PREDIS

Effects of gamma irradiation on the behavior of radioactive waste containment matrices: MKPC

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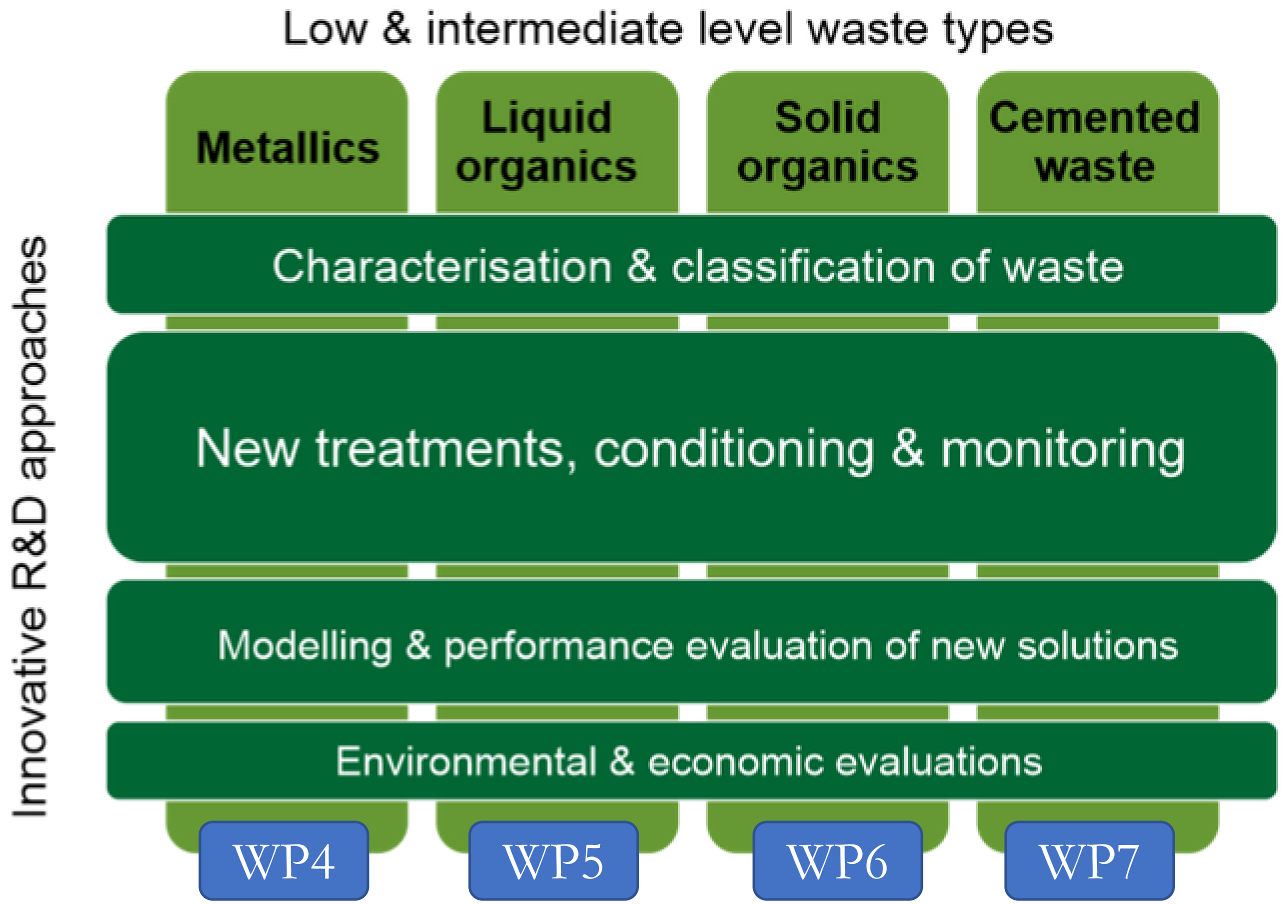
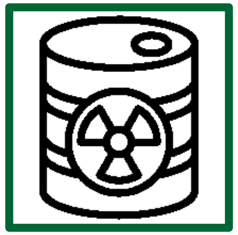
This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 945098.

PREDIS Project





Develop a new reference solution for the storage and final disposal

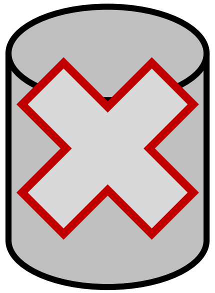
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Why Magnesium Potassium Phosphate Cement (MKPC)?

