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Synthesis and characterization of kaolinite-based geopolymer: Alkaline activation effect on calcined kaolinitic clay at different temperatures

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Abstract

In the present work we sought to determine the most convenient calcination temperature of Tunisian kaolinitic clay in order to produce a more reactive metakaolin and to determine the most suitable potassium hydroxide (KOH) and sodium hydroxide (NaOH) concentration to produce geopolymer cements with good physical and mechanical performance, less energy consumption and low carbon dioxide emission. This product would play the role of a construction material able to replace Portland cement. The kaolinitic clay fractions collected from Tabarka (Tunisia) were first calcined at different temperatures ranging from 550 °C to 1 100 °C. Calcined fractions were then activated by potassium hydroxide and sodium hydroxide solutions with concentrations of between 5 M to 18 M. The mineral and chemical composition of raw and geopolymer samples was characterized by X-ray diffraction, infrared spectroscopy and thermal analysis, whereas the mechanical and physical properties of hardened samples were characterized respectively by compressive strength, porosity and water absorption. The results obtained showed that the temperature required to obtain a metakaolin with the highest degree of reactivity is approximately 700 °C. The various physical properties reached optimum values at this temperature and for base concentration equal to 13 M. These values decreased at higher temperature and concentration.

1. Introduction

The geopolymeric cement is a new generation of the inorganic material which is different from the Portland cement in terms of microstructure and chemical composition. In 1970 Davidovits [1] addressed the synthesis of geopolymer from inorganic material comprised of silica and alumina. The term geopolymer comes from the analogy between this inorganic material and organic polymers. They contain no dangerous solvents, are incombustible and do not release toxic fumes or gases [1]. They are characterized by their rapid curing ability at room temperature, low shrinkage and permeability, good resistance to acid and heat, and excellent durability [1, 2]. Kuenzel et al [3] showed that geopolymers synthesized from metakaolin and filler have increased compressive strength and reduced porosity. They are essentially produced from materials rich in aluminosilicate such as kaolinitic clay, metakaolin, fly ash, mixed with hydroxide alkali and alkali silicate solutions at ambient conditions [4]. Head et al. [5] studied the effect of the concentration of sodium hydroxide solution on the compressive strength of kaolinite-based geopolymer. The results showed that optimal resistance is obtained for samples prepared with a sodium hydroxide solution with a concentration of 12M and cured for 3 days. When the concentration of sodium hydroxide solution is increased, the SiO_2/Na_2O ratio is decreased. The increase in the Na_2O content improves the dissolution of kaolinitic clay. However, this excess content is not beneficial for the strength development of the kaolinitic geopolymer.

Chakchouk et al. [6] studied the physical properties of Tunisian clay samples from different locations. Clays rich in kaolinite have demonstrated the highest resistance. The presence of some clay minerals such as illite, montmorillonite and muscovite does not improve pozzolan activity despite their high levels of silica, alumina and iron. Moreover, Van Jaarsveld and Van Deventer [2]studied the effect of alkali metals on the properties of geopolymer based on fly ash. They demonstrated that during the synthesis, alkali metal cations play a major role in the dissolution step of the raw material, and in the nucleation process which leads to the formation of geopolymer structure.

Generally, calcined materials react better than uncalcined ones. According to Komnitsas and Zaharaki [7], the calcinations of raw materials for the manufacture of geopolymer materials helps release silicates and aluminates, which would increase the degree of responsiveness, and the impurities in raw material may undergo secondary reactions affecting the reaction kinetics and the mechanical properties of the products obtained [7].

The main constant of kaolinitic clay is kaolinite with the chemical formula ($Al_2O_3.2SiO_2.2H_2O$). The metakaolin produced from the calcination of kaolinitic clay at temperatures ranging from 550°C to 800°C transforms kaolinitic clay to an amorphous phase regarding equation (1), but keeps illite and montmorillonite clays in a crystalline state.

$$Al_2O_3.2SiO_2.2H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O \quad \text{(Eq. 1) [4]}$$

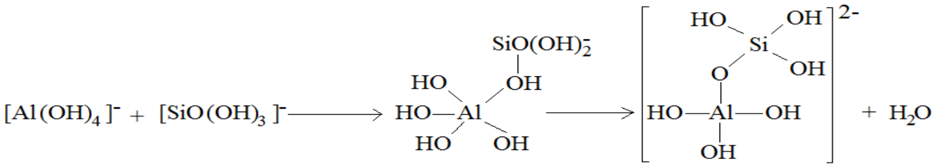
The calcination temperature of raw kaolinitic clay impacts the degree of cristallinity of the metakaolin obtained as well as its reactivity. A calcination temperature (of kaolinitic clay) at 700° C 'results in metakaolin with the highest reactivity' [8]. However, when a calcination temperature is above 850°C, it leads to the beginning of the metakaolin recrystallization and the decrease in its ability to react. Further heating (925°C to 950°C) converts the metakaolin ($Al_2O_3.2SiO_2$) to an aluminum-silicon spinel ($2Al_2O_3.3SiO_2$) (equation (2)). After calcination at 1050°C, the spinel phase ($2Al_2O_3.3SiO_2$) becomes mullite ($3Al_2O_3.2SiO_2$) and crystalline cristobalite (SiO_2) according to equation (3):

$$2(Al_2O_3.2SiO_2) \rightarrow 2Al_2O_3.3SiO_2 + SiO_2 \quad \text{(Eq. 2) [9]}$$
$$3(2Al_2O_3.3SiO_2) \rightarrow 2(3Al_2O_3.2SiO_2) + 5SiO_2 \quad \text{(Eq. 3) [9]}$$

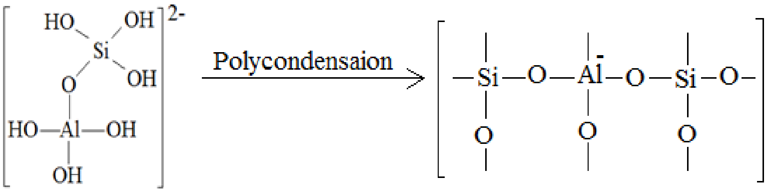
Due to its disordered structure, metakaolin displays an important reactive potential when it is activated in alkali solution [4, 10]. In geopolymer synthesis, two activators are typically used: alkaline hydroxide solutions or a blend of alkaline silicate solutions with alkaline hydroxide [11]. The difference between these two activators is that the first has very low silicate content. The method consists in dissolving the structure of metakaolin aluminosilicate and in a condensation of the free species of silicate and aluminate to form another structure with amorphous character. The dissolution and hydrolysis of aluminosilicate materials in alkaline solutions can be schematically expressed by the following reaction equations (4) and (5):

$$Al_2O_3 + 3H_2O + 2OH^- \longrightarrow 2Al(OH)^{-4} \quad \text{(Eq. 4) [11]}$$
$$SiO_2 + H_2O + OH \longrightarrow [SiO(OH)_3]^- \quad \text{(Eq. 5) [11]}$$

The condensation reaction between $[Al(OH)_4]^-$ and $[SiO(OH)_3]^-$ species may be expressed by the reactions (6) and (7):



(Eq. 6) [11]



(Eq. 7) [4]

The negative charge of Al^{3+} in IV-fold coordination in equation (7) is compensated by the cations K^+ or Na^+[12].

The metakaolin dissolution increases with NaOH concentration. Alonso and Palomo's results [13] showed that the alkaline activation of metakaolin with sodium hydroxide concentrations higher than 10M leads to the formation of an aluminosilicate. The dissolution kinetic and the advancement of the reaction depend on cationic species (Na^+, K^+) in alkaline solution and their concentrations [14]. Na^+ ions in basic solution are known to increase amorphous phase dissolution by association with silicate monomers, and K^+ ions are known to increase gel growth by association with aluminosilicates anions[4].

