Delayed Molecular Hydrogen Production in Portlandite Under Irradiation: Reaction Mechanisms and Consequences for the Storage of Radioactive Waste

Thibaut Herin, Stéphane Poyet, Pascal Bouniol, Sophie Le Caër

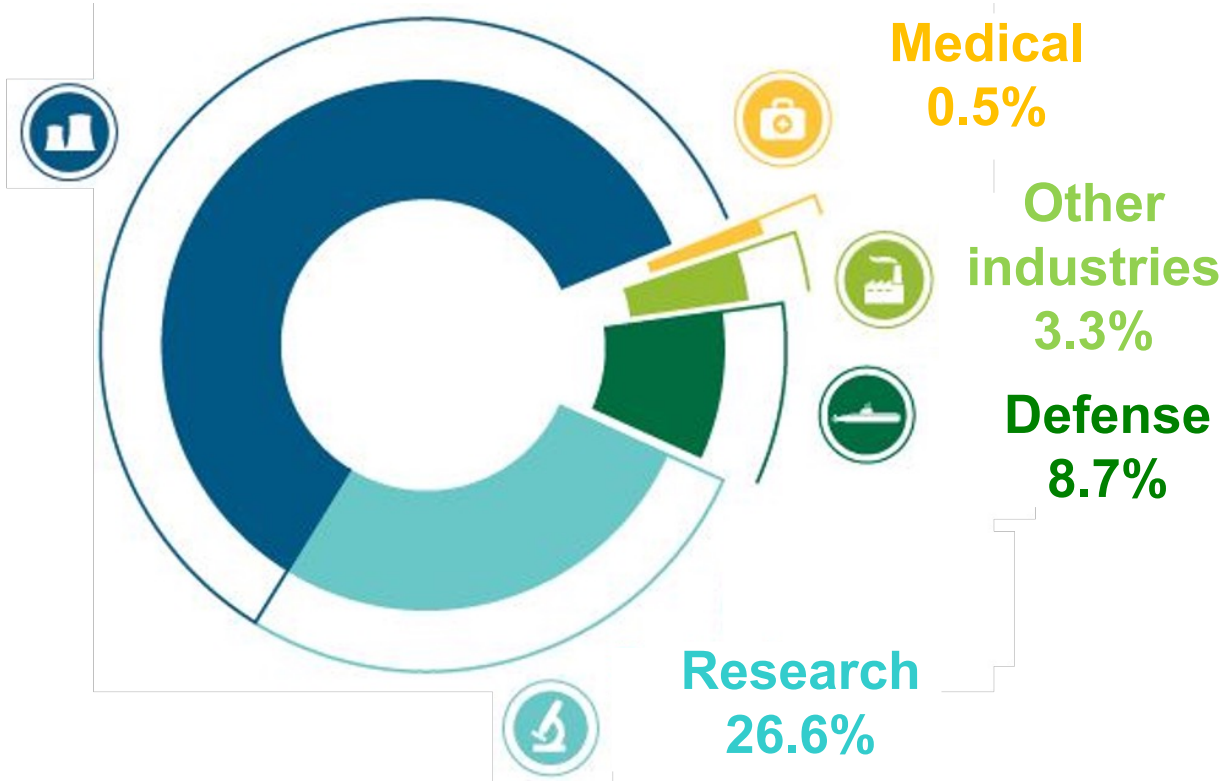
CEA/Saclay, 91191 Gif-sur-Yvette, France

sophie.le-caer@cea.fr

Background to the study

- **Every year, France produces significant amounts of radioactive waste (60 000 m^3).**
  - 70% of electricity is generated by nuclear power
  - Nuclear deterrence, naval nuclear propulsion, radiotherapy, research centers, etc.

Different sources of radioactive waste in France



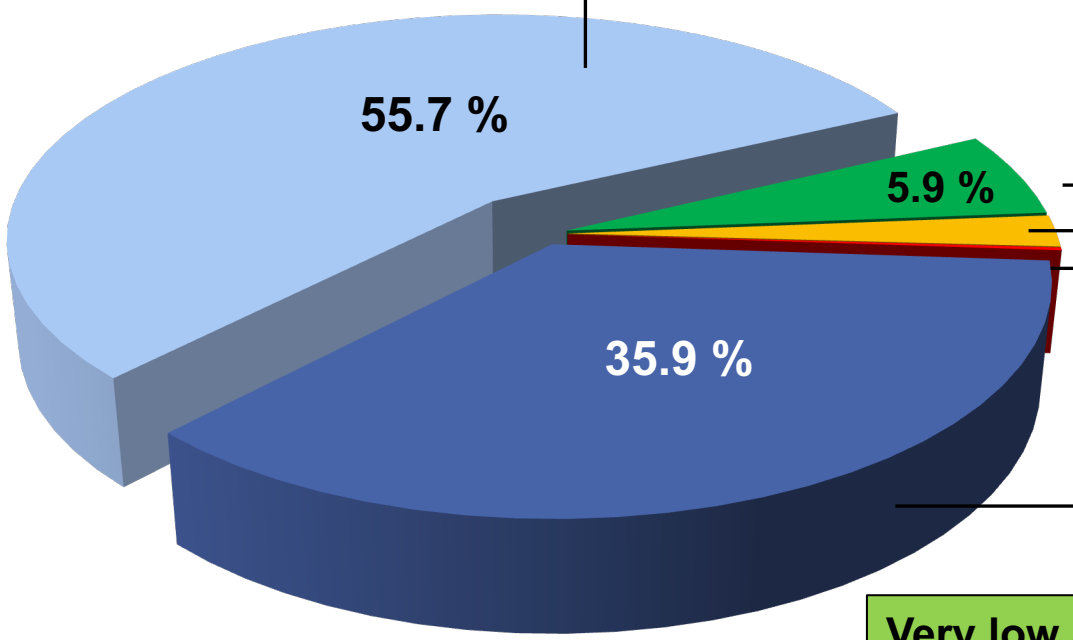
In 2021, the volume of radioactive waste is estimated at 1.76 million m^3

Equivalent to 3 French stadiums

Different types of radioactive waste

Types of radioactive waste

Several types of radioactive waste classified by activity and lifetime



Low and medium activity short-lived
Radioactivity: 0.12

Long-lived low-level activity (LLL-LL)
Radioactivity: 0.01

Long-lived average activity (LLA)
Radioactivity: 2.7

High activity (HA)
Radioactivity: 97.2

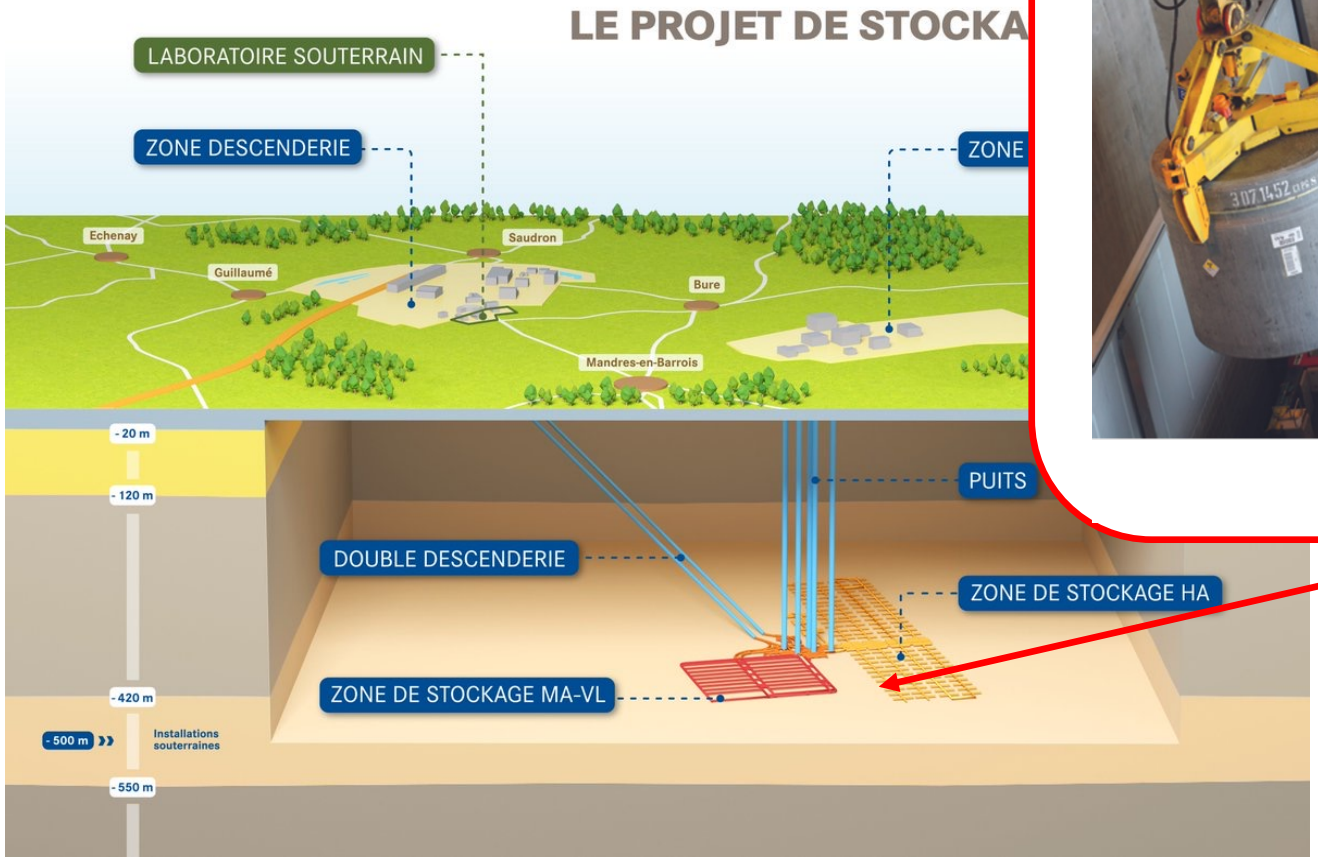
Very low activity (VLA)
Radioactivity: 0.0004

Breakdown of radioactive waste by volume

- **Short life (less than 300 years): surface storage**
- **Long life (several hundred thousand years): deep disposal**

Solution chosen for LLA and HA waste

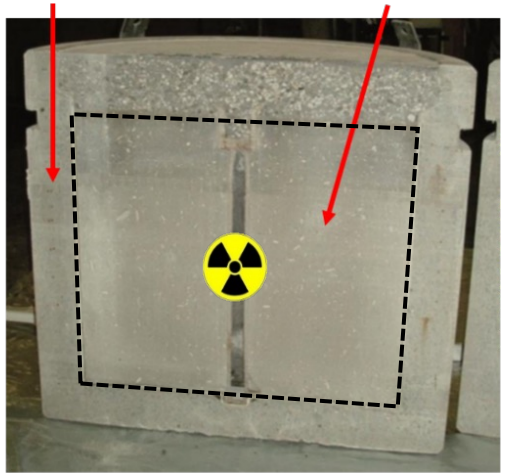
Deep geological disposal



Objective: isolate waste for several millions years

Packaging of LLA waste

Concrete shell *Cemented waste*



Cemented sludge and radioactive concentrates (EDF)

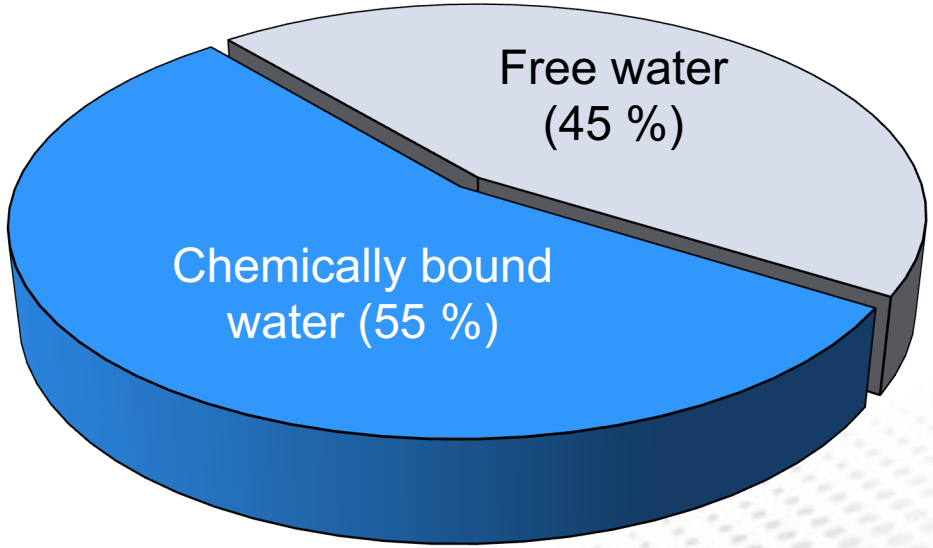
- **Cementitious materials:**
  - Low-cost materials
  - Well-known materials
  - Radiation-resistant materials
  - Basic environment