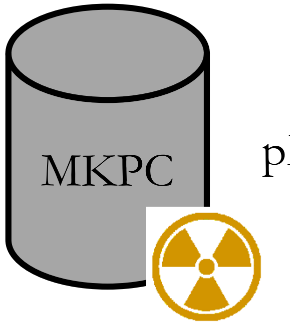
Radioactive
Metallic Waste

⬇

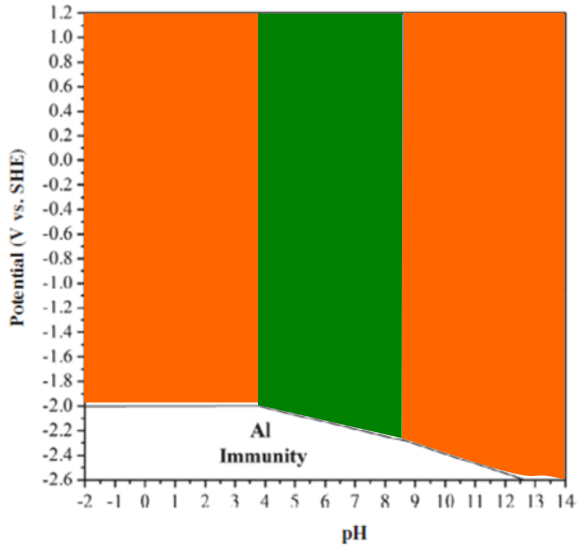
Al
Be

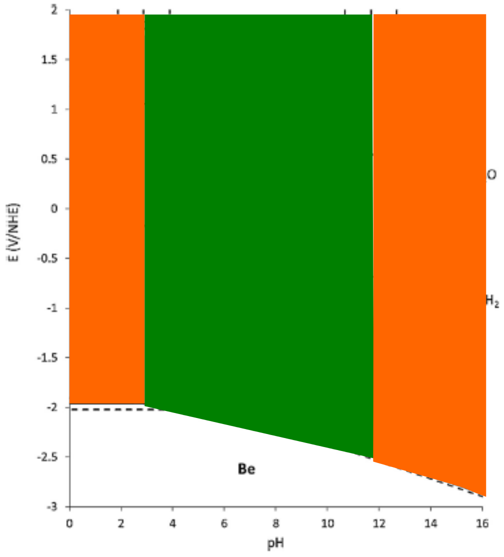


pH ≈ 11-12



pH ≈ 4-9





Corrosion

↓

H_2 release

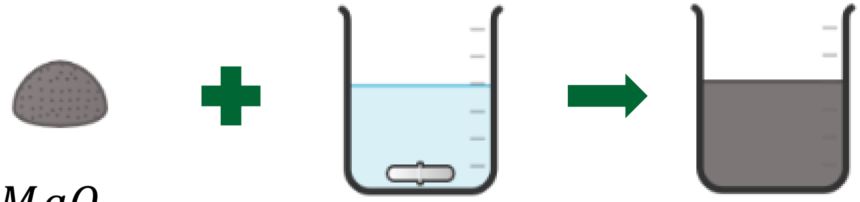
↓

Dissemination

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Experimental Protocol - MKPC Formulation

Mixing



- MgO
- KH_2PO_4
- Fly Ash
- Sand

- Water
- H_3BO_3 (retardant)

Stirring for ~5 minutes

$$MgO + KH_2PO_4 + 5H_2O \rightarrow \underbrace{MgKPO_4}_{\text{K-Struvite}} + 6H_2O$$

Ratio	Value
MgO/KH_2PO_4 (molar)	1
Fly Ash/(MgO + KH_2PO_4) (mass)	1
Sand/(MgO + KH_2PO_4) (mass)	1
H_3BO_3/(MgO + KH_2PO_4) (mass)	0.02
Water/(MgO + KH_2PO_4) (mass)	0.51

Chartier, D. *et al. Journal of Nuclear Materials* **541**, (2020).

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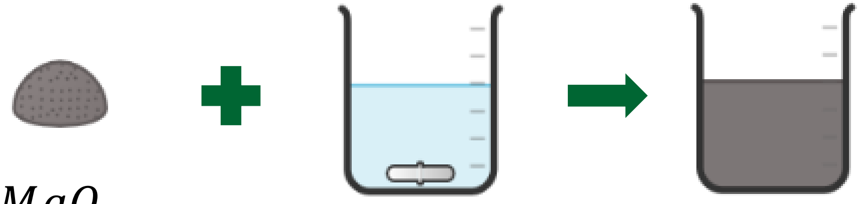

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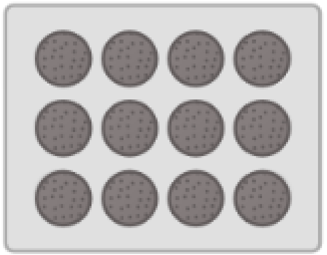
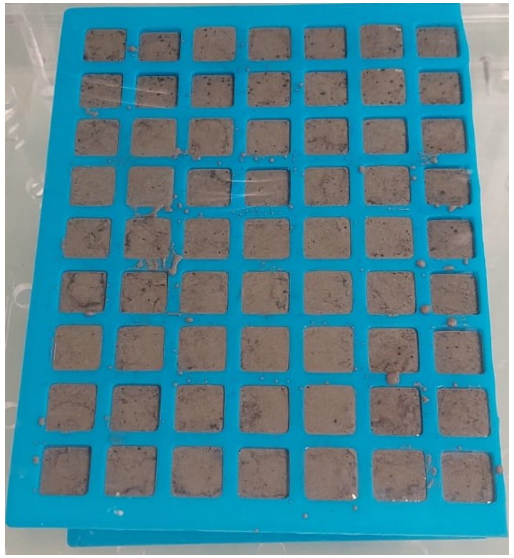
Chartier, D. *et al. Journal of Nuclear Materials* **541**, (2020).

