Modeling of liquid nuclear waste vitrification: focus on the chemical processes

Z. Nabyl *[1], S. Schuller [2], R. Podor [3], J. Lautru [3], G. Quintard [3], C. Castano [1], A. Artico [1], V. Benavent [1], M. Delaunay [1], E. Sauvage [1]

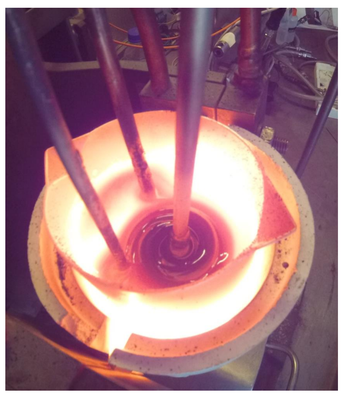
[1] CEA/DES/ISEC/DPME/LDPV, Université de Montpellier, Marcoule, France
[2] CEA/DES/ISEC/DPME, Université de Montpellier, Marcoule, France
[3] ICSM, UMR 5257 CEA-CNRS-UM2-ENSCM-F-20207 Bagnols sur Cèze, France

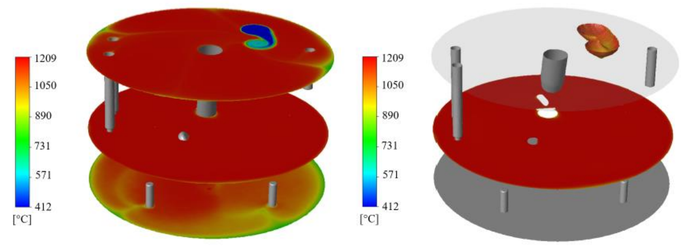
* zineb.nabyl@cea.fr

CONTEXT AND OBJECTIVES

- High-level nuclear waste: processing in **glass**, stable and sustainable at the atomic scale
- Vitrification process in France:
  - **Nitric solution** of nuclear fission and actinide product
  - **Calcination** of nitric solution with calcination additive
  - **Addition of calcine and glass frit** in the vitrification melter
- **3D multi-physics modeling of high-level nuclear waste vitrification process** in cold crucible [1,2]
- Chemical and thermal reactions during calcine dissolution in the glass [3,4]
- Other way of vitrification, by **liquid feeding:** liquid radioactive waste directly added at the surface of vitrification melter → **No modeling of liquid feeding vitrification process yet**

→ Acquire the chemical data needed to model liquid radioactive waste vitrification process
→ Predict and optimise vitrification process by liquid feeding





Modeling of vitrification process in cold crucible. Coupling of the 0D thermal kinetic model to the 3D model [3].

Vitrification of simulated nuclear waste at experimental scale, with a mechanical agitator

Drying of the solution (UOX type) → Crushing → Mixing with glass frit powder (glass frit:glass ratio of 0,76) → Thermal treatment

METHODOLOGY

- Characterize the **secondary phases** and the **chemical reaction** between the liquid solution and glass frit
- Determine the **chemical kinetic** of the liquid dissolution in the glass frit