Water in cement

Portland cement

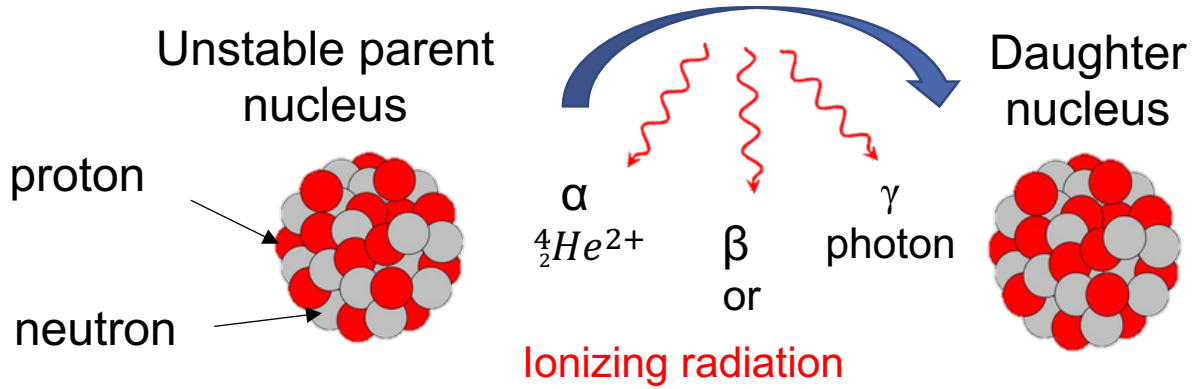
The role of water

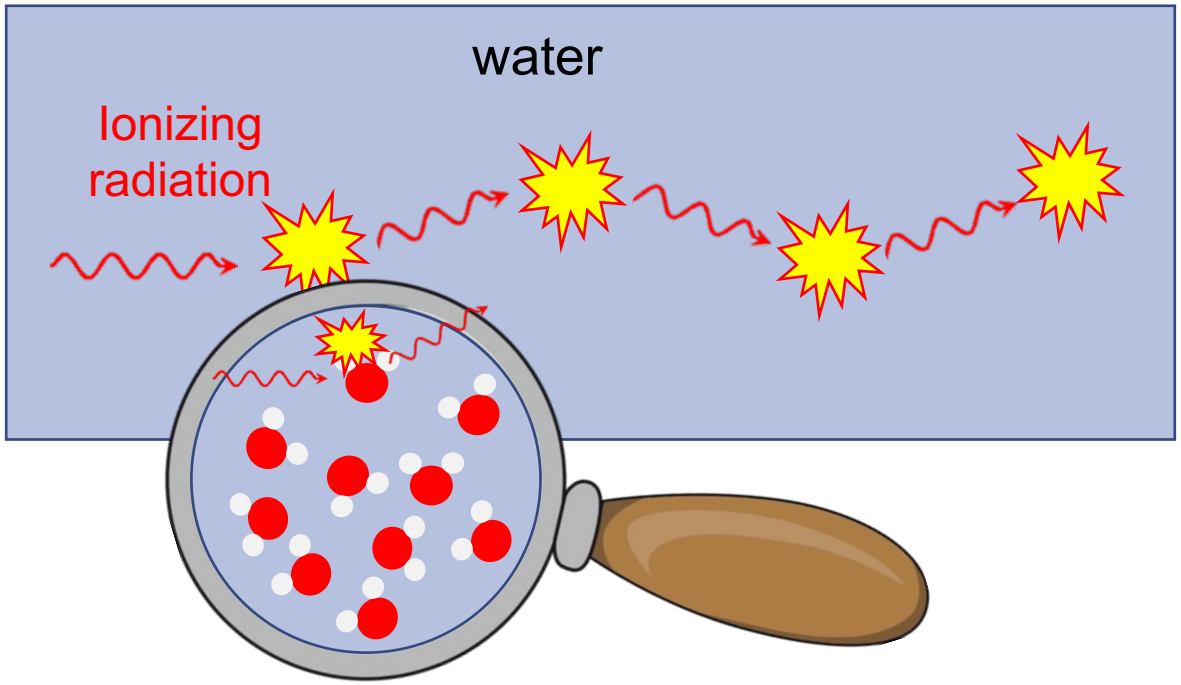
- Produce a material with rheological behavior compatible with processing
- React with cement to form cementitious hydrates (cement hydration)
- In theory: $\frac{mass\ water}{mass\ cement} \sim 0.23$
- In practice: $\frac{mass\ water}{mass\ cement} \sim 0.42$

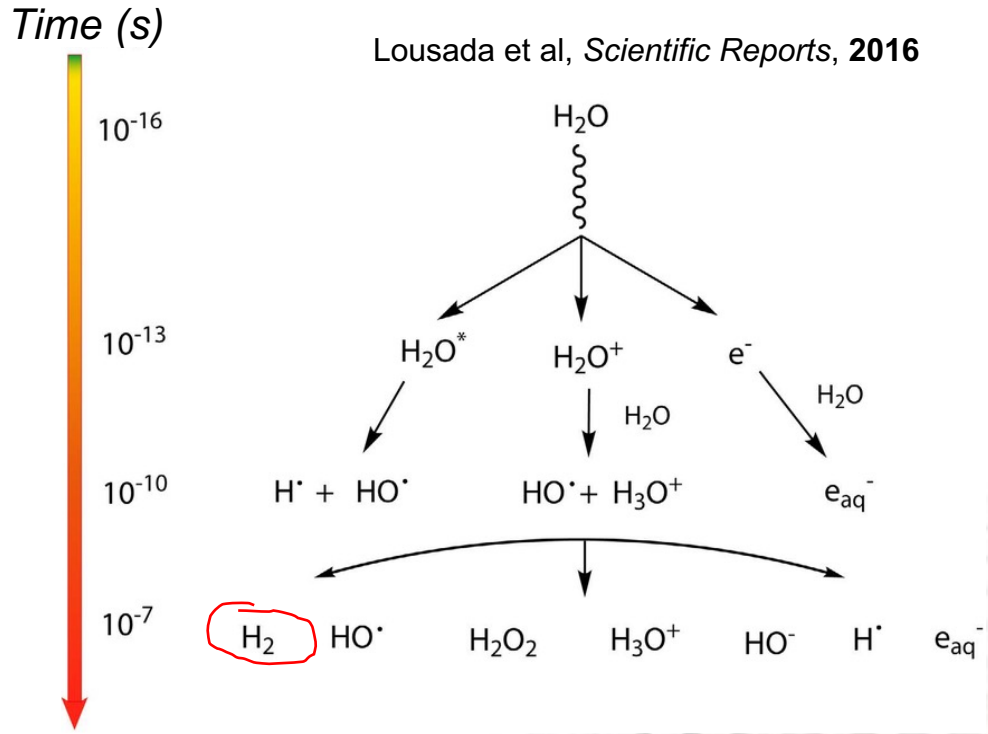


Water distribution in cement paste

Interaction of water with ionizing radiation







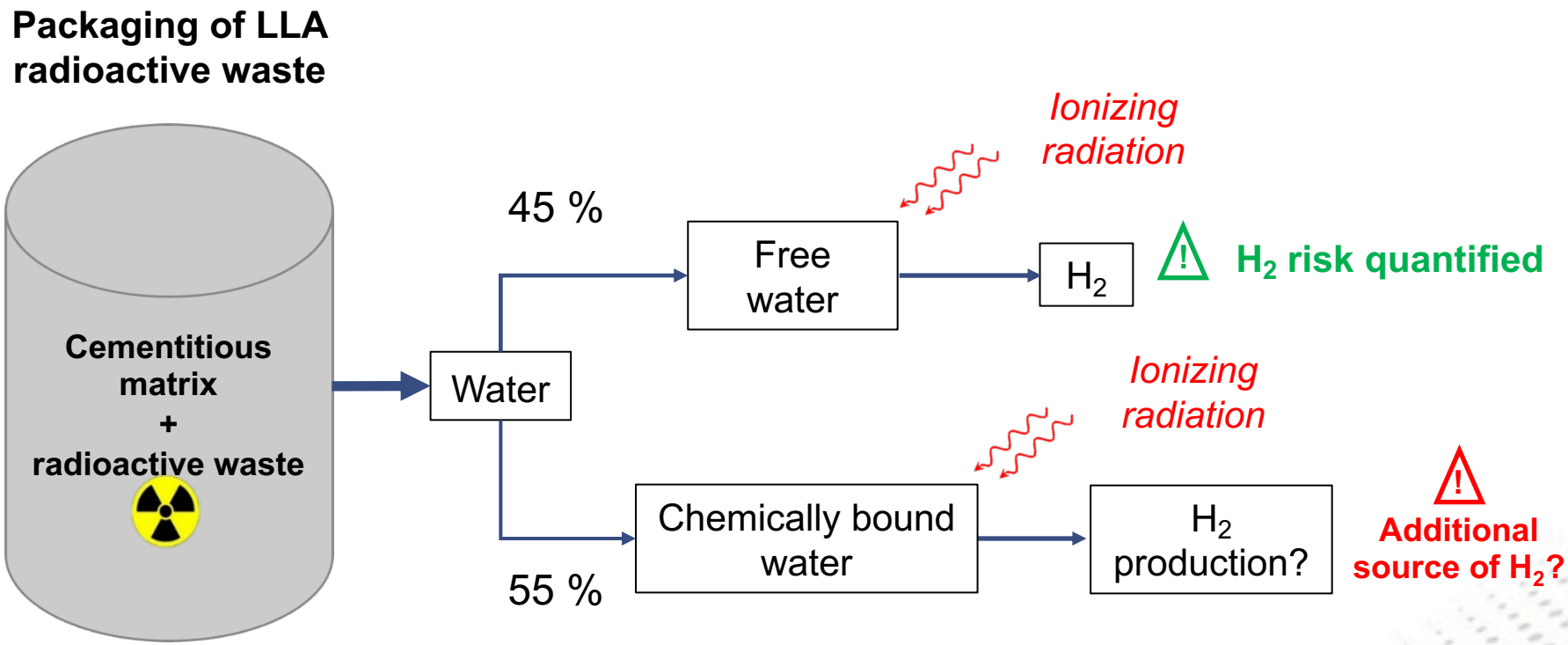
Lousada et al, *Scientific Reports*, **2016**

The dihydrogen risk

Why is H_2 potentially problematic?

- A potentially explosive gas under certain conditions
- Explosive limit of H_2 in air: 4% by volume

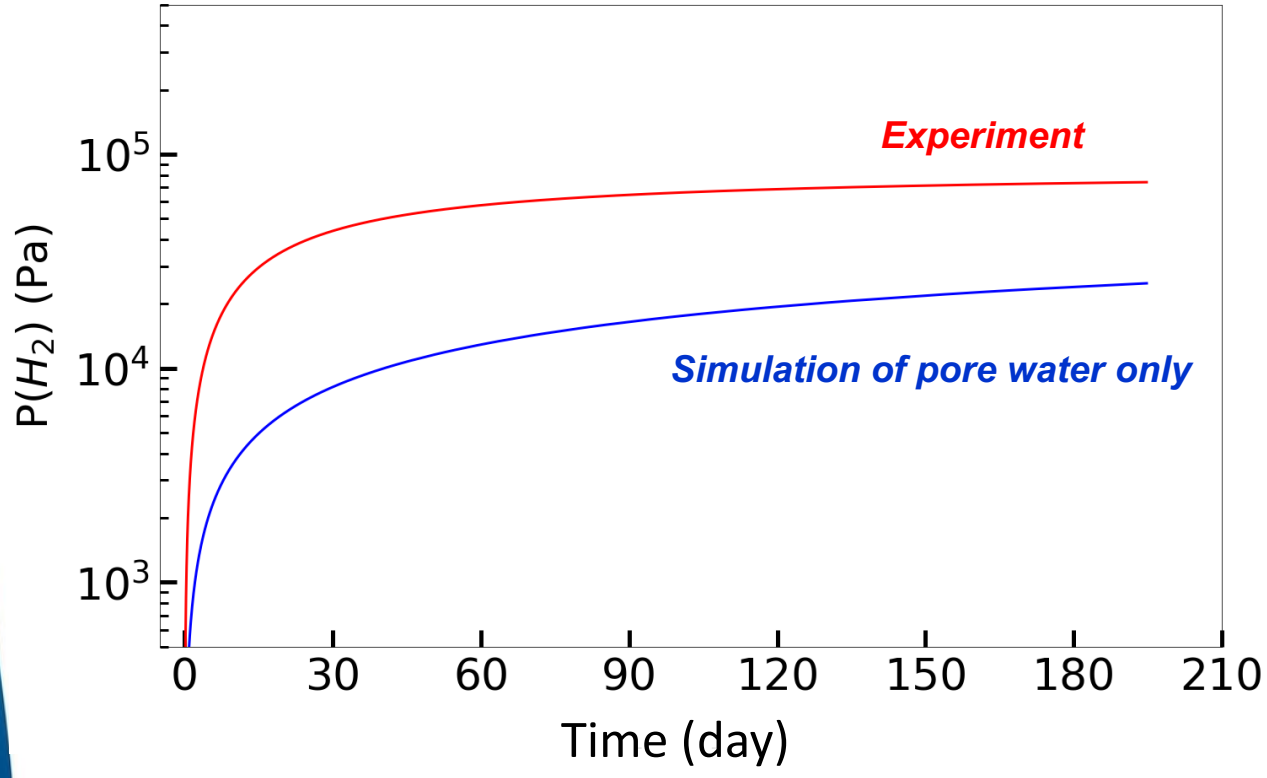
Need to assess the various H_2 source terms



