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Experimental study of XRD, FTIR and TGA techniques in geopolymeric materials.

Carlos A. Rosas-Casarez, Susana P. Arredondo-Rea, José M. Gómez-Soberón, Jorge L. Alamaral-Sánchez, Ramón Corral-Higuera, M.J. Chinchillas-Chinchillas and Octavio H. Acuña-Agüero.

***Abstract*— The alkali activation of fly ashes produces a solid and compact material having similar properties to those of portland cement (PC) with characteristics of sustainable high value; these materials with high silica and aluminum are referred to as geopolymers. These new materials are a new generation of environmentally friendly cement, so it is very important to study their properties to validate their implementation; for which the application of new techniques currently being used. The work presented in this study focuses on establish the usual procedures of the techniques of X-ray diffraction (XRD), Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) in its specific application to geopolymer base, or also called fly ash. Likewise, is determined the behavior of these materials for each of the above techniques.**

***Keywords*— Fly ashes, alkali activation, geopolymers, sustainable, XRD, FTIR and TGA.**

I. Introduction

A. *General context*

Spectacular technological progress has been made in the last few years through the development of materials such as 'geopolymers'[1], similarly, the characterization techniques studying of these materials have evolved.

Nowadays, the intense global market and its changes of opportunity are forcing the development of new materials with clean technology to reduce the high cost of processing and wear of natural resources and environmental pollution. Located in a sustainable global environment and specifically related in the field of construction, the manufacture of PC across the planet produces alarming figures regarding its contamination, specific CO_2 emissions reaches values of about 2.5 billion ton / year worldwide; and that's why there is a need to study this type of new materials to use alternatively the PC and in the other hand to count with the infrastructure needs of the current population and the regulations governing them, and otherwise to be also friendly to the environment [2-5].

Carlos A. Rosas-Casarez, Susana P. Arredondo-Rea, Jorge L. Alamaral-Sánchez, Ramón Corral-Higuera, M.J. Chinchillas-Chinchillas and Octavio H. Acuña-Aguero.
Universidad Autónoma de Sinaloa.
México.

José M. Gómez-Soberón,
Universidad Politécnica de Cataluña.
Spain.

Geopolymers are materials product of a mixed of Supplementary Cementitious Materials (SCM) with a high content of silica (Si) and aluminum (Al) with a alkali solution (usually NaOH or KOH), which require in addition a curing process at moderate temperature. In previous works it was found that the major product of this reactive mixture is formed by amorphous aluminosilicate gel (NASH) with similar characteristics and properties to those of a "zeolite precursor" [6]. The presence of soluble silica modifies the kinetics of the reaction, causing the formation of gel with a high content of Si, and that this comes to affect the rate of crystallization and the nature of the zeolite formed. Finally, when thermal curing is increased, the gel is polymerized and becomes highly ordered structure [7-8]. Thus, to understand the physical and chemical properties of the geopolymers are required its characterization by various techniques; being therefore important to know which techniques to use and how to apply them it in these procedures.

B. *XRD, FTIR and TGA in geopolymers*

Several studies show that the techniques of XRD, FT-IR and TGA help understand the behavior of geopolymer and for this reason they have been of great importance to scientists in new research.

Despite the substantial amorphous nature of geopolymers, XRD is often used to identify new formed phases, define the degree to which starting materials have reacted and assess the level of amorphicity of the final products. FTIR analysis is considered as an appropriate method to study the structural evolution of amorphous alumino-silicates exhibiting high heterogeneity. Infrared absorption bands enable identification of specific molecular components and structures. Termogravimetric analysis may be used to define water evaporation mechanisms causing losses of material weight as a result of controlled heating, usually allow a choice of atmosphere during testing. Inert atmospheres such as nitrogen or argon can be used to eliminate secondary atmospheric reactions such as oxidation [9]. In the table 1 mentions some researchers who have worked with geopolymer and were used XRD, FTIR and TGA in different publications.

TABLE I.- RESEARCH ABOUT XRD, FTIR AND TGA TECHNIQUES IN THE TOPIC GEOPOLYMERS

AUTOR	YEAR	XRD	FTIR	TGA
ALONSO, S.	2001			
ANTONIC, J.	2007			
CRIADO, M.	2010			
DUXSON, P.	2005			
FERNANDEZ-JIMENEZ, A.	2007			
HAQ, E.	2014			
PALOMO, A.	2007			
PROVIS, J.	2007			
REES, C.	2007			
SILVA DE VARGAS, A.	2011			
VAN DEVENTER, J S J.	2007			
WANG, J.	2012			
ZHANG, Y.	2005			

Note: Own elaboration from: Provis, J.L. and J.S.J. Van Deventer, Geopolymers: structures, processing, properties and industrial applications. 2009: Elsevier and literature review

II. Methodology

The fly ash used in this research was activated with an alkaline solution of NaOH, solution / ash ratio used was 0.4, being the most common, were placed in plastic molds and were then demolded at 24 hours of their manufacture, finally were placed in sealed bags and kept at a relative humidity of 99% and temperature of 85 ° C. The geopolymeric pastes produced can be seen in figure 1.

