Synthesis and characterization of inorganic polymers from the alkali activation of an aluminosilicate.

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Abstract. This paper presents the results of the synthesis and characterization of inorganic polymers (IP) from aluminosilicates: bentonite (BT) and pumice (PP). The synthesis of IP, was carried out by two methods involving alkaline activation, at room temperature and 80 ± 5 °C, using as activating agent sodium silicate both commercial and analytical (Na₂SiO₃). Sodium hydroxide (NaOH) at 3 M, 7 M and 12 M was added. A lower degree of polymerization was obtained by using analytical precursors subjected to room temperature and 80 ± 5°C. Replacement of heating by the use of the commercial activating agent with greater alkalinity allows the formation of a 3D network. The materials were structurally characterized by FTIR spectroscopy with Attenuated Reflectance (ATR), Scanning Electron Microscope (SEM) and X -ray diffraction (DRX).

1. Introduction.
In the last decades research has been conducted to improve mechanical, electrical properties and durability of Portland Cement. Geopolymers combining properties of polymers and ceramics which are obtained from chemical reaction called geopolymerization. This reaction is carried out in three steps:(i) dissolution in alkaline solution, (ii) reorganization and diffusion of dissolved ions with formation of small coagulated structures and (iii) polycondensation of soluble species to form hydrated products. On that process the raw material -aluminosilicate compounds of silicon and aluminum oxide- are activated by an oxidizing agent [1-3].

Results of the synthesis of two polymers or inorganic geopolymer (IP) by two methods, using two sources of aluminosilicates, are presented in this work: Bentonite (BT) and Pumice (PP) modified and activated at two temperatures (room temperature and 80 ± 5°C). The samples were characterized structurally by experimental techniques: Attenuated Total Reflectance Infrared Spectroscopy (ATR-FTIR), Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD)

2. Experimental.
As aluminosilicates source two clays correspond to bentonite (BT) obtained from Chemical Campota, Bogota (Colombia) and pumice (PP) extracted from Sabaneta, Antioquia (Colombia) are used. IP synthesis was performed by alkaline activation at room temperature and at 80 ± 5 °C in metallic containers of 1L capacity. Activating agent was sodium silicate (Na₂SiO₃) both, commercial and analytical degree, and sodium hydroxide (NaOH) 3, 7 and 12 M in 2:1 proportion. Sand 1:1 was also

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added to clay. The reaction mixture was left during 31 hours with vigorous stirring. Final product was
dried at room temperature for 6 hours to obtain a hard paste which was ground to 4.77 mm of particle
size according to ASTM C94 /C 94 M -09) [4]. The raw materials and the as-synthesized geopolymers
were analyzed by Attenuated Total Reflectance Fourier Transformed Infrared Spectroscopy (ATR-
FTIR Bruker Tensor 27). SEM images were obtained by field emission gun environmental scanning
electron microscopy (FEI Quanta 650 FEG SEM), under the following analytical conditions:
magnification = 2000-5000x, WD = 9.2-10.0 mm, HV = 5-20 kV, signal = Z Cont detector = ETD. X-
Ray Diffraction (Bruker D8 ADVANCE diffractometer system), operating in DaVinci geometry with
CuKα1 radiation at 40 kV and 30 mA.

3. Results and discussion

3.1. Geopolymerization reaction

Geopolymers bentonite (BT IP) and pumice (PP IP) were synthesized by two different methods (1 and
2) from the BT and PP aluminosilicates respectively, which by its lamellar structure guide the reaction
gopolymerization in a plane by increasing the speed of the same [5]. The method 1 involves two
temperatures between 20 -100 °C and the use of an activating aqueous medium provided by sodium
silicate (Na2SiO3) of commercial grade for rapid polymerization of the aluminosilicate employed [1].
Initially this synthesis was performed at two temperatures, room temperature and to 80 ± 5 °C, the first
non-disbanded the raw material in the activating solution, while the second disbanded precursors to
later present the restructuring and polycondensation thereof for formation of the polymeric matrix.
In method 2, a different activating solution was used: equimolar ratio 2:1 silicate and analytical
sodium hydroxide (Na2SiO3/NaOH) at 3, 7 and 12 M, with the purpose of to evaluate the effect on
gopolymerization by increasing alkalinity in the reaction mixture [6]. This method, however, does not
work well at any temperature. The dissolution of the raw materials was not given in the activating
solution, not even by increasing the concentration of NaOH and by raising the relationship
of SiO2/Na2O at the reaction medium[7]. So that synthesis of BT IP and PP IP was possible at 80 ± 5 °C
and commercial Na2SiO3 higher alkalinity only.

