
Development and Characterization of Geopolymers Based on a Kaolinitic Clay

Soungalo Ouattara¹, Brahim Sorgho¹, Moustapha Sawadogo¹, Youssouf Sawadogo¹, Mohamed Seynou¹, Philippe Blanchart², Moussa Gomina³, Lamine Zerbo^{1,*}

¹Laboratory of Molecular Chemistry and Materials (LC2M), University Joseph KI-ZERBO, Ouagadougou, Burkina Faso

²Institute of Research in Ceramic (IRCER), European Ceramic Center, Limoges, France

³Laboratory of Crystallography and Material Sciences (CRISMAT), National Graduate School of Engineering of Caen (ENSICAEN), Caen, France

Email address:

lamine_zerbo@yahoo.fr (L. Zerbo)

*Corresponding author

To cite this article:

Soungalo Ouattara, Brahim Sorgho, Moustapha Sawadogo, Youssouf Sawadogo, Mohamed Seynou, Philippe Blanchart, Moussa Gomina, Lamine Zerbo. Development and Characterization of Geopolymers Based on a Kaolinitic Clay. *Science Journal of Chemistry*. Vol. 9, No. 6, 2021, pp. 160-170. doi: 10.11648/j.sjc.20210906.15

Received: November 12 2021; **Accepted:** December 9 2021; **Published:** December 24, 2021

Abstract: Geopolymers today constitute an alternative to be considered with the aim, not of completely replacing cement, but of widening the possibilities available at the time of decision-making because this type of clay-based binder has a low impact environmental and thermal compared to Portland cement. The methods used to obtain eco-friendly building units from waste materials can be separated into three general categories: firing, cementing and geo-polymerization. The reaction of solid aluminosilicate materials with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material called a 'geopolymer. Geopolymers based on clay materials from Burkina Faso were developed and then characterized for use in construction. The results of the characterization of the clay mineral material referenced TAN as well as its calcined forms TAN-700 and TAN-800 have shown by several analysis techniques (DRX, IR, ICP-AES) that TAN contains kaolinite (71%), quartz (20%), illite (4%) and goethite (2%). TAN-700 and TAN-800 are essentially made of quartz. These clays are each mixed with the alkaline solution (sodium hydroxide solution 8 mol.L⁻¹) in a mass ratio (alkaline solution/clay) ranging from 0.33 to 0.36. The results of the mechanical and mineralogical tests of the geopolymers produced showed that the grade GP-MK₀ produced had the best performance favorable for its use in construction. Indeed, its linear shrinkage (3.44%) is low and the compressive strength (22.50 MPa) is greater than 4 MPa. This performance of GP-MK₀ is due to the formation of a phase rich in silica and in alumina (Na₂(AlSiO₄)₆(OH)₂·2H₂O).

Keywords: Clay, Development, Geopolymer, Characterization, Construction

1. Introduction

Clays are natural mixtures of phyllosilicate minerals that can be combined with other minerals (feldspars, quartz, etc.). They occupy a preponderant place in the mineral world, scientific research and environmental sciences. Its abundance, availability and accessibility make clays of interest to specialists in the field of construction materials because of their thermal conductivity and resistance [1, 2]. Today, the demand for new infrastructure and new buildings has increased due to the continuous increase of the human

population in the world. Thus, construction technology faces an enormous environmental challenge to develop ecological building materials (binders). Portland cement production contributes 7% of the carbon dioxide emitted to the atmosphere. Numerous studies have been carried out to alleviate the problem of air pollution. In the field of construction, geomaterials (adobes, geopolymers) of all types are therefore the subject of intense research. These so-called "geomaterials" are a solution to solve both the environmental problem, sustainability and the thermal problem. To remedy these problems, previous studies have proposed very

interesting solutions such as chemical and/or physical stabilization of earth materials with a cementitious binder [3–5]. Unfortunately, the use of portland cement for soil stabilization still gives them a strong negative environmental impact linked to the production of clinker [6]. The addition of this type of binder in earth bricks also degrades the thermophysical properties of these materials causing problems of thermal comfort [7]. Geopolymer material could then be an alternative solution in the construction of civil infrastructure. Compared to portland cement, geopolymer materials can reduce CO₂ emissions by 80% to 90% [8] and have better mechanical properties and durability similar to that of cement [9, 10]. Previous studies have indicated that geopolymer concrete can achieve a compressive strength greater than 60 MPa after thermal hardening [11, 12]. This material also has excellent durability to the most aggressive acids and is more resistant to sulfate attacks than Portland cement reinforcing steel mortars [13–15]. In addition, they have low density, low water absorption, negligible shrinkage and high resistance to chemicals and fire [16]. Alkaline aluminosilicates commonly called geopolymers by Davidovits, are "gels" of amorphous silicoaluminates, very dense obtained by attacking an alkaline solution of silicate on an ore containing alumina and silica. This type of material has the advantage of being able to be formulated from a wide range of aluminosilicate minerals other than kaolin and metakaolin, such as fly ash, blast furnace slag, or natural minerals such as clays. The common alkaline activator used to prepare geopolymers is a liquid combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na₂SiO₃) or potassium silicate (K₂SiO₃) [17–19]. The exact mechanism of geopolymerization is not yet fully understood, but it is believed to include three main steps: (1) dissolving Al and Si in a highly alkaline solution and diffusing the dissolved species through the solution, (2) the polycondensation of Al and Si complexes with the solution and the formation of a gel and (3) the hardening of the gel which gives the final geopolymer product [20]. Burkina Faso, like other countries in the West African sub-region, is full of many potentials in clay matter spread over almost the entire national territory. This local resource, widely available, is mainly used for the manufacture of traditional or modern building materials (bricks, floor tiles, sandstone tiles, etc.) as well as for the manufacture of many pottery items, because it seems to be the way the most

economical for many of the population to access housing [21]. However, it is well known that earthen constructions suffer from a resistance deficit, are confronted with the phenomena of systematic cracks due to shrinkage and come up against problems linked to their sensitivity to water (rainwater attacks). Taking into account all these factors and considering the weakly exploited clay potential of Burkina, we mainly focused our work on the development and characterization of geopolymers based on a TAN referenced clay from Tanghin-Dassouri (Burkina Faso) as well as his forms calcined at 700 and 800°C referenced respectively TAN-700 and TAN-800. In this article, the physical, chemical and mineralogical characterization of TAN, TAN-700 and TAN-800, the formulation of geopolymers from TAN, TAN-700 and TAN-800 samples as well as their performance (resistance to compression and bending, linear shrinkage, apparent density and total porosity, percentage of water absorption) are reviewed.

2. Materials and Experimental Methods

2.1. Raw Materials

2.1.1. Raw Materials of Aluminosilicate Powders

The kaolinitic clay used in this study is called TAN and taken from the clay site of Tanghin-Dassouri located about 25 km from Ouagadougou (Burkina Faso). The geographic coordinates of this site are 01.42° west longitude and 12.15° north latitude. Raw clay has a reddish-brown color with whitish spots (Figure 1). It contains a significant amount of quartz. TAN was homogenized, ground, and sieved to 141 µm. After these steps, it was calcined at 700°C and 800°C to have respectively the calcined clays TAN-700 and TAN-800, more reactive in the presence of an alkaline solution as shown by the work of Najet [22]. Indeed, calcined clays such as metakaolin are amorphous and have a higher reactivity during the geopolymerization reaction compared to non-calcined clays [22]. The first phase consists of a temperature rise at a heating rate of 5°C/min, followed by a phase during which the temperature is kept constant (700 or 800°C) for 2 hours and, finally, a phase in the oven. The aspects of the clays before and after calcination are presented in Figure 1. The calcination was carried out in an oven of the NABERTHERM C250 type. TAN, TAN-700 and TAN-800 are the sources of aluminosilicates.



