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Evaluating the Solubility and Homogeneity of Plutonium in an Alkali Borosilicate Glass

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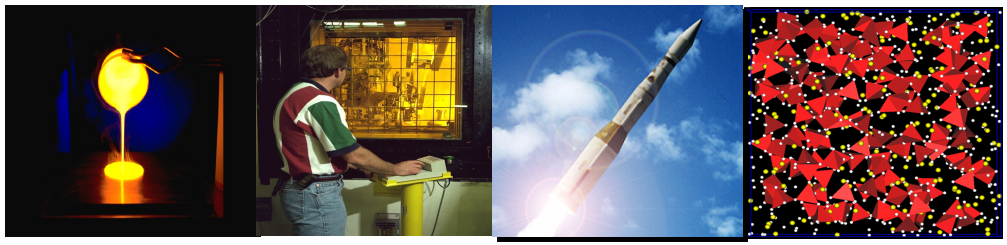


Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

EM Tech Exchange – Atlanta, GA

Print Close

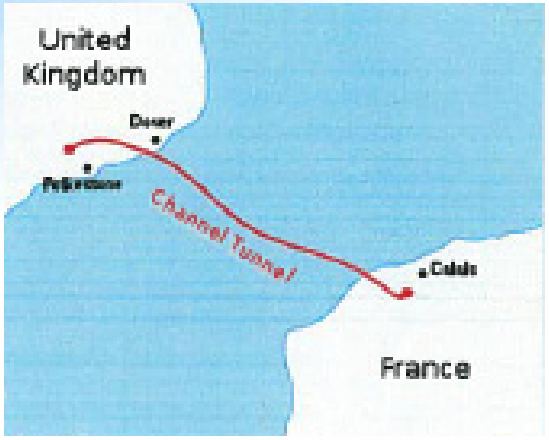
Outline

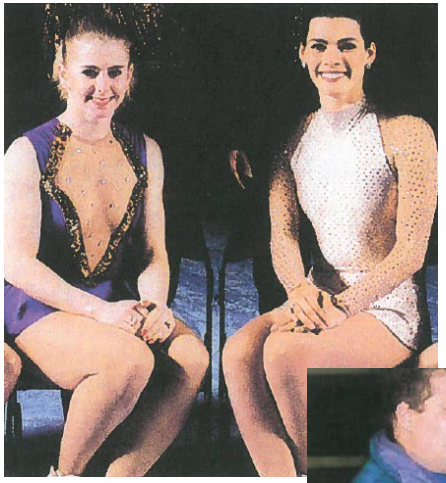
- Background
- Glass composition options
  - Vitrification processes
- Hf as a surrogate for Pu in borosilicate glasses
- Lanthanide borosilicate (LaBS) glass
- Alkali borosilicate glass
  - Initial studies
  - Present study – Pu behavior in HLW glass
- Pu behavior in the DWPF melter
- Summary

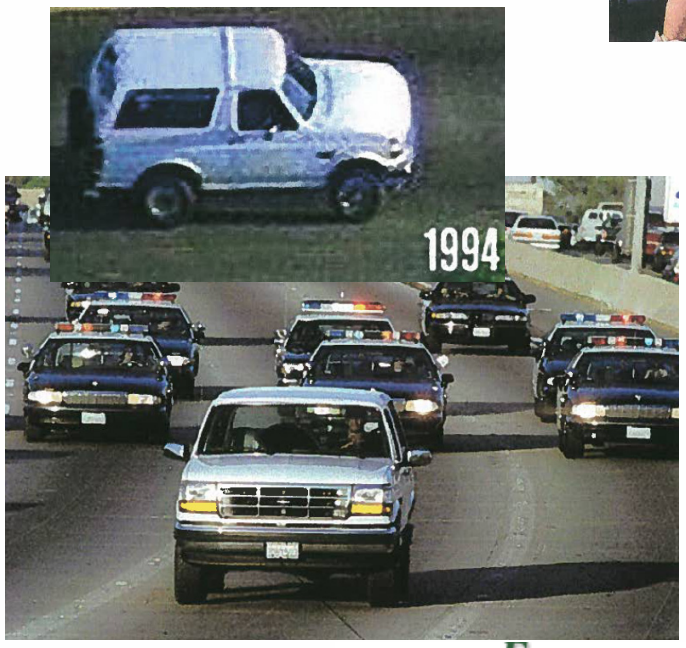
Background

- U.S. National Academy of Sciences, 1994
  - U.S. and Russian surplus weapons Pu is a “clear and present danger”
- U.S. to disposition up to 50 metric tons of surplus Pu
  - Protect surplus Pu from theft or diversion and reintroduction into nuclear arsenals
  - Bulk of U.S. material to be dispositioned by fabrication in mixed oxide (MOX) fuel and burned in a nuclear reactor
  - Remaining material could be immobilized for geologic repository disposal
- Glass and crystalline ceramics have been studied as immobilization forms
  - Vitrification studies commenced in 1994 timeframe

Events from 1994







1994

Candidate Pu Glass Forms

- **Lanthanide borosilicate (LaBS) glasses**
  - Based on high lanthanide concentration glasses originally developed for optical applications
  - Capable of high Pu loadings with good tolerance to impurities

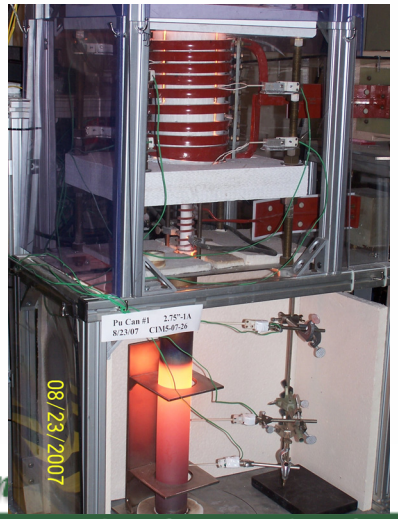
Pros	Cons
Excellent aqueous durability	High neutron dose from α,n reaction
Processing facilitates materials accountability/criticality control	High glass melting temperatures

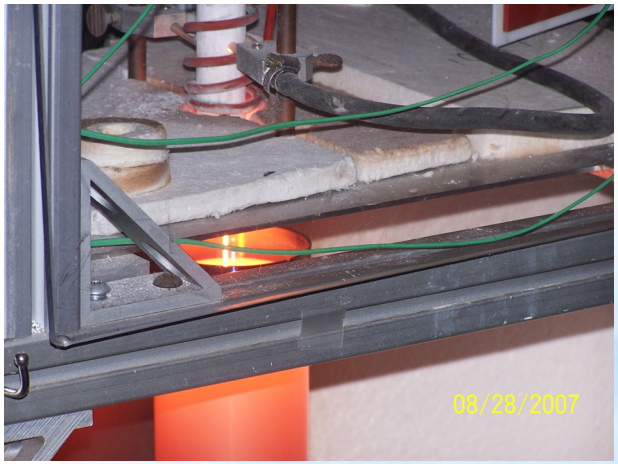
- **Alkali borosilicate glasses**
  - Based on current compositions used for high level waste (HLW) vitrification
  - Can only accommodate relatively low Pu concentrations but large-scale radioactive processing demonstrated

Pros	Cons
Established glass compositions	Safety (criticality) and materials safeguards must be established
Established vitrification processes	

