19-06-2020
ABR-BVS – Radiation Effects on Materials

The effect of gamma irradiation on CaO-Fe_xO_y-SiO_2 slag based inorganic polymers

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NuTeC
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KU LEUVEN

Inorganic Polymers (IPs)

What is an IP ?

Why IPs ?

IPs in nuclear industry

Effects of γ irradiation of Fe-rich IPs

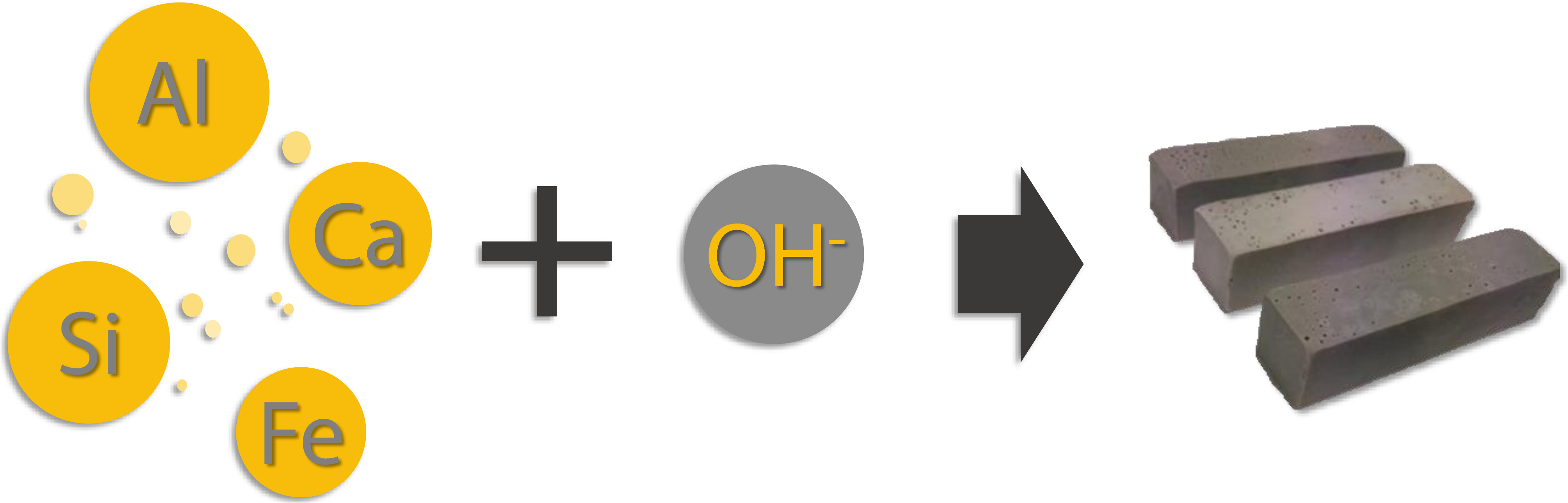
as safety material for nuclear industry

What is an IP?

What is an IP?

The production process

Alkali Activation



Amorphous precursor

Copper slag, plasma slag, metakaolin, fly ash, …

Alkali activation solution

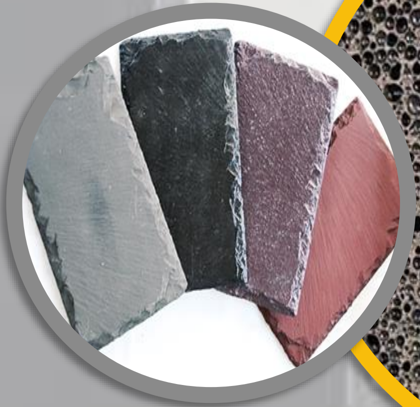
Alkali hydroxides, silicates, carbonates, sulphates, …

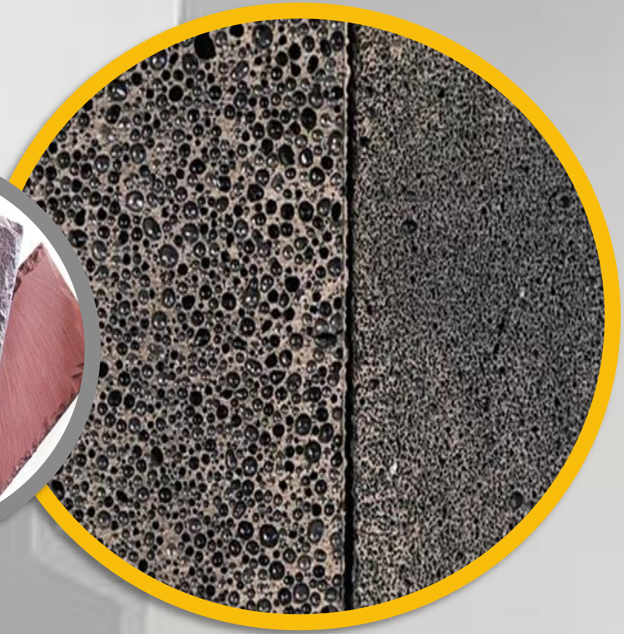
Inorganic Polymer

Geopolymer, alkali activated material, geocement, …

What is an IP?

The end product

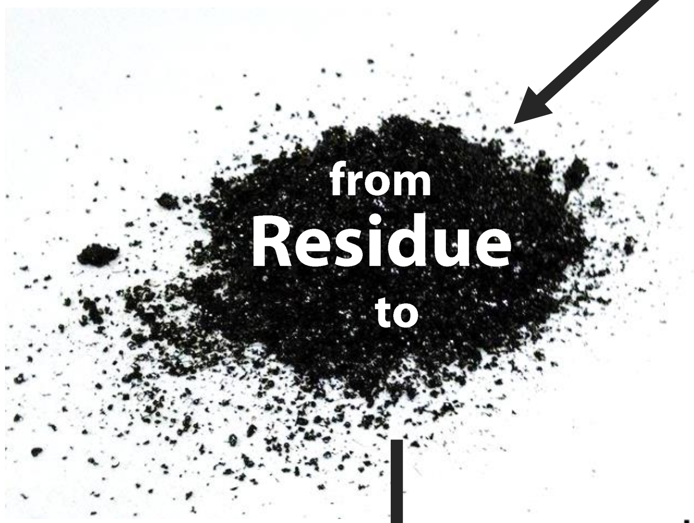




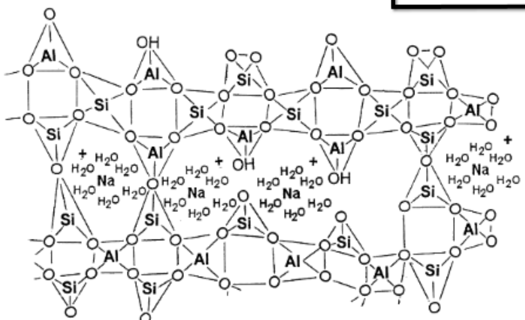
Application
Optimized
Mix Design

What is an IP?

