

EFFECT OF CALCINATION TEMPERATURE OF TUNISIAN CLAYS ON THE PROPERTIES OF GEOPOLYMERS

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Geopolymers are amorphous three dimensional aluminosilicate materials that may be synthesized at room or slightly higher temperature by alkaline activation of aluminosilicates obtained from industrial wastes, calcined clays and natural minerals. Among the different family of geopolymers, two Tunisian clays (a kaolinite clay from Tabarka and illite/kaolinitic clay from Medenine) are tested for their feasibility of geopolymers at low temperature. The unfired and calcined clays were dissolved in strongly alkaline solution in order to produce consolidated materials whose pastes were characterized by their compressive strength. Hardened geopolymer samples were also submitted to X-Ray diffraction, FTIR spectroscopy and scanning electron microscopy analyses. The geopolymer strength is related to the structure and reactivity of the clay generated by thermal treatment and to the role of associated minerals in clays. The amorphous character of obtained geopolymers and the displacement of the IR wavenumber are signature of geopolymerisation reaction.

INTRODUCTION

Development of products from a country's natural resources and waste is very important to improve its local economy. Tunisia has many clay deposits in big quantities. The vast majority of existing deposits shows a lack of chemical and mineralogical characterization which complicates their suitability for valorization. Few authors [1] used Tunisian sample clays from different locations calcined at different temperatures and tested their potential use as pozzolanic materials. These natural clays could be potentially used as raw materials for the synthesis of a novel class of materials called geopolymers. Geopolymers are a novel class of materials that are formed by the polymerization of silicon and aluminum species [2]. The principal binding phase in geopolymers is an amorphous aluminosilicate gel that consists of a three dimensional framework of SiO_4 and AlO_4 tetrahedral linked by corner-shared O atoms [3]. The negatively-charged tetrahedral Al sites in the network are charge-balanced by alkali metal cations such as Na^+ and/or K^+ [2]. Geopolymers possess many advanced properties such as fast setting and hardening, excellent bond strength, [2] long-term durability and good fire and acid resistance [4]. Due to such properties, geopolymers have the potential to be used in several industrial applications [5]. In addition, the most important advantage of geopolymer is their low manufacturing energy consumption and low CO_2 emission [6], which make them to be a "Green Material" [7]. The original

raw material used by Davidovits is metakaolinite, activated by alkali hydroxide and/or alkali silicate [8]. Many researchers [9, 10], have demonstrated that many others aluminosilicates materials could be used as raw materials for geopolymers, such as fly ash, furnace slag, silica fume and kaolinite and some natural minerals. Xu et al. [11] investigated geopolymerization of sixteen natural aluminosilicate minerals with the addition of kaolinite. However there is a lack of investigation on elaboration of geopolymers from natural clays because clay generally consists of a mixture of different clay minerals and associated non clayey minerals. Few studies [12] proved that common clays like illite/smectite clays are suitable as raw material for the preparation of geopolymer.

The variability of clay composition and parameters of the thermal activation process complicate a general statement about the suitability of clay resources for the production of geopolymers as shown in different papers with partly controversial position [12]. However, there is no literature which discusses the effect of natural clay calcination on the properties of the post obtained geopolymers. Only Lecomte [13] reported that Vickers hardness values of geopolymers are improved (from 191 ± 6 to 217 ± 5 MPa) with kaolin calcination temperatures (700 - 800°C) and that the reason for this increase was not analyzed yet and was still unclear. Furthermore, Elimby et al. [14], have demonstrated that compressive strength of the hardened geopolymer samples was between 11.9 and 36.4 MPa: it increased

with samples from the clay fractions calcined between 500 and 700°C but dropped above 700°C. Prud'homme et al., [15] have studied the influence of the clay used in terms of clay reactivity in preparation of foam geopolymers using structural data (FTIR, XRD, and SEM).

In a previous work [16], the structural evolution of two Tunisian clays on calcination is studied in detail to predict their behavior during geopolymerization. It was demonstrated that temperature calcination influenced the amorphous character of clays. The aim of this work is based on the synthesis and structural characterization of geopolymers by using two Tunisian clays. The synthesized products are characterized by-ray diffraction, FTIR Spectroscopy and SEM as well as their mechanical properties.