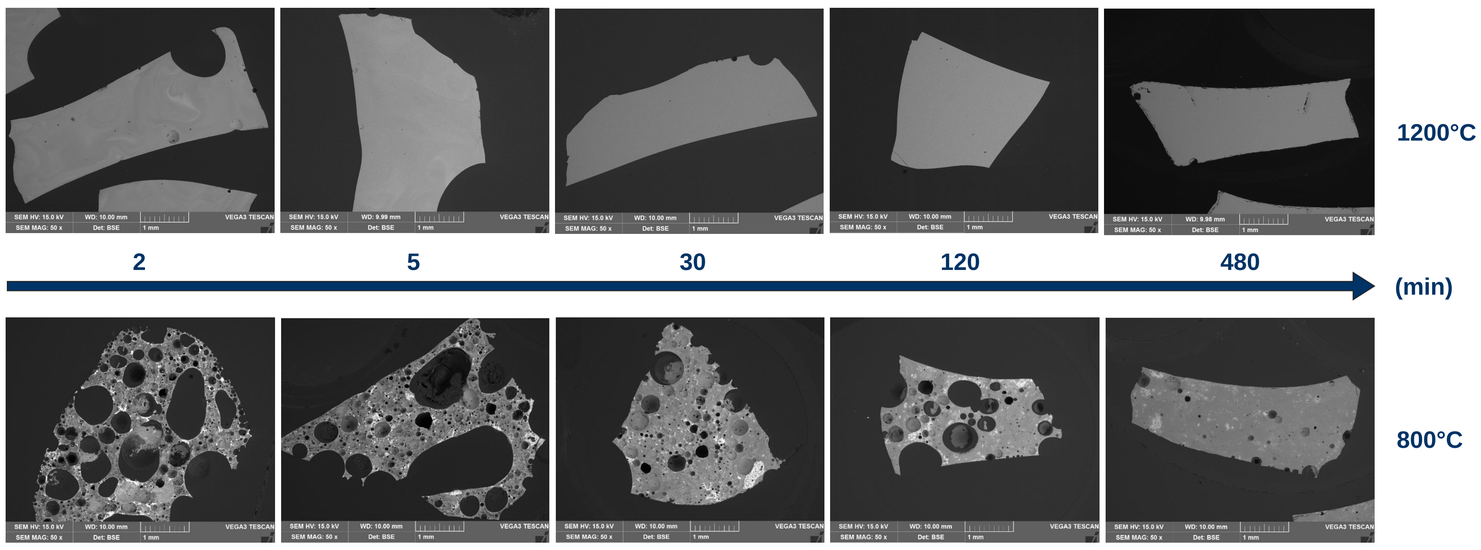
Noyes-Witney equation (1897) $C_i(t) = C_{is}(1 - e^{\frac{-t}{\tau_i}})$

- **Experiments of thermal treatment**, in muffle furnace at **800 to 1200°C** and during **2-5-30-120-480 minutes** (25 samples)
- Study of **glass microstructure** and **phase identification**
- Analytical protocol to study **glass composition and element concentration evolution** (SEM)

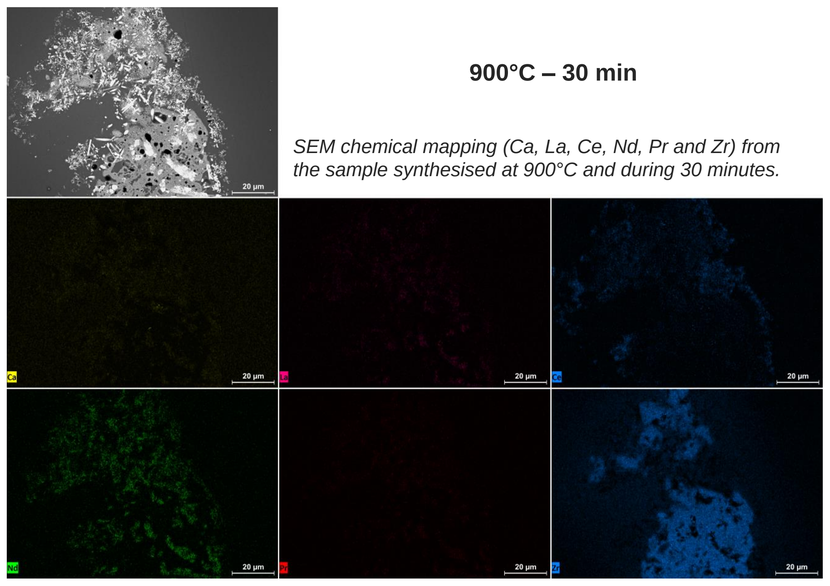
→ Parameterization of concentration evolution; kinetic parameters relative to waste liquid dissolution in glass frit

GLASS CHARACTERISATION

- Evolution of **glass morphology** and **secondary compound formation and dissolution** in function of temperature and time
- Order of dissolution in the glass: **Ca-REE silicate, Ce- oxide, Zr- (Ce-) oxide**



BSE images of the glass morphology and secondary phase evolution in time at 800 and 1200°C.

