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FORMULATION OF ALTERNATIVE CEMENT MATRIX FOR SOLIDIFICATION/STABILIZATION OF NUCLEAR WASTE

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Lille University, France

May 22, 2019

Supervisors: Prof. C. A. Davy (Centrale Lille), Dr M. Rivenet (ENSCL), UCCS UMR CNRS 8181 and J. Garcia (Orano)

Meet the Presenter

Mr. Matthieu De Campos is a second year PhD student at the University of Lille, within the Solid Chemistry axis of the UCCS laboratory (Catalysis and Solid Chemistry Unit). He is a member of the research team CIMEND (“ChImie, Matériaux Et procédés pour un Nucléaire Durable” i.e. “Chemistry, Materials and Processes for Sustainable Nuclear Activities”). This research team is involved in a joint laboratory between the University of Lille and Orano, the Laboratoire de Recherche Commun Cycle du Combustible et Chimie de l’Uranium (LR4CU) (for Joint Research Laboratory on Fuel and Uranium Chemistry).

The LR4CU is focused on generating added value to fuel cycle by-products and optimizing nuclear processes. The aim is to increase the TRL levels for futures industrial applications. His PhD research aims at adding value to low-radioactive metallic materials, by considering them as reagents for the synthesis of cementitious matrix. His research activities, funded by Orano, are based on a multidisciplinary approach combining Civil Engineering and Solid State Chemistry. In 2017, he graduated from Artois University with a Masters’ Degree in Materials Chemistry for Energy and the Environment.

As one of three students to win the Elevator Pitch Challenge (EPiC) contest during the October 2018 GIF Symposium meeting in Paris, Mr. Campos has been awarded the opportunity to give this presentation.

Email: Matthieu.De-Campos@univ-lille.fr

Outline

- Nuclear waste ?
  - Nuclear waste management
  - French nuclear system & waste management
  - Dismantling challenge
- Difference between MKP & OPC
  - Stabilization/solidification
  - MKP cement
  - OPC cement
- PhD work
  - Key points
  - Tests miniaturization
  - Conclusion

Nuclear Waste Management

- Nuclear waste?

It is any material, without any use, which contains radionuclides in higher concentrations than the values considered admissible (by the competent authority) for such materials (International Atomic Energy Agency, IAEA)

Can we magically make nuclear waste disappear?

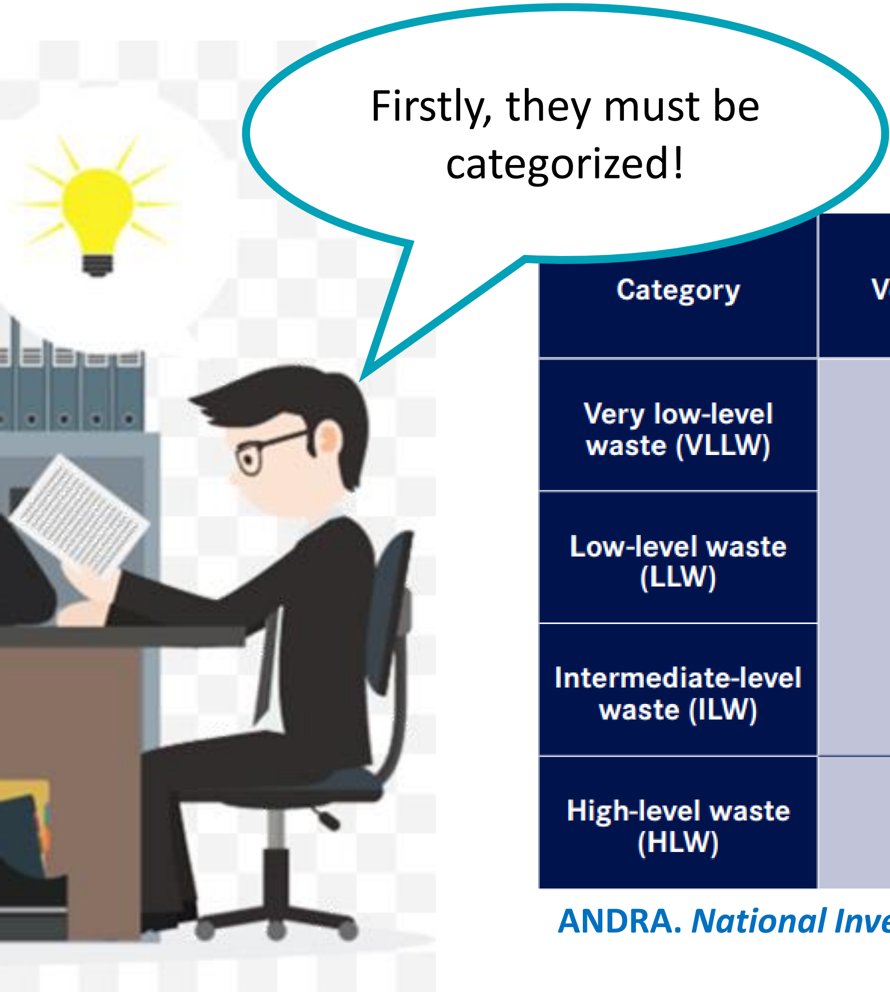
What to do with nuclear waste?

Can they have an impact on the environment?

What to do with Nuclear Waste ?

- ✓ Classify waste according to their level of radioactivity
- ✓ Managing waste according to the half-life time of radioelements
- ✓ Create processing channels based on this information :
  - Radioactive decay management
  - Surface storage
  - Deep storage
- ✓ **How to store them safely?**

French Classification of Nuclear Waste



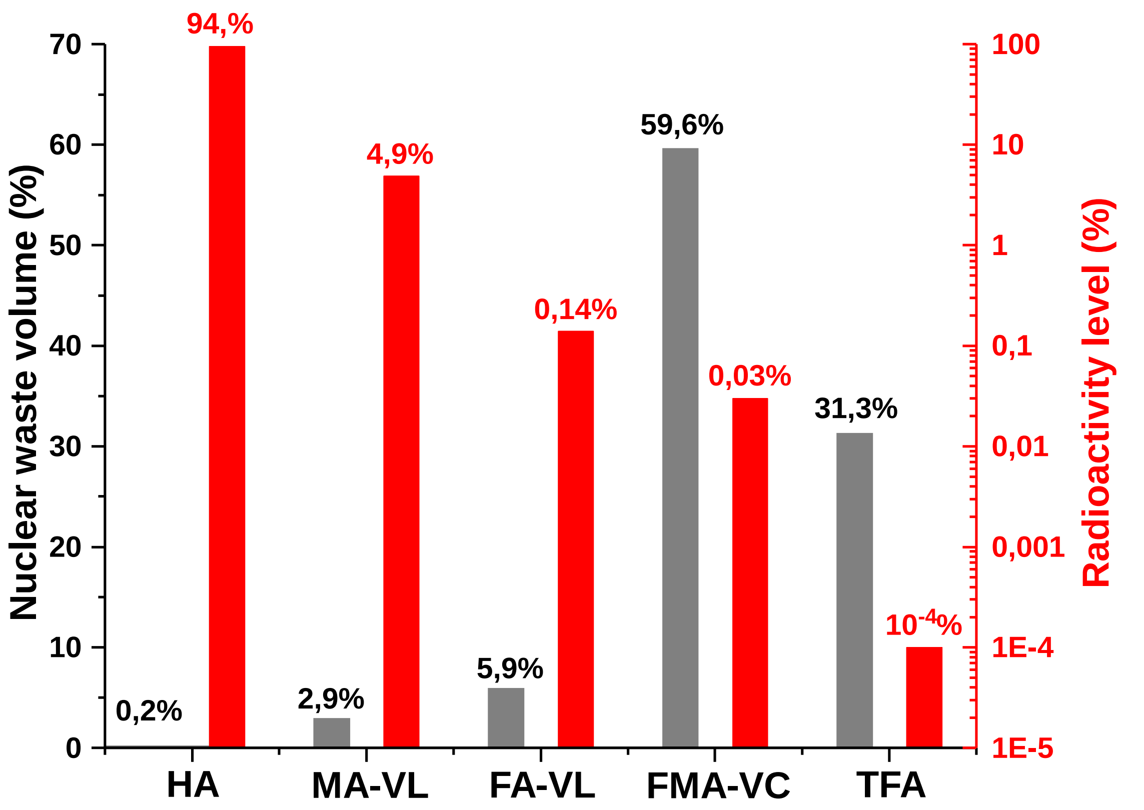
Category	Very short-lived waste	Short-lived waste	Long-lived waste
Very low-level waste (VLLW)	VSLW Management through radioactive decay	VLLW Surface disposal (Industrial facility for grouping, storage and disposal)	
Low-level waste (LLW)		LILW-SL Surface disposal (Aube and Manche disposal facilities)	LLW-LL Near-surface disposal under development
Intermediate-level waste (ILW)			ILW-LL Deep geological repository at the project phase
High-level waste (HLW)	Not applicable		HLW

ANDRA. *National Inventory of Radioactive Materials and Waste*. 2018.

→ Separation of nuclear waste into 6 categories

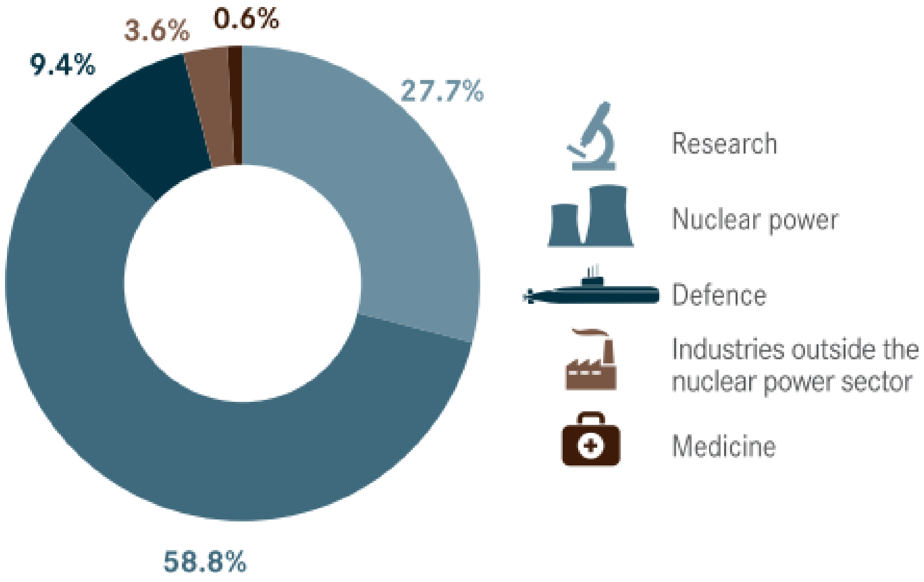
Volume & Radioactivity Level of Nuclear Waste

Volume & radioactivity distribution of nuclear waste



Manage each type of waste by :

