Glass High Level Waste Forms:

Current Experience and Future challenges on physical and chemical properties of Nuclear Glass

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Plan

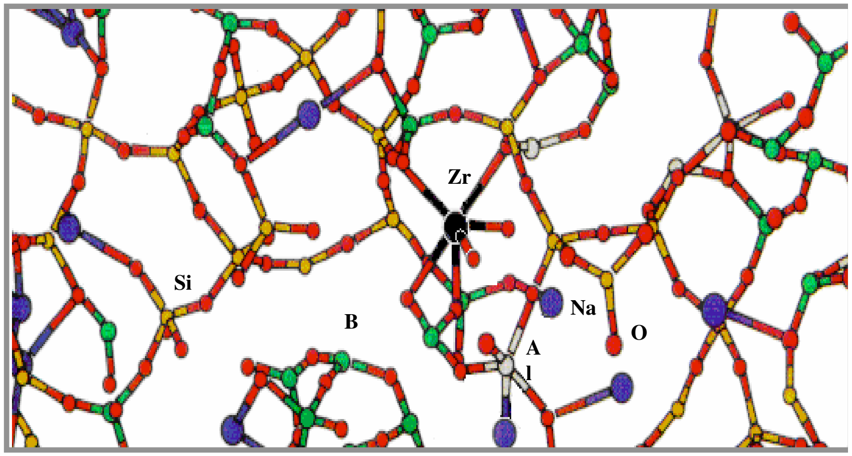
1. HLW Vitrification in Borosilicate :
   - ⇨ The current industrial experience
   - ⇨ Some key physical and chemical properties of the glass waste form

2. The Glass melting phenomenology

3. On-going R&D on New Glasses

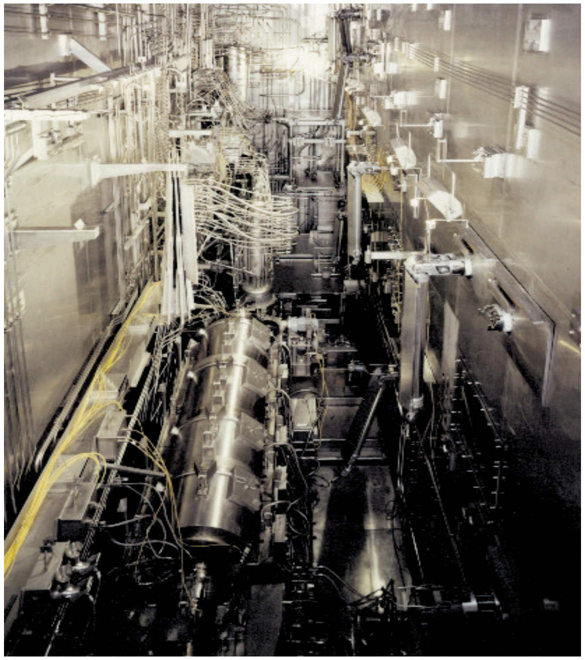
Glass Waste Form : Finding a compromise between …

- Material properties :
  - FP solubility (~30 elements !)
  - Long term Behavior :
    - Chemical stability
    - Physical stability
    - Thermal stability

