# GEOPOLYMER-BASED MATRICES FOR CONDITIONING RADIOACTIVE WASTE

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*Abstract*

Geopolymer is considered as a potential matrix for conditioning different problematic radioactive waste, including liquid organic waste. This paper outlines the formulation of geopolymer (GP) matrices based on local raw materials: granulated blast furnace slag (by-product from iron industry) and volcanic tuff. Mechanical tests were performed according to SR EN 196-3 standard, setting time was estimated using a VICAT equipment, while the compression strength was measured using a MATEST equipment. Alkali-activated binders, also called geopolymers (GP), are produced through the reaction of an aluminosilicate precursor with an alkaline activator. Based on oxide composition, the materials selected for GP formulations tested in this study are used to obtain cement mortars. The results obtained for the geopolymer matrices were comparable with the characteristics of Portland cement-based matrix, indicating the potential of the geopolymers tested to be used for conditioning different categories of radioactive waste.

***Keywords:*** *Geopolymer, Radioactive waste, Aluminosilicates precursor, Portland cement*

## Introduction

Conditioning matrices based on Portland cement are the most used in the radioactive waste management. The production of Portland cement is responsible for about 0.8 tons of $CO_2$ equivalent per ton produced and contributes to about 8% of anthropogenic $CO_2$ emissions. Not only for reducing the $CO_2$ emissions, but also to find suitable conditioning matrices for so called problematic radioactive waste, new matrices such as geopolymers or alkali-activated materials are studied.

The concept of geopolymer is composed by the prefix "geo" which corresponds to "earth" in Greek and refers to the content of Al and Si (both of which are highly present in the earth's crust) and "polymer" corresponding to its structure made up of various Al and Si monomers.

Geopolymers are inorganic binders, first defined by Davidovits [1] with reference to mineral materials with 3D aluminate-silicate network. Geopolymers are amorphous materials, in the class of alkali-activated binders, produced through the reaction of an aluminosilicate precursor with a concentrated alkaline activator. Geopolymer includes $SiO_4$ and $AlO_4$, so that the negative charge of the $(AlO_4)^{5-}$ tetrahedron is balanced by the charges on extra-framework cations (i.e., $Na^+$, $K^+$).

The hardening mechanism of geopolymers, called geopolymerization, usually occurs at ambient temperature, this reaction being essentially based on the poly-condensation of aluminosilicates tetrahedrons. Geopolymerization is the reaction between a concentrated alkali silicate solution and an aluminosilicate source. Researchers have different opinions on the reaction mechanism that occurs during geopolymerization, but most of them agree that the geopolymerization has three main stages [2], as follows:

1) The dissolution of aluminosilicate materials in the concentrated alkali solution forms the free silica and the alumina tetrahedron unit.
2) The transfer, solidification/gelation of materials, the condensation reaction of alumina and silica hydroxyl to form the inorganic geopolymer gel phase. At this stage, water is discharged from the structure due to the hydrolysis process [3].
3) As the gel phase hardens, it condenses in a 3D network of silico-aluminate that forms the geopolymer.

The optimum aluminosilicate precursors to be used for geopolymer formulation are rich in $SiO_2$ and $Al_2O_3$, and may be either natural materials (such as clays) or industrial by-products. Clays are abundant worldwide and mostly consist of Si and Al oxides. The most suitable clay for geopolymer formulation is the kaolinite, whose pozzolanic activity is achieved when calcined at temperatures between 600 °C and 800 °C. The fly ash and blast furnace slags are the most promising industrial by-products for geopolymer formulation. Low-calcium fly ash is an industrial by-product resulted from the coal combustion in power plants, mostly containing Si oxides, but also significant amounts of Al and Fe oxides. Blast furnace slag (BFS) is a by-product of iron industry and contains Ca and Mg aluminosilicates and higher content of CaO, which allows production of the C-S-H phase. It can be considered that geopolymers can be a viable method of recycling waste and reducing greenhouse gas emissions. Most studies have found that a wide range of waste can be recycled through the alkaline activation process.

In case of geopolymers, the factors that influence their physical, chemical and mechanical properties are the following: the average particle size, the Si/Al ratio, the amount of Ca, the type and concentration of the alkaline activator, the conditions of hardening/maintenance, as well as the curing temperature. Compared with conditioning matrices based on ordinary Portland cement (OPC), geopolymers are more resistant to sulphate and acid attack, and carbonation [2], making geopolymers promising matrices for immobilization of different radioactive waste categories, including liquid organic waste.

