



Thermal Transformation of Kaolinite Clays: Analyzing Dehydroxylation and Amorphization for Improved Pozzolanic Performance

K. AZIZI^{1,*}; J. MAISSARA¹; M. ELMAHI CHBIHI¹; Y. NAIMI¹

Laboratory of Physical Chemistry of Materials, Faculty of Sciences Ben M'Sick, Hassan II University of Casablanca, Morocco

Abstract

This study explores the impact of heat treatment parameters on the dehydroxylation and amorphization processes of kaolinite-based materials, in particular natural kaolin clays. It develops a quantitative method for estimating the amorphous phase in heat-treated kaolinite, using differential thermal analysis/thermogravimetry (DTA/TGA), mass spectrometry, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Kaolin clays, subjected to controlled heat treatments between 600°C and 800°C, undergo significant structural transformations. The study identifies the degree of dehydroxylation (DTG) as a crucial measure of kaolinite performance after heat treatment, calculated as a function of sample weight loss. The transition from a crystalline to an amorphous phase strongly influences pozzolanic activity, characterized by its ability to react with portlandite (Ca(OH)₂) in water-rich environments. The materials used, including clay from the Benslimane region of Morocco, were finely ground and subjected to various thermal treatments. Thermal analyses revealed characteristic patterns of mass loss and phase transformation. XRD and FTIR analyses provided detailed information on structural changes, confirming the amorphization of kaolinite after dehydro.

Keywords: Kaolinite, Dehydroxylation, Amorphization, (DTA)- (TGA), X-ray, Infrared, Pozzolanic activity, Amorphous phase,

Full length article *azizi khalid, e-mail: khalidazizimaphar@gmail.com

Doi # <https://doi.org/10.62877/127-IJCBS-24-25-19-127>

1. Introduction

The thermal transformation of kaolinite clays, particularly their dehydroxylation and amorphization, plays a critical role in enhancing their pozzolanic performance. Kaolinite, a common clay mineral, undergoes significant structural changes when subjected to controlled heat treatment, leading to the formation of metakaolin, a highly reactive amorphous phase. This study aims to explore the impact of heat treatment parameters on the dehydroxylation and amorphization processes of natural kaolin clays, focusing on their implications for industrial applications such as cement additives [1–3]. Kaolin clays are widely used in the construction industry due to their ability to improve the mechanical properties and durability of cement-based composites. The pozzolanic activity of kaolin clays, which refers to their ability to react with calcium hydroxide (portlandite) in the presence of water, is significantly influenced by their thermal treatment. The transformation from crystalline kaolinite to amorphous metakaolin is essential for enhancing this pozzolanic activity [1,4,5]. This study employs a range of analytical techniques to characterize the structural changes in kaolinite clay during thermal treatment. Differential thermal analysis (DTA) and

thermogravimetric analysis (TGA) are used to monitor the mass loss and phase transformations, while X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) provide detailed insights into the crystallographic and chemical changes. The degree of dehydroxylation (DTG) is quantified as a function of the sample's weight loss, providing a crucial measure of the kaolinite's performance after heat treatment [6,7].

Kaolin clays from the Benslimane region in Morocco were selected for this study. These clays were finely ground and subjected to various thermal treatments to induce dehydroxylation and amorphization. The results highlight the critical temperature range for achieving optimal pozzolanic activity, which is found to be between 400°C and 600°C. Beyond this range, the kaolinite structure transforms into metakaolin, marked by a significant increase in reactivity and potential for industrial application [8–11]. The findings of this study are expected to contribute to the development of high-performance materials in the construction industry. By understanding the thermal behavior of kaolinite clays and optimizing their treatment processes, it is possible to enhance their reactivity and effectiveness as cement additives. This research underscores the importance of precise temperature

control during heat treatment to achieve the desired structural transformations and improve the pozzolanic performance of kaolin clays [12]

2. Materials and methods

The kaolinite clay used in this study, referred to as Clay A, was obtained in bulk from the Benslimane region in Morocco. The raw Clay A clay was finely ground using a laboratory ball mill for 60 minutes, and the particle size distribution was determined by passing the ground clay through a 45 μm sieve. The finely ground clay was then placed in porcelain crucibles and calcined using a Nabertherm laboratory muffle furnace. The calcination temperatures were selected based on preliminary thermal analysis results, with each sample maintained at the designated temperature for a specified duration to ensure complete transformation. Thermal analysis of the raw clay was carried out using a DT-TGA instrument (DTG-60H TGA, Shimadzu). The heating rate was set at 10°C per minute, from room temperature up to 1000°C, with a nitrogen flow rate of 150 mL per minute serving as the purge gas. The chemical composition of the raw clay was determined using the X-ray fluorescence (XRF) technique before the calcination process. X-ray diffraction (XRD) measurements were performed using a Bruker/Siemens XRD diffractometer with $\text{CuK}\alpha$ radiation at a wavelength of 1.54060 Å. Data collection was conducted over a 2θ range of 5° to 65°, with a step size of 0.02° 2θ . Additionally, Fourier-transform infrared spectroscopy (FTIR) was carried out using a Shimadzu instrument, equipped with a LiTaO₃ detector and the NIOS2 Main 00.02.0064 software. The resolution was set at 4 cm^{-1} to ensure detailed identification of functional groups present in the clay samples. High-resolution scanning electron microscopy (HR-SEM) micrographs were obtained to observe the microstructural changes in the clay after heat treatment, providing further insights into the material's morphological characteristics.