Pu LaBS Glass – Cylindrical Induction Melter

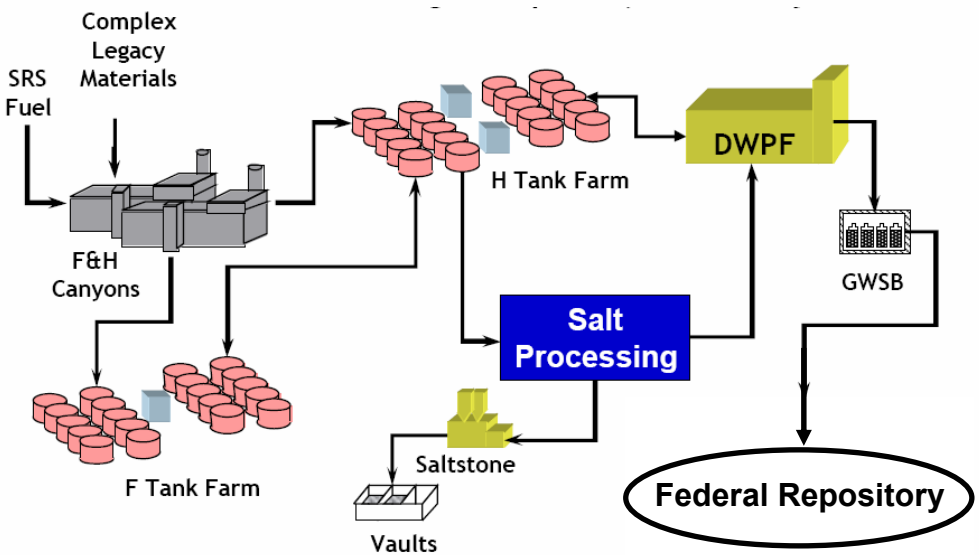
- Pt/Rh Vessel (6” ID x 20” H)
- Represents full-scale unit required for production!
- Batch process – facilitates safety and material accountability
  - Feeding (dry powder)
  - Melting
  - Pouring

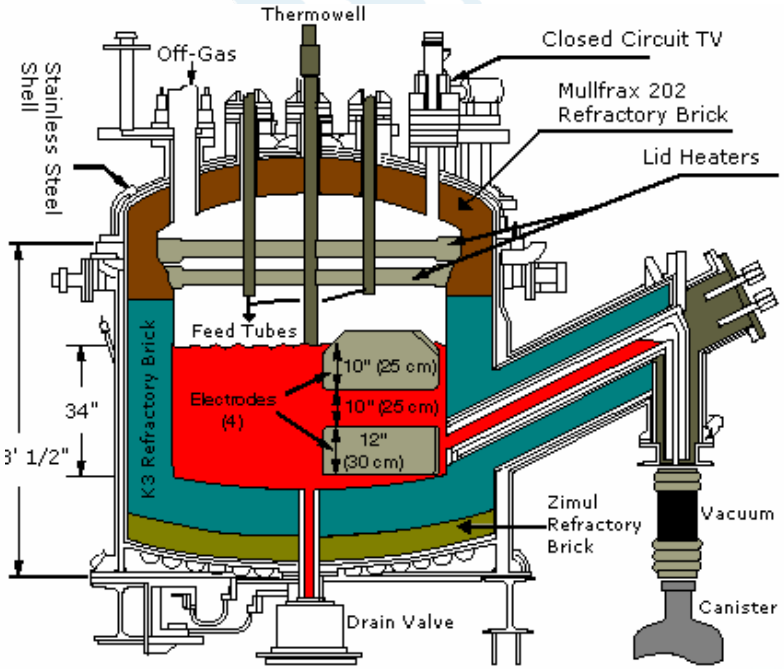




Alkali Borosilicate Glass Processing

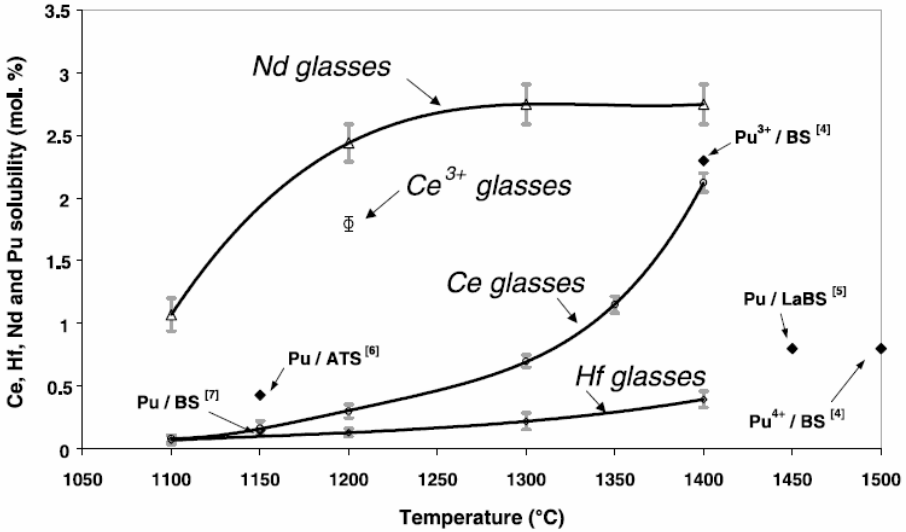
- Pu materials could be dissolved and entered into HLW system
- Pu glass then processed through DWPF in Joule heated ceramic-lined melter





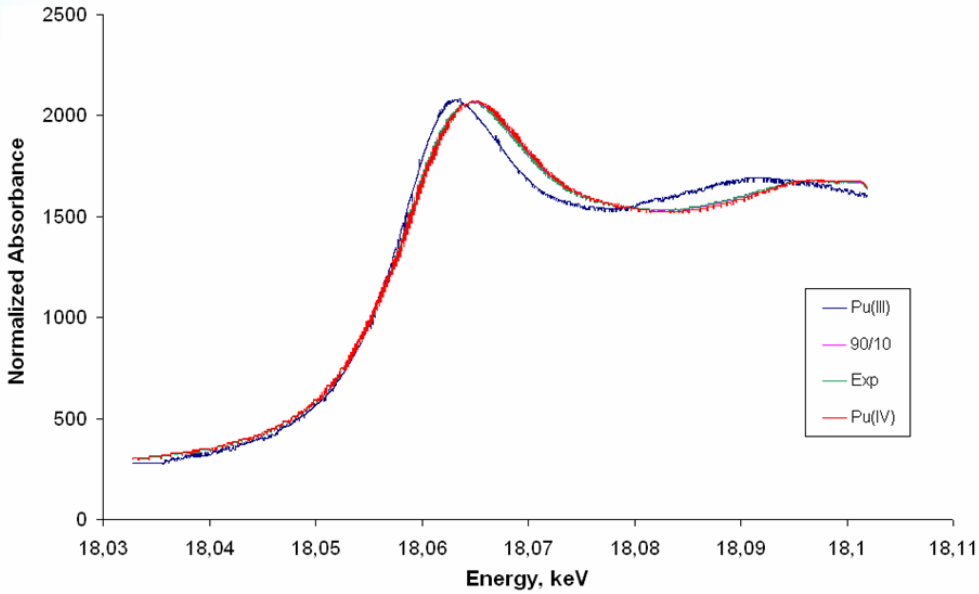
Hf as a Surrogate for Pu in Borosilicate Glasses (1/3)

- **Working with Pu surrogates simplifies glass testing**
- **CeO_2 widely used *chemical* surrogate for PuO_2**
  - **But, oxidation state change ($Ce^{4+} \rightarrow Ce^{3+}$) at high temperatures limits usefulness as surrogate for glass testing**
- **HfO_2 proven to be better surrogate for PuO_2 in glasses**
  - **Solubility**
  - **Oxidation state**
  - **Local environment**

