Inclusion of geopolymers derivate from fly ash and pumice in reinforced concrete

A M Montaño¹, C P González², D Castro³, G Baron¹ and R Atencio¹

¹Universidad Industrial de Santander, Bucaramanga, Colombia
²Universidad Pontificia Bolivariana, Floridablanca, Colombia
³Instituto Politécnico Nacional, Ciudad de México, México
⁴Instituto Venezolano de Investigaciones Científicas, Maracaibo, Venezuela

E-mail: claudia.gonzalez@upb.edu.co

Abstract. This paper presents results of a research project related to the development of alkali-activated geopolymers, synthesized from alumina-silicate minerals (fly ash and pumice) which are added to concrete. Alkali sources used in geopolymer synthesis were sodium hydroxide and sodium silicate solution. New materials were structurally characterized by Infra-Red spectroscopy (IR) and X-Ray Diffraction (XRD). Concretes obtained after geopolymers addition as Portland cement substitutes at 10%, 20% and 30%, were mechanically analysed by compression resistance at 7, 14, 28 and 90 drying days. Results were referred to standard concrete of Portland cement allows to know cementitious characteristics of geopolymers are lower than those for standard, but it keeps growing at longer drying time than Portland cement. By Electrochemical Impedance Spectroscopy (EIS) it is found that this new material shows high electrical resistance and have been proved as a protection agent against corrosion in reinforced concrete exhibiting anticorrosive properties higher than those showed by the conventional concrete mixture.

1. Introduction

Geopolymers (GPs) are produced from aluminosilicates, sources of silicon oxides and aluminium, which are activated by an alkaline agent. GP have characteristics similar to those of cement, which allows them to be used as a cementing agent. In previous works [1-5] it is reported that the substitution of GPs confers to the mixture mechanical properties and durability. In this paper, we report the results obtained by synthesizing geopolymers from the activation of fly ash (FA) and pumice (PP) with different concentrations of NaOH (3M, 7.5M and 12M) as alkaline agent. Obtained geopolymers were structurally characterized by experimental techniques such as: Infra-Red spectroscopy (IR) and X-Ray Diffraction (XRD). Subsequently, GPs were added to a concrete mixture, replacing the cement content in 10%, 20% and 30%. Obtained concretes were mechanically evaluated by compression resistance in specimens of 7, 14, 28 and 90 days of setting. Finally, the electrical response of the GPs with better mechanical behaviour was evaluated by Electrochemical Impedance Spectroscopy (EIS), placing the test specimens at accelerated corrosion conditions for 44 days.
2. Experimental

Synthesis of the GPs was initiated by adding the aluminosilicate to the solution of the alkaline agent to the base products: FA from thermoelectric plant TERMOZIPA, located in the municipality of “Tocancipa, Cundinamarca, Colombia” and PP extracted from “Sabaneta, Antioquia, Colombia”. Alkaline agents used were a solution of NaOH and a solution of sodium silicate (Na₂O=8.6%, SiO₂=27.8% and H₂O=63.2%). Obtained mixture was then heated at a temperature between 60 and 100°C for 6-12h, obtaining a viscous paste, which was allowed to dry at room temperature for 24 hours, until curing. Thereafter, this slurry was ground to a particle size of 4.75mm (No. 4 sieve, according to ASTM E-11-87). NaOH concentrations of 3M, 7.5M and 12M were used. Structural characterization was performed using IR and RXD. Concretes were then made using the following aggregates: crushed stone with a maximum size of 19mm and fineness modulus sand of 1.97, both coming from the river “Pescadero, Santander, Colombia”; Portland cement type I, Diamante®. Cylinders with 75mm diameter and 150 mm high were prepared, with a setting time of 7, 14, 28 and 90 days. The designs of the concrete mix were made according to the process followed by Tecnoconcretes S.A. [6].

3. Result and discussion

3.1. Structural characterization

3.1.1. Infra-red spectroscopy IR. Figures 1 and 2 shows IR spectra of the geopolymers obtained from fly ash GF and those obtained from pumice (GP), respectively. It is observed the characteristic band of the vibrations produced by the Si and Al oxides, displaced to lower values (1030-1018 cm⁻¹) for both geopolymers, with respect to the base products, with a variation also in the intensity.

