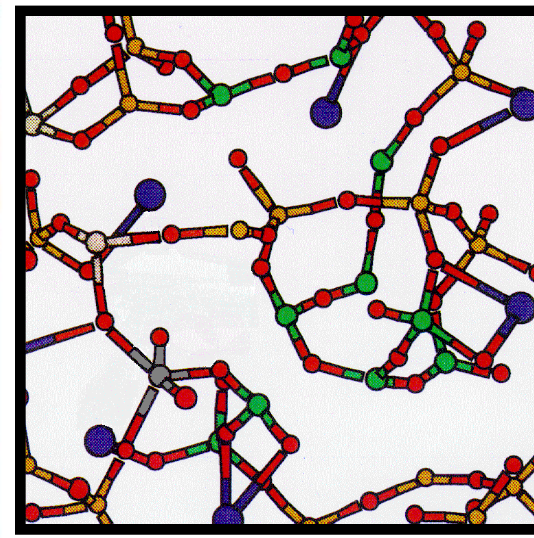
How to synthetize a good glass ?

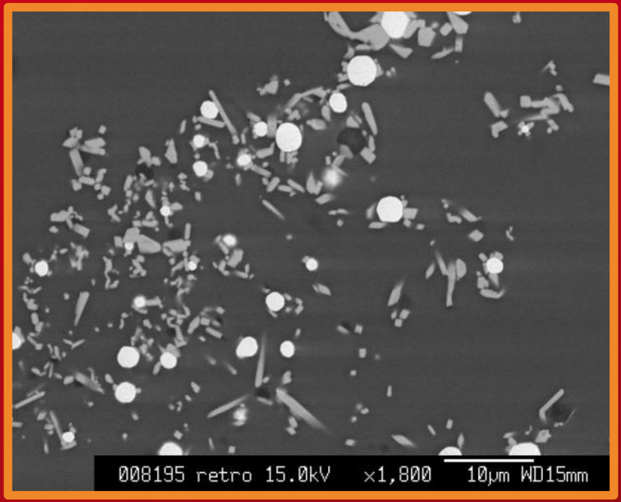
From Fission Products Nuclear Glass to New Glasses



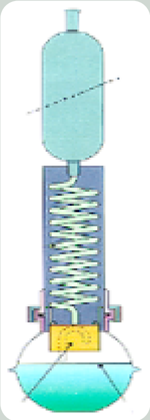
Florence Bart
Nuclear Energy Division – Marcoule Center

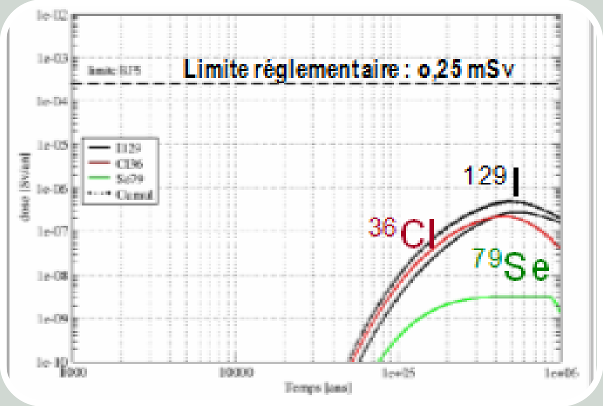
JOINT ICTP – AIEA WORKSHOP 10-14 SEPTEMBER 2018 – TRIESTE

What is a « Good » Glass ?



The answer is evolving with time





At the early beginning (50')

« A glass that can be poured is a good glass »

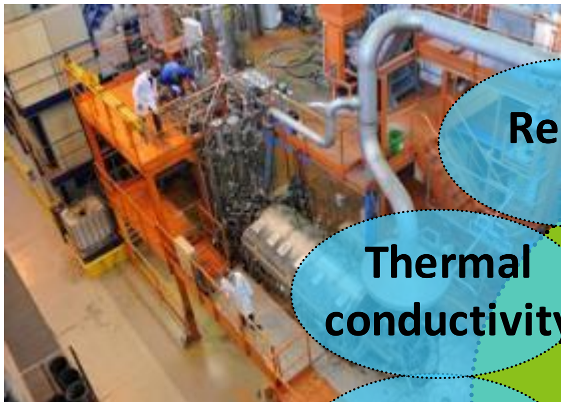
Intrinsic durability of the glassy material

Radionuclide release in function of time, in specific storage conditions

[Origin](#)

A good glass is defined thanks to an iterative process between material and process developpement

TECHNOLOGICAL FEASIBILITY



Glass melt properties

LOADING RATE

Redox

Chemical reactivity

Solubility (Mo, Cr, Ru, S, …)

