



Glass formulation for nuclear waste containment

DE LA RECHERCHE À L'INDUSTRIE

Joint ICTP-IAEA International School on Nuclear Waste Vitrification – 23 - 27 Septembre 2019 - TRIESTE

E. Régnier



CEA-Marcoule

Nuclear energy R&D

... since 1955



CEA Marcoule center (~5000 peoples)

Research facilities

**ICSM Institut for
Separation Chemistry**

Vitrification
Process development
Material science

Cementation
Decontamination

ATALANTE
Reprocessing
Separation chemistry
Conditioning matrices
Fuel fabrication
Interim storage of spent fuels

I. Nuclear waste to be vitrified

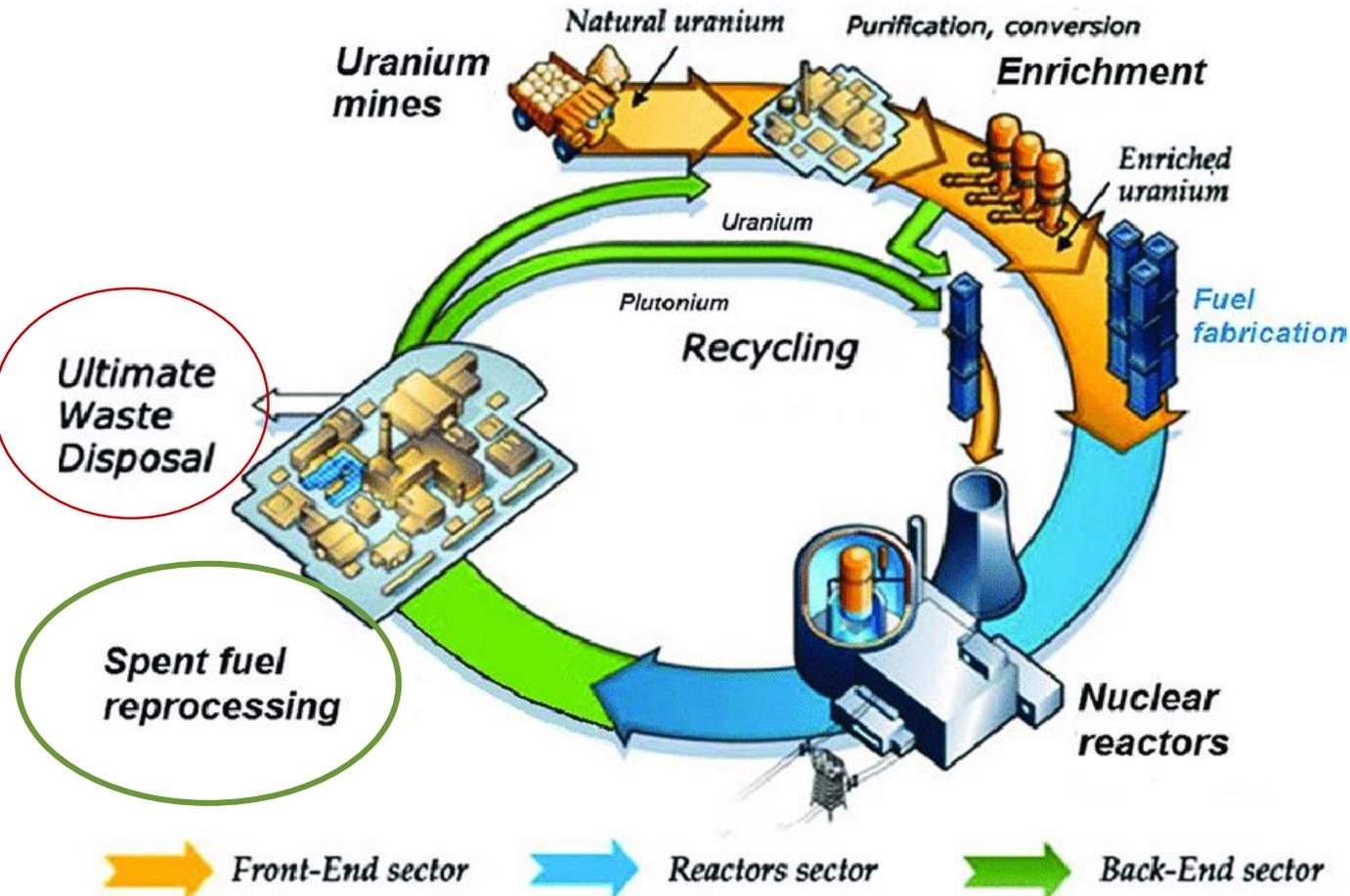
- 1) Origin of nuclear waste
- 2) Objectives of nuclear waste containment

II. Some basic knowledge on glass

- 1) Glass structure
- 2) Glass formers / modifiers / intermediates
- 3) Role of radioelements in the glass structure

III. How to formulate a nuclear glass?

- 1) Which constraints have to be respected?
- 2) Methodology to formulate a nuclear glass
- 3) CEA experience in nuclear glass formulation



<https://www.jnfl.co.jp/en/business/uranium/>

⇒ Nuclear waste produced at all stages of the Nuclear Fuel Cycle (from mines to spent fuel reprocessing)

+ Decommissioning & Dismantling (D&D) operations

https://www.researchgate.net/figure/Uranium-and-nuclear-fuel-cycle-sectors_fig11_317779578

Waste classification

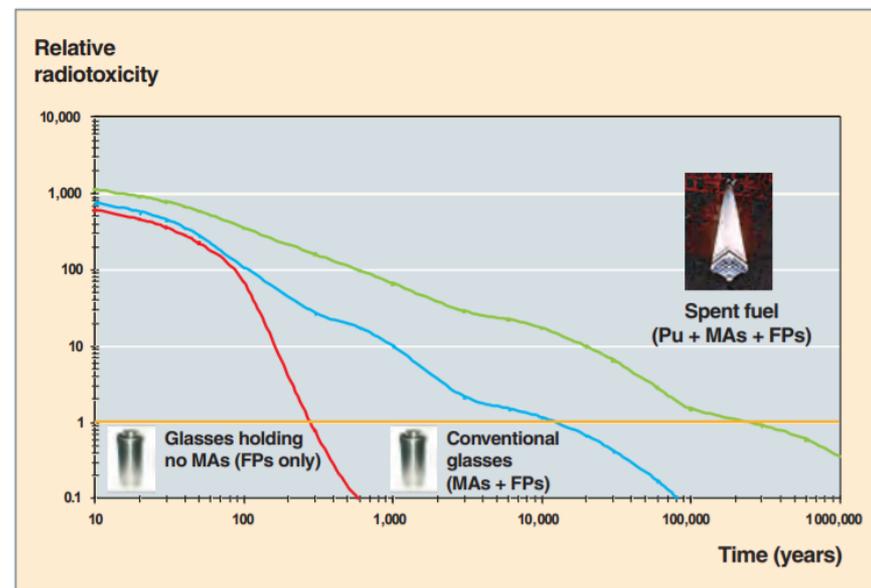
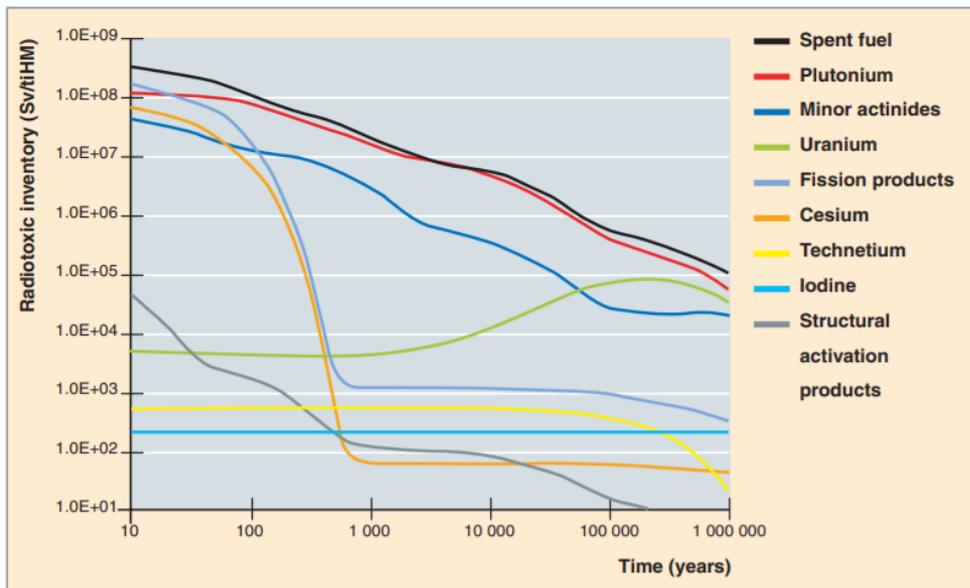
	Very short lived	Short lived	Long lived
Very low level (VLLW)	VSLW (managed first through on-site decay and then disposed of as conventional waste)	VLLW (disposed of at the CSTFA facility located in the Aube district)	
Low level waste (LLW)		LILW-SL (disposed of at the CSFMA facility (Aube))	LLW-LL (near-surface repository)
Intermediate level waste (ILW)		63 % vol but 0,02 % of radioactivity	ILW-LL (deep disposal, at 500 m, under dvpt)
High level waste (HLW)		HLW (deep disposal, at 500 m, under dvpt)	

Source : ANDRA, 2014

⇒ Used fuel reprocessing (PUREX process) ⇒ The resulting Fission Products (FP) / minor Actinids (mA) solutions are the main radioactive waste of the fuel cycle: 96 % of radioactivity (but 0,2 % vol)

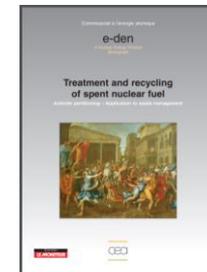
Radiotoxicity of HLW

Spent fuel / reprocessed spent fuel



⇒ Very important to propose a long term reliable solution for storage!

