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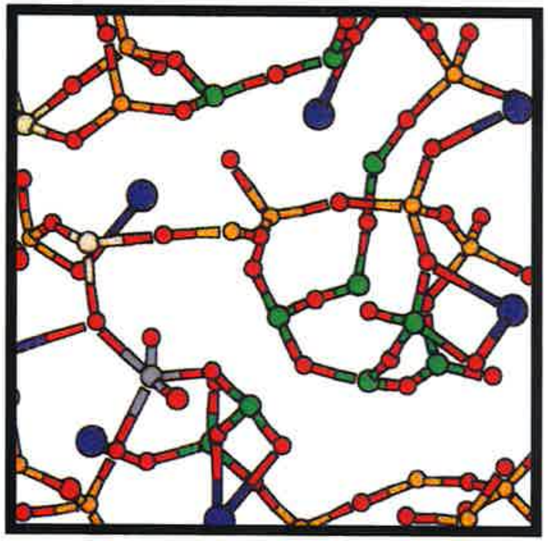
New Challenges for Vitrification

From Fission Products Nuclear Glass to new Glasses



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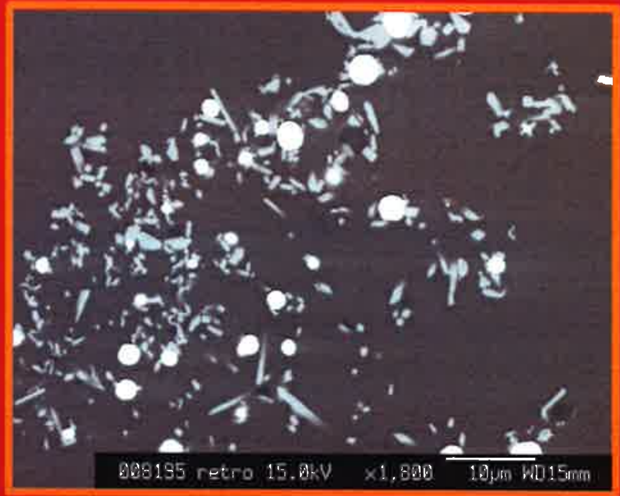
JOINT ICTP – AIEA WORKSHOP 6-10.11.2017 – TRIESTE

PART ONE

VITRIFICATION FOR FISSION PRODUCT SOLUTIONS



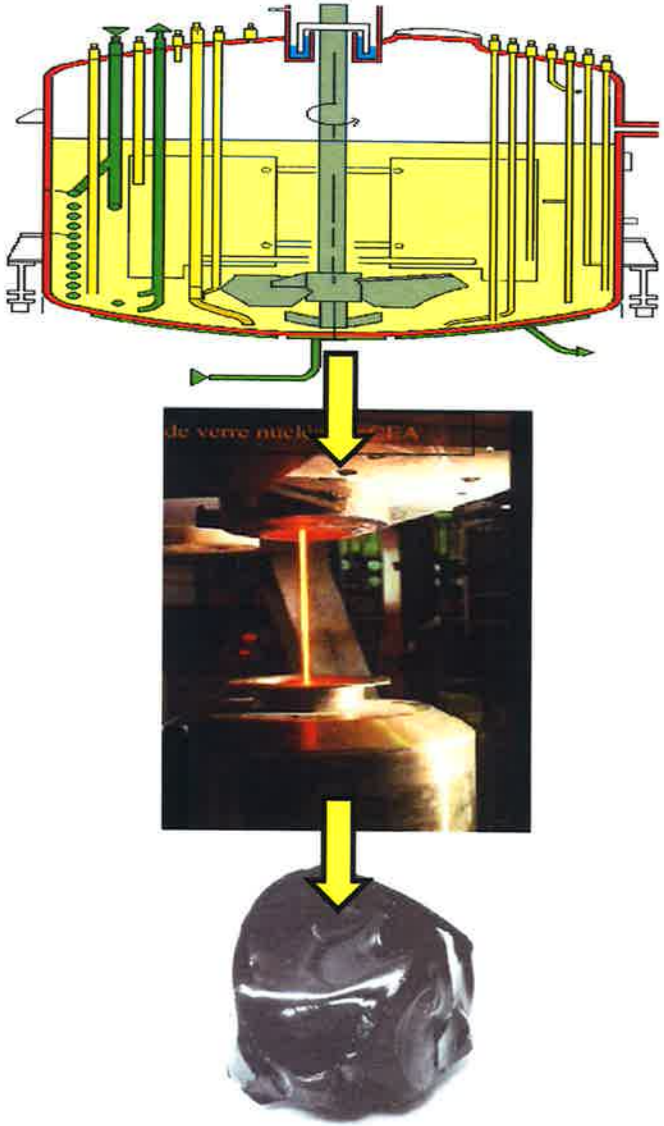
Vitrification of FP solutions

- Fission Products solutions coming from spent fuel reprocessing (PF) were produced by PUREX process

- It was not possible to store them in the liquid state for a long time : acidic stream, needed to be cooled and agitated → Solidification required

- First ideas were to transform the FP solutions into a synthetic rock, such as naturally occuring silicates minerals

- At the end of the 50', vitrification has been developed



FP solutions compositions

Fission Products

Se	Rb	Sb	Sr
Te	Y	Cs	Zr
Ba	Nb	La	Mo
Ce	Tc	Pr	Ru
Rh	Pd	Nd	Pm
Sm	Eu	Gd	Ag
Cd	In	Sn	Tb
	Dy		

Metallic species

Ru	Mo	Sb	Rh	Tc
	Pd	Sn		

Actinides

U	Np	Am	Pu	Cm

Corrosion and addition species

Fe	Cr	Ni	P	Na

- Chemically complex (more than 30 chemicals)
- Precisely defined and nearly constant for given spent fuels (slowly evolving with incresed burn-ups)