In the present work we sought to determine the most convenient calcination temperature of kaolinitic clay to obtain the reactive metakaolin and to determine the most suitable KOH and NaOH concentration to produce geopolymer cements with the best mechanical performance. The present investigation particularly focuses on Tunisian kaolinitic clay mineral and its ability to form a cement geopolymer after thermal and alkaline activation. Kaolinitic clay is highly present in Tunisia (north-west and Cap Bon) and is used in the manufacture of brick and ceramic. The clay used for the study was calcined at a temperature ranging from 550 °C to 1100 °C and was characterized by X-ray diffraction, infrared spectroscopy and thermal analysis. The calcined clays were then activated by NaOH and KOH solutions at concentration of 5, 8, 10, 13, 15 or 18M. The compressive strength and the water adsorption of the hardened geopolymer cement paste samples were determined after 28 days.

2. **Materials and method**

2.1. *Materials*

The clay used in this project is raw kaolinitic clay collected from Tabarka (Tunisia). It was first dried under ambient atmosphere at room temperature for a period of 24 hours to facilitate its grinding. It was crushed in a mortar with a pestle and finally sieved to obtain particles smaller than 106 μm. The chemical composition of the raw kaolinitic clay is shown in Table 1. The amount of silica is relatively high (53.2%) due to the presence of quartz. The amount of alumina is also quite high (27.3%). The high contents of silica and alumina content explains why this material was chosen as a source of aluminosilicates for the geopolymerisation reactions. Note that kaolinitic clay has a low CaO content, and its K_2O content (1.92%) is in relation with the presence of illite mixed with kaolinite. From the potassium content and from the empirical formula of illite $K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{2+}{}_{0.1}Si_{3.5}O_{10}(OH)_2\cdot(H_2O)$, the quantity of illite may be estimated at 13.2% (M_{illite} = 389.34g/mol) with the hypothesis that all potassium is brought by illite. The material has a high ignition loss as measured by DTA/TGA thermal analysis due to the deshydratation of clays and the dehydroxylation of kaolinite.

Table 1 Chemical composition of raw kaolinitic clay ([1] LOI: Loss of ignition)

Oxyde	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	LOI [1]
wt %	53.2	27.3	1.9	0.3	1.38	0.07	1.92	13.89

The alkaline solutions were prepared from coarse-grained sodium hydroxide NaOH from Sigma-Aldrich (purity: 99%, density: 2.13 g/cm^3) and potassium hydroxide KOH also from Sigma-Aldrich (density: 2.04 g/cm^3). The 5, 8, 10, 13, 15 or 18M NaOH or KOH solutions were prepared and cooled down to room temperature, sheltered from the air to avoid carbonation, 24h prior to use.

2.2 *Method*

Calcination of kaolinitic clay:

After grinding, the clay powder is divided in four fractions and each was calcined into a programmable electric oven (Nabertherm B 180) for 2 hours at 550, 700, 900 or 1100°C. The metakaolin thereby obtained is cooled down to room temperature and conserved in hermetic plastic bags.

Sample preparation:

First, each fraction of metakaolin powder, calcined at a temperature ranging from 550 to 1100°C, was mixed with a solution of KOH (15M, d = 1.54) or NaOH (15M, d =1.45) for a few minutes at room temperature. The liquid/solid mass ratio (g/g) = 1.1 for all samples. The mixture was homogenized for 3 to 5 minutes. The fresh kaolin-based geopolymer pastes were then poured into PVC cylindrical moulds, and entrapped air bubbles were eliminated by vibration. To avoid water evaporation and carbonation the molds were sealed with a thin plastic film. The samples were cured at room temperature for 24h. Following demolding, the samples remained in storage at room temperature without any special protection for another 28 days.

After testing the calcination temperature, the kaolin heated to the temperature which gave the highest compressive strength values after mixing with 15M NaOH or KOH is chosen for testing with various concentrations of KOH and NaOH based on the same preparation protocol. The liquid/solid mass ratio (g/g) for each formulation, density and concentration of each solution of KOH and NaOH is given in Table 2.

Table 2 Density and concentration of alkalis solutions and liquid/solid mass ratio for each formulation.

Potassium geopolymers			Sodium geopolymers		
KOH concentration	KOH solution density	liquid/solid mass ratios (g/g)	NaOH concentration	NaOH solution density	liquid/solid mass ratios (g/g)
5	1.14	0.83	5	1.15	0.83
8	1.32	0.96	8	1.27	0.92
10	1.39	1.01	10	1.33	0.97
13	1.49	1.08	13	1.40	1.01
15	1.54	1.12	15	1.45	1.05
18	1.61	1.17	18	1.52	1.1

- Compressive strength: Compressive strength tests were carried out to evaluate the strength development for cylindrical specimens, with a 1:2 diameter-to-length ratio [2, 15, 16], after 28 days of curing using a EZ50 Lloyd testing machine. The load was *controlled* at a constant displacement rate of 5mm/min in all tests [17]. Three specimens were tested for each calcination temperature and each alkaline solution concentration.
- Density: The real density of the material produced by mixing a powder, such as geopolymer cement, is less than its theoretical density. The density is determined using Archimedes' method. This method used is based on the gravimetric method wherein the samples are soaked in water. (For materials that do not react with water, the immersion liquid may be distilled water. For materials which may be expected to react with water, an organic liquid must be used. Water was used for our samples).

  Three specimens of each formulation were studied. The density measurement was performed as follows:

  The sample is oven dried at a temperature of 40 °C, until at least two successive weighings were identical. M_1 is the mass of the sample.

  The sample is saturated with water, in a vacuum, according to the following procedure: place the specimen in a sealed container. Pump air from the container to obtain a pressure of about 0.47 bar, this pressure was maintained for half an hour at room temperature to remove air from the pores of the specimen. Then, fill the container with distilled water, until the specimen is completely immersed and kept in water, while maintaining the vacuum for an hour until the water sufficiently penetrates deep into the pores of the specimen. The sample, placed on the tray in the water, is weighted; M_2 is the mass obtained. Weigh the wet sample in air; M_3 is the mass obtained.

  Calculation of density:

$$\boldsymbol{d} = \frac{\rho_{sample}}{\rho_{water}} \quad \text{(Eq. 8)}$$

$$\boldsymbol{\rho_{sample}} = \frac{\boldsymbol{mass_{sample\ in\ air}}}{\boldsymbol{Volume_{sample}}} \quad \text{(Eq. 9)}$$

To determine the volume of the sample using hydrostatic weighing: the sample is immersed in water, and is subject to buoyancy forces (Archimedes' principle). Any object immersed in a liquid receives a vertical thrust (from bottom to top), which is equal to the mass of the volume of the displaced liquid). Weigh the sample in water, the mass measured (M_2) will be equal to the mass of the wet sample in air (M_3) minus the mass of the volume of liquid displaced by the sample. Therefore, the sample volume is equal to (M_3-M_2).

$$\boldsymbol{\rho_{sample}} = \frac{\boldsymbol{M_1}}{\boldsymbol{M_3 - M_2}} \quad \text{(Eq. 10)}$$

$$\boldsymbol{d} = \frac{\boldsymbol{M_1}}{(\boldsymbol{M_3 - M_2})}\, \boldsymbol{d_{water}(T)} \quad \text{(Eq. 11)}$$

d_{water} (T): water density at the temperature of weighings.