EXPERIMENTAL

Sample preparation

Two Tunisian clays are used as solid precursors in this study: (T) Tabarka clay which is essentially kaolinitic and (M) Medenine clay which is illito-kaolinitic rich in hematite [16]. The composition of the clays is given in Table 1 in terms of the oxide weight percentage. Before sieving at 125 μm , the clays are calcined for 5 hours in a static condition at a heating rate of 10°C/min at the following temperatures: 700°C, 800°C, 850°C and 900°C in opened atmosphere. The geopolymers are prepared by mixing clays with KOH pellets (85.7 % purity supplied by Aldrich) previously dissolved in potassium silicate

(SiO₂ = 16.37 %, K₂O = 7.56 %, density = 1.2,76 % of water, supplied by Chemical Labs, USA). The reactive mixture was mixed for 5 min at 700 rpm and then placed in an opened polystyrene sealed mold in an oven at 70°C for 48 hours in order to complete the polycondensation reaction. Subsequently, the mold was closed into oven⁸ at 70°C for 2 hours. Then the material is removed from the opened mold and placed in ambient air (25°C, 40 % HR) during 21 days for curing. The identification and the composition of synthesized geopolymers are presented in Table 2. Samples are identified as ${}_{\theta}G_{SiK}^{M,T}$ where θ is the calcination temperature of clay, M or T is the origin of clay, KOH and SiK are the masses of KOH and potassium silicate solution respectively, for 1 g of clay. For example, the compound ${}_{0.18}G_{0.5}^{700T}$ is obtained from Tabarka clay calcined at 700°C with 0.18 g of KOH and 0.5 g of potassium silicate.

Characterization methods

For the dilatometry experiments, specimens were prepared by powder casting the sample in a 5 mm-diameter stamper at a pressure of 5 bars. The sample length was 5 mm and the ends were flat. The samples were analyzed in a Netzch dilatometer (Model DIL 402 PC) up to 1100°C at a heating rate of 5°C/min in air. A single-crystal sapphire cylinder was used as the calibration standard.

FTIR spectra were obtained from a Thermo Fischer Scientific 380 infrared spectrometer (Nicolet) using the attenuated total reflection (ATR) method. A drop of geopolymer reacting mixture was deposited on the diamond

Table 1. Composition of the clays in wt. %, main characteristic of raw materials. LOI: lost of dignition, D50: average particle size diameter.

Oxide (wt. %)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	MgO	LOI (wt. %)	D50 (μm)	S _{BET} (m ² g ⁻¹)
Medenin	2.4	67.5	18	6.5	0.1	2.9	2.6	9.2	5	32
Tabarka	-	67.7	28.5	2.1	-	1.4	0.2	9	3	21

Table 2. Different synthesized compositions and their identification.

Clay origine	Calcination temperature (°C)	SiK (g)	KOH (g)	Sample identification	Sintering temperature (°C)
Medenin	25	0.5	0.18	${}_{0.18}G_{0.5}^{25M}$	954
	700	0.5	0.18	${}_{0.18}G_{0.5}^{700M}$	960
	800	0.5	0.18	${}_{0.18}G_{0.5}^{800M}$	970
	850	0.5	0.18	${}_{0.18}G_{0.5}^{850M}$	975
	900	0.5	0.18	${}_{0.18}G_{0.5}^{900M}$	1023
Tabarka	25	0.5	0.18	${}_{0.18}G_{0.5}^{25T}$	908
	700	0.5	0.18	${}_{0.18}G_{0.5}^{700T}$	911
	800	0.5	0.18	${}_{0.18}G_{0.5}^{800T}$	900
	850	0.5	0.18	${}_{0.18}G_{0.5}^{850T}$	946
	900	0.5	0.18	${}_{0.18}G_{0.5}^{900T}$	972

crystal and protected by a little bell from environmental pollution during the spectrum acquisition, which was performed regularly until the end of geopolymerisation. The IR spectra were gathered between 500 and 4000 cm^{-1} with a resolution of 4 cm^{-1} . OMNIC (Nicolet Instruments), the commercial software, was used for data acquisition and spectral analysis. The spectra are then recorded every 10 min for 13 h to obtain the superposition of 72 raw spectra. Measurements were carried out at different times.

X-ray patterns were acquired via X-ray diffraction (XRD) experiments on a Bruker-AXS D 5005 powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda_{K\alpha} = 0.154056 \text{ \AA}$). XRD patterns were obtained using the following conditions: dwell time: 2 s; step: 0.04°. Crystalline phases were identified by comparison with PDF standards (Powder Diffraction Files) from ICDD.

The morphology of the final products was observed using a PhilipsXL30 scanning electron microscope (SEM) at 15 kV coupled with an EDX spectrometer. Prior to observations, an Au/Pd fine layer was deposited on the samples.