Designing a glass formulation for FPs

Specification = to produce durable homogeneous glass

→ Material : performance demonstration

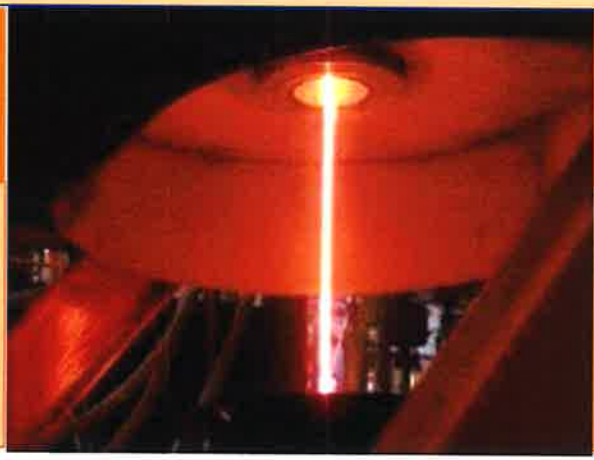
→ Process : large quantities to be produced, half-continuous process, including pouring of the melt into containers

Chemical compatibility with the waste

Solubility (Cr, Ru, Rh, Pd, Ce, Pu, SO_4, Cl)
No phase separation (Mo, SO_4, Cl, P)
No devitrification (Mo, P, F, Mg, …)
Maximize the waste loading

Process / Technology

Melting temperature
Viscosity, reactivity, residence time,
Electrical cond.



Glass performance storage/disposal

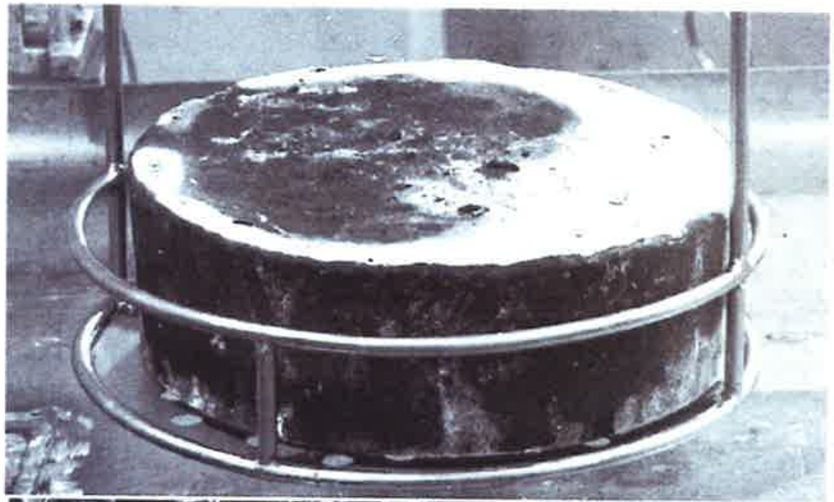
Thermal stability
Chemical durability
Resistance to self–irradiation

The first steps : Gulliver and Piver

Gulliver (1964 – 1967)

First French Vitrification pilot : heating of a gel, produced by FP impregnation of a clay material, in a refractory pot

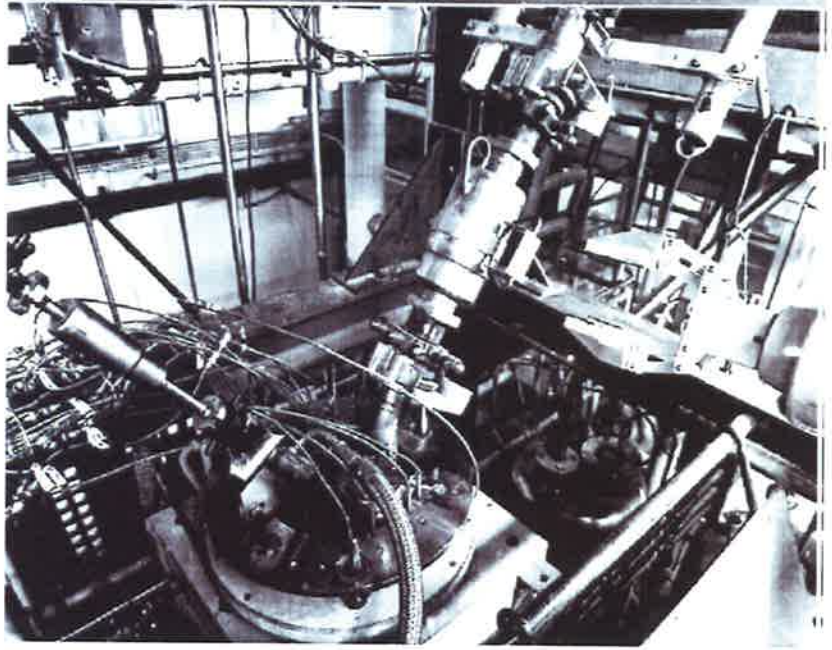
→ 170 kg of nuclear glass (10 kg per block)