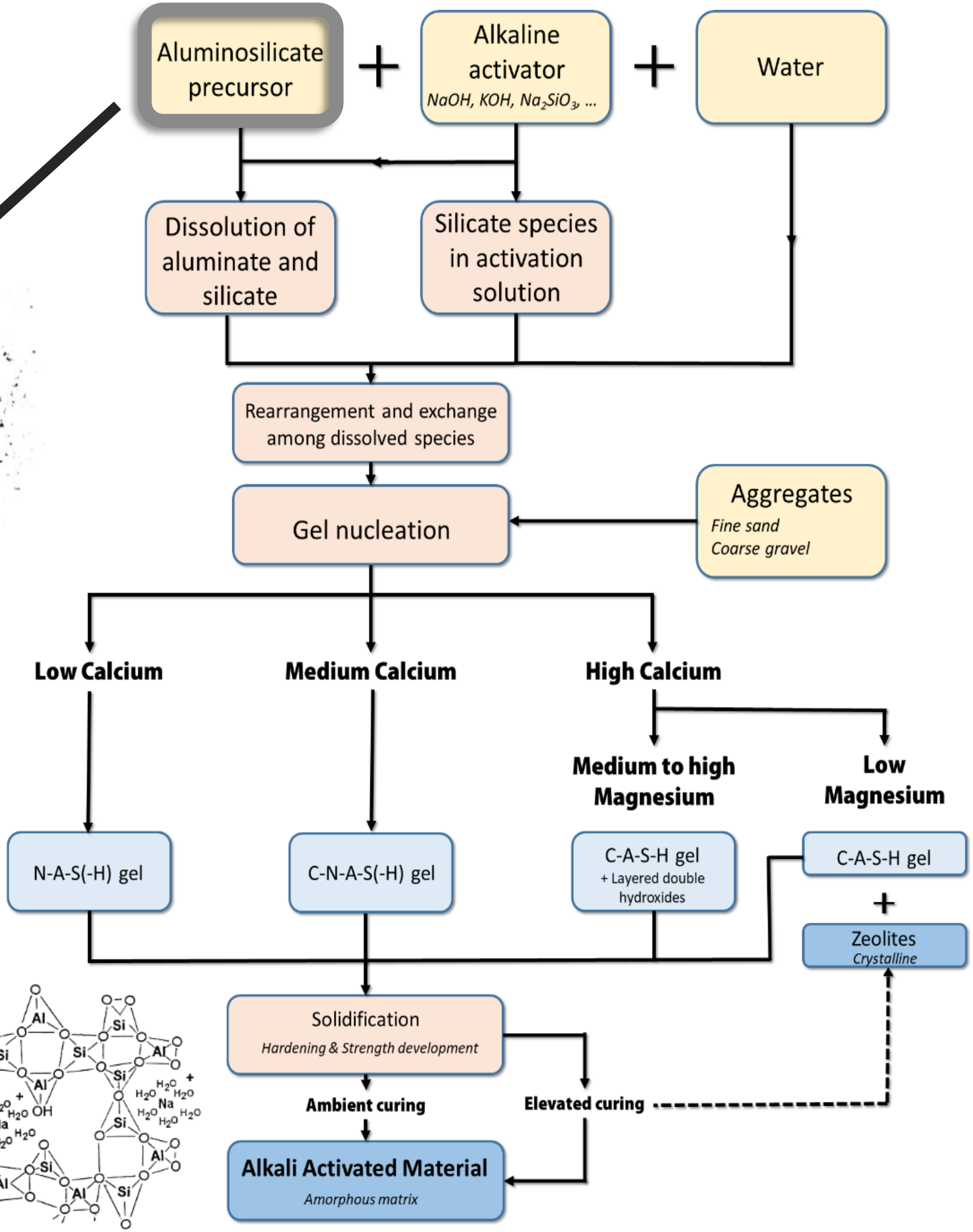
The chemistry in 4 steps

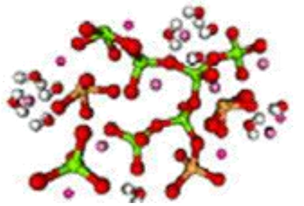


Tetrahedral network

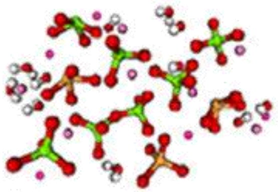


Shi et al.., 2011. New cements for the 21st century: The pursuit of an alternative to Portland cement. Cem. Concr. Res. 41, 750–763.



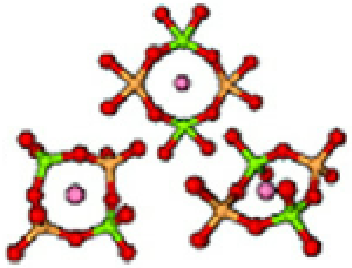


1. Dissolution

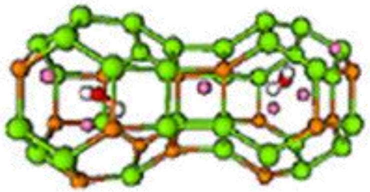


2. Reorganization

3. Nucleation



4. Polymerization



Why IPs?

Why IPs?

Closing the loop – from residue to construction material

Inorganic Industrial Residues

can be used as an input material, reducing disposal of residues as

Fly Ash

Red Mud

Blast Furnace Slag

Phosphogypsum

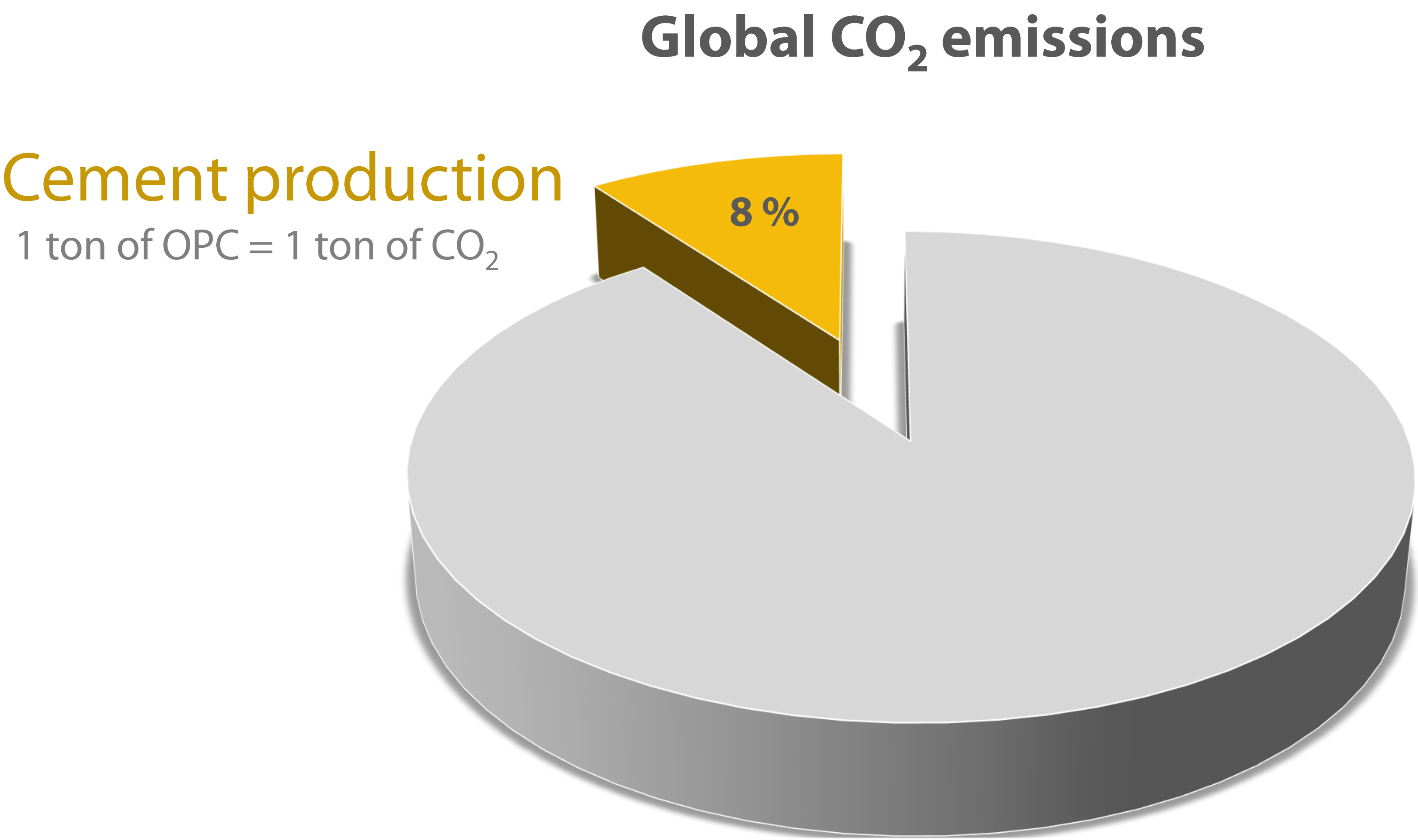
Plasmaslag

and can moreover offer a safe potential for (re)using materials containing

Naturally Occurring Radionuclides

Why IPs?