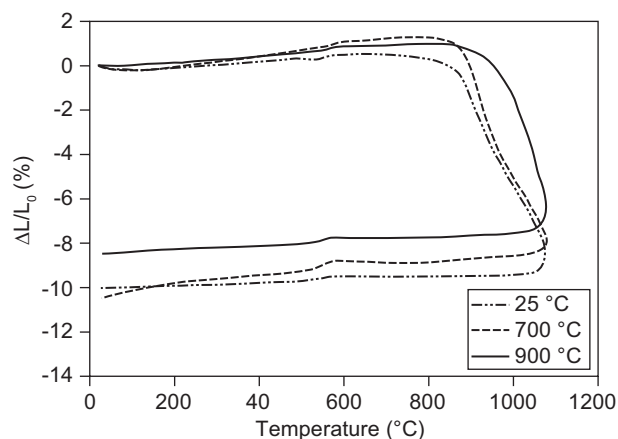
The compressive strength of samples stored for 21 days were determined using LIyodEZ20 machine moving at constant cross-head displacement of 0.2 mm/min. Specimens were cylindrical, 35 mm in diameter and 70 mm in high. Samples surfaces were polished flat and parallel to avoid the requirement for capping. All values presented in the current work are an average of 10 samples. The experimental error is obtained from the average of standard deviation of the 10 samples.

RESULTS

Formation of consolidated materials

Behavior of clays in temperature

The feature of calcined (25, 700 and 900°C) Medenine and Tabarka are evaluated using dilatometry measurements (Figure 1). Dimensional variations were



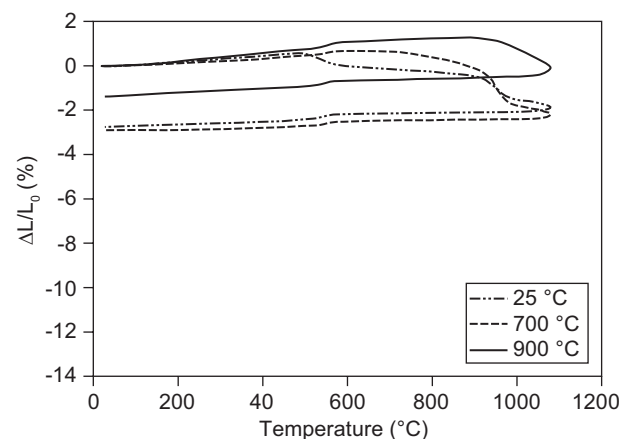
a) Medenine clays

present in both types of clays, which reflected phase transformations. In spite of the sample, the peak observed at 572°C was due to the $\alpha \rightarrow \beta$ transition of quartz. Moreover, whatever the clays, the dilatometric curves reveal three events at temperatures around 20, 450 - 600 and 900 °C. The first is due to the loss of free water molecules (more pronounced in unfired clay) and the second to the dehydroxylation of kaolinite phase. The third event is linked simultaneously to the formation of the mullite nuclei and the apparition of silica viscous flow. All of the calcined clays show at least 1 % in size at 800°C due to the reorganization of hydroxyl groups. Depending on the clay, the sample evidences sintering at higher temperatures. Irrespective of the thermal treatment, the degree of sintering was more pronounced for Medenine than Tabarka clay. This difference has been attributed to the high amount of iron oxide in Medenine (6.5 % against 2.1 % for clay T). It has been already proved that from 900°C, iron oxide start to diffuse in kaolin. They permit to promote the transformation of mullite, which go with contraction of material [17]. So a higher content of iron oxide leads to the formation of a higher amount of mullite explaining the difference of expansion for both materials. The clay Tabarka curve divergence at 700°C was attributed to the presence of the viscous flow, which was due to the evolution of metakaolin as well as the other clays until 980°C. At this temperature, mullite nuclei were observed. Subsequently, the decrease in the shrinkage rate was due to the transfer of the viscous flow to the other silicate species, which delayed the sintering process. The shrinkage was less significant if the clay was treated at a higher temperature.

These analyzes will help to determine the sintering temperature of clays calcined at different temperatures (Table 1) in order to estimate the phases not advantageous to polycondensation reactions.

In situ IR spectroscopy

The FTIR Spectroscopy analysis is a method which not only provides information on the geopolymers ma-



b) Tabarka clays

Figure 1. Dilatometric curves of Medenine clays (a) Tabarka clays (b) at 25, 700 and 900°C.

materials, but also considered as possible and a simple method for geopolymerization reaction monitoring. This reaction involves a material restructuring.

The spectra presented in Figure 2 were recorded for consolidated materials synthesized from Medenine and Tabarka clays calcined at 700°C (${}^{700}_{0.18}G_{0.5}^T$). Whatever recorded spectra, at $t = 0$ min, the bands on the spectra, at 3300 cm^{-1} and 1620 cm^{-1} are attributed to Si–O–H bond and to the water t , respectively (Innocenzi, 2003) [18]. Their intensities gradually diminished with time due to the water consumption by polycondensation reactions. The bands located in the 1100 - 950 cm^{-1} range are generally attributed to Si–O–R⁺ present in the aluminosilicate compounds (with R⁺ = Si, Al, K) [19]. The decrease of the OH band intensity with curing time and the presence of Si–O–R⁺ band are characteristic of the formation of consolidated materials. Besides, we notice the persistence of bands attributed to the presence of illite (830 cm^{-1}) and quartz (797 and 776 cm^{-1}), initially present in the raw material and which don't contribute to the polycondensation mechanism. In the case of geopo-

lymers resulting from calcined Tabarka clay (Figure 2b), the most important shifts are also recorded in ${}^{700}_{0.18}G_{0.5}^T$ and ${}^{800}_{0.18}G_{0.5}^T$. Here again this behavior is related to the disorder generated by the thermal treatment of the corresponding clay [20].