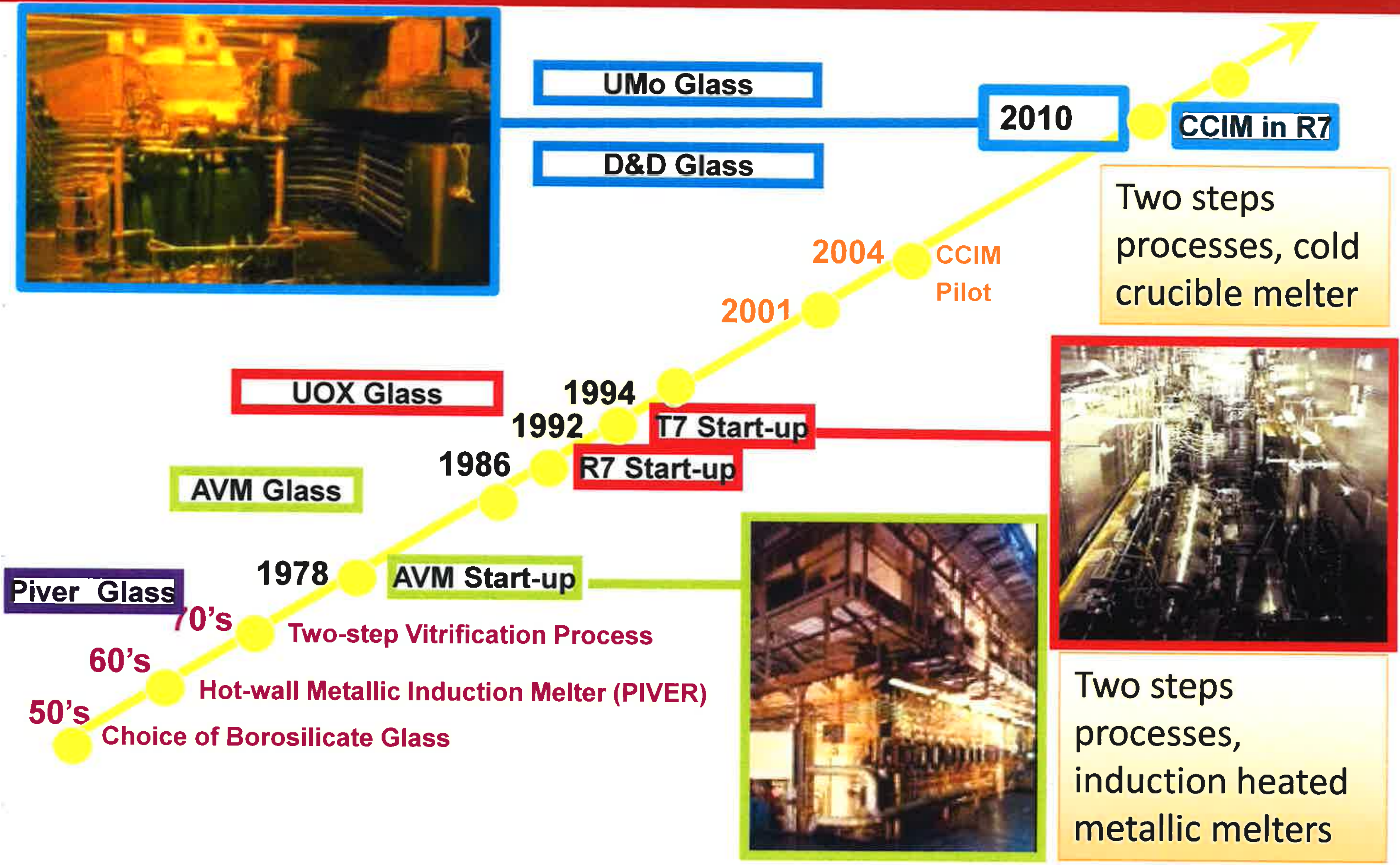
Piver (1969 – 1980)

Semi-industrial process : glass is melted by batch, in a metallic melter, heated by induction, and then poured

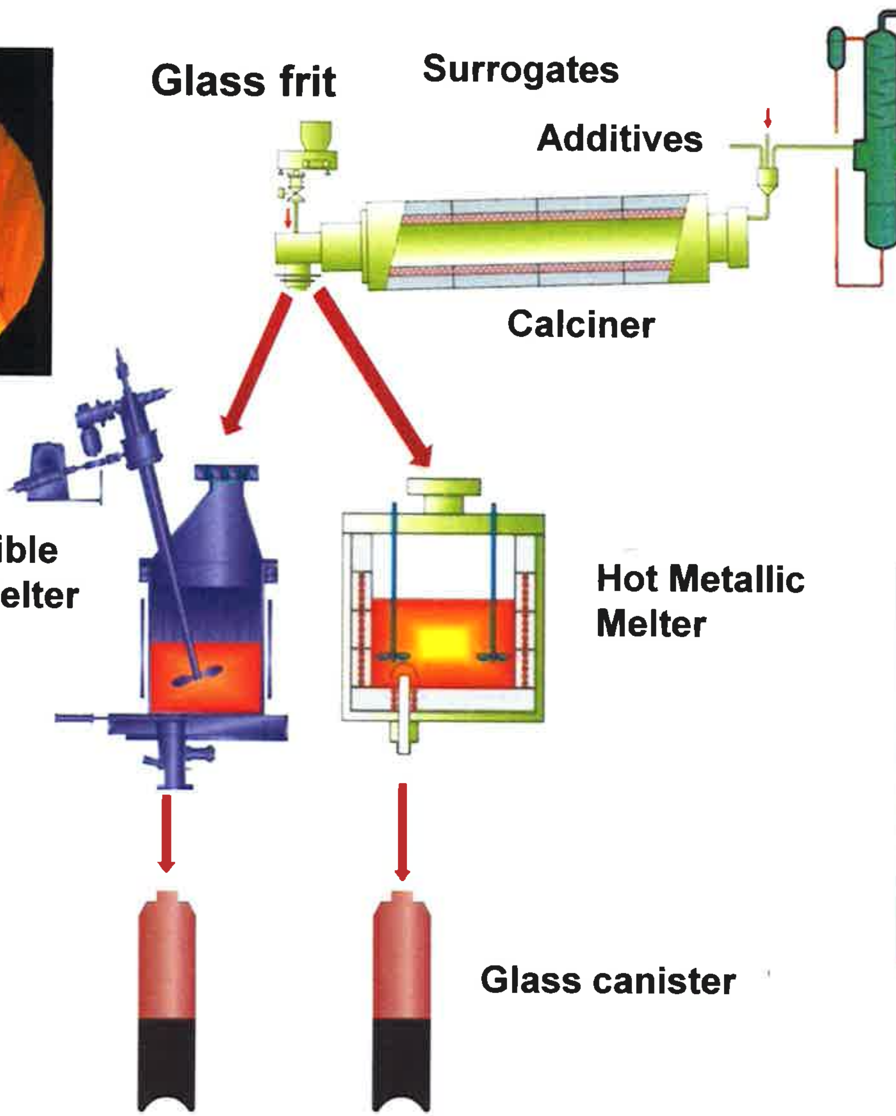
→ 13 tons of nuclear glass (25 m^3 of HLW FP solution)