Source : <https://hal-cea.archives-ouvertes.fr/cea-01153306/file/cea6-en.pdf>



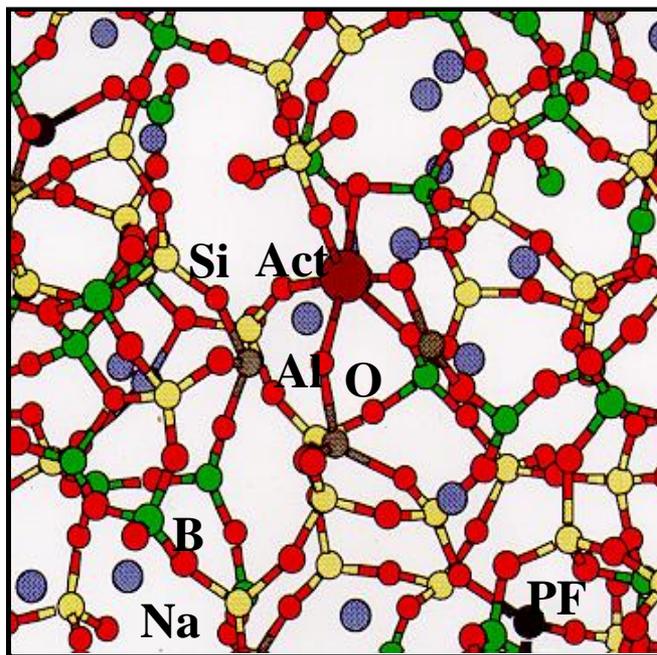
- ▶ The highly radioactive and very complex FP **solutions** are produced by the PUREX process. They contain ~40 chemical elements that must be **continuously stirred and cooled** to dissipate their thermal power.
- ▶ Conserving them in the liquid state is **not a sustainable option** => France (as well as US, UK, Canada) began to study solidification process in the 50's.

Fission Product / minor actinides solution

1 H Hydrogen 1.00794																	2 He Helium 4.003														
3 Li Lithium 6.941	4 Be Beryllium 9.012182																	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797								
11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050																	13 Al Aluminium 26.9815385	14 Si Silicon 28.0855	15 P Phosphorus 30.9737614	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948								
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The aim is to confine radionuclides by establishing chemical bonds



Remind: ~40 elements in the waste solution

► The program began by attempting to produce synthetic minerals such as mica $K[Si_3Al][Mg_3]O_{10}(OH)_2$ or feldspar $((Na,K)AlSi_3O_8)$, but glass soon proved to be the only material capable of immobilizing all the elements present in such complex solutions.

Mica-phlogopite



⇒ Choice of glass in Canada, France, US, Germany, USSR.

► In France, the first radioactive glass was synthesized at laboratory scale at CEA in 1957

⇒ **Birth of vitrification in the 50's**

⇒ **A new application of the glass was born: containment glasses**

⇒ Needs of R&D on:

- Material (specific composition of nucl. glass, long term behavior)
- Process



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- 1) Glass structure
- 2) Glass formers / modifiers / intermediates
- 3) Role of radioelements in the glass structure

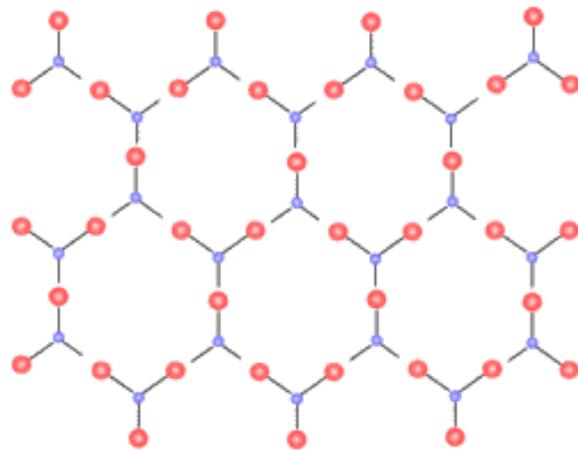
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Glass structure: a disordered structure

Cristallized state (SiO_2):

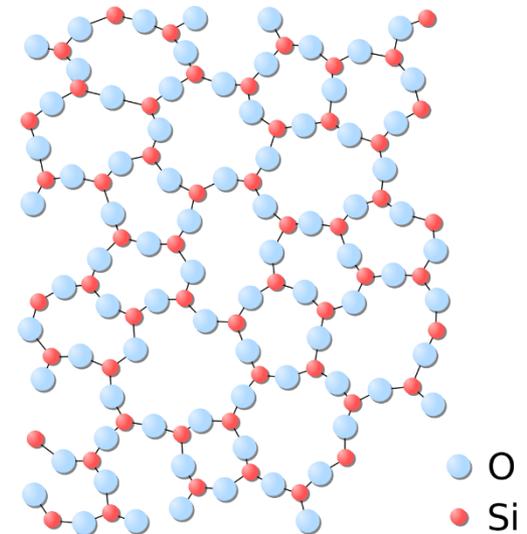
- Repetition of elementary patterns
⇒ **Ordered material**



● Oxygen
● Silicium

Vitreous state (SiO_2):

- Assembly of connected polyhedra
⇒ **No long range order**



Thanks to its disordered structure, glass is able to incorporate many different elements within its structure. However, the role of each element in this structure differs from an element to another.

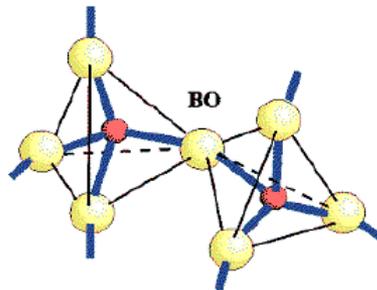
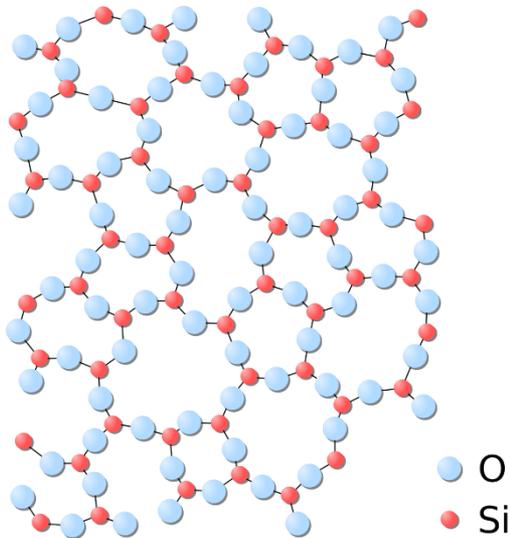
- Network formers -

SiO_2 , B_2O_3 , GeO_2 , P_2O_5

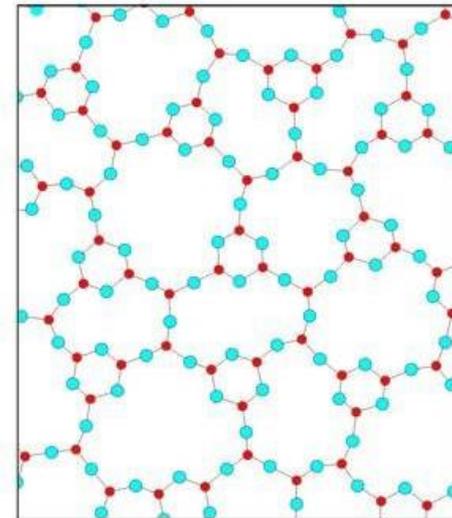
⇒ Able to form a glass alone (iono-covalent links)