Thermal conductivity

Glass waste form

Phase separation crystallization

Electrical conductivity

Chemical durability

Viscosity

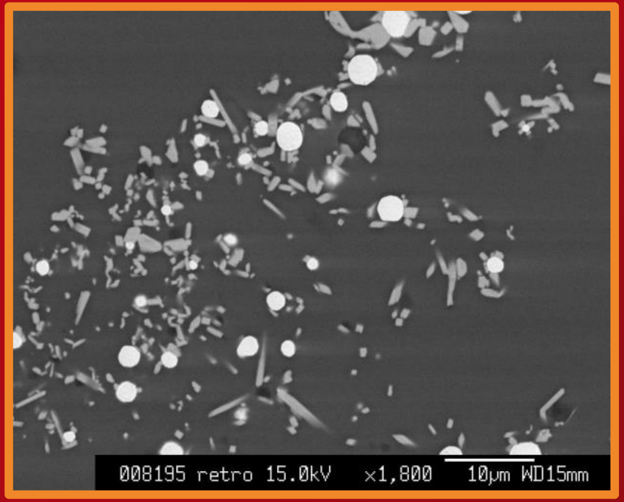
Radiation stability

Thermal stability

Glass Long term behavior

Glass properties

Glass Formulation



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Solubility limits

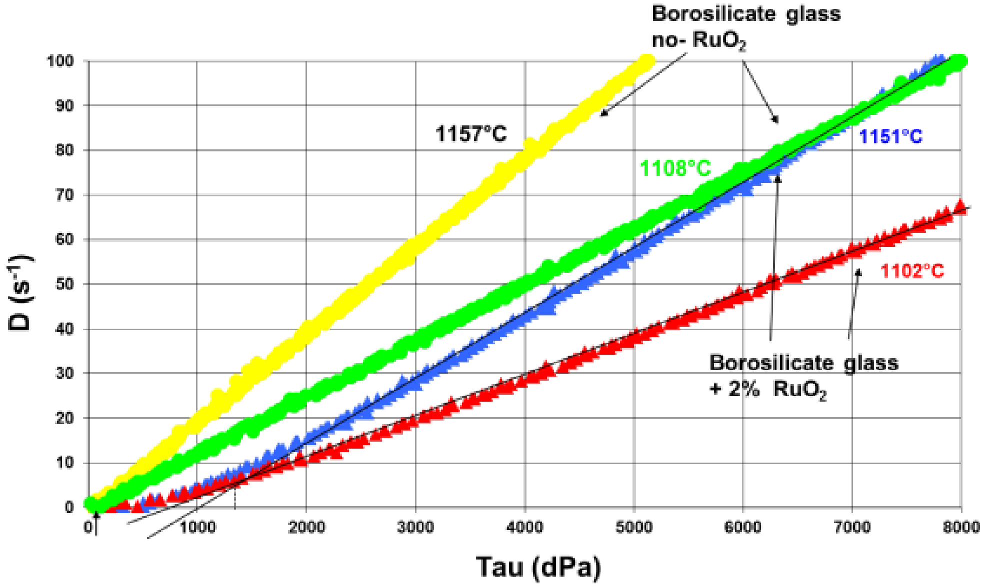
Major critical chemical elements coming from nuclear waste to be vitrified

- **Mo** → Phase separation and molybdates crystallization
- **Ru, Pd, Rh, Ag** → Chemical reactivity, particle settling, electrical conductivity, viscosity
- **Nd, La, Pr, Ce, P** → Apatite crystallization
- **Fe, Ni, Cr** → Spinel crystallization
- **Ru, Cs, Tc** → Volatility

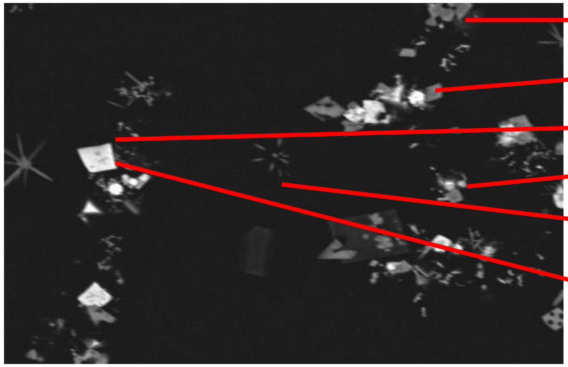
Important properties

Viscosity

Melting process can be impacted by noble metal content in glass melt (Convection, Pouring rate, Capacity)