- Water porosity: The water porosity method was used to quantify the percentage of pores accessible to water [18]. It is the ratio of the volume of voids (pores open on the surface) to the apparent volume of the sample. We determined the porosity of the samples, from the approach followed to determine the density. So we first calculate the volume of open pores according to the following equation:

$$\boldsymbol{V_{pores}} = \frac{\boldsymbol{M_3 - M_1}}{\boldsymbol{\rho_{eau}}} \qquad \text{(Eq. 12)}$$

  The open porosity was then calculated:

$$\%\boldsymbol{P} = \frac{\boldsymbol{V_{pores}}}{\boldsymbol{V_t}} \times \mathbf{100} \qquad \text{(Eq. 13)}$$

  V_t is the total volume of the sample.

  To determine V_t, the wet sample was placed in a graduated cylinder. The variation of the water level, which is the total volume of the sample, was then determined.

$$\%\boldsymbol{P} = \frac{\boldsymbol{M_3 - M_1}}{\boldsymbol{V_t}} \times \mathbf{100} \qquad \text{(Eq. 14)}$$

The percentage of water absorption is always less than the percentage of the material's porosity. The difference in mass (M_3-M_1) is the amount of water adsorbed, the percentage of water absorption (Wa) being expressed by the following equation:

$$\boldsymbol{W_a} = \frac{\boldsymbol{M_3 - M_1}}{\boldsymbol{M_3}} \times \mathbf{100} \qquad \text{(Eq. 15)}$$

- X-ray diffraction: Mineralogical qualitative analysis of raw and calcinated kaolinitic clay and kaolin-based geopolymer samples were realized by X-ray diffraction (XRD). The diffractograms collected on ground specimens were performed using a PANalytical XPert-V diffractometer (with a copper anode: λ Cukα1 = 1.54Å, and an X'Celerator RTMS detector. Monochromator: 4 Ge 220 Cu). The XRD patterns were measured from 5° to 80° 2θ at a scan rate of 2°/min. The crystalline and potentially newly-formed phases were identified by analyzing the positions of the peaks using the software package supplied with the instrument and the ICPDF 2 or 4 mineralogical database.

- FTIR analysis: The functional groups of the samples synthesized were identified by Infrared Spectroscopy using a PerkinElmer Model 180 spectrometer (the analyzed interval of the wavenumber range from 4000 to $450cm^{-1}$). Samples are prepared in tablet form composed by 300mg of KBr with 3mg of clay.

- Thermal analysis: Simultaneous thermogravimetric (TGA) and differential thermal analyses (DTA) were performed on raw clay. Thermal gravimetric analyses are used to measure the sample's mass changes as a function of temperature to provide information on phase composition and retained water, whereas differential thermal analyses were used to bring out the heat exchange accompanying a chemical reaction or a phase change occurring in a sample. The experiments were carried out (using SETARAM, SETSYS) between 30 °C and 1200 °C at a constant heating rate of 10°C/min.

- Optical microscope: The textural characteristics of geopolymers (morphology) have been studied on fractured surface geopolymer specimens using Motic BA310 POL optical microscope.

3. Results and discussion

3.1. *Mineralogical characterization of raw and heated kaolinitic clay*

Figure 1 presents XRD patterns of a raw and kaolinitic clay specimen heat-treated at 500, 550, 700, 900 and 1100°C for 2 hours. The X-ray diffractogram of the kaolinitic clay is shown in Figure 1.

It exhibits the characteristic peaks of kaolinite (7.15Å; 3.57Å). It also shows the presence of the characteristic peaks of quartz (3.34Å, 2.45Å, 1.81Å) and of illite (10.01Å). On the X-ray diffractograms of kaolin heat-treated at temperatures above 550°C, a bump appears that is larger at 700 °C, which justifies the amorphous character of metakaolin. Also, the diffraction peaks corresponding to kaolinite have completely disappeared. In the range from 700 to 1 100 °C, the remaining peaks were attributed to quartz (24.24 °C; 30.94 °C, 42.64 °C; 58.85 °C) and illite (10.28 °C).

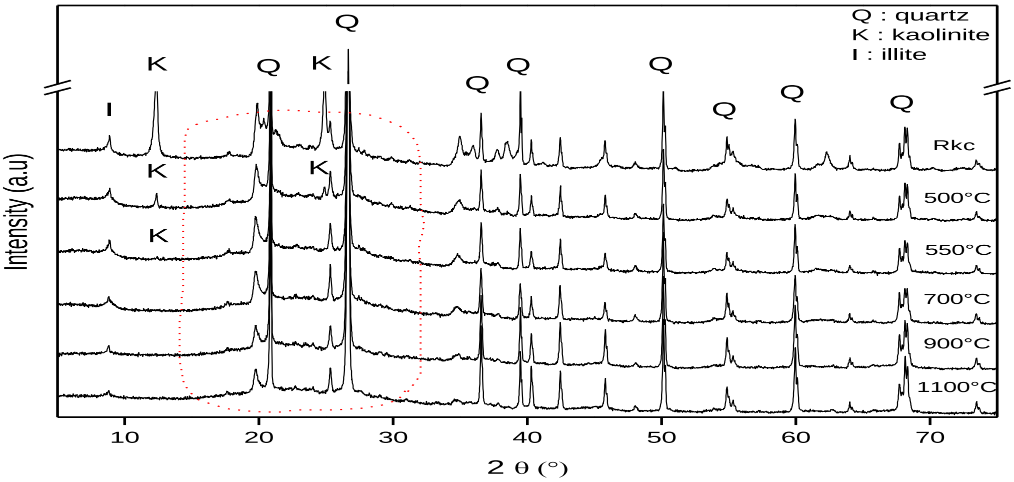


Figure 1: X-ray diffraction patterns on heat-treated and raw kaolinitic clay (Rkc) at different temperatures for 2 h

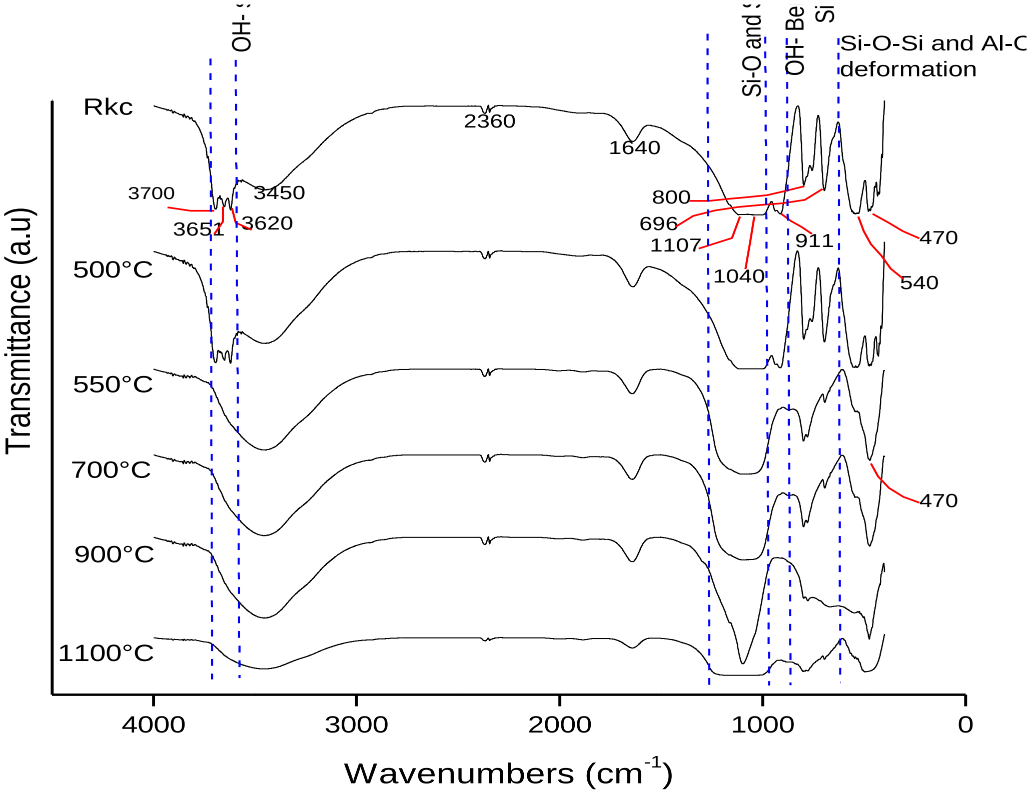


Figure 2: IR spectra of heat-treated and raw kaolinitic clay (Rkc) at different temperatures for 2 h.