⇒ SiO_4 , BO_4 / BO_3 ... polyhedra linked by their tops

SiO_2 glass



SiO_2 - B_2O_3 glass



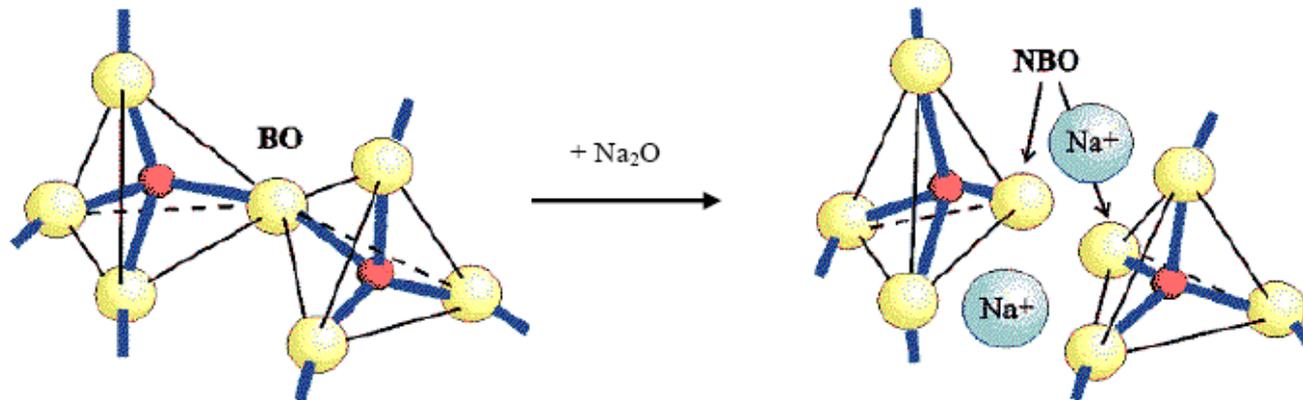
Edited by:
Adrian C. WRIGHT, Steven A. FELLER
and Alex C. HANNON

- Network modifiers -

Alkaline, Alkali earth, some transition elements and rare earthes

- ⇒ Are not able to form glasses alone (cristallize) (ionic links)
- ⇒ In glass network: break the bonds

example of Na^+ in SiO_2 glass



Effect on the glass properties:

- Decrease the melting temperature
- Decrease the glass viscosity
- Decrease the chemical durability

- Intermediate elements -

Al_2O_3 , ZnO , ZrO_2 , PbO , TiO_2

⇒ Are not able to form glasses alone (cristallize)

⇒ Can reinforce or break the bonds (depends on their content, on glass composition...)

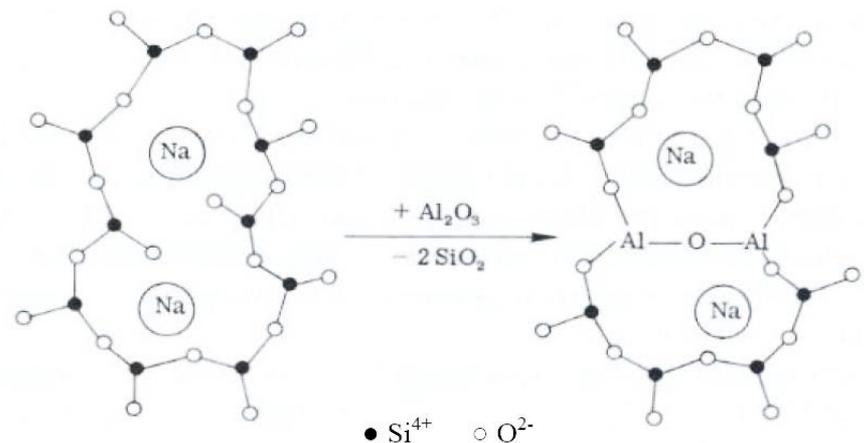
Case of Al_2O_3

⇒ Can form $[\text{AlO}_4]^-$ tetrahedrons as well as $[\text{SiO}_4]^-$ if positive charges are available

⇒ Possible with alkaline ions

⇒ But if $\text{Al}_2\text{O}_3/\text{A}_2\text{O} < 1$, then not enough alkalines to compensate $[\text{AlO}_4]^-$ charges

⇒ $\text{Al} \rightarrow [\text{AlO}_6] = \text{modifier}$.



- Summary -

Formers	Intermediates	Modifiers
SiO_2	Al_2O_3	Li_2O
GeO_2	PbO	Na_2O
B_2O_3	ZnO	K_2O
P_2O_5	CdO	CaO
As_2O_3	TiO_2	BaO
As_2O_5		
V_2O_5		

(can be found in every books on glass science)

Fission Product / minor actinides solution

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Fission Products (FP)
 Addition elements

Actinides
 Adjuvants

Corrosion products

Remind

Network formers: SiO_2 ,
 B_2O_3 , GeO_2 , P_2O_5

Network modifiers:
Alkaline, Alkali earth,
some **transition elements**
and **rare earthes**

Intermediates: Al_2O_3 , ZnO ,
 ZrO_2 , PbO , TiO_2

⇒ Most of the elements present in the FP solutions:
unknown behavior in glass (no data from traditional glass industry)
⇒ Knowledge had to be acquired

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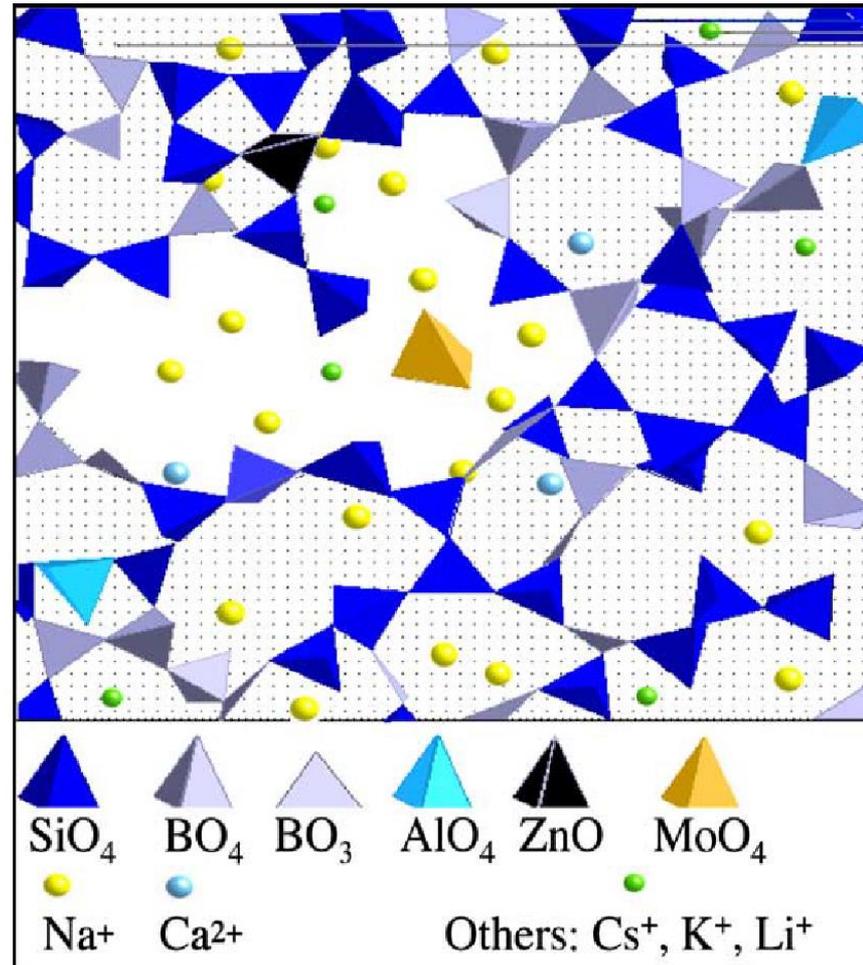
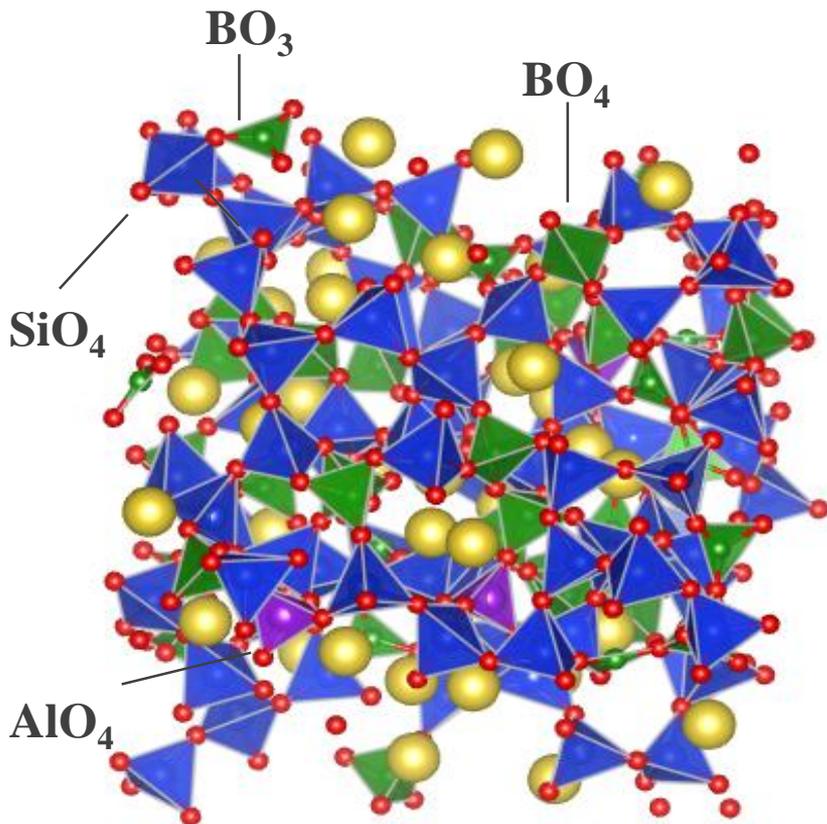
Knowledge acquired for nuclear borosilicate glass

Transition elements mainly act as intermediate elements. They have almost no impact on glass durability and viscosity, but can crystallize (cf. spinel).