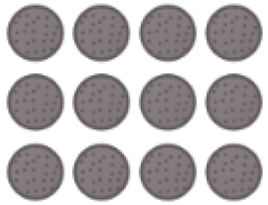
Casting





Silicon Mold

Demolding



Demolding after ~6h

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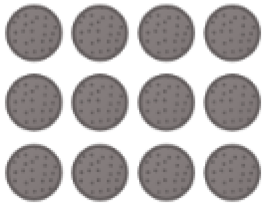
Experimental Protocol - MKPC Curing and Irradiation

Curing



Standard values for the evaluation of durability properties (i.e. compression)

Irradiation

Argon Atmosphere

ARRONAX

GSM D1 Gamma irradiation station
120 TBq $_{137}$**Cs** Eγ=0,66MeV
Dose rate: **0.45 kGy/h**

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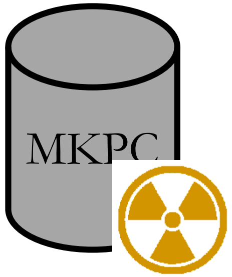
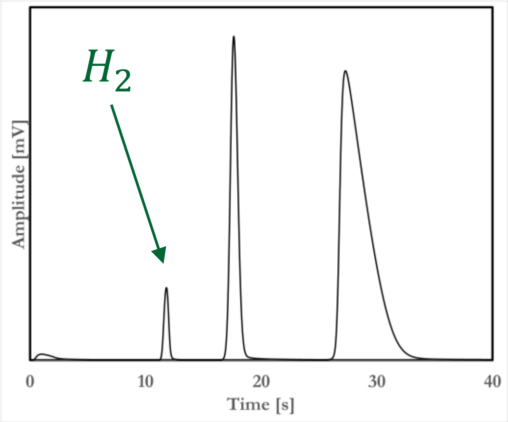
Methods

μ-GC Analyses

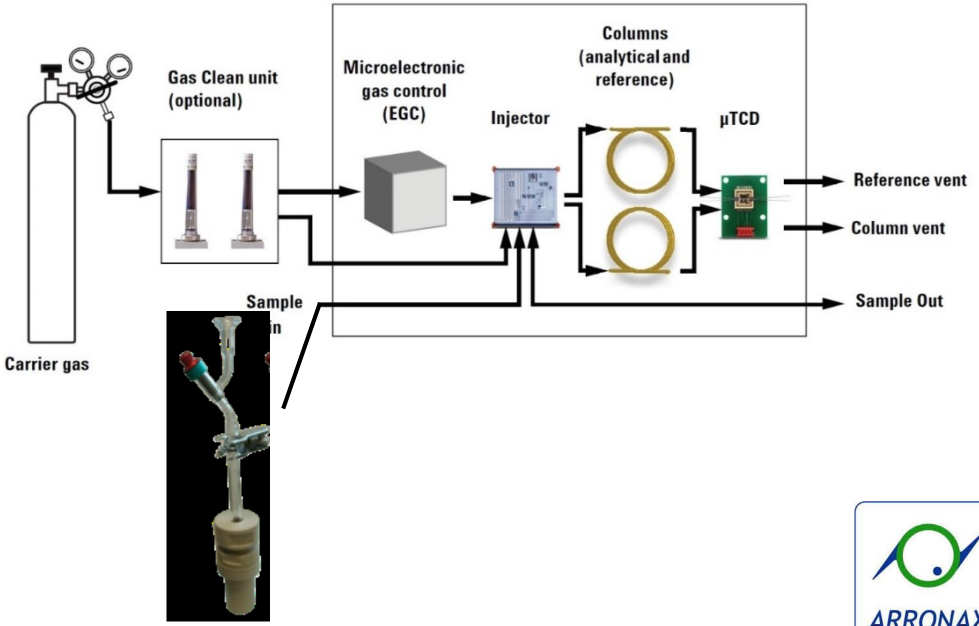
H_2 release



Radiolysis
due to the irradiation



Quantitative Analysis



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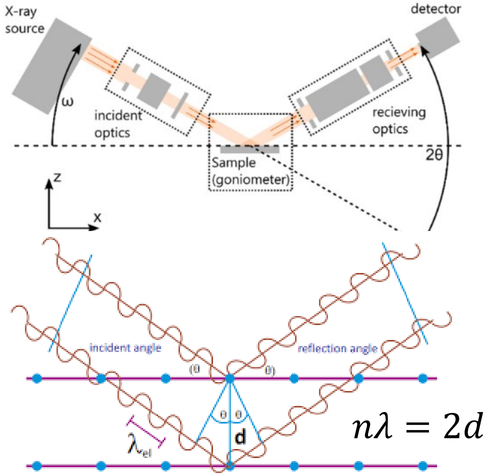
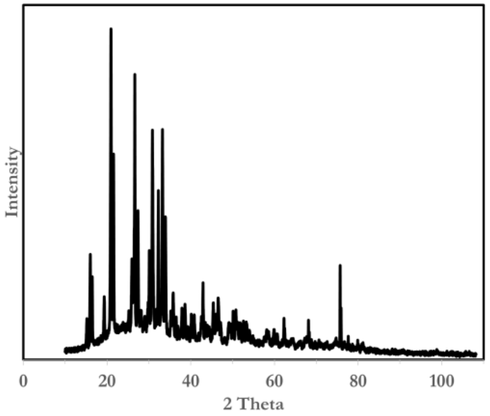
Methods