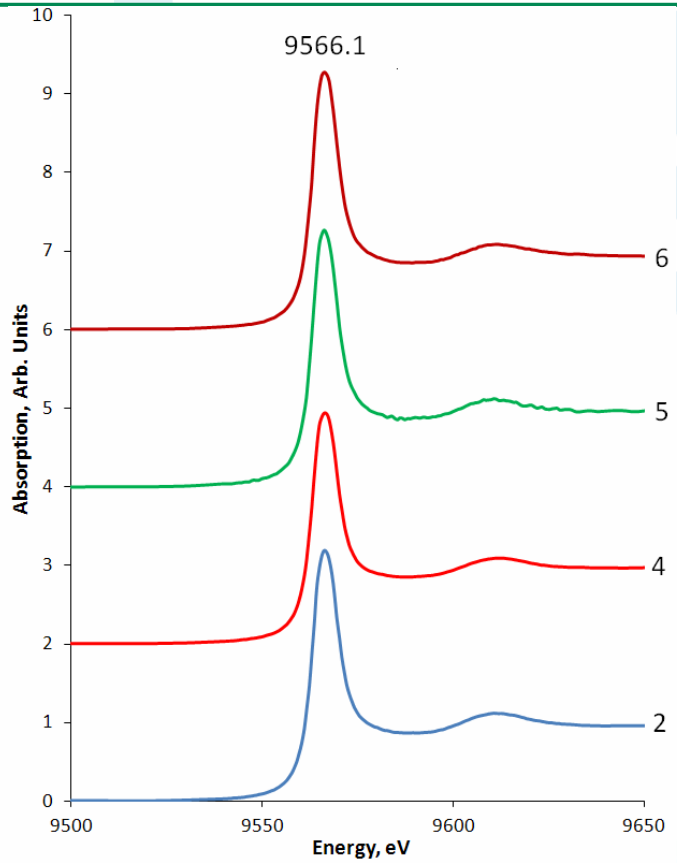


C. Lopez, et al., Journal of Nuclear Materials, 312, pp. 76-80, 2003

Hf as a Surrogate for Pu in Borosilicates Glasses (2/3)



XANES spectra of Pu LaBS Frit X @ 9.5 wt % PuO_2



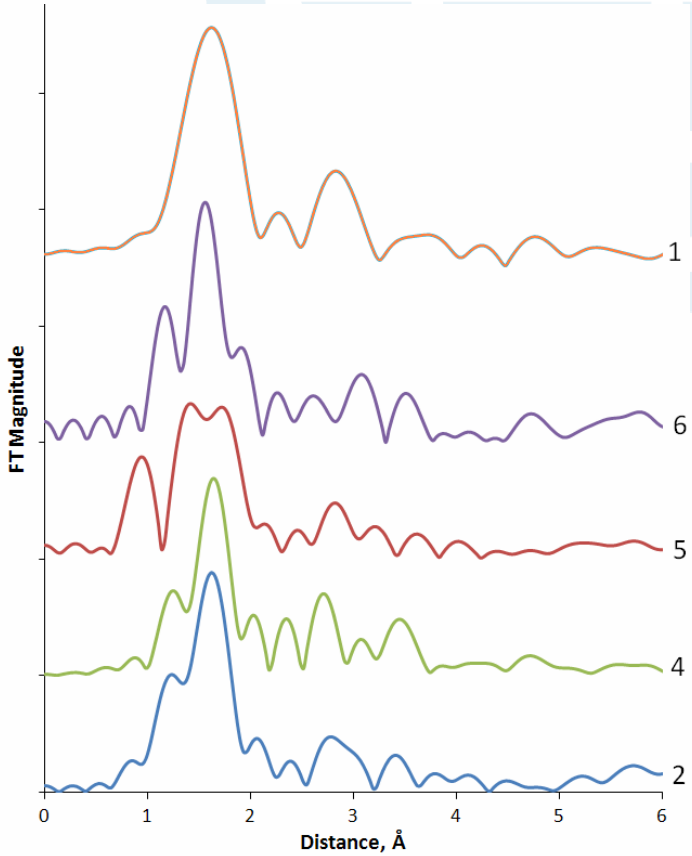
XANES spectra of HfO_2 LaBS glasses

2 – LaBS Frit X w/ 9.5 wt % equiv. HfO_2
4 – LaBS Frit X w/ 5 wt % equiv. HfO_2
5 – LaBS Frit A w/ 9.5 wt % equiv. HfO_2
6 – LaBS Frit A w/ 5 wt % equiv. HfO_2

- **Pu and Hf exist in +4 oxidation state in the glass**

Hf as a Surrogate for Pu in Borosilicate Glasses (3/3)

- EXAFS used to evaluate local structure of Pu and Hf in LaBS glasses
- Spectra (using Fourier Transform analysis) show the relative bond lengths for Pu and Hf similar in LaBS glass
- Evidence for slightly different coordination of Hf vs. Pu (Pu in "axially squeezed" octahedra with 5 equidistant oxygens and 1 at shorter distance)



1 – LaBS Frit X @ 9.5 wt % PuO_2

2 – LaBS Frit X w/ 9.5 wt % equiv. HfO_2

4 – LaBS Frit X w/ 5 wt % equiv. HfO_2

5 – LaBS Frit A w/ 9.5 wt % equiv. HfO_2

6 – LaBS Frit A w/ 5 wt % equiv. HfO_2

LaBS Glass Compositions

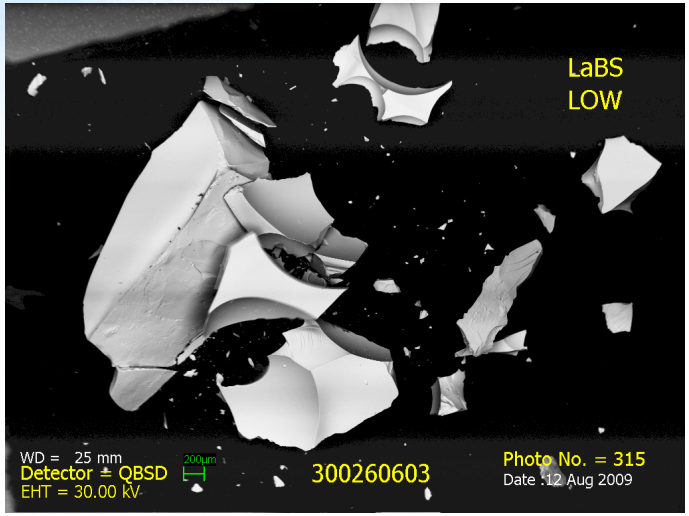
- In mid-1990s, LaBS glass developed to disposition excess plutonium
  - Based on high rare earth (RE) optical glasses
- LaBS "Frit A" demonstrated >10 wt % incorporation of Pu
- LaBS "Frit B" identified as initial reference frit
  - Included both Gd and Hf for enhanced criticality control
- LaBS "Frit X" more recent reference composition
  - Improved actinide solubility and processing properties

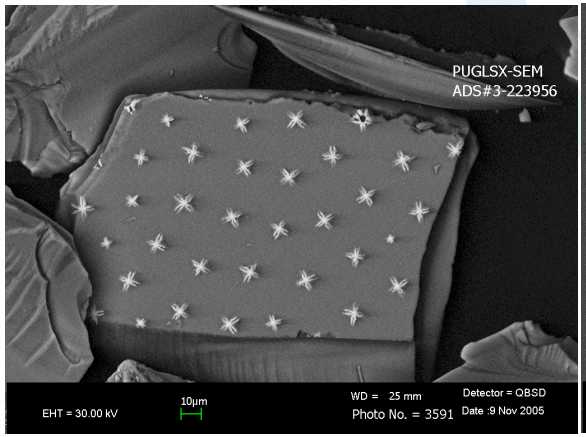
Oxide	LOEFFLER	FRIT A	FRIT B	FRIT X
Al_2O_3	16.9	21.5	21.3	10.00
B_2O_3	3.4	11.7	11.6	13.00
BaO	4.0	--	--	--
Gd_2O_3	--	8.6	12.8	13.50
HfO_2	--	--	6.6	7.0
La_2O_3	17.4	12.4	8.1	19.00
Nd_2O_3	20.4	12.8	8.2	15.00
PbO	10.4	--	--	--
SiO_2	27.5	29.2	28.9	20.00
SrO	--	2.5	2.5	2.50
ZrO_2	--	1.3	--	--