Concerning the IR spectra of raw and heated kaolinitic clay shown in Figure 2, the adsorption peaks at approximately 3450 cm^{-1} and 1640 cm^{-1} reflect the stretching and bending vibration frequencies of the hydroxyl groups, respectively [19]. The absorption peaks at 3651 cm^{-1} and peak at 911 cm^{-1} characteristic stretching vibration of Al-OH indicate that clay is dioctahedric , i.e. that two out of three octahedrons are occupied by cations in the octahedral sheet of the clay [4]. The valence vibration peak at 3700 cm^{-1}, as well as the peak at 696 cm^{-1}, proves that the clay is kaolinite, and the bands at about 1107 cm^{-1} and 1040 cm^{-1} characterize stretching vibrations of Si-O and Si-O-Si, respectively [19] [20]. The absorption peak at about 2350 cm^{-1} is due to adsorptive CO_2 vibration. In comparing the IR spectra of the calcined samples to that of raw kaolinitic clay (Fig. 2) it is observed that the peak at 470 cm^{-1} characteristic of Si-O was reduced after calcination. IR spectra are in agreement with XRD measures with the disappearance of the characteristic absorption bands of kaolinite at 696, 911, 3 621 and 3700 cm^{-1} which means that amorphization by dehydroxylation has occurred.

Figure 3 presents Thermogravimetric (green curve) and Differential Thermal (blue curve) analysis (TGA-DTA) of the raw kaolinitic clay. The TGA curve shows that the material has a total mass loss of 14% at 1000°C. In particular, the weight loss of 4% that spreads between room temperature and 200°C corresponds to material dehydration and the endothermic peak on the DTA curve confirms this results. The endothermic peak, which spreads between 400 and 600°C with a maximum at 530°C corresponds to the dehydroxylation of kaolinite and the formation of metakaolin ($Al_2O_3.2SiO_2$) [21]. This result is confirmed on the TG curves on which an important mass loss of 8% occurs. From this mass loss and the 13.94 % mass loss estimated theoretically from the molecular weight of kaolinite (258.16 g/mol of $Al_2O_3.2SiO_2.2H_2O$), the percentage of kaolinite is estimated at 57.4 % of the hydrated material. An exothermic peak on the DTA curve is also present at 977°C with a negligible loss of weight on the TG curve. This corresponds to the crystallization of illite to mullite ($3Al_2O_3.2SiO_2$) [21, 22].

Finally, if the kaolinite represents 57.4% of the raw kaolin and 4% the adsorbed water content, quartz and illite (the other phases in kaolinitic clay) should represent 13.2 % (from chemical analysis) and 25.4 % (to reach 100 %) respectively (the minor phases are neglected in this calculation).

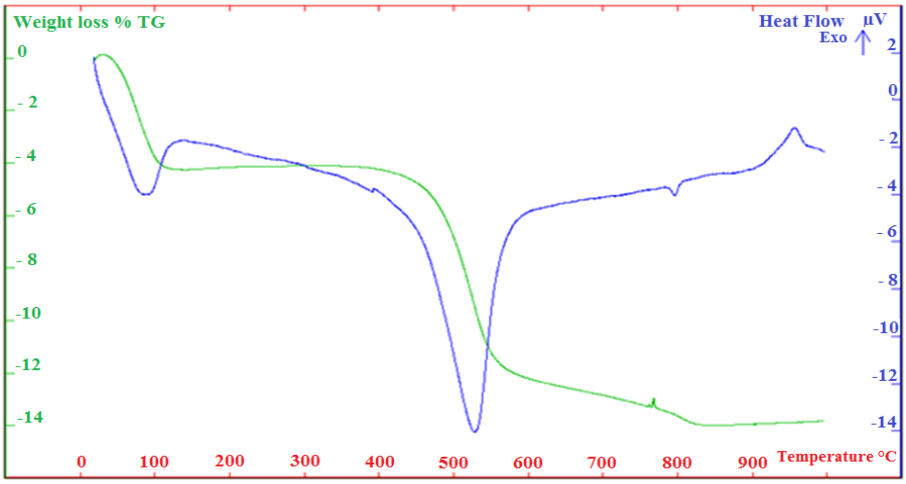


Figure 3: Thermogravimetric (TGA, green curve) and differential thermal analysis (DTA, blue curve) of the raw kaolinitic clay.

In conclusion, the XRD and IR measurements demonstrated that the heat treatment of the clay fractions at temperature above 550°C is enough to transform kaolinite into metakaolinite which is in accordance with the thermal analyses (DTA and TG). The latter shows that the dehydroxylation of kaolinite spreads between 400°C and 600°C.

3.2. *Characterization of synthesized geopolymers*

3.2.1. *Physical proprieties of geopolymers*

The mechanical strengths measured on geopolymers obtained from kaolinitic clay heated at different temperatures are shown in Figure 4. The results show that the maximum value of compressive strength is reached at 700°C. This value is approximately 34.4 MPa when KOH is used and 30 MPa when NaOH is used. So, this temperature is the best suited to synthesize geopolymer with high strength. For temperatures above 700°C, the compressive strength of metakaolin-based geopolymer decreases because, at these temperatures, the metakaolin obtained is in crystallized form, so poorly reactive. In fact, the "halo" or dump observed on the XRD spectra pattern (Figure 1), in the region of 24° <2θ <33°, characterizes the presence of amorphous (reactive) mineral phases in the metakaolin. Its decreases from 700°C to 1100°C translates to a decrease of this amorphous phase and an increase of the crystallized phase (less reactive) [23]. Thus, the metakaolin obtained at temperatures above 700°C are poorly reactive and therefore they are poorly activated by the addition of soda and potash solutions.

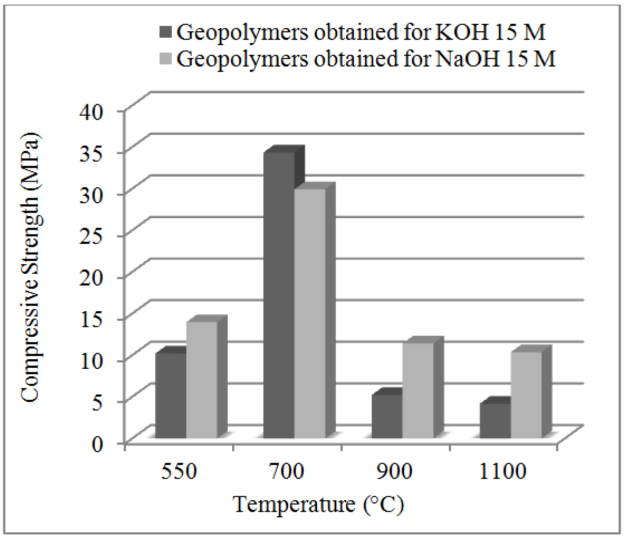


Figure 4: Geopolymer compressive strength result for different heated temperatures of kaolinitic clay and KOH and NaOH 15 M (Three cylinders of each sample were tested, averaging the experimental values obtained).