XRD Analyses



$$n\lambda = 2d \sin\theta$$



Qualitative Analysis

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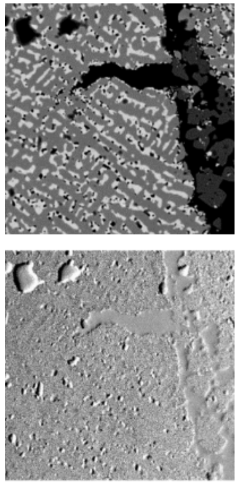
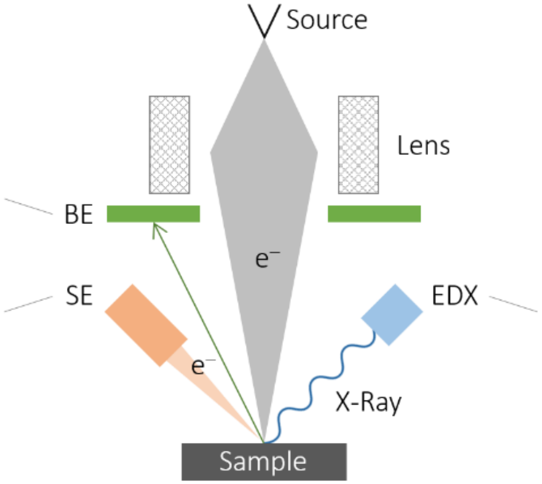
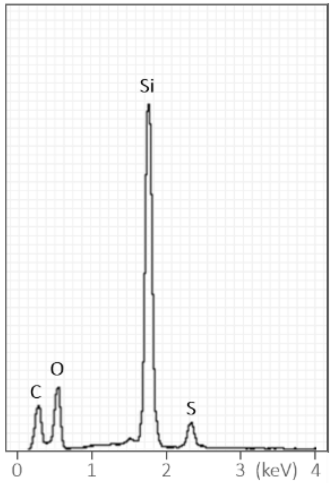
Mineralogy and Microstructural Characterization

SEM - EDX Analyses







Quantitative Analysis

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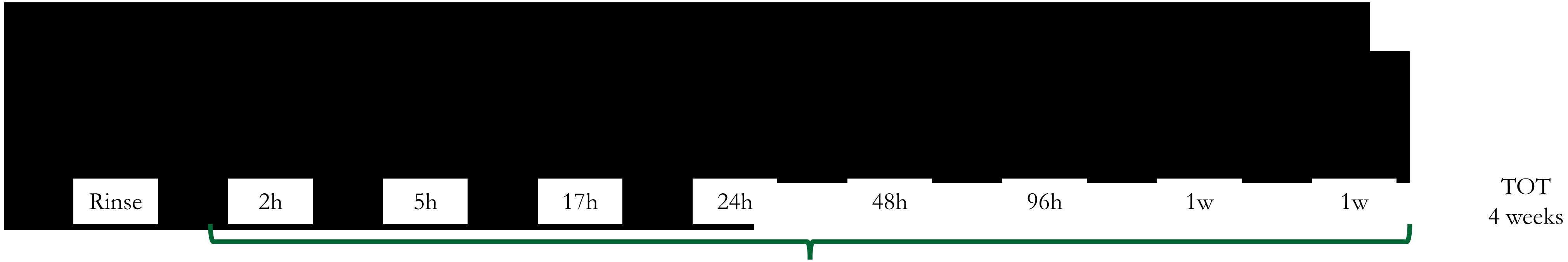
Methods

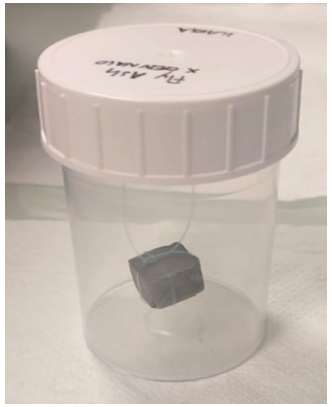
Guida Tecnica 33. Ispettorato Nazionale per la Sicurezza Nucleare e la Radioprotezione. **2023**.

Leaching Test

ANSI-ANS 16.1 - 2003

Resistance of the MKPC to the water immersion





Each solution is analyzed to obtain the amount of **element released** from the sample

- Ion Chromatography (Mg, K)
- ICP-MS (Si)

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Methods

Guida Tecnica 33. Ispettorato Nazionale per la Sicurezza Nucleare e la Radioprotezione. **2023**.