Fission products will generally act as intermediate elements. They tend to increase the resistance of glasses against water corrosion, increase glass viscosity and tend to lead to phase separation (Mo) or crystallization (RE_2O_3 , Ce, Mo).

Specific case of platinum elements: insoluble elements in borosilicate glasses. They have almost no impact on glass corrosion by water, modify the glass rheology, and act as nucleating agents for crystallization.

More complex glasses?



Complex glasses \Rightarrow a combination between an experimental approach / a statistical approach / basic knowledge on glass science is needed

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When formulating nuclear glasses:

- Elements coming from the waste solution are sustained:

Fission products / minor actinides solutions (FPS)

Fission products (FP)
 Addition elements

Actinides
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Constraint 1:

All elements from the nuclear waste have to be incorporated in the glass structure

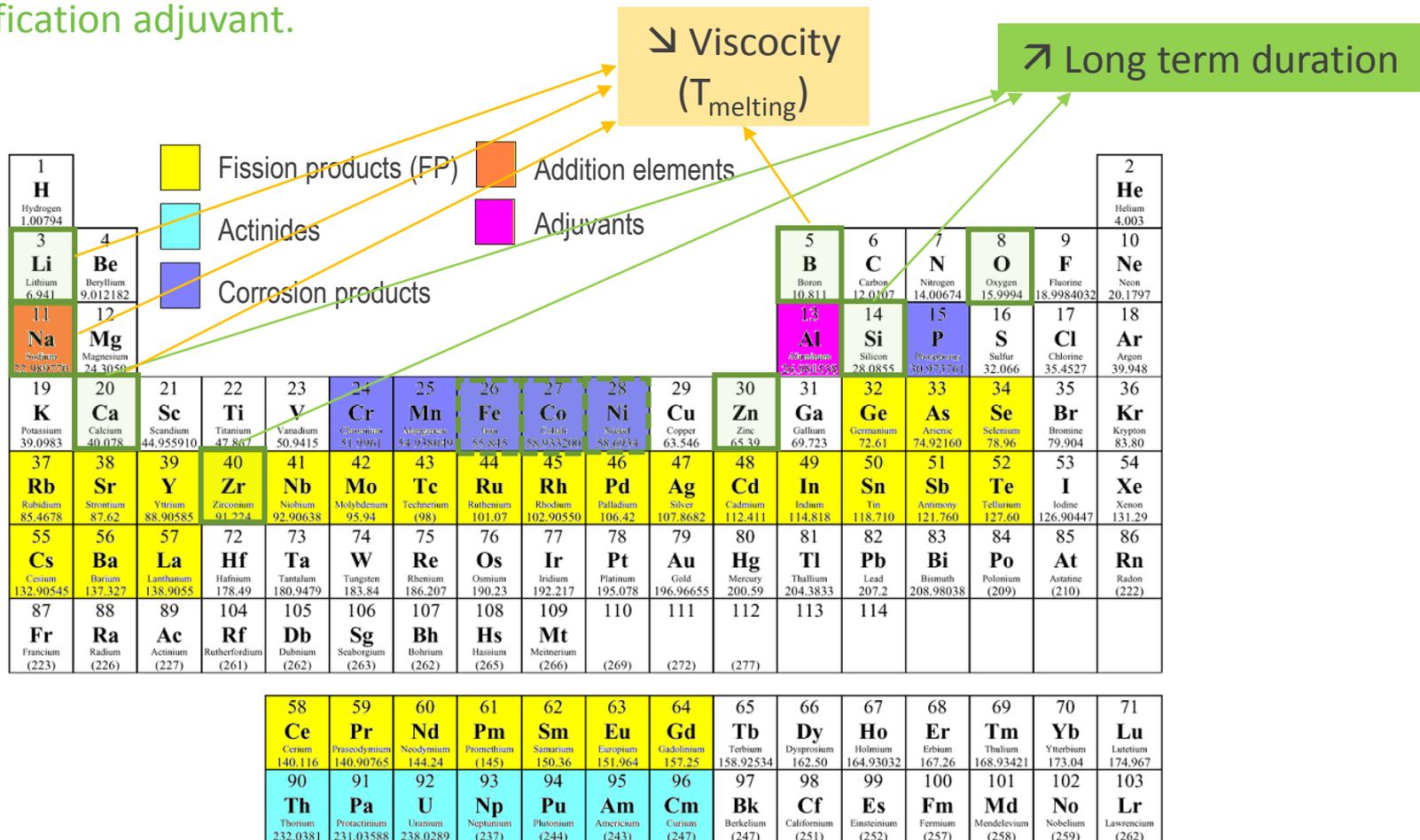
Constraint 2:

Loading rate has to be maximized to minimize storage cost

NB:
These elements are not glass formers

When formulating nuclear glasses:

- Elements coming from the waste solution are sustained,
- Glass formers (generally absent from the waste solution) have to be added = vitrification adjuvant.



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

Waste incorporation in the glass

- * Solubility of radioelements in glass (Mo, transition metals, rare earths, actinides, SO_4 , Ag,...)
- * Reactivity waste – glass adjuvant

**Technical feasibility at industrial scale**

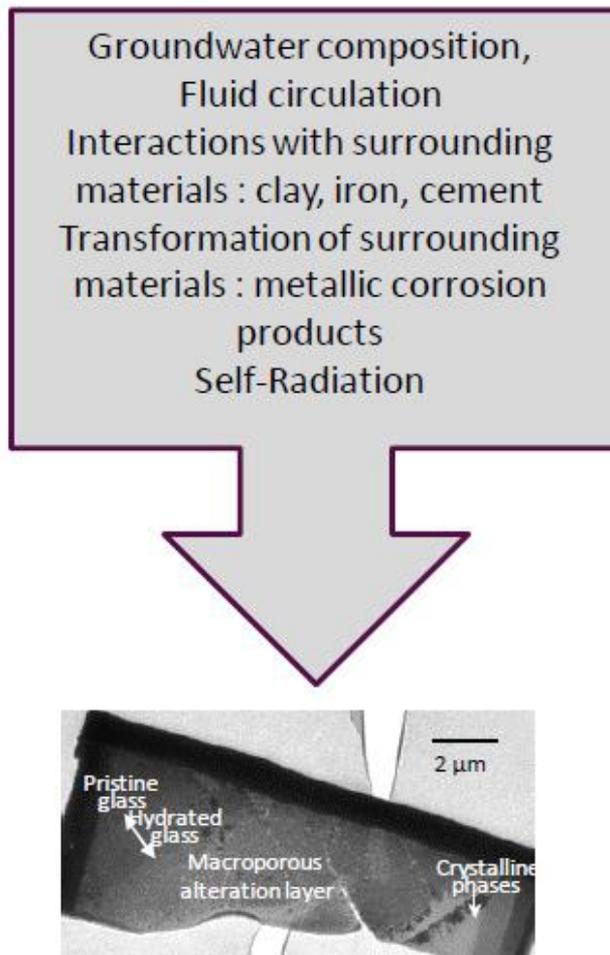
- * T_{melting}
- * Rheology (cf. cast possibility),
- * Redox
- * Reactivity (cf. production capacity)
- * Thermal and electrical conductivities

Long term behavior of glass (storage)