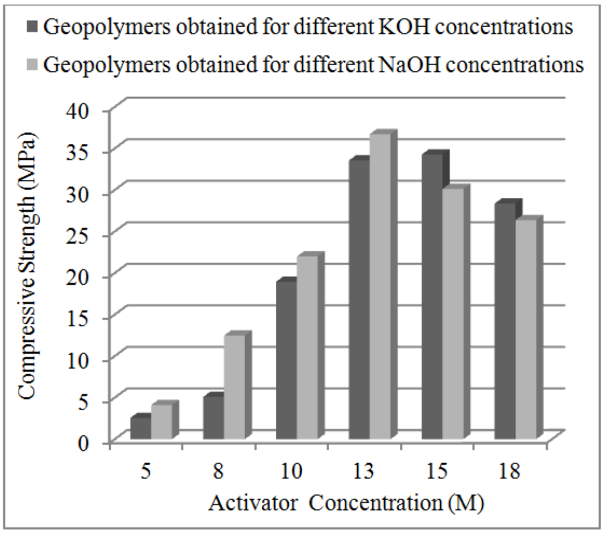


Figure 5: Geopolymer compressive strength result for heated kaolinitic clay at 700 °C and different base concentrations (Three cylinders of each sample were tested, averaging the experimental values obtained).

Figure 5 shows the compressive strength of geopolymers obtained from the kaolinitic clay calcined at 700 °C followed by activation by various concentrations of KOH and NaOH. The maximum values of compressive strength are obtained for KOH activator at 15 M (33.5 MPa) and NaOH activator at 13 M (36.7 MPa).

When the KOH concentration is above 15 M, the compressive strength decreases (Fig. 5). This behavior could be due to the high concentration of K^+ ions in the tetrahedral cavities [24]. On the other hand, the decrease of compressive strength when the NaOH concentration is above 13 M, could be explained by the formation of cracks on the cured geopolymer samples resulting from efflorescence caused by the reaction of excess sodium hydroxide with atmospheric carbon dioxide (CO_2) [14]. Figure 6 shows the formation of efflorescence on the surface of cured geopolymer samples which induces cracks in the materials.

Figure 6: Formation of the white carbonate on surface of specimens known as efflorescence which usually induced degradation of binder

The water porosity, density and water absorption rates of the samples obtained from kaolinitic clay calcined at various temperatures and KOH and NaOH (15M) are listed in Table 3. The physical properties obtained from kaolinitic clay calcined at 700 ° C and after mixing with different concentrations of KOH and NaOH are listed in Table 4.

Table 3 Water porosity, density and water absorption rates of hardened geopolymer cement paste obtained for different calcination temperatures of kaolinitic clay (500, 700, 900 and 1100°C) and with KOH or NaOH 15M as activators.

Calcination temperature of kaolinitic clay (°C)	Potassium geopolymers				Sodium geopolymers			
	Compressive strength (MPa)	Water porosity (%)	Density (g/cm^3)	% water absorption	Compressive strength (MPa)	Water porosity (%)	Density (g/cm^3)	% water absorption
550	10.2	24.5	1.95	15.2	13.9	22.2	1.91	13.4
700	34.4	24.3	1.96	14.1	29.9	22.1	2.14	12.9
900	5.2	27.2	1.86	16.9	11.4	25.2	1.98	15.0
1100	4.1	28.3	1.94	17.4	10.4	26.0	1.91	15.4
550	10.2	24.5	1.95	15.2	13.9	22.2	1.91	13.4

Table 4 Porosity, density and water absorption rates of hardened geopolymer cement paste obtained with kaolinitic clay heated at 700°C and after activation with different KOH or NaOH concentrations.

KOH or NaOH concentration	Potassium geopolymers				Sodium geopolymers			
	Compressive strength (MPa)	Water porosity (%)	Density (g/cm^3)	% water absorption	Compressive strength (MPa)	Water porosity (%)	Density (g/cm^3)	% water absorption
5	2.6	26.5	1.89	16.5	4.1	24.1	1.94	15.9
8	5.1	26.0	1.86	15.9	12.5	23.9	1.97	14.5
10	18.9	24.9	1.90	14.9	22.0	22.9	1.98	14.3
13	33.5	23.5	1.98	14.1	36.7	22.0	2.11	13.8
15	34.3	24.4	1.92	14.6	30.1	21.9	2.09	13.2
18	28.4	24.3	1.90	14.9	26.4	22.2	2.08	13.9

The results in both tables may partially explain the compressive strength test results. The maximum of density value corresponds to the highest compressive strength measured on samples. The water porosity and water absorptions were in the range of 23.5 % to 28.3 %, and 14.1 % to 17.4% respectively when KOH is used, and in the range of 21.9 % to 26.0 % and 12.9 % to 15.9 % when NaOH is used.

In each table, the various physical properties (such as water adsorption in relation with water porosity) decrease and then increase. A minimum of porosity and water adsorption corresponds to the optimum values for the heating temperature of kaolinitic clay at 700 °C and the base concentration at 13 M. The density behaves similarly, increasing to the optimum values and then decreasing.

Porosity, density and the percentage of water absorption are interrelated. Thus, the highest compressive strength is correlated with lower porosities and % of water absorption, and it is probably linked with less heterogeneity and defects in the material.

The very open microstructure of some samples can be considered as one of the reasons leading to the formation of efflorescence in geopolymer that causes the decrease in compressive strength.

Figure 7 presents the OM images of fractured geopolymer specimens synthesized by different heated temperatures of kaolinitic clay and KOH or NaOH 15 M and cured at room temperature for 28 days. Figure 8 presents the OM images of fractured geopolymer specimens synthesized by heated kaolinitic clay at 700 °C and different base concentrations, and cured at room temperature for 28 days.

The OM images of geopolymer fractures surface show a matrix with many irregular pores generated by the air bubbles encapsulated. All micrographs in Figure 7 and micrographs (c) and (f) in Figure 8 show a more heterogeneous matrix with large amount of particles, with lumpy texture, which attribute to efflorescence characteristic of alkali carbonate. However, micrographs (a) and (d) in Figure 8 show matrix containing particles with some porosity. While micrographs (b) and (e) in Figure 8 show a more compact matrix.

