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Investigation on the use of volcanic tuff in acid-activated geopolymers for radionuclides immobilisation

F. Fattori[1], E. Mossini[1], G. Magugliani[1], C. Milanese[2], S. Paraboschi[2], G. D. Gatta[3], D. Comboni[3], A. Santi[1], F. Galluccio[1], E. Macerata[1], M. Mariani[1]

[1]Politecnico di Milano, Department of Energy, Piazza Leonardo da Vinci 32, 20133, Milano, Italy
[2]Università di Pavia, Department of Chemistry, Viale Taramelli 16, 27100, Pavia, Italy
[1]Università degli Studi di Milano, Department of Earth Sciences, Via Sandro Botticelli 23, 20133, Milano, Italy

INTRODUCTION

Geopolymers emerged as promising alternatives to traditional cementitious materials for the conditioning of low-to-intermediate level waste. These materials are obtained by mixing a source of amorphous aluminosilicates (**precursor**), and an either alkali or acid solution (**activator**). Although acid activation has been less extensively studied, **phosphate-based geopolymers** (PGPs), which use a **phosphoric acid** solution as activator, usually offer high mechanical strength, elevated thermal stability, and promising adsorption properties.

RESEARCH PROBLEM

- Alkaline geopolymers have demonstrated excellent retention performances for several cations, including $^{137}Cs^{+}$.
- Serious concerns arise when dealing with long lived isotopes such as ^{99}Tc, ^{93}Mo, ^{79}Se, ^{36}Cl or ^{129}I, which may be present as **anionic** species.
- PGPs have demonstrated a higher efficiency in immobilising **anions**, thanks to their positive surface charge.

OBJECTIVES

- The objective is to develop a PGP matrix capable of immobilising both **cations** and **anions** relevant for radioactive waste disposal.
- **Volcanic tuff** (VT) is rich in zeolite **chabazite** (65% w/w), a crystalline aluminosilicate with high cation-exchange capacity, selective especially for Cs^{+}.
- VT also offers significant **environmental** advantages over metakaolin or Portland cement.

METHODOLOGY

- A set of samples has been prepared at **activator solution-to-precursor** ratio of **0.9** w/w, varying activator concentration (**40%**, **60%**, and **75%** w/w **H_3PO_4 solutions**).
- The samples have been characterised using powder **XRD** and **SEM** analyses.
- The **leaching** behaviour of the samples for **Cs** and **Mo** has been investigated following the ANSI/ANS-16.1-2019 protocol.

RESULTS

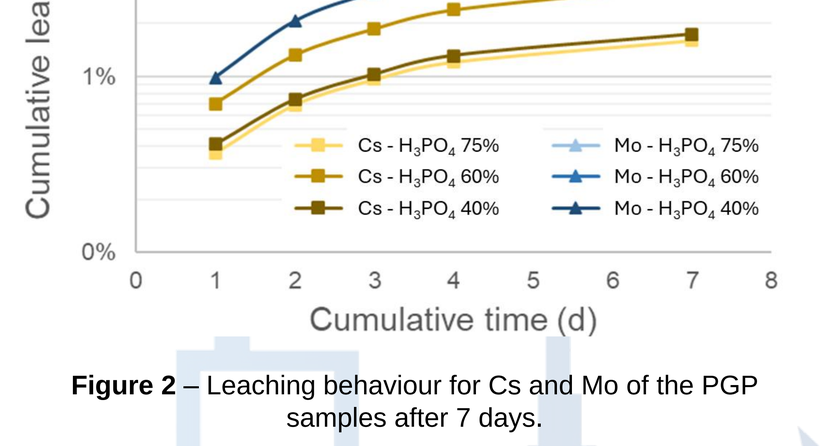

Figure 1 – Mineralogical phase compositions of the PGP samples.

Figure 2 – Leaching behaviour for Cs and Mo of the PGP samples after 7 days.