Leaching Test

ANSI-ANS 16.1 - 2003

→ Resistance of the MKPC to the water immersion

Leachability Index (LI)

Required value is <u>above 6</u>

$$LI = \frac{1}{n}\sum\left[\log\left(\frac{\beta}{D_e}\right)\right]_n \quad \text{with} \quad D_e = \sum\left[\frac{a_n/A_0}{(\Delta t)_n}\right]^2\left(\frac{V}{S}\right)T$$

Effective Diffusivity $[cm^3/s]$

Δt time interval [s]

T function of time

a_n amount of element leached

A_0 amount of element in the matrix

[redacted]

Volume $[cm^3]$ and Surface $[cm^2]$

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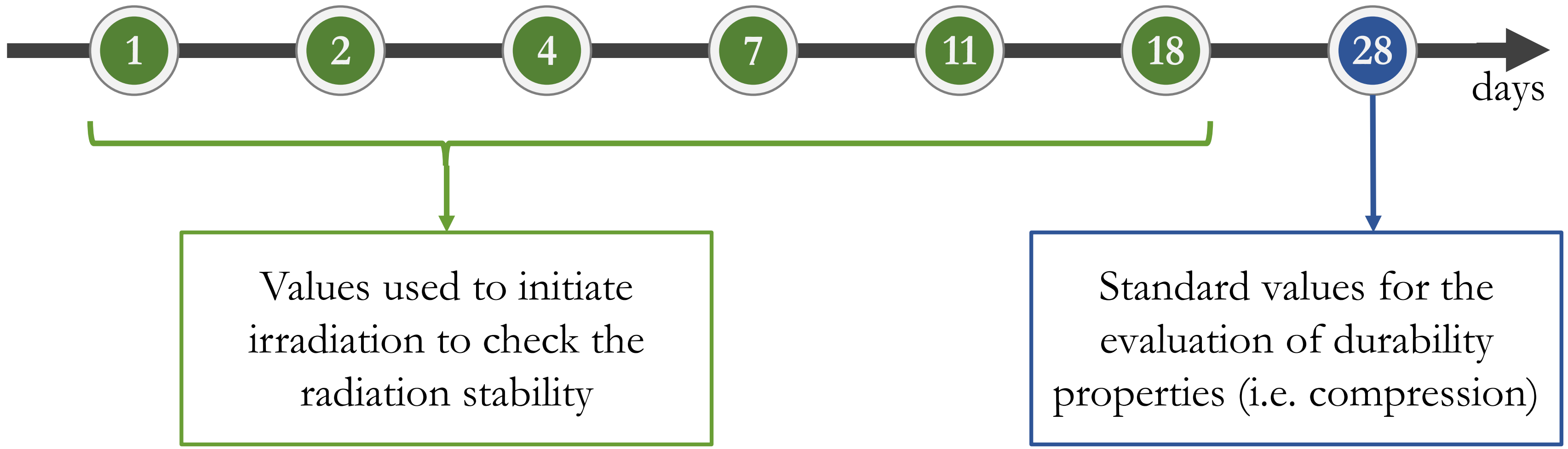
Experimental Set-up

Curing time	Total Dose	Water content	
1, 2, 4, 7, 11, 18 and 28 days	200 kGy	0%	**Real Application**



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	28 days	50, 100, 200, 500, 1000 kGy	0%	**Possible Applicability**

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Experimental Set-up

	Curing time	Total Dose	Water content	
	1, 2, 4, 7, 11, 18 and 28 days	200 kGy	0%	**Real Application**
	28 days	50, 100, 200, 500, 1000 kGy	0%	**Possible Applicability**
	28 days	200 kGy	±5%	**In-Situ Variation**

Ratio	Value
MgO/KH_2PO_4 (molar)	1
Fly Ash/($MgO + KH_2PO_4$) (mass)	1
Sand/($MgO + KH_2PO_4$) (mass)	1
H_3BO_3/($MgO + KH_2PO_4$) (mass)	0.02
Water/($MgO + KH_2PO_4$) (mass)	0.51

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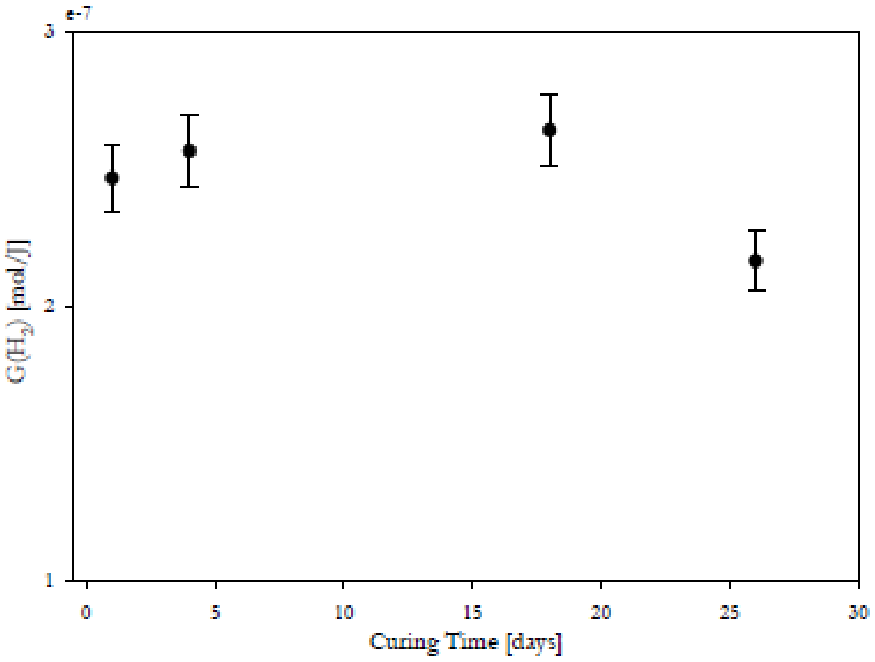
Variation of Curing Time

