PREDIS

WP6. T6.4 Immobilisation of the treat wastes by geopolymers or cement-based materials

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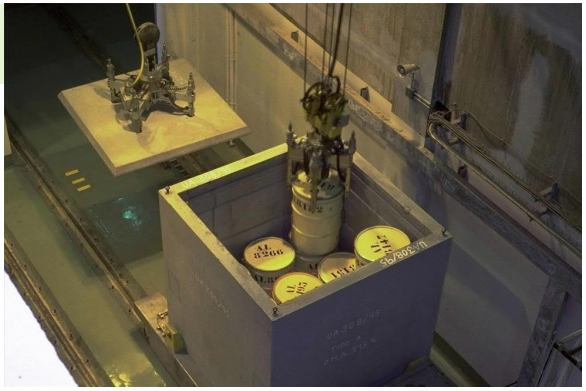
This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 945098.

Challenge and expected end products

Aim: **Organic solid waste volume minimization & immobilisation**

Initial challenges:

- Use of **existing conditioning facilities** in NPPs
- Conditioning in **220l drums**
- Waste **surrogates**: thermally-treated mixed IERs (ashes) tailored to **existing waste streams**
  - Secondary Circ. **PWR**– **B** + **traces of Sr, Cs, Co, Ni, Zn, Fe, Ag**
  - **BWR** – **$NaNO_3$**



Conditioning matrix: suitable if waste form meets Spanish Waste Acceptance Criteria

Requirements of reconditioned waste-form:

- *Homogenous waste dispersion in the matrix*
- *No bleeding risk*
- *Good interaction waste/matrix*
- Uncertainties:
  - Handling of small particle ashes (micro-nanosize) *(delivery in water suspension)*
  - Insufficient matrix fluidity / setting / hardening
  - Instability of matrix: aggressive ion interaction (PO_4^{3-}, NO_3^-, $SO_4^=$), ↓pore pH, mechanical strength loss (zeolite formation)

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Immobilisation of waste in Portland-based & geopolymer binders

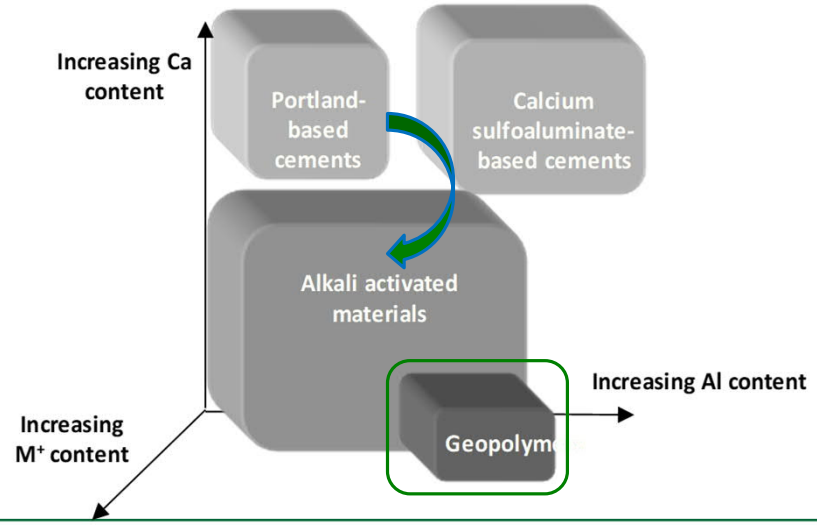
IMMOBILISATION OF RADIOACTIVE WASTES IN CEMENTITIOUS SYSTEMS

CONVENTIONAL BINDERS: Portland-based Cement

- **Binding capacity & High pH** (*OPC:13-3.5, blended:13-10) favor sorption & ion substitution*
- **Durable solid material:** low permeability
- **Safe transportation & storage**

ALTERNATIVE BINDERS (Geopolymers)

-**Improve radionuclides binding** capacity *(Cs or Sr)* **& High pH**:*13.5-13.7*
-**Reduce set retardation** caused by inactive components *(inorganic salts, borates)*



Cement type	Early-age strength	[1]Durability	[2]Chemical resistance
Portland cement	++	++	+
Blended cement	+	+++	++
High alumina cement	+++	+	+++
High sulfate cement	+	++	+++
Sulfoaluminate cement	+++	++	+++
Alkali-activated cement	**+++**	**+++**	**+++**