Figure 1. Photos of materials used: a- Clay TAN; b- Powder of TAN; c- Powder of TAN-700 and d- powder of TAN-800.

2.1.2. Alkaline Solution

The alkaline activator (alkaline solution) is prepared by

mixing sodium hydroxide and sodium silicate to obtain a final concentration of OH⁻ equal to 8 mol.L⁻¹ [23]. The sodium hydroxide solution was obtained by dissolving

soda pellets having a purity of 99.2% in distilled water. The sodium silicate solution has the following chemical composition by mass: 28.7% SiO₂, 8.9% Na₂O and 62.4% H₂O, with a modulus ratio (MS) equal to 3.2 (MS = SiO₂/Na₂O).

2.1.3. Formulation of Geopolymers

The development of geopolymers begins by grinding the TAN clay soil until a particle size close to 141 μm is obtained. After grinding, part of the sample is calcined at different temperatures (700°C, 800°C) and the other part is not heat treated. The clay (calcined or not calcined) is mixed with the binding liquor in a mass ratio (alkaline solution/clay) ranging from 0.33 to 0.36 for 10 min. After the

kneading which lasts 10 min, the mixture obtained is introduced into a prismatic mold 4cmx4cmx16cm. The molding is carried out in two stages. First, we fill the mold halfway and then we do a series of 30-hit manual shocks. Then we add the other half and repeat the same number of strokes. The mold is kept in the shade. After demolding, a heat treatment is carried out at 70°C for 24 hours. The adobes obtained are stored to undergo the various tests after a minimum of 21 days. The entire production process is shown in Figure 2.

Figure 3 presents the photos of the specimens of geopolymers formulated and Table 1 presents the notation of the samples and of the geopolymers.

Table 1. Grading of clays and geopolymers.

Clay	Mass ratio (alkaline solution/clay)	Treatment		Geopolymer
		Calcination temperature (°C)	OH ⁻ concentration of the alkaline solution (mol.L ⁻¹)	
TAN	0.29	25	0	GP ₀
	0.33	25	8	GP-MK ₀
TAN 700	0.35	700	8	GP-MK ₇₀₀
TAN 800	0.36	800	8	GP-MK ₈₀₀

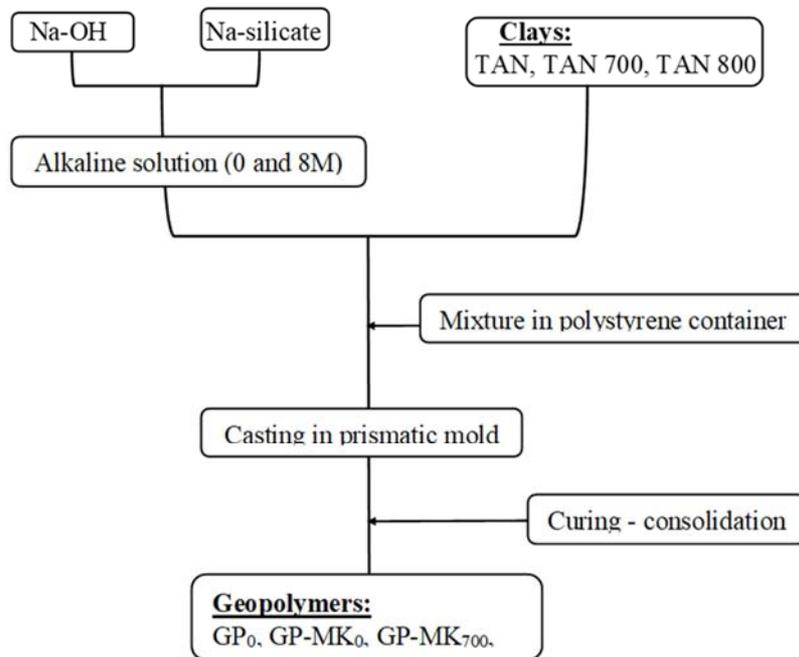


Figure 2. Geopolymers formation process.

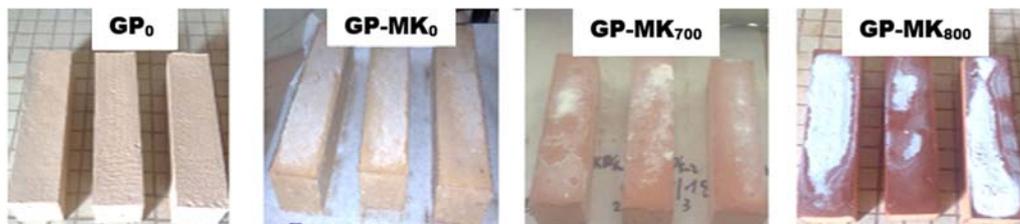


Figure 3. Appearance of geopolymer bricks.

2.2. Experimental Methods

The mineralogy of the raw materials and of the formulated

geopolymers was carried out by X-ray diffraction (XRD), infrared spectroscopy (IR) and differential thermal and thermogravimetric analysis (DTA/TG). The diffractometer

used is a Bruker AXS, operating at 40 kV-40 mA and using monochromatic graphite $\text{CuK}\alpha$ radiation. The infrared spectra were recorded in the range of 400 to 4000 cm^{-1} using a Perkin Elmer FT-IR spectrometer. Thermal analysis (ATD / TG) was carried out using a SETARAM instrument operating at 10°C/min from room temperature to 1200°C. The calcined alumina was taken as a reference. The chemical composition of the raw clay material was evaluated by inductively coupled plasma - Atomic emission spectrometry (ICP-AES). The loss on ignition was evaluated by calcining the sample up to 1000°C. The mineralogical composition of the raw sample was obtained using XRD and the results of chemical analyzes. For a chemical element "a", equation 1 was used to calculate the amount of oxide T (a).

$$T(a) = \sum MiPi(a) \quad (1)$$

where T (a): percentage of oxide constituting the element 'a', Mi percentage in mineral 'i' and Pi (a) percentage of oxide of 'a' in 'i'.

The compressive and flexural strength are the mechanical parameters of geopolymers that have been evaluated. Flexural strength is achieved on $4 \times 4 \times 16 \text{ cm}^3$ mortars with a hydraulic press fitted with a 200 kN load cell at a controlled displacement rate of 0.5 mm/min. Equation 2 makes it possible to determine the limit stress in resistance to bending [24]:

$$\sigma \text{ (MPa)} = \frac{3FE}{2le^2} \quad (2)$$

F is the intensity of the force applied, E is the distance between the two specimen supports, l is the width of the specimens, e is its thickness and σ is the stress at break. To determine the compressive strength, the half-prism resulting from the flexural strength is subjected to a load increasing monotonously until rupture. Thus, the compressive strength is the ratio of the breaking load to the cross section of the sample. the value of the resistance Rc in MPa is obtained from equation 3:

$$Rc \text{ (MPa)} = \frac{P}{S} \quad (3)$$

with: S mean value of the section in cm^2 and P the load in kN. The flexural and compressive strength tests are carried out following standard NF P 15-471 [25].