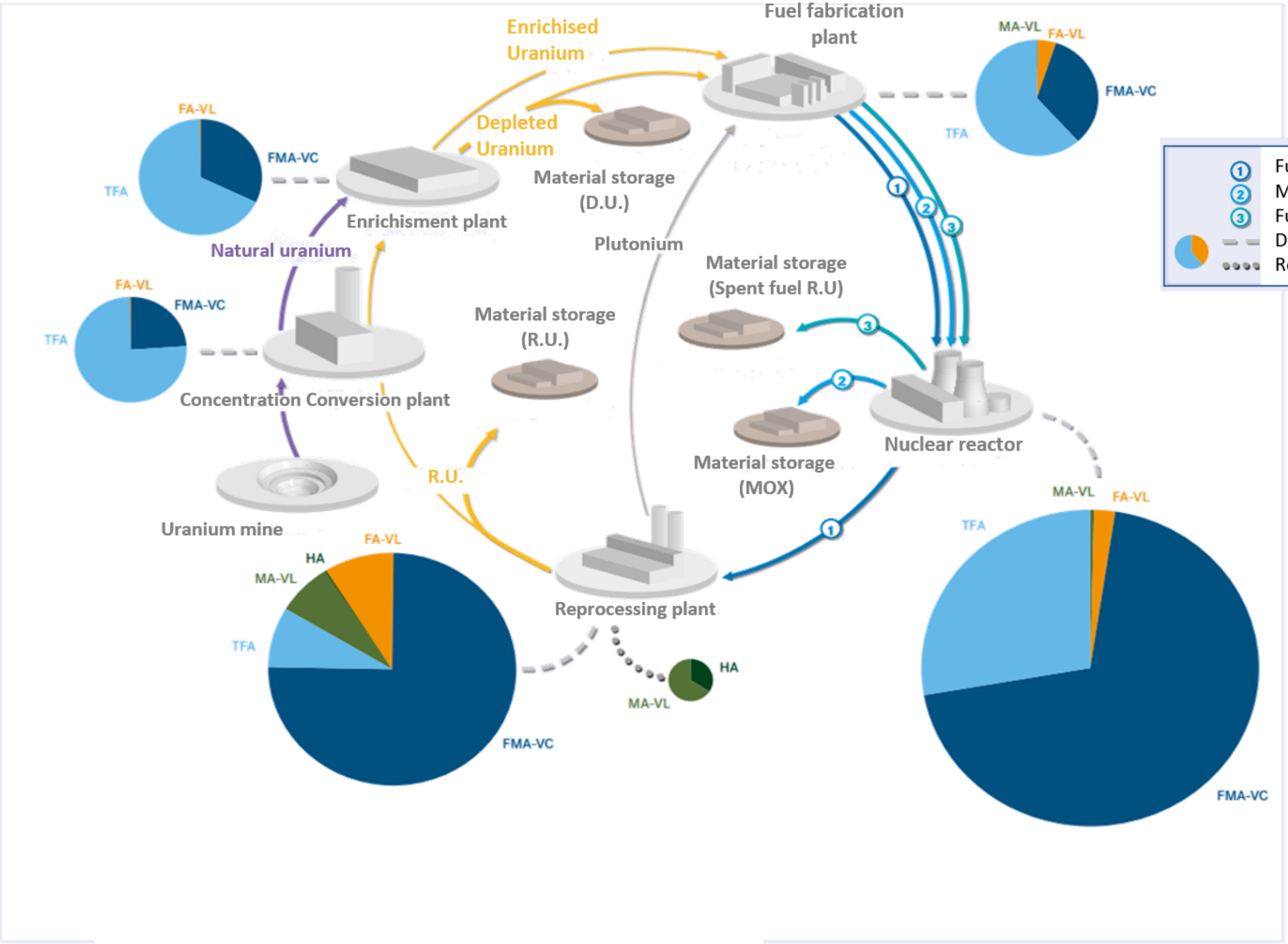
- Implementing specific solutions adapted to the hazard
- Developing specific solutions adapted to the hazard
- Adapting the solutions to their evolution over time



Where does nuclear waste come from in the nuclear cycle?

ANDRA. *National Inventory of Radioactive Materials and Waste*. 2018.

Origin of Nuclear Waste



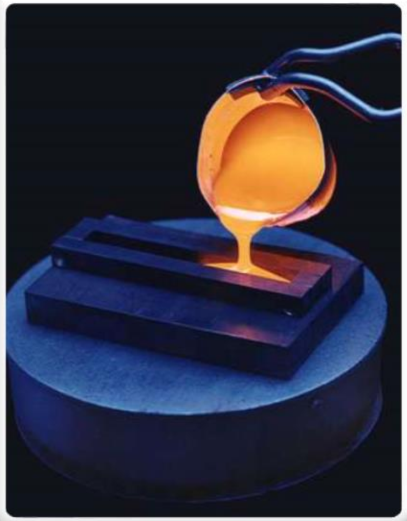
1 Fuel from enrichised natural uranium
2 MOX fuel
3 Fuel from R.U.
Dismantling waste – stock at the end of 2017
Residual waste after reprocessing spent fuel – stock at the end of 2017

- Closed cycle
- 96 % of exploitable material
- 4 % of fuel waste

Where do nuclear waste go after being generated?

The Conditioning Routes for Radioactive Waste

Vitrification of fission elements



Stabilization by solidification of nuclear waste

Packing

The common point of these conditioning routes is storage: what type of storage should be used?

Stabilization by Solidification of Nuclear Waste

GEN IV International Forum℠

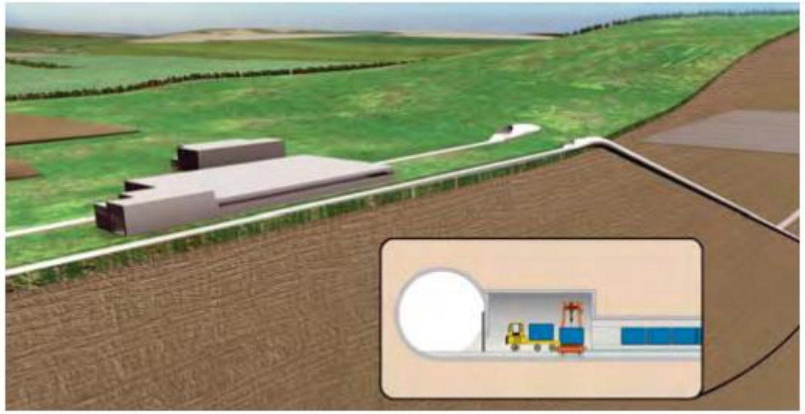
The French National Radioactive Materials and Waste Management Plan (PNGMDR) describes the prescribed management solutions for the different categories of radioactive waste.
Management solutions: 4 types of disposal facilities (2 are currently operational & 2 are being studied)

Operational management solutions :

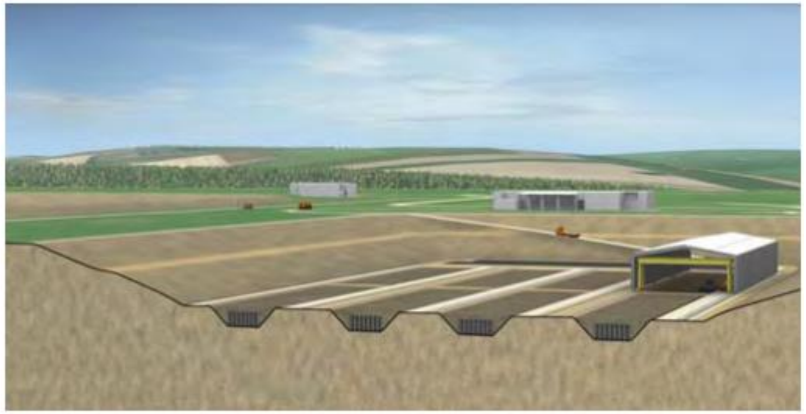
- CSTFA disposal facility → The very-low-level waste disposal facility
- CSFMA disposal facility → The low- and intermediate-level waste disposal facility

Studied management solutions:

- Near-surface repository project → Graphite waste (generated by the dismantling of Generation 1 GCRs) and radium-bearing waste.
- Deep repository project (CIGEO)



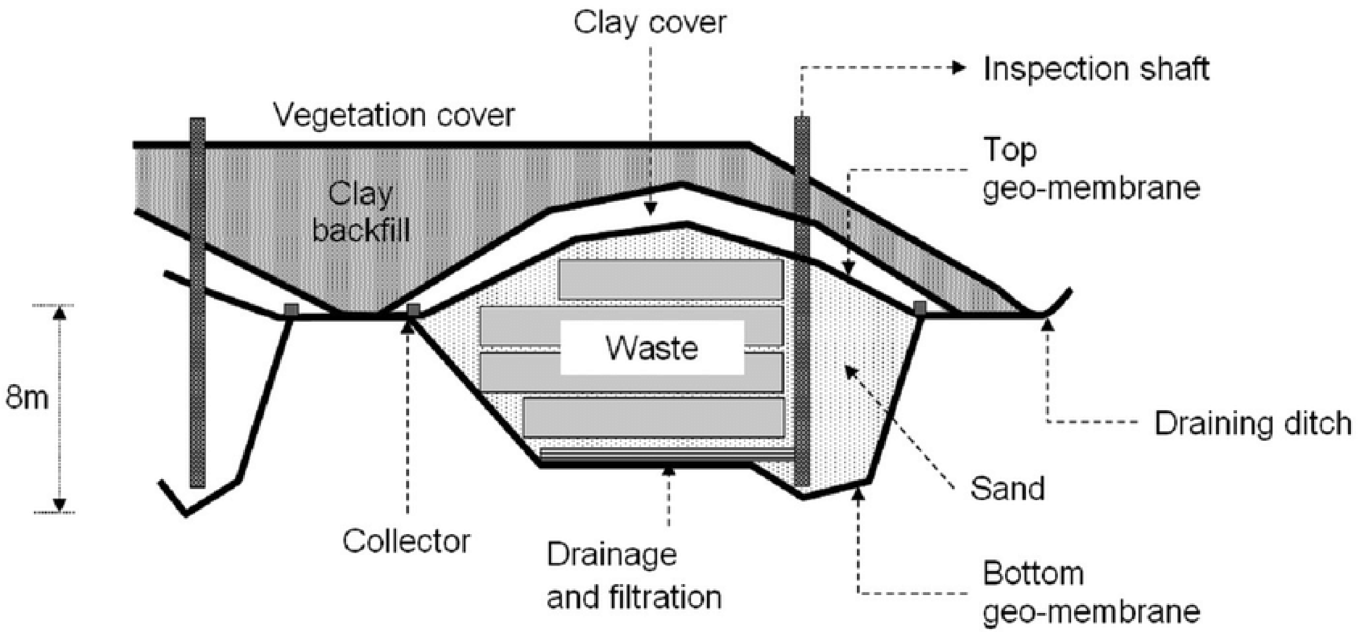
Near-surface repository with undisturbed cover



Near-surface repository with disturbed cover

Surface Storage: VLLW Disposal

The very-low-level waste disposal facility → Dismantling of decommissioned French nuclear facilities.
Waste packages are deposited in cells excavated in clay, which base is engineered to collect seepage water.