State of the art

Systemic study by Bouniol (2022)

- Comparison of experimental H_2 production (hydrated and irradiated C_3S paste) and theoretical production



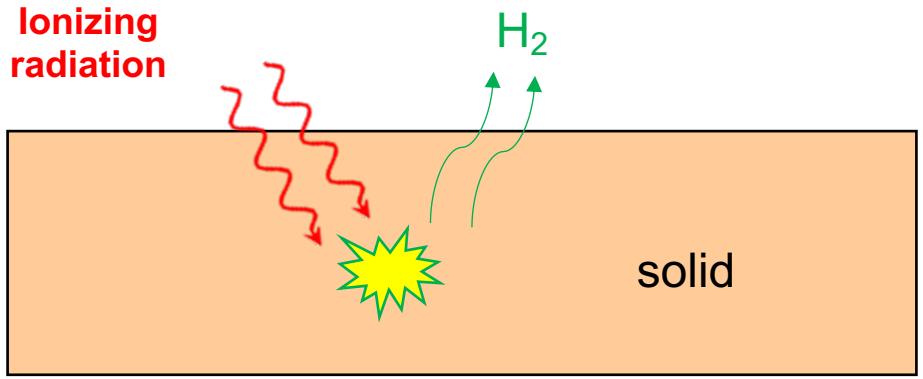
Study results

- Radiolysis of free (pore) water alone does not account for the H_2 production observed.
- Radiolysis of solid phases must exist

Bouniol P. *J Adv Concr Technol.* **2022**;20(2):72-84

Controlling the surface state of materials

Solid with no adsorbed water



Selected study configuration

Modeling cement paste

Portland cement

composition

50 - 65 % Ca_3SiO_5 ✓

15 - 20 % Ca_2SiO_4 ✗

5 - 15 % $Ca_3Al_2O_6$ ✗

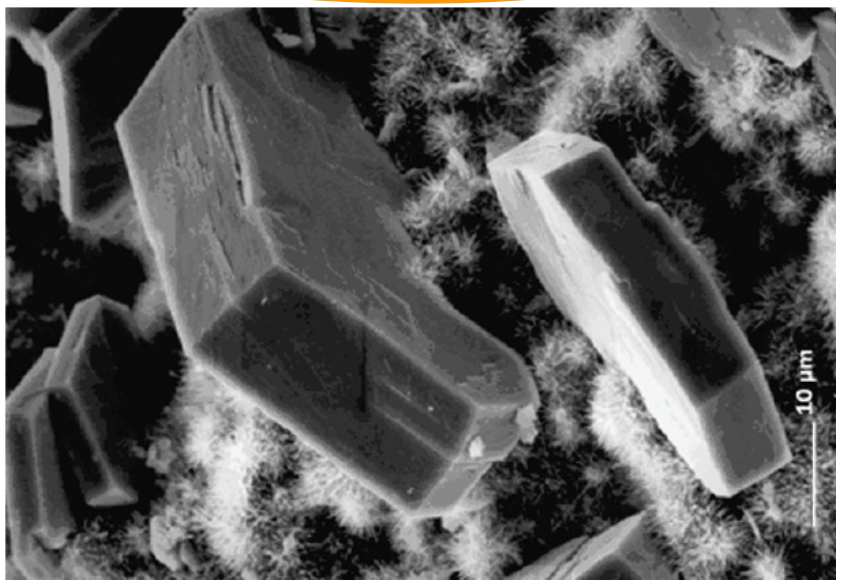
5 - 10 % Ca_2AlFeO_5 ✗

+ water →

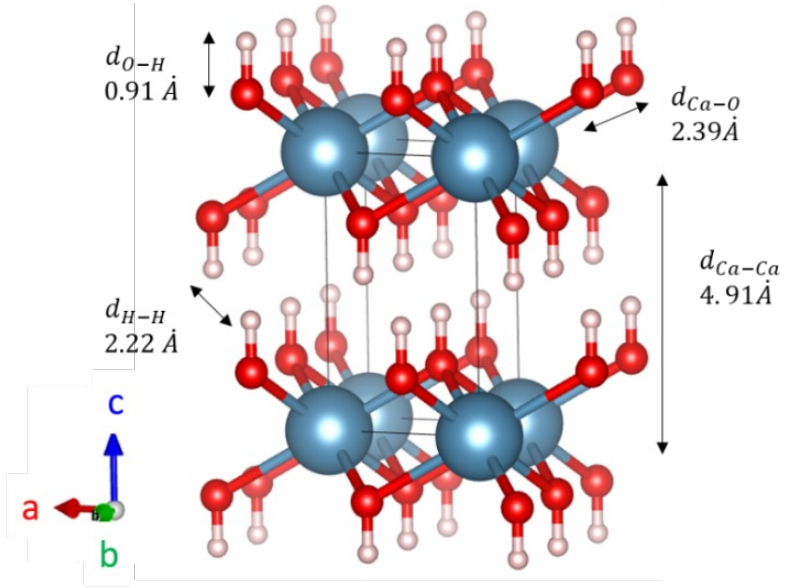
Portlandite: $Ca(OH)_2$

C-S-H: $(CaO_{1.70})SiO_2\ (H_2O)_{1.80}$

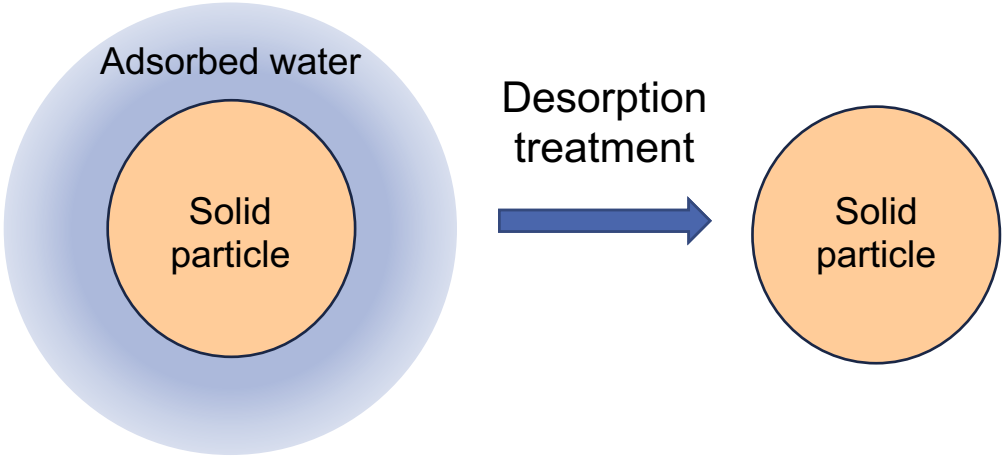
$Ca(OH)_2$



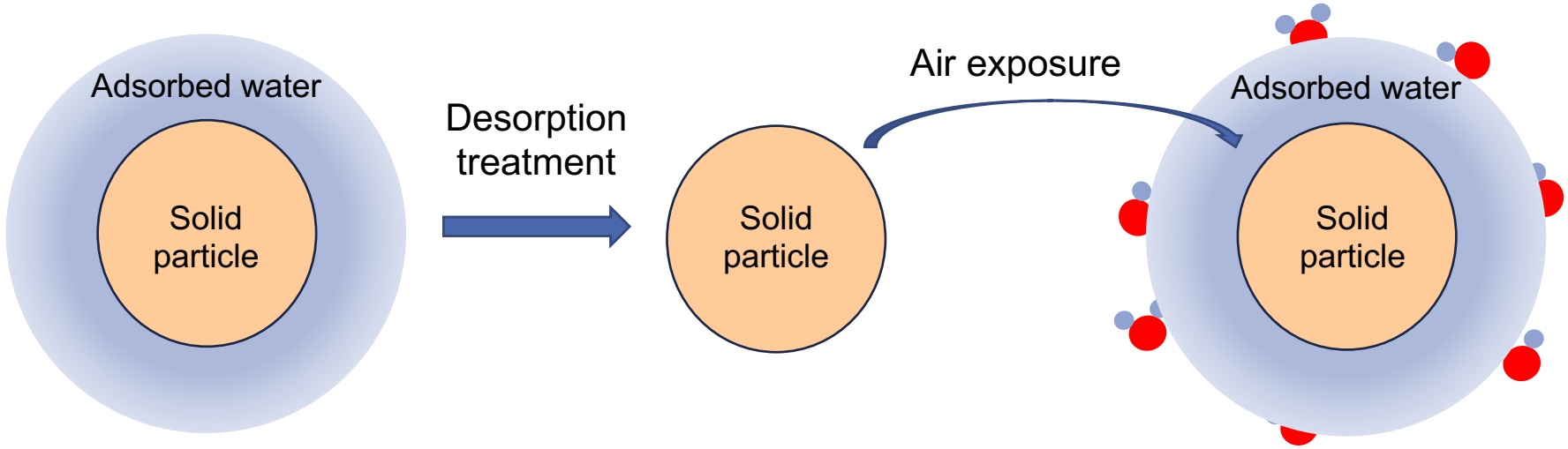
Nonat A. Chapter 2: Hydration of cements. In: La durabilité des bétons (2e Edition). Presses de l'Ecole Nationale des Ponts et Chaussées; **2008**. p. 35.



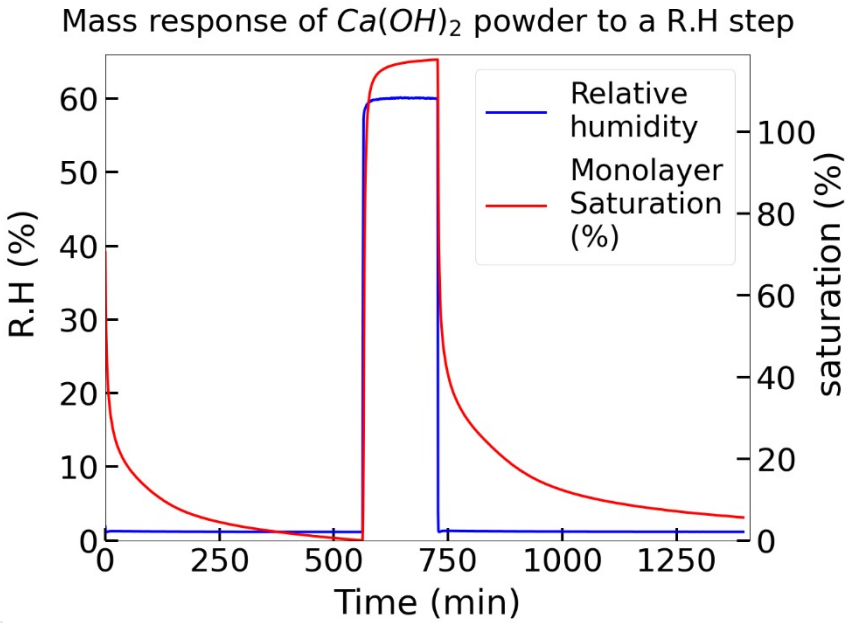
Water re-adsorption kinetics



Water re-adsorption kinetics

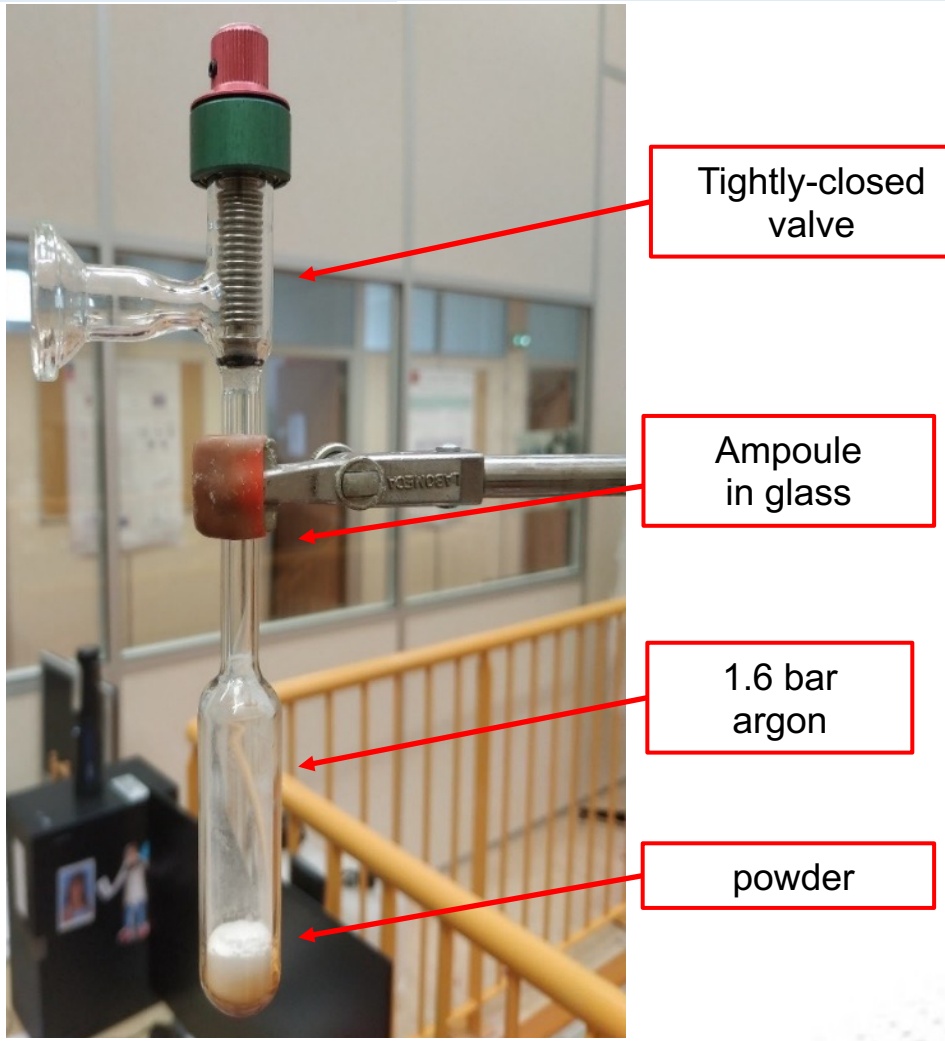


- **Measurement of water re-adsorption kinetics**
  - Use of vapor sorption dynamics (VSD)
  - Exposure of samples to a range of relative humidity 0-60%.
  - Measuring mass change