Drying shrinkage (DS) was evaluated by the relative variation of the dimensions of the material before and after drying. The difference between these dimensions of the material gives linear shrinkage. This shrinkage is determined using a caliper (equation 4) [26].

$$DS \text{ (%) } = \frac{Li-Lf}{Li} \times 100 \quad (4)$$

where DS (%) is the measured shrinkage, Li: the length of the test pieces before drying and Lf: the length of these same test pieces after drying.

The density of our geopolymers has been measured by the hydrostatic weighing method. This technique involves

weighing a dry sample, then coating it with paraffin and weighing it again. Then it is weighed the third time while it is immersed in water. Knowing the density of the paraffin (0.88), we can go back to the density of the dry material by the principle of Archimedes. The apparent density was determined using equations 5 and 6.

$$\rho = \frac{m}{V} \quad (5)$$

with

$$V = \frac{mp-mp'}{\rho w} - \frac{mp-m}{\rho p} \quad (6)$$

where ρ : density of the sample, V: volume of the sample, mp: mass of the sample waxed in the open air, mp': mass of the waxed sample immersed in water, ρw : density of water (1g/cm^3), ρp : density of paraffin (0.88 g/cm^3). As for the closed porosity (P) of geopolymers, it was deduced from the density by equation 7 [27].

$$P \text{ (%) } = \left(1 - \frac{da}{ds}\right) \times 100 \quad (7)$$

where da is the apparent density and ds the absolute density.

The water absorption test is intended to determine the amount of water absorbed by capillarity. The tests were carried out based on the AFPC-AFREM protocol [28]. This test consists to measure the increase in the mass of the test piece placed in a container whose water level is 5 mm above the underside of the test piece. In practice, this condition is obtained by placing the samples on a bed of gravel and immersing them to a depth of approximately 5 mm. The mass of the test piece is then measured as a function of time at 1, 4, 9, 16, 36, 49 and 64 minutes. To avoid the disintegration of the brick, we covered the lower part with filter paper. The values obtained make it possible to plot the amount of water absorbed per m^2 of surface as a function of the square root of time (in seconds).

The directing coefficient of the line obtained gives the water absorption coefficient A in $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}$.

3. Results

3.1. Characterization of Raw Materials

3.1.1. Chemical Characterization of Raw Materials

Table 2 presents the results of the chemical analysis of the TAN sample. From this analysis, it appears that the clay fraction contains significant amounts of silica SiO_2 (56.83%) and alumina Al_2O_3 (29.21%). TAN clay is therefore a silico-aluminate given the high contents of silica and alumina. This aluminosilicate powder is one of the main raw materials used in the preparation of geopolymers in addition to the activating solution. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ mass ratio is 1.95 for TAN against 1.18 for pure kaolinite. This value suggests the presence of free silica in the sample. The strong predominance of silica results from quartz. We also note a significant content of iron oxide (2.51%) giving it a red-brown tint. The K_2O content (0.34%) indicates that this

clay probably contains illite. TAN has relatively low levels of Na₂O (0.09%), CaO (0.01%) and MgO (0.14%). These alkali contents reflect the presence of clay minerals. Given

these results, the sample would be rich in quartz and clay minerals and would contain a moderate content of iron minerals.

Table 2. Elementary chemical analysis of TAN.

Oxyde	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	PF	Total
%	56.83	29.21	2.51	0.09	0.34	0.01	0.14	10.88	100.01

3.1.2. Mineralogical Characterization of Raw Materials

The diffractogram of TAN (Figure 4) shows that it is essentially composed of kaolinite (Al₂Si₂O₅(OH)₄), quartz (SiO₂), goethite (FeO(OH)) and illite (KAl₂Si₃AlO₁₀(OH)₂). These mineral phases are commonly present in laterites. After calcination at 700°C and 800°C, the diffractograms no longer show the characteristic peaks of kaolinite, illite and goethite (which has turned into hematite) while the quartz peaks are still present. The disappearance of the peaks of kaolinite on all the XRD diagrams of calcined powders reflects the perfect dehydroxylation of kaolinite to metakaolinite and the

amorphization of the structural network of this mineral under the effect of the calcination temperature [29]. Goethite turns into hematite under the effect of temperature (at least 300°C) [30]. By combining the results of X-ray diffraction and those of chemical analysis, the content of the crystallized mineral phases present in TAN was evaluated using a calculation technique described by Millogo *et al.* (2014) [31]. The mineralogical composition of the crystallized phases is presented in table 3. It appears from this table that the sample is rich in quartz and clay minerals (kaolinite, illite) and contains a not inconsiderable goethite content.

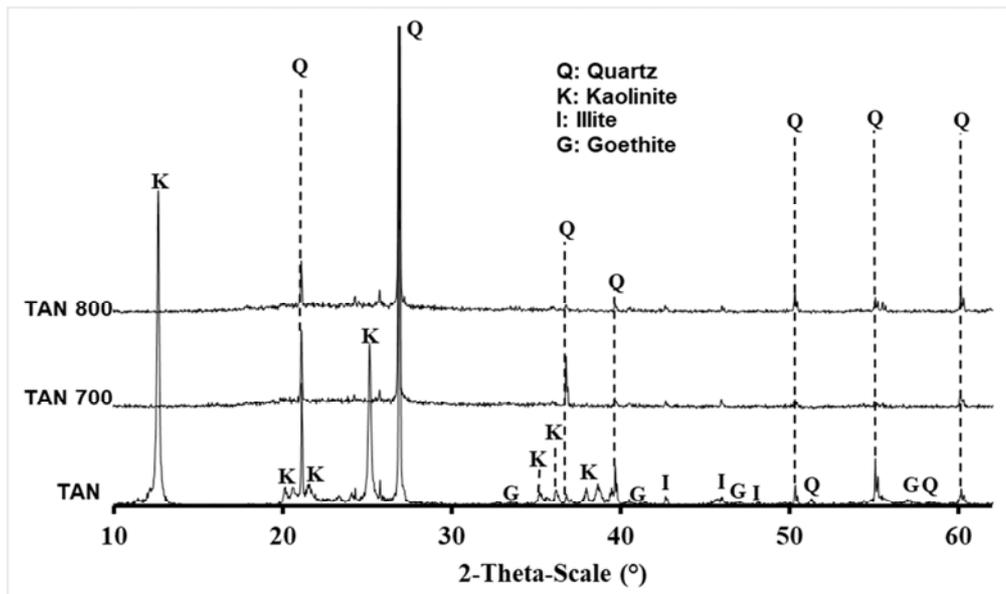


Figure 4. Diffractograms of TAN, TAN-700 and TAN-800 powders.

Table 3. Mineralogical composition of TAN.