Except to fresh clays where no variation is evidence, for all compositions (Tabarka and Medenine), we notice that the Si–O–R⁺ band shifts from 979 to 935 cm^{-1} (Figure 3). This result is in agreement with the literature data and gives evidence for polycondensation reaction. In the case of geopolymers deriving from calcined Medenine clay (Figure 3a), we note easily that the most important shift is recorded in the case of ${}^{700}_{0.18}G_{0.5}^T$ and ${}^{800}_{0.18}G_{0.5}^T$. This proves that the geopolymerisation is more developed in these samples. This result could be attributed to the disorder of the corresponding calcined clay [16]. In addition, for ${}^{900}_{0.18}G_{0.5}^T$ sample, we notice the lowest Si–O–R⁺ band shift. It seems that the reorganized structure in the corresponding calcined clay, detected by ${}^{29}Si$ NMR, makes the dissolution step in the geopolymerisation process more difficult.

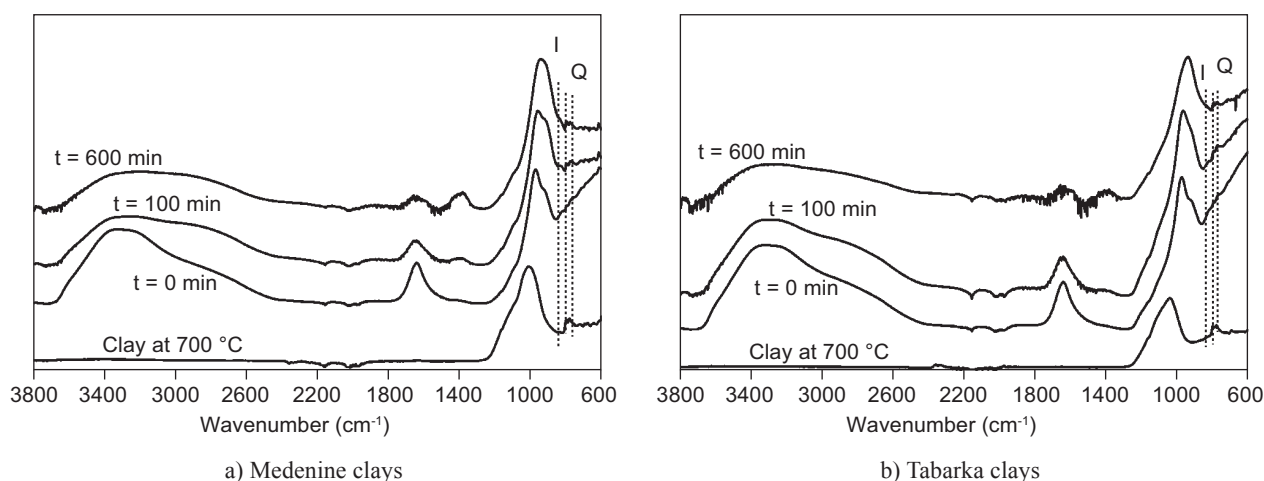


Figure 2. In situ infrared spectra of consolidated materials based on Medenine clays (a) Tabarka clays (b).