3.2 Structural analysis

3.2.1 Analysis by attenuated reflectance infrared spectroscopy (ATR)

Precursors (BT and PP) and synthesized polymers by FTIR-ATR were analyzed to further the
formation of the polymer matrix. The range of 700 – 2200 cm⁻¹ (Figure 1) is remarkable because of the
most important characteristics are evident: vibration of the Si-O and Al-O to 996 cm⁻¹ for BT and 1018
cm⁻¹ for PP; the presence of mineral oxides for both aluminosilicates materials in the region of 700-
800 cm⁻¹ is also found. Differences mainly being observed between the precursor (BT and PP) and BT
IP and PP IP in a shift to higher wave numbers in the band corresponding to the vibrations Al-O and
Si-O, attributed to the replacement of Al in the original structure of the skeleton of Si-O-Si precursor
[8]. Also weak band at 1400-1600 cm⁻¹ is related to stretching vibrations of terminal Si–OH groups in
partially hydrated PI of BT and PP. From these last two bands IP formation through structural
rearrangement of aluminosilicate sources (BT and PP) by alkaline solution is confirmed.

In addition, at FTIR- ATR spectra for synthesized IP, a displacement to shorter wavelengths for the
mineral oxides bands is observed. This fact is due to the modification of aluminosilicates (Al2O3,
2SiO2) by the activating agent (Na2SiO3), in order to obtain both ionic species: aluminate (Al (OH)₄⁻)
and monosilicate (OSi(OH)₃⁻), to form the corresponding polycondensation monomer (n(OH)₃-Si-O-
Al-(OH)₃).
3.2.2 Analysis by Scanning Electron Microscope (SEM)

The SEM of the precursor materials and the synthesized IP micrographs are presented in Figure 2. For both precursors homogeneous morphology and similar size are observed BT (Figure 2a) and PP (Figure 2c). Obtained IP exhibits a very different conformation with islands of raw materials unpolymerized, (BT IP (Figure 2b) and PP IP (Figure 2d)) immersed in a polymeric matrix. The aluminosilicates is shown unreacted (white arrows) [9]. Besides the particle size is clearly smaller for IP obtained from both clays than for BT and PP, because of compaction of materials in a cementitious mixture with better molecular organization which brings on crystallinity to the geopolymer.

3.2.3 Analysis by X-Ray Diffraction

The X-ray diffraction data for precursors (BT and PP) and the synthesized IP (BT IP and PP IP) are presented in Figure 3. Main mineral phases for BT are quartz, albite, gypsum, calcite, anorthoclase, kaolinite and montmorillonite. By alkaline activation orthoclase and muscovite appears in BT IP synthesized except by gypsum and anorthoclase [10]. Similarly for PP mineralogical phases corresponding to quartz, illite, albite, anorthite and iron oxide are found, keeping quartz and albite phases for PP IP synthesized. Cristobalite, muscovite and anorthoclase phases are observed also by activation alkaline.

It is also important to highlight the increase of intensity and resolution of the peaks for both IP, particularly in the quartz and anorthoclase phases, compared to those of precursors, due to the crystallinity achieved by geopolymerization, as it was observed by SEM.
Conclusions
The main findings of this study can be summarized as follows:
- Geopolymerization reaction was successful at high temperature and in a highly alkaline medium. On that conditions polymerization was reach at short times.
- Structural characterization by FTIR-ATR, SEM and X-Ray Diffraction of IP synthesized, shows the structural rearrangement of the aluminosilicate sources (BT and PP) with improvement in crystallinity degree. It is also found that not all the raw material is polymerized suggesting that less quantities of clay could be used.

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