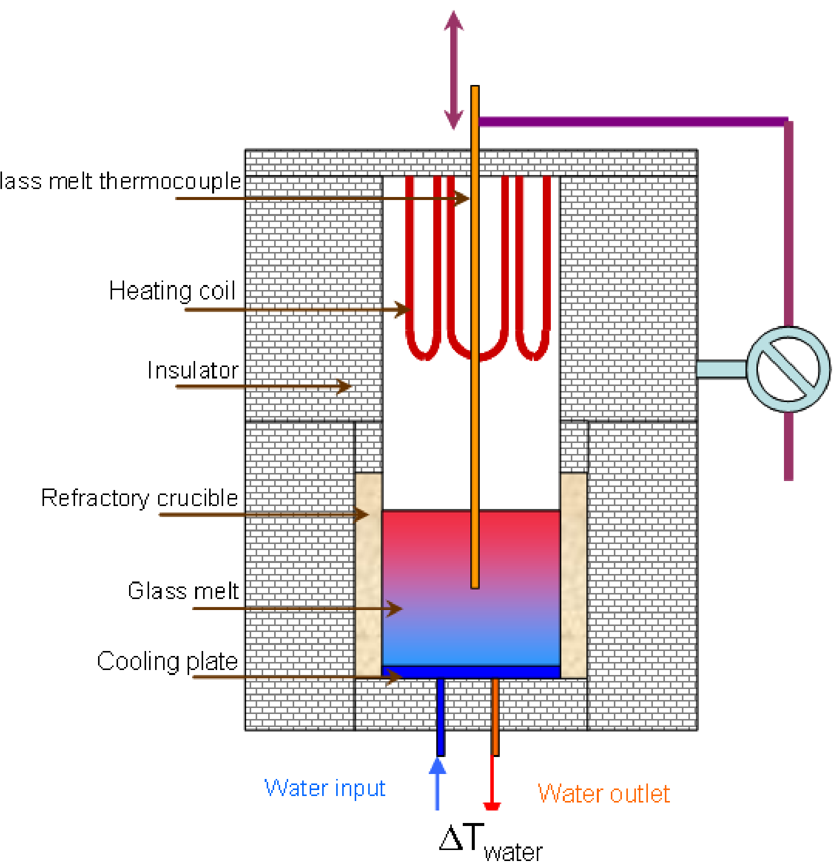


Micro-homogeneity

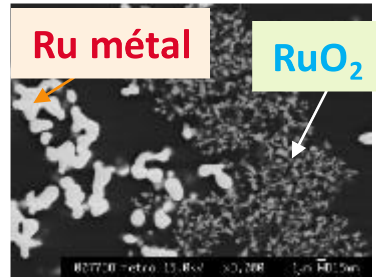


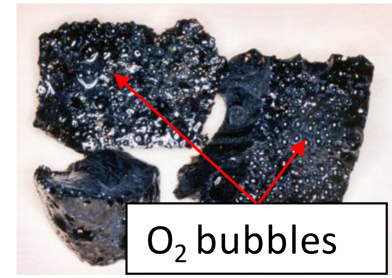
Important properties

Thermal conductivity



Redox properties





Process parameters

- Melter atmosphere
- Temperature

Input data

- Glass frit composition
- (Fe^{2+}/Fe^{3+}) in glass frit
- Waste composition
- Nitrate concentration

Thermodynamic data on redox equilibria in the glass

- Fe^{2+}/Fe^{3+}
- Ce^{3+}/Ce^{4+}
- Cr^{3+}/Cr^{6+}
- Mn^{2+}/Mn^{3+}
- Ni^{2+}/Ni^{3+}
- Ru^{0}/Ru^{4+} ....

Oxygen fugacity in the final glass

Final redox ratio $M^{m+}/M^{(m+n)+}$ of multivalent elements in the glass

Long term behaviour

Assessing long term behavior of vitreous matrices

Initial Glassy state

Thermal stability

(0-300 years : 90-70 °C)

Phase separation

Crystallization

Self irradiation

(cumulative dose : 1 dpa)

Radiation damage

(electronic and nuclear interactions, He production)

Chemical durability

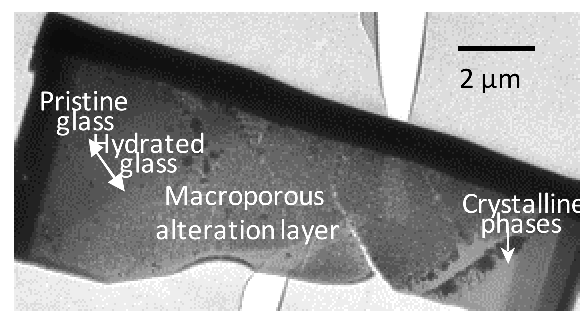
(performance assessment : 1 Ma)

Aqueous alteration

(source term: radionuclide release from the package)

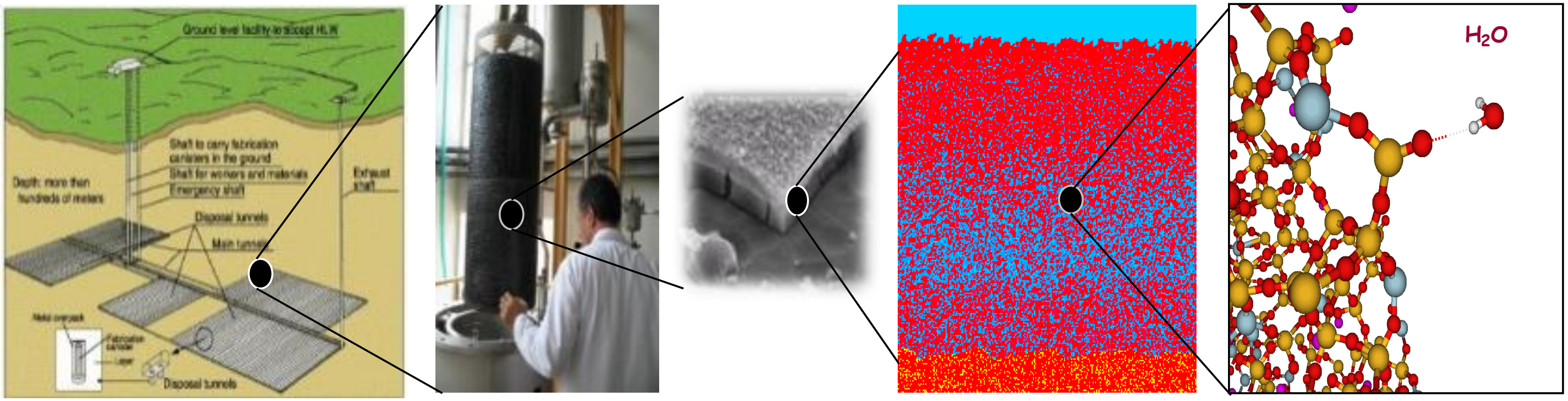
Glassy state structural modifications

Groundwater composition,
Fluid circulation
Interactions with surrounding materials : clay, iron, cement
Transformation of surrounding materials : metallic corrosion products
Self-Radiation



Glass alteration description and validation

To describe macroscopic properties…



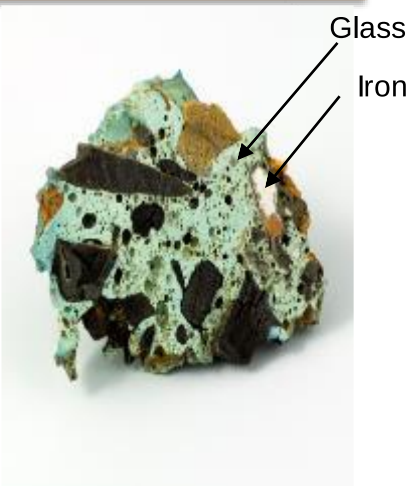
… from atomic to mesoscopic scale

Archeological and natural analogs for validation

Obsidian and basaltic glasses
(volcanic eruption)