They are isolated from the environment by:

- **a synthetic membrane surrounding the waste and linked to a monitoring system;**
- **a thick layer of clay underneath and on the sides of the disposal cells;**
- **a clay cover placed over the waste.**

During the facility use, the cells are protected by tunnel-shaped removable covers and equipped with monitoring devices.

FRENCH NATIONAL RADIOACTIVE WASTE MANAGEMENT AGENCY . *Synthesis Report Foreword*. 2009.

Surface Storage: LILW Disposal

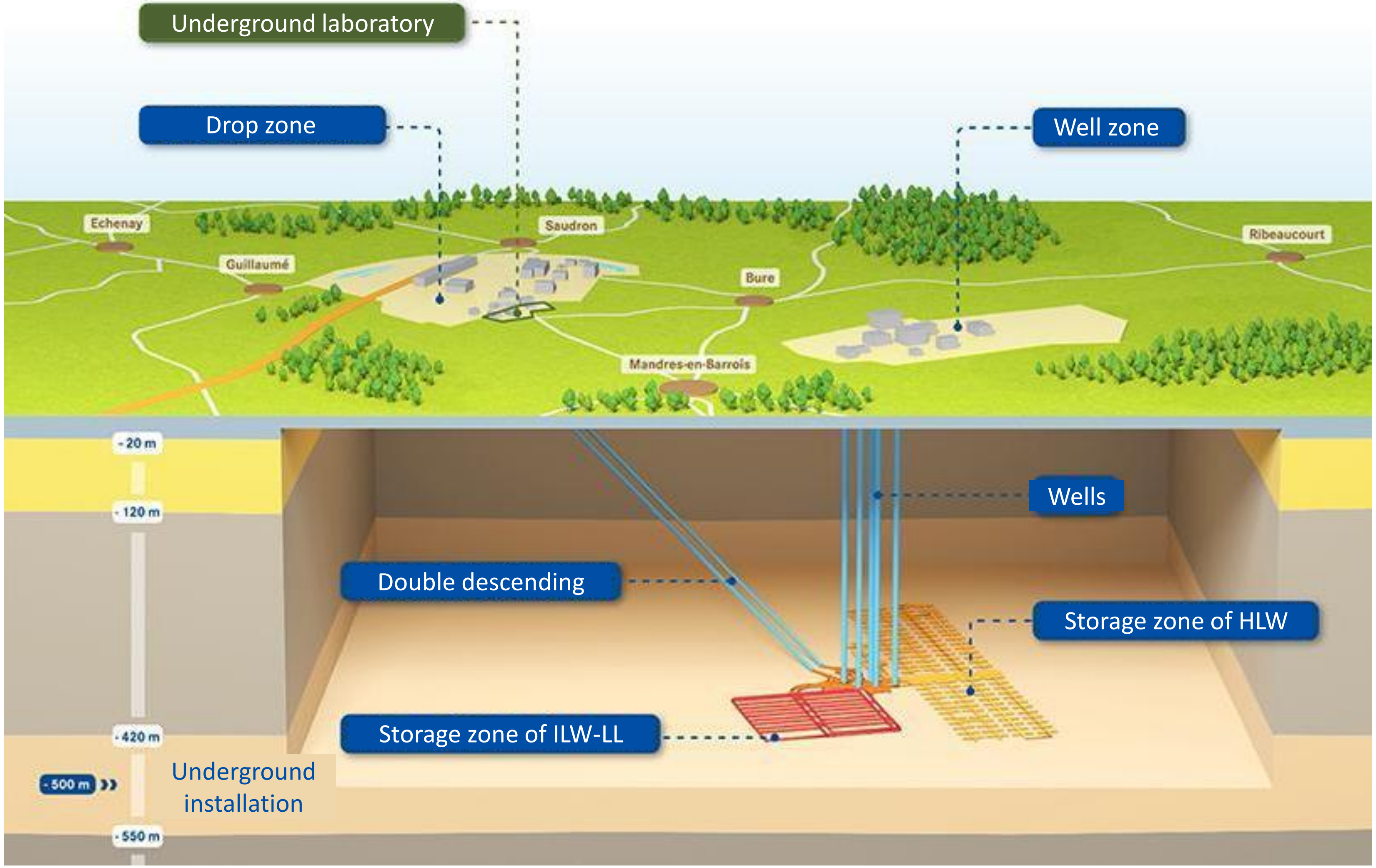
The low- and intermediate-level waste disposal facility
It is made of reinforced concrete disposal cells 25 metres square and 8 metres high.

While a cell is being filled, packages are protected from rain by movable roofs.
Once a cell is filled, it is sealed by a concrete slab and covered with a leak-tight polyurethane layer.

It is also a seismic-resistant structure: disposal cells are built on an impermeable clay layer, which acts as a natural barrier in the event of accidental dispersal of radioactive elements to the ground- water.

FRENCH NATIONAL RADIOACTIVE WASTE MANAGEMENT AGENCY . *Synthesis Report Foreword*. 2009.

Deep Storage



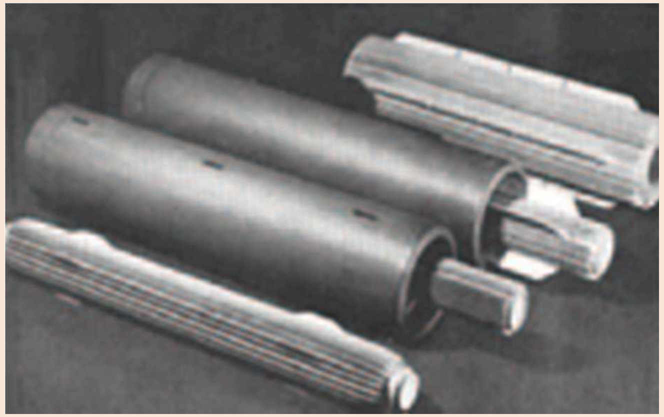
Objective: protect humans and the environment from the danger of this waste in the very long term.

- Underground disposal cells are excavated in an argillite claystone
- The site should allow the long-term containment of radionuclides contained in the waste.
- Should be in accordance with a *reversibility* principle
- Different storage zones depending on waste type

Dismantling Challenge: Case of the UNGG Reactor

EDF Uranium Naturel Graphite Gaz (UNGG) reactor – Saint-Laurent-des-Eaux (© IRSN)

≈ 1 100 to 3400 T of waste per reactor



Identity card

Name: Nuclear fuels

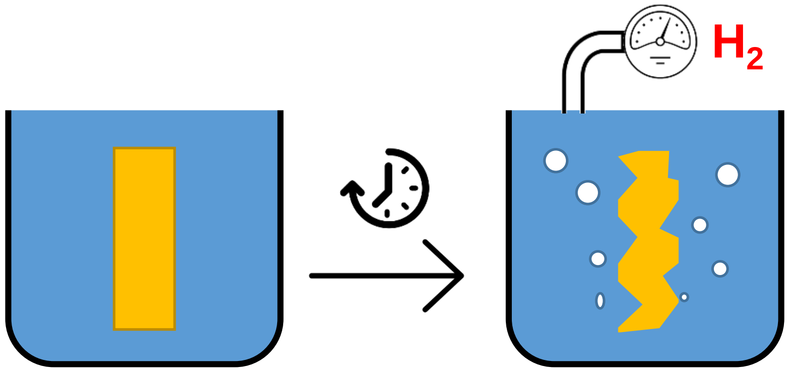
State: Spent fuels

Origin: Dimantling of UNGG reactors

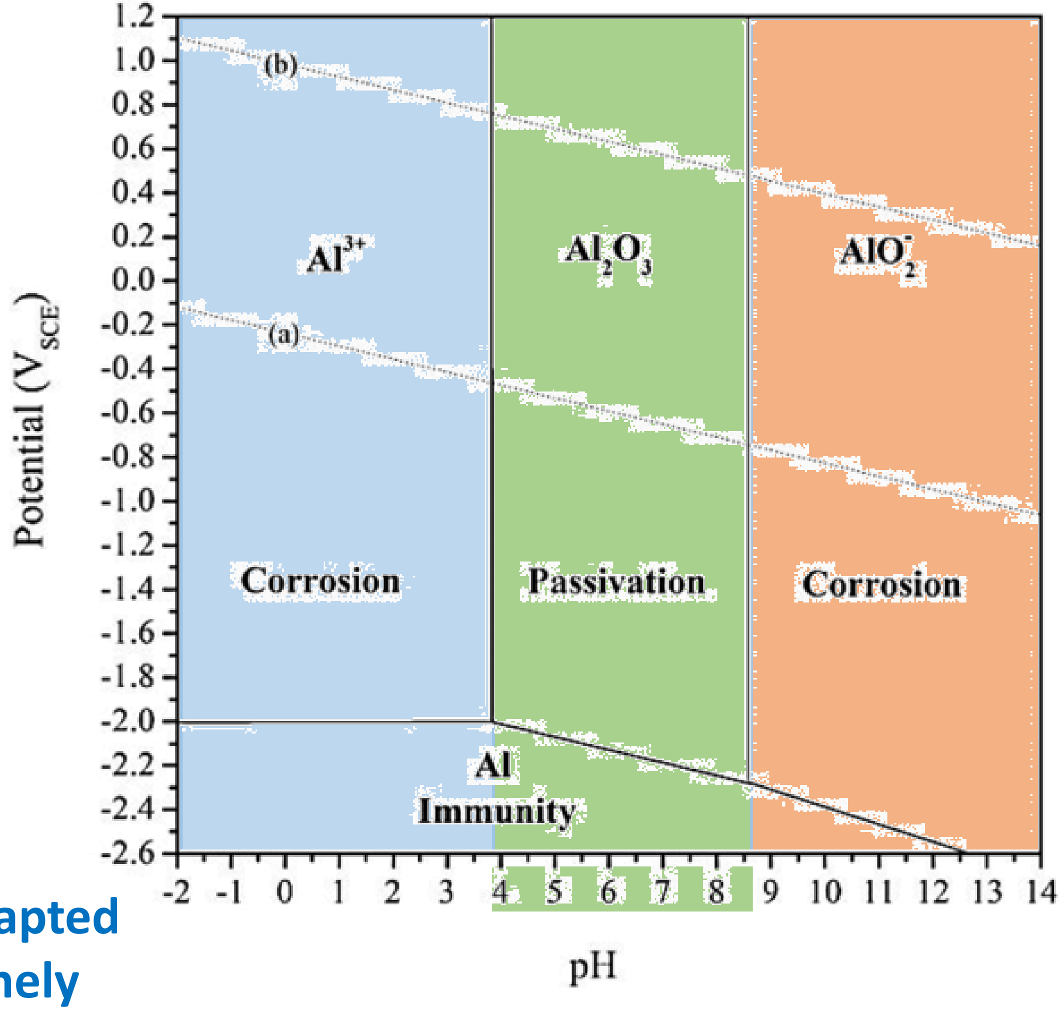
- **Period of use:** from 1966 to 1990
- **Composition:** Graphite jackets – wire stainless steel saddle - Magnesium - Uranium in the heart of Mg
- **Stored in aluminium containers**
- **Processing/conditioning:** The project is to remove a large part of the chemical reactivity by a magnesium metal dissolution process and a uranium metal corrosion process. Secondly, all waste is cemented with a specific blocking slurry to manage chemical reactivity and limit H2 production.