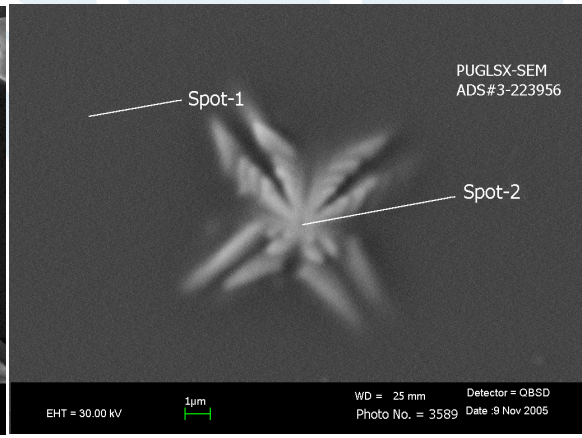
LaBS Frit X

LaBS Frit X w/ 5 wt% Pu

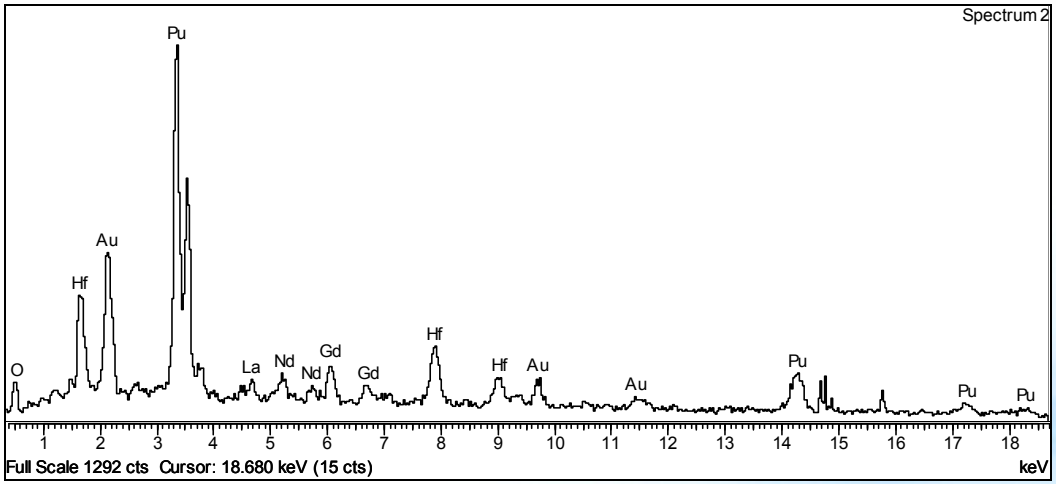
Pu LaBS Glass Microstructure







- Pu LaBS glasses are generally homogeneous – Pu dissolved in glass matrix
- At high Pu loadings (~10 wt %), some evidence of undissolved or reprecipitated PuO_2 and/or PuO_2-HfO_2 solid solution phase

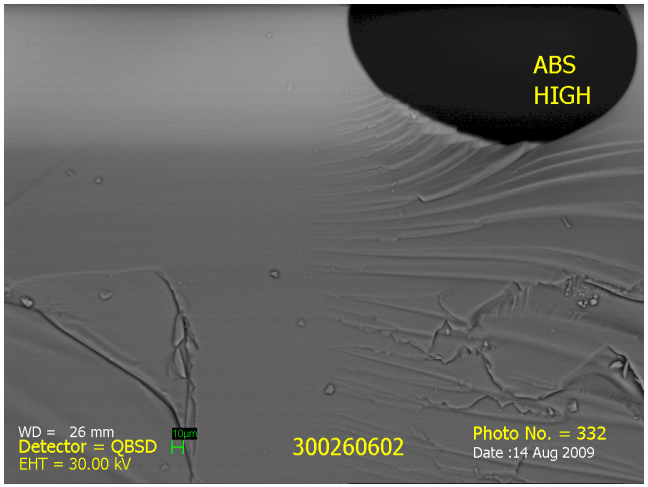


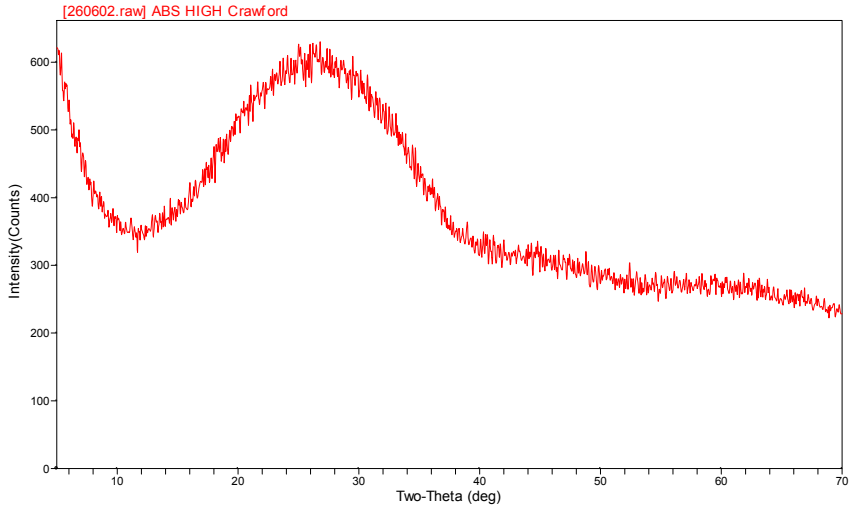
Alkali Borosilicate Glass – Initial Studies

- Current compositions used for HLW vitrification at Savannah River Site
  - Defense Waste Processing Facility – radioactive operations since 1996 (>12 million pounds of glass)
- Simplified HLW glass utilized for preliminary (feasibility) Pu testing
  - 0.5 wt % and 2 wt % PuO_2 loading
  - Complete "dissolution" of Pu observed

Oxide	Wt %
Al_2O_3	9.0
B_2O_3	6.0
CaO	2.0
Fe_2O_3	12.0
Na_2O	14.0
Li_2O	5.0
MnO	2.0
SiO_2	50.0