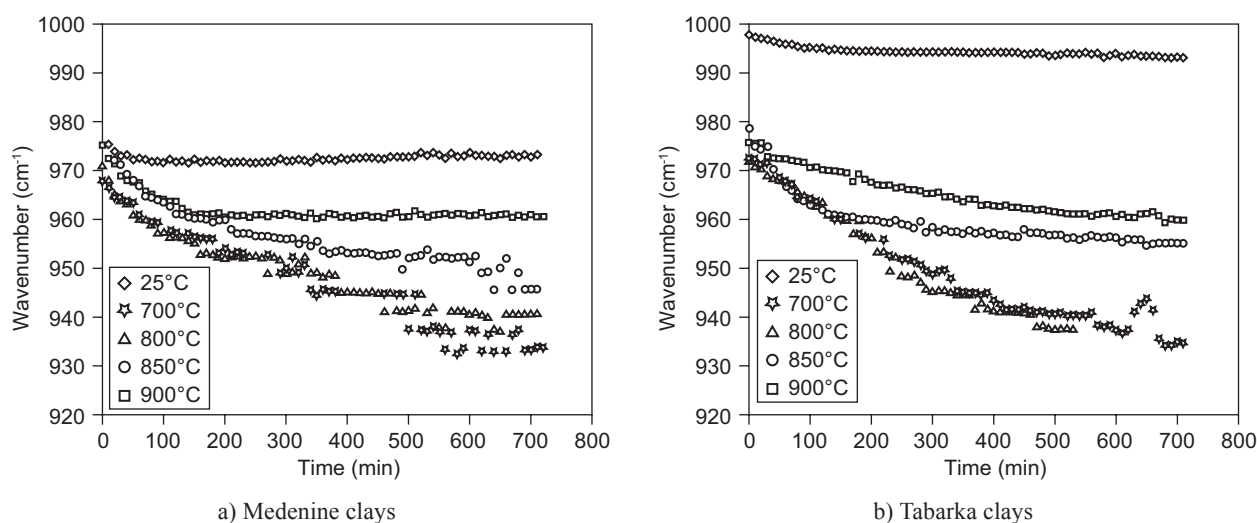


Figure 3. Evolution of the band Si–O–R⁺ as function of the time during polycondensation reaction for different compositions Medenine clays (a) Tabarka clays (b).

Physical chemistry
of consolidated materials

Mechanical properties

To understand the influence of calcination temperature of starting clays on the geopolymer synthesis and its performance, the compressive strength of geopolymers as a function of calcination temperature, based on Medenine or Tabarka clays were performed after 21 days curing. The Figure 4 shows the mechanical results of the different samples of geopolymers prepared from crude and calcined Tabarka and Medenine clays. The comparison between the mechanical strength of samples based on crude clays reveals that the composition ${}_{0.18}^{25}G_{0.5}^T$ displays a higher compressive strength than ${}_{0.18}^{25}G_{0.5}^M$. In addition, for a given temperature, the compressive strengths of geopolymers deriving from calcined Medenine clay are higher than those synthesized from calcined Tabarka clay despite the lowest metakaolin content in the corresponding raw material. It seems

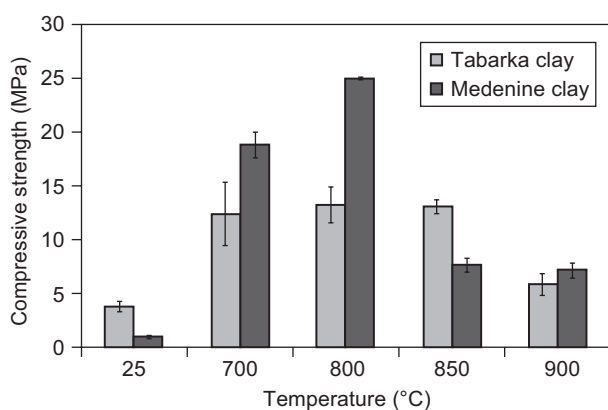


Figure 4. Values of the compressive strength of materials obtained from different clays calcined at different temperatures.