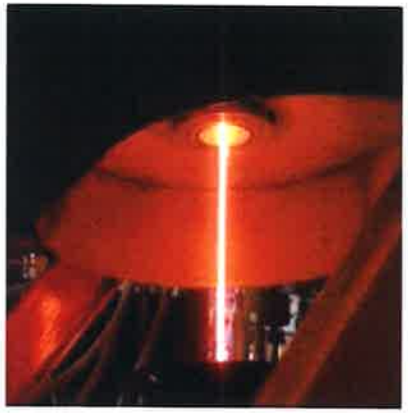


cea den Development of the nuclear glass industry



Calcination – Vitrification continuous two-steps process





From glasses... to glass-ceramics

History of glass specifications implemented at industrial scale

- 1969 — PIVER Glass
- 1986 — UOX Glass, AQ016 Specification
- 1994 — AVM Glass, AQ047 Specification
- 2007 — New UOX Glass, AQ060 Specification; MAD Glass, AQ061 Specification
- 2011 — UMO Glass, AQ059 Specification

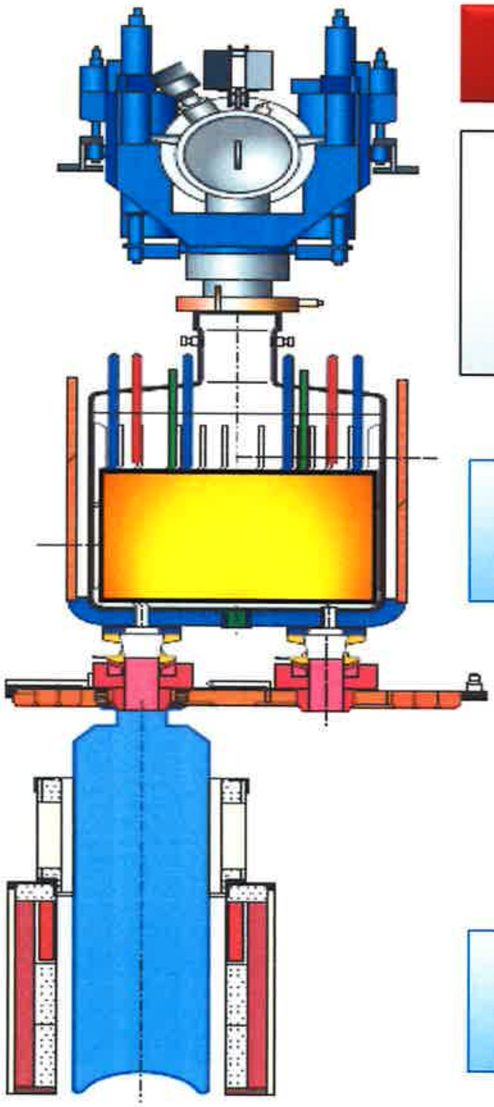
Homogeneous Borosilicate Glasses | Glass-ceramic

Legacy waste : Molybdenum-rich fission product solutions (UNGG fuels)

→ Highly corrosive ILW glass, low solubilty of Mo into BSG

→ Designing a glass-ceramic melted material
   → Homogeneous melt (1250°C)
   → Crystallization with cooling
   → Loading factor up to 13 wt%

From induction heated metallic melter...