3. Results and Discussions

Clay A is a type of clay sourced from the Benslimane region in Morocco. It was used in this study to analyze thermal transformations and pozzolanic properties after heat treatment. The chemical composition of Clay A before calcination, determined using X-ray fluorescence (XRF) technique, is as follows:

Figure 1 presents a micrograph obtained by High-Resolution Scanning Electron Microscopy (HR-SEM) of the kaolinite clay used in this study. This image allows for the observation of the microstructural characteristics of the clay before and after thermal treatment, highlighting the transformations it undergoes.

Observations from the HR-SEM Micrograph

Initial Structure: The image shows that the structure of the raw kaolinite clay is composed of well-defined, stacked platelets, typical of crystalline kaolinite.

Thermal Transformation: After thermal treatment, a disorganization of the platelets is observed, indicating partial amorphization. The platelets appear less defined, more

irregular, which is characteristic of the formation of metakaolin.

Amorphous Aspect: The structure becomes increasingly amorphous with the rise in treatment temperature, corresponding to the progressive dehydroxylation of kaolinite and the transition to metakaolin.

Crystalline-Amorphous Transition: Figure 1 visually illustrates the transition from the crystalline phase of kaolinite to an amorphous phase of metakaolin, which is essential for enhancing the pozzolanic activity of the treated clay.

Pozzolanic Applications: These microstructural transformations are crucial for the use of kaolinite clay as a cement additive, as they increase the chemical reactivity of the clay with portlandite ($\text{Ca}(\text{OH})_2$), thereby improving the mechanical properties and durability of cement composites [13,14].

In summary, Figure 1 highlights the microstructural changes in kaolinite clay under thermal treatment, clearly showing dehydroxylation and amorphization, and underscoring their importance for improving pozzolanic performance. Figure 2 in the article provides the ATG-DTG thermogram for the kaolinite clay sample from the Benslimane region. This thermogram is essential for understanding the thermal behavior and transformations of the clay as it undergoes heating. The thermogram displays two curves: the Thermogravimetric Analysis (TGA) curve, which shows the mass loss of the sample as a function of temperature, and the Differential Thermogravimetric (DTG) curve, which indicates the rate of mass loss. Initially, from 20°C to 150°C, a minor mass loss of approximately 1-2% is observed, corresponding to the evaporation of physically adsorbed water and moisture from the clay surface. The DTG curve shows a small peak in this range, confirming the gradual release of water.

From 150°C to 400°C, the TGA curve continues to show a slight decline, reflecting the removal of more tightly bound water molecules. This stage marks the pre-dehydroxylation phase where the clay structure begins to lose hydroxyl groups, but the loss is not yet significant. Between 400°C and 600°C, a pronounced mass loss occurs, indicated by a steep decline in the TGA curve and a significant peak in the DTG curve. This stage corresponds to the dehydroxylation of kaolinite, where hydroxyl groups (OH^-) are removed, resulting in the formation of metakaolin ($\text{Al}_2\text{Si}_2\text{O}_7$). The endothermic reaction associated with this transformation is evident from the DTG peak. The mass loss is substantial, reaching up to 10%, indicating intense dehydroxylation. Beyond 600°C, the TGA curve flattens, showing minimal additional mass loss. The DTG curve also levels off, indicating the completion of the dehydroxylation process. At this stage, the kaolinite has been fully converted into an amorphous phase, primarily metakaolin. The lack of significant mass loss or DTG peaks suggests that the material is now stable at these temperatures.

From 900°C to 1100°C, an exothermic peak appears on the DTA curve, corresponding to the formation of new crystalline phases such as spinel and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). This transformation is characterized by a reorganization of the amorphous phase into more ordered structures. However, the TGA curve shows only a negligible mass loss, indicating

that the primary thermal transformations have already occurred. The thermogram confirms the critical temperature range for dehydroxylation (400°C to 600°C), essential for transforming kaolinite into metakaolin with improved pozzolanic activity. The significant structural changes indicated by the mass loss and DTG peaks highlight the importance of precise temperature control during the thermal treatment to achieve the desired amorphous phase. The appearance of new crystalline phases at higher temperatures suggests potential applications for the thermally treated clay in producing high-performance materials, benefiting from the enhanced reactivity and structural properties of metakaolin. In summary, Figure 2 effectively illustrates the thermal transformations of kaolinite clay, providing insights into the dehydroxylation and amorphization processes critical for enhancing pozzolanic performance.

Figure 3 presents the X-ray diffraction (XRD) patterns of kaolinite clay samples before and after heat treatment at various temperatures. XRD is a powerful technique used to identify the crystalline phases present in a material by measuring the intensity of X-rays scattered at different angles.