Fractured archeological glass (Embiez),
1800 y. in Sea water

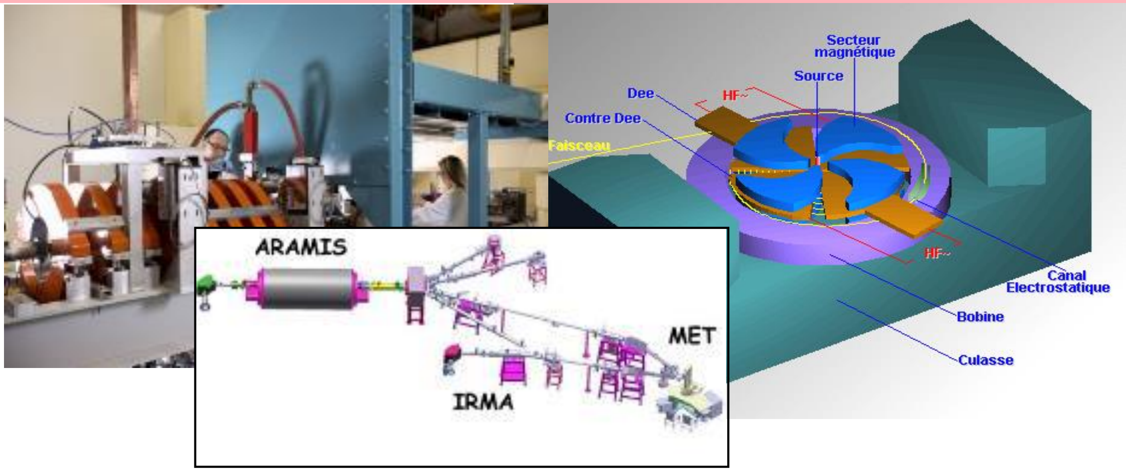
Steel production:
Blast furnace slags
from iron ore reduction
(400 y. in an iron (anoxic burial medium) and clayey environment)



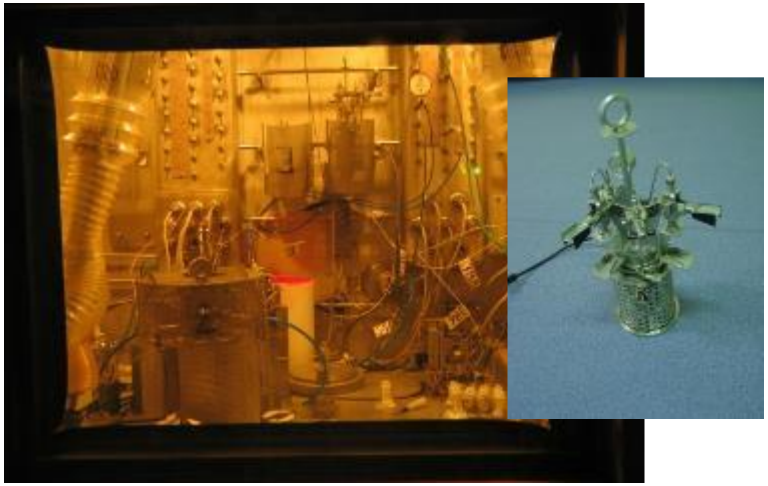
IRRADIATION DAMAGE : EFFECT ON GLASS STRUCTURE AND LONG TIME BEHAVIOUR

Doped glasses (^{244}Cm , ^{238}Pu, ^{239}Pu,….)

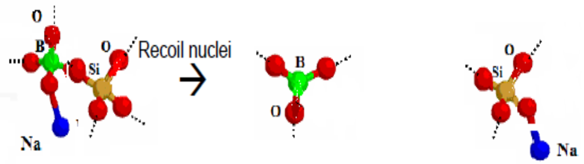
Irradiation facilities



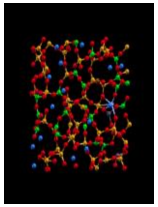
Leaching tests and measurements (effect of dose and dose rate)



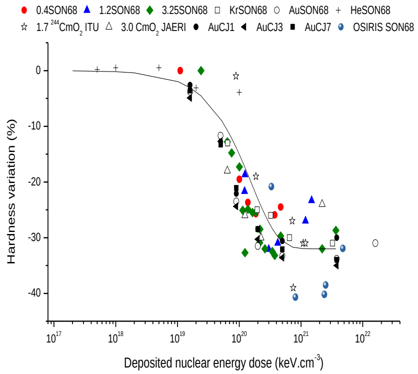
Damage / properties modelling



MD simulation of displacement cascade: accumulation of ballistic disordering



- **Thermal phase → local melting → network reorganization** (rapid thermal quenching)
- **Stabilization of a new structural state** when all the volume has been damaged one time (~ 4×10^{18} α/g)
- **Stabilization of macroscopic properties** (density, hardness…)