[redacted]

μ-GC : H_2 release



Aim: Measure the H_2 release

- Between 1 and 18 days → 2.5x10^{-7} mol/J
- At 28 days → 2.1x10^{-7} mol/J

Outcome: Variation due to longer curing time
Fresh matrix not significantly more sensitive

ARRONAX

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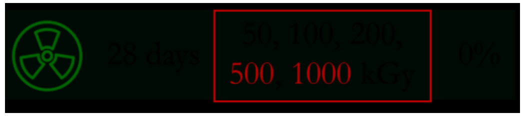
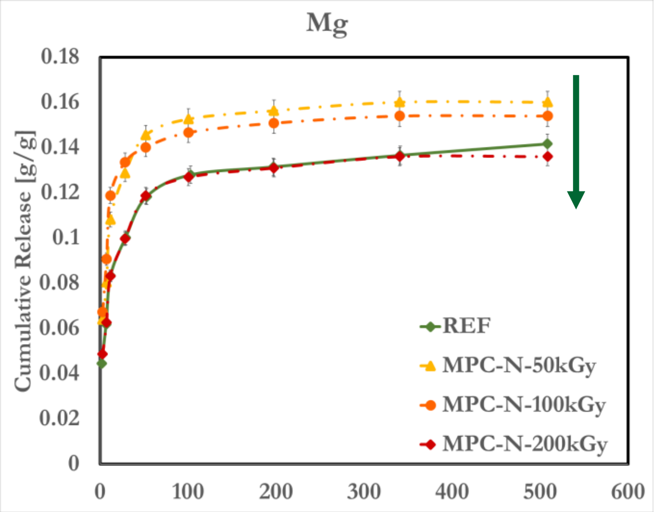
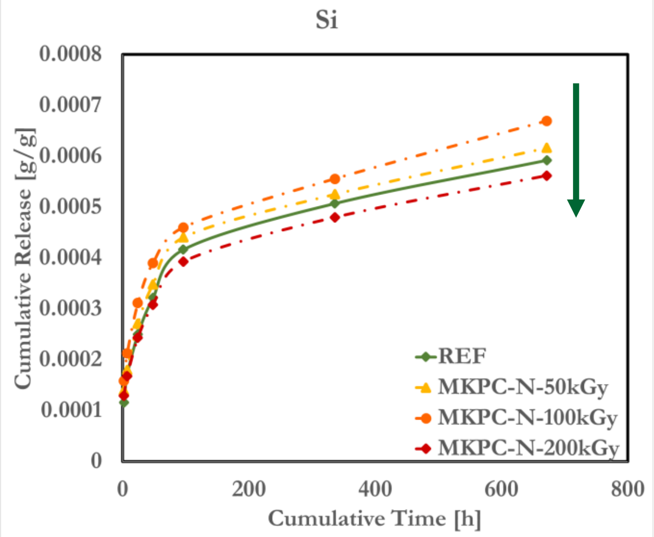
Variation of Total Absorbed Dose



Leaching Test





Aim: Understand the water resistance

➢ Higher is the total absorbed dose, lower is the element release

Mg	REF	50kGy	100kGy	200kGy
Leachability Index	9.5	9.3	9.4	9.3

Si	REF	50kGy	100kGy	200kGy
Leachability Index	12.9	12.8	12.7	12.9

*Measure of K were also performed and the LI was over the standard requirement.