Phases (%)	Kaolinite	Illite	Quartz	Goethite	Total	Balance
TAN	71	4	20	2	97	3

The IR spectra of our samples presented in Figure 5 were recorded in the frequency range from 400 to 4000 cm⁻¹ with a Perkin Elmer FT-IR type device. The infrared spectrum of TAN showed absorption bands at 3694, 3652 and 3619 cm⁻¹, which have been attributed to the stretching vibration of the OH groups of kaolinite [32, 33]. The absorption bands at 1010, 1033 and 786 cm⁻¹ would correspond respectively to the vibrations of Si-O, of symmetrical and asymmetrical elongations of the Si-O-Si bond in kaolinite [32, 34]. The Al-O stretching vibration of kaolinite was identified by the band at 795 cm⁻¹. In addition, the vibration band at 912 cm⁻¹ indicated the presence of the Al-OH bond while that at 698

cm⁻¹ indicated the presence of quartz in this material as identified on the DRX (Figure 4). The infrared spectrum of calcined clay fractions showed the disappearance of the absorption bands at 1103, 1033, 1006 and 912 cm⁻¹ and the appearance of a new broad band at 1060 cm⁻¹, expressing vibrations of asymmetric and symmetrical stretching of Si-Al-O and Si-O-Si [35] and the presence of amorphous silica. The band at 795 cm⁻¹ showed the presence of Al-O stretching vibrations. At 700°C, metakaolin reached its maximum. The disappearance of these bands on the spectra of calcined clays confirms the transformation of kaolinite into metakaolinite as already shown by DRX.

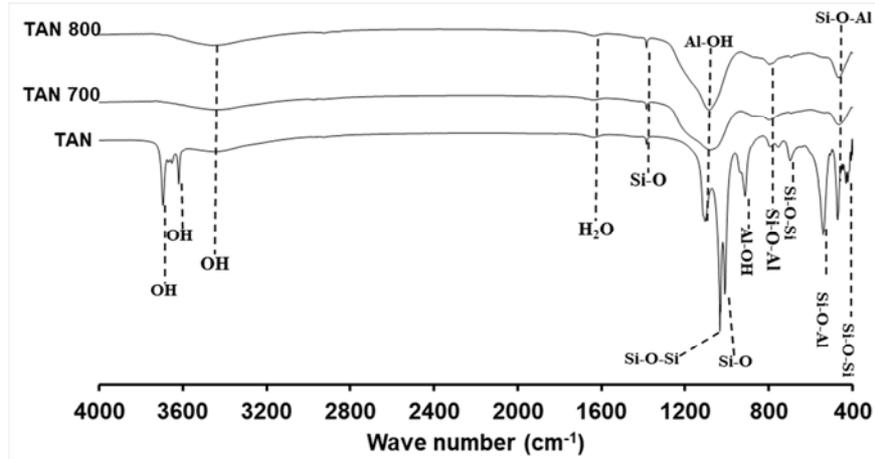


Figure 5. Infrared spectrum of TAN, TAN 700 and TAN 800.

3.1.3. Thermal Behavior of TAN

The mineralogical composition of the sample is supplemented by differential thermal analysis (ATD) and thermogravimetric analysis (ATG). The Thermogram obtained was produced at a heating rate of 10°C/min under atmospheric pressure, using SETARAM Setsys equipment. The weights of the samples and the reference alumina are 48 mg inside identical platinum crucibles. The ATD/TG curves of the TAN sample (Figure 6) show an endothermic peak at 96°C due to the departure of hygroscopic water or hydration, causing a mass loss of 1%. The endothermic peak at 300°C relates to the transformation of goethite into

hematite. The very pronounced endothermic peak at 532°C, is attributable to the dehydroxylation of clay minerals such as kaolinite and illite and its transformation into an amorphous phase called metakaolinite. The mass loss linked to this thermal accident is 11%. This dehydroxylation takes place according to the equation: $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ (kaolinite) \rightarrow $\text{Si}_2\text{Al}_2\text{O}_7$ (metakaolinite) + $2\text{H}_2\text{O}$. Finally, the exothermic peak at 952°C is due to the structural reorganization of metakaolinite into more stable structures (spinel, mullite) in addition to amorphous silica. These significant mass losses confirm the predominance of clay phases.

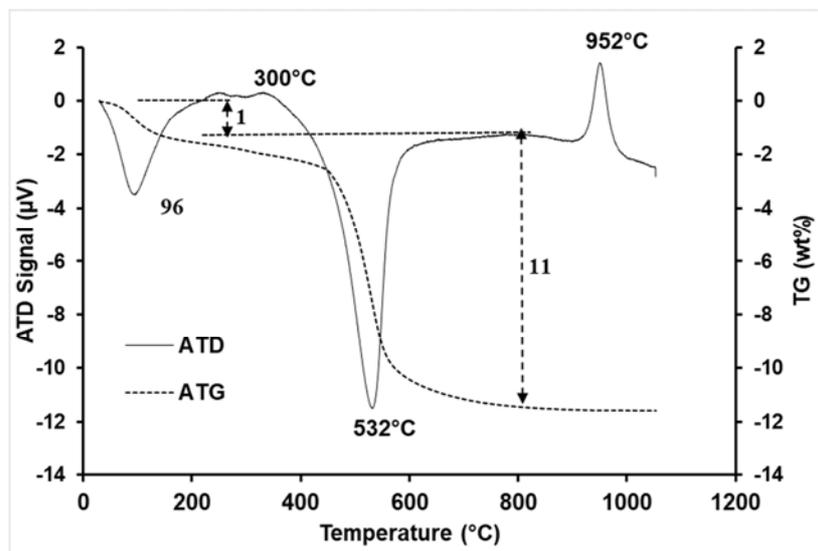


Figure 6. Thermograms DTA/TG of TAN.

3.1.4. Particle Size Distribution

The cumulative volume curves of the samples allow access to the maximum diameters corresponding to given cumulative volumes. The values corresponding to 10% (d_{10}), 50% (d_{50}) and 90% (d_{90}) of the grains of TAN, TAN-700 and TAN-800 are shown in Table 4. The comparison among the

particle size distribution of the clays shows that the samples are composed of three populations due to the presence of three main fractions. The first represents the clay fraction (<2 μm), numerous studies have shown that the particle size of clay minerals is generally less than 2 μm [36, 37]. The second is between 2 and 20 μm corresponding to the silty fraction and the last, the remaining fraction coarser than 20

μm of non-clay minerals, generally quartz. These results respectively show that 50% of the particles of TAN, TAN-700 and TAN-800 have a diameter of between 9.27 and 15.32 μm. For these three samples, the d_{10} being relatively close to 2 μm, we could say that the clay fraction is around 10%.

Table 4. Cumulative particle size parameters of raw materials.

Samples	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
TAN	2,69	9,27	28,36
TAN-700	3,43	15,32	211,39
TAN-800	2,83	9,74	42,32

3.1.5. Specific Surface Area

The specific surface area measured by the BET method is 8.75 m²/g for TAN and is close to the range of kaolinite (10 - 30 m²/g). The presence of quartz in TAN justifies this slightly low value and therefore indicates the presence of kaolinite in TAN. This result is in agreement with the results obtained from the analysis of the particle size distributions.