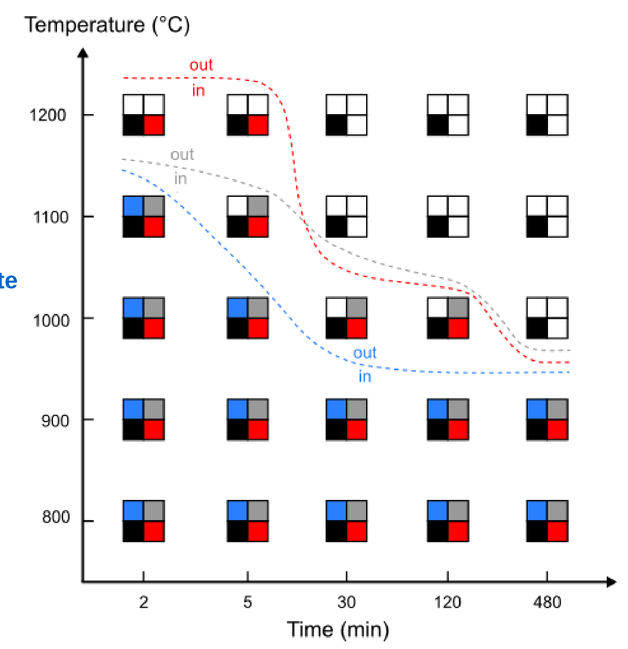


900°C – 30 min

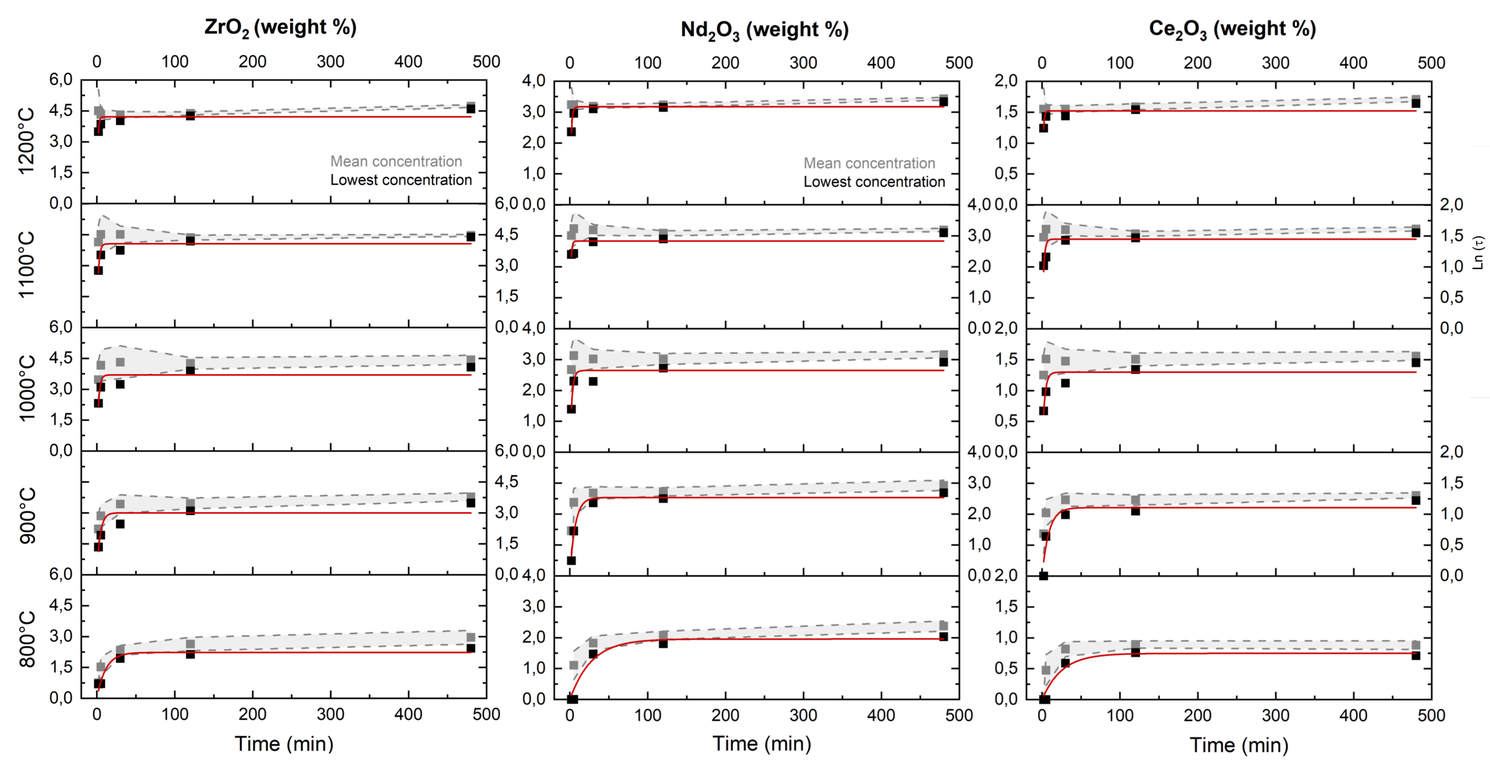
SEM chemical mapping (Ca, La, Ce, Nd, Pr and Zr) from the sample synthesised at 900°C and during 30 minutes.