Simplified DWPF Waste Glass



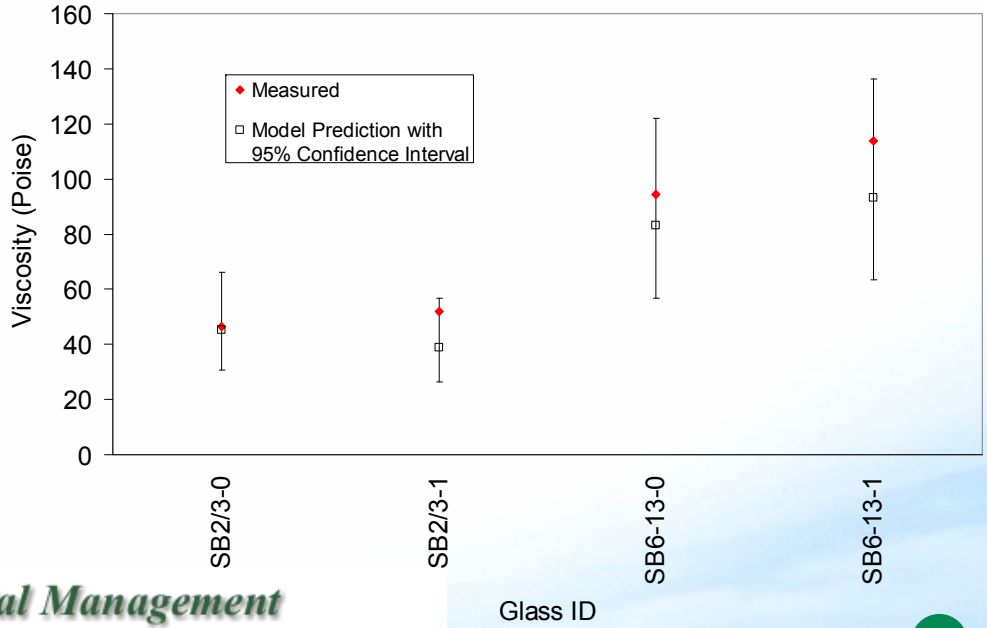


Current Study - Pu Behavior in HLW Glass

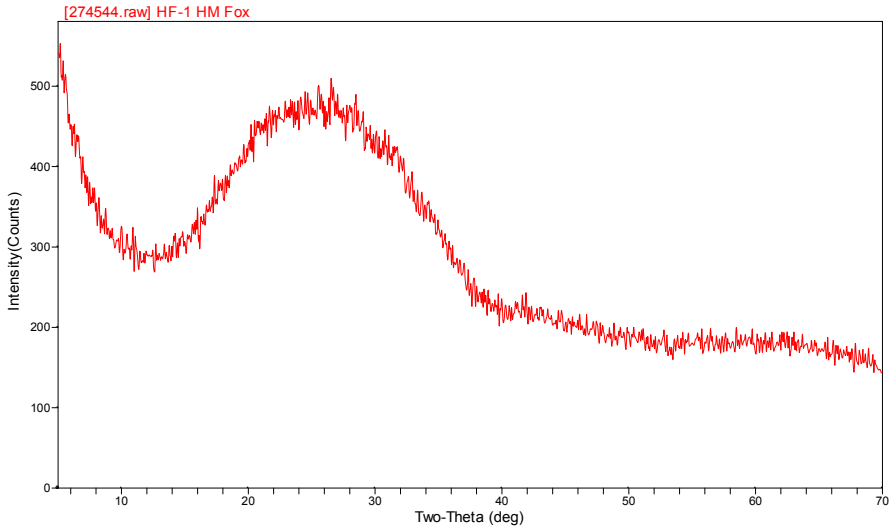
- **Literature study**
  - **"Solubility" of Pu in glass**
  - **Local environment of Pu in glass**
  - **Durability impacts**
  - **Radiation damage**
  - **Processing considerations**
- **Experimental program**
  - **Pu distribution in glass (settling, stratification, etc.)**
  - **Impact on glass properties (viscosity, durability, etc.)**
  - **Volatility/carryover/settling during processing**
    - Analyses of DWPF SB4 and SB5 pour stream samples
  - **Effect of Pu on waste/melter feed processing**
    - Fate of Pu
    - Role of neutron poisons

Pu Behavior in HLW Glass – Hf Studies (1/3)

- **Pu (Hf) surrogate glasses**
  - **Surrogate DWPF Slurry Mix Evaporator (SME) product – SB2/SB3 composite and SB6 surrogate**
  - **HfO_2 to represent 1 wt % Pu in the glass on molar basis**
    - "Well-mixed" sample using Wig-L-Bug® grinding mill
    - "Poorly-mixed" sample
- **Characterization**
  - **HfO_2 distribution using SEM/EDS**
  - **Crystallinity determination using XRD**
  - **Chemical composition**
  - **Viscosity**

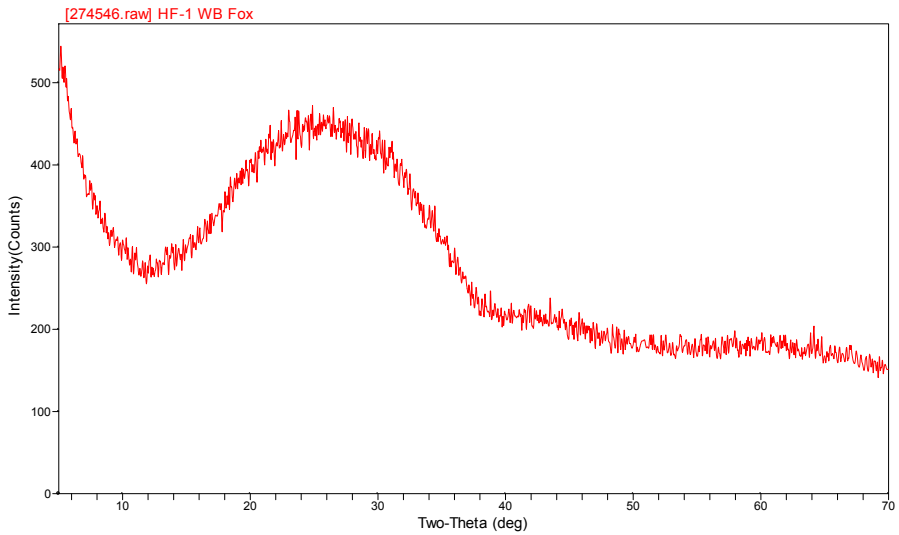


Pu Behavior in HLW Glass – Hf Studies (2/3)



SB2/SB3 poorly mixed -

Hf at 1 wt % Pu in glass on molar basis

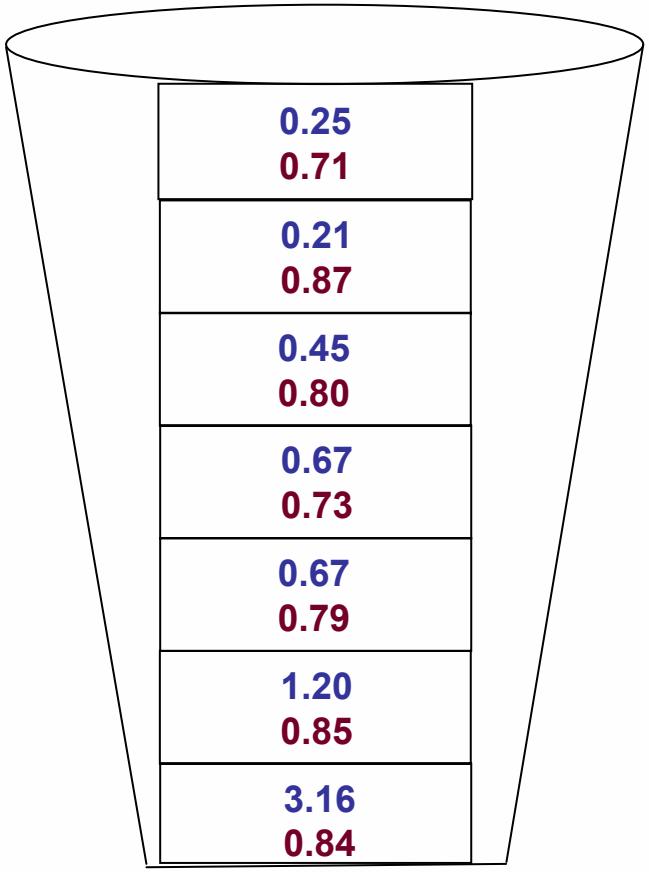


SB2/SB3 well mixed -

Hf at 1 wt % Pu in glass on molar basis

- **No evidence of Hf crystallization in either poorly mixed or well mixed samples**