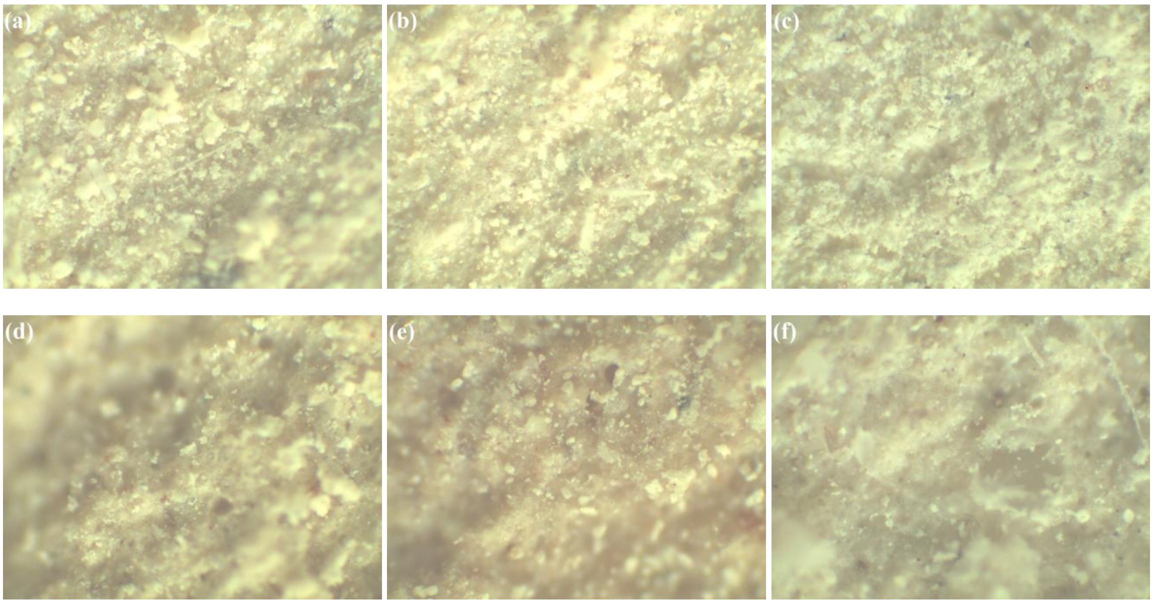


Figure 7: OM images (100 times magnified) of fractured geopolymers result for different heated temperatures of kaolinitic clay and KOH or NaOH 15 M: (a) geopolymer specimen synthesized by heated kaolinitic clay at 550 °C and KOH, (b) geopolymer specimen synthesized by heated kaolinitic clay at 700 °C and KOH, (c) geopolymer specimen synthesized by heated kaolinitic clay at 1100 °C and KOH, (d) geopolymer specimen synthesized by heated kaolinitic clay at 550 °C and NaOH, (e) geopolymer specimen synthesized by heated kaolinitic clay at 700 °C and NaOH, (f) geopolymer specimen synthesized by heated kaolinitic clay at 1100 °C and NaOH,

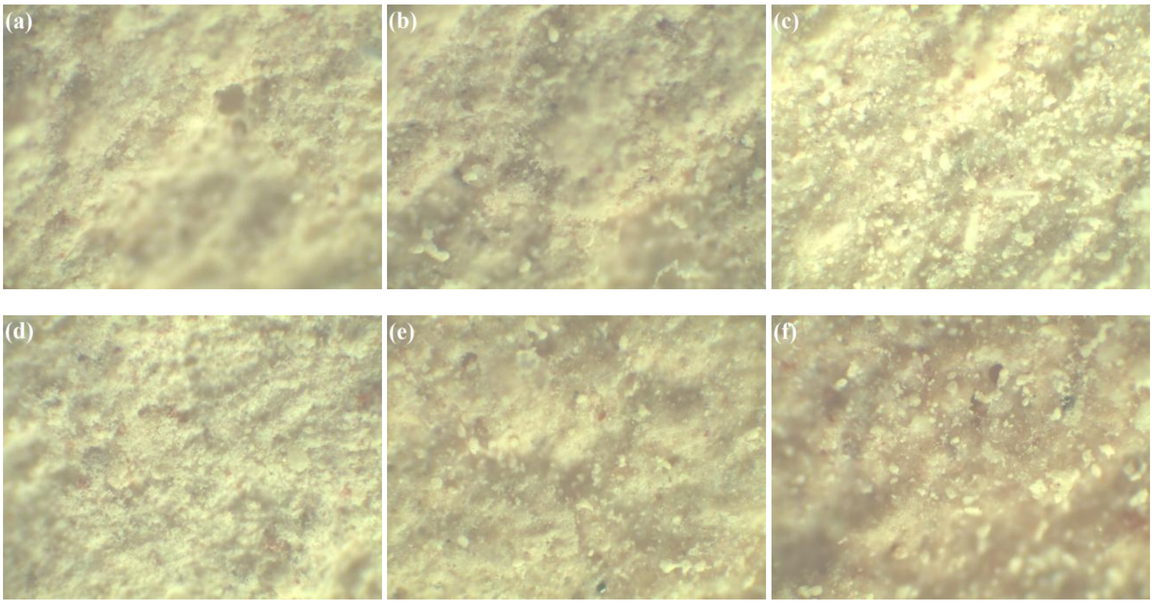


Figure 8: OM images (100 times magnified) of fractured geopolymers result for heated kaolinitic clay at 700 °C and different base concentrations: (a) geopolymer specimen synthesized by KOH 8 M, (b) geopolymer specimen synthesized by KOH 13 M, (c) geopolymer specimen synthesized by KOH 15 M, (d) geopolymer specimen synthesized by NaOH 8 M, (e) geopolymer specimen synthesized by NaOH 13 M, (f) geopolymer specimen synthesized by NaOH 15 M

This shows that the high resistance of geopolymer specimens seems to be linked to a lower porosity and a compact aspect which are controlled by the kaolinitic clay calcination temperature and the alkali solution concentration. The compressive strength is more important in geopolymers result for the kaolinitic clay calcined at 700 °C and alkaline solution concentration of approximately 13 M.

3.2.2. Mineralogical characterization of geopolymers

Figures 9 and 10 show the XRD patterns of samples obtained by mixing the clay fractions calcined at 550, 700, 900 and 1100 °C with KOH and NaOH 15 M, respectively. The X-ray diffraction patterns of mixes made of calcined kaolinitic clay at 700 °C with KOH and NaOH solutions at different concentrations are presented in Figure 11 and Figure 12, respectively.

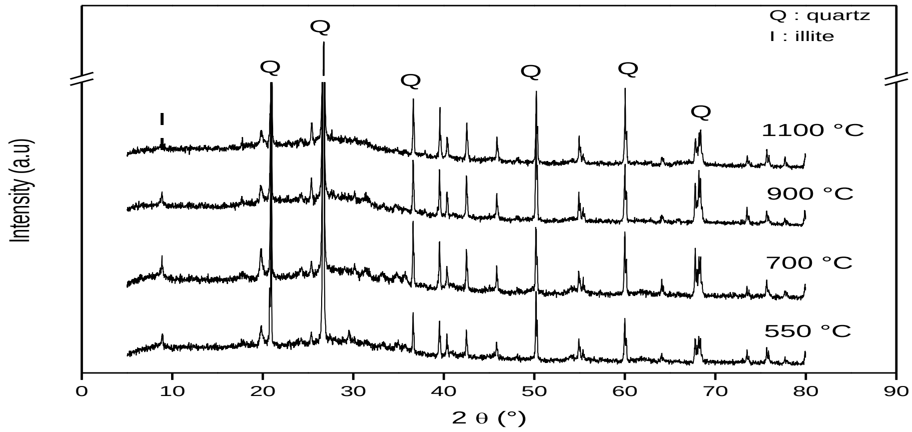


Figure 9: XRD patterns on calcined clay at 550, 700, 900 and 1100 °C and mixed with KOH (15 M)

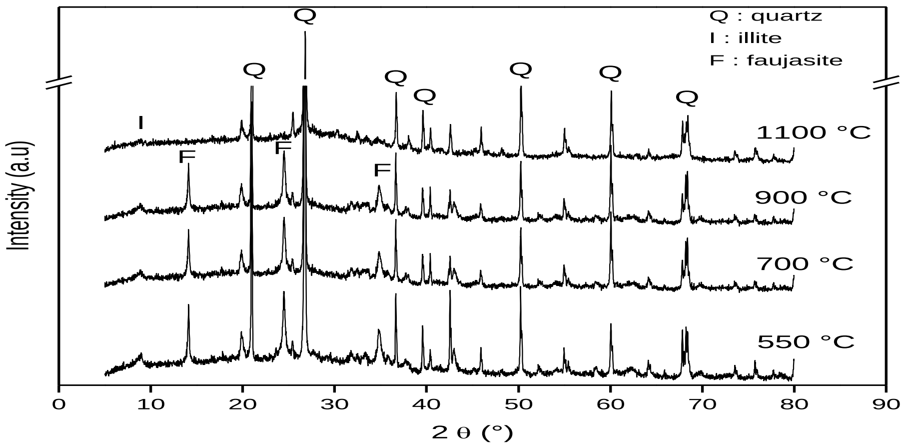


Figure 10: XRD patterns on calcined clay at 550, 700, 900 and 1100 °C and mixed with KOH (15 M)