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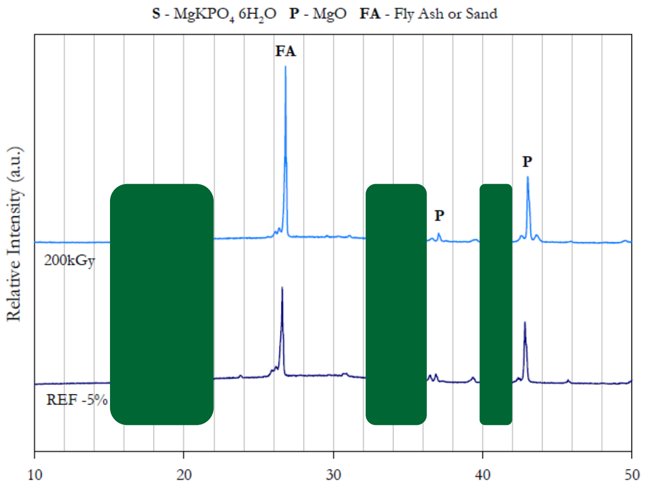
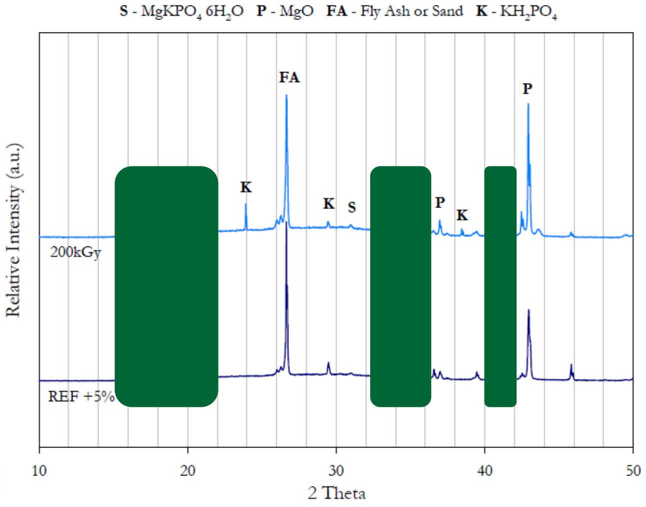
Variation of Water Content

[redacted]

XRD : structural changes



-5% water



+5% water

Aim: Understand the possible morphology modification
Particularly variation on struvite-K

- ✓ No major changes between samples
- ✓ Struvite-K peaks still visible after 200kGy

Outcome: Morphology of struvite-K
does not change with a difference
in water content

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Hall E

Bykov, G.L., et al. *Radiation Physics and Chemistry* Vol. **190** (2022): p. 109822.

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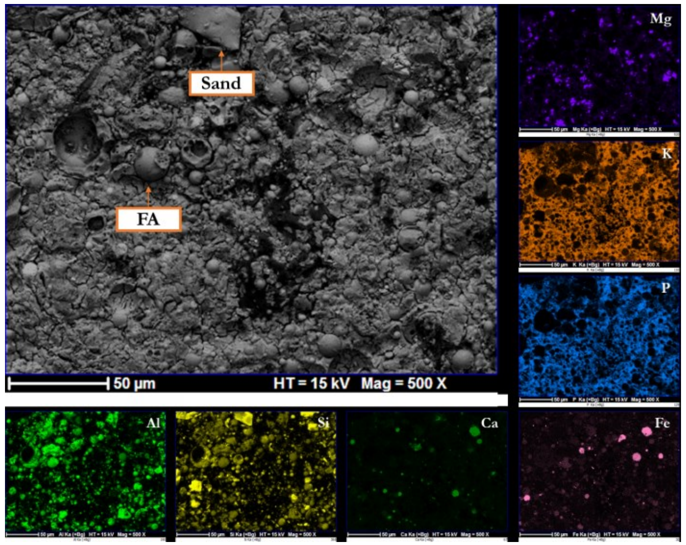
Variation of Water Content

[redacted]

SEM: structural changes

IMN
INSTITUT DES MATÉRIAUX JEAN ROUXEL



Sample	Mg/P	Mg/K	K/P
MKPC-L	1.02	0.92	1.1
MKCP-L 200 kGy	0.52-0.96	0.5-0.84	1.04-1.14
MKPC-H	0.93	0.83	1.1
MKPC-H 200 kGy	1.04-1.4	1.44-1.5	0.72-0.94

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 + 6H_2O$$

Aim: Understand the possible morphology modification
Particularly variation on struvite-K

EDX analyses underline the presence of:

(i) Unreacted MgO
(ii) Filler material (Fly ash and Sand)
(iii) K-struvite phase

Outcome: (?) Modification due to gamma irradiation
(?) Detection of different morphologies

Xu, B. et al. *Cement and Concrete Research* Vol. **99** (2017): pp. 86–94.

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Outcome

XRD	H_2	SEM	Leaching	End Objective
	Fresh matrix not sensitive			**Real Application**
K-struvite phase always present		Further characterization needed (needle or prismatic shape)	LI greater than **6**	**Possible Applicability**
				In-Situ Variation

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Future Work

Geopolymer

- New type of matrixes for the encapsulation of Liquid Organic Waste (WP5)
- Same characterization techniques

New Techniques

- Nano-Indentation (for local compression strength)

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Rennes

- Tomography (for porosity and density)