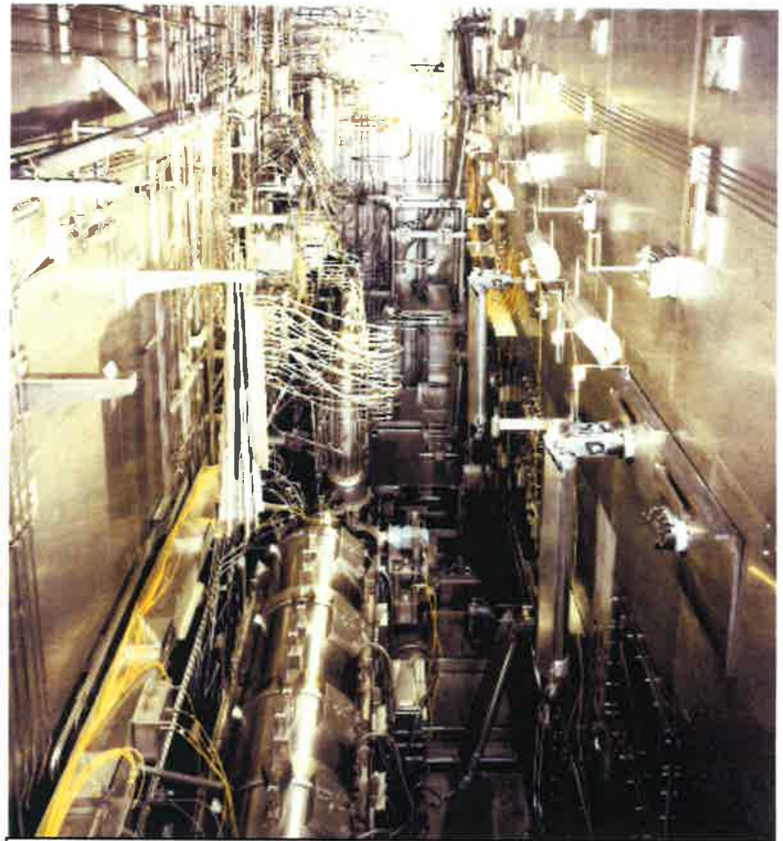


Since 1990

Thermal flux from metallic walls to molten glass

Hot Metallic Crucible
Bubblers, rotary stirrers

Pouring glass into stainless steel canister



5 vitrification lines in operation at AREVA La Hague Facility

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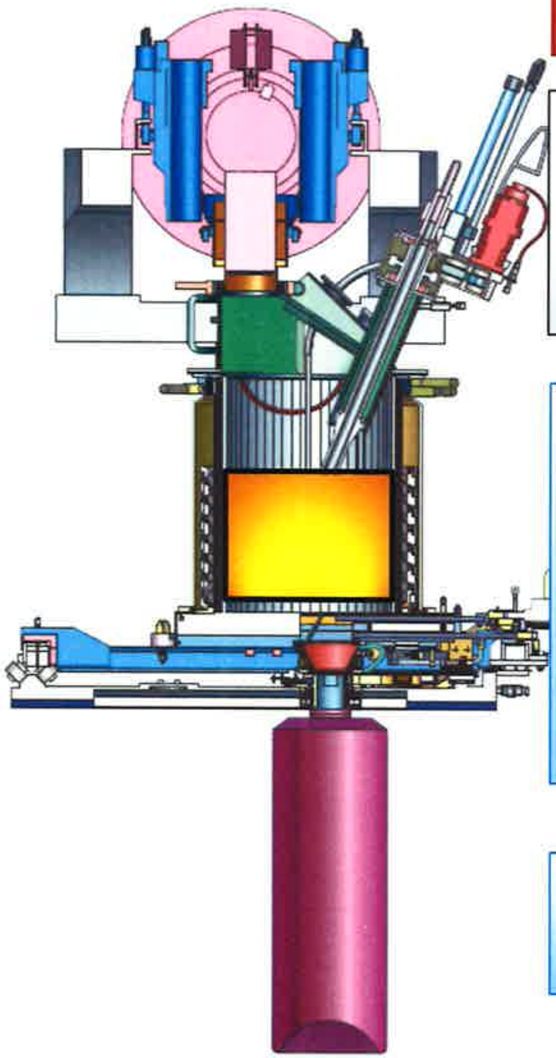
... to cold crucible technology

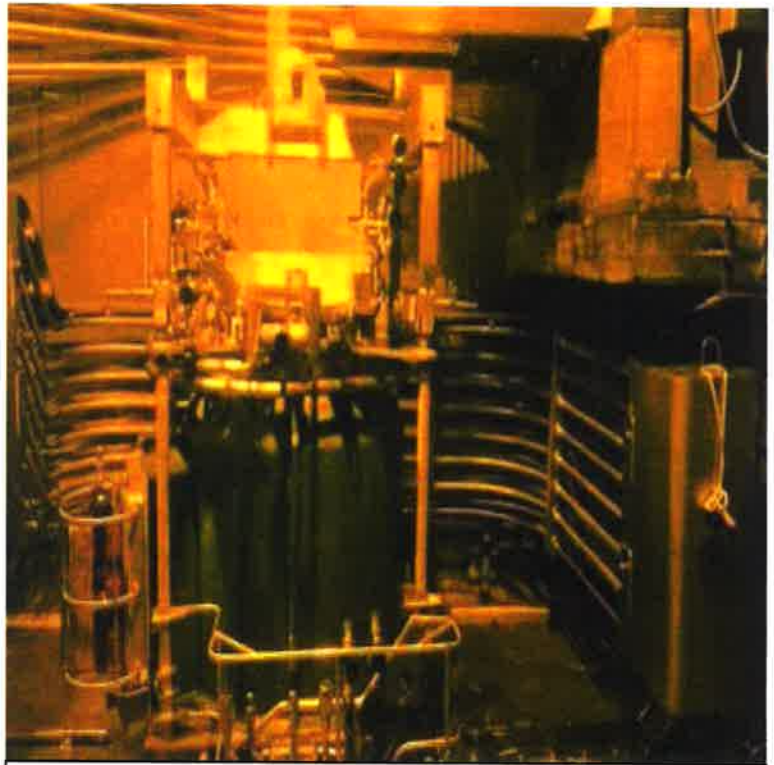


Since 2010

Thermal flux from the molten glass to the cooled crucible

Cold CrucibleWater cooled metallic structure (higher temperature, no corrosion on the melter)

Pouring into Glass canister



1 CCIM line in operation at AREVA La Hague Facility

PART TWO

NEW WASTE, NEW VITRIFICATION PROCESSES :

IN-CAN TECHNOLOGIES

Marcoule : industrial nuclear site under dismantling

New sources of HL – IL Waste

HLW coming from D&D operations

- Small quantities, sludges or solids
- Compositions are not as precisely defined as for FPS

→ **Immobilization of TRU and FP into a durable matrix**

ILW waste coming from MOX fuel production

- Alpha-bearing waste
- Organic matter + metals : gloves, power cables, metallic material or tools, dusters…

→ **Volume reduction**

→ **Organics destruction**

→ **Immobilization of TRU into a durable matrix**

High active deposits from fission products evaporators and tanks Marcoule reprocessing facility

MELOX glove box (http://www.irsn.fr)

DEM&MELT PROCESS : IN CAN MELTER

In can Melter for D&D HLW

Currently developed by CEA* for its own waste coming from D&D operations, including legacy waste management

Material and process specifications :