Initially, the untreated kaolinite clay shows characteristic peaks associated with the crystalline structure of kaolinite, indicating a well-ordered structure. After heating to 600°C, a significant reduction in the intensity of the kaolinite peaks is observed, indicating the onset of dehydroxylation, where hydroxyl groups are removed from the kaolinite structure. The emergence of new peaks or the broadening of existing peaks suggests the formation of a more disordered phase, likely metakaolin. As the temperature increases beyond 600°C, the kaolinite peaks continue to diminish and eventually disappear completely, marking the transformation of kaolinite into an amorphous phase. The presence of residual peaks can be attributed to stable impurities such as quartz and anatase, which do not undergo significant changes at these temperatures. The transition from crystalline kaolinite to amorphous metakaolin is clearly visible in the XRD patterns. The loss of distinct kaolinite peaks indicates the breakdown of the ordered crystal structure, leading to amorphization. The broadening of peaks and the appearance of diffuse scattering in the XRD patterns are typical signatures of an amorphous material. The peaks corresponding to quartz and anatase remain visible even after heating, highlighting their thermal stability. These phases are often present as impurities in natural kaolinite clays. The removal of hydroxyl groups during the dehydroxylation process is a critical step in transforming kaolinite into metakaolin. This process is responsible for the observed changes in the XRD patterns. Dehydroxylation leads to structural rearrangements, reducing crystallinity and increasing pozzolanic activity [15,16]. In conclusion, the XRD analysis in Figure 3 effectively demonstrates the thermal transformation of kaolinite clay. The reduction and eventual disappearance of kaolinite peaks with increasing temperature confirm the dehydroxylation and amorphization processes. These structural changes.

3.2. Impact of Calcination Temperature on Dehydroxylation Extent

The curves presented in Figures 4 and 5 illustrate the impact of heat treatment temperature on the degree of

AZIZI et al., 2024

dehydroxylation of kaolinite clay. In Figure 4, the mass loss curves of clay A after heating at different temperatures for 5 hours reveal three distinct regions. In Region A (20 to 400°C), the mass loss is minimal, varying by about 1 to 2%, primarily due to the evaporation of physically adsorbed water on the surface of the clay. The degree of dehydroxylation (DTG) remains below 0.18, indicating very little dehydroxylation in this temperature range. In Region B (400 to 600°C), the mass loss increases significantly, reaching approximately 10%, due to intense dehydroxylation where hydroxyl groups (OH) are removed from the kaolinite structure. The DTG rises rapidly to 0.95, indicating that dehydroxylation is almost complete in this temperature range. This transformation corresponds to the conversion of kaolinite to metakaolin, a more reactive amorphous phase. In Region C (600 to 800°C), there is almost no further mass loss, suggesting that most of the dehydroxylation is already complete. The DTG reaches its maximum value of 1, indicating that the clay is fully dehydroxylated at 800°C, with no further mass loss detected. Figure 5 further corroborates these findings by showing the degree of dehydroxylation of locally sourced kaolin clay subjected to heat treatment at different temperatures. In Region A (20 to 400°C), the DTG remains below 0.18, indicating minimal dehydroxylation, similar to the observations of mass loss in Figure 4. In Region B (400 to 600°C), the DTG rises rapidly to up to 0.95, confirming intense dehydroxylation within this temperature range. In Region C (600 to 800°C), the DTG reaches 1, confirming that the clay is fully dehydroxylated at this temperature, with no significant further changes. In conclusion, the curves in Figures 4 and 5 clearly demonstrate that heat treatment temperature has a crucial impact on the degree of dehydroxylation of kaolinite clay. Dehydroxylation begins significantly at around 400°C, peaks between 400 and 600°C, and is completed at 800°C. Precise management of the treatment temperature is essential to optimize the pozzolanic activity of the treated clay, thereby enhancing its chemical reactivity and effectiveness in industrial applications such as cement additives.

3.3. Quantitative Assessment of the Amorphous Content in Heat-Treated Kaolinite Materials

The infrared spectroscopy (IR) curves shown in the image display the spectra of two clay samples: the raw sample and the sample treated at 600°C. Here is a detailed interpretation of the two curves:

Curve of the raw sample: This curve shows several distinct peaks, notably at wavenumbers 3695, 3668, 3651, and 3620 cm⁻¹, which are characteristic of the stretching vibrations of hydroxyl (OH-) groups in the structure of kaolinite. An intense peak around 914 cm⁻¹ is also observed, which is associated with the Al-OH bond, as well as peaks at 1020, 1105, and 465 cm⁻¹ corresponding to Si-O bonds, and a band at 540 cm⁻¹ attributed to the bending of Si-O-Al. *Curve of the sample treated at 600°C:* This curve shows a significant reduction in the bands at 3695, 3668, 3651, and 3620 cm⁻¹, indicating partial dehydroxylation of the clay due to the thermal treatment. This is typical of the process of transformation of kaolinite into metakaolin. The peak at 914 cm⁻¹ is almost absent, suggesting an alteration of the Al-OH bonds.