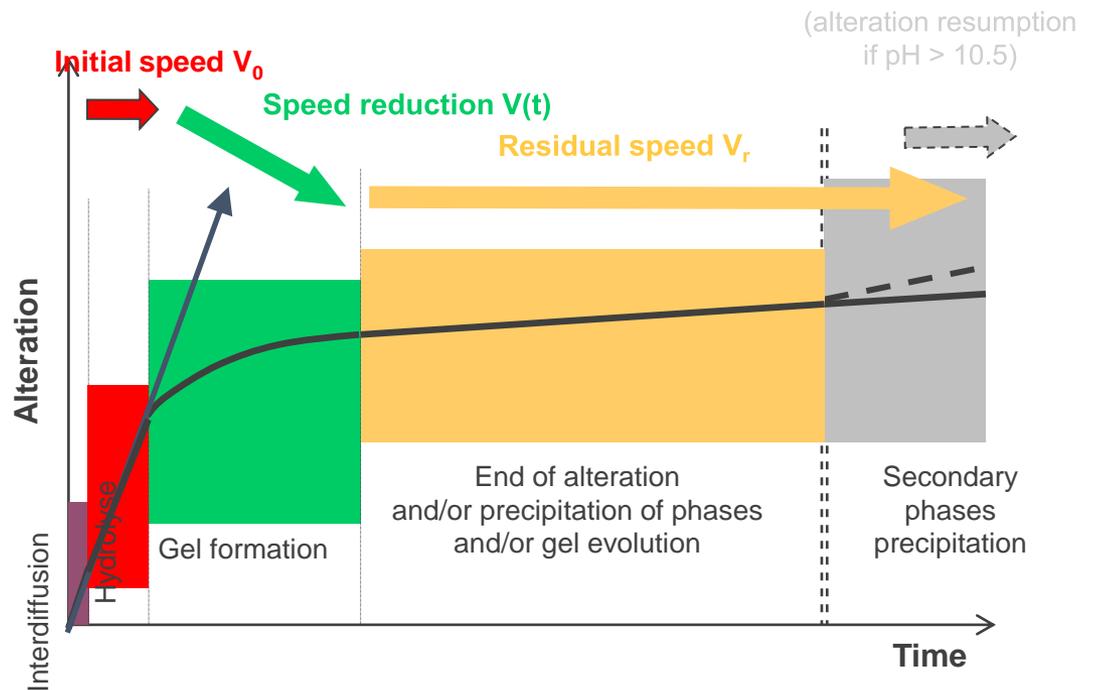
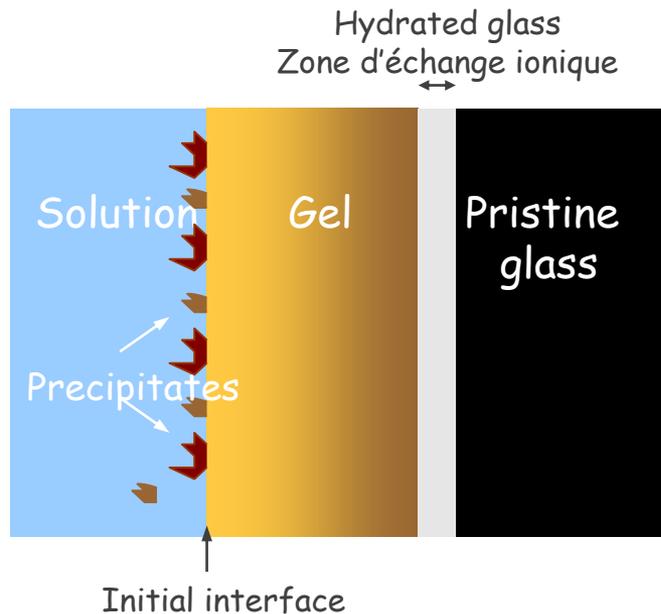
- * Thermal stability
- * Chemical durability
- * Auto-irradiation resistance

Cf. Christian LADIRAT talk

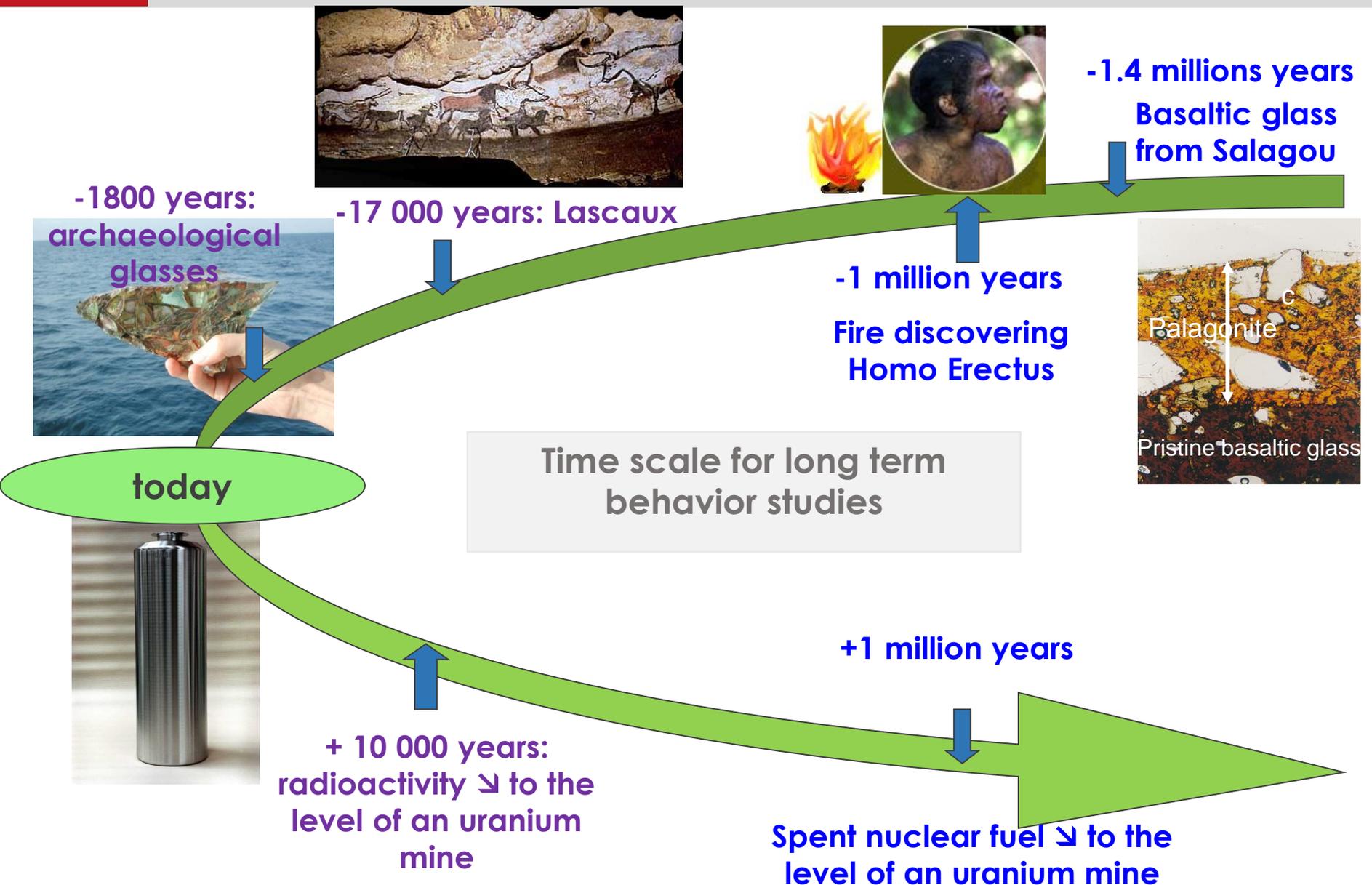
Glass – water interactions => RN release from the package



Glass – water interactions => RN release from the glass package



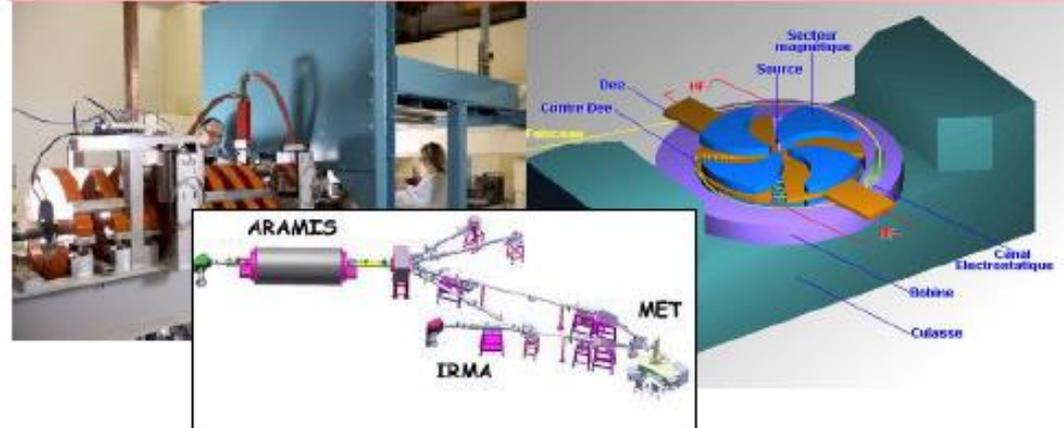
The RN release speed depends on glass composition, but also groundwater composition, fluid circulation, interactions with surrounding materials (clay, iron, cement), transformation of surrounding material (metallic corrosion, self-irradiation...)



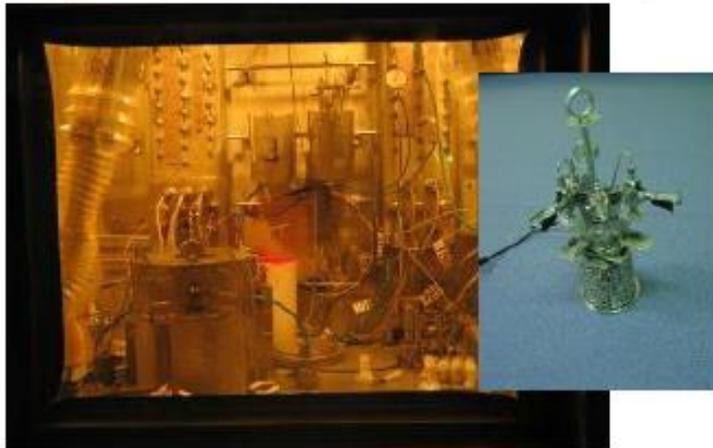
Doped glasses (^{244}Cm , ^{238}Pu , ^{239}Pu ,...)