A. Palomo et al. . Mater. Construcc. (2014)

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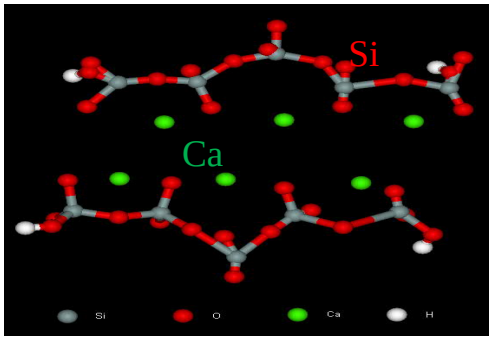
CONVENTIONAL BINDERS (commercial products)

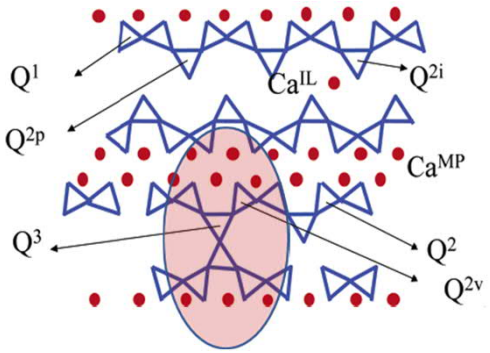
OPC:
- 70% Calcium silicates (CSH)
- 20% Ca(OH)2 (CH)
- 10% Ettringite…

Blended cements:
(*BFS, FA, MK, SF)*
- More CSH
- Less CH
- Aluminates (ettringite, monocarb aluminates..

CSH (amorphous gel)



Al incorpopration in C-(A)-S-H



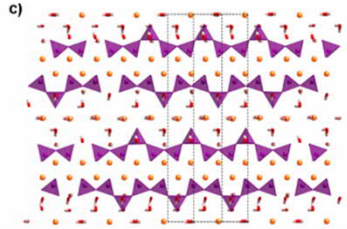
E. L'Hôpital et aCement and Concrete Research 75 (2015) 91–103l

GEOPOLYMERS: chemical interaction between silicoaluminates (Precursors) with low or high Ca contents from natural sources (such as clays) or artificial (industrial by-products) and **highly alkaline solutions (or Alkaline Activators)**

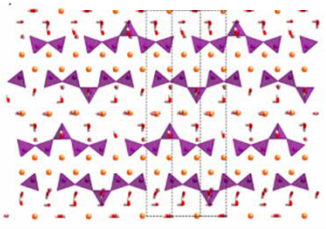
PRECURSORS:
METAKAOLIN (MK), BLAST FURNACE SLAG (BFS), FLY ASH (FA)

ACTIVATORS:
(NaOH or HS, KOH, Na_2SiO_3 or MS, etc..)

C-A-S-H

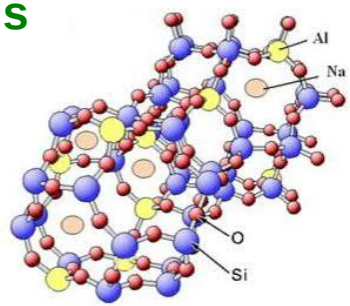


Amorphous Gels



F. Puertas et al. J. Eur. Ceram. Soc.(2011)

N-A-S-H



I. Lodeiro et al. Woodhead Publishing Book (2014)

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Development of organic waste conditioning material in PREDIS

Requirements for waste-binder matrixes design:

Applicability Criteria:

- *Availability of raw matrix components and*
- *Commercial products (Metakaolin, BFS, Activators..)*

Technical Criteria & Assessment parameters in binder design (*literature source*):

In Fresh state:

- *Good Mix Fluidity: (Flow > 200 mm after 150 min)*
- *Proper Initial/final setting time: (> 4 h/< 24h)*
- *Low Heat of hydration: (i.e < 180 kJ kg-1 after 24 h)*

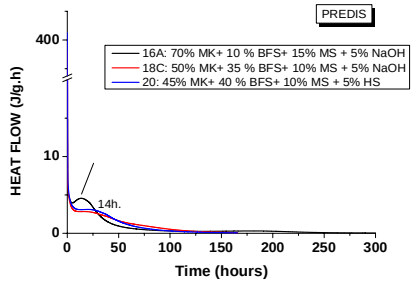
1. *Minimum Bleeding*

In Hardened state:

- *Mechanical strength: (between 4 MPa and 40)*
- *Good compactness and low porosity*

ONE PART GEOPOLYMERS
(solid activator, "Ready mix")

- MK range (45-70 % wt.)
- BFS range (10-40%wt.)
- HS + MS range (5-15% wt.)