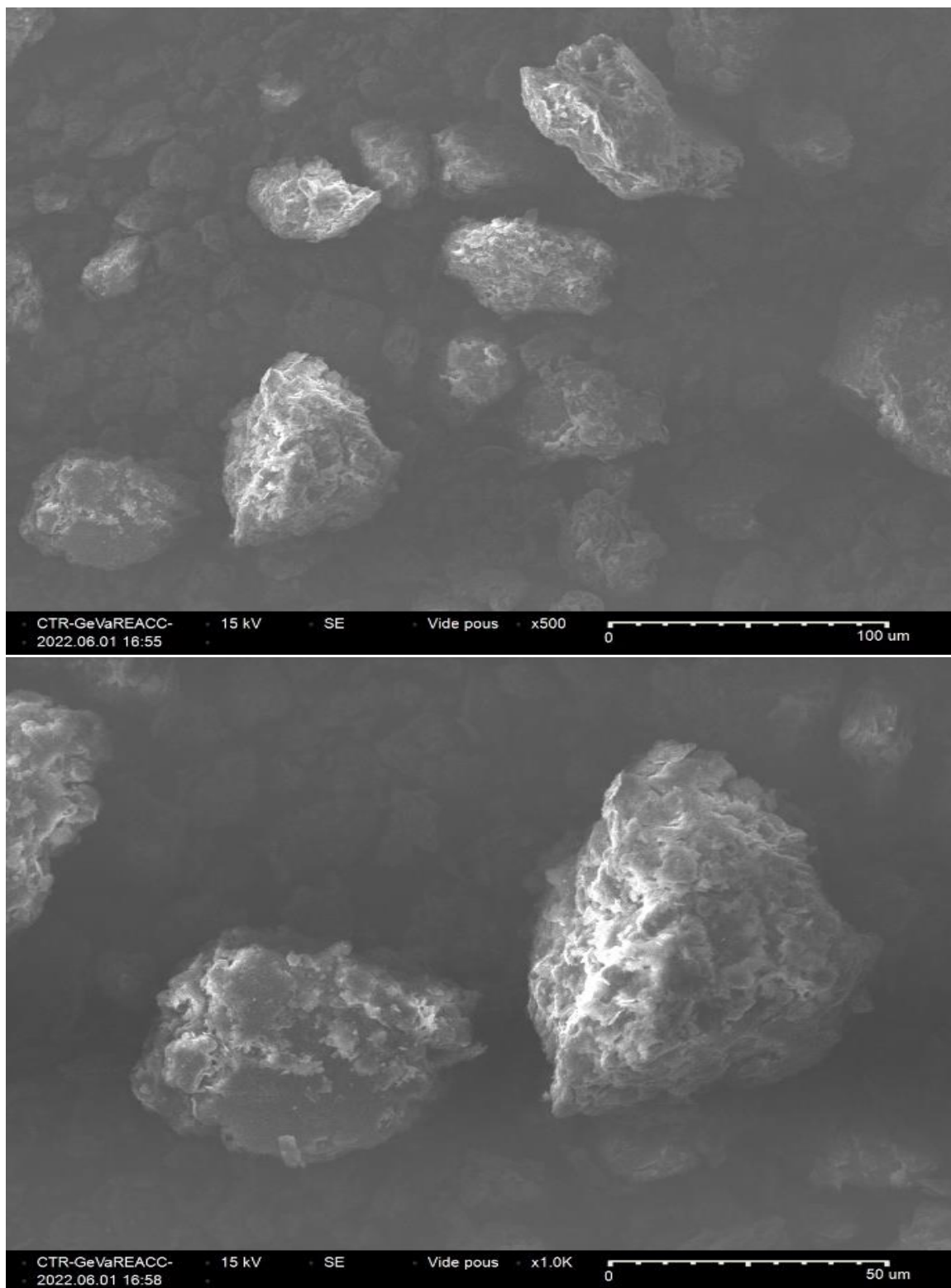


Fig. 1. HR-SEM micrograph of the clay

Table 1: Chemical Composition of Benslimane Clay Before Calcination

Compose	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
Clay A	0,582%	11,79%	27,168%	0,331%	2,795%	0,566%	0,94%	8,431%