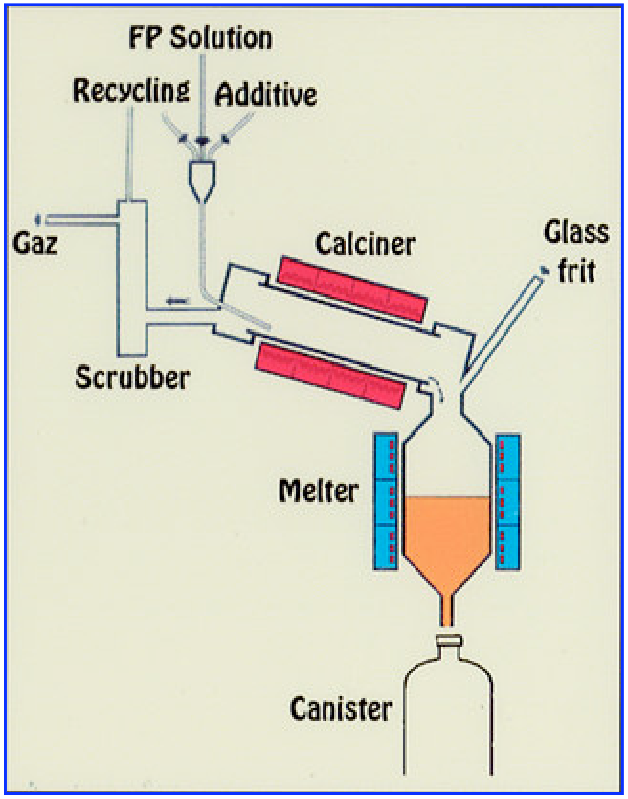


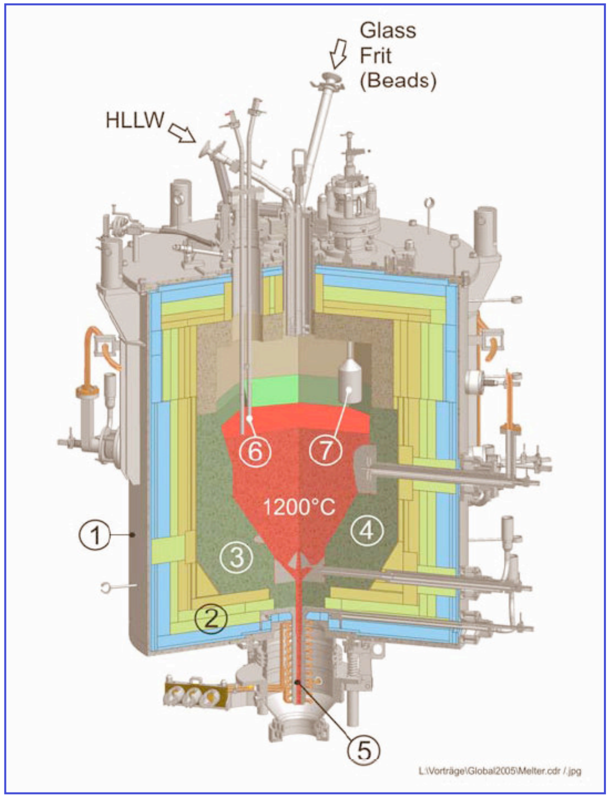
- Volume reduction

- Technological feasibility in a shielded cell
  - Melting temp.→ homogeneous melt
  - Pouring feasibility (viscosity)
  - Few secondary technological wastes (volatility, …)



The current Vitrification Technologies …





<u>France, UK</u>

(Metallic Hot melter heated by induction- 1100°C)

<u>Russia, Belgium, Japan, Germany, USA</u>

(Ceramic melter, heated by electrodes)

Some Industrial Data…

Facilities	Period	Production		
		Number of Canisters	Glass mass (tons)	Activity (TBq)
AVM R7 T7	1978- 2003	12,340	4902	1.7×10^8
WVDP (USA) DWPF	1996-2002	285 1,337	485 2,440	9×10^5
MAYAK (R)	1987-1997	5,126	2,362	1.5×10^5
PAMELA (B)	1985-1991	2,201	490	4.5×10^5
WVP (GB)	1990-1999	1,300	520	