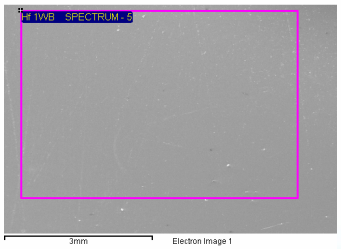
Pu Behavior in HLW Glass – Hf Studies (3/3)

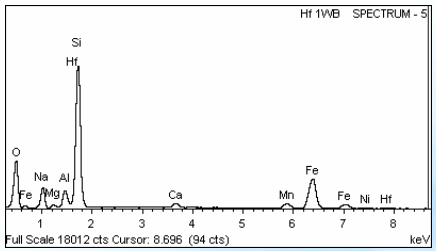


X.XX = wt % HfO_2 unmixed batch

X.XX = wt % HfO_2 well-mixed batch

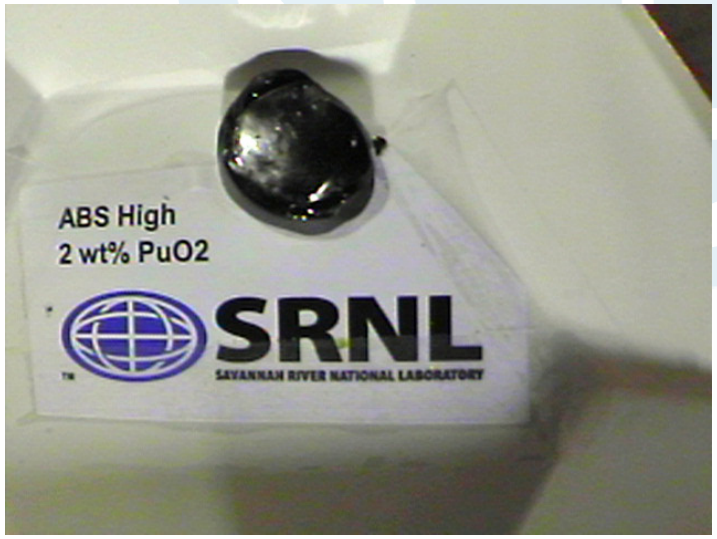
- Hf surrogate glasses analyzed using SEM/EDS
  - Semi-quantitative using EDS internal standards
  - Area scans and line scans
- HfO_2 to represent 1 wt % Pu in the glass
  - 0.76 wt % target in glass
  - 0.86 wt % based on major elements in glass (i.e. elements analyzed by EDS)

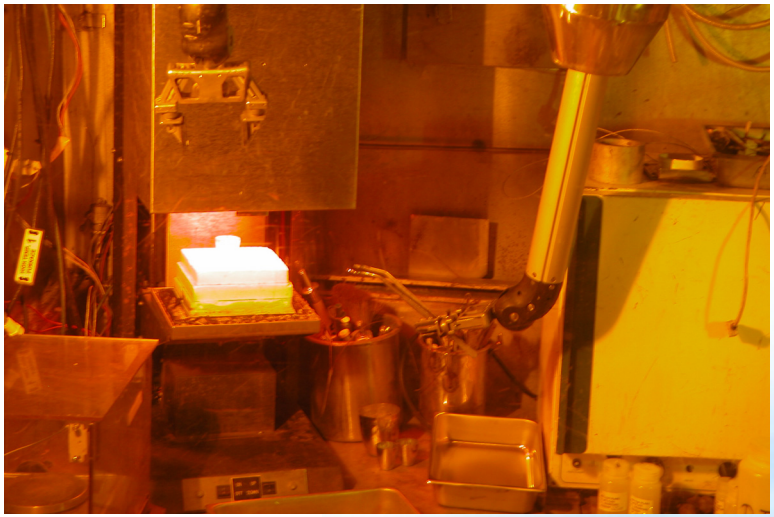




Pu Behavior in HLW Glass - Pu Studies (1/6)

- **Pu glasses prepared**
  - **Actual SB6 DWPF qualification SME feed**
  - **Surrogate SB6 SME feed**
  - **1 wt % Pu in the glass**
    - "Well-mixed" sample using Wig-L-Bug® grinding mill
    - "Poorly-mixed" (hand-mixed) sample
- **Glass characterization**
  - **Chemical composition**
    - On actual SB6 SME glass with Pu
  - **Crystallinity – XRD**
    - On both actual SB6 SME glass and surrogate SB6 SME glass
  - **Durability – PCT-A**
    - On actual SB6 SME glass with Pu
  - **Pu distribution - SEM/EDS using Pu internal standard**
    - On sectioned crucible melts of surrogate SB6 SME glass with Pu
    - SEM analysis on glass shards of actual SB6 SME glass





Pu Behavior in HLW Glass - Pu Studies (2/6)

Actual SB6 w/ Pu

Actual SB6 Analyzed Glass Composition with 1 wt % Pu

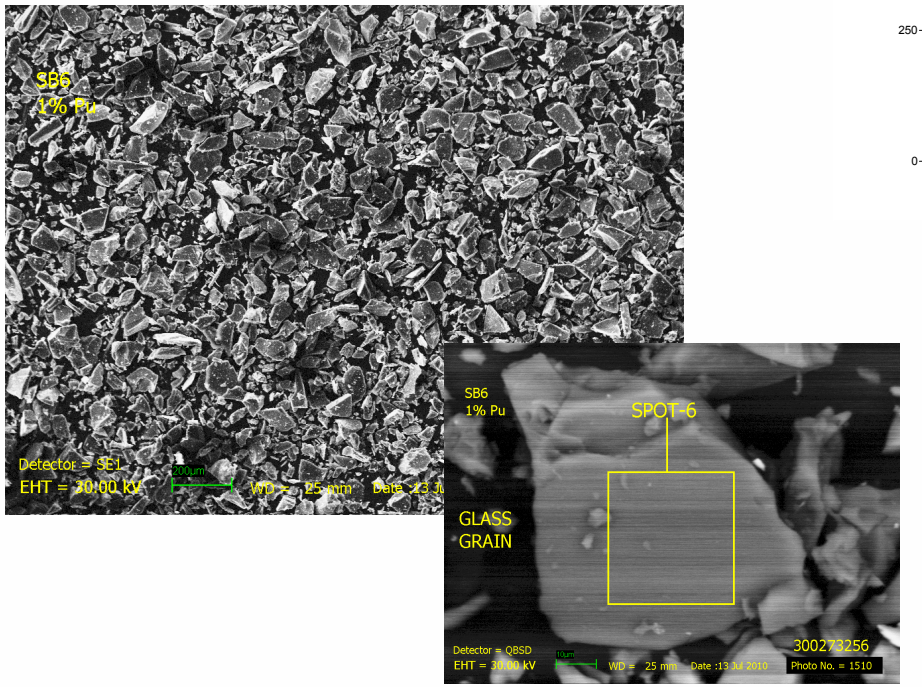
Oxide	Weight %		Oxide	Weight %
Al_2O_3	8.88		Na_2O	13.08
B_2O_3	5.15		Nd_2O_3	ND
BaO	0.05		NiO	1.02
CaO	0.38		P_2O_5	0.13
Ce_2O_3	0.02		PbO	ND
Cr_2O_3	0.35		SO_4^{2-}	0.30
CuO	0.12		SiO_2	51.13
Fe_2O_3	8.29		SrO	0.02
K_2O	0.04		ThO_2	1.40
La_2O_3	0.04		TiO_2	0.020
Li_2O	5.17		U_3O_8	1.23
MgO	0.18		ZnO	0.04
MnO	2.44		ZrO_2	0.14
MoO_3	0.01		**PuO_2**	**1.11**

