

OPTIMIZATION OF THE ALKALINE ACTIVATION PROCESS OF DIFFICULT-TO-TREAT INORGANIC WASTES

García-Triñanes P. *, Pereiro G., Bao M.

University of Santiago de Compostela, ETSE Chemical Engineering Department,
Santiago de Compostela, SPAIN

Abstract

Several types of waste from different industrial sectors have been studied; namely fly ashes, thermal processing wastes from the ceramic industry, siliceous slags, aluminium hydroxide dry sludge and glass residues.

The recovery process of these wastes is difficult and has no clear market alternative. Therefore, based on their composition, it is interesting to investigate the recycling of these materials by means of new techniques such as alkaline activation.

In view of the above, this research is based on eco-efficient processing, for which different mixtures were tested, both at room temperature and 60 °C, focussing on the influence of this variable on the curing reaction and the resulting mechanical and structural properties.

The particle size tested was always smaller than 200 microns in every case, and a physicochemical characterization of the different raw materials was carried out by setting up a series of experiments and determining features such as degree of activation, the influence of curing time or the importance of the activation solution for each mixture.

Finally, the cylindrical pieces obtained were tested applying compressive stress in order to analyze the mechanical performance of the proposed cement systems.

Originality:

The novelty of this work lies in the nature of the siliceous raw materials used in the alkaline activation process. The research conducted has provided an alternative that avoids the use of Portland cement (the predominant source of CO₂ in the construction industry) and it has also defined the compositions of the alkaline dispersions and the curing conditions to achieve improved mechanical properties.

Similarly, it is worth mentioning the application of eco-efficiency criteria throughout the different trials, which use minimum quantities of reagents in each case, thus improving process economics.

Main contributions:

- An alternative strategy to enhance the value of mineral wastes or by-products with difficult commodity viability.

- This research deals with the composition of the alkaline dispersions suitable for fast curing based on environmental criteria; it also looks into the direct influence on the mechanical behaviour of the solid cement pieces obtained, engaging in key variables like temperature, particle size, specific surface or the chemical nature of the raw materials.

Keywords: *Industrial wastes, aluminosilicates, geopolymers, structure and mechanical properties*

* Corresponding author: pablo.garcia.trinanes@usc.es Tel:+34 881 811 000 Ext. 16769, Fax +34 881 816 702

1. Introduction:

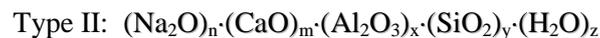
Geopolymers have a similar origin to those of many minerals and rocks that make up the Earth's crust, consisting of compounds of alkaline metals (group I and II), in conjunction with aluminosilicate systems as is the case of zeolites, micas or feldspars.

Therefore, these are systems rich in SiO_2 and Al_2O_3 containing positive alkaline metals with a generic composition:



Or

Systems made up by alkaline earth metals that have high calcium content with a typical composition:



Geopolymeric materials are synthesized by the alkaline activation of an aluminosilicate source (Type I or Type II, even both) forming a gel phase with binder properties. This geopolymerization is originated by the inorganic three-dimensional polycondensation in a strongly alkaline environment (Komnitsas, 2007; Duxson, 2007).

The breakdown of Si-O-Si bonds allows the penetration of the Al atoms into the amorphous structure of the raw materials, therefore the original composition of the aluminosilicates employed, their entropic state, the surface phenomena, the kinetics of the reaction, and the conditions of the curing stage are some of the multiple factors which play a decisive role in the development of the microstructure and, consequently, in the properties of the geopolymers.

In recent years there has been an enormous interest in these kinds of materials (Fernández-Jiménez, 2009; Allahverdi, 2009; Houry, 2009) especially because of their potential application properties and, above all, due to their environmental benefits, although many issues remain unresolved regarding the mechanisms that control the activation process (Duxson, 2005; Zivica, 2005; Chao, 2010).

This research aims to provide a brief report of the understanding of the early stage of the geopolymerization process based on four different industrial wastes as precursors, highlighting several worthy alternatives for their recovery and opening up eco-friendly opportunities for their management.

The suitability of fly ashes (*FLA*), ferroalloy slags (*SiMn*), clay brick wastes (*ARF*) and glass wastes (*PV*) was studied using specific protocols depending on their mineralogical and chemical composition, fineness, water content, etc (...) and employing, as far as possible, other suitable by-products as reagents in the process of geopolymerization. This approach looks to enhance the advantages of geopolymerization using cheaper raw materials throughout the treatment process.

In line with this, waste from the aluminium processing industry, mainly composed by Al_2O_3 was used to supply a reactive source of four coordinated Al to balance the deficiencies of some of the mentioned raw materials.

