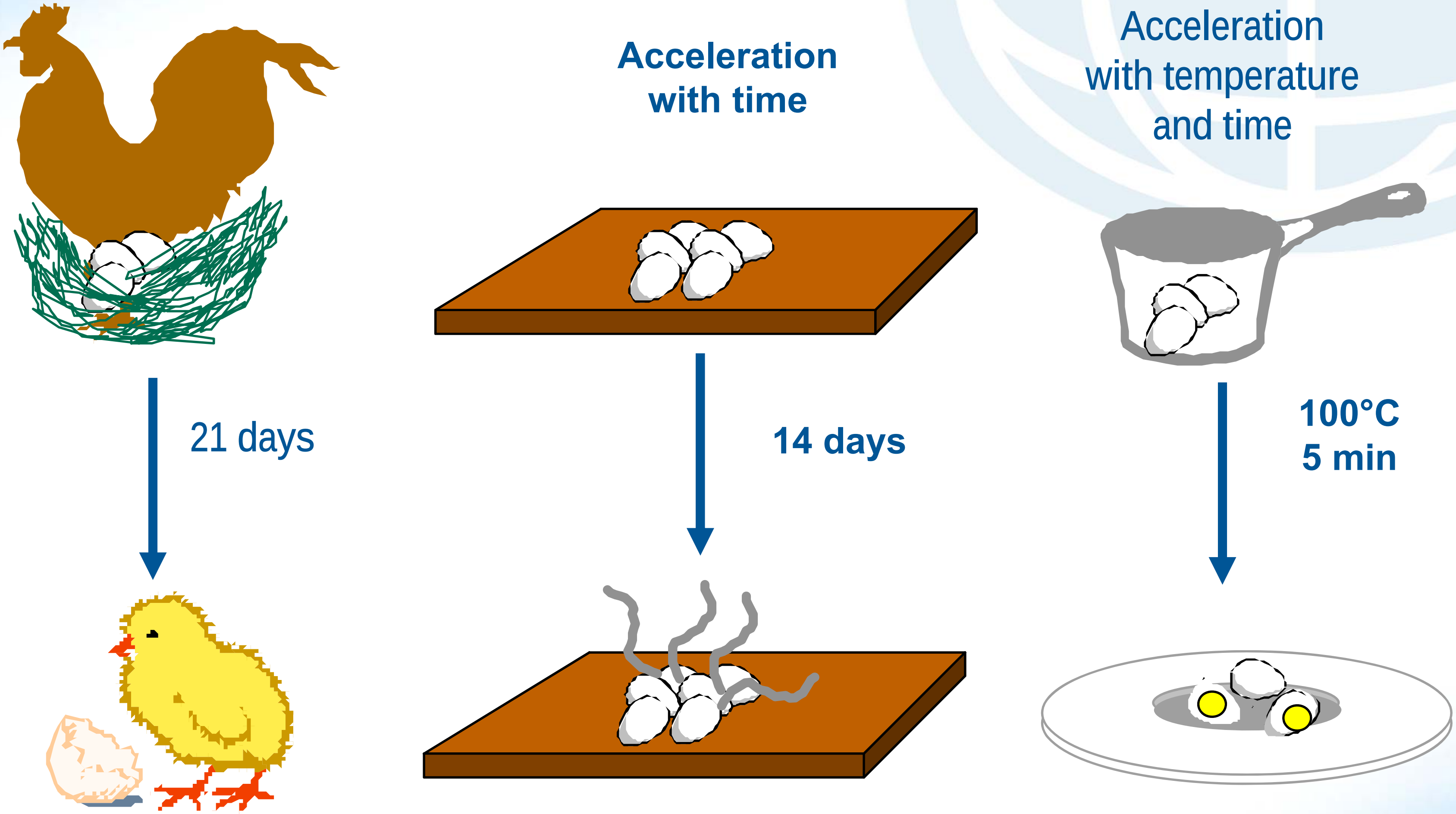
NO

YES

To “Analyze and Qualify Data” Box

SRNL

Accelerating the Correct Mechanism in Short Term (ST) Testing to Simulate LT is Very Important