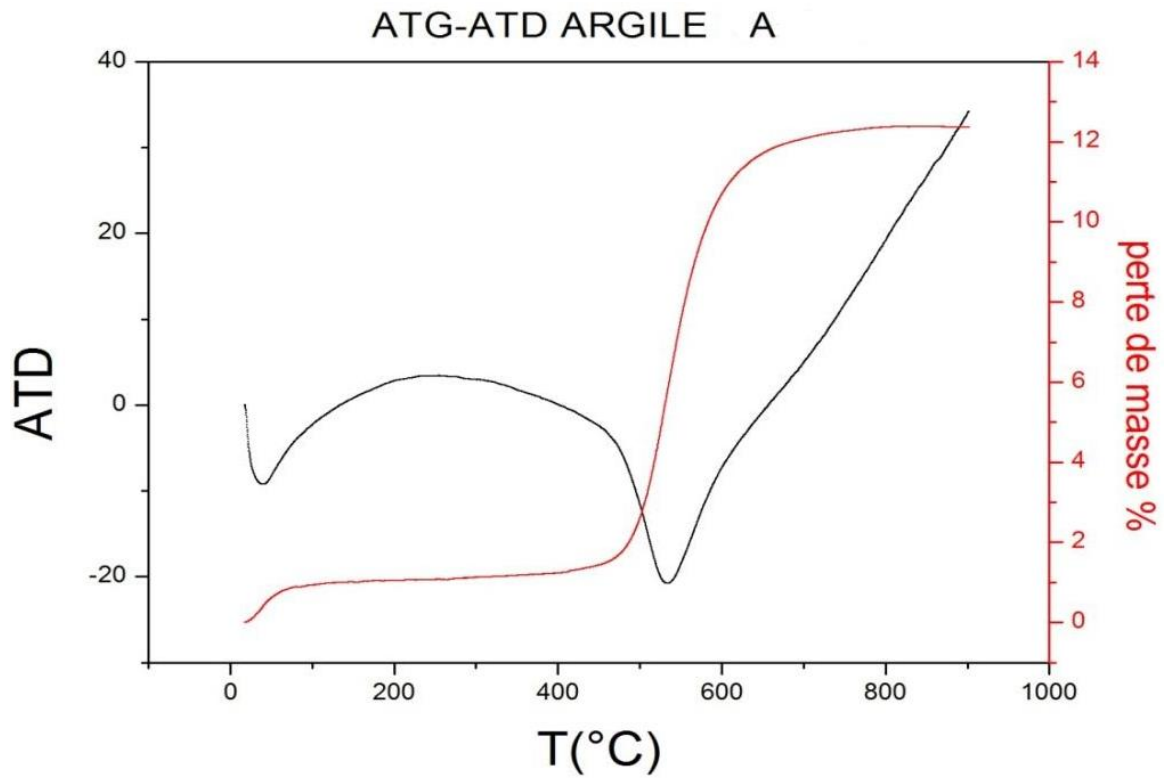


Fig. 2. ATG -DTG Thermogram of Ben Slimane Clay

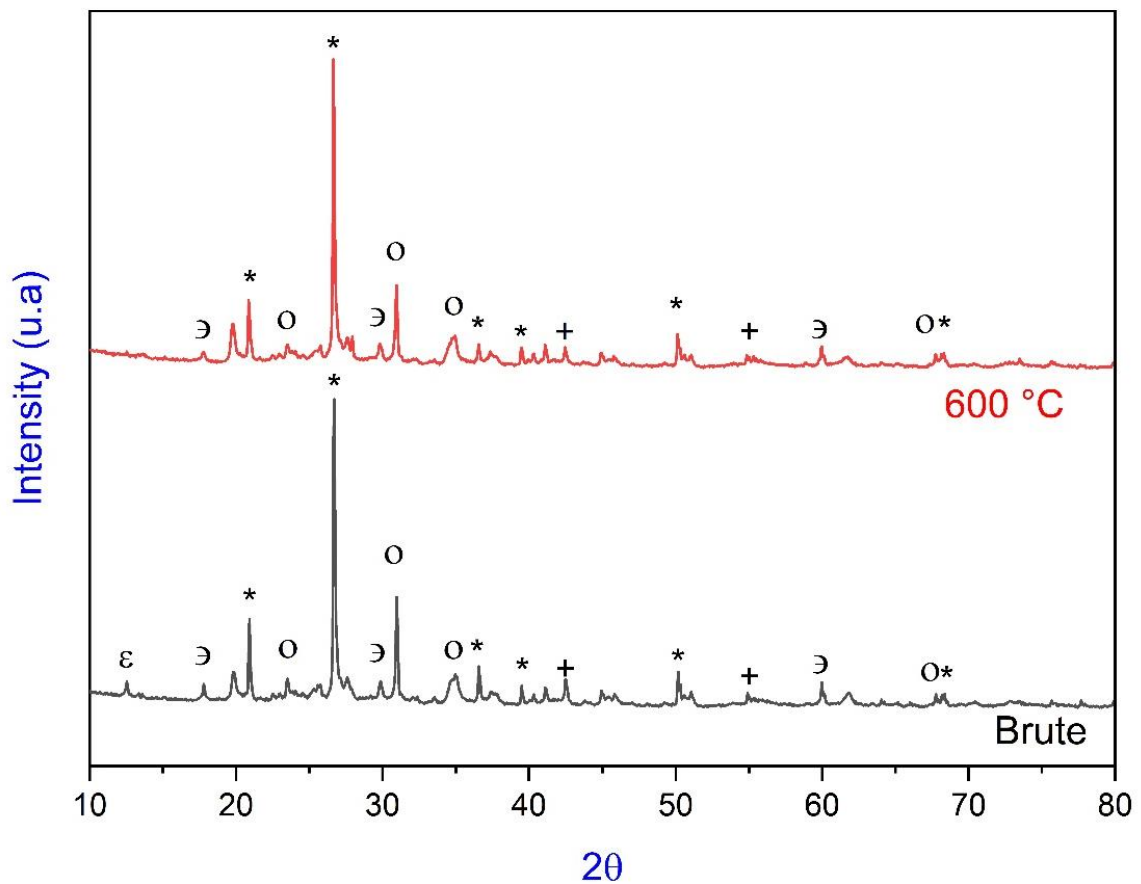


Fig. 3. DRX before and after heat treatment

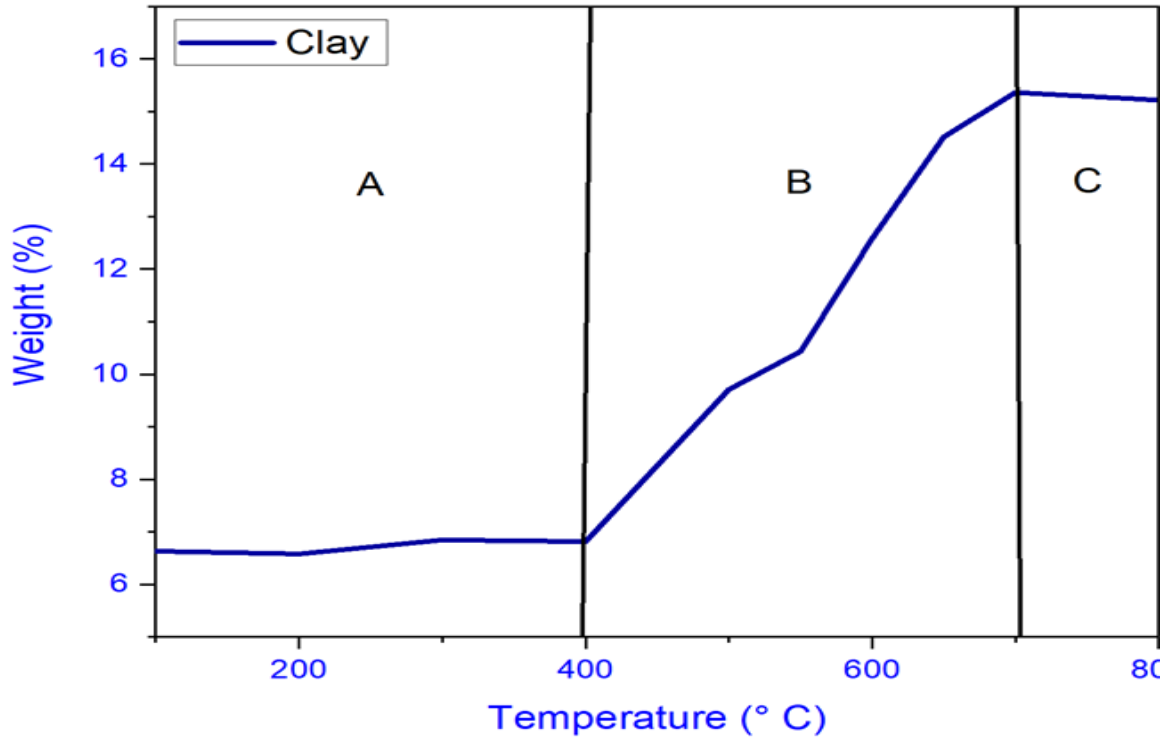