Other authors (Shi, 2006; Temujin, 2009) have reported that temperatures ranging from 600 to 900 °C are absolutely necessary in the pretreatment of most of the aluminosilicates; nevertheless the experiments presented below do not resort to the thermal treatment of the raw materials, with the corresponding reduction in energy costs.

In essence, the present work details findings on the manufacturing process for novel kinds of concretes which are candidates to replace standard Portland cement, thus reducing CO_2 emissions and providing new alternatives to other expensive materials.

2. Materials and methods:

The raw materials studied in this paper are the following:

a) Fly ashes (FLA)

Fly ashes are collected during the pulverized coal burning process. The original sample provided by ENDESA As Pontes (NW, Spain) was sieved to obtain a particle size lower than 125 microns.

b) Ferroalloy slags (SiMn)

Slags from the silico-manganese industry are usually deposited in landfills. This material from FERROATLÁNTICA S.L. (NW, Spain) was received as gravels with a variable particle size inferior to 25 mm. Therefore, in the pretreatment stage, it was crushed using a Retsch mill and then micronized to achieve a particle size smaller than 125 microns.

c) Clay brick wastes (ARF)

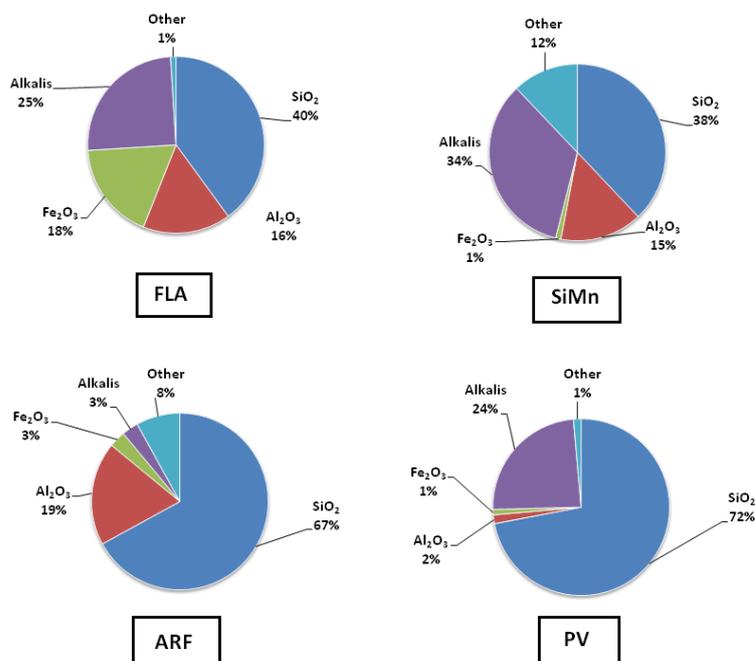
Clay bricks are wastes from the manufacture of ceramic products; in this case from PRODUCTOS ULLA S.L. (NW, Spain). In particular, refractory bricks, tiles, or ornamental ceramic products. A dry ball milling method of pre-screened crushed material was used to produce ground ARF, with a particle size distribution lower than 125 microns.

d) Glass powder wastes (PV)

This material consists mainly of used green glass bottles collected from an urban bottle bank that were crushed by rollers and then pulverized using a ball mill, to obtain a powder with a particle size smaller than 125 microns.

2.1. Characterization

The chemical composition of the four samples was obtained by quantitative chemical analysis and Figure 1 depicts the percentages of each of them.



It is worth mentioning that the category alkalis include the species Na₂O, K₂O, MgO and CaO. These substances can be included in the same group because they compensate the negative charge of the network described by SiO₄ and AlO₄ during the poly-condensation reaction.

Based on the SiO₂ content we can further establish two different groups:

- High SiO₂ content:
ARF, PV
- Medium SiO₂ content:
FLA, SiMn

Figure 1. Chemical composition of the four samples.

Regarding physical characterization, Figure 2 displays the bulk density as a whole with the average particle size (d_{50}) and the specific surface area, the latter determined using a Micromeritics Gemini 2360 Surface Area Analyzer for each sample. The measurement of the particle size distribution for the raw materials (on the right) was carried out using a Sedigraph 5100 obtaining the equivalent spherical diameter of the samples over a size range from 125 to 0,50 μm (repeated three times for each sample).