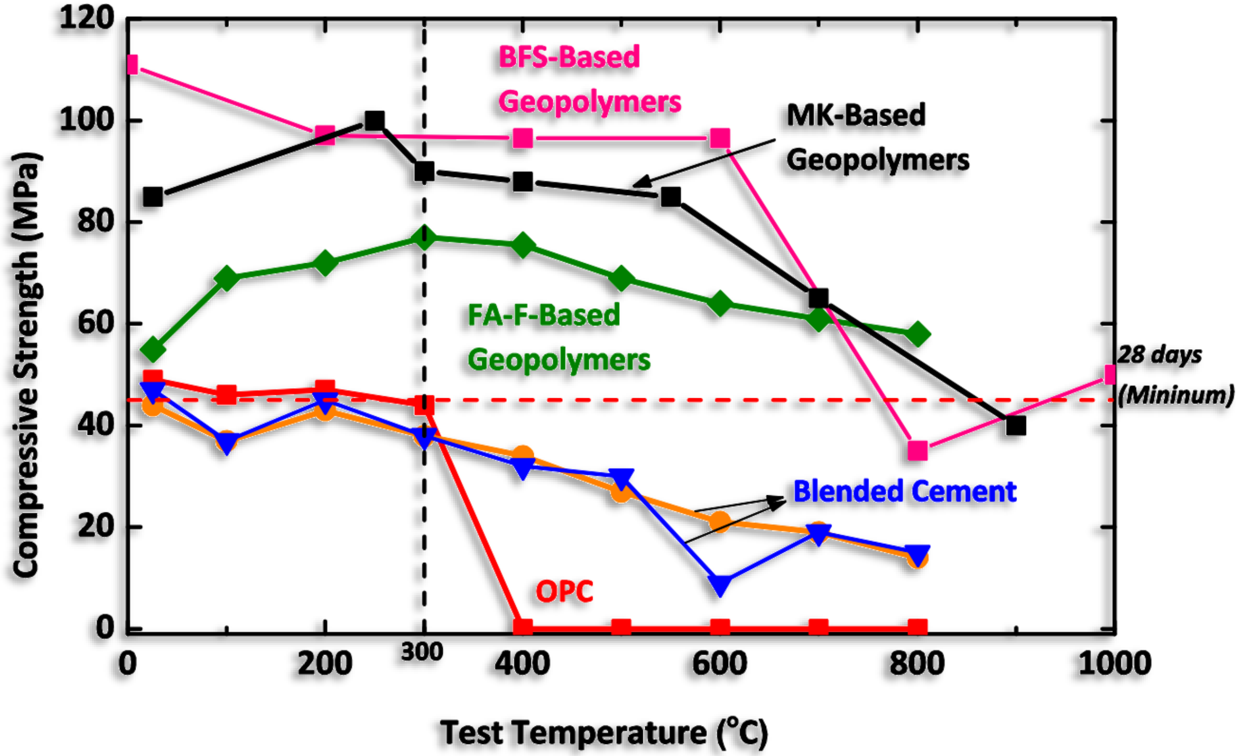
Reduced carbon footprint



Why IPs?

Tailor-made materials with excellent performances

Design 4 Application



- ✓ High (early) strength
- ✓ Controllable porosity
- ✓ High chemical resistance
- ✓ High temperature resistance
- ✓ Low water content
- ✓ High alkalinity
- ✓ Good immobilization capacity
- ✓ No important ASR

Possibilities of IPs in nuclear industry

B. Mast, Y. Pontikes, W. Schroeyers, B. Vandoren, and S. Schreurs,
“00135 Alkali Activated Materials - The use of alkali activated materials in nuclear industry,”
in Comprehensive Nuclear Materials, 2nd ed., 2020.

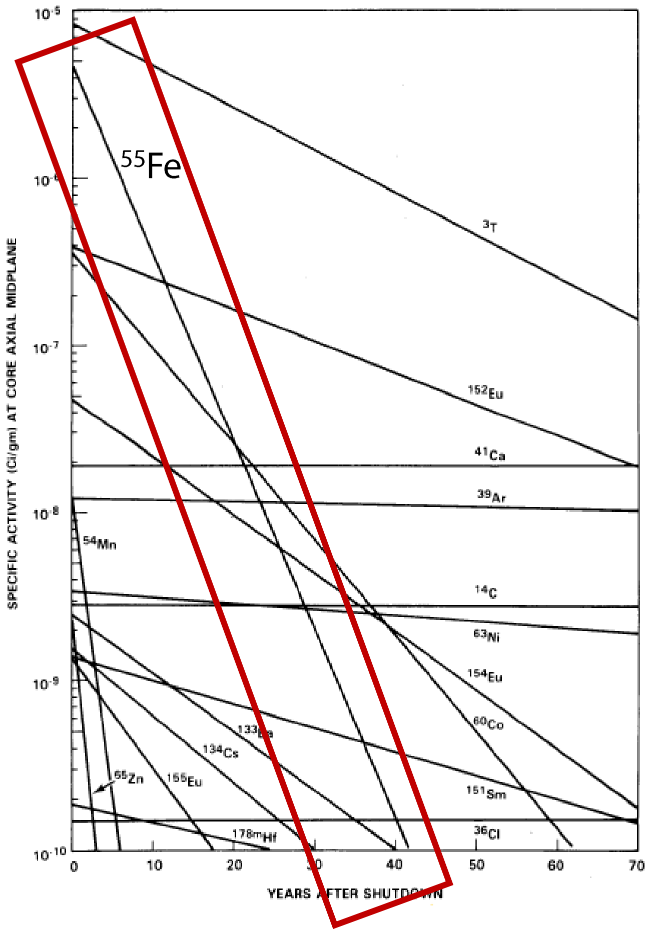
IPs as shielding material

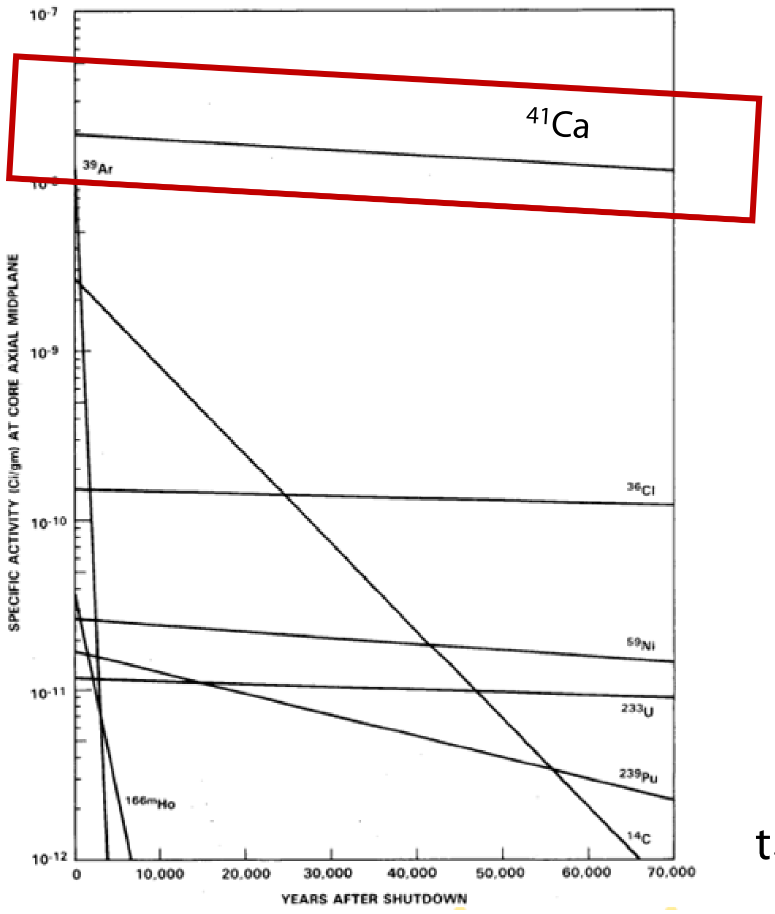
- Low radiolytic H_2 yield
- No damage as a result of dehydration
- Good shielding of γ-radiation
- Activation with $Ba(OH)_2$ improves the shielding performance due to high atomic number
- Boron can subsitute Al for good neutron shielding
- Better neutron shielding than aged OPC concrete
- Neutron activation of ^{40}Ca can be reduced