![Figure 1. IR spectra of GF with different NaOH concentrations.](image1)

![Figure 2. IR spectra of GP with different NaOH concentrations.](image2)

The behaviour of Figures 1 and 2, possibly is due to the transformation of the precursor aluminosilicate (Al₂O₃·2.5SiO₂) to the ion orthosialate, by the presence of the alkaline agent. This agent activates the bonds of the oxides, forming the two species, the aluminate ion (Al(OH)₄⁻) and the monosilic acid (OSi(OH)₃⁻), responsible for forming the monomer (n(OH)₃-Si-O-Al-(OH)₃) intermediate of the polycondensation. Bands located between 600 cm⁻¹ and 800 cm⁻¹ are related to the tension vibrations of the Al-O bond. The bands located between 400 cm⁻¹ and 600 cm⁻¹ are associated with vibrations by deformation of the Si-O-Si and Al-O-Si bond. A broadband from 2500 to 3700 cm⁻¹ approximately, indicates the presence of water in both minerals [7]. Peak located at 1641 cm⁻¹ for GP and at 1638 cm⁻¹ for GF, corresponds to the vibration by deformation of the H-OH bond, since the high alkali content in the polymer network decreases the pore size, thus avoiding the evaporation of water.
The higher intensity of the band is associated to the greater number of water molecules present in GF 12M and GP 3M, because in these geopolymers the highest degree of geopolymerization is achieved. Broad and very intense band at 3452 cm⁻¹ for GF and at 3453 cm⁻¹ for GF, results from the tension vibrations of the group –OH of linking water, present in free molecular form, or adsorbed on the surface or going into pores of the geopolymer. Band located in the region of 1025-800 cm⁻¹ are due to Si-O bond flexion vibrations from the sodium silicate, this band is centered at 1029 cm⁻¹ for GP and at 1025 cm⁻¹ for GC. Signal at 1410 cm⁻¹ for the GP and at 1404 cm⁻¹ for the GC is attributed to CO₂ tension vibrations of the carbonate present in the geopolymers. The presence of carbonates is due to the interaction of the material with the CO₂ of the environment, in this case to form sodium carbonates (Trona and Temonatrite).

**3.1.2. X-Ray diffraction.** Figure 3 shows the XRD patterns obtained for FA and GF, with the different concentrations of NaOH: 3M, 7.5M and 12M. In FA diffractogram mineral phases were identified: Quartz (SiO₂); Mullite [Al₈Si₆O₁₈(Al,Fe)₃]; Hematite (Fe₂O₃); Magnetite (Fe₃O₄); Berlineite (AlPO₄); Rutilo (TiO₂) and Anatasa (TiO₂) and the presence of an amorphous phase in between 20 to 30° 2θ, this phase is also found in the IR spectra [8]. This behaviour agrees with that reported in the literature for this mineral [9]. In diffractograms for GF, this amorphous phase is also observed, but with a lower intensity and with a shift of 0.5° in 2θ. All diffractograms of GF also present the formation of new crystalline phases that are not present in the ash; these phases are attributed to the dissolution of the structure of the aluminosilicate with the alkaline solution. Ions resulting from the reaction form phases such as: Termonatrite, Albite, Calcite, Muscovite, Clinochlorine, Microcline, Trona and Anortoclase, which generally consist of sodium, potassium, magnesium and aluminium aluminosilicates. Trona, Calcite and Temonatrite are carbonates, formed mainly by the reaction of the alkaline ions of the geopolymer network with the CO₂ present in the environment. In these materials two crystallographic phases of FA are conserved: Quartz and Mullite; The characteristic reflections of these phases have shifts of the order of 0.09⁰ in 2θ. Phases mentioned above are found in the three GF, except trona, which is only found in GC 12M, mainly because this geopolymer is obtained with excess sodium. In GF 7.5M and GF 3M, anortoclase is present, which is not present in GF 12M, indicating that at higher concentration of NaOH, more carbonate phases appear, that is to 12M the highest degree of geopolymerization is achieved.

**Figure 3.** X Ray diffraction patterns of GF with different NaOH concentrations. **Figure 4.** X Ray diffraction patterns of GP with different NaOH concentrations.
Figure 4 shows the XRD patterns obtained for PP and GP, with NaOH concentrations: 3M, 7.5M and 12M. In the PP diffractogram the mineral phases were identified: Anortita [Al$_2$Ca (SiO$_4$) ]; Magnetite (Fe$_3$O$_4$); Anortoclase, syn (Na$_{0.71}$K$_{0.29}$Al$_{2}$Si$_3$O$_{10}$); Halite, potassium, syn (K$_{0.8}$Na$_{0.2}$Cl); Alpha quartz (SiO$_2$); Wuestita, syn (Fe$_{0.97}$); Muscovite [(K, Na) (Al, Mg, Fe)$_2$ (Si$_{3.1}$Al$_{0.9}$) O$_{10}$(OH)$_2$] and as in the case of FA, an amorphous phase in between 15°-35°2θ but of greater intensity. Diffractograms for the GP at different concentrations also present the amorphous phase existing in PP, but with less widening and intensity. This phase was also observed by IR spectroscopy. It is observed the formation of new crystallographic phases that are not present in PP, these phases result from the dissolution of the structure of the aluminosilicate in the alkaline medium. In these materials two crystallographic phases of PP: quartz and Muscovite are conserved, the characteristic reflections of these phases present shifts of 0.08° in 2θ. The phases named above are in the three GP, except Trona, which is only found in GP 3M; probably due to the fact that the SiO$_2$ and Al$_2$O$_3$ present in PP are activated at a lower concentration of NaOH, that is to say that with 3M has been achieved the highest degree of geopolymerization [10].