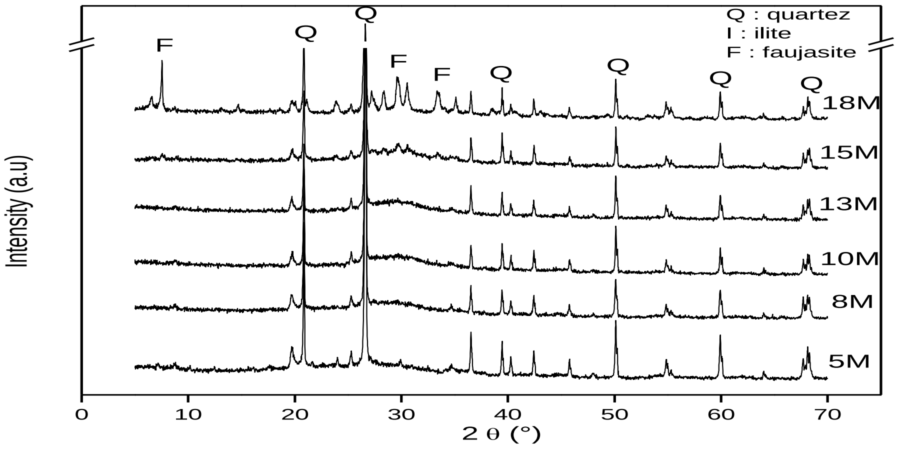


Figure 11: XRD patterns on calcined clay at 700°C and mixed with different KOH concentrations

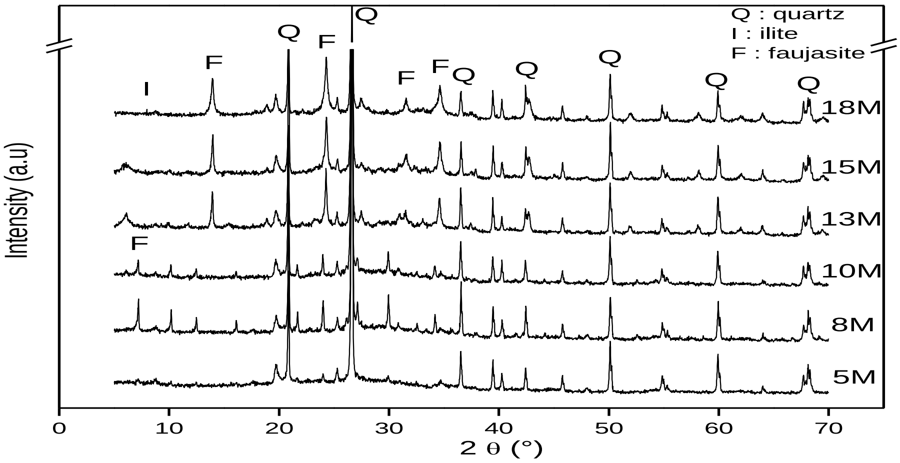


Figure 12. XRD patterns on calcined clay at 700 °C and mixed with different NaOH concentrations

All the X-ray diffractograms recorded show the presence of the characteristic peaks of quartz (3.34 Å; 2.45 Å, 1.81 Å) and illite (10 Å) which means that these minerals are not dissolved during geopolymerization, they remain as a crystalline phase in the geopolymer cement. The diffractograms of the samples obtained from kaolinitic clay calcined at 700°C and at different concentrations of KOH (5, 8, 10, 13 and 15M) are quite similar (Fig.11) except in the case of the 18M KOH sample which reveals the presence of faujasite-K ($K_2Al_2Si_{2.4}O_{8.8,}6.7H_2O$) [25] due to the excess of KOH. Similarly, the X-ray diffractograms on Figures 10 and 12 corresponding to samples synthesized using NaOH (except diffractogram obtained from kaolinitic clay calcined at 1100 °C) show the appearance of faujasite-Na ($Na_2Al_2Si_{2.4}O_{8.8,}6.7H_2O$) [25].

X-ray diffractograms show also the presence of a large peak in the region of 28° < 2θ < 34°. This halo peak indicates the formation of an amorphous alumino-silicate phase corresponding to the geopolymer materials [4, 26].

Figure 13 shows the IR spectra of metakaolin (kaolinitic clay heated at 700 °C), the Figures 14 and 15 show, the IR spectra patterns of samples obtained by mixing the clay fractions calcined at 550, 700, 900 and 1100 °C with 15M-KOH and 15M-NaOH solutions, respectively. The IR spectra patterns of samples obtained with calcined kaolinitic clay at 700 °C and mixed with different concentrations of KOH and NaOH solutions are presented in Figures 16 and 17, respectively.

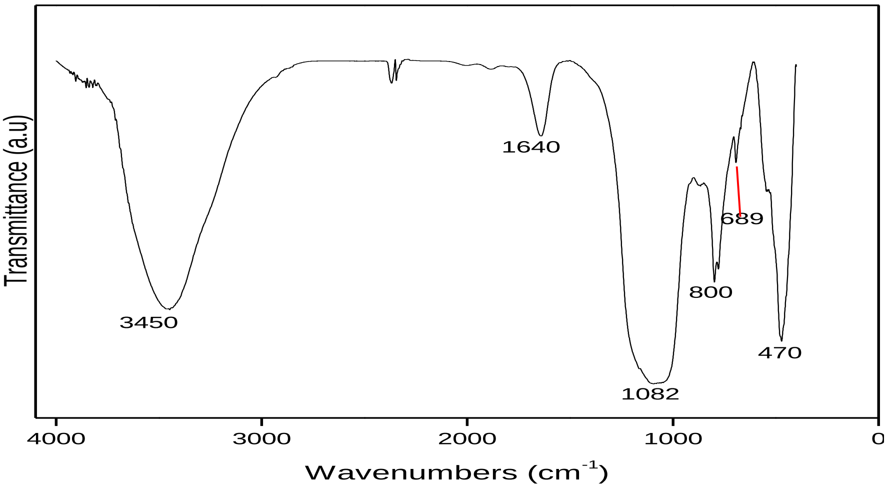


Figure 13: IR spectra of metakaolin (calcined kaolinitic clay at 700 °C)

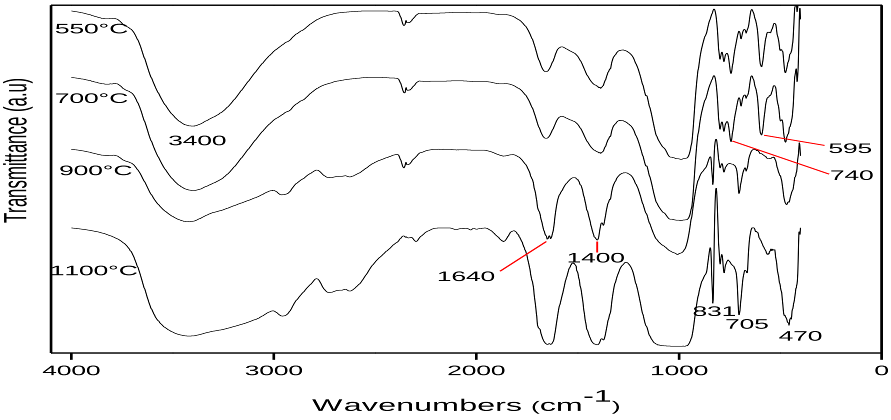


Figure 14: IR spectra patterns of samples obtained by mixing the clay fractions calcined at 550, 700, 900 and 1100 °C with 15M-KOH solutions