IPs as shielding material

- **Neutron activation of ^{40}Ca can be reduced**

$t_{1/2}=2.74$ a





$t_{1/2}=9.9 \cdot 10^4$ a

IPs as conditioning material

Advantages

- Absence of $Ca(OH)_2$
- Reduced water content
- High alkalinity
- Excellent fire resistance
- Low porosity

Mechanisms

- Uptake as charge-balancing ion in the structure
- Incorporation in aluminosilicate structure
- Formation of precipitates as hydroxides or carbonates
- Adsorption on self-generated or introduced zeolite structures
- Chemisorption and electrostatic interactions

IPs as conditioning material

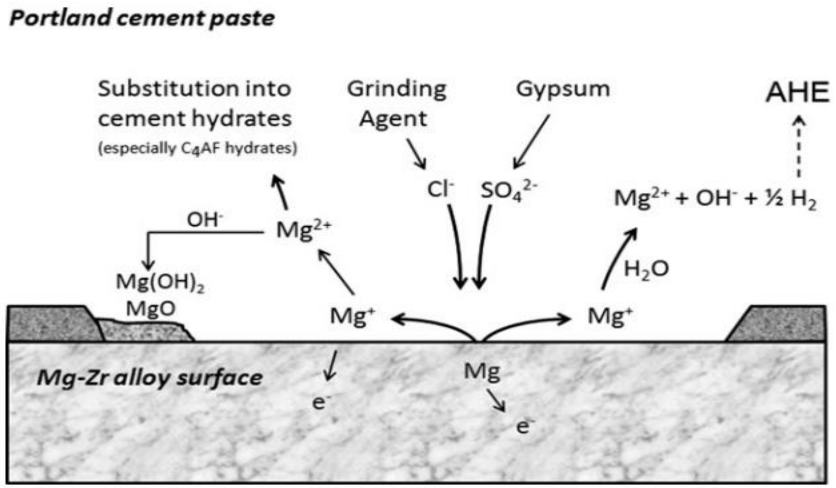
Example: Mg-Zr alloys

At high pH:
High hydrogen gas generation as result of $Mg(OH)_2$ formation

Solution:
Addition of sodium fluorine as Mg corrosion inhibitor → formation of passivation layer

Problem in OPC:
Formation of CaF_2 precipitates → deterioration
Destabilization of protection layer

Solution:
Ca-free low alkaline IPs



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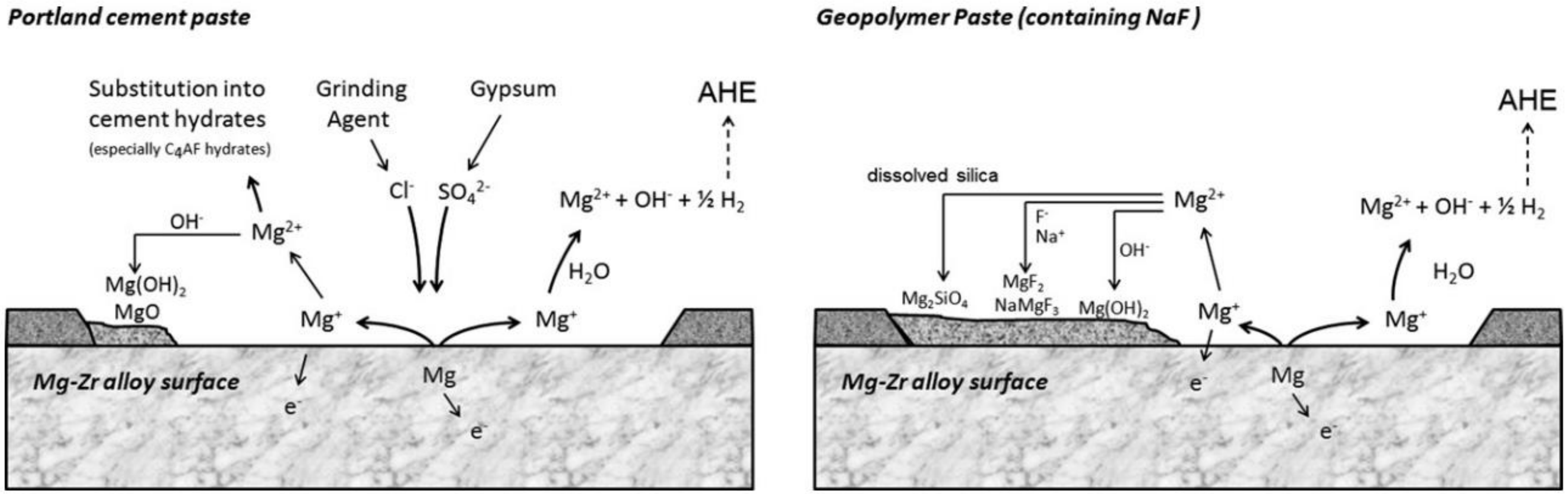
IPs as conditioning material

Example: Mg-Zr alloys

Solution:
Ca-free low alkaline IPs

- Formation of $MgSiO_4$ passivation layer



Effects of gamma irradiation on Fe-rich inorganic polymers

B. Mast et al., "The effect of gamma radiation on the mechanical and microstructural properties of Fe-rich inorganic polymers," J. Nucl. Mater., vol. 521, 2019.