VITRIFICATION PROCESSES

Glass

Glass - Ceramic

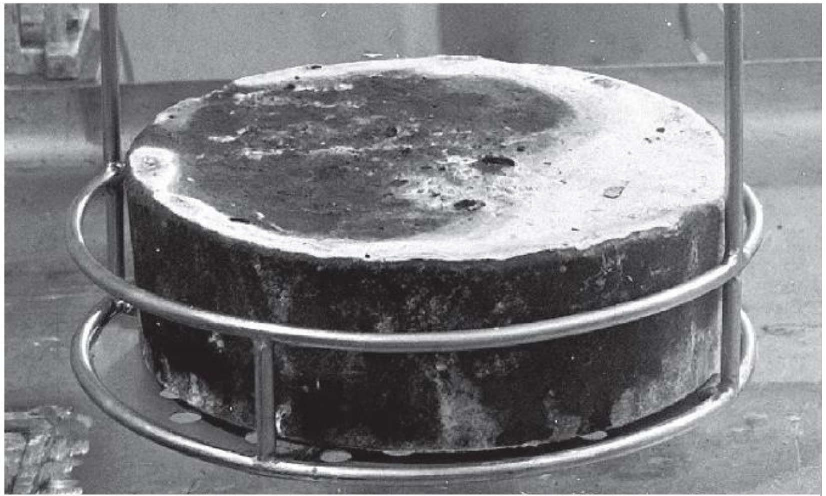
Glass /Metal Matrice

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

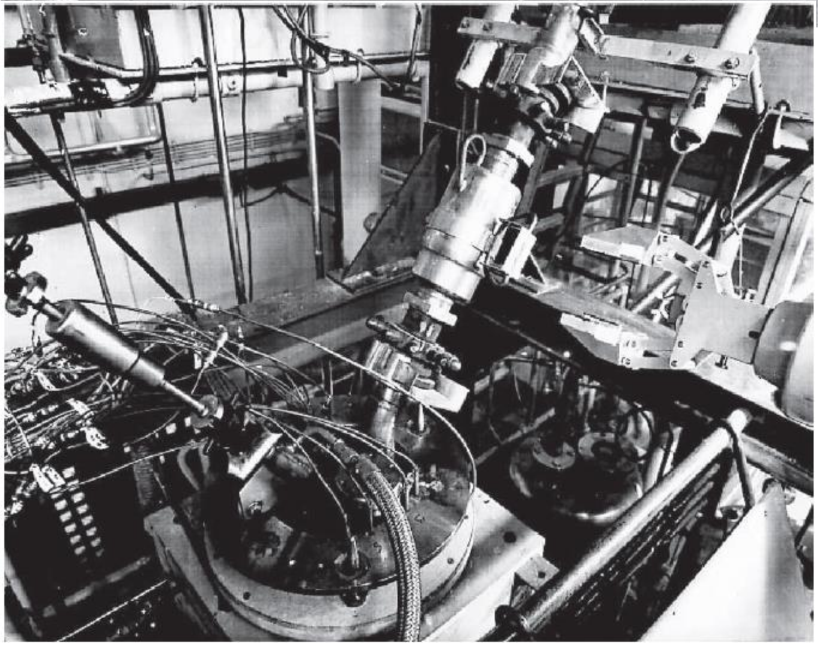
→ 170 kg of nuclear glass (10 kg per block)



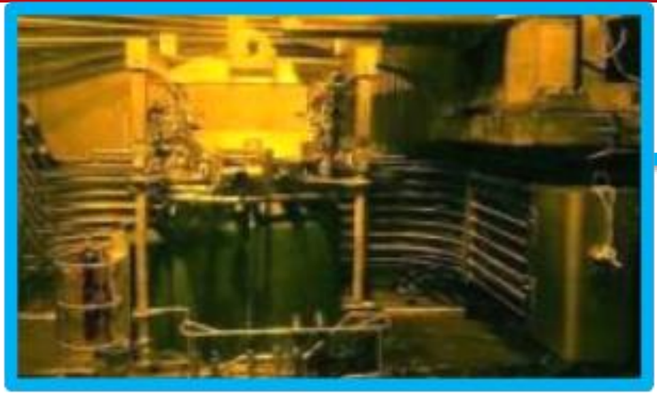
Piver (1969 – 1980)

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)



Development of the nuclear glass industry



UMo Glass

D&D Glass

2010 — CCIM in R7

Two steps processes, cold crucible melter

2004 — CCIM Pilot

2001

1994

1992 — T7 Start-up

Two steps processes, induction heated metallic melters

UOX Glass

1986 — R7 Start-up

AVM Glass

1978 — AVM Start-up

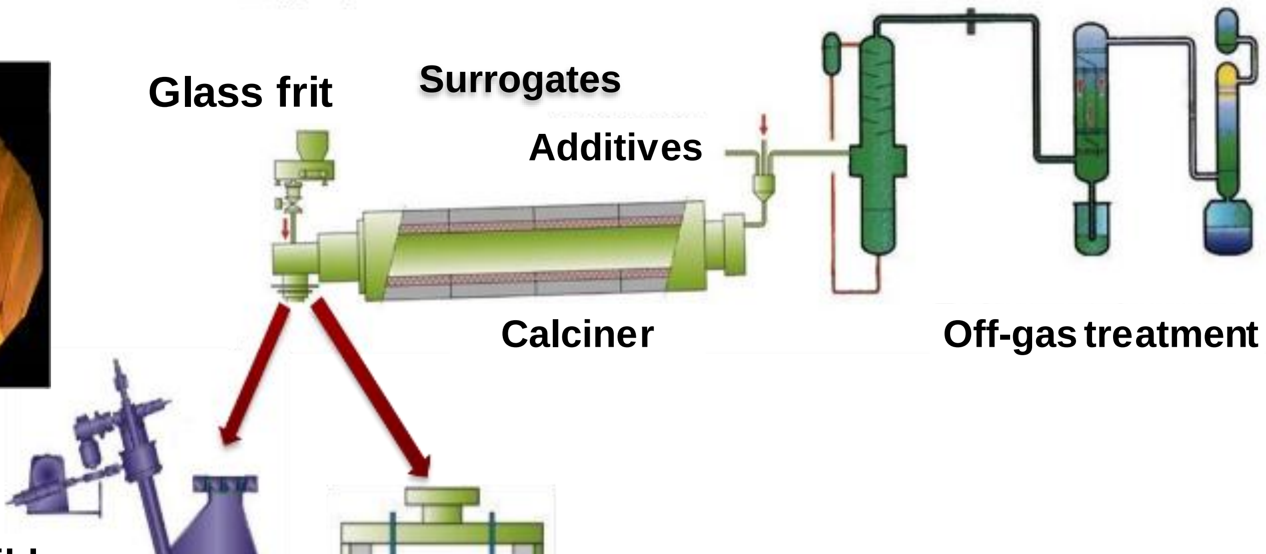
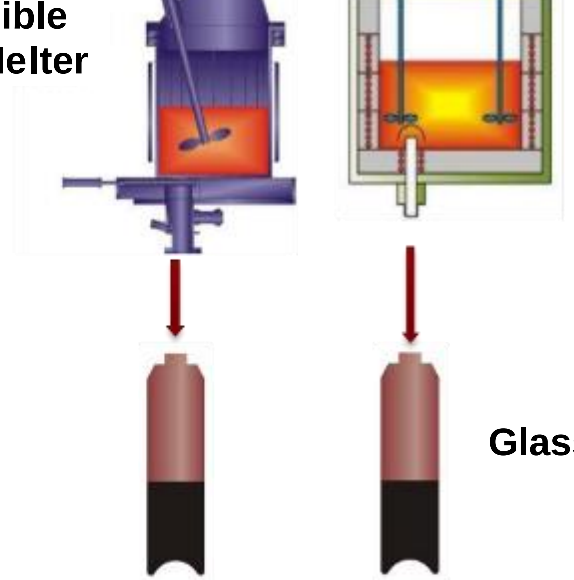
Piver Glass