Figure 1.- fly-ash based geopolymer pastes.

A. *XRD*

The X-ray diffractometer D8 Advance, Bruker mark (figure 2) using CuKα radiation was used. The samples were examined in the range 2θ, ranging from 5 ° to 90 ° and in steps of 0.033 / s. The diffractograms show the intensity of the observed diffraction function of angle of incidence and the intensity is characteristic of each crystalline component present in the sample. The identification of the different phases present can be realized by comparison with spectra of patterns available in the global database (by using the software X'pert HighScore Plus).

Figure 2.- X-ray diffractometer D8 Advance, brand: Bruker.

The standardized test embodiment of this process can be listed as follows and seen in figure 3 and figure 4.

1. - Obtaining of the geopolymeric sample with a fineness of typical talcum powder type, using for this an agate mortar for grinding, the usual amount required is approximately 10 gr.
2. - Using a spatula for placing the powder in a sample holder (the filling should be done in stages and without allowing the sample around the hole of the sample holder to agglomerate).
3. - Filling the sample holder, it must be flush using a piece of glass with a smooth surface.
4. - Finally, the glass must be removed taking care to avoid anomaly and introduce the sample holder for exposing the surface X-ray diffractometer.

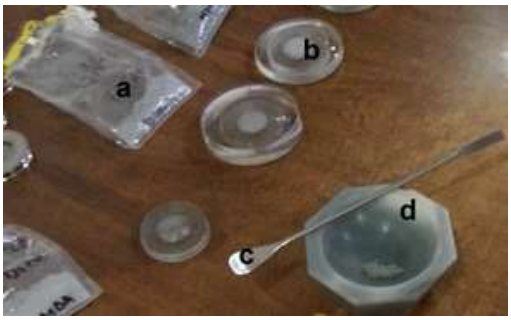

Figure 3.- Minor equipment and sample preparation in X-ray diffractometer instrument; a) geopolymer sample, b) sample holder, c) spatula d) agate mortar and spatula.

Figure 4.- Sample preparation procedure for X-ray diffractometer.

B. *FTIR*

The method used for testing was an equipment of Infrared Spectroscopy FTIR-Alpha 1, Brand Bruker, Vertex Series (figure 5). The samples for this analysis were prepared by the KBr tablet method; which consists to put the solid sample mixed with a transparent alkali halide (KBr) in a mold which is subjected to a clamping force to obtain a clear pill that allows its intrusion in the analysis equipment.

Figure 5.- infrared spectroscopy equipment, FTIR- Alpha 1, brand: Bruker.

The spectral range that was used to characterize this type of material was between 500 and 4000 cm^{-1}. The allocation of the bands has been made taking into account the commonly accepted patterns in the study of the silicates.

It is noteworthy to mention that the contribution of applying this technique in the characterization of a geopolymer, is what allows us to observe the movement of band that can present as well as the appearance of new bands attributable to the formation of new chemical compounds. The specific procedure for the preparation of these samples is described below (see Figure 6):

1. -Obtaining the geopolymeric sample with a fineness of typical talcum powder, with an approximate amount of 2 gr.
2. -Placing the sample in an agate mortar and make the white mixed with KBr in the ratio of 20:1 geopolymer / Kbr.
3. -Add the product in the sample holder and compress hard, to adhere the sample perfectly.
4. -Enter the sample holder in the infrared equipment and activate the software with the above parameters.

Figure 6.- Sample preparation procedure for FTIR.

C. *TGA*

Thermogravimetric analysis was performed with a thermobalance TA Instruments SDT 2960 Symultaneus (figure 7). The device consists of an electronic balance which is placed inside an oven, the device is coupled to a control microprocessor and a processing station data. Samples in the form of fine powder are slid and placed inside the analysis equipment for testing, they are then calcined to 1000 ° C temperature range that increase 10 ° C per minute.The preparation process of the samples can be described as follows (see figure 7).

1. – Obtain the geoplymeric sample by reducing a fine powder in an amount of 1 g.
2. - Add the material in the sample holder very carefully and verify that 5/6 of the total volume are covered.
3. - With the sample prepared and by using lab forceps, the sample holder is introduced into the analysis equipment, as shown in figure 7.
4. - The software is activated, in this case the SDT Q600 V is 20.9 Build 20 with the aforementioned parameters.

Figure 7.- Sample placement for TGA analysis.

III. Results

The following results are examples that allows to see the type, form and detail of the information provided by these three techniques in the characterization of geopolymers; this does not imply that all these are similar to those presented then, since it is necessary to consider that there may be multiple parameters such as the type of fly ash, the type of alkaline activator, age of curing material, silica-aluminum relations present, the percentage of reactive silica, among others [9].