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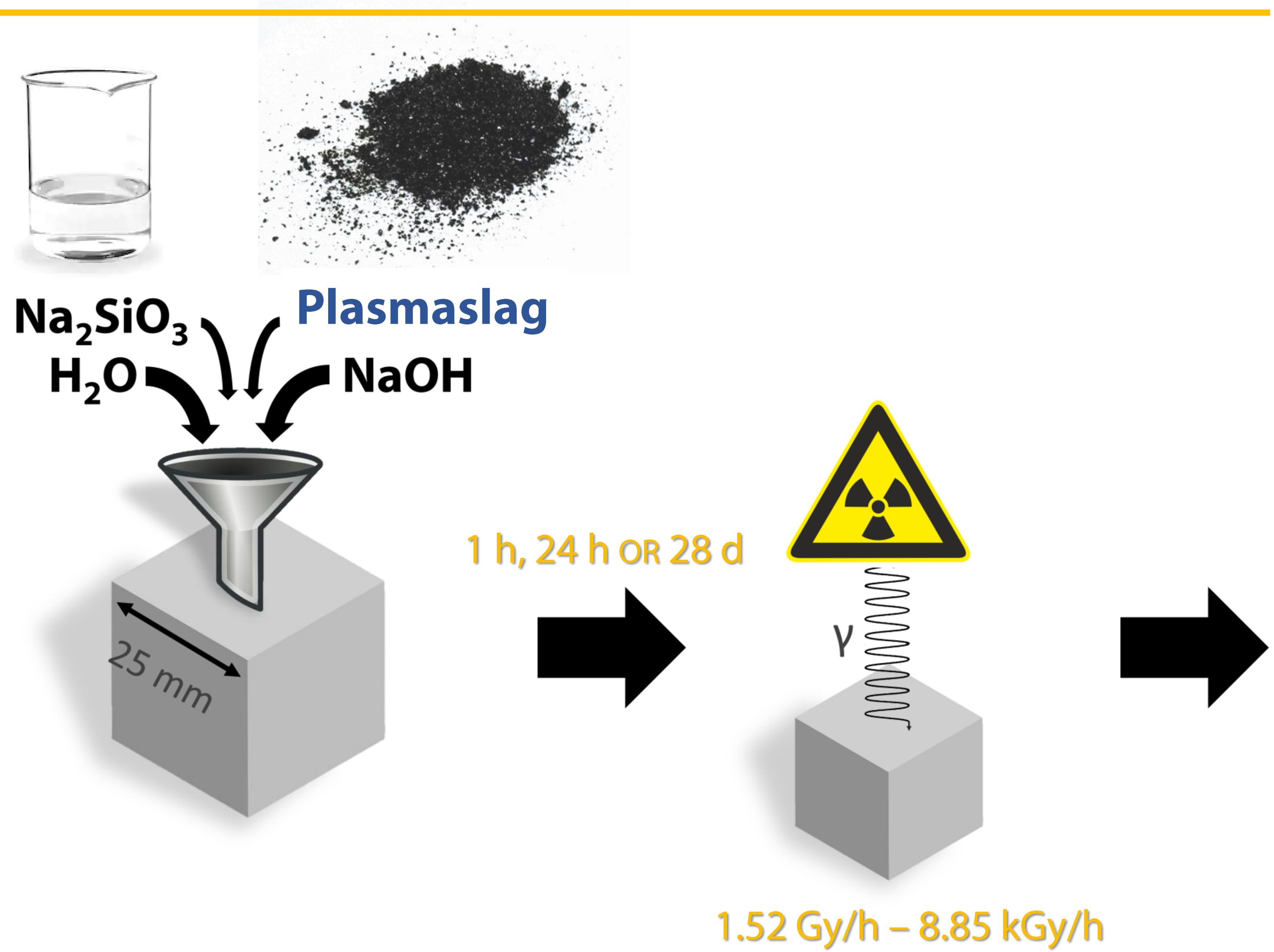
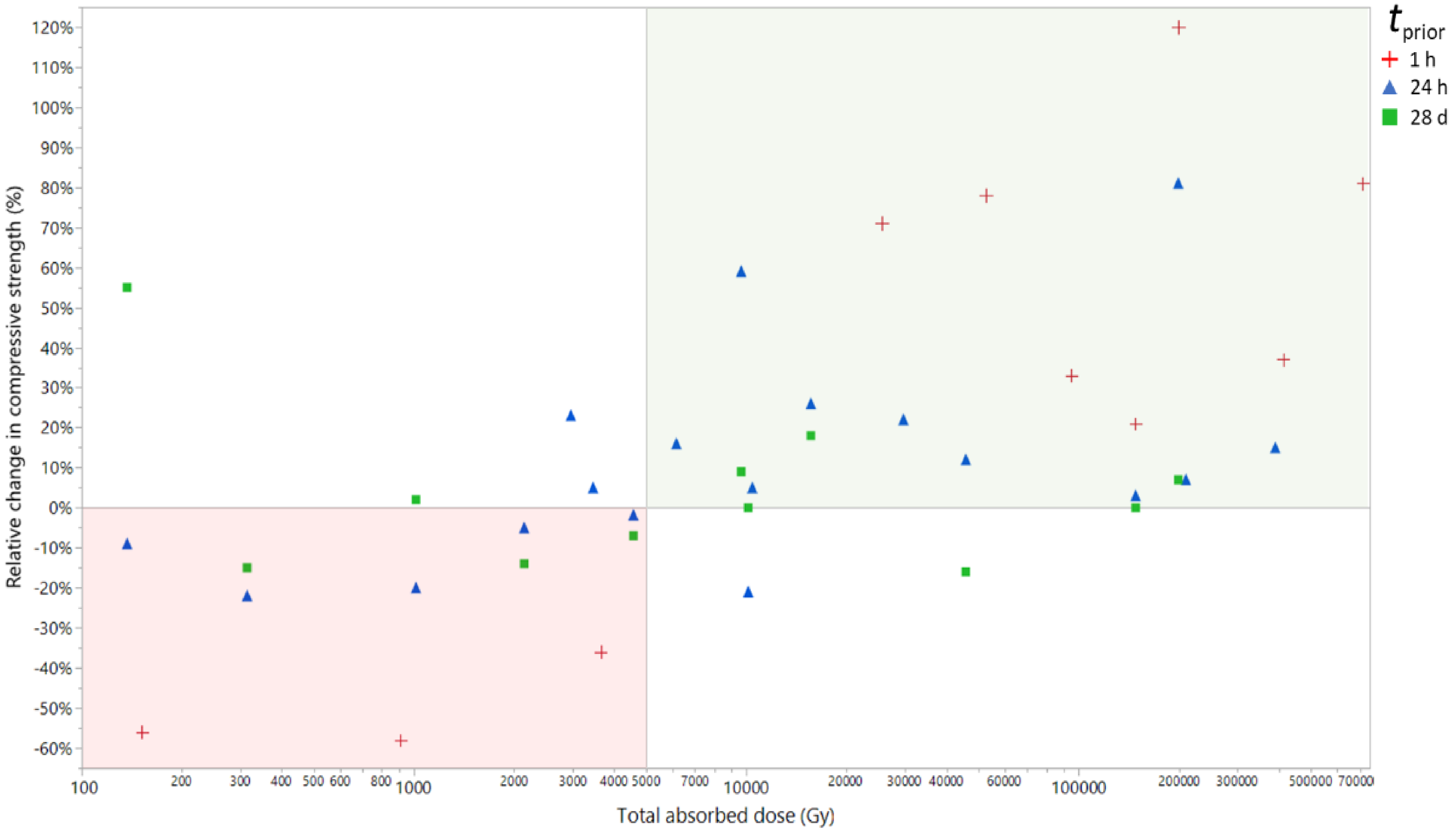


Evaluation:

- Nanoindentation
- Compression strength test
- ATR-FTIR
- NMR
- MIP
- SEM
- TGA
- ^{57}Fe Mössbauer spectroscopy

Effect of gamma irradiation on Fe-rich inorganic polymers

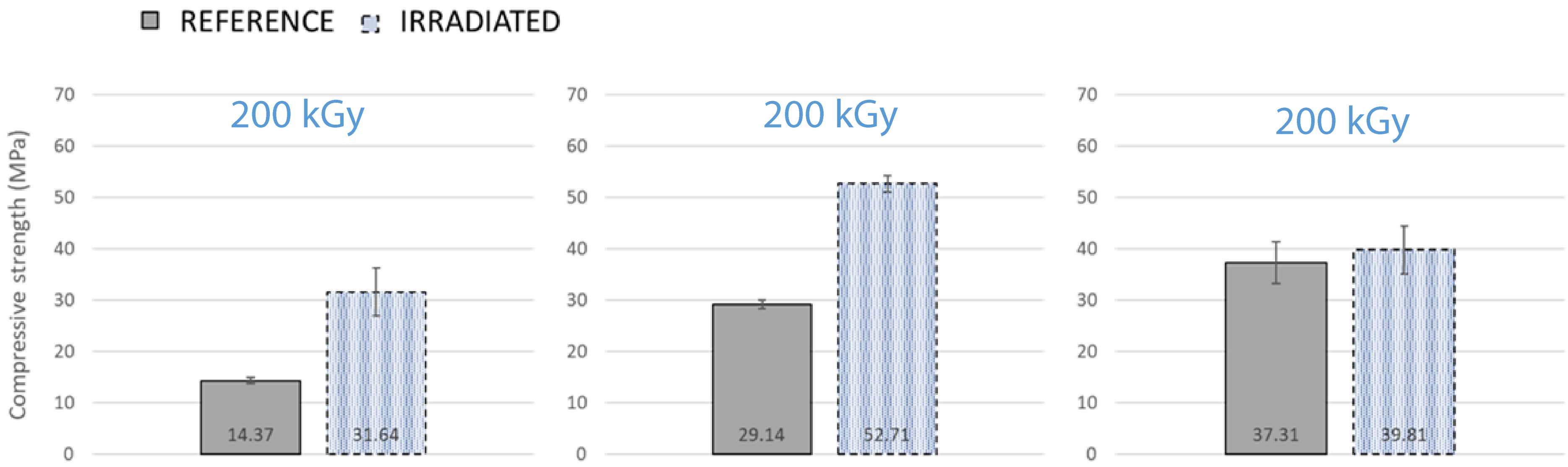
Increase in compressive strength > 5 kGy