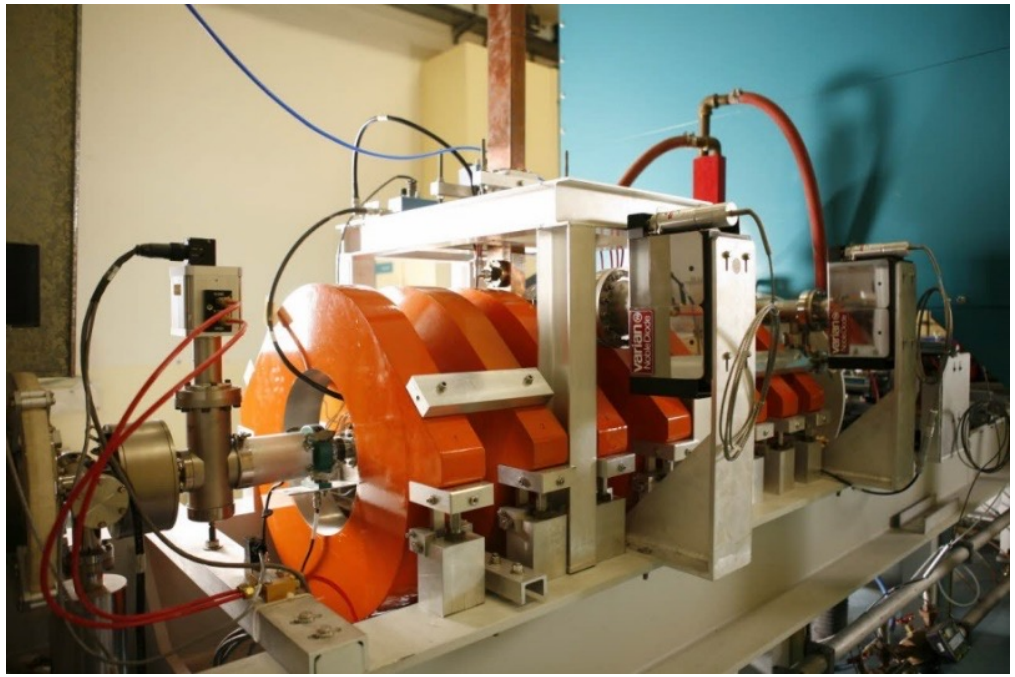
Measurement of H_2

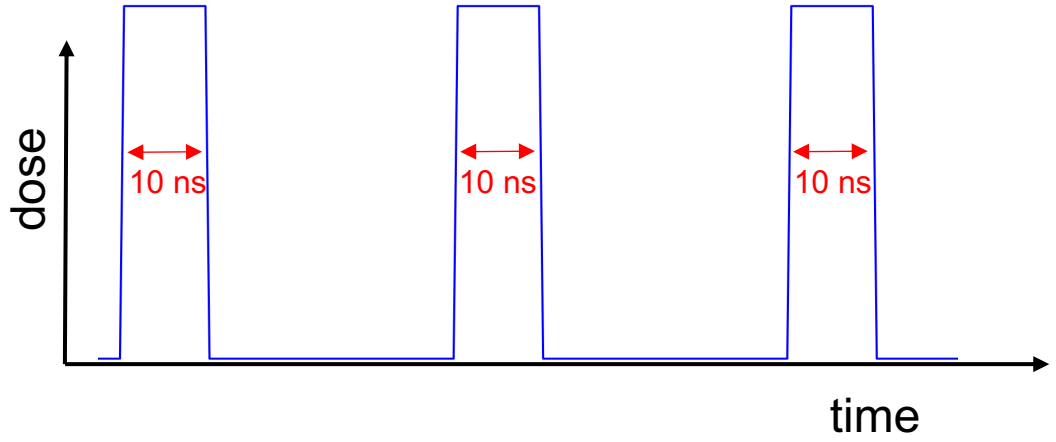
- **Sample preparation**
  - Minerals in powder form
  - Desorption and irradiation treatment in the same ampoule
  - Possibility of sampling ampoule atmosphere after irradiation
  - Measurement of H_2 production by gas-phase micro-chromatography (μ-GC)



Sample storage in glove box with ultra-pure argon & H_2O content < 0.5 ppm

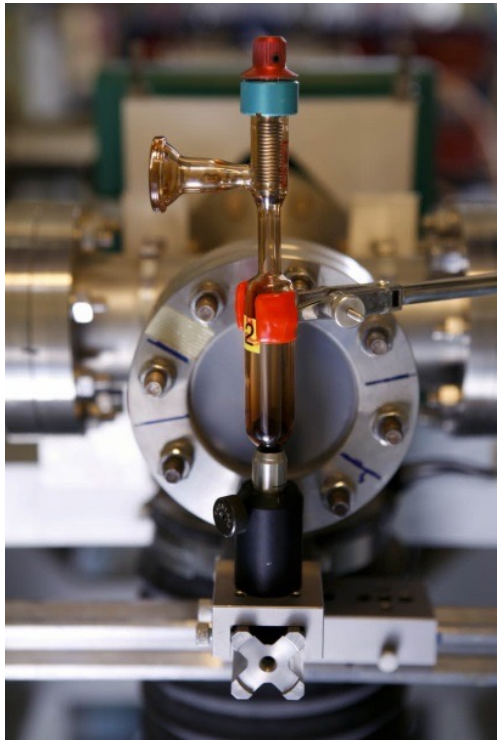
The ALIENOR linear electron accelerator





Ampoule positioning

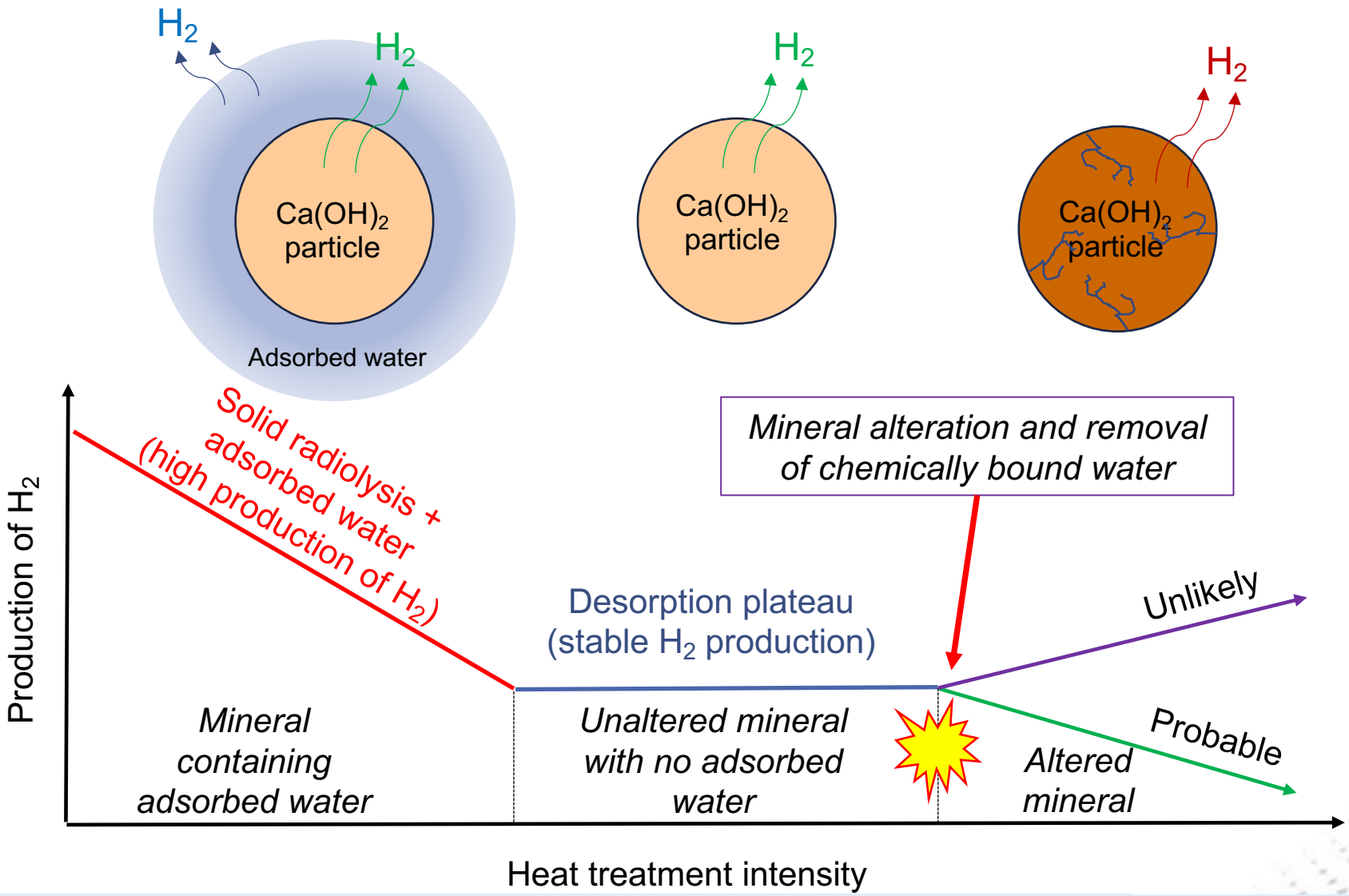
Irradiation with Jorge VIEIRA



10 MeV electrons
Pulse duration: 10 ns
Repetition frequency: 1-10 Hz
Dose: 20 Gy/pulse
Dose rate: 2 ×10¹⁰ Gy/s

Removal of adsorbed water from portlandite

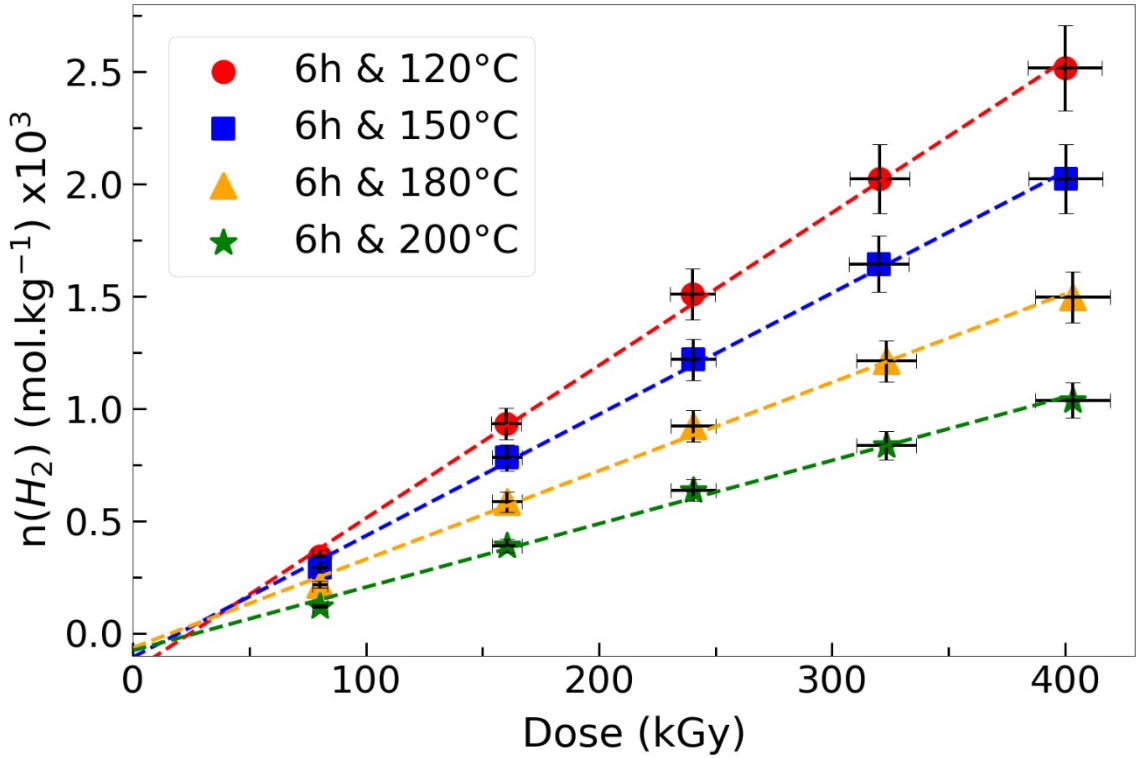
Using radiolysis to check for the presence of adsorbed water