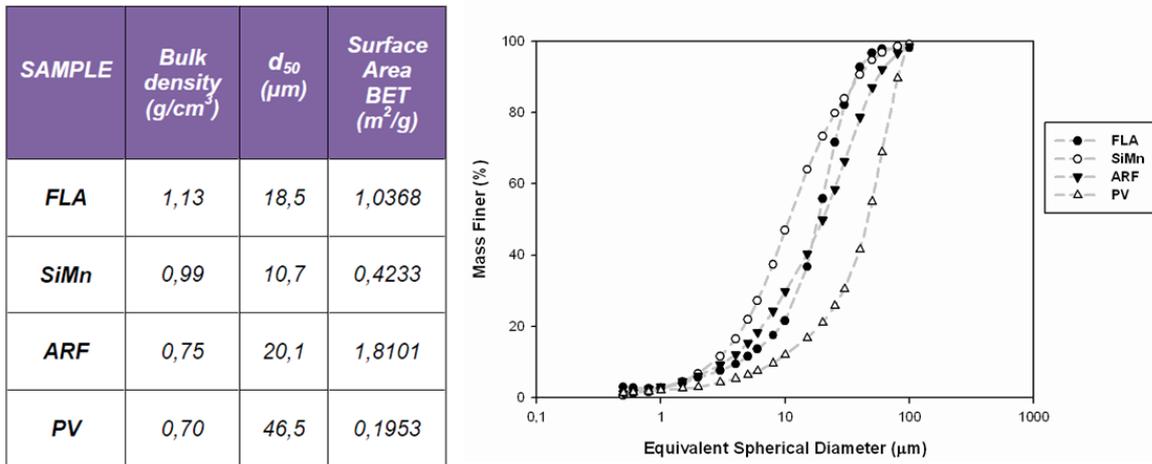


Figure 2. Physical characterization of the raw pulverized materials.

The mineralogical composition (Figure 3) was determined by the X-ray diffraction method (Siemens D5000 Diffractometer) revealing that the fly ashes (FLA) are mainly formed by crystalline phases such as SiO_2 , the mineral form of Fe_2O_3 (hematite), $\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$ (mullite) and FeAl_2O_4 (hercynite). Regarding the SiMn sample, the XRD peaks reveal the presence of mineral phases corresponding to a hydrated aluminum silicate $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 3\text{H}_2\text{O}$ (allophane) and to $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ (xonotlite).

With regard to ARF, it is constituted by SiO_2 , by an aluminum silicate mineral KAlSi_3O_8 (microcline), by Fe_2O_3 (hematite) and by a layered structure of another aluminum silicate (muscovite). Finally, the PV specimen is typically an amorphous solid and crystalline planes are not detectable.

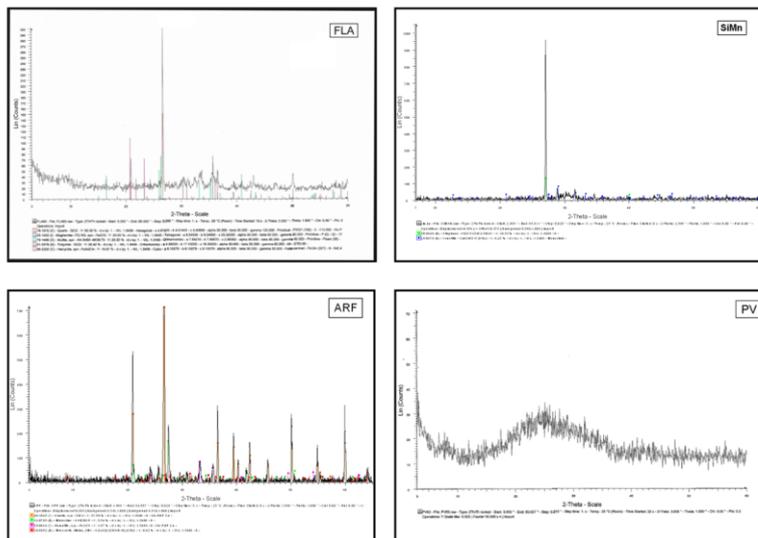


Figure 3. X-ray diffraction patterns of solids: FLA, SiMn, ARF and PV.

2.2. Geopolymers preparation

The first stage of the geopolymer preparation involved mixing each pulverized raw material with an aluminium sludge (ALO) which contains 43 % of Al_2O_3 , 19 % of sodium calcium hydrogen carbonate, 37 % H_2O and traces of aluminium silicate. This sludge was dried in an oven at 120°C for 24 h and then crushed and sieved. The particle size of the supplement ALO was always lower than $200\ \mu\text{m}$.