3.2. Characterization of the Geopolymers Produced

3.2.1. Linear Shrinkage, Water Absorption, Porosity and Density of Geopolymers

After drying, the geopolymers undergo size changes either by shrinking or by swelling. These modifications to a certain extent may compromise the use of these materials in buildings, as their durability will be affected. These various modifications are followed by measuring the dimensions before and after drying of the geopolymers. The values of the coefficient of linear expansion determined on the samples are

represented as a function of the calcination temperatures (Figure 7a). The linear shrinkage of the bricks obtained is relatively low and decreases with the calcination temperature. For the calcined samples, we observe practically no shrinkage, whereas this is not negligible for the geopolymer bricks formulated from raw clay. Figure 7b shows the results of the absorption of water by capillarity of the different synthesized geopolymers. In this figure, the absorption coefficient (in kg.m⁻².s^{-1/2}) is given by the directing coefficient of each of the straight lines obtained with correlation coefficients greater than 0.98. The water absorption coefficient increases with the calcination temperature. The absorption coefficients of geopolymers formulated from raw clay are lower than those of calcined clays. It is even smaller for the geopolymer GP-MK₀ in which the alkaline solution has been added. The density of our test pieces was determined by hydrostatic weighing. As for the porosity, it was deduced from the value of the density. The evolution of the density and porosity of the specimens as a function of the temperature is given in Figure 7c. The density and porosity evolve in the opposite direction. The denser the geopolymer, the less porous it is and vice versa. The geopolymers obtained from raw clay have a higher density than those obtained with calcined clays (GP-MK₇₀₀ = 1.62 and GP-MK₈₀₀ = 1.73). Here, the effect of the alkaline solution is not felt, because the densities of the two geopolymers (GP₀ = 1.88 and GP-MK₀ = 1.91) are substantially identical. In Figure 7d, the shrinkage and the porosity have variations that are well correlated with the variation in the absorption of water.

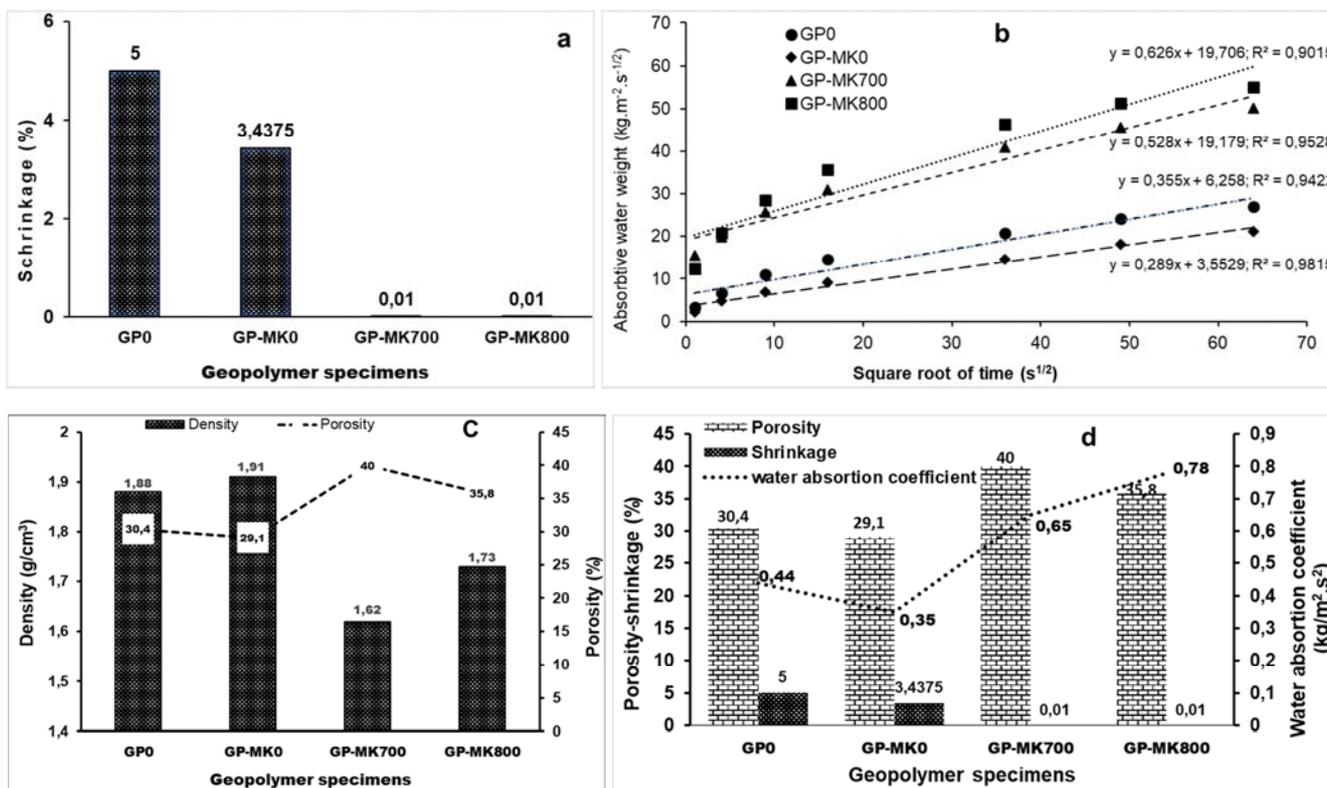


Figure 7. Physicochemical properties of specimen: a: shrinkage; b: absorption of water by capillarity; c: Density-porosity; d: Correlation between physicochemical properties.

3.2.2. Mechanical Resistance of Specimen

The purpose of building material is to react effectively to the compressive and tensile forces to which it is subjected. Its primary quality is therefore based on its ability to resist this pressure without deforming [38]. Figure 8 shows us the results of the mechanical resistances of the formulated geopolymers. It appears that the mechanical resistances decrease with the calcination temperature. A very marked increase in mechanical strengths is observed for the geopolymer GP-MK₀. The alkaline solution accelerates the geo-polymerization reaction which strongly affects the mechanical strengths. This observation is not the same for bricks GP-MK₇₀₀ and GP-MK₈₀₀. This should rather be seen in the GP-MK₇₀₀ and GP-MK₈₀₀ geopolymers formulated from the TAN 700 and TAN 800 samples, since their calcination leads to the production of metakaolinite which is reactive with alkaline solutions [39].

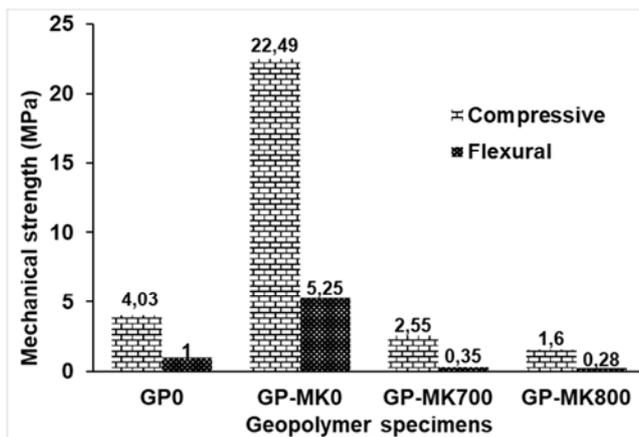


Figure 8. Flexural and compressive strength of test pieces.

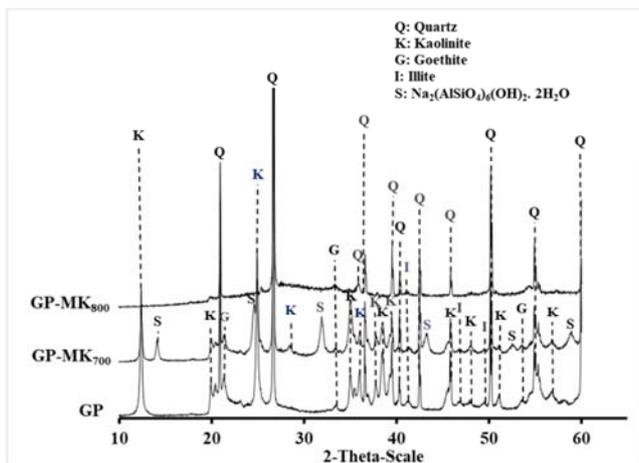


Figure 9. Diffractograms of GP₀, GP-MK₀ and GP-MK₇₀₀ powders.