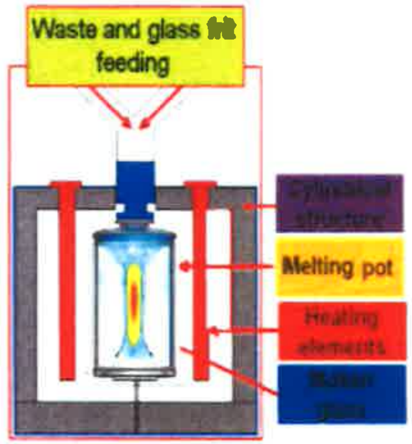
- Flexible and adjustable to waste with a composition poorly defined : mixed effluents such as zeolites, co-precipitation sludges, powders of fuel debris (FP and alpha components)
- Final waste package must be suitable with existing routes and/or on-site storage facilities
- Compact size of the process, compliant with existing hot cells under dismantling
- "Dismantling tool" that shall be itself dismantled after use (for re-use)
- Low quantities of secondary waste
- Minimum investment and operation cost

**PIA project, national financial support, in collaboration with ANDRA, AREVA and ECM technologies*

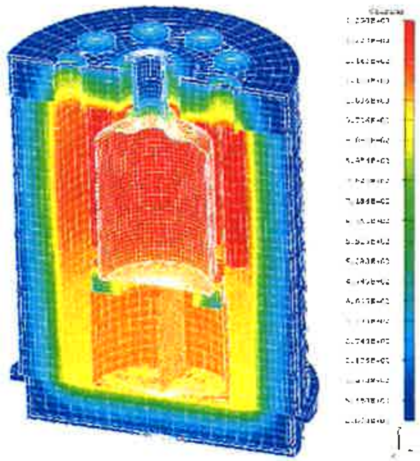
In Can Melter : Main Features

Process development criteria :

- ❑ One step IN CAN vitrification (no calciner)
- ❑ Container is used as a crucible renewed for each batch (no pouring)
- ❑ Resistance heating, thermal homogeneization (no stirrer)
- ❑ Design for liquid or solid feeding in a melting pot
- ❑ Operating temperature < 1100°C



Principle of process

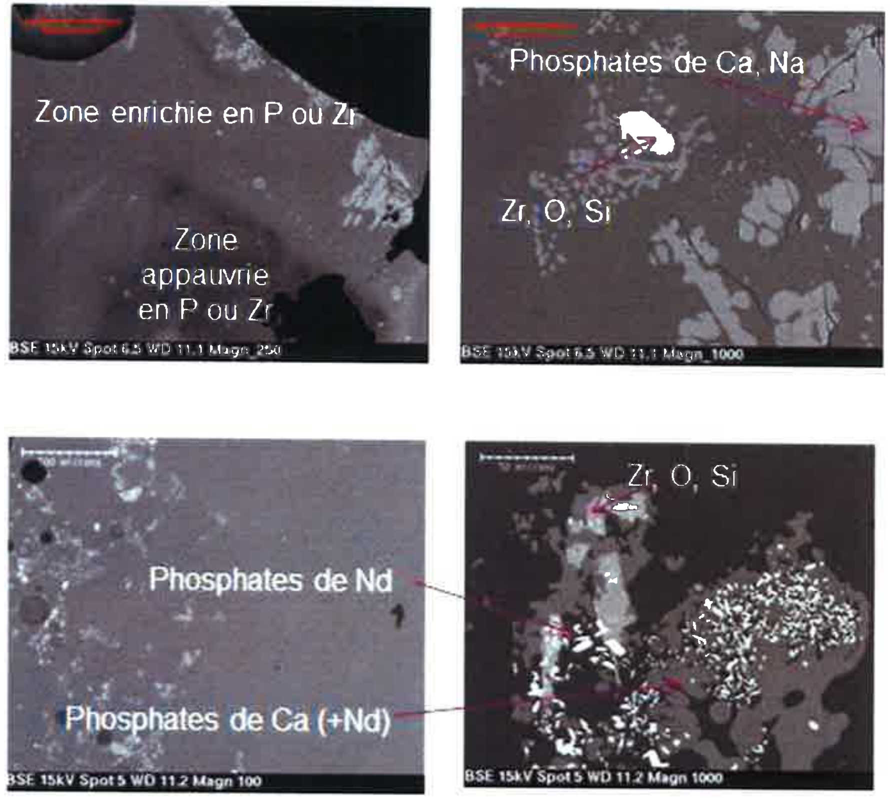


*PIA project, national financial support, in collaboration with ANDRA, AREVA and ECM technologies

In can Melter Glass

Formulation criteria :

- Minimization of FP volatilization (Cs)
- Adjustable to accomodate composition uncertainties and variabilities
- High content for P, Zr, Mo (a few wt%),
- Low viscosity melts to ensure homogeneization thanks to thermal convection



Microstructure of a simulated borosilicate glass enriched with P and Zr oxydes showing numerous crystallizations

Material Science Challenges

- To develop flexible glass formulations :
  - At relatively low elaboration temperature to avoid Cs volatilization
  - Suitable for P, Zr and Mo, elements that have a low solubility in borosilicate glasses
  - Compliant with variations of the feeding stream, characteristic of old deposits remaining in facilities that have been shut down, currently under dismantling
- To develop final package description :
  - Source terms are needed, since these packages are designed for deep disposal