Removal of adsorbed water from portlandite

Desorption treatment

- Water removal by heat treatment under primary vacuum (0.1 - 1 mbar)
- Treatment of increasing intensity
- Measuring H_2 radiolytic yield



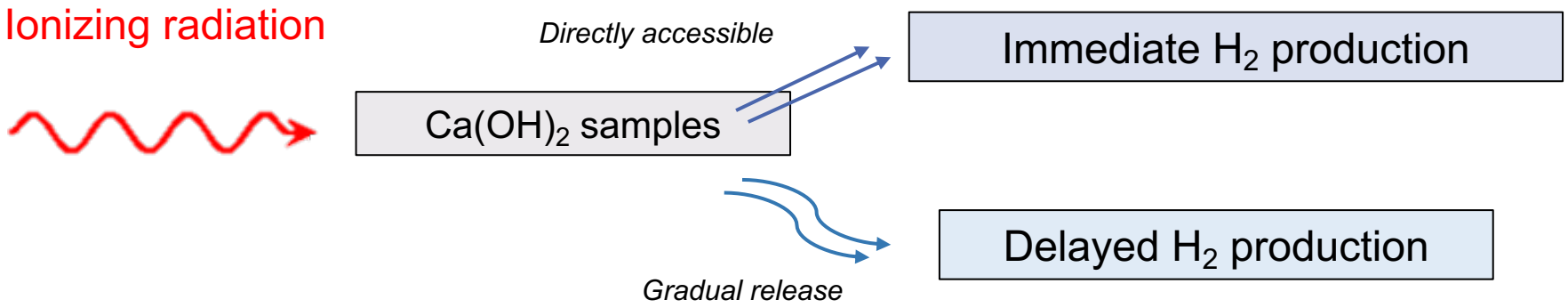
Time/temperature mapping

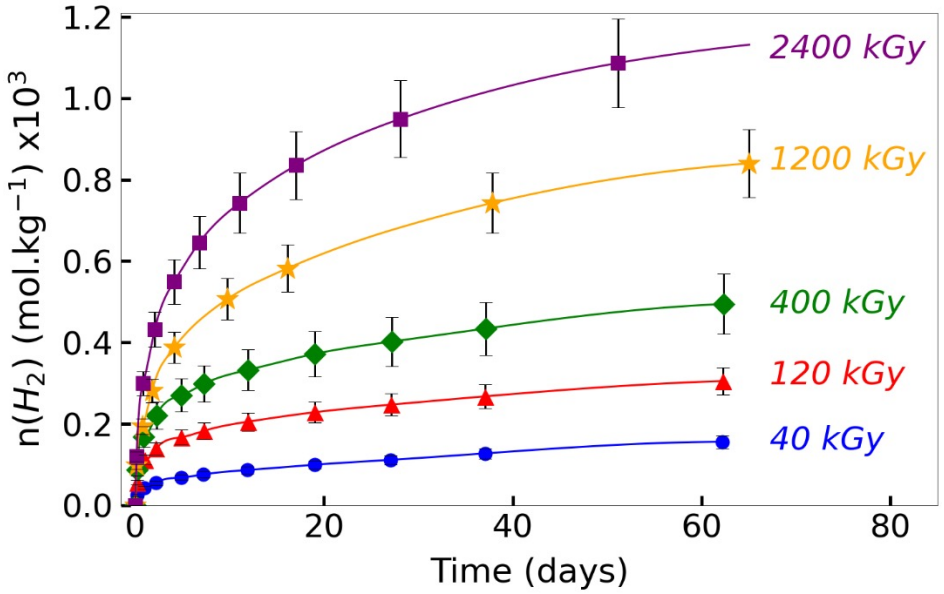
Time \ Temperature	120°C $G(H_2)$ (mol.J^{-1}) ×10^9	150°C $G(H_2)$ (mol.J^{-1}) ×10^9	180°C $G(H_2)$ (mol.J^{-1}) ×10^9	200°C $G(H_2)$ (mol.J^{-1}) ×10^9
6 h	6.8 ± 0.7	5.4 ± 0.5	3.9 ± 0.4	3.0 ± 0.3
16 h	4.9 ± 0.5	4.8 ± 0.5	3.5 ± 0.4	3.6 ± 0.4
64 h	5.5 ± 0.5	3.6 ± 0.4	3.0 ± 0.4	3.4 ± 0.4

Herin et al., *Rad. Phys. Chem.*, 243, 113715 (**2026**)

Delayed production of H_2 in portlandite

- **After initial irradiation, portlandite progressively releases H_2**



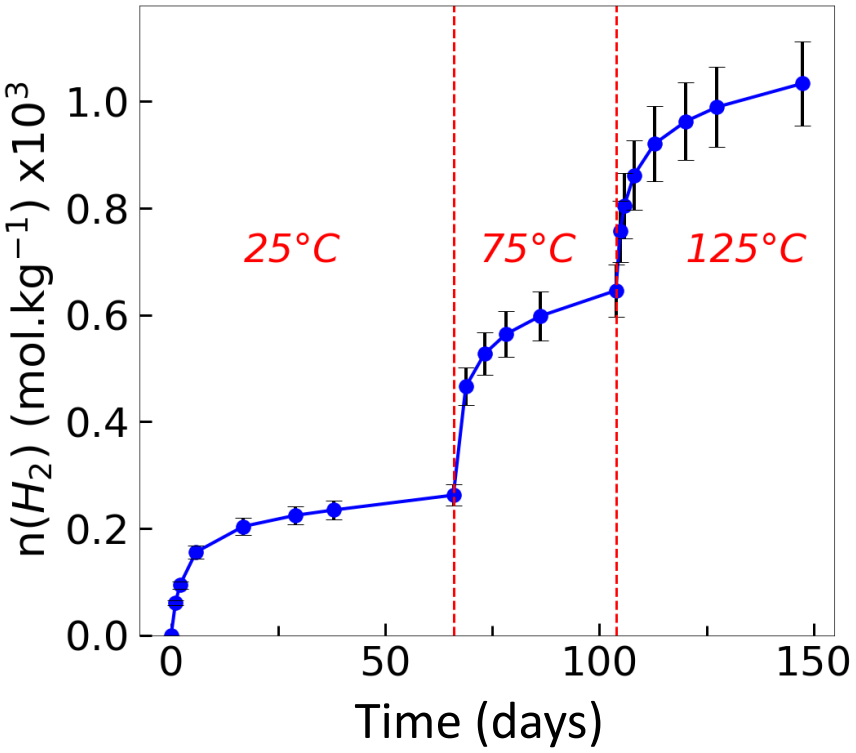


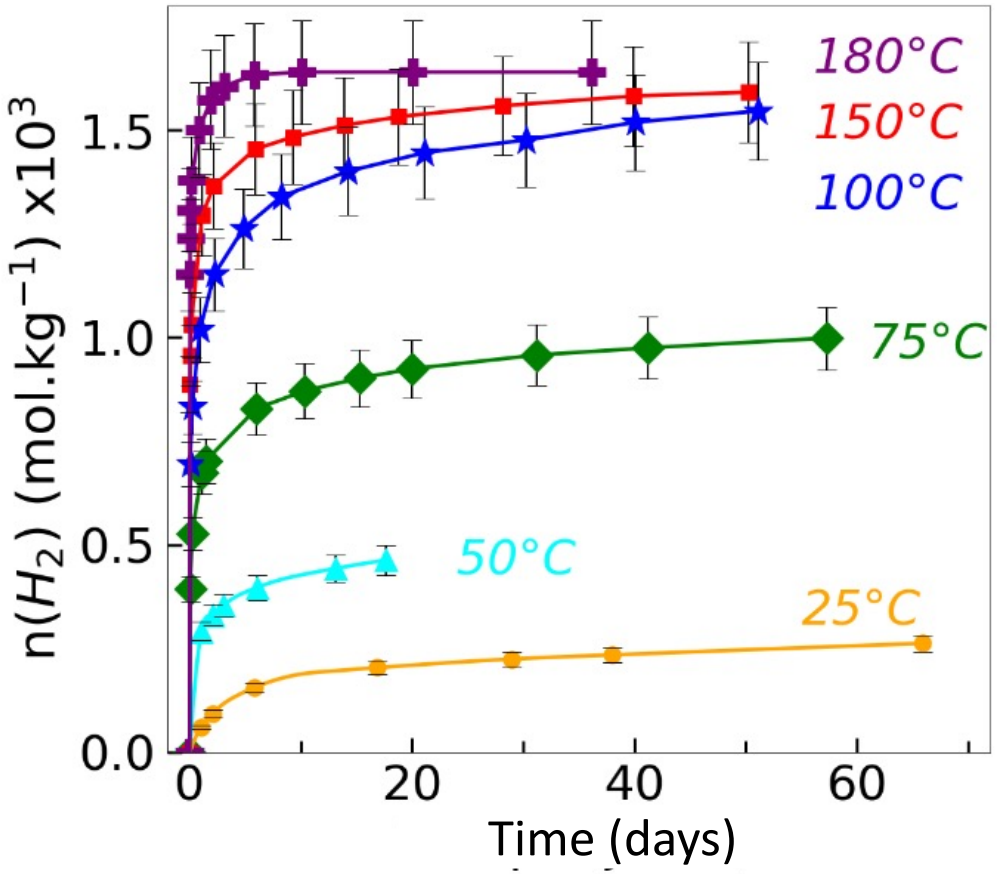
- **Delayed production of H_2**
  - Similar phenomenon demonstrated on aluminum oxy(hydroxides) by Kaddissy (2016)
  - H_2 not directly accessible
  - Delayed production increases with the initial dose delivered

Herin et al., *J. Phys. Chem. C*, 127, 20245 (**2023**)

Influence of temperature on delayed H_2

- **Delayed production is heat-activated**
  - Irradiation at 400 kGy and delayed production monitoring for several temperatures
  - Convergence at temperatures above 100°C





Type of H_2 considered	$G(H_2)$ (mol.J^{-1})
Immediate	3.0×10^{-9}
Immediate + delayed	1.2×10^{-8}

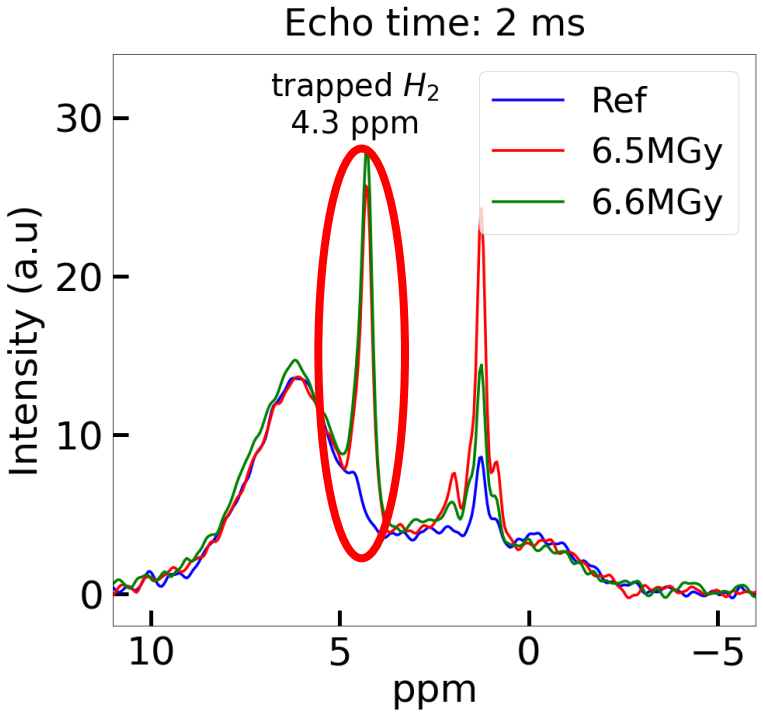
Horie et al. *J. Phys. Chem. C*, 127, 20245 (**2023**)