R7T7 Industrial Glass

Oxides (Major)	Nominal compo.	Range of comp.	Properties	Nominal Comp.	Domain of compos.
SiO_2	45,1	42,4 - 51,7			
B_2O_3	13,9	12,4 - 16,5	Viscosity	110 dPa.s (1100°C)	87 – 310 dPa.s (1100°C)
Al_2O_3	4,9	3,6 - 6,6			
Na_2O	10,1	8,1 - 11,0			
CaO	4,0	-	T_g	502°C	500 - 533°C
Other…	…	…			
FP Ox.+ZrO_2+fines + Minor actinide ox.	12,9 + 0,37	7,2 – 18,5	$r_{0\ (100°C)}$ ($g.m^{-2}.d^{-1}$)	2	1,6 – 4,1
			$r_{f\ (90°C)}$ ($g.m^{-2}.d^{-1}$)	< 10^{-4}	10^{-4}-10^{-3}
			Thermal stability	<2% vol. $CaMoO_4$, CeO_2, spinelles	Identical to the nom. Comp.

The Melting Phenomenology (glass frit+calcine)

Glass Frit → Calcine

↓

Impregnation of the Calcine

↓

Partial dissolution

↓

Local saturation

↓

Crystal precipitation

↓

Agitation

↓

Dilution

↓

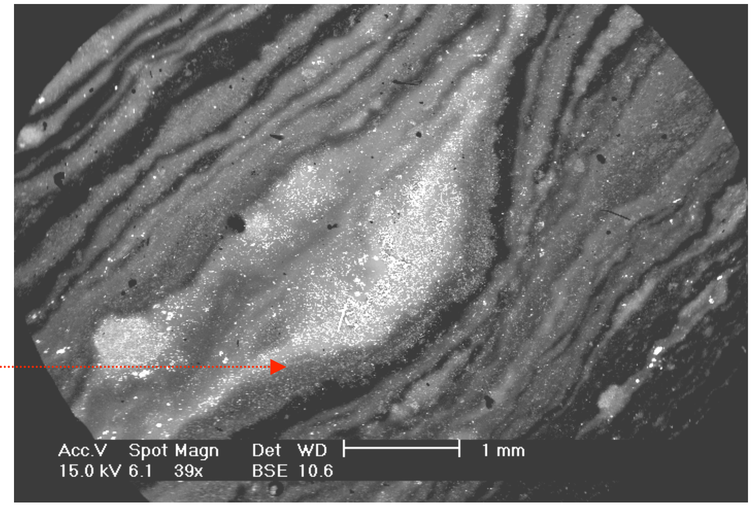
Crystal dissolution

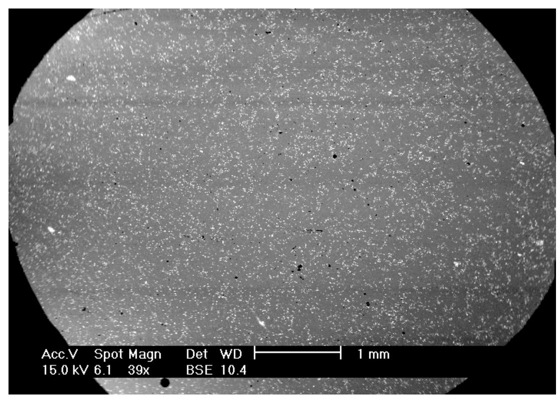
↓

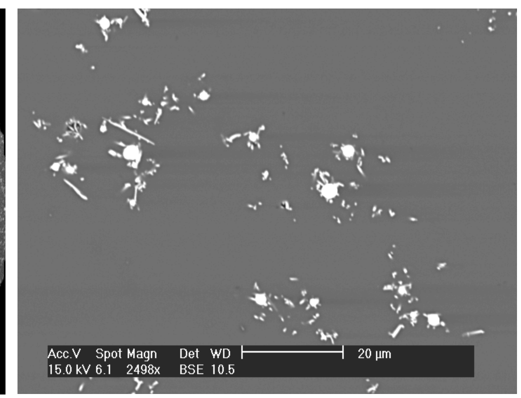
Homogenization of the molten liquid

↓

GLASS







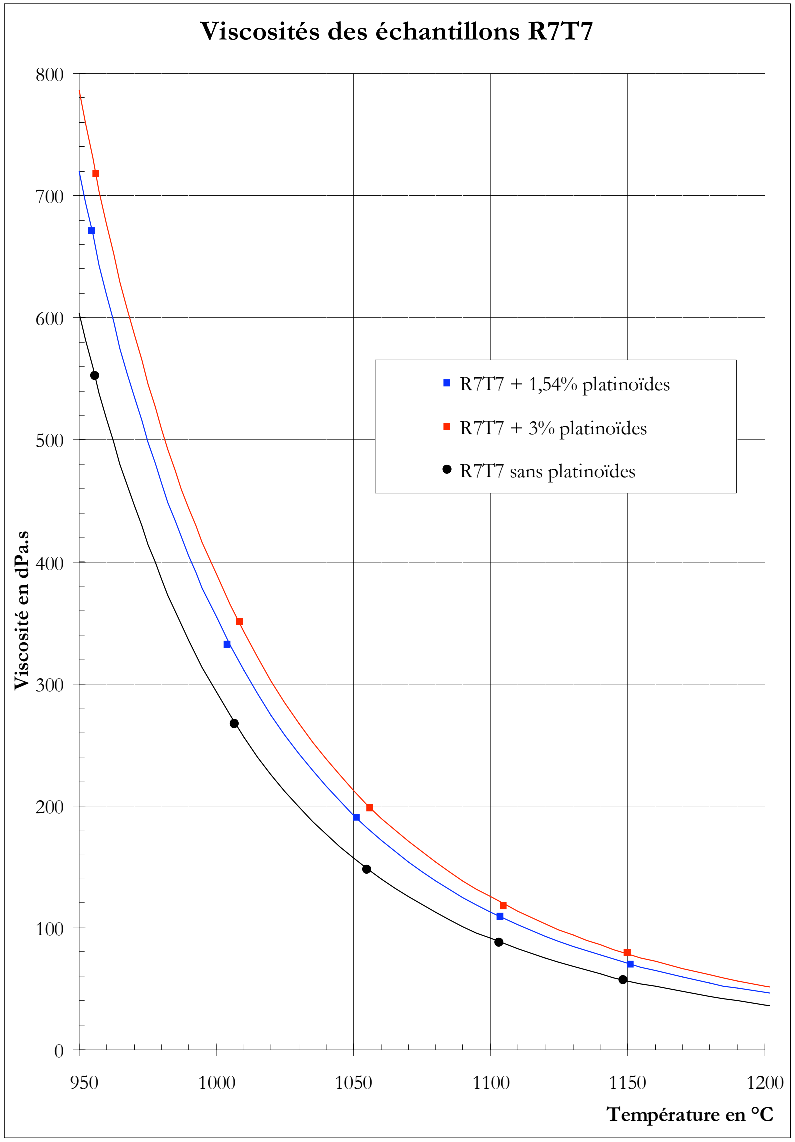
HT melting = RN solubilisation in a ionic and covalent network by chemical reactions at the molten state

The key role of the « Insoluble »noble metals

RuO_2, Pd, Rh have strong impacts on the properties of the melt :

- Chemical Reactivity,
- *Viscosity*,
- Electrical conductivity (for LFCM and CCM)
- Crystallization (nucleation)

Viscosity of the melt



→ Non Newtonian behavior (Pseudo-plastic)

