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SNETP Forum

Experience on the immobilisation of Ion Exchange Resins in Geopolymeric and Alkali-Activated Materials (AAM): Spanish experimental programme

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In Spain, typically, Spent Ion Exchange Resins (SIERs) are cemented in Ordinary Portland Cement (OPC) matrices with different additions. However, conditioning of Ion Exchange Resins, especially the highly-borated IERs, exhibit problems such as delayed setting or microcracking generated by the swelling of the beads. In order to avoid these problems that limit the SIERs content in the waste packages, new materials are being developed for their encapsulation. CIEMAT-CSIC-UAM groups were working on different alternatives to conventional cementation methods, including a one-part geopolymer and two alternative Alkali-Activated Cementitious blends (Blast Furnace Slag (BFS)/Fly Ash (FA)).

Conditioning of Spent Ion Exchange Resins (SIERs)

SIERs are one of the largest volume waste streams to be treated and disposed. Table below summarizes challenges that need to be addressed for their conditioning and disposal.

Challenges in treatment and conditioning of SIERs	
Conditioning	*Stability issues with cementitious matrices:* mechanical and chemical stability of the cement matrix when immobilising SIERs. *Contaminants interfering with Cement Hydration*: (B, Zn, nitrates, organic acids…) Problems: *swelling*, *delayed gel formation*, and *reduced strength*.
Storage & Disposal	Mechanical and chemical behavior of waste packages: *potential swelling*, *corrosion*, and *complexing substances* that increase radionuclide mobility.

To avoid these problems, that limit the SIERs content in the waste packages, new materials are under development, such as geopolymer and Alkali-Activated Materials.

Geopolymers and Alkali-Activated Materials (AAMs)

Geopolymers and Alkali-Activated Materials have gained global interest as an alternative to standard Portland cement (OPC) blends.

Metakaolin and/ or slag-based systems have demonstrated to be robust solutions, able to stabilize diverse waste streams (RLOW, SIERs, evaporator concentrates, sludges…).

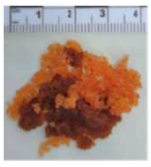
These type of matrices allow the implementation of **simplified cementation process routes,** as they generally show faster curing than OPC binders and eliminate the need for waste pre-treatment.

Among their most interesting characteristics for waste conditioning:

- **Suitability** for wastes containing **setting retarders** (B, Zn…).
- higher fluidity: can lead to potentially **higher waste loadings.**
- higher efficiency for the immobilization of radionuclides and heavy metals due to their zeolitic-like structure.

In the case of SIERs, the use of geopolymers allow increasing waste loadings, up to 25wt.%, even for high boron contents

Experimental program



Mixed-bed Ion Exchange Resins

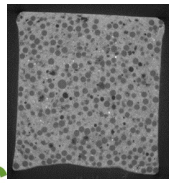
IRINEMA

Immobilization of SIERs in Geopolymers and AAM

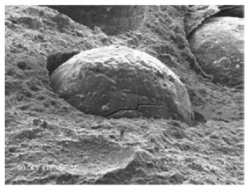
Two strategies

Thermally-treated Ion Exchange Resins (tt-IERs)

PREDIS



Cross-section of a tt-IERs-GP specimen



IER bead embedded in the AAC matrix

Direct immobilisation

- Encapsulation of highly-borated IERs
- Two **alkali-activated cementitious (AAC)** blends
  - Based **on BFS with partial FA substitution**:
    - 100-85 wt.% of slag
    - 0-15 wt.% of ash
  - Two *activating solutions*:
    - sodium carbonate (C)
    - sodium silicate (S)

Thermal treatment + immobilisation in GPO

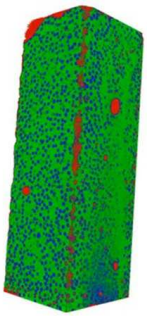
Low thermal-gradient treatment (P.T. 450°C)

- Avoid loss of volatile elements (Cs, B…)
- Retention of RNs of interest in the ashes
- Volume reduction: 80% initial volume

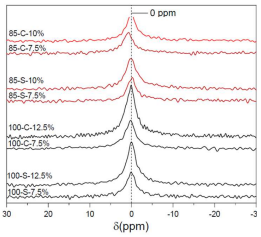
+

Development of a **one-part Na-MK geopolymer**

- Reduced operational risks
- Solid raw materials and activator
- Avoid the use of highly-activated solutions



3D-µCT image of a ttIERs specimen



^{11}B MAS-NMR spectra of the AAC pastes with 7.5, 10 and 12.5wt% of IERs at 28 days of curing

Continuation in **EURAD-2 WPs 6 & 7**

eurad 2 European Partnership on Radioactive Waste Management

- **WP6 STREAM** (Sustainable treatment and immobilisation of challenging wastes) → **Scaling-up & prototyping**
- **WP7 L'OPERA** (Long-term performance of waste matrices) → **Long-term performance under national disposal conditions**

will be addressed in EURAD2-WPs

Main outcomes

Compared to the currently in-use cements, the ***geopolymer*** and ***AACs*** matrices developed in PREDIS and IRINEMA projects showed:

- **Increased waste loading:** up to 20wt.% for both:
  - IERs beads
  - thermally-treated wastes
- **Good chemical compatibility** with both types of wastes
- **Increased mechanical performance**
- **Acceptable workability for high waste loadings**

- **Leaching behaviour** in cementitious, disposal site groundwater and ultrapure media:
  - **Improved leaching** rates for **Cs** and **Sr**
  - **Boron leaching** slightly increased compared to OPC reference matrices.
  - Increased Al and Si leaching of geopolymer matrices in cementitious medium (pH 12.4)

Acknowledgements

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