The mixture of the supplement with each raw material was activated using a solution prepared by dissolving the slurry obtained from the calcinated mix of sodium hydroxide pellets, silica sand and an adjuvant, in the appropriate quantity of boiling water, forming the silicic acid sodium salt composed by 13,8 % SiO_2 , 24,8 % Na_2O , 61,4 % H_2O (density= $1,286\ \text{g/cm}^3$).

After putting the original powders and the activation solution together and mixing them intensively, an optimum amount of fresh water was added to elaborate the fresh pastes, which were in turn vibrated and then moulded in triplicate in covered cylindrical polipropilene containers. The liquid/solid ratios of the pastes varied from 0,38 to 0,44 and the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranged from 3,70 to 6,10.

2.3. Curing conditions

All the specimens were cured for 7 days at room temperature and at 60°C and after that, the solid pieces obtained were dried for 72 hours at 40°C .

3. Results and discussion:

After ten days, a wide variety of solid structures was observed after the drying stage. These results were strongly influenced by the raw material and by the processing variables. Figure 4 shows the results obtained when comparing the effect of curing temperature on 7-day compressive strength for the different geopolymer mixtures establishing differences between the samples cured at room temperature (rt) and those produced by heating (60 degrees).

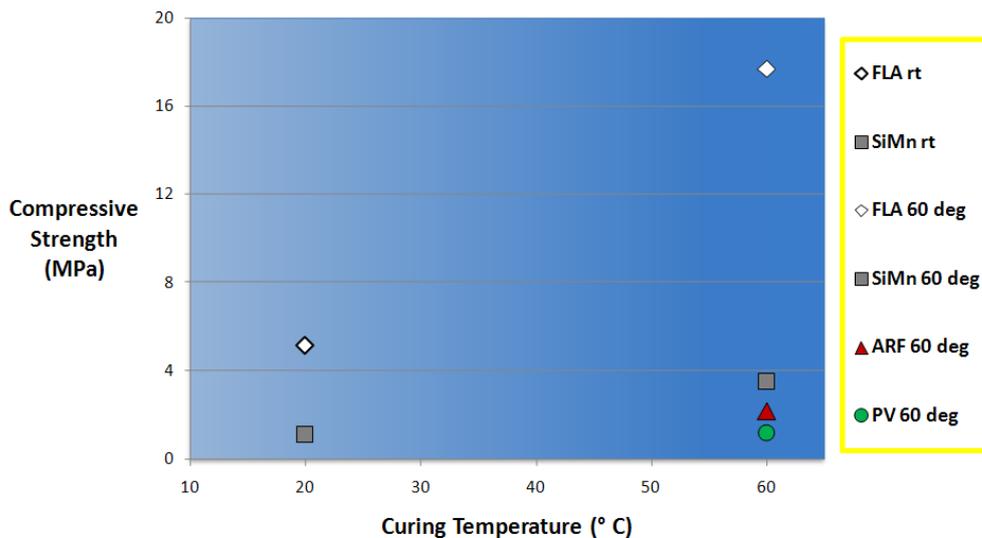


Figure 4. Effect of curing temperature on 7-day compressive strength for the 4 geopolymers.

All the products were analyzed by means of Field Emission Scanning Electron Microscopy and by X-Ray Diffraction in order to investigate the structural characteristics and the phase compositions of the geopolymers. Figure 5 shows the SEM micrographs of the cross sections of the solid structures after the resistance test (uniaxial compressive strength). These SEM images clearly show the presence of continuous pores, especially in the samples obtained from SiMn and PV.

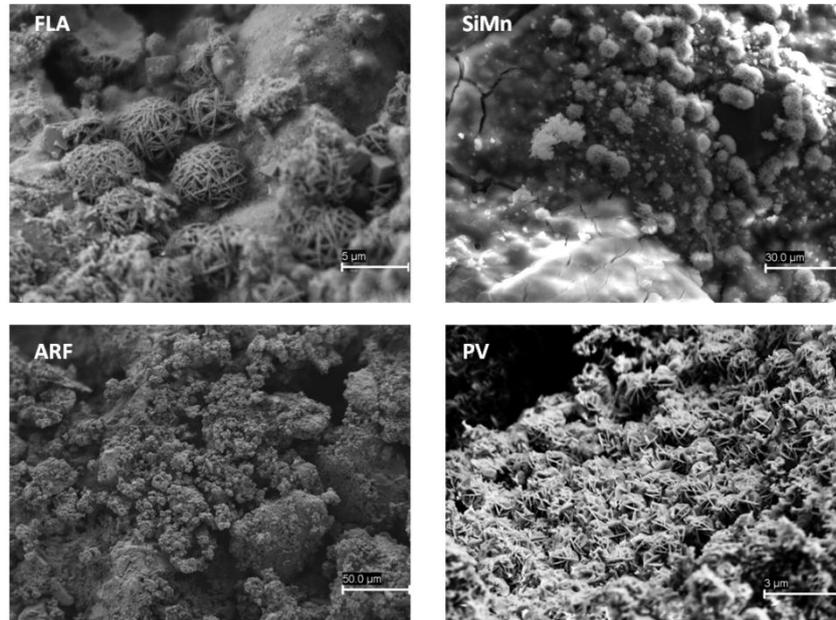


Figure 5. SEM micrographs of cross section of: FLA, SiMn, ARF and PV.