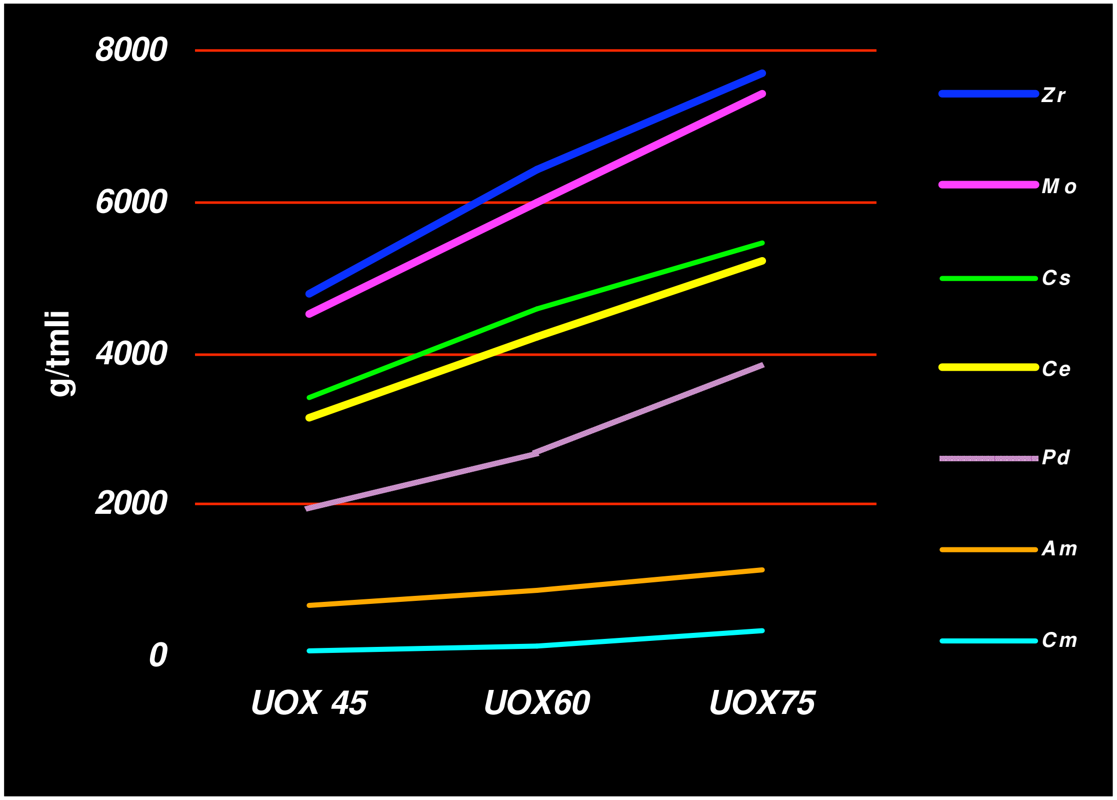
On-going R&D : futur challenges

- Current "R7T7" BS-glass
  - Loading charge limited to ≤ 18,5 wt.% FP Ox.
  - $T_m \leq$ 1100°C (metallic hot melter)

- New UOx fuels to get higher Burn-up
  - → FP ↑ ($/t_{ihm}$)
  - → Increasing the Loading charge in the Glass
    - » Feasibility up to 25 wt.% FP Ox.?
    - » Specific heat ↑ (3 kW/glass canister ?)

Fuel		Current UOX	Future UOX
^{235}U enrichm.		3,5 %	4,9 %
Burn-up		33 GWd/t	60 GWd/t
Lifetime in reactor		3 y.	~ 5 y.
Spent fuel composition (kg)	U	955	924
	Pu	10	13
	Fission Products	34	61
	Minor Actinides	0.6	1.8

FP evolution with the fuel burn-up (normalised per ton of initial heavy metal)



Three major consequences (at least !) to check :

- Compatibility of the FP with a glass network
- Thermal stability of the Glass
- Alpha radiation stability of the Glass

The options for the Glass Waste Forms…

Extension of the current R7T7 glass domain

1. More refractory glass waste form, but :
   - $Tg \sim Tg_{(R7T7)}$

New Glass families

2. REE-borosilicate glass (LaBS)
   - $Tg = Tg_{(R7T7)} + 50°C$

3. Alumino-silicate glasses/Glass-Ceramics :
   - $Tg \geq 700°C$

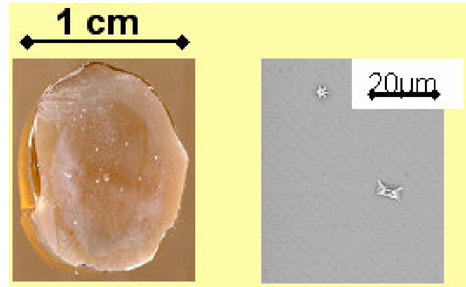
$T_m \geq 1200°C$

How to proceed ?