70's — Two-step Vitrification Process

60's — Hot-wall Metallic Induction Melter (PIVER)

50's — Choice of Borosilicate Glass

Calcination – Vitrification continuous two-steps process

From glasses... to glass-ceramics

History of glass specifications implemented at industrial scale

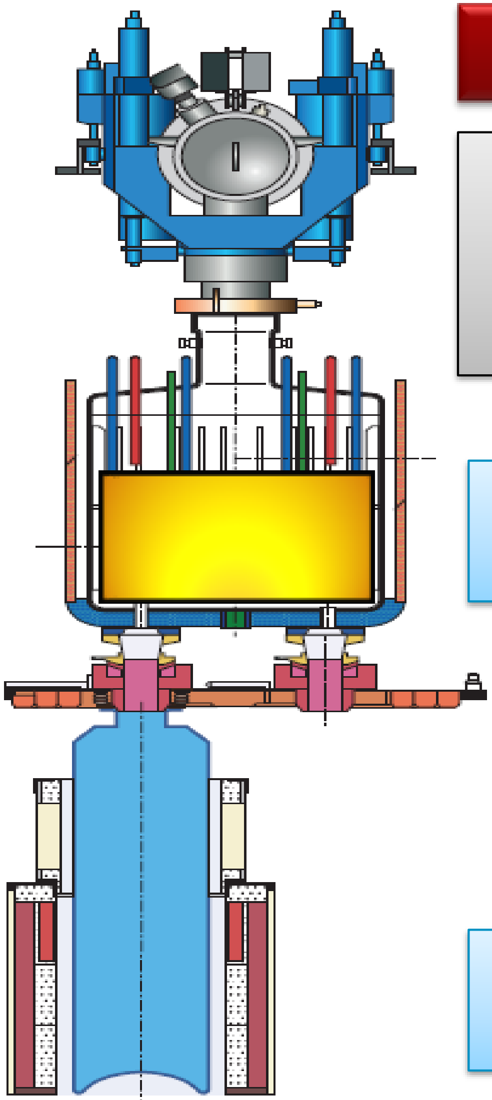
- **1969** — PIVER Glass
- **1986** — UOX Glass, AQ016 Specification (For hot crucible melter)
- **1994** — AVM Glass, AQ047 Specification
- **2007** — New UOX Glass, AQ060 Specification (With new curium limit); MAD Glass, AQ061 Specification (Decontamination effluent glass for cold crucible)
- **2011** — UMO Glass, AQ059 Specification; UOX Glass, AQ063 Specification (For cold crucible melter)