Acceleration with time

Acceleration with temperature and time

21 days

14 days

100°C
5 min

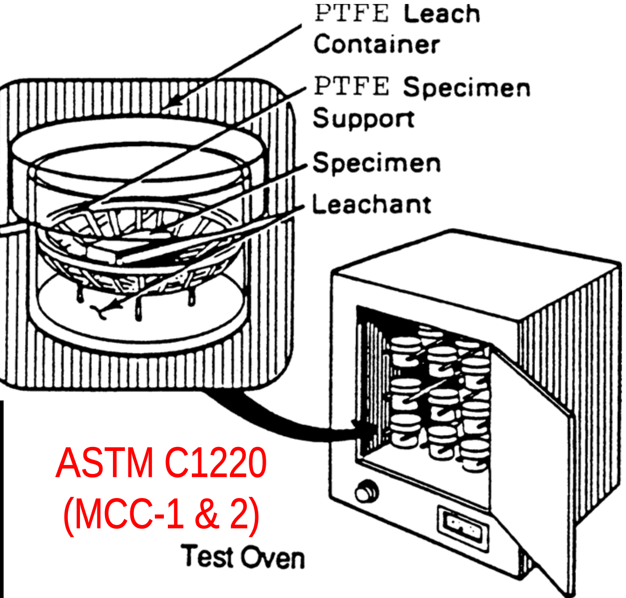
* As defined at the August, 1998 NAS/NRC Workshop on Test Methods and Models to Simulate Accelerated Aging of Infrastructure Materials

Accelerated Tests Developed from 1980

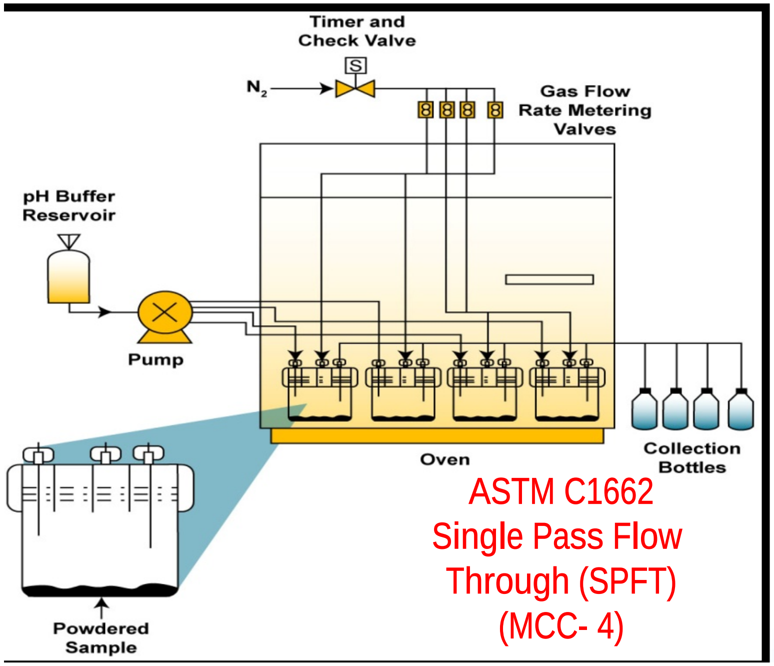
Waste Form (1980-Pres)	
Chemical Durability	**MCC-1, 2, 3, 4, 5** (Soxhlet)
Aging Effects (thermal and radiation)	**MCC-6, 7, 12, 13**
Volatility	**MCC-8.9,16**
Physical Strength	**MCC-10, 11, 15**
Canister Container	
Corrosion Resistance	**MCC-101, 102, 103, 104**
Repository Interactions	
Canister/container corrosion	**MCC-105**[a]
Waste Form Durability	**MCC-14**[a]

[a] The repository interactions tests are divided into site-specific subcategories, e.g., MCC-105.1 (basalt).

ASTM C1663
Vapor Hydration
Test (VHT)

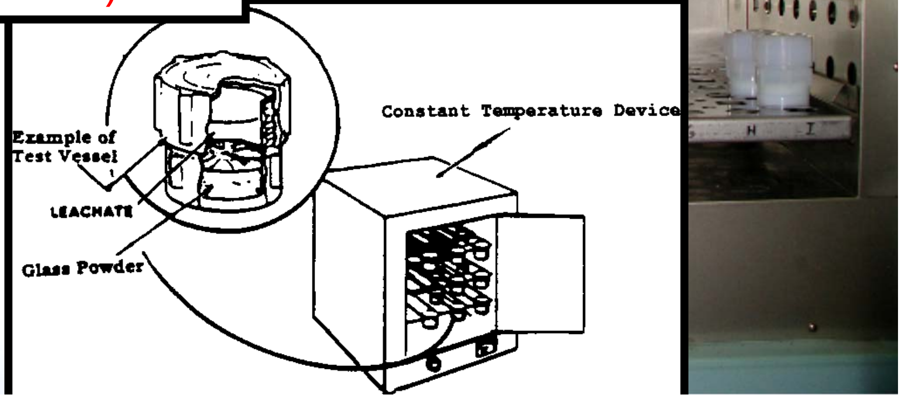


ASTM C1220
(MCC-1 & 2)