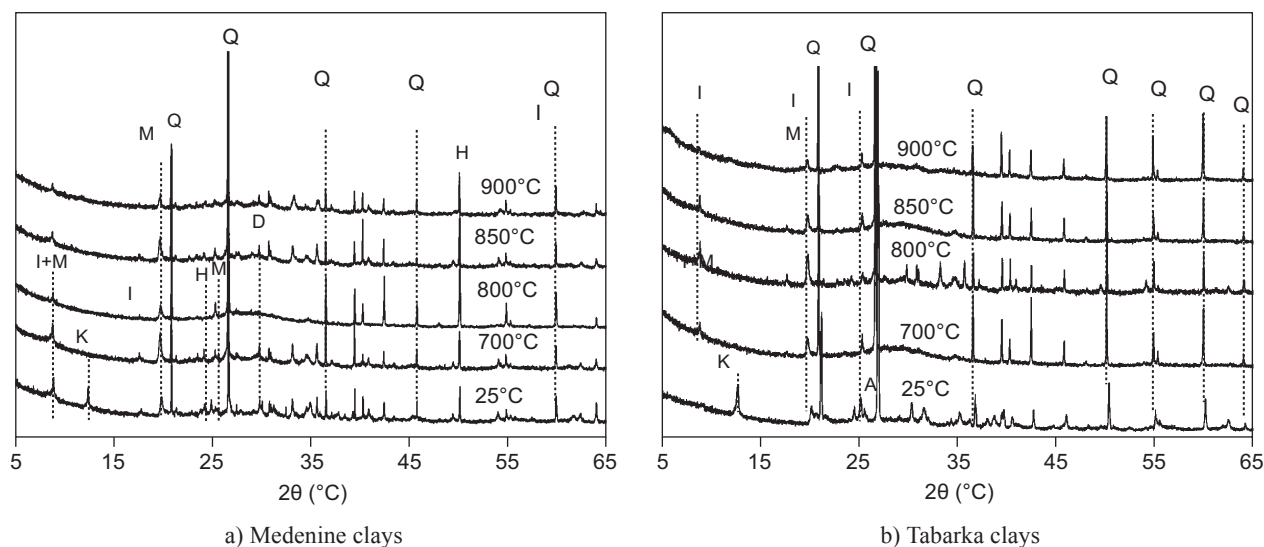


Figure 5. X-Ray patterns of synthesized materials based on Medenine clay (a) and Tabarka clay (b); K - kaolinite (04-013-2830), Q - quartz (04-012-0490), I - illite (00-002-0462), M - muscovite (04-012-1956), H - hematite (04-008-8479), D - dolomite (01-089-5862), A - TiO_2 (04-014-0494).

that the associated minerals such as quartz, illite and hematite in Medenine clay play the role of reinforcement in the geopolymer structure. In effect, another works in the laboratory have make in evidence the role played by the sand addition [21] on mechanical properties. In addition, the compressive strength of geopolymers based on Medenine calcined clay ${}_{0.18}G_{0.5}^M$ increases to obtain its maximum value (25 MPa) for a calcination temperature of 800°C then decreases for calcination temperatures of 850°C and 900°C while for geopolymers based on Tabarka calcined clay, the compressive strength increases to obtain its maximum at temperature calcination almost 700 - 800°C and 850°C then decreases for higher temperature of calcination (900°C). The developed resistance could be directly related to mineralogy composition of clays especially kaolinite content in the clay (58 % in T and 32 % in M).

Structure and microstructure
of consolidated materials

The XRD patterns of geopolymers samples based on crude clays ${}_{0.18}G_{0.5}^M$ and ${}_{0.18}G_{0.5}^T$ are presented in Figure 5. All the XRD patterns display peaks attributed to crystalline phases found in the starting clays such as hematite, quartz, muscovite, dolomite. The X-ray patterns of geopolymers obtained from fresh clays at room temperature evidence lower amorphisation in comparison to compounds synthesized from calcined clays. In effect, XRD patterns of geopolymers (${}_{0.18}^{700}G_{0.5}^M$, ${}_{0.18}^{800}G_{0.5}^M$, ${}_{0.18}^{850}G_{0.5}^M$, ${}_{0.18}^{900}G_{0.5}^M$, ${}_{0.18}^{700}G_{0.5}^T$, ${}_{0.18}^{800}G_{0.5}^T$, ${}_{0.18}^{850}G_{0.5}^T$, ${}_{0.18}^{900}G_{0.5}^T$) show an amorphous pattern centered at 26° characteristic of geopolymer state [19]. Figure 6 presents the micrographs of various compounds based on Medenine and Tabarka fresh and calcined clays. The microstructure of (${}_{0.18}^{25}G_{0.5}^M$, ${}_{0.18}^{25}G_{0.5}^T$) evidence a coating of particles by the silicate solution in relation with the few amount of amorphous

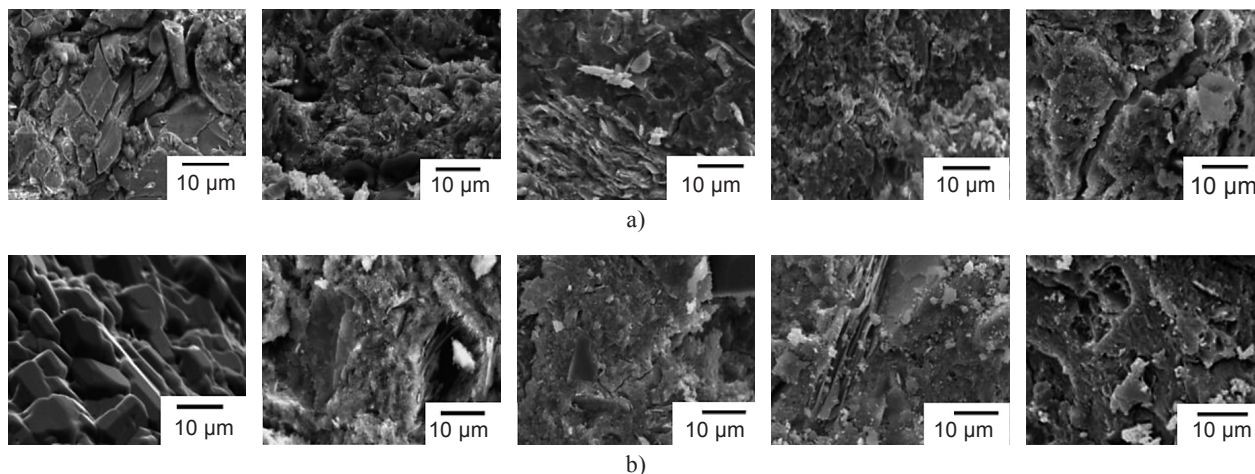


Figure 6. SEM micrographs of various consolidated materials synthesized from Medenine clays (a) and Tabarka clays (b).