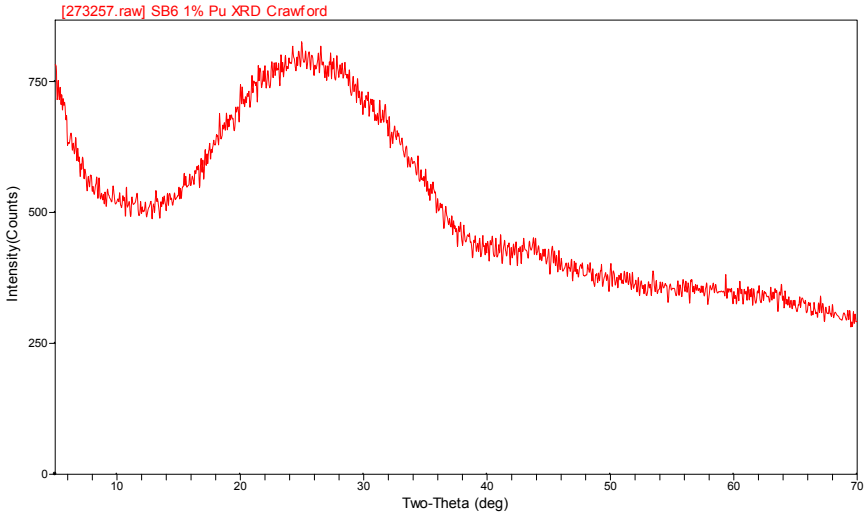
- **ICP-AES and ICP-MS results (for major cations) indicated glass composition close to targeted**
  - **Sum of oxides = 100.74**
  - **Pu elemental content = 0.98**

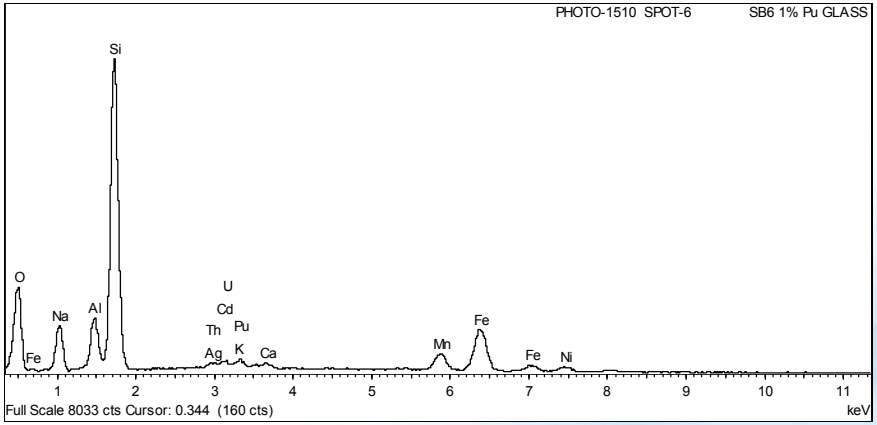
Pu Behavior in HLW Glass - Pu Studies (3/6)

Actual SB6 w/ Pu

- **XRD and SEM completed on actual SB6 SME glass with Pu (Wig-L-Bug® mixed)**
- **No evidence of crystallization or undissolved PuO_2**



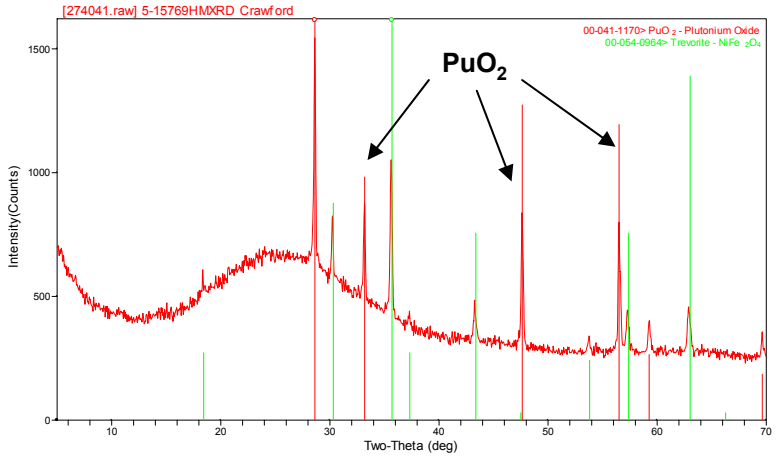


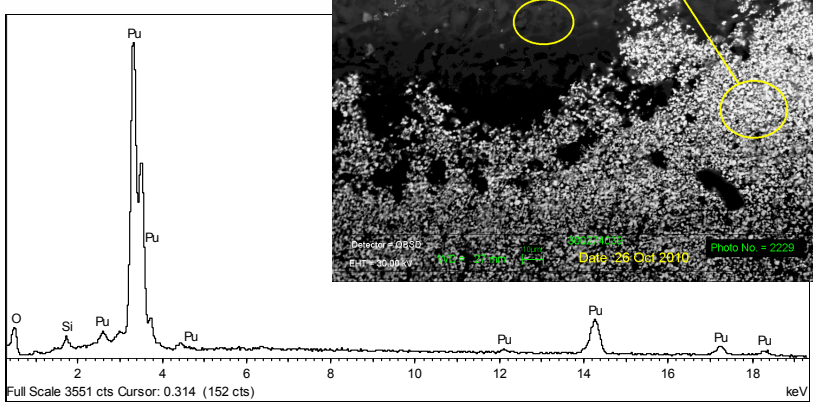


Pu Behavior in HLW Glass - Pu Studies (4/6)