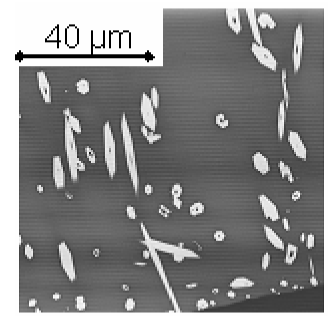
- New Glass additives (↑REE, ↓ B, …)
- New technological Vitrification Process

REE-Borosilicate Glass

SiO_2	51
Na_2O	12
B_2O_3	9
CaO	5
Al_2O_3	4
Nd_2O_3	8
La_2O_3	4
CeO_2	3
Pr_2O_3	2
ZrO_2	3



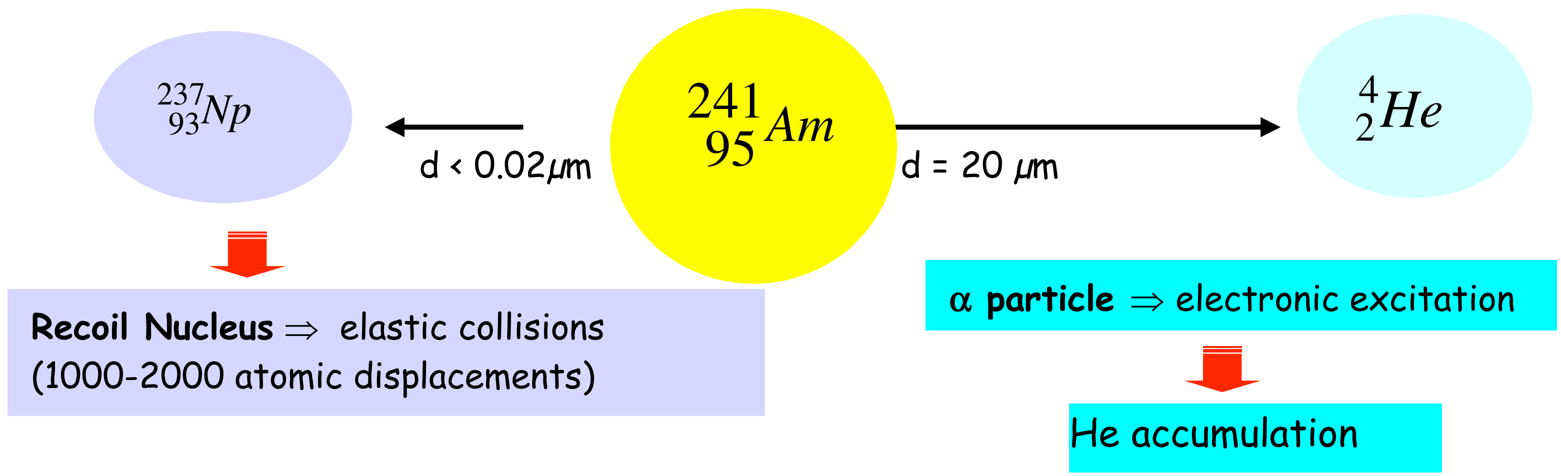
$Ca_2REE_8(SiO_4)_6O_2$



REE (17 ox. wt%) :