Effect of gamma irradiation on Fe-rich inorganic polymers

Increase in compressive strength > 5 kGy

8.85 kGy/h up to 200 kGy

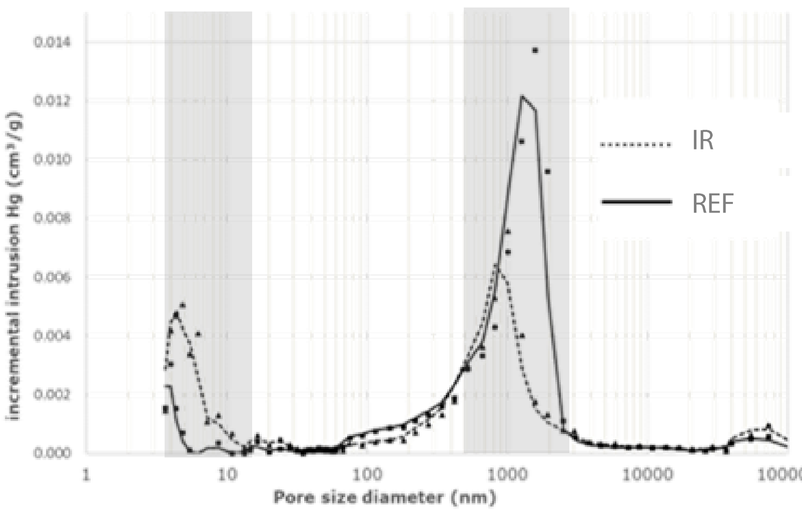


t_{prior}: 1 hour (paste) 24 hours (wet solid) 28 days (solid)