The fallowing graphs of XRD, FTIR and TG were obtained from the geopolymer paste studied and the effect that they gave in their correct preparation, due to both the creation of the geopolymer as the experimental process described above.

A. *XRD*

The presented diffractogram (figure 8) shows characteristic peaks of a geopolymer material based on their intensity.

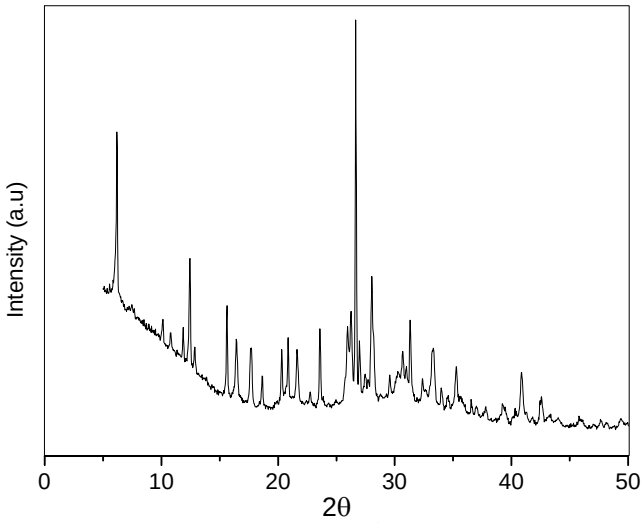

Figure 8. - XRD pattern of geopolymer.

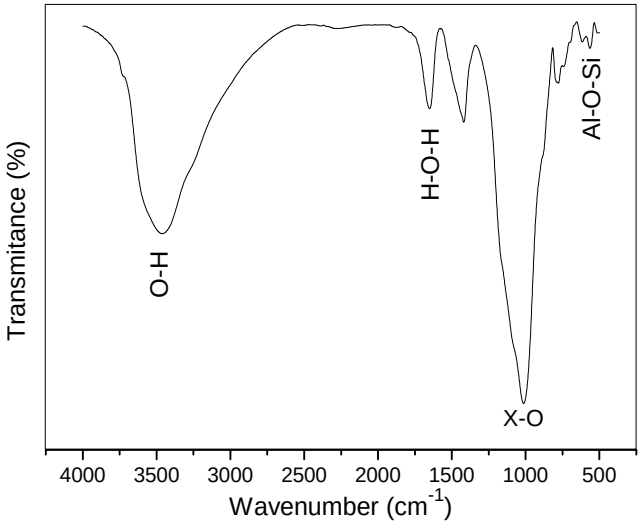

Figure 9.- FTIR spectra of geopolymer.

This technique allows the determination of the different phases between the reference sample and the sodium hydroxide-activated and can verify its existence, emergence of new phases, loss, etc.

These XRD diffractograms present relevant peaks at different intensities, being usual crystalline phases such as quartz, hematite, and some types of zeolites; the latter are formed by blending fly ash with the alkaline activator, so the resulting type will depend on the zeolite cation having hydroxide of sodium [10], and this is how this technique that allows differentiation.

Moreover, you can also observe a rise between 20 and 33 ° in 2θ, which is a normal behavior in amorphous materials.

The intensity of the peaks depends on the crystallization of the phases, which may be attributed to age of cured or to any of the before mentioned parameters causing variables on the geopolymers. Finally, we must say that their interpretation will require strong knowledge in chemistry and the reaction of the components present in the samples.

B. *FTIR*

Figure 9 shows an example of the characteristic bands of this test, for a geopolymer example with fly ash, the usual infrared spectrum of this type of materials is characterized by different types of bands:

The most characteristic band is located between 900 and 1100 cm^{-1}, which is important in these studies, it is attributed to the asymmetric stretching "X-O" (where X represents to Si or Al) and is the one present in the gel of hydrated sodium aluminosilicate. The magnitude of this band is mainly attributed to the amorphous nature of the material, as well as short-range ordering of Si and Al tetrahedron.

Moreover, this graph also allows us to deduce the degree of transmittance in the band and which depends of factors such as the cured age or the degree of reactivity, among other [11-12].

Also, these materials tend to report small bands located between 600 and 650 cm^{-1} and bands between 790 and 800 cm^{-1}, which are attributed to the bonds present in the fly ash source (quartz and mullite).

Finally, two more bands were located, the first band was between 1600 and 1650 cm^{-1}, the second band around 3450 cm^{-1}, both bands usually correspond to present bond in the geopolymer hydration, ie, corresponding to water molecules present in the material and in the NASH gel.

C. *TGA*

Figure 10 shows the usual thermogram of fly ash based-geopolymer. In this can be highlighted the main decreases in the slope of the curve located between 0 ° C to 1000 ° C.