Chemical Reactivity: Example of Aluminium Metal

Reactivity of aluminium depending on the porous solution (which depends on cement nature)



Corrosion & dihydrogen production
→ potential explosive behavior



If pH < 3

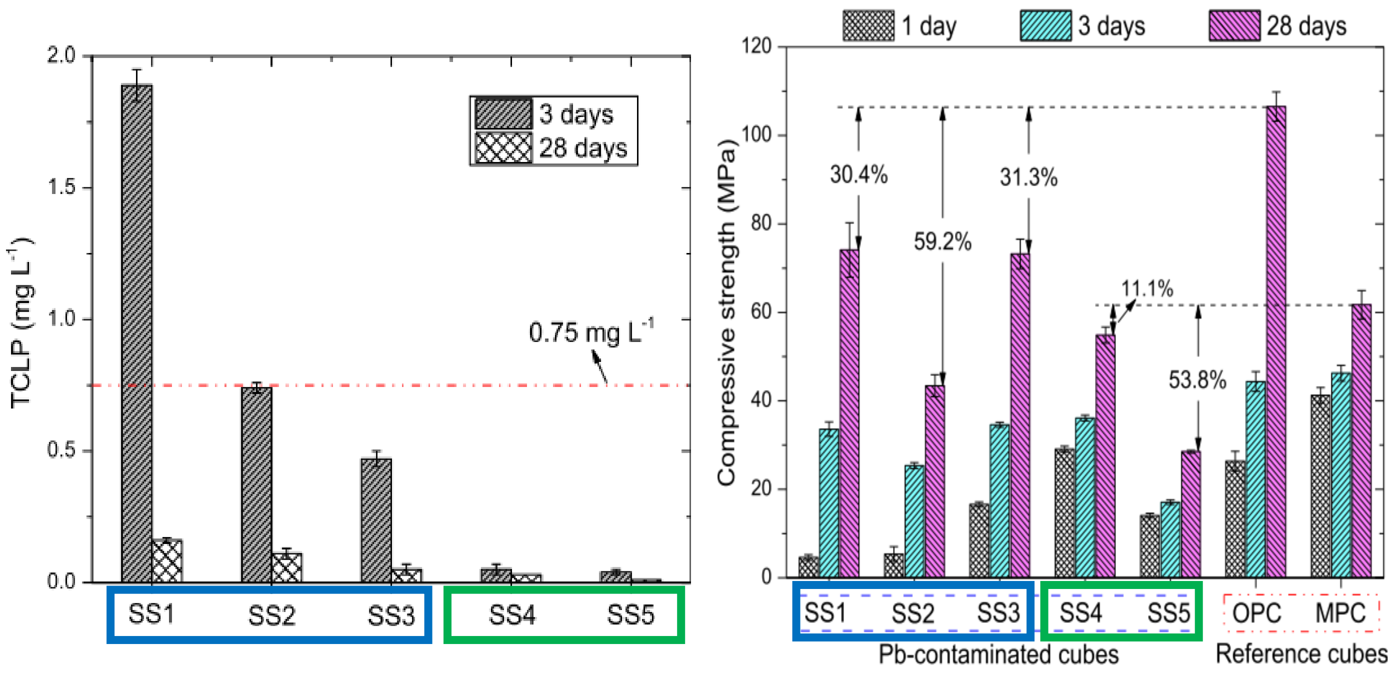
$$2\,Al + 6H^+ \rightarrow 2\,Al^{3+} + 3\,H_2$$

If pH > 9

$$2\,Al + 2\,HO^- \rightarrow 2\,AlO_2^- + 3\,H_2$$

Use of a specifically adapted cement, namely Magnesium potassium K Phosphate cement (MKP)

Stabilization/solidification (S/S)



OPC

SS1 = Only OPC
SS2 = OPC + 50% FA
SS3 = OPC + 5% KH_2PO_4

MKP

SS4 = MKP Mg/P = 3
SS5 = Same MKP +50% FA

- 5 formulations with 0.01 Pb-to-cement mass ratio
- Quantity of lead leached is lower in the MKP matrix
- Higher mechanical properties are obtained for Portland cement
- Less mechanical loss in the case of MKP

OPC-based S/S of soluble Pb → Physical encapsulation by calcium-silicate-hydrate (C-S-H) gels (present in Portland cement)
MKPC-based S/S process → Chemical stabilization with residual phosphate and physical fixation by K-struvite cement.

MKP is a more efficient and chemically stable inorganic binder for the Pb S/S process (compared to Portland cement)

Wang, Yan Shuai, et al. *Chemosphere*, vol. 190, no. October, Elsevier Ltd, 2018, pp. 90–96.

Difference Between MKP & OPC

Main difference
*between **OPC** and **MKP** cements*

Hydration reaction

Acid / Base reaction

MKP history

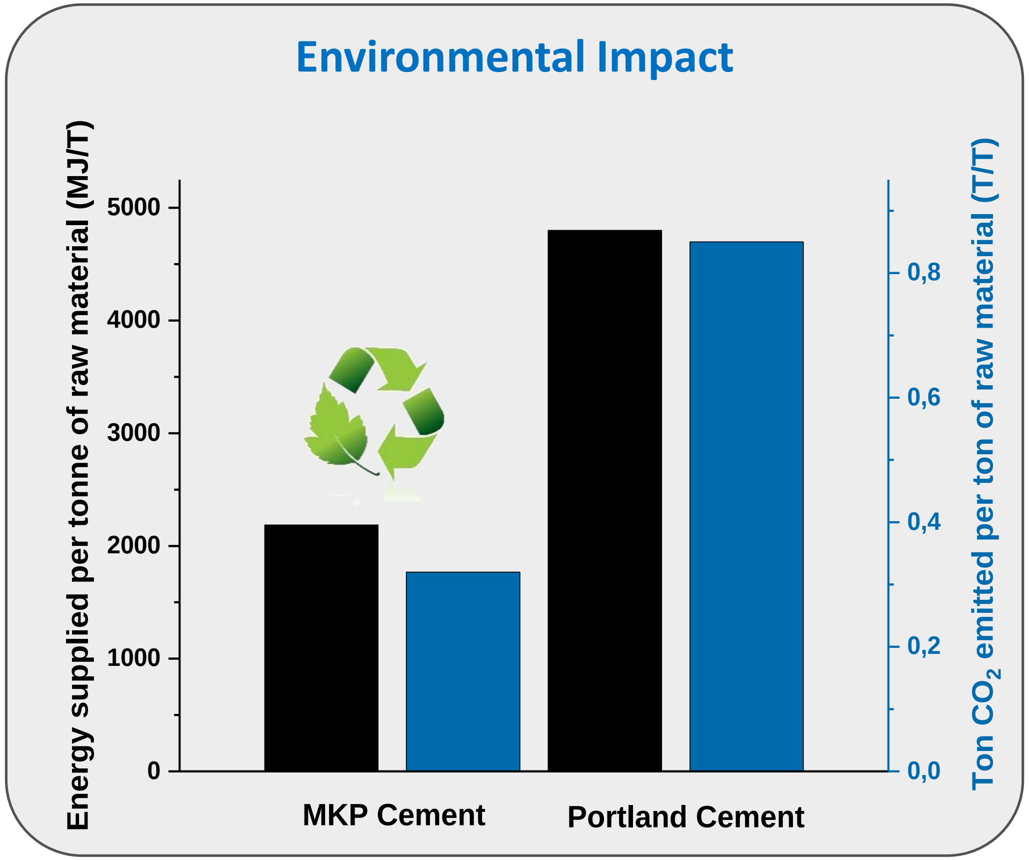
1945-1947
Shotcrete
(MgO + phosphorized liquid))

1960
Repair material
for steelworks

1970
Fast repair
material for highways

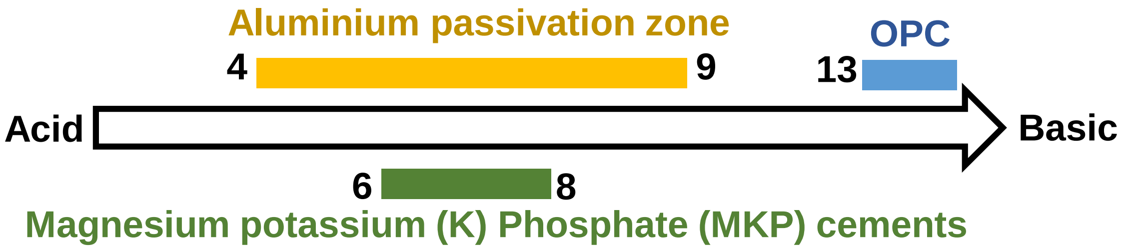
1974
"SET45" sets in 45 minutes
(Mix of powders called "premix" + Water)