Mechanical strengths ranges
(7days) : 15-45 MPa

REFERENCE SYSTEMS

- CEM I (OPC)
- CEM III (50-70%BFS)

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Work Strategy

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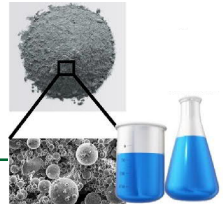
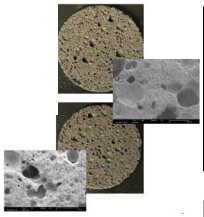


OPTIMIZATION OF IMMOBILISING MATRICES (Geopolymer/porland-based binder)

Conditioning material

- Geopolymer Binder
- Portland-based Binder

CONDITIONING MATRIX

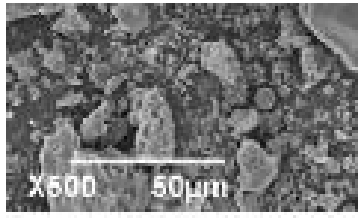


WASTE FORM

WASTE: Incineration

- Grain (PWR)
- Powder (BWR)
- IERs surrogates

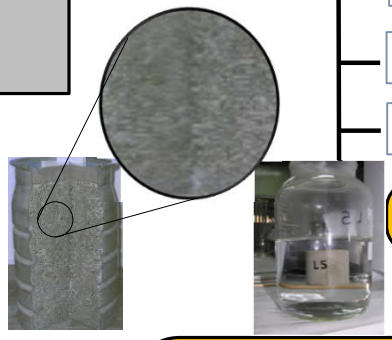
Thermally-treated IERs (ashes)



MATRIX QUALIFICATION → **National WACs**

OPTIMIZATION OF WASTE LOAD Screening based on requirements WAC

- Dimensional stability
- Chemical interaction waste/matrix Physic/mech. Propert.
- Porosity
- Immersion
- Thermal cycles



LEACHING TESTS — Tracers ^{90}Sr, ^{137}Cs

STRUCTURAL & ELEMENTAL CHARACTERIZATION (pre- and post-leaching characterization)

XRD, SEM, FTIR, µ-CT
MIP, BET
mechanical resistance

ICP-OES, ICP-MS, GC

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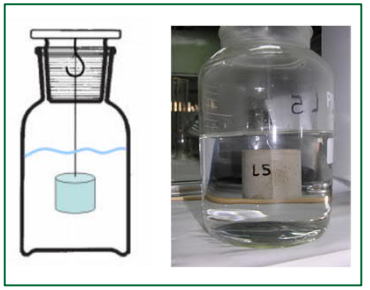
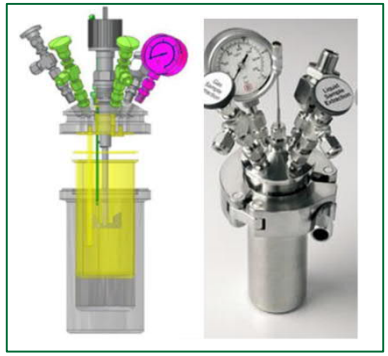
PERFORMANCE: Short- and long-term leaching Risk

Assessment of durability of waste forms under representative disposal conditions

Samples to be leached	Monoliths: Thermally-treated IERs surrogates (ashes immobilized in geopolymer/OPC binders
Use of active tracers	Cs-137/Sr-90
Elements of interest to be followed • Indicators of matrix degradation • Immobilised elements	Ca, Na, K,Si,Al,$SO_4^=$, Cl, $CO_3=$ B, Co, Cr, Ni, Zn, Fe, Ag, Cs, Sr, S
Associated analyses of the eluate/leachant	pH, Eh, EC (gas analysis by GC in each step of leaching)
Post-mortem analyses	Chemical matrix changes: XRD, SEM, FTIR… Dimensional stability, mechanical proper., Poros (MIP, BET), thermal cycles, immersion, free liquid,…





Leaching rate:

Vol./surf of specimen

$$R_n = \frac{a_n}{a_0} \cdot \frac{V}{S} \cdot \frac{1}{t_n}$$

→ Step lap time

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Acknowledgment

ENRESA and waste producers, (**ENDESA- ANAV & IBERDROLA – Cofrentes NPP**, for their active collaboration in the materials supply, the definition of the waste streams and the tailoring of the chemistry for the IERs surrogates.

Materials supply of cement producers: Portland Valderrivas, Cementos Lemona, Tudela Veguin & Arcire S.A.

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