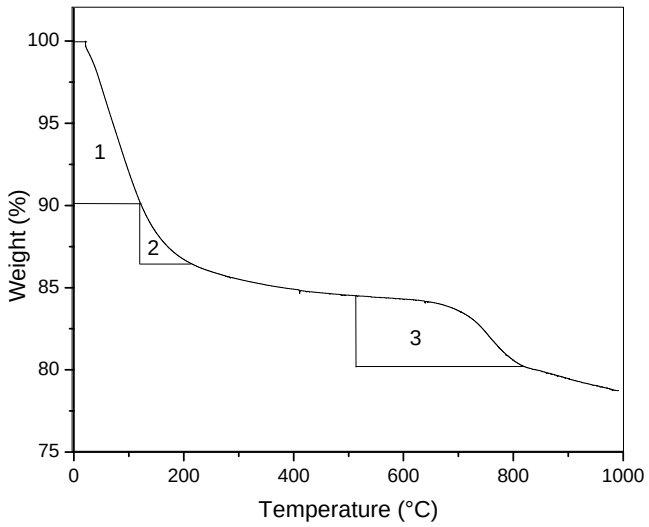

Figure 10.- thermogravimetric analysis of geopolymer.

The first major decline is associated with the dewatering process, which generates a 10% weight loss in the temperature ranges from 0 to 120 ° C (number 1 in figure 10).

This process is associated with adsorbed free water or evaporable water present on the surface and porosity of sample; however, this hypothesis is currently being refuted by research that involves to loss of hydrated sodium aluminosilicate gel. The second significant thermal degradation occurs between 120 and 200 °C (number 2 in figure 10) and is specifically associated with the presence of NASH gel.

Finally, can be observed a weight loss in the carbonates range between 450 and 800 ° C, as shown in figure 10 and marked with number 3, which may be associated with the presence of these, produced by external means.

In short, this technique allows differentiating and probing the structural variants and the presence of compounds in a material by relating its water binding capacity for each compound against the effect of temperature, to thereby be used as a comparative technique between different materials.

IV. Conclusions

A. *Generals*

To obtain geopolymers with desirable properties is necessary to take into account factors and issues such as the type of fly ash, the alkaline activator and the curing temperature, among others, the results reported that the techniques of XRD, FTIR and TGA allow correlate these factors with favorable properties; thus the process of preparing and testing methodology are important factors to consider for a successful experimental characterization.

B. *Specific*

The geopolymer contains amorphous structure but turn different crystalline phases, mainly zeolites, which are directly related to the alkaline activator used.

The chemical bonds that appear in the FTIR bands correspond to the molecules present in XRD results and states that the geopolymer was properly activated by the presence of the gel NASH. More than 60 % of the losses from TGA correspond to the range of temperature between 0 and 200 °C, which refers to the generated product in the Alkali activation of fly ashes.

The techniques of XRD, FTIR and TGA are of invaluable help and complementary between them, in turn, these results can be correlated in the physical and chemical properties of a geopolymer.

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About Authors:

C. A. Rosas-Casarez.
Title: Civil engineer and candidate to Master in Materials at Autonomy University of Sinaloa, Mexico.
Research areas: Concrete Technology, sustainable concretes characterization techniques applied to pastes, mortars and concretes, and sustainability in construction

S. P. Arredondo-Rea.
Title: PhD in Materials Science Research Center for Advanced Materials, Mexico.
Research areas: Concrete Technology, sustainable concretes characterization techniques applied to pastes, mortars and concretes, and sustainability in construction

J. M. Gómez-Soberón.
Title: PhD from the Technical University of Catalonia.
Research areas: Concrete recycled, porous structure of concrete, sustainable construction, minimization, reuse and recycling in construction, ICT in teaching, virtual campus teachers.

J. L. Almaral-Sánchez.
Title: PhD in Science (Materials), CINVESTAV-Querétaro, Mexico.
Research areas: Properties and modification of materials, inorganic-organic hybrid materials, zeolites, nanotechnology, sustainable materials and steel corrosion.

R. Corral-Higuera.
Title: PhD in Science (Materials), CIMAV-Chihuahua, Mexico.
Research areas: Concrete Technology, sustainable concretes characterization techniques applied to pastes, mortars and concretes, and sustainability in construction.

M. J. Chinchillas-Chinchillas
Title: Civil engineer and candidate to Master in Material at Autonomy University of Sinaloa, Mexico.
Research areas: Concrete recycled, sustainable construction, minimization, reuse and recycling in construction.

O. H. Acuña-Aguero
Title: Civil engineer and candidate to Master in Materials at Autonomy University of Sinaloa, Mexico.
Research areas: Use of recycled aggregates in concrete. Behavior of the chloride diffusion in recycled concrete.