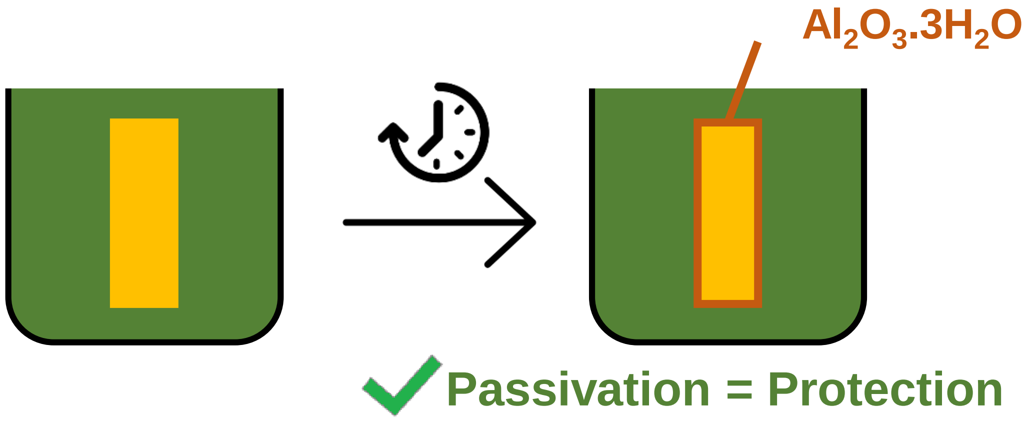
2018
Increased research

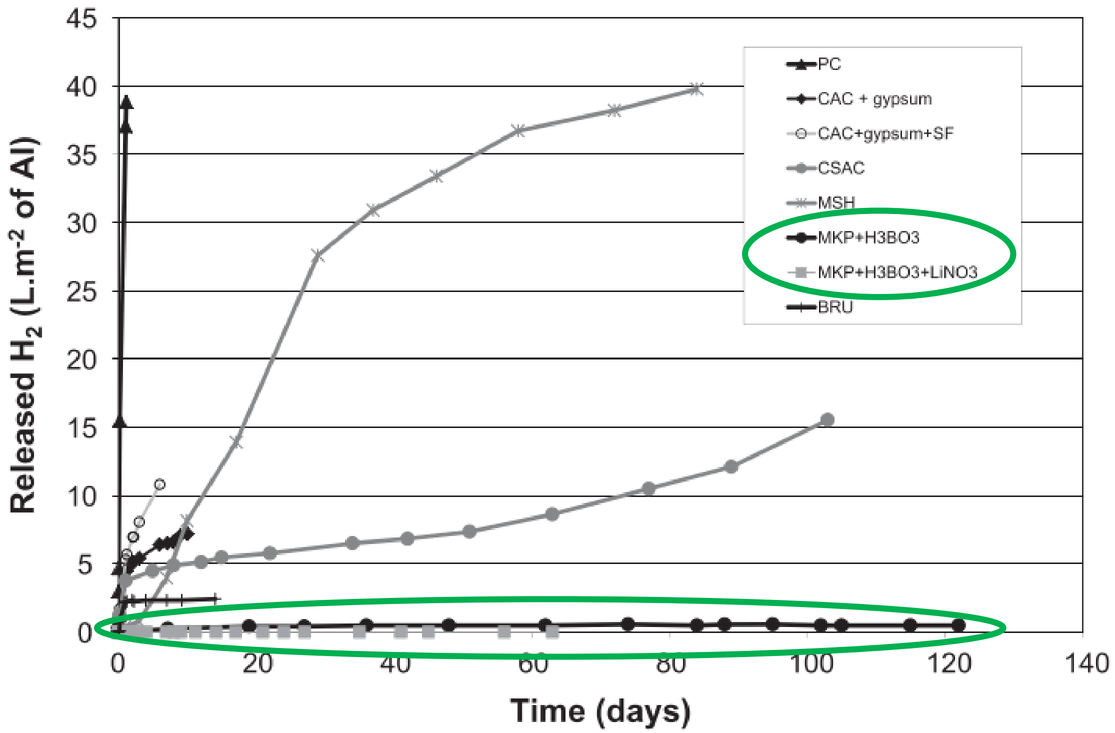


A. S. Wagh, *Chemically Bonded Phosphate Ceramics. 21st century materials with diverse applications.* 2004.

Difference Between MKP & OPC







PC: Portland cement
CAC: Calcium aluminate cement
CSAC: Calcium sulfoaluminate cement
MSH: Magnesium siliceous binder
BRU: Brushite cement
MKP: Magnesium potassium phosphate cement

Cau Dit Coumes, C., et al. *Journal of Nuclear Materials*, vol. 453, no. 1–3, Elsevier B.V., 2014, pp. 31–40.

Magnesium Potassium Phosphate (MKP) Cement

Formation of MKP cement:

$$« \; KH_2PO_4 + MgO + 5\,H_2O \rightarrow MgKPO_4 \cdot 6H_2O \; »$$

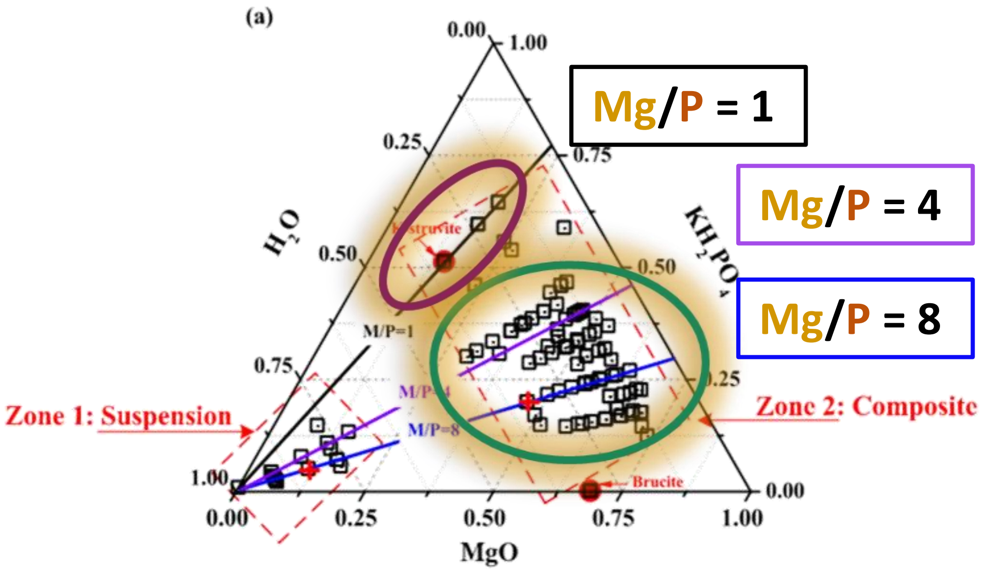
- Theoretical molar ratio $MgO/KH_2PO_4 = 1$

- For best mechanical performance Mg/P = 6

Drawback : Hydration of magnesium oxide

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Can damage the cementious matrix due to volume change (swelling)



Why use over-stoechiometric formulations?

Xu, Biwan, et al. *Cement and Concrete Research*, vol. 108, no. September 2017, Elsevier, 2018, pp. 140–51.
Ma, Hongyan, et al. *Materials and Design*, vol. 64, Elsevier Ltd, 2014.
Qureshi, Tanvir, and Abir Al-tabbaa. *Proceedings of the Int. Conference on Ageing of Materials & Structures*, no. May, 2014.

MKP Cement: MgO Optimization

Why use over-stoechiometric formulations ?

Mg/P=1 | Mg/P=5

Swelling

Effect of over-stoechiometric MgO ?

Physical + Chemical → Physico-chemical

If there is a physical effect of MgO on stoichiometry, what would be the effect of replacing it with mineral additives?

→

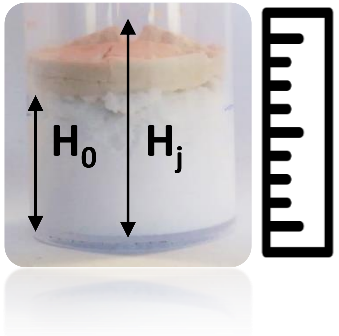
Investigation

Use of fly ash (FA)

Use of silica fume (SF)

MKP Cement: Swelling Inhibition

Volume variation



$$\Delta V = \frac{H_j - H_0}{H_0}$$

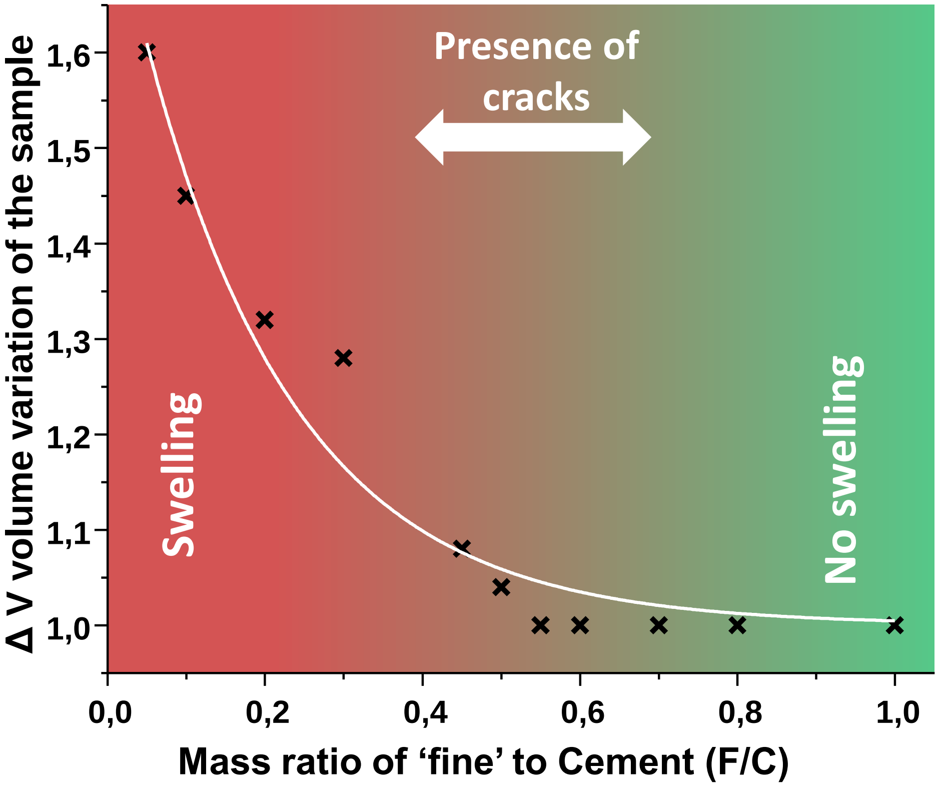
With H_j height at j days

$\Delta V > 1 = swelling$

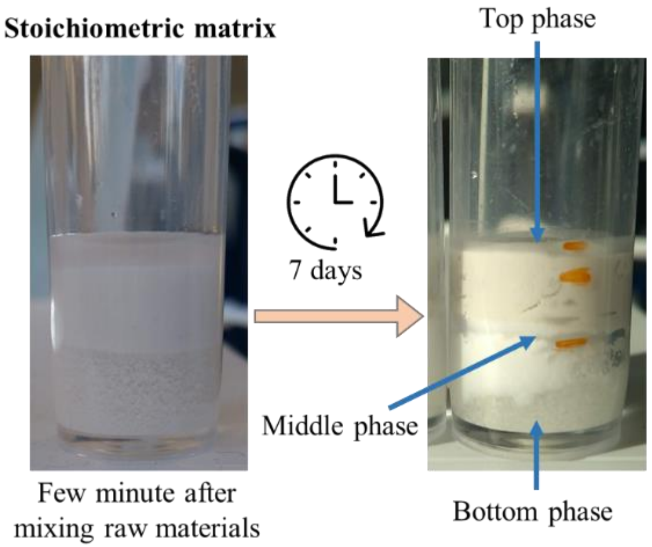
Sample after 28 days

0.05 0.1 0.2 0.3 0.4 0.6 0.8 1

Evolution of swelling according to F / C (Results for silica fume at 28 days)