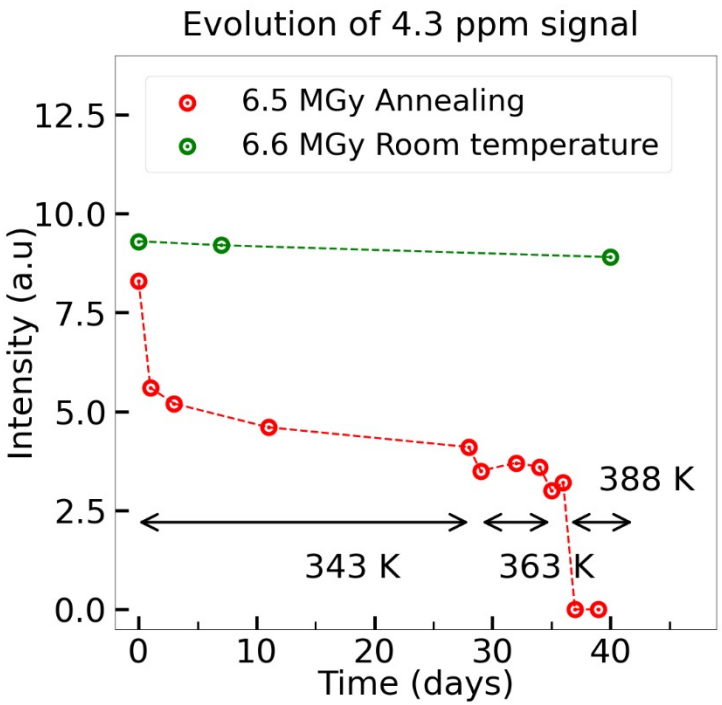
Origin of delayed H_2

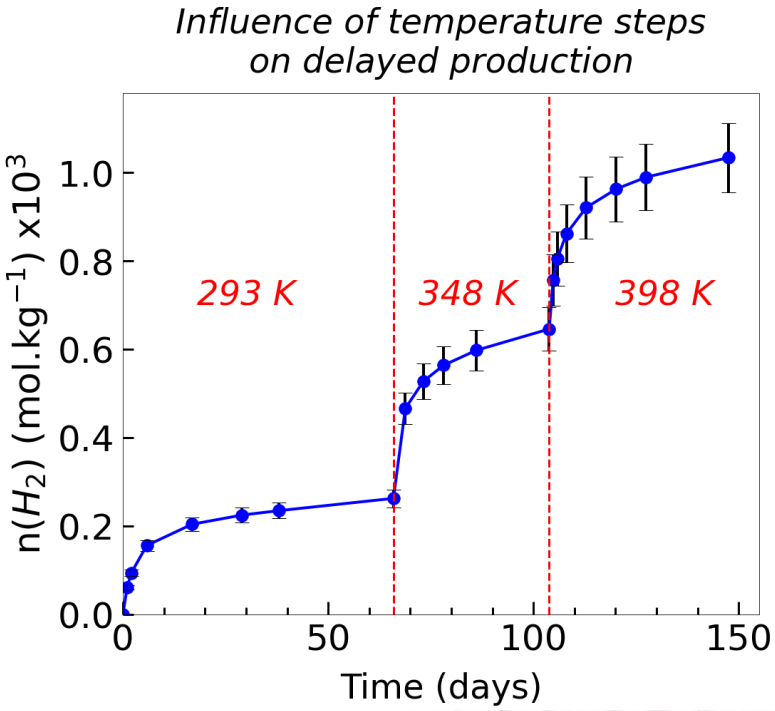
^{1}H NMR analysis of irradiated portlandite samples

In collaboration with Thibault Charpentier (CEA Saclay/NIMBE/LSDRM)

- Appearance of a signal at 4.3 ppm in irradiated samples (trapped H_2)
- Tracking the intensity of the 4.3 ppm peak with temperature







Good correlation with µ-GC measurements

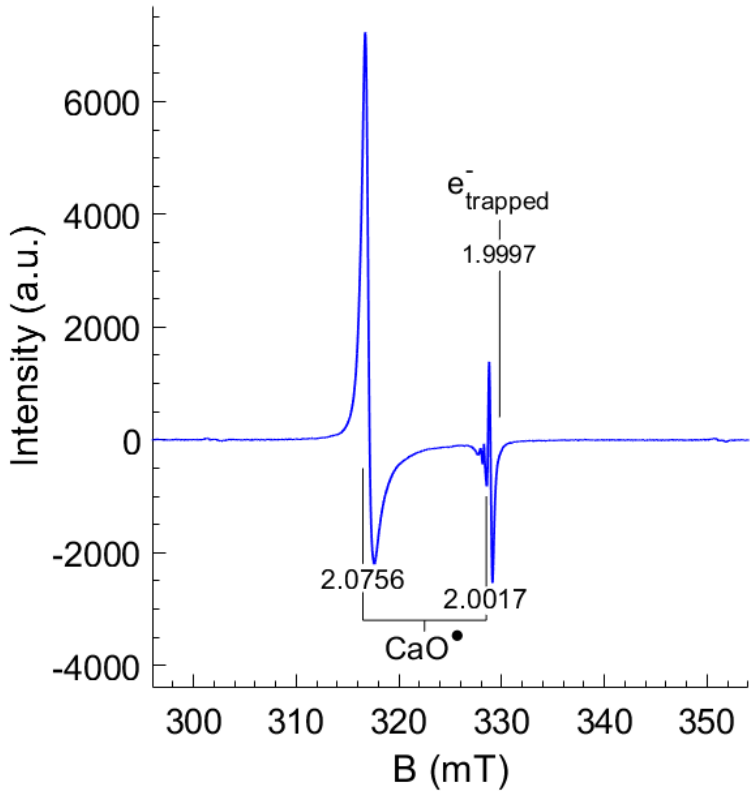
Herin et al., *J. Phys. Chem. C*, 127, 20245 (**2023**)

Electron paramagnetic resonance analysis of $Ca(OH)_2$

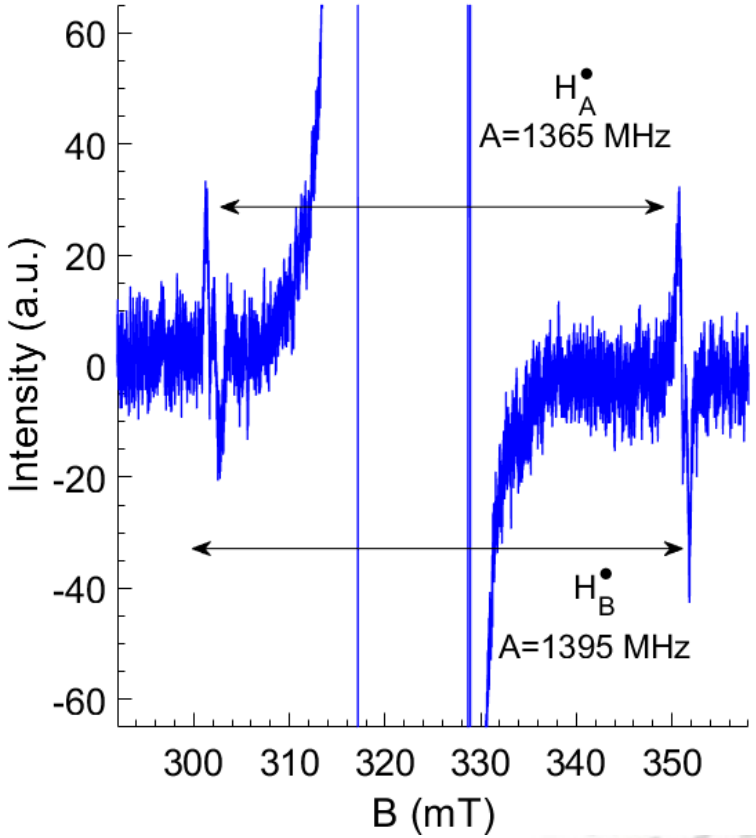
- **Electron paramagnetic resonance (EPR) spectroscopy**

In collaboration with Antonino Alessi (CEA Saclay/LSI)

  - Method for detecting radical (paramagnetic) species formed during irradiation
  - Irradiation of $Ca(OH)_2$ samples in liquid nitrogen at 20 kGy and EPR detection at -150°C



Zoom



- **Presence of paramagnetic species: $CaO^{\bullet}$ (in the volume), $e^-_{trapped}$ (on the surface) and $H^{\bullet}$**

Herin et al., *J. Phys. Chem. C*, 128, 19529 (**2024**)

Mechanism of H_2 production in portlandite

- **The presence of $CaO^{\bullet}$ is an argument in favour of radiolysis of CaO-H bonds**

Primary event

Irradiation $\rightsquigarrow h^+ + e^-$

Ionic mechanism

$$CaOH + h^+ \rightsquigarrow CaO^{\bullet} + H^+$$

$$H^+ + e^- \rightarrow H^{\bullet}$$

Excitonic mechanism

$$e^- + h^+ \rightsquigarrow exciton$$

$$exciton + CaOH \rightarrow CaO^{\bullet} + H^{\bullet}$$

$$n(CaO^{\bullet}) = n(e^-) + n(H^{\bullet})$$

Equality never observed in practice

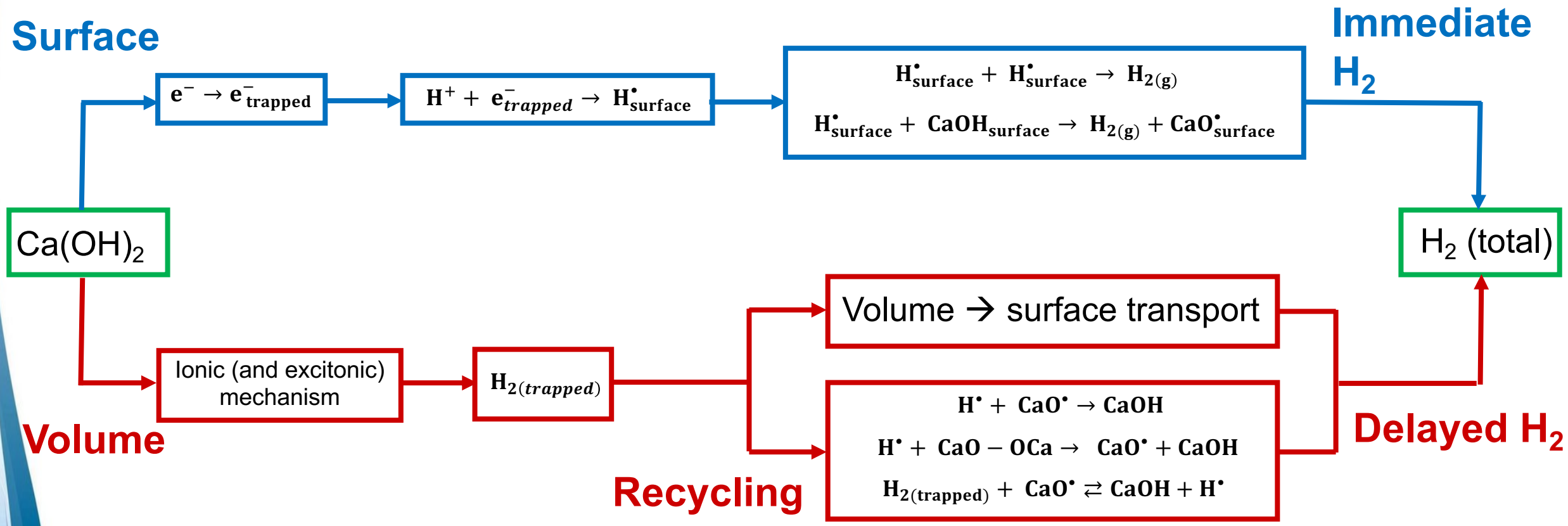
$$H^{\bullet} + H^{\bullet} \rightarrow H_2$$

or

$$CaOH + H^{\bullet} \rightarrow H_2 + CaO^{\bullet}$$

Herin et al., *J. Phys. Chem. C*, 128, 19529 (**2024**)

Mechanisms of H_2 production in portlandite



Herin et al., *J. Phys. Chem. C*, 128, 19529 (**2024**)