Effect of gamma irradiation on Fe-rich inorganic polymers

Mercury Intrusion Porosimetry: thin pore wall reorganization

200 kGy

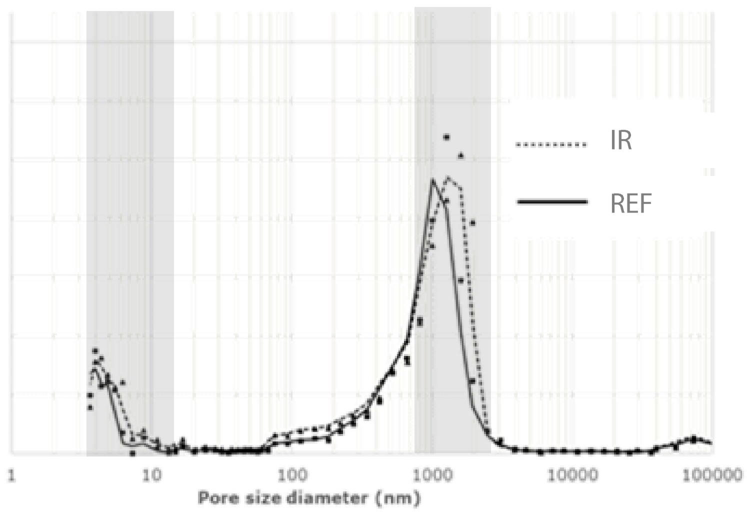


1 h

Decrease in porosity

Shift to smaller pore sizes

200 kGy

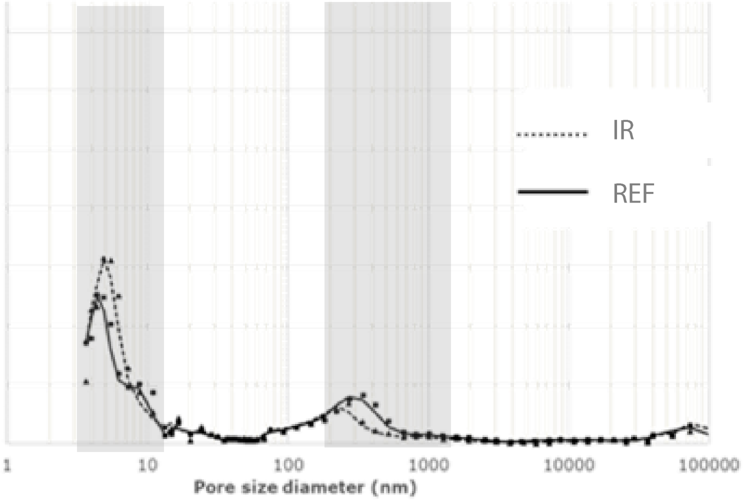


24 h

Increase in porosity

Shift to larger pore sizes

200 kGy

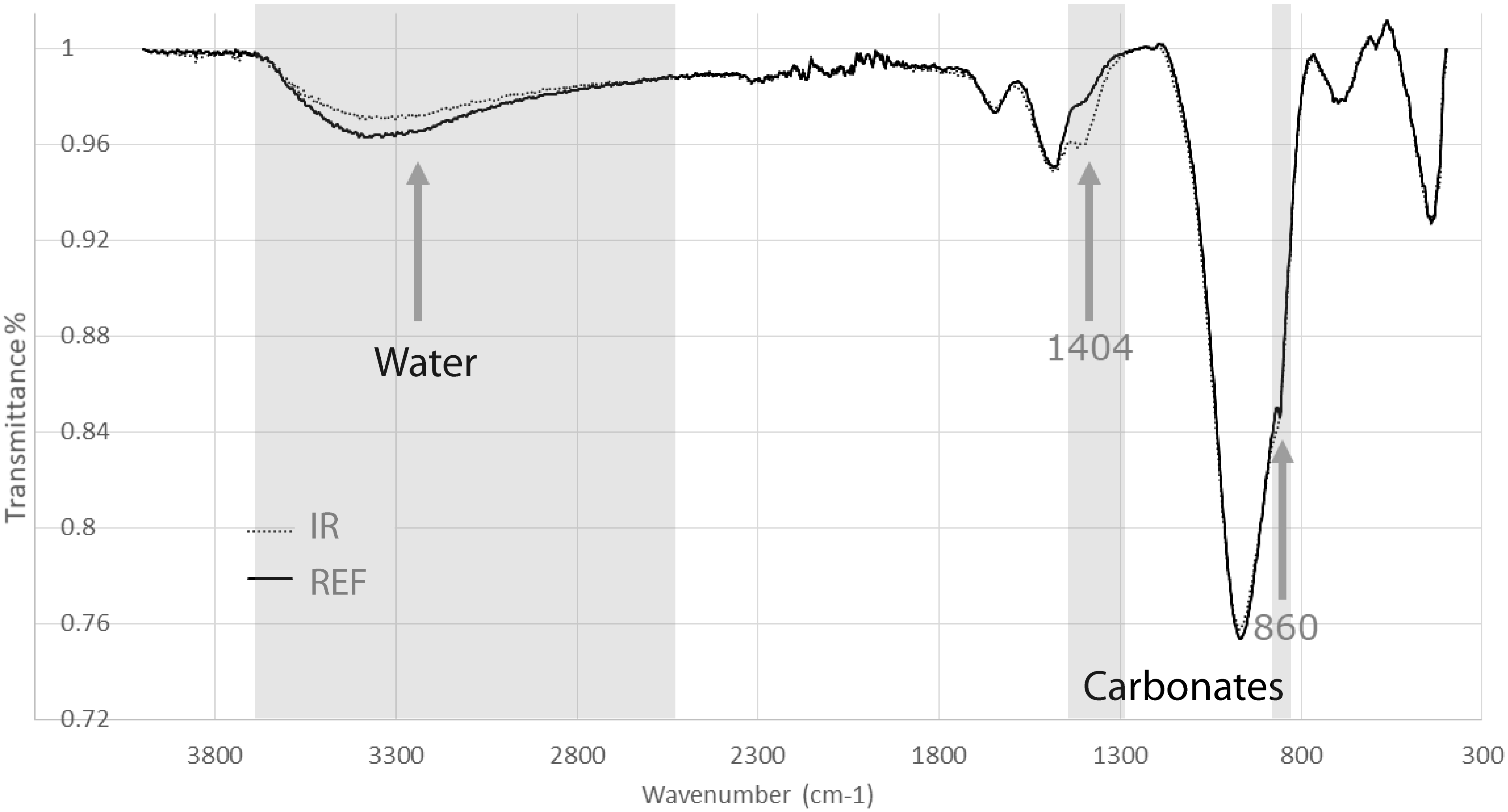


28d

No change in porosity

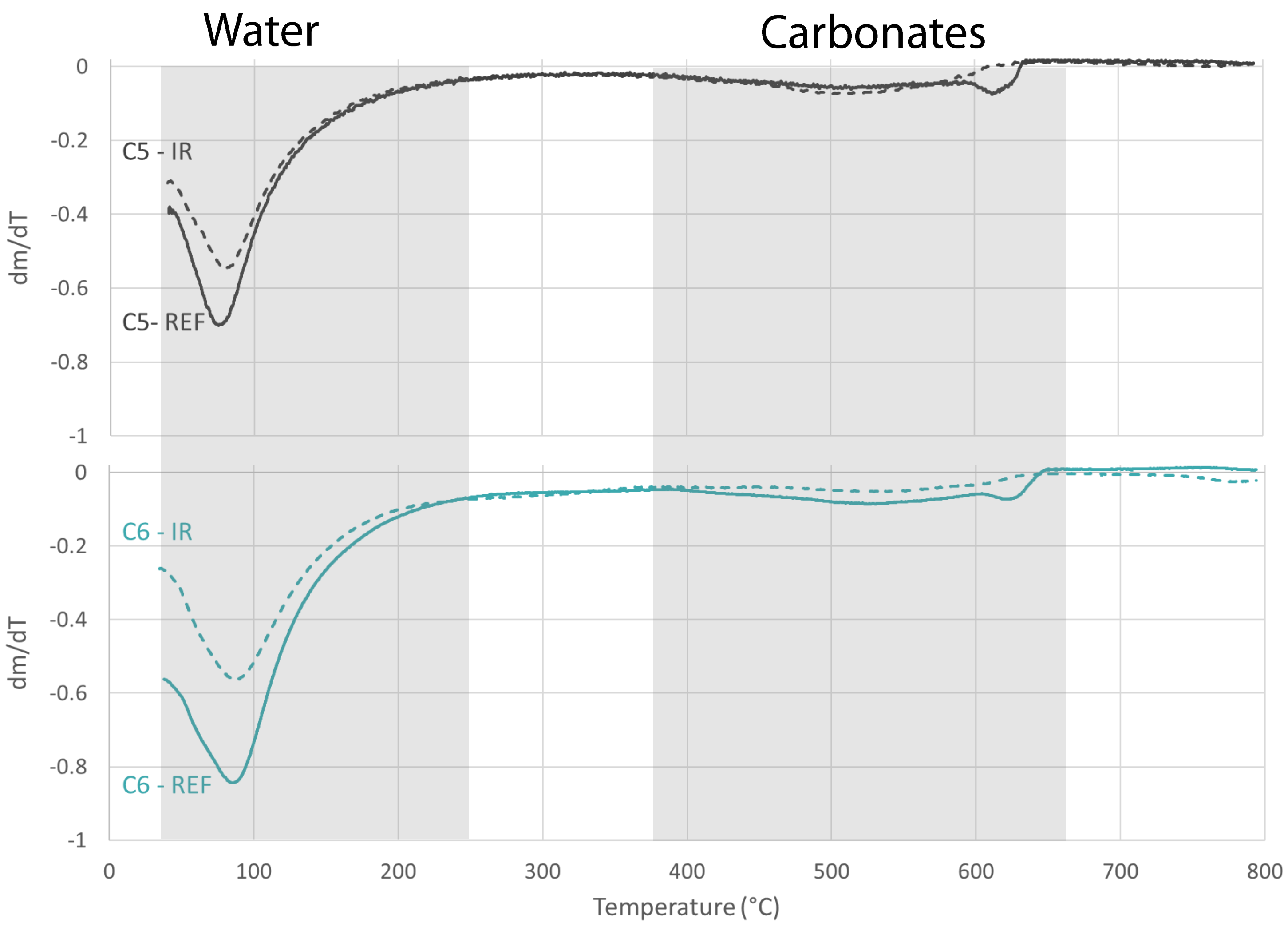
Effect of gamma irradiation on Fe-rich inorganic polymers