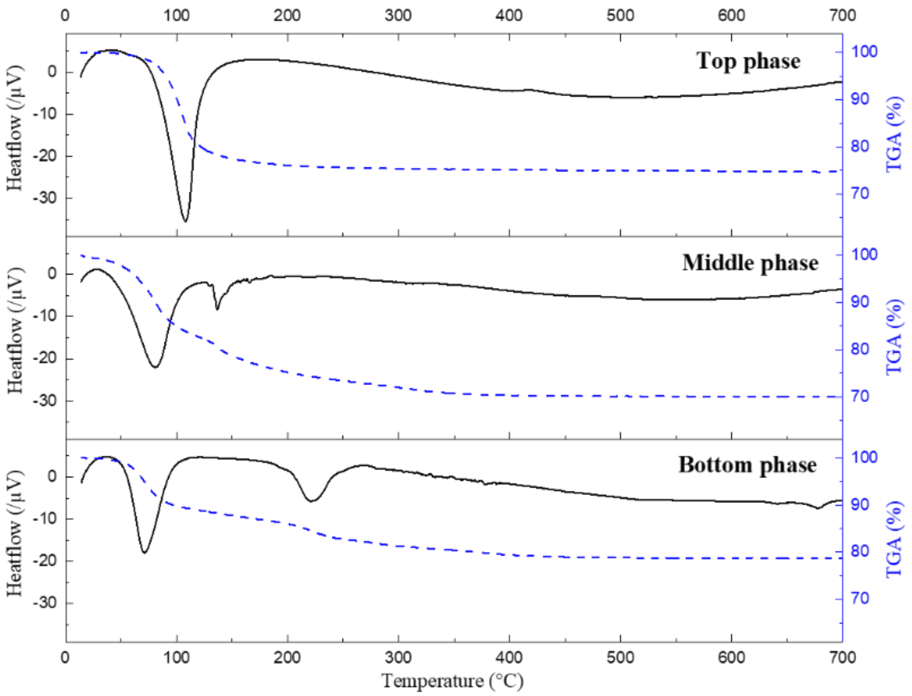
MKP Cement: Stoichiometric Matrix



Analysis of the swelling by TGA/TDA and by X-ray diffraction

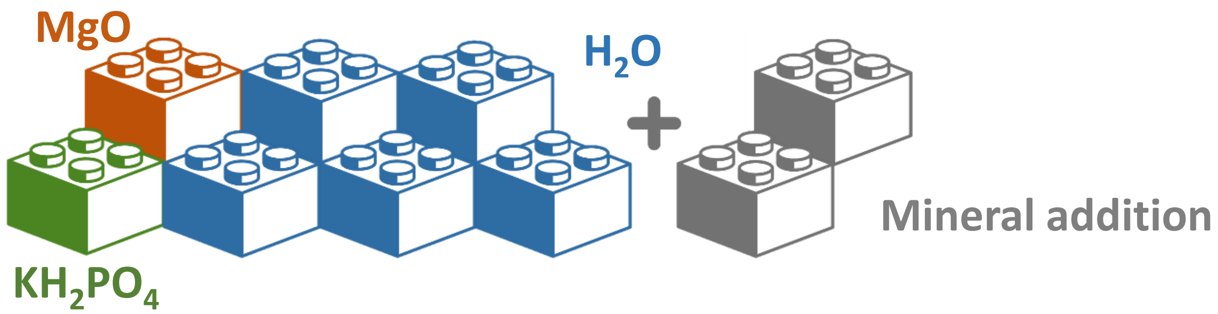
Segregation of constituents with an increase in the amount of acid at the bottom of the sample

Hypothesis: Composition difference with pH gradient



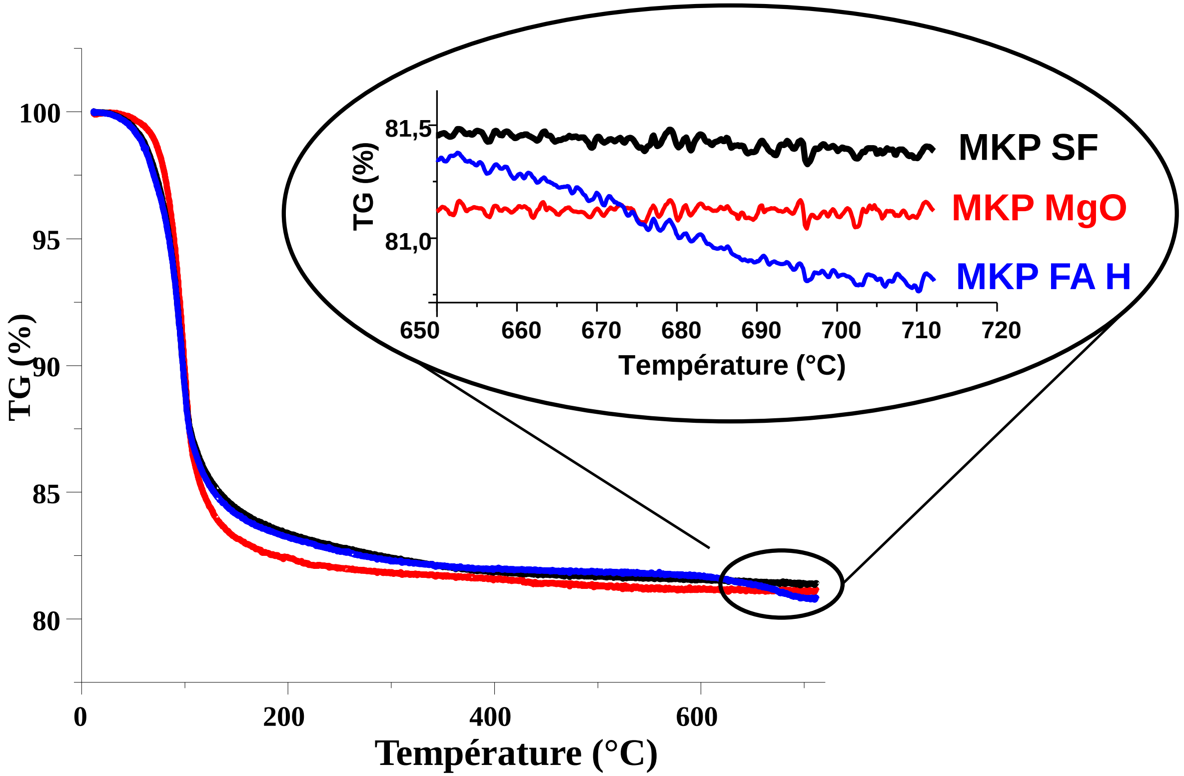
The addition of mineral powder avoids phase segregation and homogenizes the different components.
Now, what is the quantity of binder phase?

Magnesium Potassium Phosphate Cement



Mass ratio Fine/Cement (F/C) = 1

- Conversion into volumetric proportion (due to the difference in mineral density)
- 3 formulations using MgO, FA & SF



	Silica fume	FA Harnes	MgO
	Mg/P = 1	Mg/P = 1	Mg/P = 5,38
$R_{K\text{-}Struvite}$:	43,4 %	40,7 %	46,4 %

Thermal decomposition :

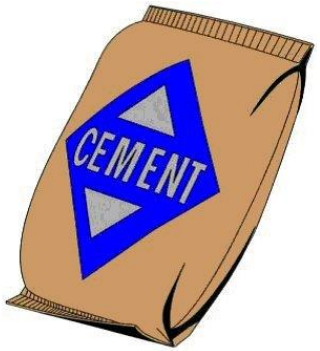
$$MgKPO_4 . 6H_2O \xrightarrow{\Delta} MgKPO_4 + 6\,H_2O$$

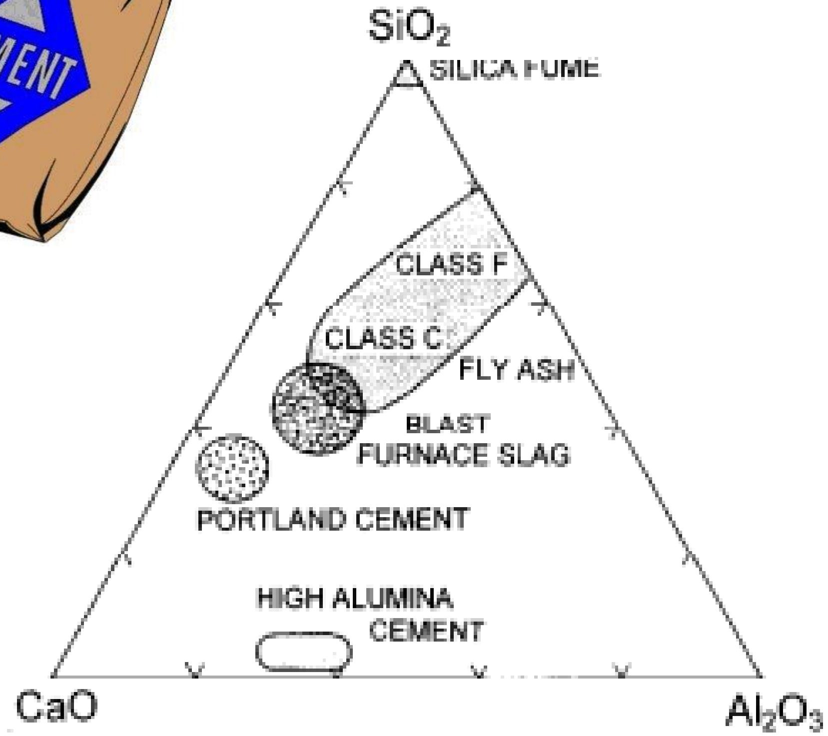
Water quantity is determined to access the K-Struvite quantity

MKP Cement: Mechanical Characterization

- **Depending on its mechanical properties, the application of the final matrix will be different:**
  - High strength (> 60 MPa) → structure material
  - Normal to low strength (<60 MPa) → Blocking material for stabilization/solidification
- **Possibility to work with a Mg/P = 1**
- **Possible substitution of over-stoichiometric MgO with waste powder, in order to make cheaper matrices (and reduce cost in MgO)**
- **Fly ash addition decreases the mechanical performance of MKP cement matrix**
- **In progress work: study of dimensional stability**

Portland Cement





Ordinary Portland Cement (OPC) is a hydraulic binder produced by firing a mixture of limestone and clay at over 1400°C. The product obtained after "baking" and quenching is called clinker.

Composition:

CaO, SiO_2, Al_2O_3 & Fe_2O_3

Type of reactions: **Hydration by multiple reactions (solid solution CSH)**

$$\begin{matrix} C_3S \\ C_2S \end{matrix} + H_2O \xrightarrow{\Delta} CSH + Ca(OH)_2$$

$$C_3A + \underset{Gypsum}{3\,C\bar{S}H_2} + 26\,H_2O \xrightarrow{\Delta} \underset{Ettringite}{C_3A, 3C\bar{S}H_{32}}$$

Characteristic: **Alkaline pore solution**

Used in stabilization/solidification of heavy metals

Glasser, F. P. *Journal of Hazardous Materials*, vol. 52, 1997, pp. 151–70.
Santos, Ana C. P., et al. *Construction and Building Materials*, vol. 78, Elsevier Ltd, 2015, pp. 40–49.