**Materials and methods**

This study summarizes the work performed to define geopolymer (GP) compositions based on local raw materials.

Considering the oxide composition needed to formulate a GP matrix by alkaline activation, the starting materials selected for the first set of geopolymer formulations are:

- *Industrial sources of aluminosilicates*
  Romanian granulated blast furnace slag (BFS) from Liberty Steel Galati, by-product with basic character (see Fig. 1). In order to be used in geopolymer formulation, the BFS was dried, grounded and sieved to fineness up to 75 µm.
- *Natural source of aluminosilicates*:
  Romanian volcanic tuff from Bârsana (see Fig. 1). The tuff was calcined at 800 °C to increased its reactivity.
- *Standardized sand* (CEN EN 196-1) usually used to obtain mortars based on Portland cement (see Fig. 1).




Fig. 1. Raw materials (BFS, volcanic tuff and sand) prepared to be used for geopolymer reference formulations # 1

The oxide compositions for the raw materials are reported in Table 1, while the diffractograms of the BFS and volcanic tuff are presented in Fig. 2. The frequently phases identified in the composition of the volcanic tuff are albite, anorthite, and dolomite, respectively.

Table 1. Raw materials oxide composition

| **Oxide** | *Blast furnace slag* | *Volcanic tuff* |
|---|---|---|
| $SiO_2$ | 34.72 | 55.45 |
| CaO | 44.56 | 9.83 |
| $Al_2O_3$ | 11.00 | 10.97 |
| MgO | 4.47 | 1.18 |
| $Fe_2O_3$ | 0.80 | 2.55 |

As activation solution, a mixture of sodium hydroxide (8 M NaOH) and commercial silicate ($Na_2SiO_3$) solution (25.5% $SiO_2$, 7.5% $Na_2O$ and 66% $H_2O$) was used. The solution dissolves Si and Al ions from the precursor to form $Si(OH)_4$ and $Al(OH)_4$ – monomers in solution.

Three geopolymer matrices were formulated (GP1, GP2 and GP3 respectively) and tested in comparison with a mortar based on Portland cement type CEM II. The composition for each matrix is described in the Table 2, while the molar rations of the most important oxides for geopolymer formulation are reported in Table 3.

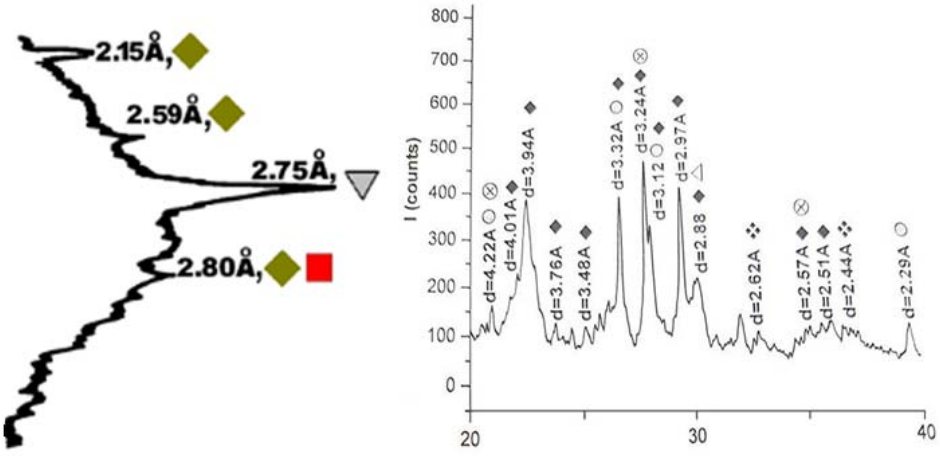



Fig. 2. Diffractogram for granulated blast furnace (right) and Volcanic tuff (left)

All geopolymer mortars were cured for 28 days, at room temperature (20 ± 5 °C), inside protective foil to avoid water evaporation.