Fig.4. Curves of Mass Loss of Clay A After 5-Hour Heat Treatment at Various Temperatures.

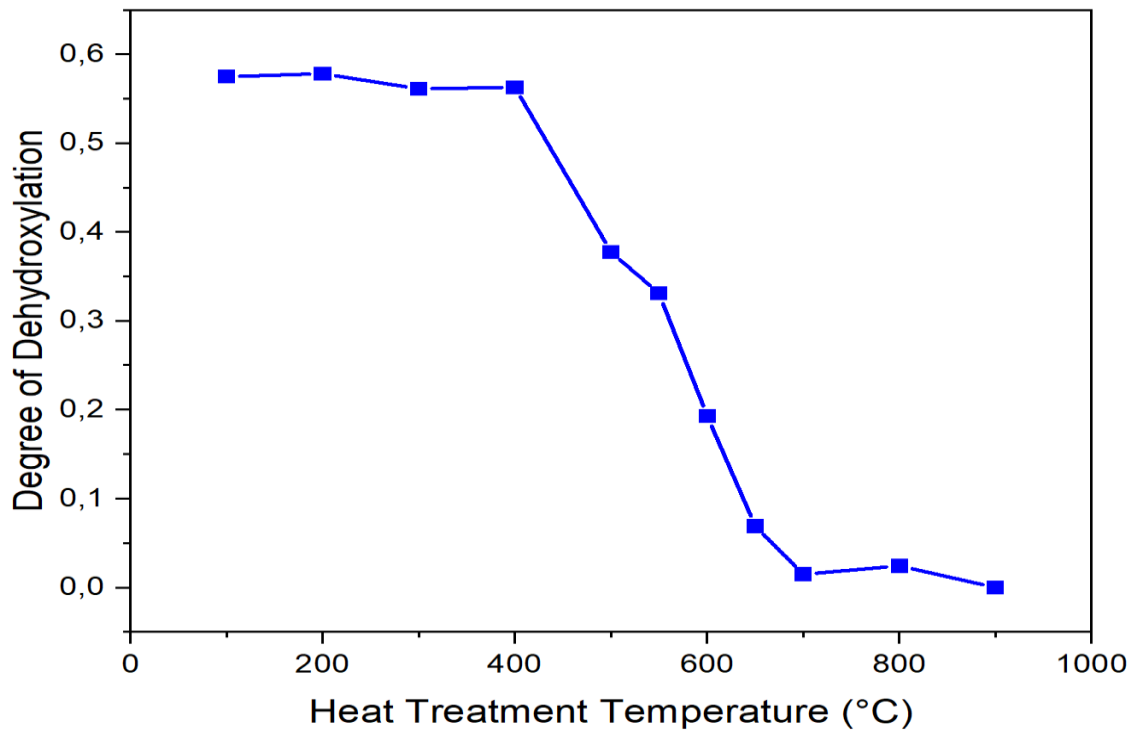


Fig.5. Degree of Dehydroxylation of Kaolinite Clay After Heat Treatment at Different Temperature