Portland Cement

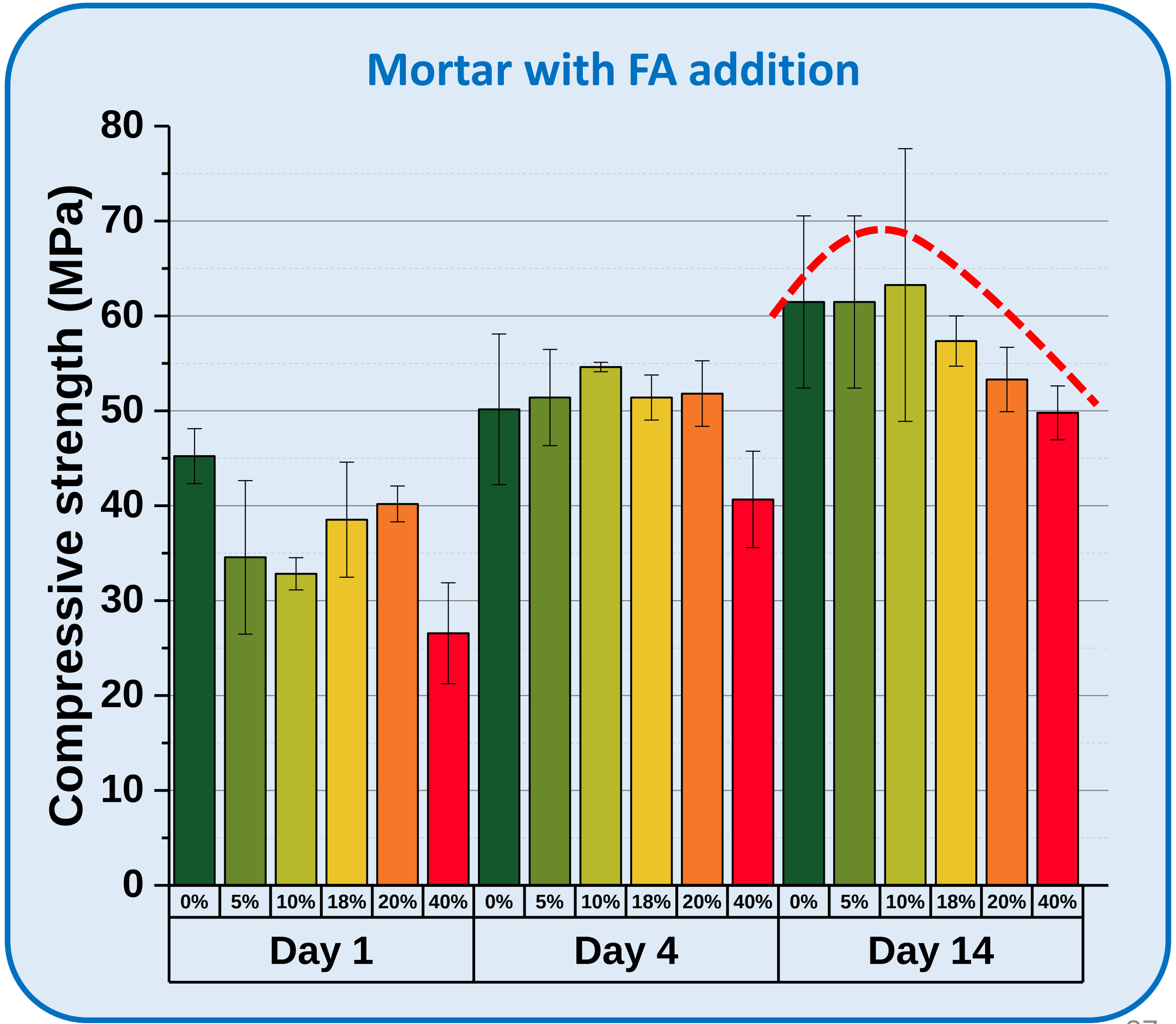
How to add mineral powders to OPC mortar?

Physical integration → Fill in the gaps

Use of an accelerated protocol for strength development

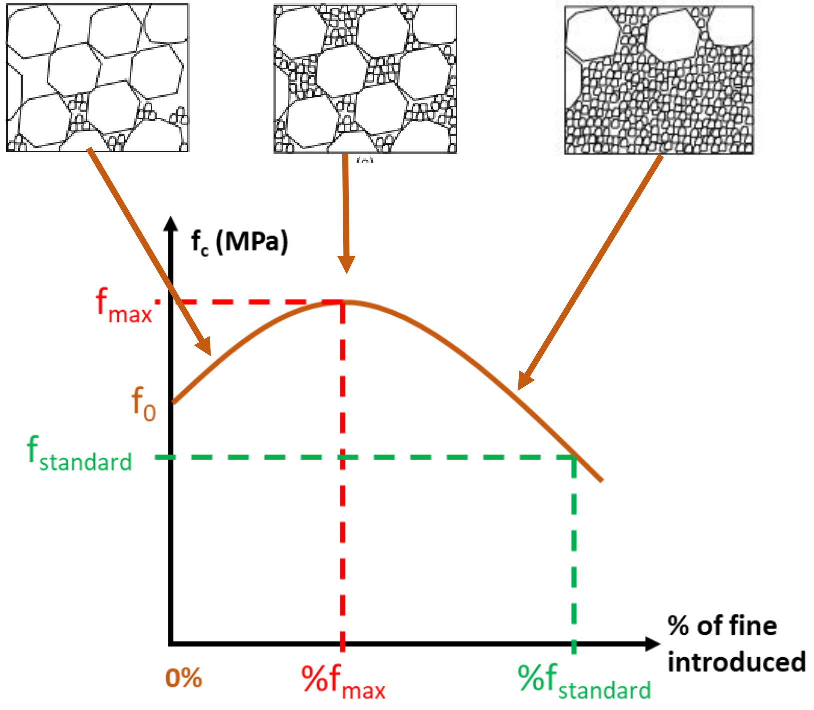
Best compressive strength → 10% Fly ash / Cement mass

The formulation has a significant impact on compressive strength



Physical Integration?

- **Compressive strength depends on the granular skeleton**
- **3 possible cases**



Filler addition can increase compressive strength
and decrease fluid transport (permeability) and hence, durability

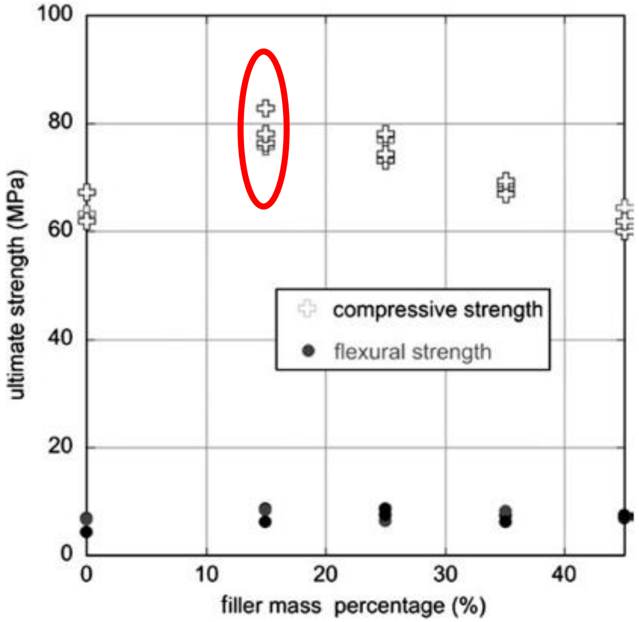


Fig. 11. Variation of ultimate compressive stress σ_{ucs} and ultimate flexural stress σ_{UFS} as a function of filler mass percentage.

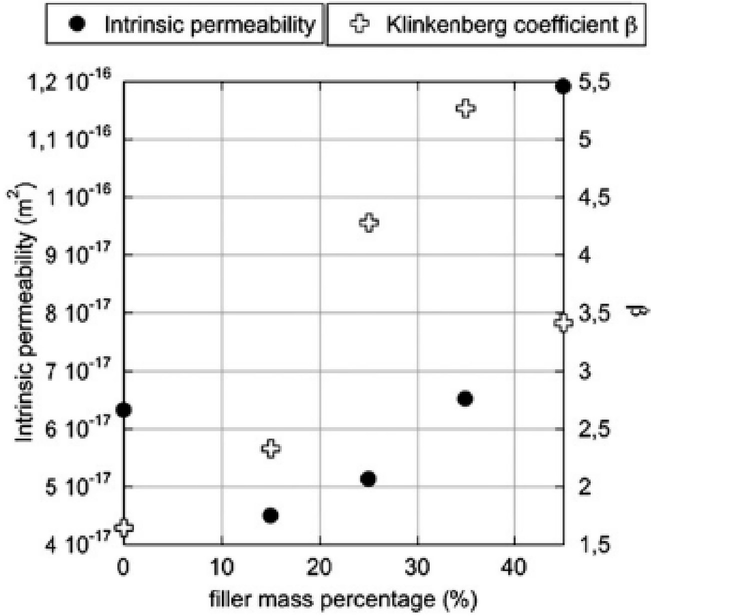


Fig. 13. Variation of intrinsic permeability and Klinkenberg coefficient β as a function of filler mass percentage.

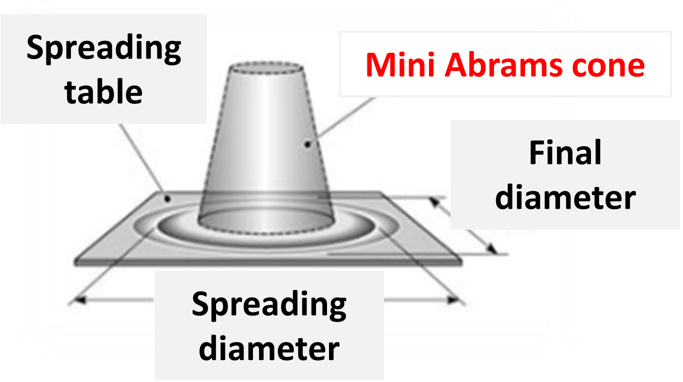
A. E. R. Westman and H. R. Hugill, “The packing of particles,” *J. Am. Ceram. Soc.*, vol. 13, no. 10, pp. 767–779, Oct. 1930.
F. De Larrard, “Structures granulaires et formulation des bétons,” *Etudes Rech. des Lab. des ponts chaussées*, vol. OA 34, p. 414, 2000.
Benachour, Y., et al. *Cement and Concrete Research Journal*, vol. 38, pp. 727–736, 2008.