phase in X-ray patterns. In this case, the clay reacts slowly with the solution in agreement with the work of Gao et al.[22]. In contrast, the micrograph of ${}_{0.18}^{700}G_{0.5}^M$, ${}_{0.18}^{800}G_{0.5}^M$, ${}_{0.18}^{850}G_{0.5}^M$, ${}_{0.18}^{900}G_{0.5}^M$, ${}_{0.18}^{700}G_{0.5}^T$, ${}_{0.18}^{800}G_{0.5}^T$, ${}_{0.18}^{850}G_{0.5}^T$, ${}_{0.18}^{900}G_{0.5}^T$ reveals a mixture of the microstructure of geopolymer compound and the presence of platelets clays of illite which do not react according to X-ray patterns.

DISCUSSION

The different results obtained when taking these various compositions has highlighted the importance of heat treatment temperature of different clays. Indeed, when there is no heat treatment, the consolidation of the material is made by coating of different clay which results in a material whose mechanical strength is low. Once there is calcination, the mechanical properties increase and the study of the displacement of infrared bands as a function of time reveal the formation of bonds of Si-O-Al. All these results are to be correlated to the rate of amorphous phases present in the starting compounds.

In order to verify the correlation of all these pro-

perties, it has been reported in the Figure 7. The IRTF displacement and the specific stress according to temperature of calcination. This figure shows clearly that the Si-O-R⁺ band shift can be correlated with the specific compressive strength [s(N·m²)/r(g·cm⁻³)]. This result can be explained as follows: when the geopolymeric network is more developed and consequently the compressive strength is higher, the wavenumber of Si-O-R⁺ band decreases because the structure is more rigid and consequently the shift is more important. The geopolymers resulting from clays calcined at 700 and 800°C have the highest compressive strengths because the disorder of the corresponding raw material induced by the thermal treatment is the most important. The compressive strength drops for higher calcination temperatures (850°C for Medenine clay and 900°C for Tabarka clay) because the clay structural reorganization proved previously [16] limits the attack of the raw material by the basic solution. Variations noted namely a decrease of these two parameters as a function of increasing heat treatment clays are largely due to the presence of the amorphous phase even for a silicate solution. Such variations have already been mentioned by

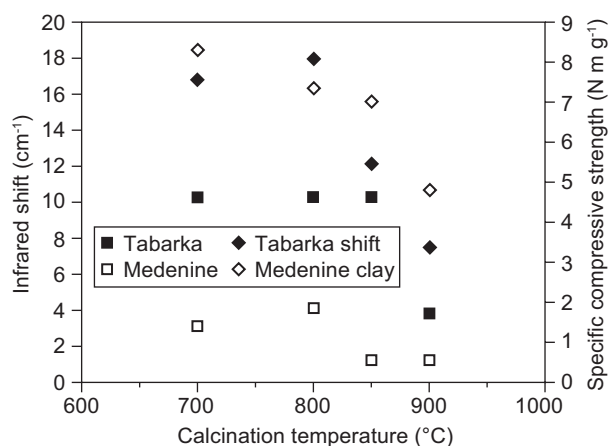


Figure 7. The evolution of σ/ρ and Si-O-R⁺ band shift versus the calcination temperature for all samples.

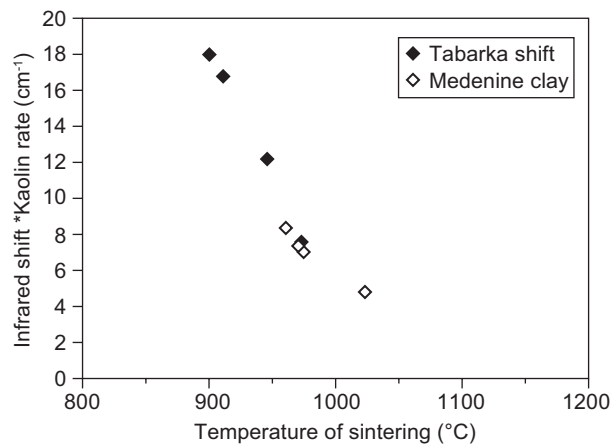


Figure 8. Evolution of Si-O-R⁺ band shift versus the temperature of sintering for all samples.

Autef et al. [21] but variations Si/Al ratio in the mixture. This same type of law suggests that in our case the rate of amorphous phase depending on the temperature of calcination is the same as the availability of Si/Al ratio.