Simulation of delayed H_2 production after irradiation of portlandite

Diffusion model assumptions

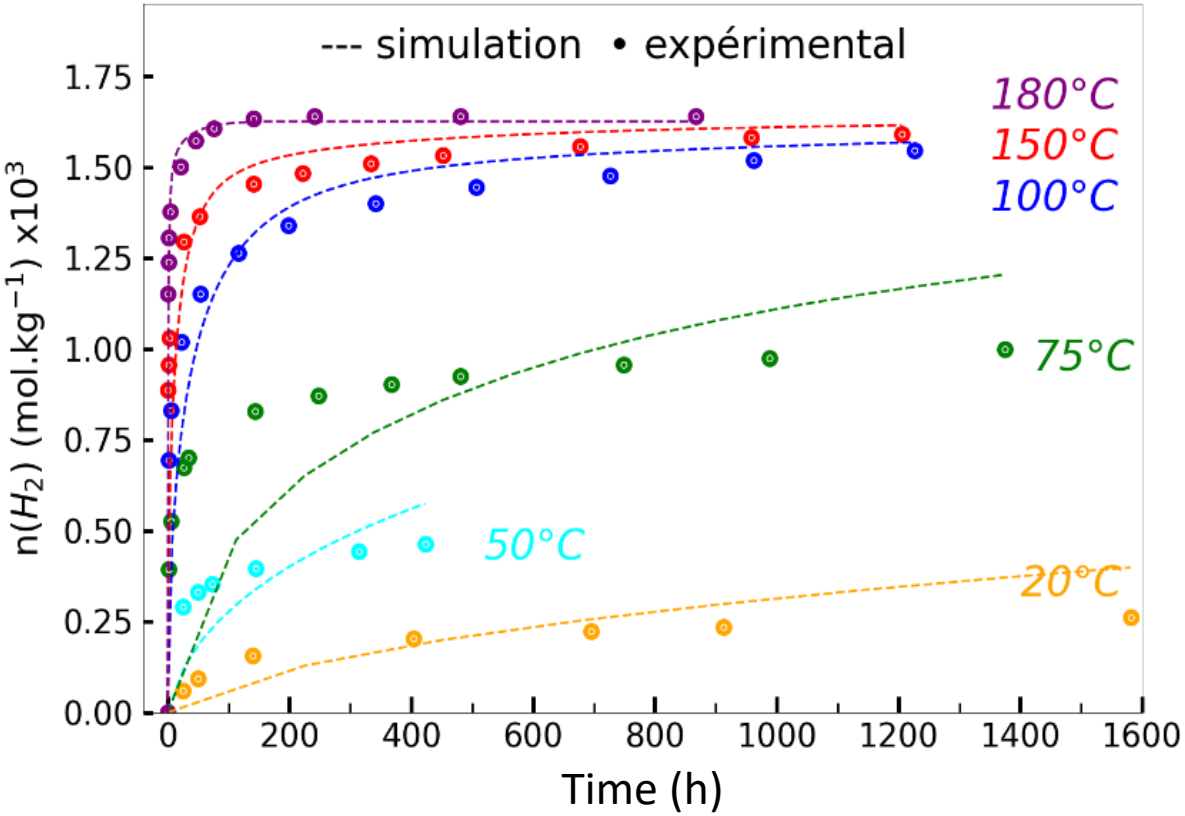
- Spherical particles
- Isotropic diffusion with radial geometry
- Fickian diffusion
- Homogeneous initial concentration

Equations of the diffusion model

$$\frac{\partial u}{\partial t} = D_T . \Delta u(r,t)$$

$$u(r = r_{max}) = 0$$

$$P_{H_2}^{tot}(t, D_T) = \alpha \sum_{j=1}^{n} n_j . P_{H_2}(t, R_j, D_T)$$



Problems

- Poor model convergence at low temperatures
- At least one of the hypotheses is false

Sub-diffusion modeling

- **H_2 transport in portlandite is a sub-diffusive process**
- **Evidenced by Honorio de Faria and Trifa using molecular dynamics calculations**

$< d^2 > \sim t$: Fickian diffusion

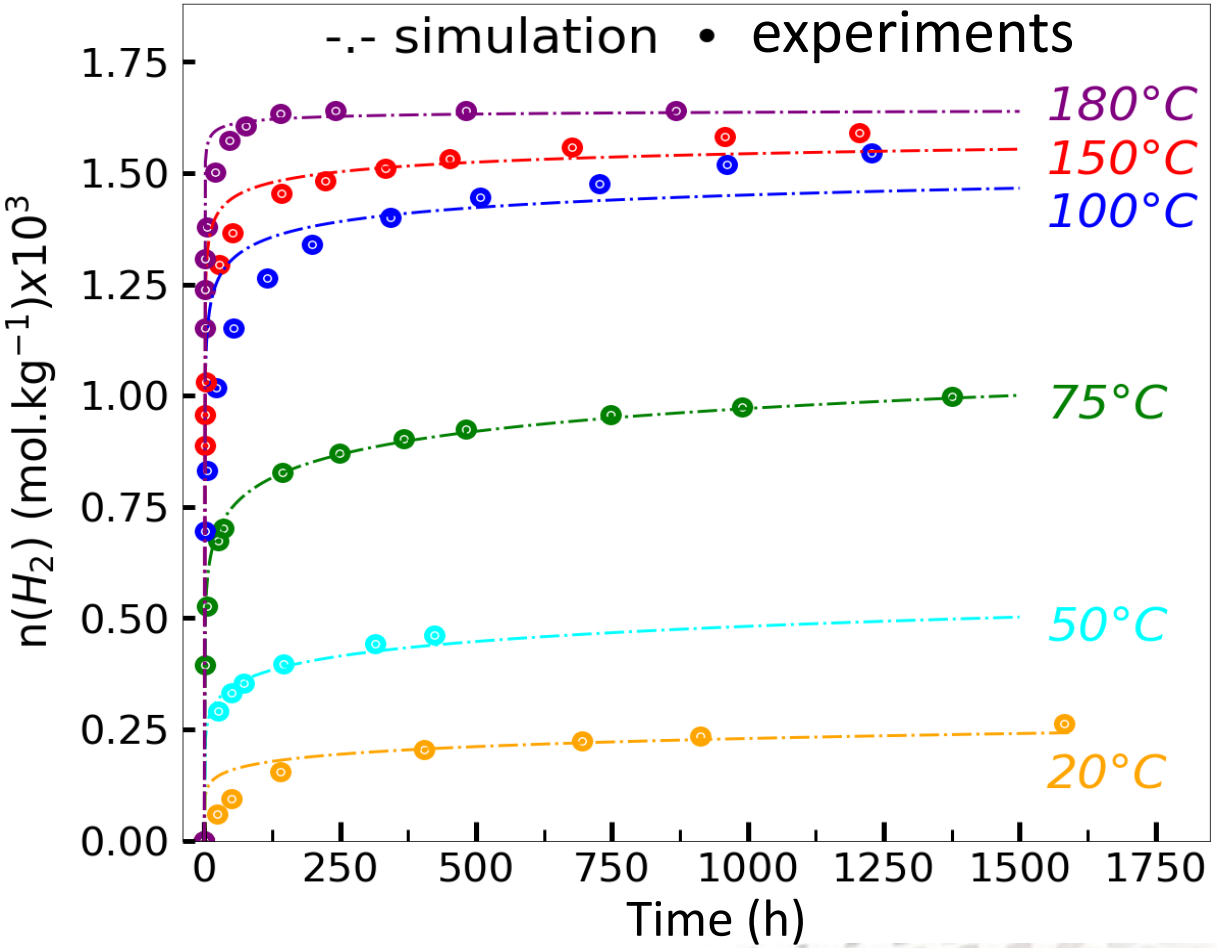
$< d^2 > \sim t^{\gamma}$ and $\gamma < 1$: subdiffusion

Subdiffusion model equations

$$\frac{\partial u}{\partial t} = \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\left[K_\gamma . \Delta u\right]$$

$$u(r = r_{max}) = 0$$

$$P_{H_2}^{tot}(t, D_T) = \alpha \sum_{j=1}^{n} n_j . P_{H_2}(t, R_j, D_T)$$



Honorio et al., *J. Phys. Chem. C*, 128, 19085 (**2024**)

Using a more "realistic" portlandite

- **In cement, portlandite crystals are micrometric (1 to 100 µm).**

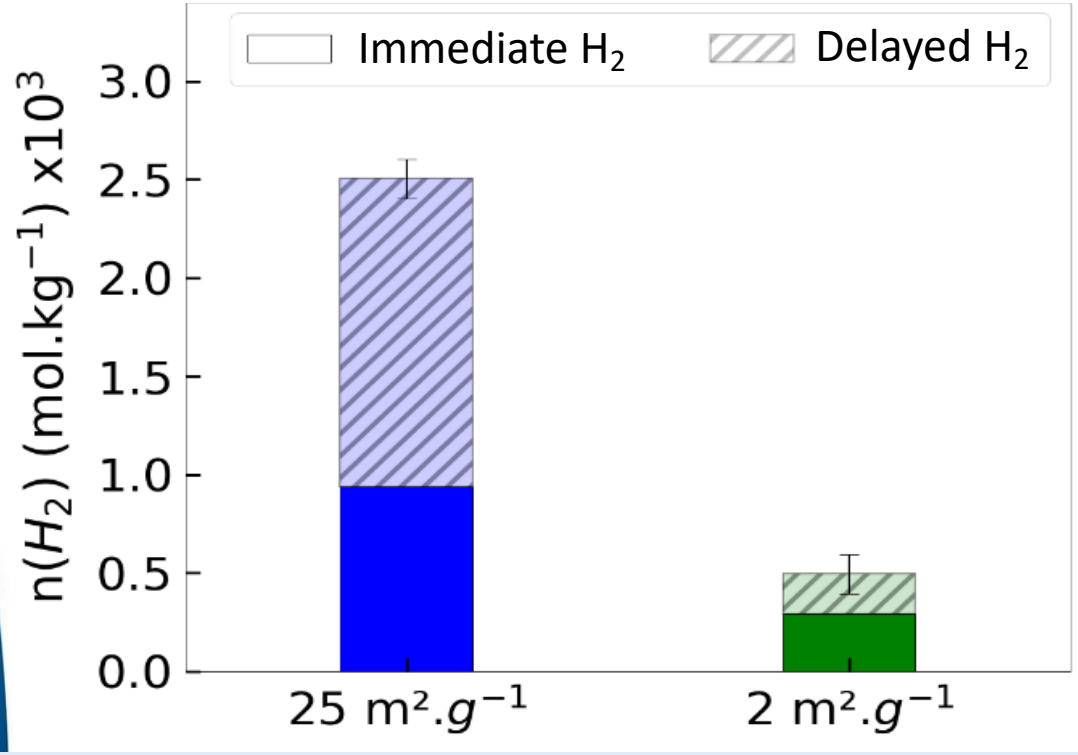
$Ca(OH)_2$ (standard)

- **Typical size: 100 nm**
- **Specific surface area: 25 $m^2.g^{-1}$**

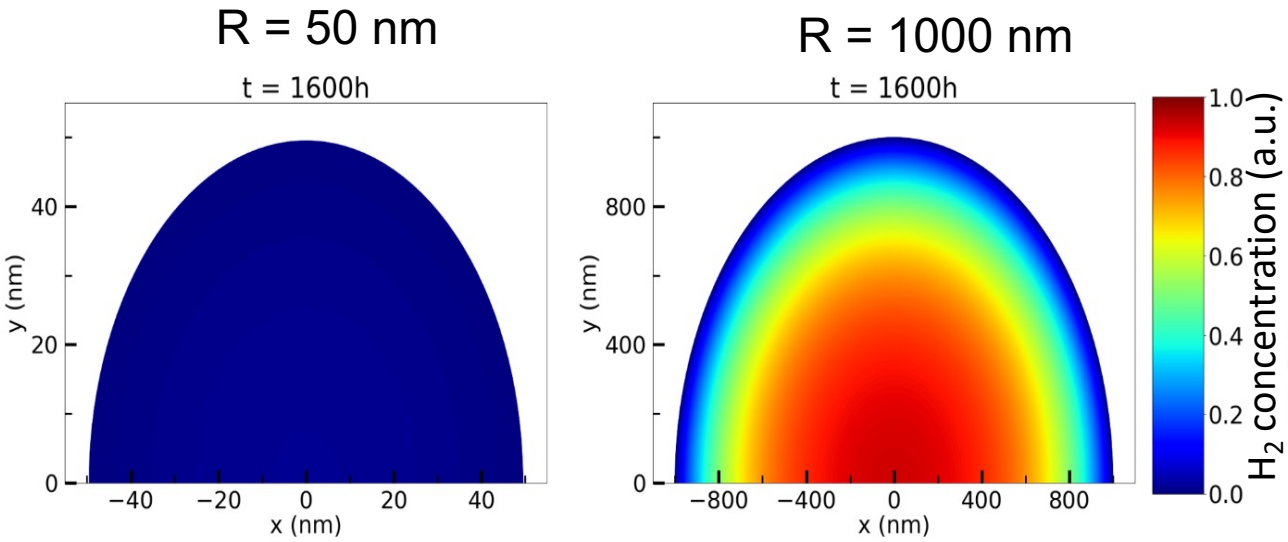
Thermal cycling in a hydrothermal reactor

$Ca(OH)_2$ (recrystallized)

- **Typical size: 1-2 µm**
- **Specific surface area: 2 $m^2.g^{-1}$**



Simulation of the H_2 concentration profile in portlandite particles



Conclusions

Study assumptions

- Cement can be assimilated to tricalcium silicate (Ca_3SiO_5)

$$6\,Ca_3SiO_5 + 18\,H_2O \rightarrow Ca_{11}Si_6O_{20}(OH)_6\,.8H_2O + \mathbf{7\,Ca(OH)_2}$$