Surrogate SB6 w/ Pu

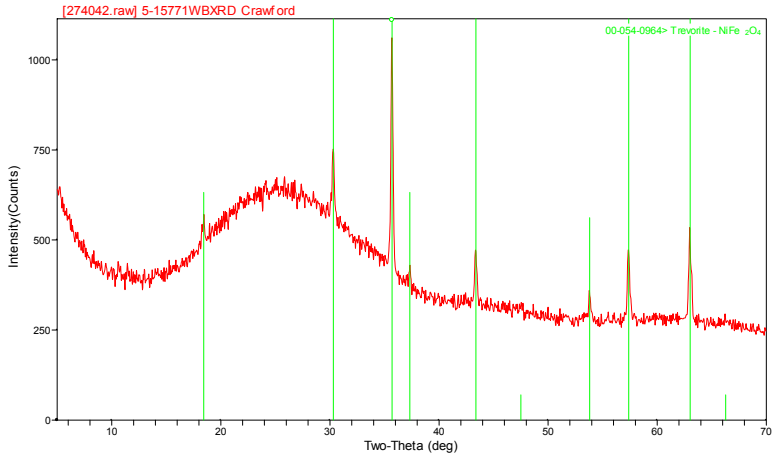
Hand Mixed Samples

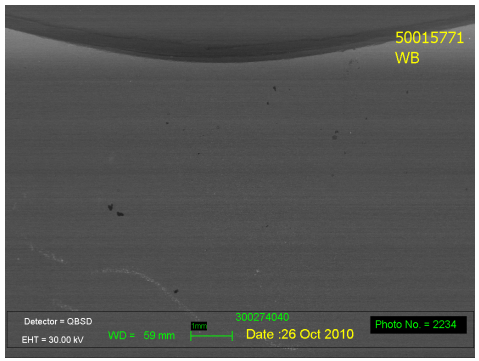


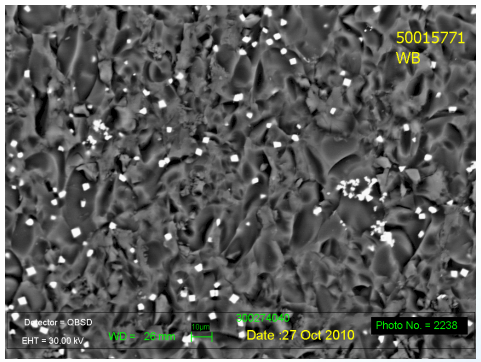


Evidence of undissolved PuO_2 in hand-mixed melt

Wig-L-Bug ® Mixed Samples



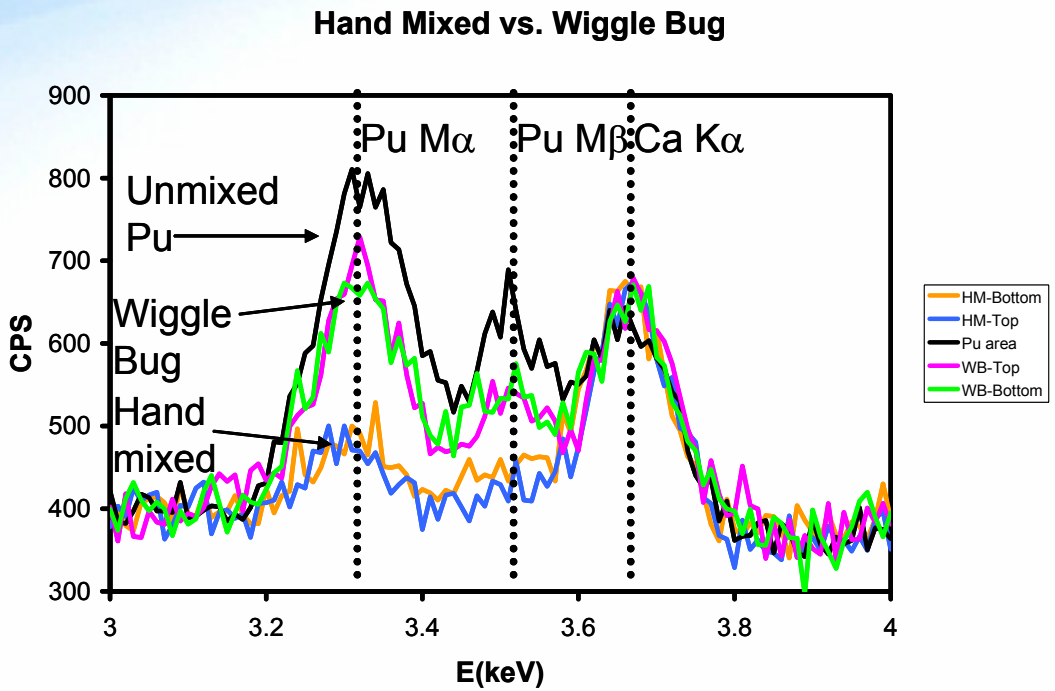


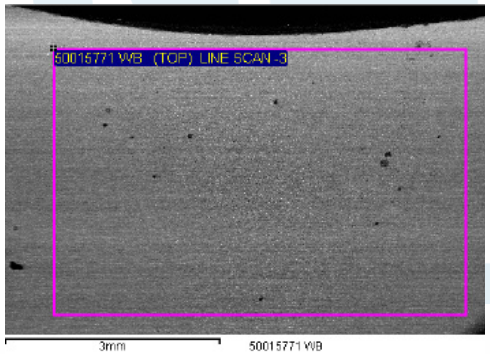


No evidence of undissolved PuO_2 in Wig-L-Bug® mixed sample – only trevorite (spinel) crystals observed

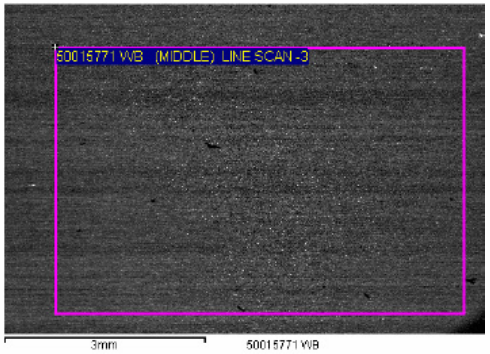
Pu Behavior in HLW Glass - Pu Studies (5/6)

Surrogate SB6 w/ Pu

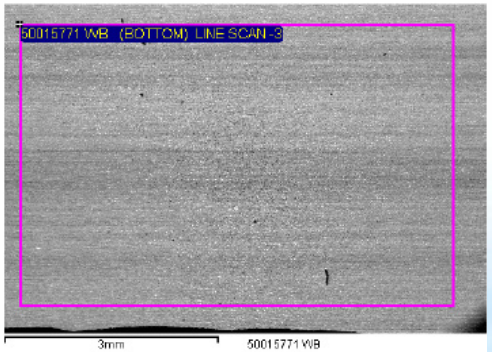




Top



Middle



Bottom

- Analyses of EDS Pu Mα line (Pu Mβ line overlaps with Ca Kα line)
- Wig-L-Bug® sample Pu Mα lines consistent at top and bottom → consistent Pu concentrations
- Hand-mixed Mα lines of similar intenstity BUT lower relative to Wig-L-Bug ® lines due to undissolved PuO_2

Pu Behavior in HLW Glass - Pu Studies (6/6)

Actual SB6 w/ Pu

- **ASTM C-1285 Product Consistency Test - Method A (PCT-A)**
  - **Samples are ground to a defined particle size range (-100,+ 200 mesh)**
    - Solids are washed in ethanol to remove fines
  - **Small mass of ground sample placed in measured volume of water**
    - Controlled surface to volume ratio (e.g. 1.5 g glass to 15 ml water to provide S/V = 2000 m^{-1}
  - **Sealed vessels (triplicate samples) held at 90 °C for 7 days**
  - **Leachate is filtered and analyzed**
  - **Normalized release values based on measured compositions**

Glass ID	NL (B) g/L	NL (Na) g/L	NL (Li) g/L	NL (Si) g/L	NL (Pu) g/L
ARM	0.47	0.49	0.58	0.27	--
EA	17.45	13.33	9.89	4.05	--
SB6 Qual	0.63	0.90	0.81	0.46	--
SB6 Qual w/ 1 wt % Pu	0.58	0.70	0.68	0.42	0.04

Pu Behavior in DWPF Melter

- **DWPF SB4 and SB5 pour stream samples recently analyzed in SRNL**
  - **SB4 and SB5 had the highest concentrations of Pu processed in DWPF to date**
  - **But, still about two orders of magnitude lower than in current Pu glass studies!!**
- **Comparison of Pu concentrations in pour stream samples to Pu concentration in melter feed can provide some insight into fate of Pu in melter**
  - **SB4: $Pu_{Melter\ feed}$ = 0.0078 wt %; $Pu_{Pour\ Stream}$ = 0.0086 wt %**
  - **SB5: $Pu_{Melter\ feed}$ = 0.015 wt %; $Pu_{Pour\ Stream}$ = 0.013 wt %**

Pu appears to be incorporated into glass and discharged from melter at these levels

Summary

- Glass waste forms have been studied for disposition of excess weapons-useable plutonium
  - LaBS glasses – high concentrations of Pu in waste form
  - Alkali borosilicate glasses – lower concentrations using existing high level waste vitrification technology
- HfO_2 determined to be most suitable PuO_2 surrogate for borosilicate glass studies
- Current emphasis is on alkali borosilicate option
  - Studies conducted to evaluate
    - Pu solubility in the glass – crystalline phase formation, distribution within glass
    - Impact of Pu addition on glass properties – viscosity and durability
    - Behavior of Pu in the glass melter
- Results to date indicate no impact for up to 1 wt % Pu in the alkali borosilicate glass
- Parallel testing underway to evaluate Pu waste/melter feed processing

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