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…

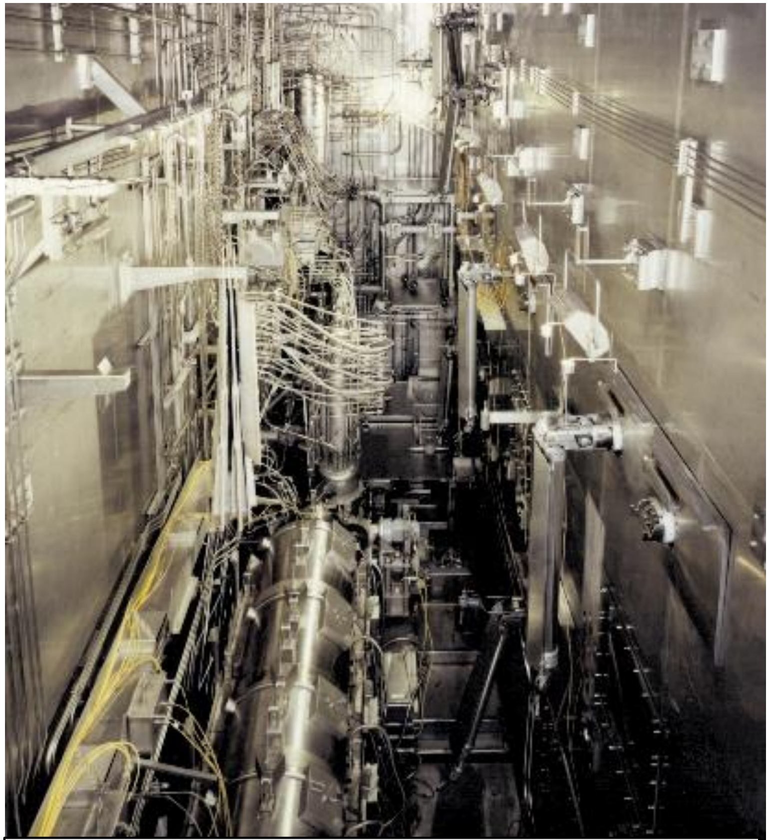


Since 1990

Thermal flux from metallic walls to molten glass

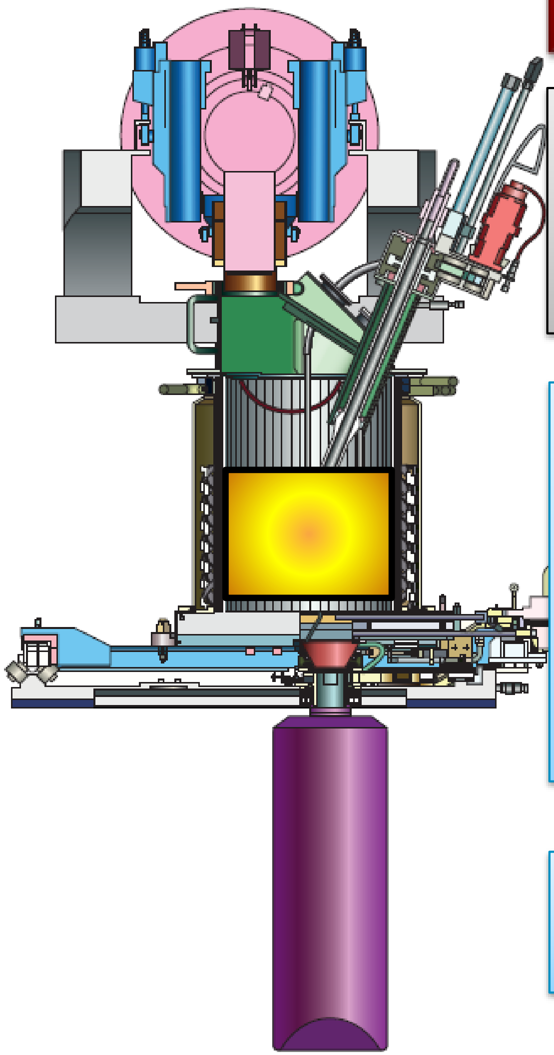
Hot Metallic Crucible
Bubblers, rotary stirrers

Pouring glass into stainless steel canister



5 vitrification lines in operation at AREVA La Hague Facility

… 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 ORANO La Hague Facility

NEW WASTE, NEW VITRIFICATION PROCESSES :

IN-CAN TECHNOLOGIES

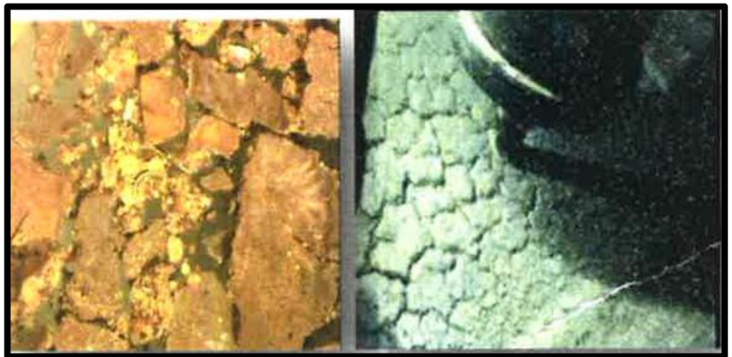
Marcoule : industrial nuclear site under dismantling

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**



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

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**

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

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 :

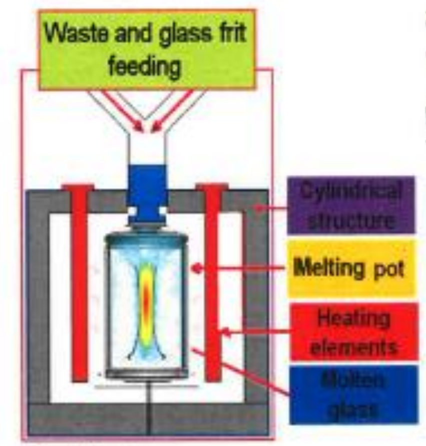
- Flexible and adjustable to waste with a composition poorly defined : mixed effluents such as zeolites, co-precipitation sludges, powders of fuel debris (FP and alpha components)
- Final waste package must be suitable with existing routes and/or on-site storage facilities
- Compact size of the process, 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