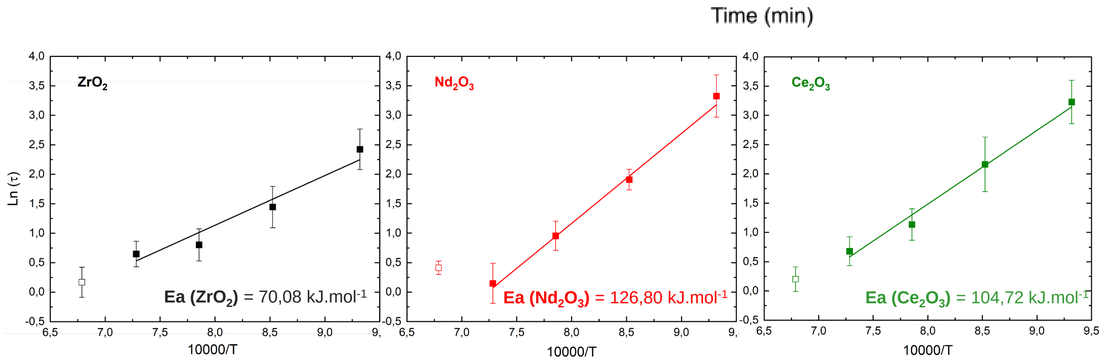
DISSOLUTION KINETIC

- Parameterization of concentration evolution to describe the **lowest kinetics of the secondary phase dissolution**
- C_s (saturation concentration) and **τ** (saturation time) for Zr, Ce and Nd), at each temperature
- **Ea** (activation energy) and **A** (pre-exponential factor)
- Secondary phase formation:
  - **Zr- (Ce-) oxide and Ce- oxide → inherited from the dried solution**, dissolution in the glass frit
  - **Ca-REE- silicate → intermediate compounds**, formation from the dried solution dissolution



Phases:
Ca-REE- silicate
Ce- oxide
Zr- (Ce-) oxide
Glass





CONCLUSION

- **Acquisition of parameters** at laboratory scale to model the vitrification process by liquid feeding in cold crucible
- **Proxy of the kinetic reaction** (Zr-Ce- oxides, Ca-REE- silicate)
- Perspectives: experiments at intermediate scale (liquid directly at the surface of the glass melt) → **to a global 3D modeling of the elaboration of nuclear glass by liquid feeding**

References: [1]. Sauvage E., PhD thesis (2007); [2] Barba Rossa G., PhD thesis (2017); [3] Paraiso K., PhD thesis (2021); [4] Paraiso et al., Journal of Nuclear Materials, 569, 153878 (2022).