4. Discussion

The development of a geopolymer material mainly involves mixing the aluminosilicate powder and the activating solution. This has been the subject of several studies to determine the ideal proportions leading to the best

properties. The work of Xu and Van Deventer [40] has shown that a mass ratio between the alkaline solution and the solid matter (aluminosilicates and alkaline crystals) of between 0.3 and 0.4 should be used to guarantee better dissolution of the aluminosilicates. They also reported that a mass ratio higher than 0.4 caused a drop in the mechanical strengths of the samples with high porosity. On the other hand, Kong et al [41] have shown that a mass ratio of 0.8 between the alkaline solution and the aluminosilicate powder would make it possible to have good workability of the paste and to increase the mechanical strengths of the geopolymer binders. However, defining a representative formulation of geopolymers remains a delicate task due to a multitude of influencing factors such as the nature of the sources of aluminosilicates, the concentration and the type of alkaline solution used for activation of aluminosilicates, rate of powder amorphization, curing temperature, particle size, etc. The properties of geopolymer binders depend mainly on their formulation, but also on these influencing parameters. Thus, the results obtained in the course of our work prompt a discussion on the physical, mechanical and mineralogical characteristics of the geopolymer binders produced from TAN, TAN-700 and TAN-800. The particle size distribution is one of the most important physical parameters having an impact on the synthesis of geopolymers from aluminosilicates as well as on the resulting products because an important part of the reaction takes place at the particle-liquid interface. Thus, for a given aluminosilicate raw material, the smallest and most porous microstructure particles are the most active in an alkaline medium [42, 43]. Table 4 shows that only 10% of our clays have a particle size close to 2 μm attributable to the clay fraction which is one of the essential reagents in the geopolymerization reaction. The TAN specific surface, determined by the BET method, is 8.75 m²/g. This is low compared to that of certain aluminosilicate materials. According to the work of Kirschner et al. [44], the specific surfaces of many aluminosilicate materials used for the synthesis of geopolymers vary between 16 and 29 m²/g. Thus, TAN and its calcined forms could have low reactivity. The results in Table 4 and the value of the specific surface show that there is a strong correlation between the particle size distribution and the specific surface: the smaller of particles of a material, the larger of their specific surface. Since the stress value increases with the decrease of particle size. In addition, the sieve used after grinding is 141 μm. This could explain the low mechanical resistance values observed especially for GP-MK₇₀₀ and GP-MK₈₀₀ since the value of the stresses increases with the decrease in the size of the particles. Figure 7a shows that the shrinkage of all geopolymer bricks is low (≤ 5%). For samples GP-MK₇₀₀ and GP-MK₈₀₀ formulated from calcined clays, we do not observe any shrinkage and this would be due to the presence of coarse particles contained in the calcined materials, thus resulting in faster contact, therefore less shrinkage [44]. Those obtained from raw clay have a significant shrinkage GP₀ = 5% and GP-MK₀ = 3.4%

which could be due to the presence of very fine clay particles contained in the materials. Drying then leads to the departure of excess water which results in the bringing together of the clay particles. This bringing together of the particles causes packing of the material, which causes a contraction representing the phenomenon of shrinking which becomes more significant when the particles initially present are distant from each other. Also note that the shrinkage is lower for GP-MK₀ by the fact that the water evaporates faster than the alkaline solution which acts as a binder. In addition, according to previous studies [45, 46], the increase in the ferric oxide content leads to good resistance to shrinkage during geo-polymerization. The significant content of iron oxide (2.51%) in TAN could be responsible for its low shrinkage observed. Figure 7c shows the apparent density and the total porosity of the geopolymer samples as a function of the calcination temperature. The density varies between 1.62 and 1.91 g/cm³ and the maximum density is observed in GP-MK₀. This high density obtained highlights significant gelation and good gel condensation. In fact, the polycondensation is followed by the release of trapped water during the dissolution of the aluminosilicates [47]. During the heat treatment at 70°C which lasted 24 hours, the samples undergo a slower dissolution of the raw materials and a slow condensation of the gel, which leads to the formation of porosity. This hardening at 70°C is accompanied by a significant outflow of water during the condensation of the geopolymer gel and promotes the presence of considerable porosity. We find that the geopolymers GP₀ and GP-MK₀ obtained from raw clay have a higher density than those obtained with calcined clays GP-MK₇₀₀ and GP-MK₈₀₀. This may be due to the good cohesion between the particles of the raw clay and implies that the raw clay contains very few pores. The porosity of these samples is between 30.4 and 40%. The variations observed can be linked to the evaporation of water filling the pores. A significant loss of water negatively impacts the condensation reaction leading to the formation of micro-cavities which increase the number of pores [48]. Gao and al. report that the apparent density of geopolymers is sensitive to the weight ratio between liquid and solid adopted during the formulation of the geopolymer paste, and would increase with low values of the liquid / solid ratio [48]. Thus, the weight ratio, respectively equal to 0.35 and 0.36 for GP-MK₇₀₀ and GP-MK₈₀₀ slightly greater than the ratio (solution / solid) of GP₀ = 0.29 and GP-MK₀ = 0.33 adopted in our study could be at the origin of these low apparent density values observed (or high porosities) in GP-MK₇₀₀ and GP-MK₈₀₀. These high porosities could also lead to lower mechanical strengths. The absorption coefficients of geopolymers formulated from raw clay are lower than those of calcined clays (Figure 7b). The coefficient is even lower for the geopolymer GP-MK₀ in which the binder has been added. Indeed, kaolinitic clays because of their small sizes can be inserted among the grains of the clay matrix to favor the shrinking of the pore size [49]. The alkaline solution also contributes to a decrease in pore size. The results of water absorption by capillarity correlate perfectly with those of