Table 2. Amounts of row materials used to formulate GP1, GP2, GP3 and CEM II matrices

| Composition [g] | CEMII | GP1 | GP2 | GP3 |
|---|---|---|---|---|
| Cement, CEM II | 225 | - | - | - |
| BFS | - | 225 | 175 | 157.5 |
| Volcanic tuff | - | - | 50 | 67.5 |
| Sand | 675 | 675 | 675 | 675 |
| NaOH | - | 100 | 100 | 100 |
| $Na_2SiO_3$ | - | 50 | 100 | 100 |
| $H_2O$ | 112.5 | 50 | - | - |
| Sand (wt. %) | 66.67 | 61.36 | 61.36 | 61.36 |

Table 3. Molar ration of the oxides for GP1, GP2, GP3 geopolymer matrices

| Composition [mol/mol] | GP1 | GP2 | GP3 |
|---|---|---|---|
| $SiO_2$ / CaO | 0.91 | 1.38 | 1.53 |
| $SiO_2$ /$Al_2O_3$ | 3.67 | 4.61 | 4.76 |
| $SiO_2$ / $Na_2O$ | 22.72 | 14.25 | 14.70 |
| $H_2O$/$Na_2O$ | 39.32 | 17.47 | 17.47 |
| W/B | 0.7 | 0.62 | 0.62 |

To assess the mechanical properties of the three geopolymer formulations, according to SR EN 196-3, the following tests (see equipments in Fig. 3) were performed:
• setting time: measured with VICAT equipment
• compression strength: measured with MATEST equipment.

After testing the mechanical properties of the three geopolymers, the formulation GP2 was further optimized to incorporate oil waste (set #2 of tests), and performances of the resulted waste forms were evaluated.



Fig. 3. Equipments used for mechanical testing: VICAT equipment (right) and MATEST equipment (left)

**Results and discussion**

The mechanical performances (initial and final setting times and compression strength) for the matrices prepared in the first set of formulations are listed in Table 4, together with the density of the cured mortars.

Table 4. Characteristics of the investigated matrices

| | | CEM II | GP1 | GP2 | GP3 |
|---|---|---|---|---|---|
| **Setting time** | **initial** | 2h 20min | 45 min | 2h 40 min | 4h 30min |
| | **final** | 6h 20min | 2h 15 min | 4h 15 min | > 8 h |
| **Mechanical strength, [MPa]** | | 54.614 | 19.340 | 34.970 | - |
| **Density, [g/cm$^3$]** | | 2.214 | 2.113 | 2.107 | 1.974 |

The maximum value for compression test was obtained for GP2 geopolymer composition (34.97 MPa), while for GP1 matrix the mechanical strength had the minimum value. The GP3 matrix was not used for mechanical testing as it has a long final setting time and a very fragile structure.

Nevertheless, for all investigated matrices, the mechanical strength was above the limit for waste acceptance for disposal (5 MPa), indicating the tested GPs potential to be used for different categories of radioactive waste conditioning.

For the second set of formulations, Shellspirax oil was used as surrogate for pump oil type radioactive waste. To increase the amount of $Na_2O$ in the activation solution, the concentration of sodium hydroxide was increased to 10M. The granulated blast furnace slag (BFS) used in this set of tests came from different slag batch, with a slightly different oxide composition (see Table 5).

Table 5. Oxide composition of the BSF slag used for the second set of GP formulations

| BFS composition | [wt.%] |
|---|---|
| CaO | 37.61 |
| $SiO_2$ | 25.29 |
| $Al_2O_3$ | 5.22 |
| MgO | 3.85 |
| $Fe_2O_3$ | 3.08 |
| $SO_3$ | 1.77 |
| MnO | 0.62 |
| $K_2O$ | 0.52 |
| CuO | 0.31 |
| LOI | 21.73 |

Tween 80 (5% of oil volume) was used as emulsifier to increase the waste loading (waste percentage in the geopolymer mortar).

For oil incorporation in the geopolymer, the following mixing sequence was applied:

- Shellspirax oil was mixed for 5 minutes on a stirring plate with adequate amount of Tween 80 and the emulsion was continuously stirred until it was added over the GP.
- The activating solution was added to BFS (< 50 μm) and mixed for 2 minutes in a small scale planetary mixer.
- The adequate amount of sand was added and mixed for 2 more minutes.
- The emulsion formed by the oil and Tween 80 was added and mixed for 5 more minutes.

The resulted mortar was cured at room temperature into small moulds.

In the first set of tests, it was tried to fit the oxide molar rations from the previous GP2 formulation, the amount of additional water added in the GP being calculated for water to binder ratio of 0.45.

The amounts of raw materials used to formulate a GP mortar with no waste incorporated and for two GP mortars containing 15% and 19%, respectively, oil incorporated are presented in Table 6.