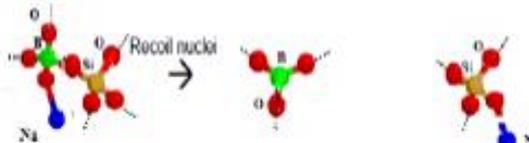
Irradiation facilities



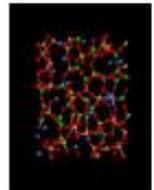
Leaching tests and measurements (effect of dose and dose rate)



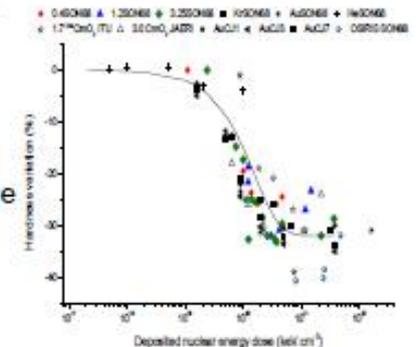
Damage / properties modelling



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 ($\sim 4 \times 10^{18} \alpha/\text{g}$)
- ❑ Stabilization of macroscopic properties (density, hardness...)



I. Nuclear waste to be vitrified

- 1) Origin of nuclear waste
- 2) Objectives of nuclear waste containment

II. Some basic knowledge on glass

- 1) Glass structure
- 2) Glass formers / modifiers / intermediates
- 3) Role of radioelements in the glass structure

III. How to formulate a nuclear glass?

- 1) Which constraints have to be respected?
- 2) Methodology to formulate a nuclear glass
- 3) CEA experience in nuclear glass formulation

How to formulate a nuclear glass?

⇒ No unique formulation methodology

Nuclear Glass formulation depends on:

- the type of waste (composition, variability, radioactivity level)

* **FP solution** => limited composition domain

* **rinse flows,**

* **D&D operations,**

* **technologic waste** => Metallic phase, organic elements, minerals...

} Compositions not as precisely defined as for FPS

=> Reducing conditions

- the type of process

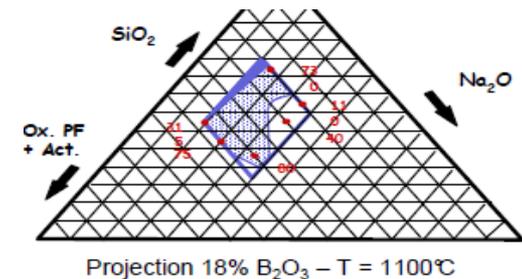
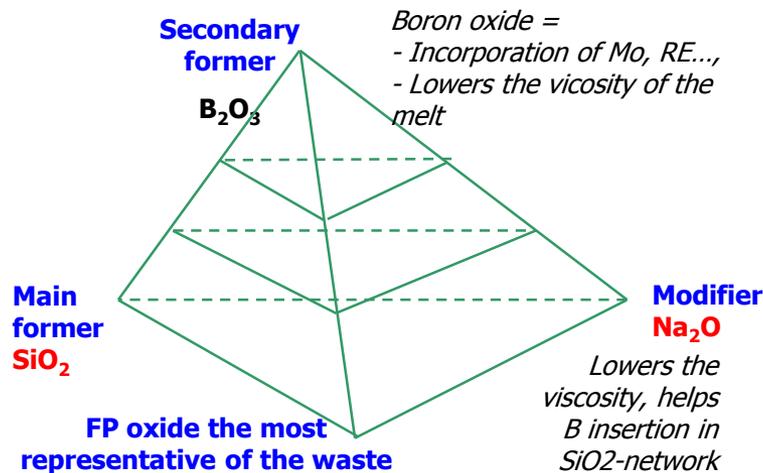
* **hot metallic crucible** => cast, mechanical stirring

* **CCIM** => cast, induced currents, mechanical stirring

* **In-can melter (resistif furnace)** => no cast

⇒ Formulating a nuclear glass requires:

- A clear description of the waste (nature, composition, variability, radioactivity level...)
- A good knowledge on glass structure (=> identify key elements, define how to simplify the glass composition for specific studies,...)



- A good knowledge of process constraints (T_{max} , cast / no cast, redox conditions...)

⇒ a combination between an experimental approach / a statistical approach / basic knowledge on glass science is needed

Methodology

1) Waste features

- Nature
- Mean composition
- Variability

2) Process constraints

- Max T_{melting}
- Cast ?
- Melt homogeneity needed?

3) Long term behavior constraints

- Long term / middle term performances
- Homogeneous glass / crystallized glass

4) Define a few reference glass compositions based on

- Mean waste composition
- Capitalized knowledge on glass formulation
- Glass formulation modelling (cf statistical approach – see Damien PERRET talk)

5) Test these few reference glass compositions

- Glass elaboration
- Glass characterization
- First long term behavior tests

Lab scale
(inactive materials)



Technological scale
(inactive materials)



Long term behavior (water
intractions + radiations)



Specification document



Industrialization



Nuclear glass formulation: methodology

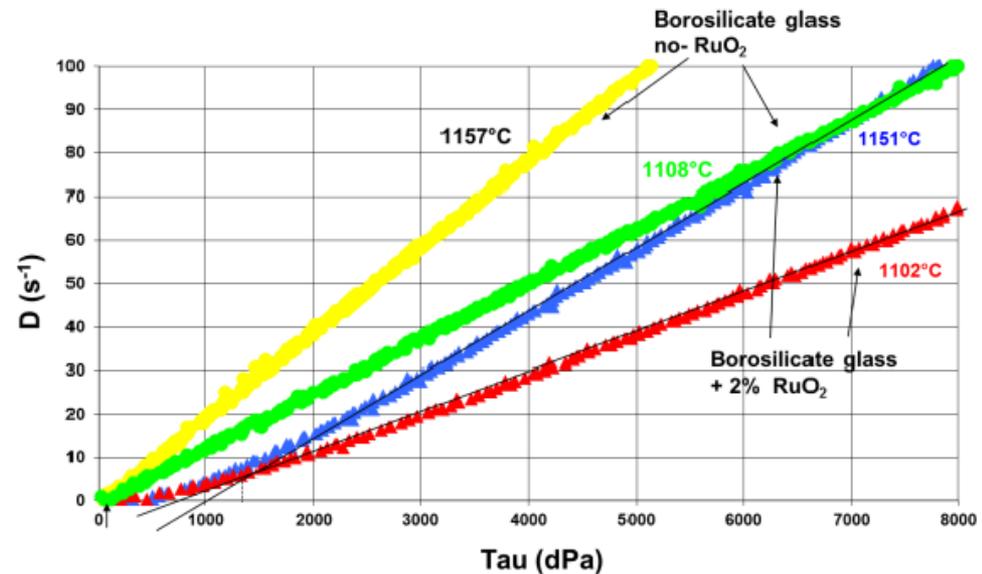
Glass melting at lab scale



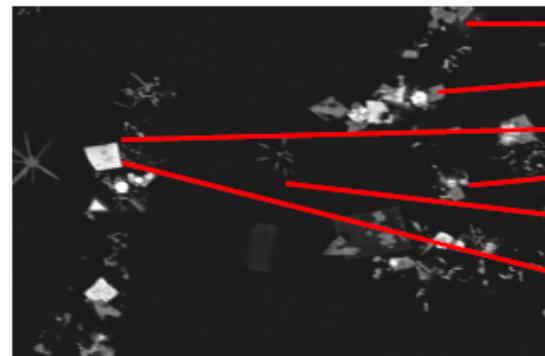
Viscosity



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

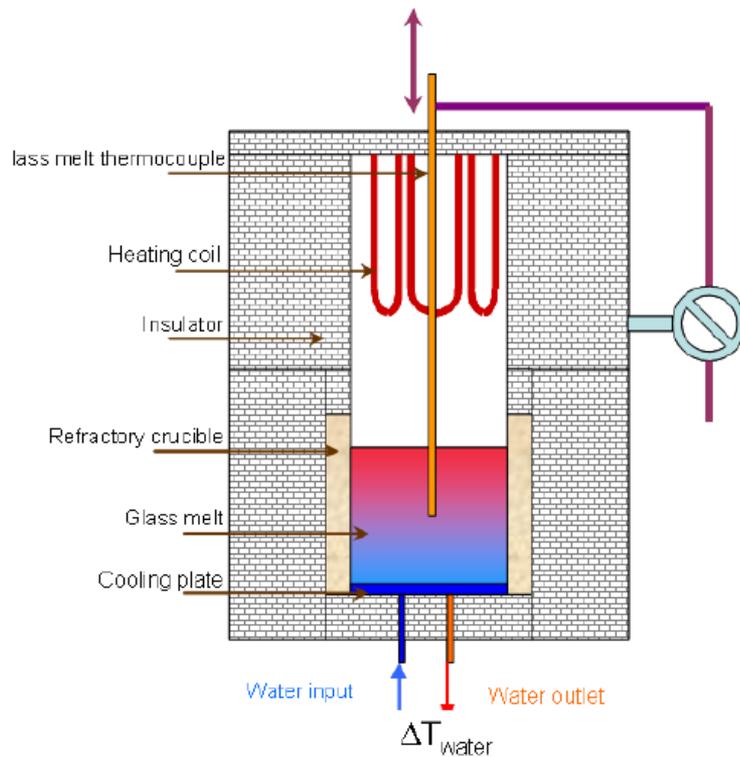


Micro-homogeneity

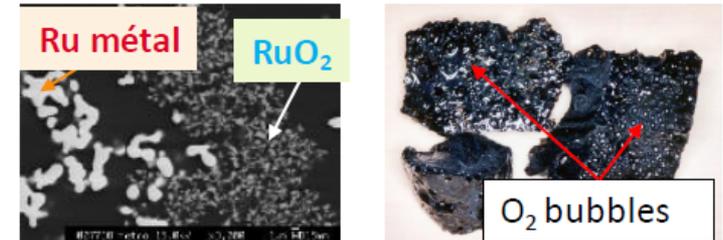


- Chromites
- Palladium-Tellure
- Cerium oxide
- RuO₂
- Silicophosphate
- Ca-molybdate