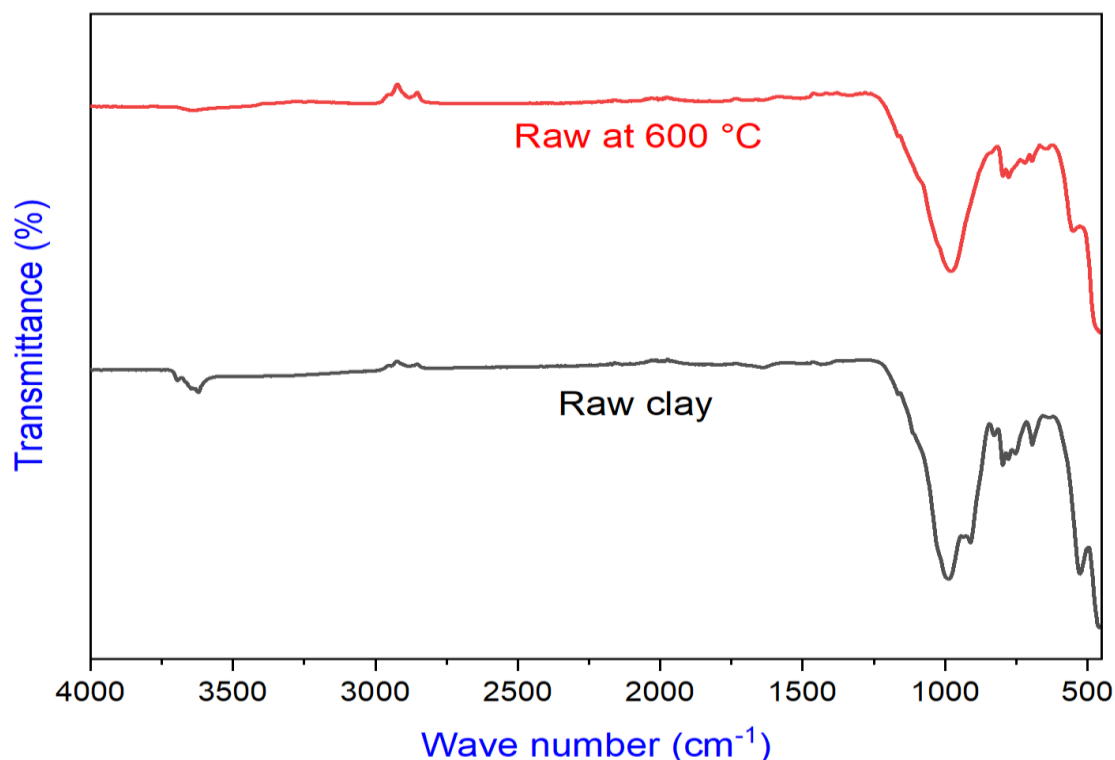


Fig. 6. FTIR before and after heat treatment

The other bands, especially those associated with Si-O and Si-O-Al, also appear to be altered, although less drastically than the OH bands. Implications of the observed changes: The disappearance or reduction of the hydroxyl bands and the alteration of other spectral bands confirm a significant structural transformation of the clay, transitioning from kaolinite to a more amorphous structure such as metakaolin [12,17]. These changes are generally associated with an increase in the reactivity of the clay, which can be leveraged in various industrial applications such as cements and composite materials. These spectroscopic observations, aligned with the applied thermal treatments, provide direct evidence of the alteration of the chemical and structural properties of the clay due to the effect of temperature.

4. Conclusions

This study has highlighted the substantial transformation of kaolinite clay into metakaolin through controlled thermal treatments, a process marked by significant dehydroxylation and amorphization. The results demonstrate that the amorphous state of metakaolin is essentially the product of the loss of hydroxyl groups and a molecular restructuring that reduces the initial crystallinity of kaolinite, thereby increasing its pozzolanic reactivity. Amorphization, observable through techniques such as DTA/TGA, XRD, and FTIR, has proven crucial for optimizing the pozzolanic properties of the material. The dehydroxylation curve shows a clear transformation of the material, with a notable reduction in peaks corresponding to hydroxyl groups at temperatures between 400 and 600 °C, where metakaolin is formed. This transformation is corroborated by the reduction or disappearance of XRD peaks

for kaolinite, with the emergence of more amorphous and less ordered phases.

The structural modifications due to amorphization confer properties on metakaolin that enhance its reaction with portlandite in cement mixtures, illustrating its potential to improve the durability and mechanical strength of cement composites. Indeed, transitioning from a well-ordered crystalline structure to an amorphous structure increases the material's specific surface area, enhancing its pozzolanic activity through better chemical reactivity with cement components. In conclusion, the amorphous state of metakaolin, achieved through the dehydroxylation process, plays a pivotal role in enhancing the performance of cement-based composites, offering improved structural integrity and chemical resistance. This deepened understanding of the transition from crystalline to amorphous states opens up prospects for the development of innovative, high-performance materials tailored through precisely controlled thermal treatment processes.