Table 6. Amounts of raw materials used to GP matrices

| **Composition [g]** | **GP mortar with no waste** | **GP mortar with oil waste** | |
|---|---|---|---|
| | | **15 wt.%** | **19 wt.%** |
| BFS | 93.00 | 93.00 | 93.00 |
| Sodium silicate solution | 2.98 | 7.17 | 7.17 |
| 10 M NaOH | 12.28 | 11.51 | 11.51 |
| Additional water | 33.40 | 31.69 | 31.69 |
| Sand | 56.00 | 56.00 | 56.00 |
| Waste | - | 35.50 | 47.40 |
| Tween 80 | - | 1.78 | 2.37 |

All GP mortars presented good workability and normal fluidity. For both waste loading rates (15 wt.% and 19 wt.%, respectively) homogeneous mixtures with no waste separation were obtained.

The setting time was less than 24 h for all mortars, but for matrices with oil incorporated very limited mechanical strength was developed after 28 days of curing.

For the third set of tests, using the same batch of BFS the molar ratios of $SiO_2/Na_2O$, $SiO_2/Al_2O_3$ and $Na_2O/Al_2O_3$ were optimized to increase the mechanical strength, resulting the composition reported in Table 7 (GEO-WO).

Table 7. Composition of GP matrix used for 3rd set of tests

| **Composition [g]** | **GEO-WO** |
|---|---|
| BFS | 348.6 |
| Sand | 210 |
| 10 M NaOH | 43.2 |
| $Na_2SiO_3$ | 27.0 |
| Additional water | 118.8 |
| Oil | 133.2 |
| Tween 80 | 6.6 |
| Compressive strength, [MPa] (average of the 3 samples) | 7.439 |

From GEO-WO composition, GP mortar was poured in three standardized cubic forms (see Fig. 4) to get adequate waste forms for mechanical strength measurements using MATEST equipment, according to SR EN 196-3 standard.

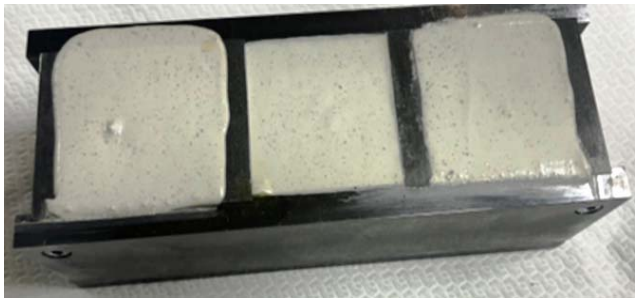


Fig. 4. GEO-WO geopolymer poured in forms

GP mortar was kept in the cubic moulds for 24 hours, that were carefully de-moulded without breaking the edges (see Fig.5). For the next 28 days, all three GP matrices were kept at room temperature for curing.



Fig. 5. GEO-WO geopolymer demoulded cubes

After 28 days of curing, the mechanical strength of the three specimens was between 7 MPa and 8 MPa, with an average value of 7.439 MPa, above the waste acceptance criteria for disposal.

## Conclusions

Numerous studies have been conducted to clarify and understand the geopolymer matrices and evaluate the potential of these materials to be used in conditioning of different categories of radioactive waste.

The tests performed and the results presented in this paper demonstrate the importance of the oxide composition of the aluminate precursor used for geopolymer formulation, mainly the Si/Al ratio and the Ca amount, on the mechanical properties of the resulted geopolymer.

The amount of $Na_2O$ and $SiO_2$ in the activation solution proved to influence the geopolymerization reaction and the mechanical strength of the resulted geopolymer mortar. For the same granulated blast furnace slag, optimizing $Na_2O$ content in the activation solution and the $SiO_2$ ratios in BFS to $Na_2O$ in activation solution, $Na_2O$ in activation solution to $Al_2O_3$ in BFS, and $SiO_2$ in activation solution to $Al_2O_3$ in BFS, it was possible to obtain geopolymer with oil incorporation rate higher than 15wt.% with a mechanical strength exceeding the minimum value for waste acceptance for disposal (> 5 MPa).

These preliminary results are encouraging and require further studies to optimize the composition of the geopolymer in order to increase the mechanical strength.

The use of the blast furnace slag as a basic material in the process of synthesis of a geopolymer binder presented a special interest for this experimental work as this is a by-product of Liberty Steel Galati and using it in a conditioning matrix can contribute to solve the environmental problem generated by the storage of large amount of slag.

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