Thermal conductivity



Redox properties



Input data

- Glass frit composition
- (Fe²⁺/Fe³⁺) in glass frit
- Waste composition
- Nitrate concentration

Process parameters

- Melter atmosphere
- Temperature

Thermodynamic data on redox equilibria in the glass

- Fe²⁺/Fe³⁺
- Ce³⁺/Ce⁴⁺
- Cr³⁺/Cr⁶⁺
- Mn²⁺/Mn³⁺
- Ni²⁺/Ni³⁺
- Ru⁰/Ru⁴⁺.....

Oxygen fugacity in the final glass

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

Examples of glass formulations

FP solutions

- * Precisely defined and nearly constant for given spent fuels (slowly evolving with increased burn-ups)
- * Long term reliability needed (Hot metallic crucible / CCIM)
- * Furnace process with glass casting

⇒ Borosilicate glass

- * Homogeneous melt (except platinumoids elements)
- * limited crystallization in the final glass
- * Loading factor up to 18 wt%

Examples of glass formulations

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

* Highly corrosive ILW glass, low solubility of Mo into BSG

⇒ Designing a glass-ceramic melted material

- * Homogeneous melt (1250°C)
- * Crystallization with cooling
- * Loading factor up to 13 wt%

Examples of glass formulations

ILW waste contaminated with alpha emitters

- * Mainly arising from glove boxes used for MOX production (Melox facility)
- * Organic matter (30%) + metals (70%): gloves, power cables, metallic material or tools, dusters...

⇒ Aim:

- * **Volume reduction**
- * **Organics destruction**
- * **Immobilization of TRU into a durable matrix**

⇒ **Formulation of a new glass / metal package**

* Suitable for actinide incorporation : RN shall be confined in the glassy phase, not in the metallic part => Partition coefficients are understudy, depending on compositions

* **Description of a new ILW waste package**

- Leaching behaviour of the vitreous phase
- Corrosion mechanisms of the metallic part of the package
- Combination of both parts in expected disposal conditions



Examples of glass formulations

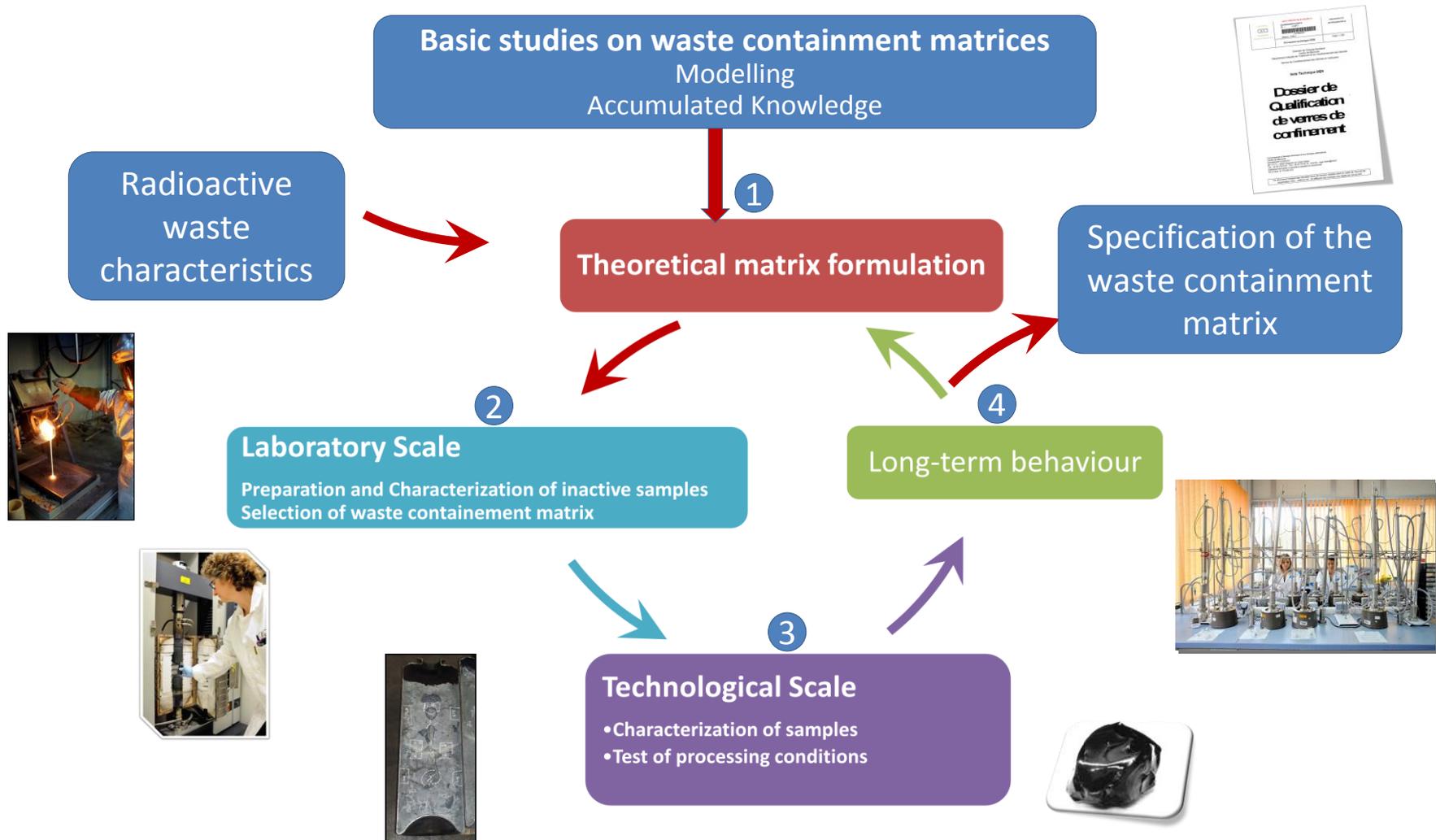
D&D operations, including legacy waste management

Material and process specification

- * 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

Glass formulation challenge:

- * Glass formulation that can be melted at low T 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 underdismantling