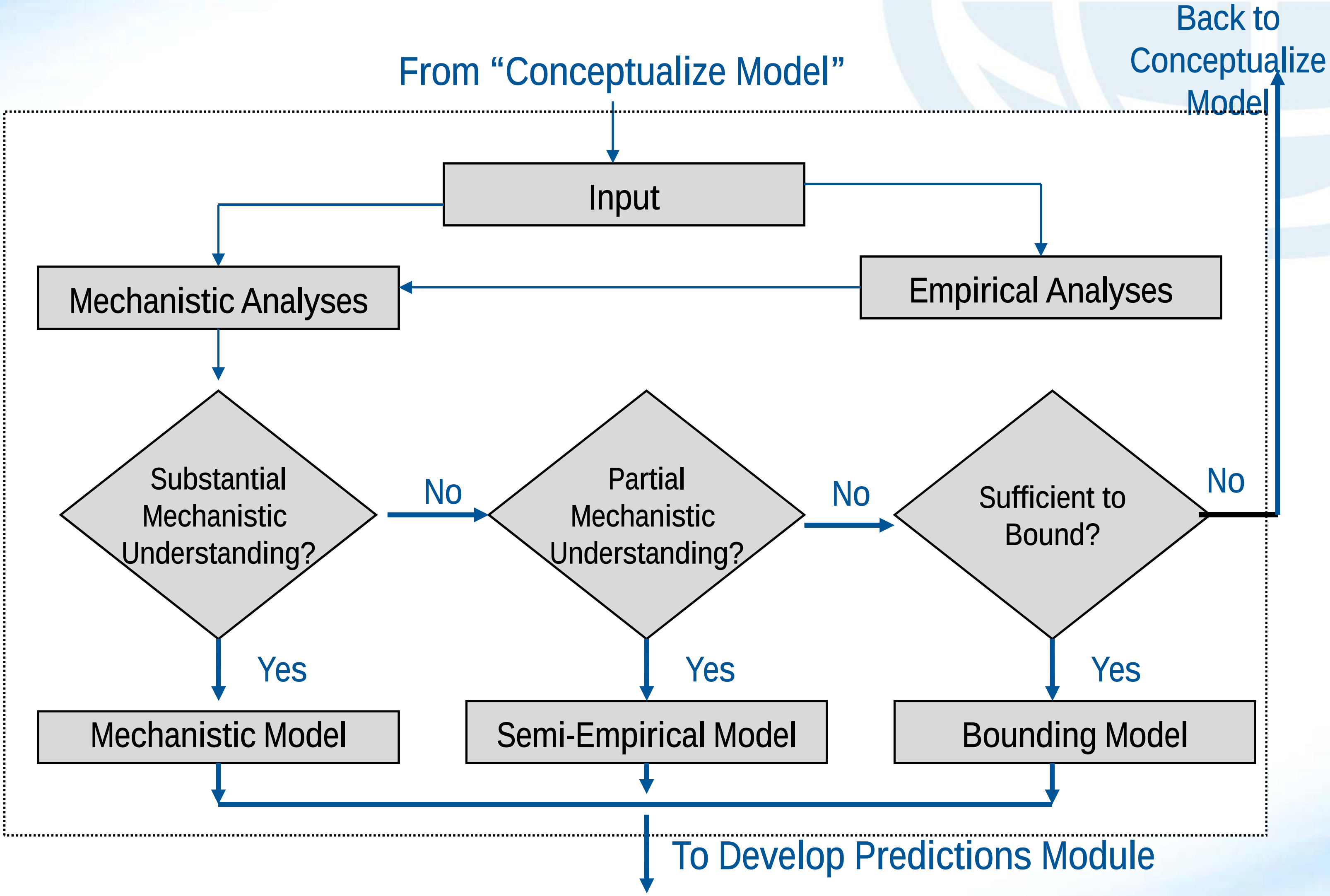


ASTM C1662
Single Pass Flow
Through (SPFT)
(MCC- 4)

ASTM C1285
Product Consistency
Test (PCT)
(MCC- 3)



ASTM C1174 “Perform Modeling” Module



From “Conceptualize Model”

Back to Conceptualize Model

Input

Mechanistic Analyses

Empirical Analyses

Substantial Mechanistic Understanding?