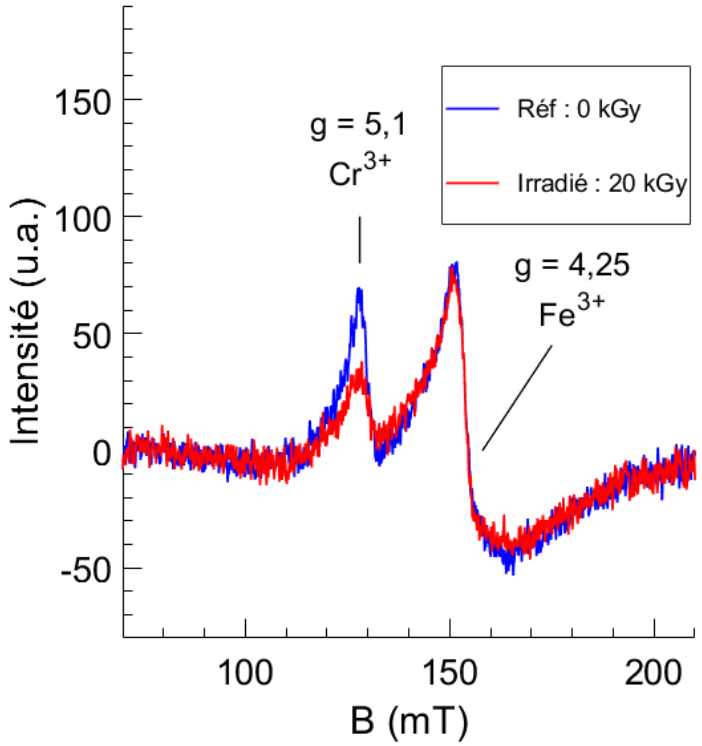
- **The total absence of adsorbed water is necessary to study the radiolysis of bound water without any parasitic contribution.**
- **The notion of radiolytic yield can be rather tricky in the case of a solid.**
  - Production delayed over several days (and specific surface area effects....)
- The **immediate production of H_2** is due to **surface phenomena.**
- **The delayed production of H_2** is due to dihydrogen molecules trapped in the crystalline structure, which diffuse slowly towards the surface via sub-diffusion.
- **EPR spectroscopy** can be used to propose reaction mechanisms for irradiated portlandite by identifying radiation-induced defects.
- **High H_2 retention capacity for micrometric particles**

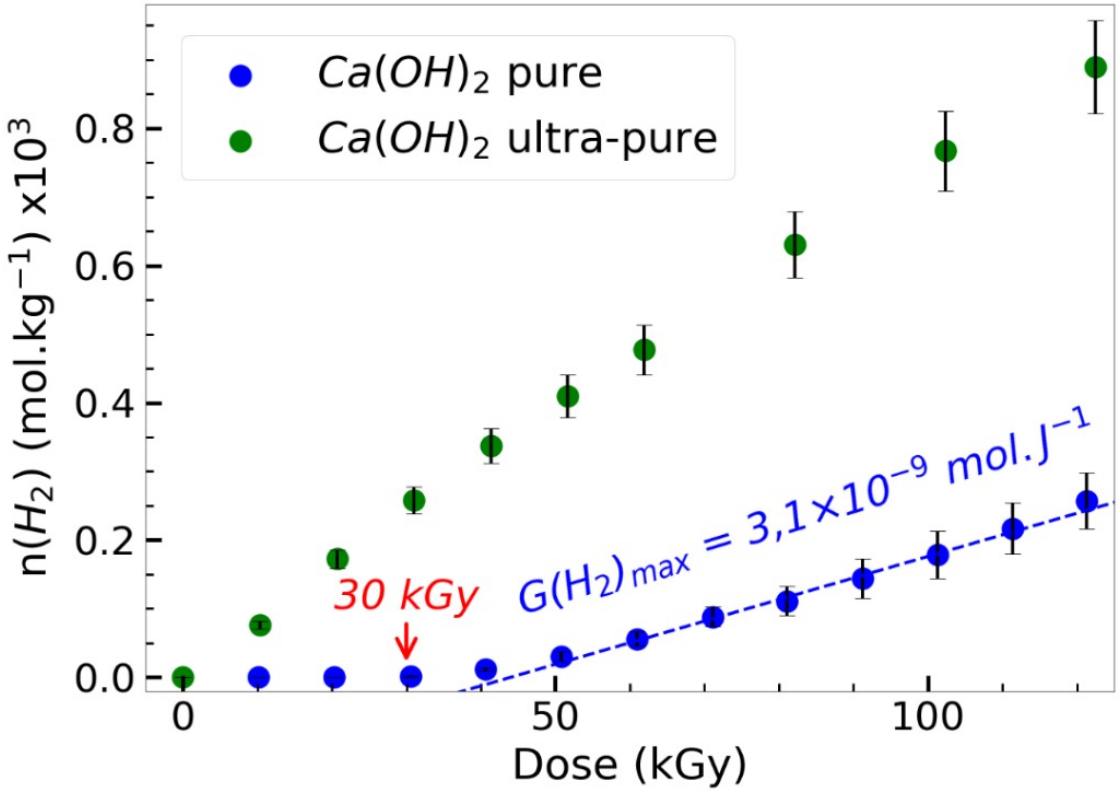
Thank you for your attention

Influence of portlandite purity

$Ca(OH)_2$ pure	$Ca(OH)_2$ ultrapure
CaO (99.95% purity)	CaO (99.998% purity)

- **Irradiation of high-purity portlandite**
  - Disappearance of dose offset
  - Higher H_2 production





- **EPR analysis of standard portlandite**
  - Irradiation at 20 kGy at room temperature
  - Decrease in Cr^{3+} and Mn^{2+} with irradiation

State of the art

- **Radiolytic yield:**

$$G(X_i) = \frac{\Delta n(X_i)}{Dose \times m}$$

$\Delta n(X_i)$: quantity produced/destroyed (mol)
Dose: Gray ($J.kg^{-1}$)
m: irradiated mass (kg)

- **Reference yields:**

Measuring radiolytic yields on cement paste

Author	Treatment prior to irradiation	$G(H_2)$ $(mol.J^{-1}) \times 10^8$
Yin et al (2019)	*R.H. = 30%.	**3.6**
	Lyophilization	**3.3**
Le Caër et al. (2017)	T = 110°C + R.H. = 11%	**1.3 – 2.3**
	T = 110°C + R.H. = 0% (0°C)	0.3 – 0.5
Ishikawa et al (2019)	T = 40°C	**1.4**
	T = 120°C	0.06

* *Relative humidity*

- ❑ **Irradiation with free water**
- ❑ **Attempt to remove adsorbed water**

Extrapolation to a real material

Laboratory materials

- Portlandite: $Ca(OH)_2$

ALIENOR Accelerator

Results

- Radiolysis of solid phase and production of H_2
- Proposition of production mechanisms
- Portlandite stores some of the H_2 produced

- **Laboratory results are difficult to transpose to an operational context**
  - Use of an irradiation source with a more realistic dose rate
  - How much H_2 should be counted for portlandite?
  - Is the portlandite used representative of the portlandite in a cementitious matrix?

Influence of dose rate

Operating context

Radioactive waste packages
$t_0 \sim 10 - 100$ Gy.h^{-1}

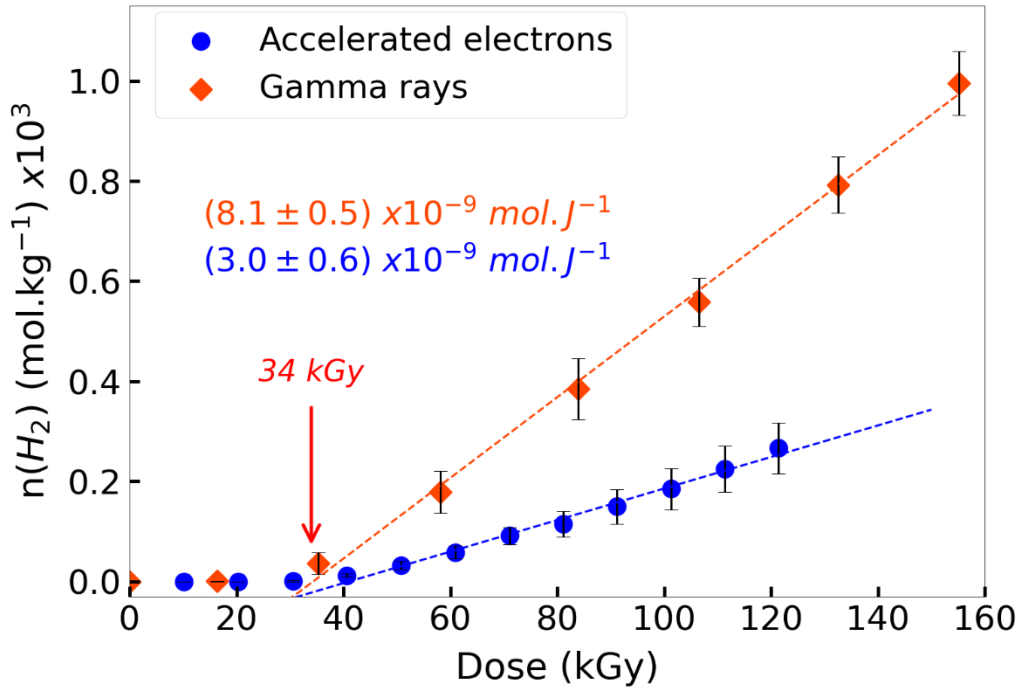
Laboratory

ALIENOR Accelerator
10^{13} Gy.h^{-1}

Gamma source ^{137}Cs
270 Gy.h^{-1}

« Immediate » H_2 production

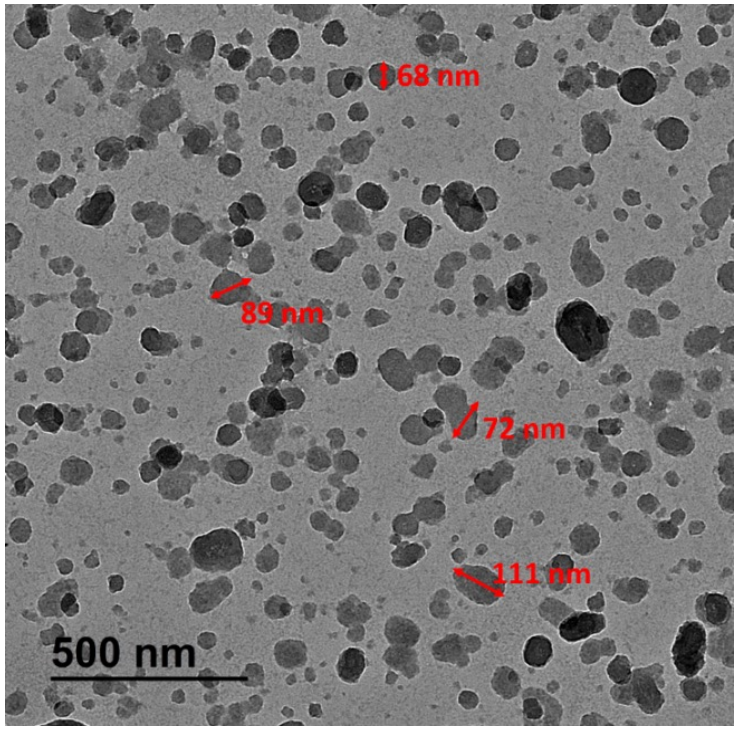
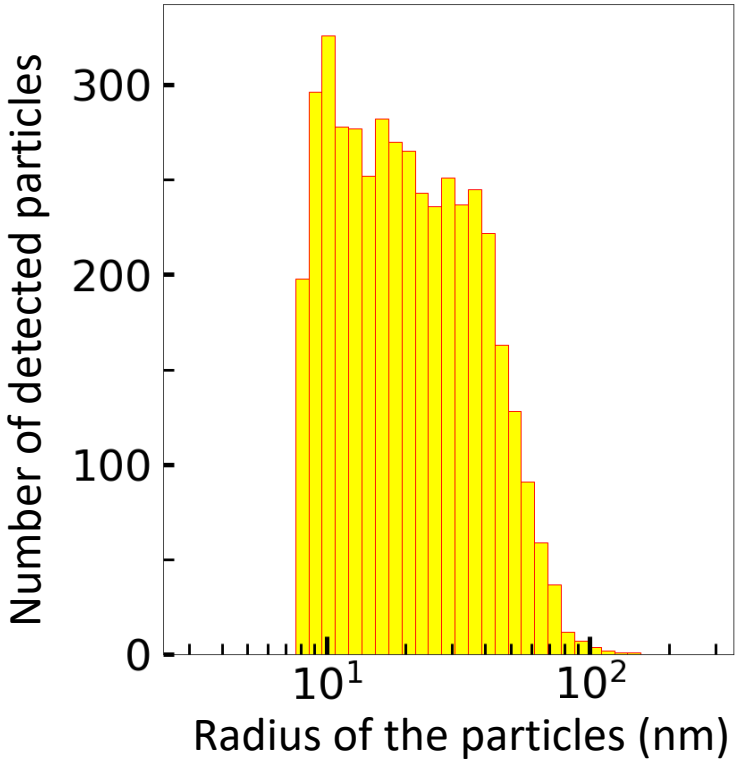
$Ca(OH)_2$



- Molecular hydrogen production follows the same trend regardless of whether the irradiation is done with gamma rays or accelerated electrons;
- **The H_2 radiolytic yield is 2 to 3 times higher with gamma irradiation**, despite its dose rate being several orders of magnitude lower than that of electron irradiation.

How much H_2 should be considered in portlandite? Can we model H_2 transport?

- **Modeling delayed H_2 transport**
- **Determination of portlandite particle size**
  - Observation by TEM (Transmission Electron Microscopy)
  - Image analysis to obtain particle size distribution



Processing