Infrared Spectroscopy: radiation-altered carbonation & dehydration



Effect of gamma irradiation on Fe-rich inorganic polymers

Thermogravimetrical analysis: radiation-altered carbonation & dehydration

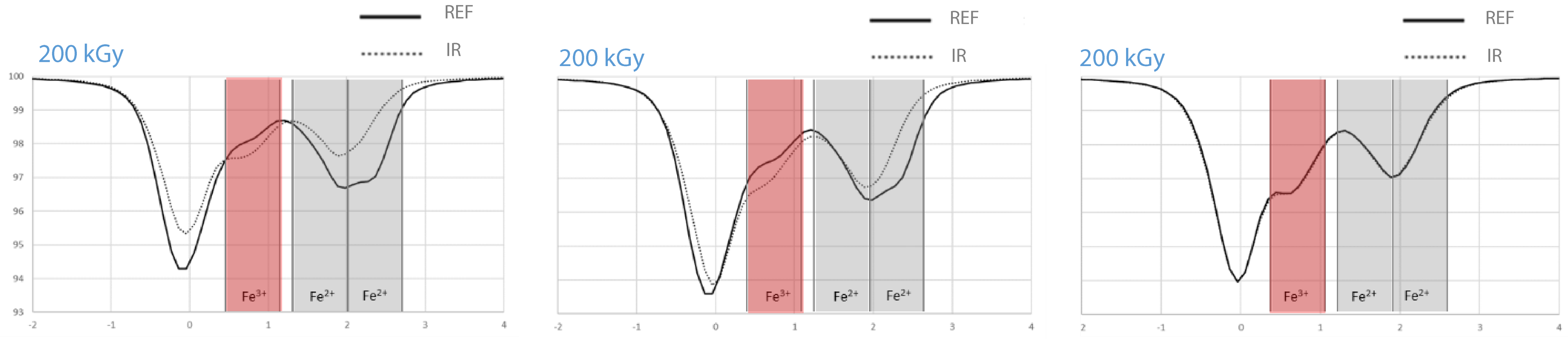


Effect of gamma irradiation on Fe-rich inorganic polymers

^{57}Fe Mössbauer spectroscopy: radiation-induced iron oxidation

Fe^{2+}

Fe^{3+}



1 h | 24 h | 28d

	1 h	24 h	28d
Fe^{3+}_{REF}	20 %	24 %	43 %
Fe^{3+}_{IR}	39 %	38 %	43 %

Effect of gamma irradiation on Fe-rich inorganic polymers

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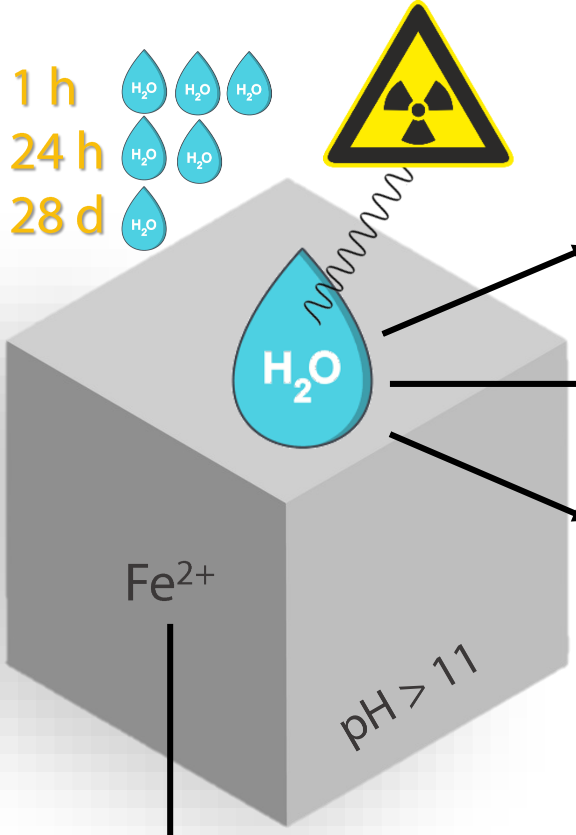


H_2

H_2O_2: strong oxidant → Fe^{2+} oxidation

O_2 acts as catalyst for $^{\bullet}e_{aq}^{-}$ and $^{\bullet}OH$ removal

Fenton Reactions:

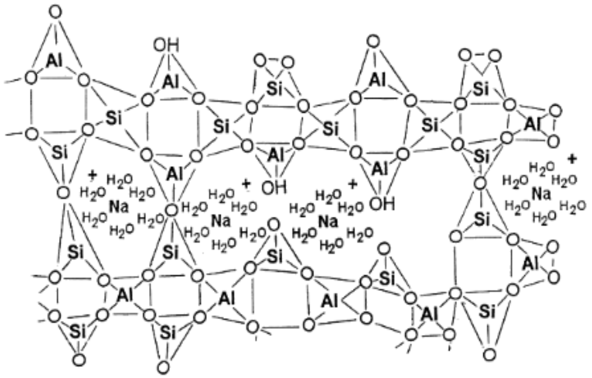
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+$

Very strong oxidants

Fe^{2+} oxidation:

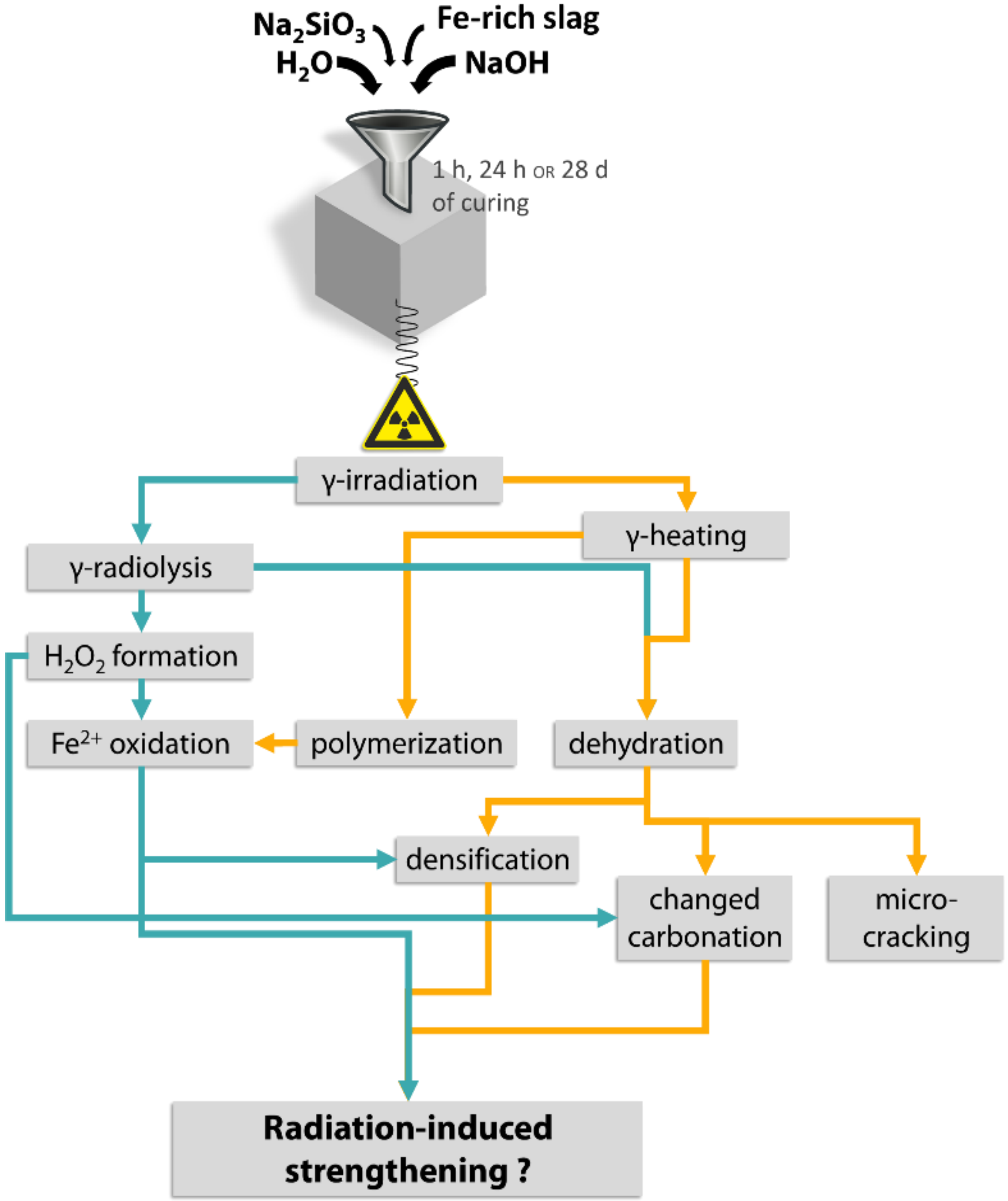
- Formation of FeO(OH) nanoparticles
  - Nucleation sites for polymerization
- Fe^{3+} incorporation in tetrahedral network



Strength Increase

Effect of gamma irradiation on Fe-rich inorganic polymers

Summary



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as safety material for nuclear industry

Related work

[1] B. Mast, I. Gerardy, Y. Pontikes, W. Schroeyers, B. Reniers, P. Samyn, G. Gryglewicz, B. Vandoren, S. Schreurs, "The effect of gamma radiation on the mechanical and microstructural properties of Fe-rich inorganic polymers," J. Nucl. Mater., vol. 521, 2019.

[2] B. Mast, Y. Pontikes, W. Schroeyers, B. Vandoren, and S. Schreurs, "The use of alkali activated materials in nuclear industry," in Comprehensive Nuclear Materials, 2nd ed., R. Konings, Ed. Elsevier Inc., 2020.

[3] B. Mast , A. Cambriani, A. P. Douvalis, Y. Pontikes, W. Schroeyers, B. Vandoren, S. Schreurs, "The effect of high dose rate gamma irradiation on the curing of CaO-FeOx-SiO2 slag based inorganic polymers: Mechanical and microstructural analysis," J. Nucl. Mater., 2020.

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Opening new horizons

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