References

- [1] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, *Cem. Concr. Compos.* 37 (2013) 319–327. <https://doi.org/10.1016/j.cemconcomp.2013.01.002>
- [2] R.M. Torres Sánchez, E.I. Basaldella, J.F. Marco, The effect of thermal and mechanical treatments on kaolinite: Characterization by XPS and IEP measurements, *J. Colloid Interface Sci.* 215 (1999) 339–344. <https://doi.org/10.1006/jcis.1999.6241>.

- [3] Y. Li, P. Wang, Z. Wang, Evaluation of elastic modulus of cement paste corroded in brine solution with advanced homogenization method, *Constr. Build. Mater.* 157 (2017) 600–609. <https://doi.org/10.1016/j.conbuildmat.2017.09.133>.
- [4] S. Hollanders, R. Adriaens, J. Skibsted, Ö. Cizer, J. Elsen, Pozzolanic reactivity of pure calcined clays, *Appl. Clay Sci.* 132–133 (2016) 552–560. <https://doi.org/10.1016/j.clay.2016.08.003>.
- [5] S. Bajji, M. Oubani, F.E. Bammou, Y. Bahammou, A. Saba, Y. Naimi, Mineralogical, Geotechnical, Thermal and Mechanical Characterizations of an Energy-Efficient Building Material: Clay Stabilized by Wood Ashes or Crushed Waste from Traditional Pottery, *Chem. Africa* (2024) 3466. <https://doi.org/10.1007/s42250-024-00988-1>.
- [6] M. Valipour, F. Pargar, M. Shekarchi, S. Khani, Comparing a natural pozzolan, zeolite, to metakaolin and silica fume in terms of their effect on the durability characteristics of concrete: A laboratory study, *Constr. Build. Mater.* 41 (2013) 879–888. <https://doi.org/10.1016/j.conbuildmat.2012.11.054>.
- [7] S. Ferreiro, D. Herfort, J.S. Damtoft, Effect of raw clay type, fineness, water-to-cement ratio and fly ash addition on workability and strength performance of calcined clay – Limestone Portland cements, *Cem. Concr. Res.* 101 (2017) 1–12. <https://doi.org/10.1016/j.cemconres.2017.08.003>.
- [8] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, *Cem. Concr. Res.* 42 (2012) 1579–1589. <https://doi.org/10.1016/j.cemconres.2012.09.006>.
- [9] S. Ferreiro, M.M.C. Canut, J. Lund, D. Herfort, Influence of fineness of raw clay and calcination temperature on the performance of calcined clay-limestone blended cements, *Appl. Clay Sci.* 169 (2019) 81–90. <https://doi.org/10.1016/j.clay.2018.12.021>.
- [10] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Kaolinitic calcined clays: Factors affecting its performance as pozzolans, *Constr. Build. Mater.* 28 (2012) 276–281. <https://doi.org/10.1016/j.conbuildmat.2011.08.064>.
- [11] D.L. Carroll, T.F. Kemp, T.J. Bastow, M.E. Smith, Solid-state NMR characterisation of the thermal transformation of a Hungarian white illite, *Solid State Nucl. Magn. Reson.* 28 (2005) 31–43. <https://doi.org/10.1016/j.ssnmr.2005.04.001>.
- [12] J. Madejová, FTIR techniques in clay mineral studies, *Vib. Spectrosc.* 31 (2003) 1–10. [https://doi.org/10.1016/S0924-2031\(02\)00065-6](https://doi.org/10.1016/S0924-2031(02)00065-6).
- [13] S.A. Moshizi, A. Malvandi, Different modes of nanoparticle migration at mixed convection of Al₂O₃–water nanofluid inside a vertical microannulus in the presence of heat generation/absorption, *J. Therm. Anal. Calorim.* 126 (2016) 1947–1962. <https://doi.org/10.1007/s10973-016-5560-1>.
- [14] M. Lobo-Sánchez, G. Nájera-Meléndez, G. Luna, V. Segura-Pérez, J.A. Rivera, G. Fetter, ZnAl layered double hydroxides impregnated with eucalyptus oil as efficient hybrid materials against multi-resistant bacteria, *Appl. Clay Sci.* 153 (2018) 61–69. <https://doi.org/10.1016/j.clay.2017.11.017>.
- [15] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3), *Cem. Concr. Res.* 107 (2018) 124–135. <https://doi.org/10.1016/j.cemconres.2018.02.016>.
- [16] A. Elimbi, H.K. Tchakoute, D. Njopwouo, Effects of calcination temperature of kaolinite clays on the properties of geopolymer cements, *Constr. Build. Mater.* 25 (2011) 2805–2812. <https://doi.org/10.1016/j.conbuildmat.2010.12.055>.
- [17] J. Maissara, H. Karym, M. El Mahi Chbihi, M. Moutaabbid, M. Abatal, S. Benmokhtar, Enthalpy of Dissolution and Dehydration of Two Moroccan Clays, *World J. Eng. Technol.* 06 (2018) 119–127. <https://doi.org/10.4236/wjet.2018.61007>.