linear drying shrinkage, porosity and density. Figure 8 shows the variation in the compressive and flexural strength of the geopolymers produced as a function of the calcination temperature. Mechanical resistance in bending as in compression evolves in the same direction. There is a very marked increase in mechanical strengths for grade GP-MK₀ which has mechanical strength in compression (22.49 MPa) and in bending (5.25 MPa). Its value is very high compared to those of other geopolymers which have mechanical strengths in compression ≤ 4 MPa and in bending ≤ 1 MPa. The improvement in the resistance of GP-MK₀ is explained by a strong geopolymerization reactivity that took place between the raw clay and the alkaline solution. Rather, this should be seen in geopolymers formulated from the TAN-700 and TAN-800 samples, since their calcination leads to the production of metakaolinite which is more reactive with alkaline solutions [39]. This situation could have its explanations through the conditions of elaboration of the geopolymers that we chose which consisted in the difference of the standard conditions, not to put the bricks after just the shaping in plastic bags to avoid the carbonation with carbon dioxide from the air [50]. We also think that certain factors would also be at the origin of its low mechanical resistances especially noted at the level of GP-MK₇₀₀ and GP-MK₈₀₀ such as the SiO₂/Al₂O₃ ratios = 1.95; R₂O/Al₂O₃ = 0.015 (where R = Na⁺ or K⁺) contained in our aluminosilicate powder (TAN) which are clearly lower than the values required by Kamalloo et al [51] who shows through his work that to obtain a very high compressive strength (70-80 MPa), the SiO₂/Al₂O₃, R₂O/Al₂O₃ and H₂O/R₂O ratios of the mixture should be respectively from 3.6 to 3.8, from 1.0 to 1.2, and from 10 to 11. Moreover, it clearly shows that the increase in the H₂O/R₂O ratios, which corresponds to the increase in the amount of water, drastically lowers the mechanical performance. The concentration of the alkaline solution (8M) used in our study would be relatively low to obtain strong mechanical performance. Indeed, Wang and al studied the properties of geopolymers using the NaOH solution as an activator and reported that the compressive strengths, the flexural strengths and the bulk density of the geopolymers increase with the concentration of NaOH to 4 at 14M [52]. High concentrations of the alkaline solution increase the pH, which leads to an increase in the dissolution and solubility of the mineral residues of aluminosilicates. Figure 9 represents respectively the diffractograms of the geopolymer binders GP₀, GP-MK₀ and GP-MK₇₀₀ as a function of the calcination temperature. The GP₀ diffractogram shows that it consists of quartz, kaolinite, goethite and illite. That of GP-MK₇₀₀ shows that it is essentially made of quartz. As for that of GP-MK₀ we observe in addition to the phases identified in the diffractogram of GP₀, a new mineral phase, of formula (Na₂(AlSiO₄)₆(OH)₂·2H₂O) noted S this new phase was certainly formed as a result of the geopolymerization reaction between the alkaline solution and the minerals structurally destroyed during grinding. The formation of this new phase would therefore be at the origin of the good mechanical performance of GP-MK₀.

5. Conclusion

From the results presented, it is clear that the work was carried out successfully. A mineral raw material from Burkina Faso used and its calcined forms are suitable for the formulation of geopolymer materials. The significant deposits of this raw material will make the production of geopolymers economical and will promote the development of the countries of the sub-region. The geopolymers obtained had appropriate technical characteristics such as absorption of water by capillarity ($0.35 \text{ Kg/m}^2 \cdot \text{s}^{1/2}$ for GP-MK₀), linear shrinkage on drying ($\leq 5\%$), porosity (0.29 for GP-MK₀) and the mechanical resistance ($\approx 25 \text{ MPa}$ for GP-MK₀). In the continuation of our research, we plan to optimize the parameters influencing the geopolymerization reaction such as the nature and concentration of the alkaline solution, the temperature of the heat cure as well as the granulometry of the aluminosilicate powder. However, in future research, we will evaluate the resistance to chemicals as well as the resistance to thermal shocks which can surely affect the properties of geopolymers for target uses.

References

- [1] Vieira C. M. F., Sanchez R., Monteiro S. N., Caractéristiques des argiles et propriétés des céramiques de construction dans l'état de Rio de Janeiro, *Constr. Build. Mater.*, 22 (2008) 781.
- [2] Gualtieri M. L., Gualtieri A. F., Gagliardi S., Ruffini P., Ferrari R., Hanuskova M., Conductivité thermique des argiles cuites: Effets des propriétés minéralogiques et physiques des matières premières, *Appl. Clay Sci.*, 49 (2010) 269-275.
- [3] D. Gavigan, J. Goggins, B. McCabe, Strength and durability performance of stabilized soil block masonry units, Conference paper in IABSE Symposium Report, (2012) 2-8.
- [4] Taallah V., Guettala A., Guettala S., Kriker A. (2014). Mechanical properties and hygroscopicity behavior of compressed earth block filled by date palm fibers, *Constr. Build. Mater.* 59. DOI: 10.1016/j.conbuildmat.2014.02.058.
- [5] P. Meukam, Y. Jannot, A. Noumowe, T. C. Kofane, Thermo physical characteristics of economical building materials, *Constr. Build. Mater.* 18 (2004) 437-443.
- [6] J. Davidovits, Geopolymer cements to minimise carbon-dioxide greenhouse-warming, *Ceram Trans.* 37 (1993) 165-182.
- [7] M. O. Boffoue, K. C. Kouadio, C. H. Kouakou, A. A. Assande, A. Dauscher, B. Lenoir, E. Emeruwa, Influence de la teneur en ciment sur les propriétés thermomécaniques des blocs d'argile comprimée et stabilisée, *Afr. Sci. Rev. Int. Sci. Technol.* 11 (2015) 35-43.
- [8] Davidovits J. Chemistry of geopolymeric systems, terminology. Proceedings of Second International Conference on Geopolymers, Saint- Quentin, France, (1999) 9-40.
- [9] Li, Z., Ding, Z., Zhang, Y. Development of sustainable cementitious materials in: International Workshop on Sustainable Development and Concrete Technology, edited by K. Wang, Beijing, China, May (2004) 20-21.
- [10] Gourley J., Johnson, G. Developments in geopolymer precast concrete. In: proceeding of fourth World Congress geopolymer, Geopolymer Institute, France. (2005) 133-137.
- [11] Kovalchuk, G., Fernandez-Jimenez A., Palomo, A. (2007) Alkali-activated fly ash: Effect of thermal curing conditions on mechanical and microstructural development-Part II 86 (3). *Fuel*. DOI: 10.1016/j.fuel.2006.07.010.
- [12] Duxson P., Provis J. L., Lukey G. C., Mallicoat S. W., Kriven, W. M., Van Deventer J. S. (2005). Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 269 (1). DOI: 10.1016/j.colsurfa.2005.06.060.
- [13] Fernandez-Jimenez A., Garcia-Lodeiro I., Palomo A. (2007). Durability of alkali-activated fly ash cementitious materials. *Journal of Materials Science* 42 (9). DOI: 10.1007/s10853-006-0584-8.
- [14] Song, X., Marosszeky, M., Brungs, M., & Munn, R. Durability of fly ash based geopolymer concrete against sulphuric acid attack. Proceedings From: The 10th DBMC, International Conference on Durability of Building Materials and Components, Lyon, France. (2005) 123-129.
- [15] Fernandez-Jimenez A. M., Palomo A., Lopez-Hombrados C. (2006). Engineering properties of alkali-activated fly ash concrete. *ACI Materials Journal* 103 (2). DOI: 10.14359/15261.
- [16] Thakur, R. N., & Ghosh, S. Effect of mix composition on compressive strength and microstructure of fly ash based geopolymer composites. *ARNP Journal of Engineering and Applied Sciences*, 4 (4), (2006) 68-74.
- [17] Kong D. L. Y., Sanjayan J. G. (2008). Damage behavior of geopolymer composites exposed to elevated temperatures. *Cement and Concrete Composite* 30. DOI: 10.1016/j.cemconcomp.2008.08.001.
- [18] Rukzon S., Chindaprasirt P., Mahachai R. (2009). Effect of grinding on chemical and physical properties of rice husk ash. *International Journal of Minerals, Metallurgy and Materials*. DOI: 10.1016/S1674-4799(09)60041-8.
- [19] Nazari A., Riahi S., Bagheri A. (2012). Designing water resistant lightweight geopolymers produced from waste materials. *Materials and Design*. DOI: 10.1016/j.matdes.2011.09.016.
- [20] Ferone C., Liguori B., Capasso I., Colangelo F., Cioffi R., Cappelletto E., Di Maggio R., Thermally treated clay sediments as geopolymer source material, *Appl. Clay Sci.* 107 (2015) 195.
- [21] Zerbo Lamine, Transformations thermiques et réorganisation structurale d'une argile, Editions Universitaires européennes, (Août 2014) 978-3-8417-3766-3.
- [22] S. Selmani, E. Najet, F. Gouny, S. Bouaziz, E. Joussein, A. Driss, A. Sdiri, S. Rossignol, Physical-chemical characterization of Tunisian clays for the synthesis of geopolymers materials, *Journal of African Earth Sciences* 103, (2015) 113-120.
- [23] Bai. C., Colombo, P. Processing, properties and applications of highly porous geopolymers: A review. *Ceram. Int.* 44, (2018) 16103-16118.