Physical Integration of Nuclear Waste

- **Applications ?**
  - Formulation for specific waste encapsulation
  - Stabilization/Solidification of nuclear waste
- **Industrial specifications**
  - Mechanical resistance
  - Good rheology
  - Thermal resistance
  - Maximum incorporation of this material
- **Demonstrate feasibility to enable to scale-up while unlocking the technological locks**

Test Miniaturization

Physical characterization: workability



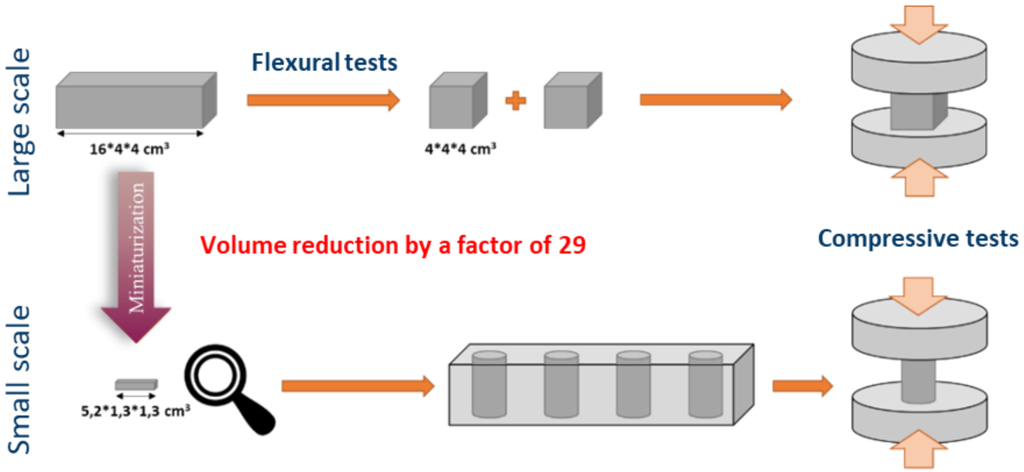
Access to rheological behavior

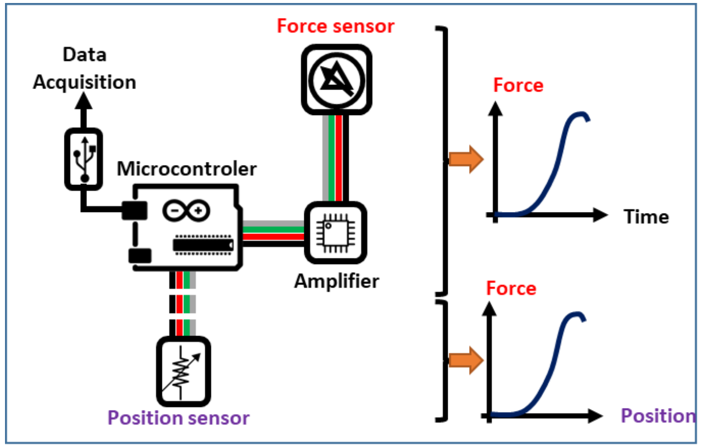
Physical characterization: mechanical test

Access to compressive strength

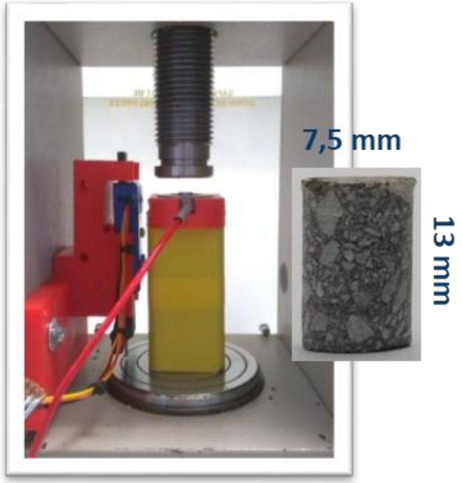
Compressive Test Miniaturization

Methodology used for mechanical tests:



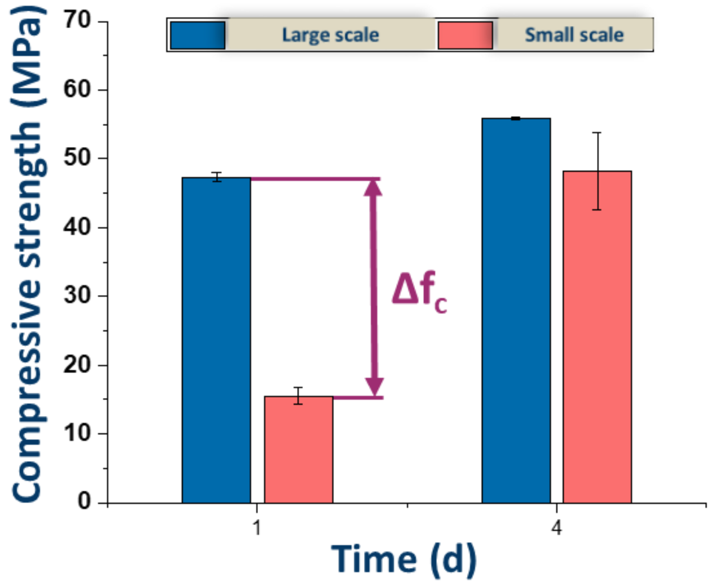


Compression tests on specimens of 4*4*4 cm^3



Compression tests on specimens of Ø7,5 mm *H13 mm

Compressive results at 1 and 4 days for the same formulation



Difference due to volume change

Compressive Test Miniaturization

Volume change = Compressive strength difference at 1 day!

<u>Hypothesis:</u>

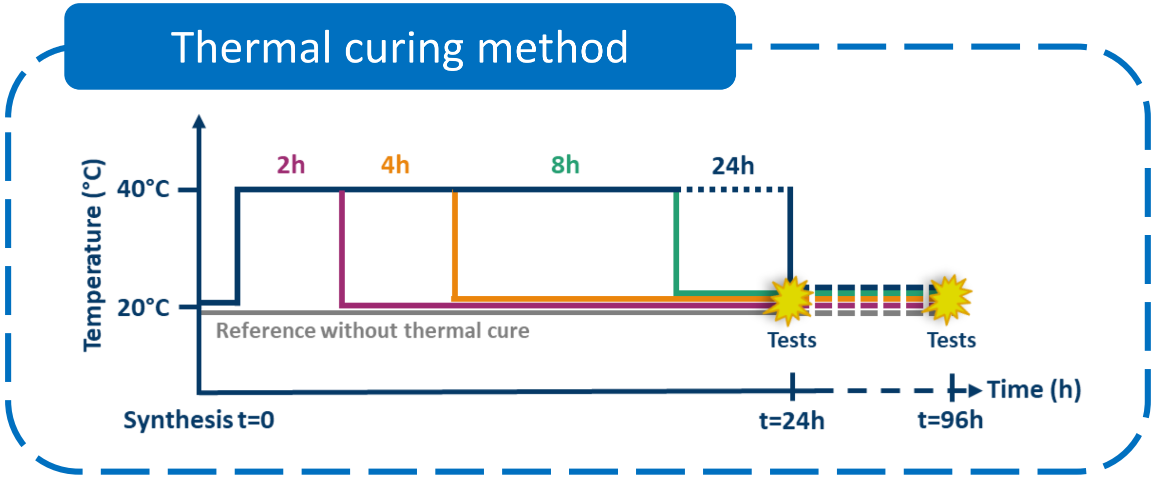
Decrease in reaction kinetics related to volume change (Small/Large scale) by a factor of 29

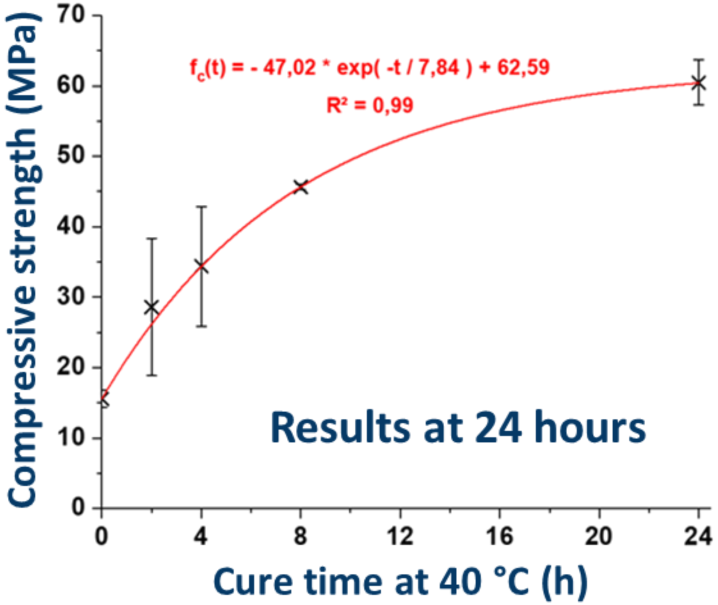
Heat of hydration is dependent on sample volume (Lee et al. 2014)
This influences the reaction kinetics

Arrhenius law type:

$$k' = A * e^{\left(-\frac{E_a}{RT}\right)}$$

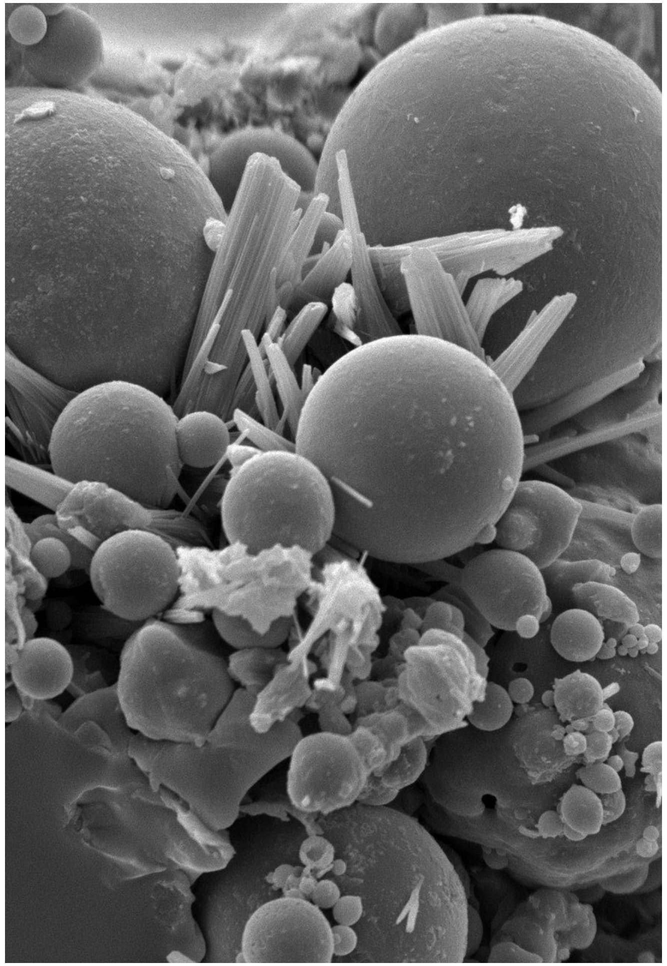
→ Influences kinetics → influences the hydration products
→ Influences compressive strength





Lee, Byung Jae, et al. *Materials*, vol. 7, no. 12, 2014, pp. 7861–74.

Conclusion



Dismantling generates many different type of wastes.
The chemical nature of this waste is the main difficulty in managing it during dismantling.

This is why the development of new adapted cementitious matrices is important to ensure safe handling & protect humans from their toxicity.

The formulation of innovative matrices requires:

- Implementation of specifications according to the intended use
- Use of a cementitious matrix appropriate to the waste
- Formulation tests
- Performance optimization (physical, leaching…)
- Understand the physico-chemical phenomena involved

The use of these new materials will make it possible to answer different challenges, which involve safety, technological, environmental and financial issues

GEN IV International Forum℠

Upcoming Webinars

19 June 2019	Interactions Between Sodium and Fission Products in Case of a Severe Accident in a Sodium-cooled Fast Reactor	Mr. Guilhem Kauric, CEA, France
31 July 2019	Security Study of Sodium-Gas Heat Exchangers in Frame of Sodium-cooled Fast Reactors	Dr. Fang Chen, CEA, France
29 August 2019	Lead Containing Mainly Isotope ^{208}Pb: New Coolant, Moderator and Neutron Reflector for Innovative Fast Nuclear Reactors	Dr. Evgeny Kulikov, National Research Nuclear University “MEPhI,” Russia