LCV

Joint Vitrification Lab

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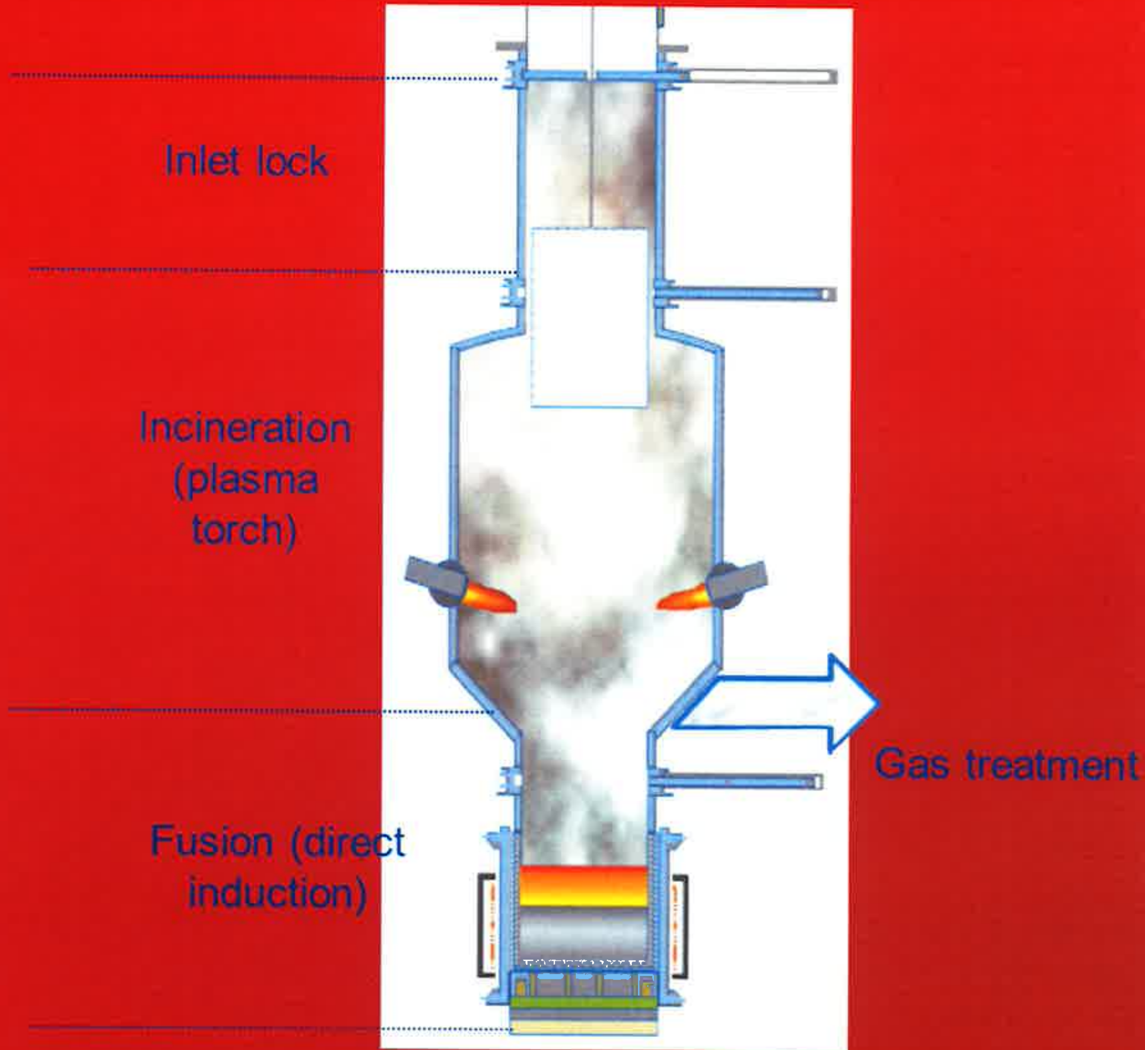
INCINERATION AND VITRIFICATION PROCESS : IN CAN MELTER



PIVIC Project is addressing the alpha emitters waste issue

- **Intermediate Level Waste contaminated with alpha emittters:**
  - Mainly arising from glove boxes used for MOX production (Melox facility)
  - Mixed waste made of 30% organic matter/70% metallic content
- **Original conditioning option (compaction) not suitable for disposal because of organic matter radiolysis and hydrolysis that may result in**
  - Hydrogen release → overpressure, explosion issues
  - Corrosive species release → waste package corrosion issues
  - Complexing species release → potential increse in RN mobility in deep disposal
- **Aternative conditioning option is under study, with the following requirements :**
  - Full destruction oforganic matter
  - RN conditioned in a mineral matrix

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http://www.dailymotion.com/video/x5mbkt1

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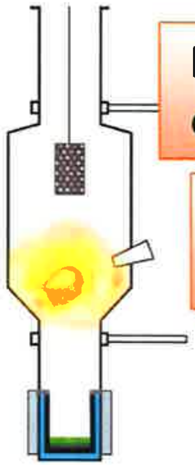
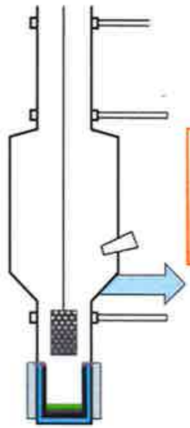