I. Nuclear waste to be vitrified

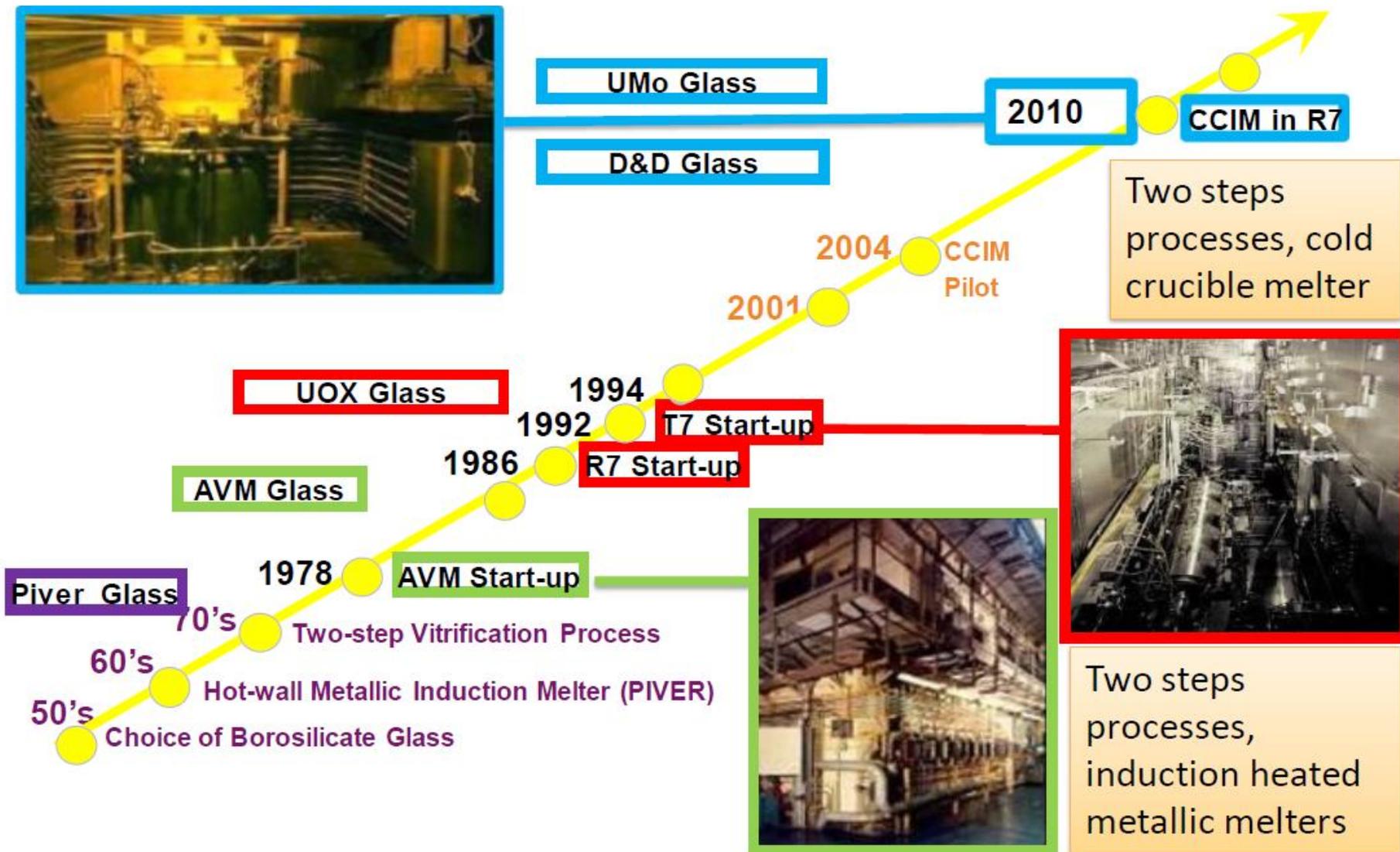
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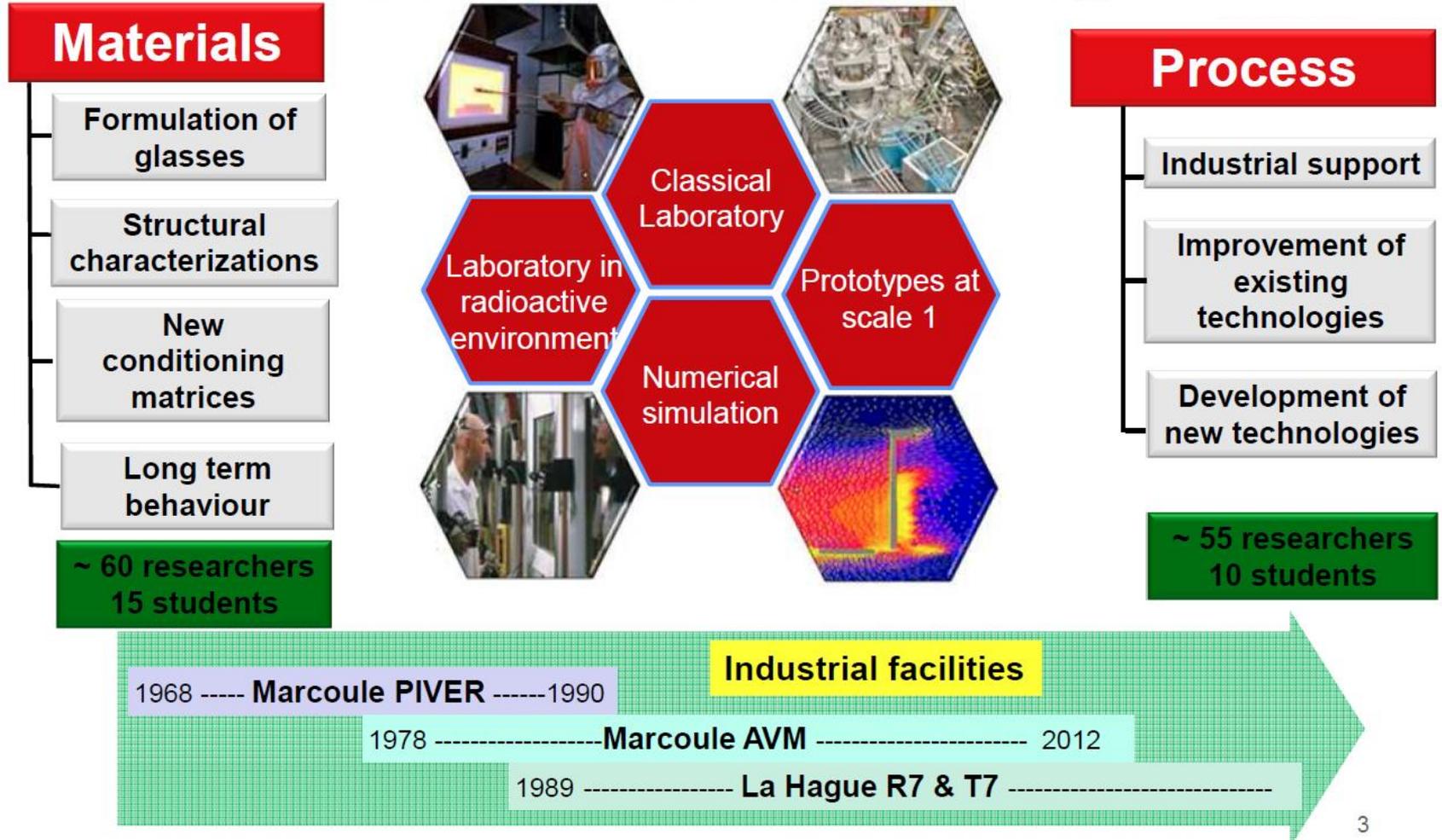
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HLW vitrification: from research to industry

From laboratory scale to industrial prototype

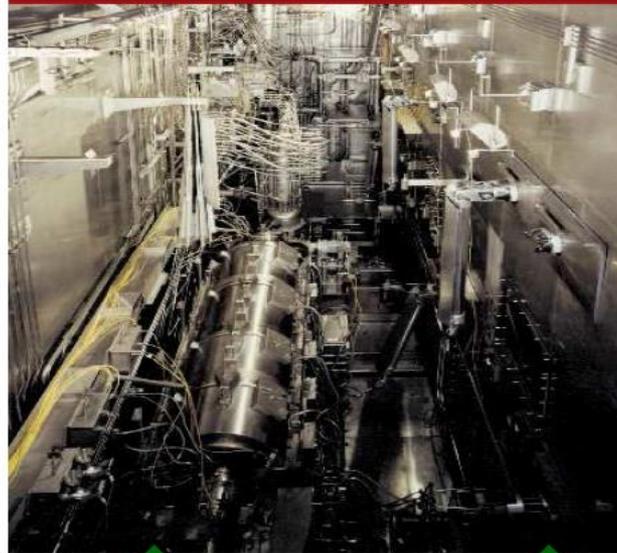


R&D in support of vitrification processes

Vitrification prototype
PEV Marcoule

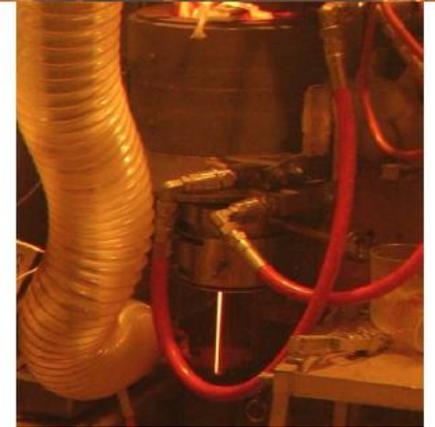


Hot cell for vitrification: La Hague



Support scale 1
Non-radioactive
environment

Vitrification prototype in hot cell
DHA Atalante



Support
Radioactive
environment

- ❑ More than 50 years of R&D on glass formulation / vitrification process at CEA
- ❑ Vitrification of 95% of the radioactivity coming from fuel recycling
- ❑ Production sites : Marcoule (1978 – 2010) La Hague (since 1989),

	Canisters (Number)	Mass of glass (Metric ton)	Activity (TBq)
AVM	3306	1220	22x10 ⁶
R7T7	17667	7032	269x10 ⁶
Total	20973	8252	291x10 ⁶



- ❑ Continuous adaptation and evolution of the process up to industrial scale
- ❑ 6 specifications of nuclear glass approved by the safety authority

► **Keys to success in HLW vitrification:**

- A major program of sustained and continuing R&D (rather than by fits and starts)
- Continuous interaction between “material definition”, “technological research” and “long-term behavior”;
- Strong synergy with industry (ORANO) leading to the creation of a Joint CEA-ORANO Vitrification Laboratory in 2010.

Thanks for your attention

Acknowledgments



Glass elaboration and characterization

V. Ansault, T. Blisson, M. Chartier, V. Debono, S. Mure, J. Renard, C. Vallat

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