- [24] Seynou, M., Ouedraogo, R., Millogo, Y., Traore, K. and Bama, B. C. A., Geotechnical, Mineralogical, Chemical and Mechanical Characterization of Clay Raw Material from Korona (Burkina Faso). *Journal de la Société Ouest Africaine de Chimie*, 27, (2009) 9-19.
- [25] NF P15-471 (1990) Méthodes d'essais des ciments: Détermination des résistances mécaniques. AFNOR-Paris.
- [26] Juan M. Perez, Jesus Ma Rincon, Maximina Romero: effect of moulding pressure on microstructure and technological properties of porcelain stoneware, *Ceram. Int.* 38 (2012) 317–325.
- [27] Dao K., Ouedraogo M., Millogo Y., Aubert J-E., Gomina M., Thermal, hydric and mechanical behaviours of adobes stabilized with cement. *Construc. Build. Mater.* 158, (2018) 84-96.
- [28] AFPC-AFREM, Durabilité des bétons-Mesure de l'absorption d'eau par capillarité,(1997).
- [29] C. Bich, Contribution à l'étude de l'activation thermique du kaolin: évolution de la structure cristallographique et activité pouzzolanique, PhD, Institut National des Sciences Appliquées de Lyon, (2005).
- [30] A. F. Gualtieri, P. Venturelli, In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction, *Am. Mineral.* 84 (1999) 895–904.
- [31] Millogo Y, Morel JC, Aubert JE, Khosrow G. Experimental analysis of Pressed Adobe Blocks reinforced with Hibiscus cannabinus fibers. *Constr. Build. Mater.*, 52, (2014) 71-78.
- [32] I. N. A.-T. Mohammad, A. Qtaitat, Characterization of kaolinite of the Baten El- Ghoul region/South Jordan by infrared spectroscopy, *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.* 61 (7) (2005) 1519–1523.
- [33] D. Akolekar, A. Chaffée, R. F. Howe, The transformation of kaolin to low-silica X zeolite, *Zeolites* 19 (5–6) (1997) 359–365.
- [34] G. Kakali, T. Perraki, S. Tsvilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, *Appl. Clay Sci.* 20 (1) (2001) 73–80.
- [35] I. Ozer, S. Soyer-Uzun, Relations between the structural characteristics and compressive strength in metakaolin based geopolymers with different molar Si/Al ratios, *Ceram. Int.* 41 (8) (2015) 10192–10198.
- [36] K. Elaiopoulos, T. Perraki, E. Grigoropoulou, Monitoring the effect of hydrothermal treatments on the structure of the natural zeolithe through a combined XRD, FTIR, XRF, SEM and N₂-porosimetry analysis, *Microp. Mesop. Mat.*, 134 (2010) 29-43.
- [37] Franco F., Cecilia J. A., Perez-Maqueda L. A., Perez-Rodriguez J. L., Gomes C. S. F., Particle-size reduction of dickite by ultrasound treatments: Effect on the structure, Shape and particle-size distribution, *Appl. Clay Sci.*, 35 (2007) 119.
- [38] S. Wild, J. M. Khatib, Portlandite consumption in metakaolin cement pastes and mortar. *Cement and Concrete Research*, 27 (1996), 137-146.
- [39] N. P. Lemougna, D. J. K. Mackenzie AND C. U. F. Melo Synthesis and thermal properties of inorganic polymers (geopolymer) for structural and refractory applications from volcanic ash. *Ceramics International*, 37 (2011), 3011-3018.
- [40] H. Xu, J. S. Van Deventer, Geopolymerisation of multiple minerals, *Miner. Eng.* 15 (2002) 1131–1139.
- [41] Kong D. L. Y., Sanjayan J. G., Sagoe-Crentsil K. (2007). Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures, *Cem. Concr. Res.* 37. DOI: 10.1016/j.cemconres.2007.08.021.
- [42] Madéjova J., Techniques in clay mineral studies, *Vib. Spectrosc.*31 (2003) 1.
- [43] Hajji L., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 118, (2014) 11-16.
- [44] S. Donatello, M. Tyrer, C. R. Cheeseman, Comparison of test methods to assess pozzolanic activity. *Cement and Concrete Composites* 32 (2) (2010), 121-127. doi.org/10.1016/j.cemconcomp.2009.10.008.
- [45] Kizhakkumodom Venkatanarayanan H., Rangaraju P. R. (2015). Effect of grinding of low-carbon rice husk ash on the microstructure and performance properties of blended cement concrete, *Cem. Concr. Compos.* 55. DOI: 10.1016/j.cemconcomp.2014.09.021..
- [46] Prud'homme E., Michaud P., Joussein E., Peyratout C., Smith A., Arrii-Clacens S., Clacens J. M., Rossignol S. (2010). Silica fume as porogent agent in geo-materials at low temperature, *J. Eur. Ceram. Soc.* 30. DOI: 10.1016/j.jeurceramsoc.2010.01.014.
- [47] A. Palomo, J. Fernández, Alkaline Activation, Procedure for Transforming Fly Ash into New Materials, in: Part I: Applications' Presented at the World of Coal Ash (WOCA) Conference in Denver, CO, USA, (2011) pp. 1–14.
- [48] K. Gao, K.-L. Lin, D. Wang, C.-L. Hwang, B. L. Anh Tuan, H.-S. Shiu, T.-W. Cheng, Effect of nano-SiO₂ on the alkali-activated characteristics of metakaolin-based geopolymers, *Constr. Build. Mater.* 48 (2013) 441–447. doi.org/10.1016/j.conbuildmat.2013.07.027.
- [49] D. Geryville, L. Hacimi, M. Cyr, P. Clastres, Amélioration et étude de l'activité pouzzolanique de certains matériaux d'aluminosilicates naturels, en: Actes de la 29^{ème} Rencontre de l'AUGC (XXIX^e Rencontres Universitaires de Génie Civil, Tlemcen, Algérie, 29-31 mai, 2011), Rd. Université Abou Bekr Belkaid 2 (2011), 148-157.
- [50] C. Ferone, F. Colangelo, R. Cioffi, F. Montagnaro, L. Santoro, Mechanical Performances of Weathered Coal Fly Ash Based Geopolymer Bricks, *Procedia Eng.* 21 (2011), 745– 752. doi.org/10.1016/j.proeng.2011.11.2073.
- [51] A. Kamaloo, Y. Ganjkanlou, S. H. Aboutalebi, H. Nouranian, Modeling of compressive strength of metakaolin based geopolymers by the use of artificial neural network Research Note, *International journal of engineering. Transactions A: basics* vol. 23 No. 2 (2010) 145-152.
- [52] H. Wang, H. Li, F. Yan, Synthesis and mechanical properties of metakaolinite-based geopolymer, *Colloids Surf. Physicochem. Eng. Asp.* 268 (2005) 1–6. https://doi.org/10.1016/j.colsurfa.2005.01.016