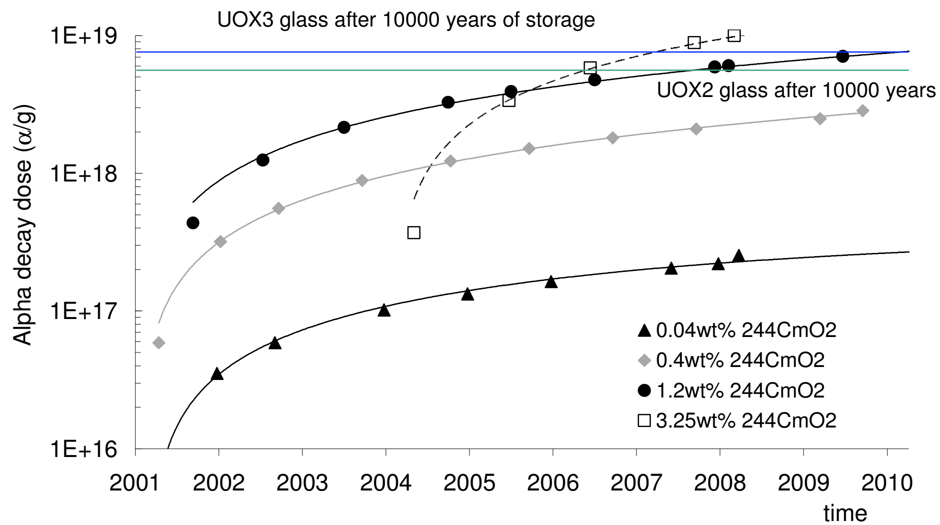
- crystallization of Si-apatite is limited
- T_g = 660°C
- $r_{0(100°C)} = 0.5\ g.m^{-2}.d^{-1}$
- → The glass network is depolymerized, but :
  - ❑ the solubility of REE-ox in water is very low !
  - ❑ REE-O-Si , REE-O-Na/Ca

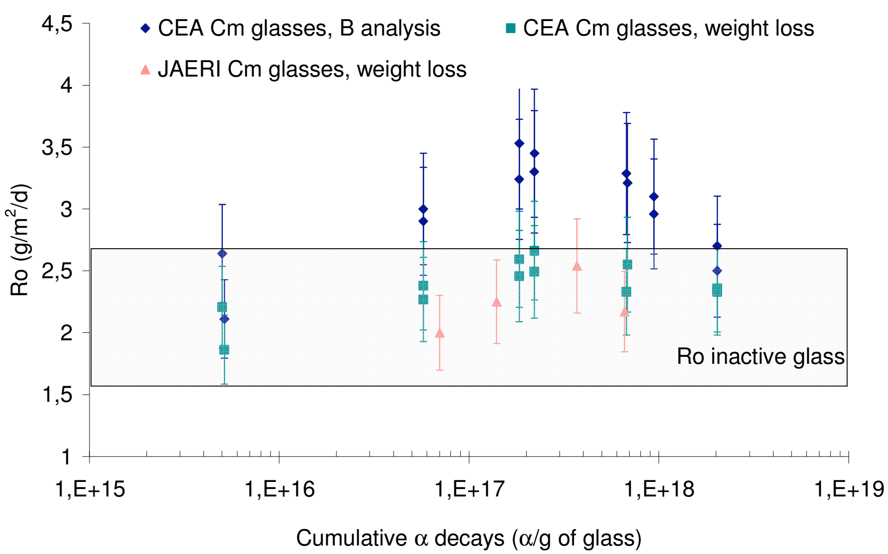
α Radiation Stability of the Glass



Current R&D to quantify the α radiation stability of Borosilicate Glass

- ^{244}Cm-doped Glass samples
- Heavy-ion bombarded glass samples





Conclusions

- Compromise :
  - Technological feasibility
  - Glass formulation (Homogeneity→ Long Term Behavior)
  - Range of composition for the waste form (flexibility)

- Industrial needs for Future Developments
  - Increasing the FP loading charge in REE-BS glass :
    - Thermal stability
    - Alpha radiation stability above 10^{19} α/g
  - Increasing the melting temperature