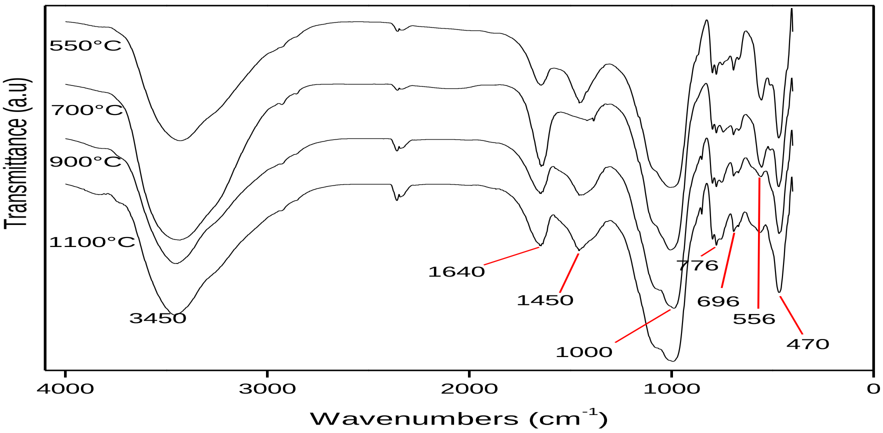


Figure 15: IR spectra patterns of samples obtained by mixing the clay fractions calcined at 550, 700, 900 and 1100 °C with 15-NaOH solutions

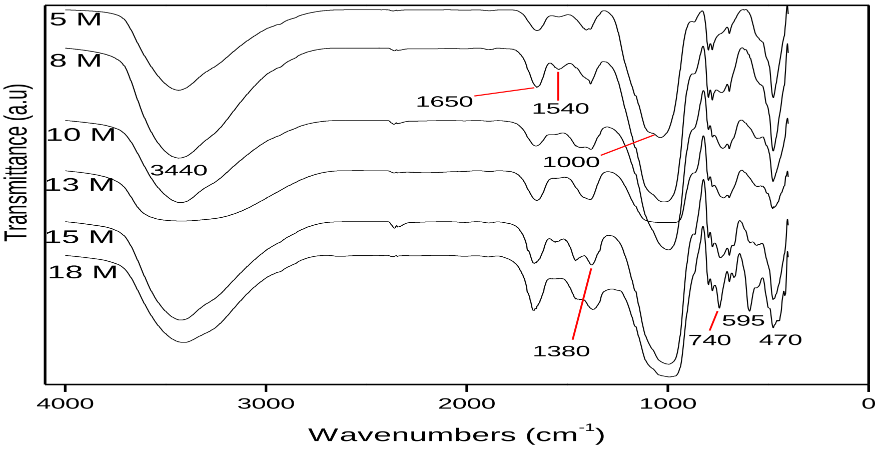


Figure 16. IR spectra of Samples obtained with the kaolinitic clay calcined at 700 °C and different KOH concentrations

The band intensity at 800 cm^{-1} in the IR spectra of metakaolin related to symmetric Si-O stretching was greatly reduced or disappeared, while a peaks around 596 cm^{-1} and 740 cm^{-1} (Figs. 14 and 16) and others peaks at 556 cm^{-1} and 689 cm^{-1} (Figs. 15 and 17) are formed. The peaks at 470 cm^{-1} are attributed to in-plane bending of Si-O and Al-O linkages [27, 28] originating from reconstruction of AlO_4 and SiO_4 species characterizing the tetrahedral structure of the geopolymer [29]. A new band also appears around 1460 cm^{-1} in all IR spectra (Figs. 14, 15, 16 and 17) which can be attributed to stretching vibrations of C-O bond of alkaline carbonate which induces efflorescence within materials. Thus, IR spectra exhibit absorption bands at 3450 cm^{-1} and 1640 cm^{-1} which correspond to stretching and deformation vibrations of O-H and H-O-H groups, respectively.

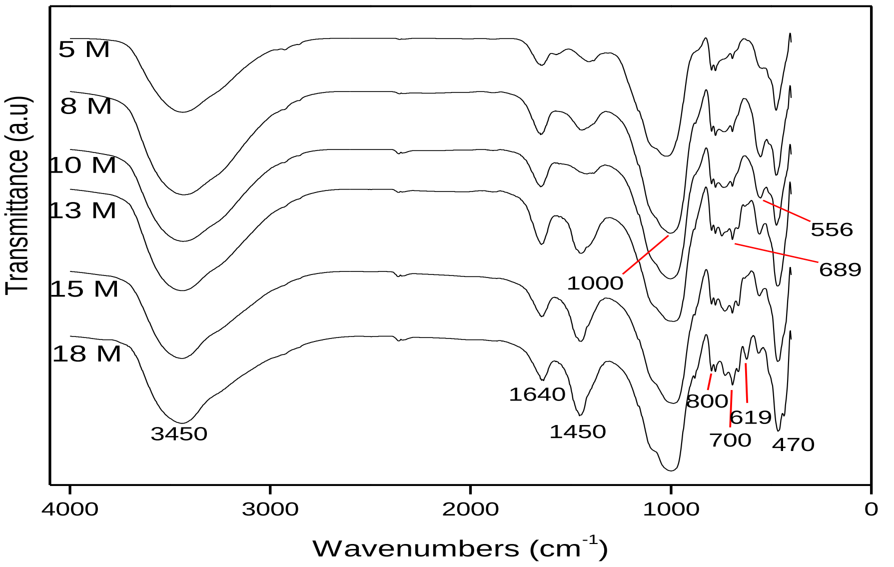


Figure 17: IR spectra of Samples obtained with the kaolinitic clay calcined at 700 °C and different NaOH concentrations

The metakaolin-based geopolymer microstructures are linked to the transformation of kaolinitic clay to metakaolin, and to the degree of polycondensation and structural reorganization of oligomers in polysialates including the pore development. The results obtained showed that geopolymers synthesized using calcined Tunisian clay at 700°C have a good compressive strength and the lower water adsorption. Also, authors have used alkaline silicates in several studies, but in this paper, we sought only to determine the most suitable potassium hydroxide (KOH) and sodium hydroxide (NaOH) concentration to produce geopolymer cements with good mechanical performance. The samples were cured at ambient temperature. Efflorescence can be reduced either by the addition of alumina-rich admixtures or by hydrothermal curing. Each of these techniques provides benefits to the binder structure by enhancing the binder structure formation process [30, 31].

Conclusions

Tunisian kaolinitic clay calcined between 550 °C and 1100 °C was activated by potassium hydroxide or sodium hydroxide to obtain geopolymer cement with good mechanical and physical proprieties. The compressive strengths of hardened samples are very low for NaOH and KOH concentrations below 10M, due to incomplete geopolymerization. Porosity is inversely proportional to compressive strength: samples which have the highest strength display relatively low porosity and samples, showing the greatest resistance, display the highest density. For all samples, the water absorption is relatively low, which provides us with information about the long term durability of the material. The most convenient temperature to obtain the most reactive metakaolin is approximately 700 °C. The density reached a maximum value at this temperature and for a base concentration of approximately 13 M, while porosity and water adsorption reached a minimum. These values decreased (increased respectively) at higher temperature and concentrations. So, the decrease of the compressive strength is due to two main factors: the crystallization of metakaolin to aluminum-silicon spinel then to mullite at a temperature from 900 °C results in a decrease in its ability to react with basic solutions and the formation of efflorescence, on the surface of cured geopolymer samples, which induces cracks in the materials.

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