3.2. Mechanical analysis
In compressive strength analyzes performed on concrete made with substitutions of 10, 20 and 30% of the cement by GF and with GP for 7, 14, 28 and 90 days of setting [11], it was found that the highest values of resistance in the GC geopolymer are observed for a 12M NaOH concentration and 10% of substitution. On the other hand, GP exhibit the highest resistance for NaOH 3M and 10% of substitution. Concrete shows an increase in resistance as the drying time increases. Conventional concrete, has its maximum resistance to 28 days of drying, reaching a value of 300Kg/cm$^2$, whereas for concrete made with the geopolymers (GF and GP), this continues to increase even at 90 days, where the GF with 12M NaOH concentration and 10% substitution reached a value of 165Kg/cm$^2$ and GPs with 3M NaOH and 10% of substitution reaches a value of 145Kg/cm$^2$.

3.3. Electrochemical impedance spectroscopy
This test was performed for those specimens that exhibited the best mechanical resistance: GF 12M and GP 3M, for a total of 7 specimens, 6 with substitutions: 10%, 20% and 30% of each geopolymer (GF and GP), and one without replacement of the portland cement, used as a reference. In the electrochemical cell, the working electrode acts as reinforcing steel of the concrete structures, and the reference electrode allows to record the potential of the reinforcing steel. For electrochemical monitoring, the EIS in AC was used with an IM6 BAS-Zahner Impedance Unit, according to ASTM G3 [12] and it was supported with Resistance to Line Polarization (LPR) in DC. Nine monitoring were carried out at 0, 1, 2, 4, 8, 11, 15, 31 and 44 days of exposure to the corrosive medium. At the beginning of the immersion in the corrosive medium, the resistance increased in the geopolymer materials, evidencing the protection of the steel by the oxide layer formed in the surface of the same. As shown in Figures 4 and 5, the corrosion resistance of the concretes modified with geopolymer material increases as the time of exposure to the corrosive medium elapses, showing a greater anti-corrosion effect by replacing conventional cement by 20% of GF and GP. At the end of the process, the electrical resistance value is 40KΩ for the GF 20% and 18KΩ for the 20% GP, compared to only 4KΩ for the reference mixture. At the early stage of the corrosion process, around day eight, there was a decrease in the steel's resistance due to the amount of chloride around it, which causes localized breakage of the protective layer formed, resulting in material wear. Afterwards the resistance increases as the formation of the anticorrosive layer on the steel stabilizes, reducing the rate of corrosion. Increase in the electrical resistance indicates the low conduction of the electricity of GF and GP, responsible for a corrosion visibly lower than that occurred in the concrete made with portland cement. Stabilization of anticorrosive layer is caused by the decrease of the chlorides dissolved in the electrolyte. These anions react with the tricalcium aluminate (Ca$_3$Al$_2$O$_6$) present in the concrete mixture, forming the Friedel salt (3CaOAl$_2$O$_3$CaCl$_2$ 10H2O). This reduces the conductivity and increases the strength of the concrete.
4. Conclusions

Sources of aluminosilicates used in this study have a high reactivity in the presence of a highly alkaline medium, where an optimum concentration of the activating solution allows to obtain geopolymeric materials with mechanical resistance up to 170 kg/cm² at 90 days of setting.

Highest values of resistance in the GF geopolymer are observed for 12M and in the GP for 3M with 10% replacement of the concrete. Based on the persistent increase of the mechanical resistance of the GF and GP, it is very interesting to continue this research, allowing even greater setting times to 90 days.

Synthesized geopolymers have a marked tendency to protect the steel, forming an anticorrosive layer between this and the concrete. The increase in the strength of the reinforcing steel has its maximum value, in the study carried out, at 44 days of exposure to the medium of accelerated corrosion, this increase in the resistance indicates that the geopolymer material is bad conductor of the electricity, allowing to elaborate Concrete with a lower corrosion rate than conventional concrete.

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Corrigendum: Inclusion of geopolymers derivate from fly ash and pumice in reinforced concrete

J. Phys. Conf. Ser 935 (2017) 012016

A M Montaño¹, C P González², D Castro³, G Gualdron² G Baron¹ and R Atencio⁴
¹Universidad Industrial de Santander, Bucaramanga, Colombia
²Universidad Pontificia Bolivariana, Floridablanca, Colombia
³Instituto Politécnico Nacional, Ciudad de México, México
⁴Instituto Venezolano de Investigaciones Científicas, Maracaibo, Venezuela

Description of corrigendum:

The corresponding author would like to correct a mistake in the author list replacing G Gualdron for G Baron