No

Partial Mechanistic Understanding?

No

Sufficient to Bound?

No

Yes

Yes

Yes

Mechanistic Model

Semi-Empirical Model

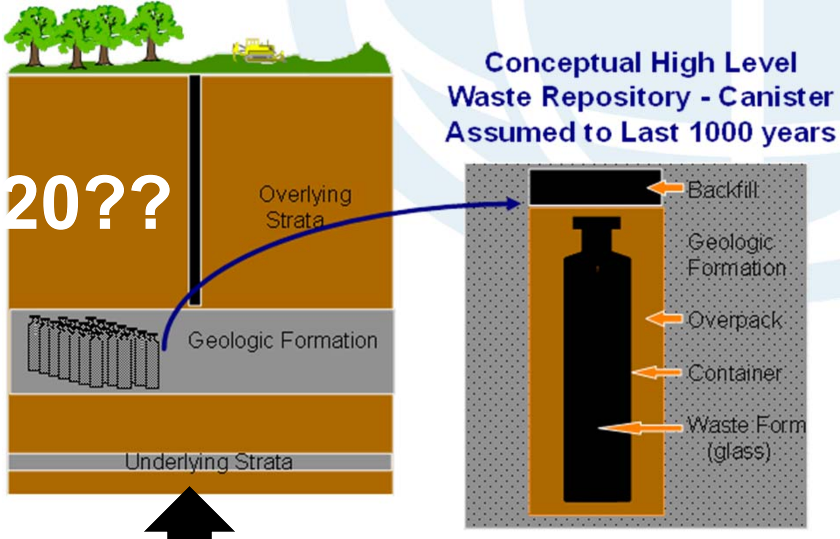
Bounding Model

To Develop Predictions Module

The Roadmap Utilizes All Test Responses and Modeling for Long Term Durability Modeling

Relate short term test results to a "repository relevant" test when a repository is chosen

Develop a glass durability standard (EA glass) meets all the repository requirements because then all the other glasses will meet the requirements

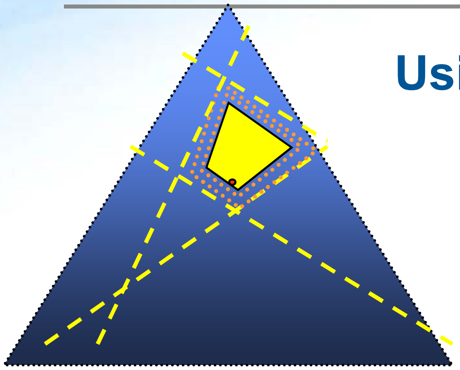


Conceptual High Level Waste Repository - Canister Assumed to Last 1000 years

Total Systems Performance Assessment-LA (TSPA-LA) for Yucca Mtn.

- **Perform LT tests as possible (HLW glass and natural analogs)**
- **Perform repository relevant tests (rock cup tests in tuff, basalt, salt, with various groundwaters, low Eh, etc.)**
- **Perform in situ tests in a repositories (WIPP, STRIPA granite in Sweden, Ballidon clay in UK)**
- **Perform materials interactions tests (glass and metal, with and without rock present)**
- **Perform accelerated ST tests (without changing the durability mechanism) with HLW glass and analogs**
- **Relate LT and ST testing (rad and non-rad testing)**

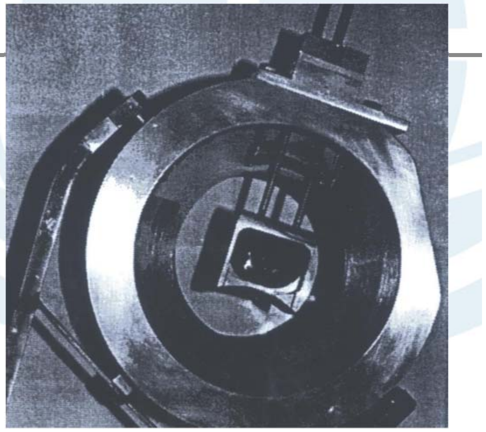
Waste Form Producers Use Process Control to Demonstrate Acceptable Performance



Using Process Control for QA/QC

QA = Quality Assurance

QC = Quality Control



Short term testing (ASTM C1285 The Product Consistency Test (PCT) can be related to acceptable performance
by the following linking relationships:

process control ↔ composition control ↔ dissolution rate control ↔ performance control ↔ acceptable performance

This strategy allows a waste form producer to ensure that the waste form that they are producing on a tonnage per year basis will be acceptable to long term performance instead of having to test each and every canister or form produced