To evidence the influence of amorphous rate in the polycondensation reactions, the IRTF shift corrected by the kaolin rate (58 % and 32 % for Tabarka and Medenine) which reflecting the amount of amorphous phase (as a function of sintering temperature determined by dilatometry studies is plotted (Figure 8). Whatever the clay, the values obtained are aligned almost on a straight line with the exception of points to 25° C. This is perfectly demonstrated the rate of amorphous phases necessary for the formation of a type network geopolymer. Indeed, the observed displacement by FTIR spectroscopy is mainly attributed to the substitution of Si–O–Si in the silicate solution by the species in solution available from kaolinite rate converted to metakaolin. Indeed, more siliceous species are available for inducing the flow and more viscous sintering temperature is weak. Moreover, it is this quantity which is after largely responsible for the availability of species leading to the formation of a viscous flow sintering and therefore the starting compound clay. These data underline the role of calcination temperature and above the amount necessary of amorphous phase which decreases with calcination temperature.

CONCLUSION

Consolidated materials have been obtained with raw and thermally activated Tunisian clays (Tabarka and Medenine) calcined at different temperatures and evaluated during formation and after synthesis. The reaction of polycondensation is proved by the shift of the Si–O–R⁺ band, the presence of amorphous dome on XRD patterns and the development of compressive strength to materials prepared from calcined clays. In presence of unfired clay, all characterization shows that the material is based on a coating of all particles by the silicate solution.

The compressive strengths of geopolymers deriving from calcined Medenine clay are higher than those synthesized from calcined Tabarka clay (at the same calcination temperature) despite the lowest metakaolin content in the corresponding raw material. It seems that the associated minerals such as quartz, illite and hematite in Medenine clay play the role of reinforcement in the geopolymer structure. The compressive strength and the development of the geopolymeric structure are directly related to the presence of free silicate species generated by the thermal treatment of the clay and as bee. At high temperature (900° for Tabarka and 850°C for Medenine clay) the compressive strengths of geopolymers decrease considerably because the clay structural reorganization

limits the attack of the raw material by the basic solution.

In addition, it is established a correlation between the sintering temperature of clays and the prediction of polycondensation reaction by infrared spectroscopy.

REFERENCES

1. Chakchouk A., Samet B., Mnif T.: Applied Clay Science 33, 79 (2006).
2. Davidovits J.: Journal Thermal Analysis 35, 429 (1989).
3. Provis J., Lukey L. G.C., Van Deventer J.S.J: Chemical Materials 17, 3075 (2005).
4. Phair J. W., Van Deventer J.S.J: Journal Mineral Engineering 14, 289 (2001).
5. Xu H., Van Deventer J.S.J: International Journal Minerals Process 59, 247 (2000).
6. Davidovits J., Comrie D.C., Paterson J.H., Ritcey D.: Concrete International 12, 30 (1990).
7. De Silva., Sagoe-Crenstil K., Sirivivatnanon V.: Chemical Concrete Research 37, 512 (2007).
8. Davidovits J. In: Proceedings of the World Congress Geopolymer, p. 9-15, Ed. Davidovits J., Saint Quentin, France, (2005).
9. Xu H., Van Deventer J.S.J.: Minerals Engineering 15, 1131 (2002).
10. Panias D., Giannopoulou I., Perraki T.: Colloids and Surfaces A: Physicochemical Engineering Aspects 301, 246 (2007).
11. Xu H., Van Deventer J.S.J.: International Journal Mineral Processing 59, 247 (2000).
12. Buchwald A., Hohmann M., Posern K., Brendler E.: Applied Clay Science 46, 300 (2009).
13. Lecomte I., Liegeois M., Rulmont A., Cloos R.: Journal Materials Research 18-11, 2571 (2003).
14. Elimbi A., Tchakoute H.K., Njopwouo, D.: Construction and Building Materials 25, 2805 (2011).
15. Prud'homme E., Michaud P., Joussein E., Peyratout C., Smith A., Rossignol S.: Applied Clay Science 51, 15 (2011).
16. Essaidi N., Samet B., Baklouti S., Rossignol S.: Applied Clay Science (2012).
17. Soro N.S. : *Influence des ions fer sur les transformations thermiques de la Kaolinite*, Ph.D Thesis, University of Limoges, France (2003).
18. Innocenzi P.: Journal of Non-Crystalline Solids 19, 309 (2003).
19. Prud'homme E., Michaud P., Joussein E., Peyratout C., Smith A., J-M classens Arri-Clacens., Rossignol S.: Journal European Ceramic Society 30, 1641 (2010).
20. Prud'homme E., Autef A., Essaidi N., Michaud P., Joussein E., Rossignol S.: Applied Clay science 73, 26 (2012).
21. A Autef, E Joussein, G Gasgnier, S Rossignol: Journal of Non-crystalline solids 366, 13 (2013).
22. Gao X.X., Autef A., Prud'homme E., Michaud P., Joussein S., Rossignol S.: Journal of Sol-Gel Science and Technology 65, 220 (2012).