- **Chabazite easily degrades** in acidic environments, disappearing completely when the H_3PO_4 concentration is **60%** or greater.
- The samples are mostly amorphous, suggesting a **high degree of geopolymerisation**.
- **Taranakite** $K_3Al_5(HPO_4)_6(PO_4)_2 \cdot 18(H_2O)$ is the main crystalline phase when using **40%** and **60%** H_3PO_4.
- Using **75%** H_3PO_4, **calcium dihydrogen phosphate** $Ca(H_2PO_4)_2$ formation is favoured.
- The release of **Mo** can be correlated to the **P/Al** molar ratio. Using **40% H_3PO_4** it is possible to obtain a higher retention when compared to **Portland cement**.
- **Cs** release is limited in all the samples, possibly because it might precipitate as **cesium phosphate** (Cs_3PO_4).
- The residual **chabazite** hinders **Cs** release when using **40%** H_3PO_4.
- When using 75% H_3PO_4, **Cs** might precipitate as insoluble **cesium dihydrogen phosphate** (CsH_2PO_4), explaining to some extent the deviation from the monotonically increasing trend.
- The overall **Cs** retention of the PGP samples is comparable to that of **alkaline geopolymers**.

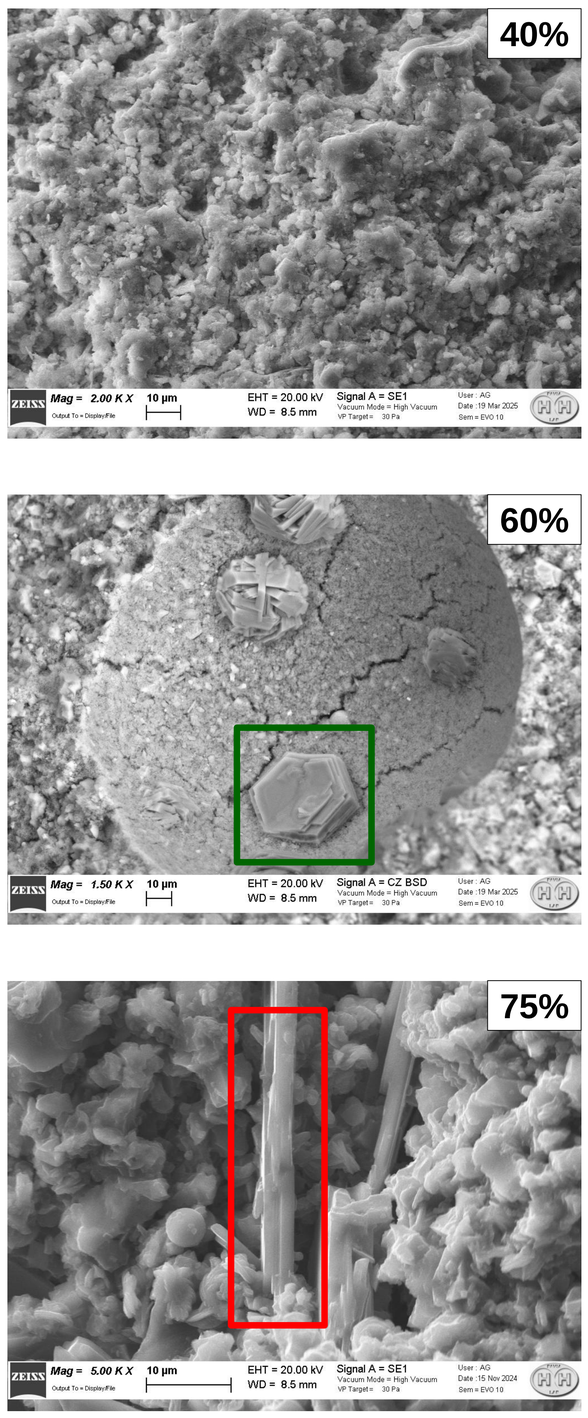

Figure 3 – SEM micrographs of the PGP samples.

CONCLUSIONS

The activator **concentration** strongly affects the samples' **mineralogical** composition. After 7 days, **Mo** cumulative releases are below 10%, except with 75% H_3PO_4. **Cs** retention is consistently high (~3%) regardless the activator concentration. Future works will be performed to investigate the leaching behaviour of other anionic species, mainly I, Se, Tc, and Cl, and the effects of the activator concentration on the mechanical properties of the samples.

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LET'S KEEP IN TOUCH!