Introduction of the waste

Organic matter is burning in the plasma

2



Gaz is released into gaz treament

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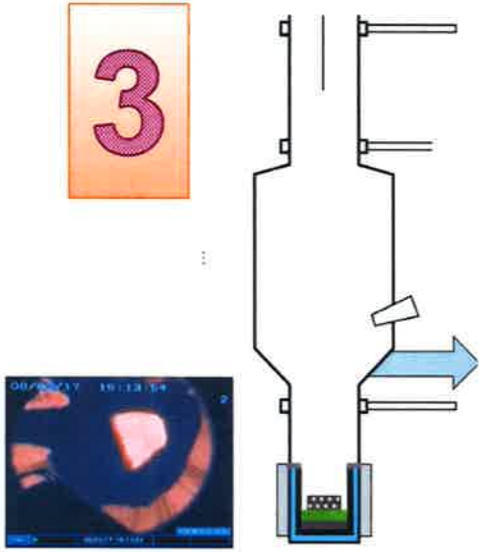
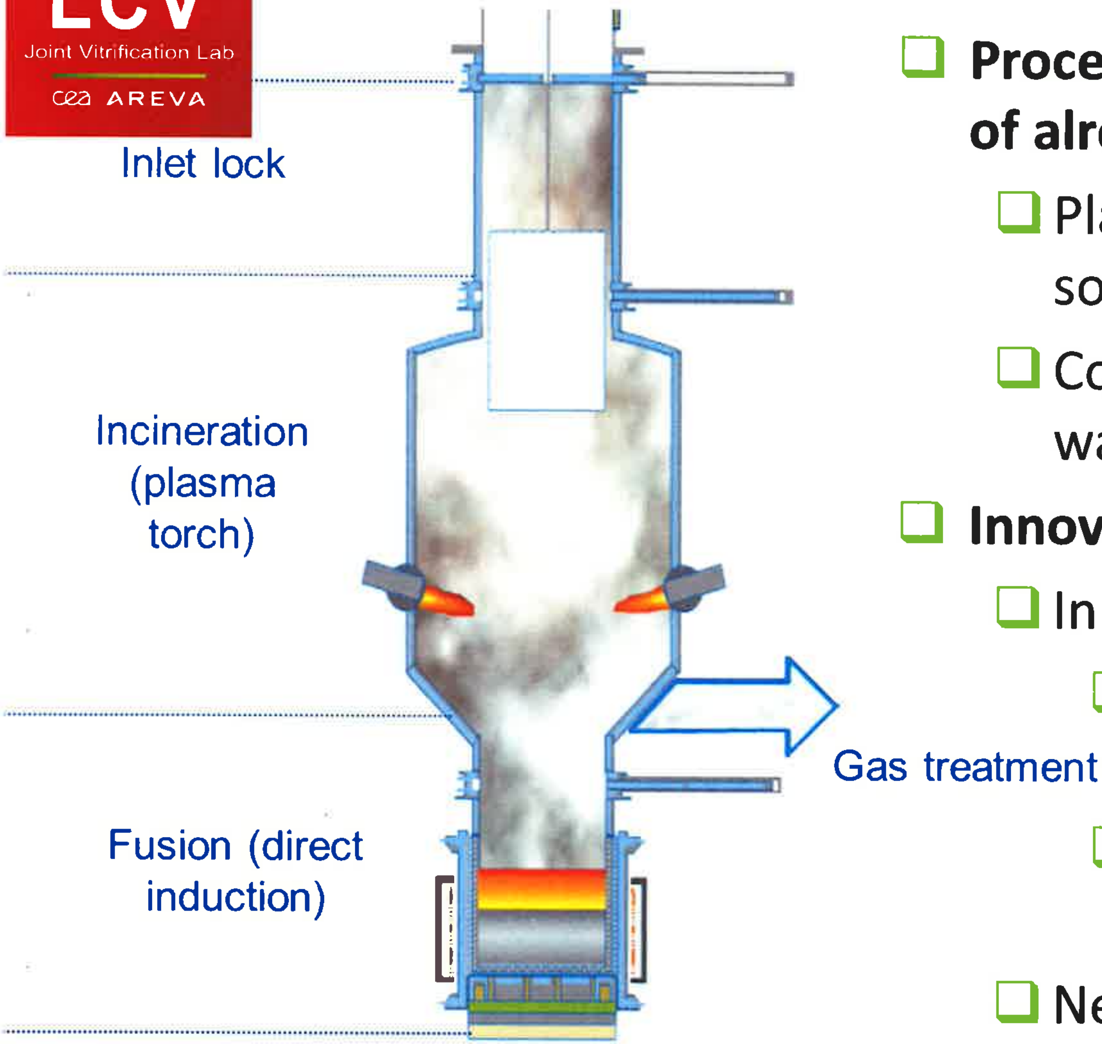


Metallic waste is heated thanks to induction

Glass fraction (green) is trapping actinides

Mixed matrices Glass / Metal

PROCESS DESCRIPTION

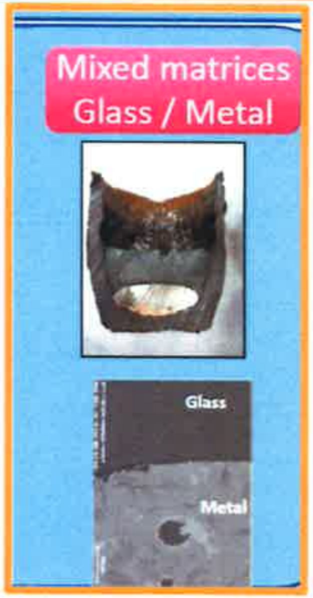


- **Process developed as a combination of already pre-existing technologies**
  - Plasma torchs for incineration of solids
  - Cold crucible technlogy for metal waste melting
- **Innovations**
  - In Can melting of a biphasic melt
    - Metallic fraction at the bottom of the can
    - Glass fraction at the top of the can
  - New kind of waste package

Material Science Challenges

- **Formulation of a new glass**
  - Suitable for actinide incorporation : RN shall be confined in the glassy phase, not in the metallic part

  → Partition coefficients are under study, depending of compositions
- **Description of a new ILW waste package**
  - Leaching behaviour of the vitreous phase
  - Corrosion mecanisms of the metallic part of the package
  - Combination of both parts in expected disposal conditions



TO CONCLUDE

From FP glasses to new glasses

- **Vitrification of fission products solution is a mature centralized industrial technology characterized by :**
  - Large capacities of production (20 to 50 kg/h of glass produced per melter, continuously)
  - Small variations of the incoming streams

- **New processes/glasses are needed for new High and Intermediate Level Waste**
  - New waste coming from dismantling operations of old facilities, larger range of chemical compositions
  - New specifications : smaller quantities of waste to be treated, geographically dispersed, need for lower cost vitrification processes
  - New glasses → New glass material science challenges to face

Thank you for your attention