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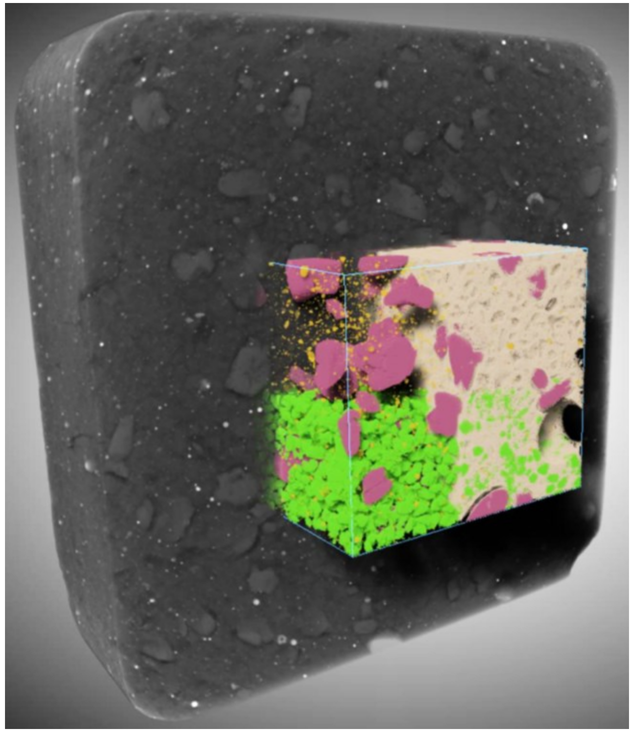

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Thanks for
your attention

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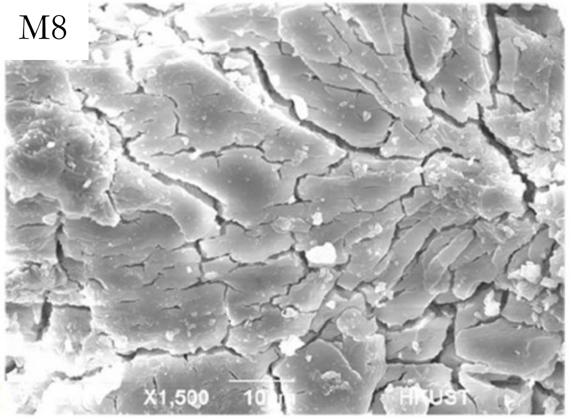
Annex 1: Needle and Prismatica Shape

Table 2
Mix proportions of the MKPC mortars.

Series	M/P molar ratio	Binder components				s/b	w/b
		Magnesia	KDP	FA[a]	Borax[b]		
M8	8.0	1.00	0.43	0.00	0.080	0.25	0.15
M8-FA-C[c]	8.0	0.70	0.30	0.43	0.056	0.25	0.15
M4.5-FA-R[c]	4.5	0.57	0.43	0.43	0.046	0.25	0.15
M4.5	4.5	0.82	0.61	0.00	0.065	0.25	0.15

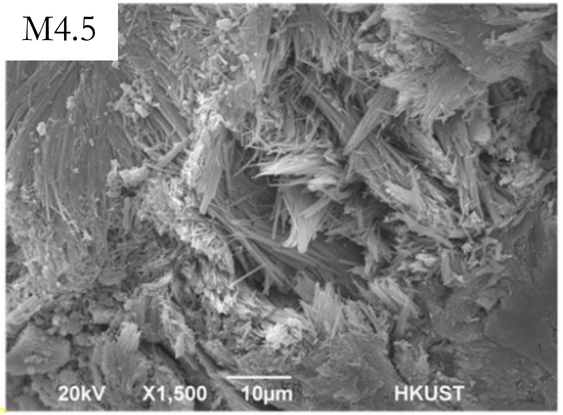
[a] The replacement levels of FA in both M8-FA-C and M4.5-FA-R are both 30 wt%, by weight of the sum of magnesia and KDP in M8.
[b] For all the MKPC mortars, the addition level of borax is 8 wt%, by weight of the magnesia.
[c] C the conventional design method, where FA is treated as inert and used to replace both magnesia and KDP; R: the other design method, where FA is treated as reactive and used to replace magnesia only.

M8



Prism shape

M4.5



Needle shape

Xu, B.; Ma, H.; Shao, H.; Li, Z.; Lothenbach, B. Influence of Fly Ash on Compressive Strength and Micro-Characteristics of Magnesium Potassium Phosphate Cement Mortars. *Cement and Concrete Research* **2017**, *99*, 86–94. https://doi.org/10.1016/j.cemconres.2017.05.008.

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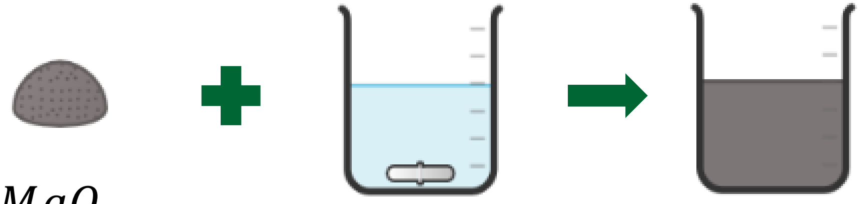
Annex 2: Raw Material

Mixing



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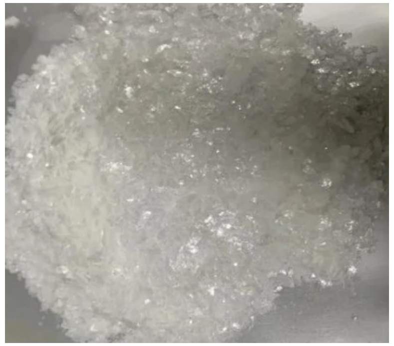
Fly Ash

Sand



H_3BO_3

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