This observation was confirmed by measuring the pore size distribution listed in Table 1 (MICROMERITICS 9305 PORESIZER). In the case of the cellular solid obtained from SiMn, the presence of big pores is attributed to the action of an air entrainment agent (surfactants or water soluble groups like SO_4 or SO_3) which causes air bubbles during the preparation of the mixture.

Table 1. Mercury Intrusion Porosimetry results for the porous samples.

View	SAMPLE	Interstitial Porosity (%)	Total Pore Area (m^2/g)	Median Pore Diameter (μm)
	SiMn	27,691	16,163	3,219
	PV	44,289	6,177	0,576

X-ray diffraction studies proved that there is a partial dissolution of the original crystalline phases in the activator solution, due to the presence of new crystalline species and the presence of the original matter with an amorphous portion. These observations are demonstrated when studying in detail the results for each of them in terms of compressive strength, since the higher the amorphous content in the matrix, the greater the resistance to compression. However, resistance is not the only desirable property of this type of inorganic polymers, because there are other potential applications such fireproof composite panels, coatings, waste encapsulation as well as membrane sieving.

4. Conclusions

- ∴ This work has successfully accomplished the development of geopolymers for industrial applications using inorganic waste materials as the main constituent.
- ∴ A supplementary source of aluminium was employed in order to provide a low-cost reagent. The method of preparation of the activator solution also makes the process economically viable since the added quantity is fixed for each type of raw material in terms of their SiO₂, Al₂O₃ and alkali content in order to specifically adjust the molar ratios of the pastes.
- ∴ In certain cases porous materials were obtained and they must be studied in depth for the sake of make them practical as insulating refractory materials (SiMn) or membrane filters (PV).
- ∴ With this information, it is imperative to fully understand the complexities of the geopolymerization process of these waste materials; it is necessary to carry out further research into the process of preparation, focussing on aspects like setting time, amorphous phase content, role of alkali metals and also into the resulting properties such as compressive strength, low shrinkage, fire resistance or permeability and their derived applications.

Acknowledgments

The authors would like to thank Professor F. Guitian (Instituto de Cerámica de Galicia) for helping during the experimental work.

References

- Allahverdi A., Najafi Kani E. 2009. Construction Wastes as Raw Materials for Geopolymer Binders. *International Journal of Civil Engineering*. 7, (3), 154-160.
- Chao Li, Henghu Sun, Longtu Li. 2010. A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements. *Cement and Concrete Research*. 40, 1341–1349.
- Duxson P., Fernández-Jimenez A., Provis J.L. et al. 2007. Geopolymer technology: the current state of the art. *J. Mater. Sci.* 42, 2917–2933.
- Duxson P., Provis J.L., Grant C. Lukey et al. 2005. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloids and Surfaces A:Physicochem. Eng. Aspects*. 269, 47–58.
- Fernández-Jiménez A., Palomo A., Revuelta D. 2009. Alkali activation of industrial by-products to develop new earth-friendly cements. *Proceeding of the 11th International Conference on Non-Conventional Materials and Technologies (NOMAT 2009; Bath, UK)*.
- Khoury, H., Alshaaer, M. 2009. Production of Building Products through Geopolymerization. *Proceeding of the Global Conference on Renewable and Energy Efficiency for Desert Regions (GCREEDER 2009, Amman-Jordan)*.
- Komnitsas K., Zaharaki D. 2007. Geopolymerisation: A review and prospects for the minerals industry. *Minerals Engineering*, 20, 1261–1277.
- Shi C., Krivenko P.V., Roy D.M. 2006. *Alkali-Activated Cements and Concretes*. Taylor & Francis, Abingdon, UK.
- Temuujin J., van Riessen A.. 2009. Effect of fly ash preliminary calcination on the properties of geopolymer. *Journal of Hazardous Materials*. 164, 634–639.
- Zivica V. 2005. Effects of type and dosage of alkaline activator and temperature on the properties of alkali-activated slag mixtures. *Construction and Building Materials*. 21, 1463–1469.