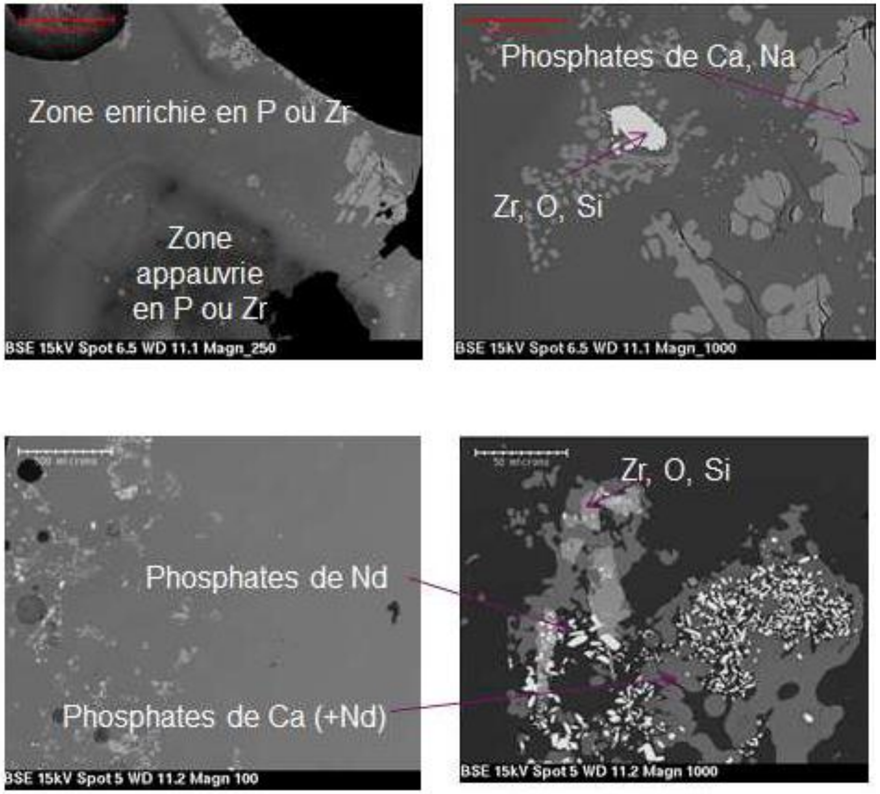


Principle of process

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

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

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

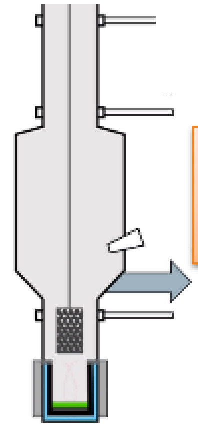
http://www.dailymotion.com/video/x5mbkt1

1

Introduction of the waste

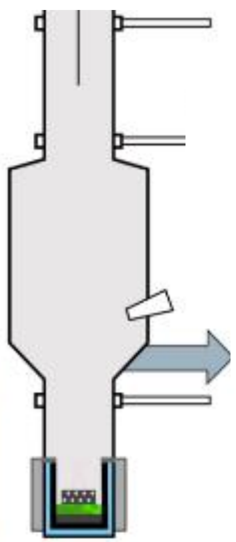
Organic matter is burning in the plasma

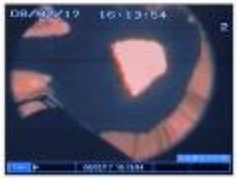
2



Gaz is released into gaz treament

3





Metallic waste is heated thanks to induction
Glass fraction (green) is trapping actinides

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

How to produce a "good glass" ?

Specification = to produce durable glass

→ Material : performance demonstration

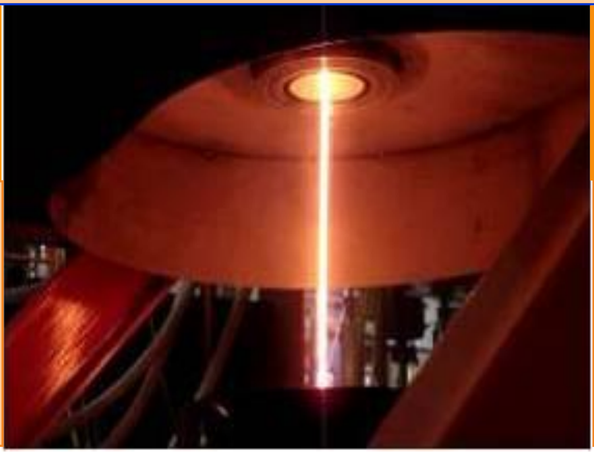
→ Process : large quantities to be produced, half-continuous process, including pouring of the melt into containers

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

From FP glasses to new glasses

- **Vitrification of fission products solution is a mature 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

DE LA RECHERCHE À L'INDUSTRIE

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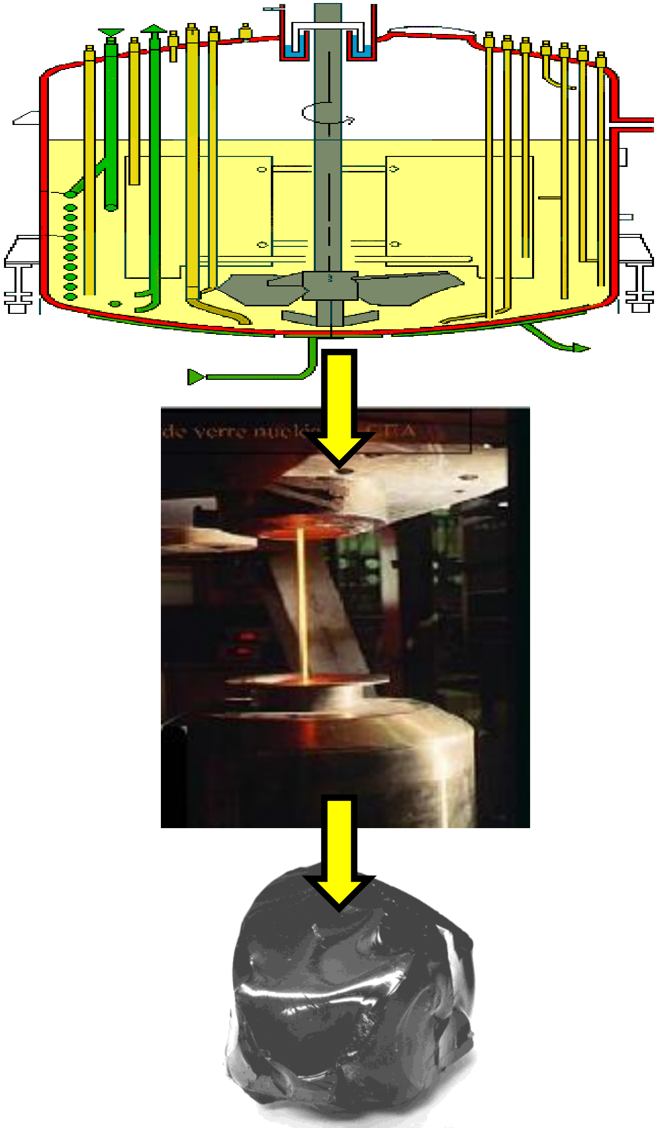
Vitrification of FP solutions Back

- 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)