ALGERIAN DEMOCRATIC AND POPULAR REPUBLIC

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

UNIVERSITY OF MOHAMED BOUDIAF - M'SILA

FACULTY OF SCIENCES

DEPARTMENT OF PHYSICS

N° : PhMat 07/2019

DOMAINE: SCIENCE OF MATTER

FIELD: PHYSICS

OPTION: PHYSICS OF MATERIALS

Memory Submitted for Obtaining

Diploma of Academic Master

Prepared by: DJAAFER Hayat

TITLE:

Analytical Study of the Local Raw Materials Used in the Construction Bricks Industry

Defended on: 01/07/2019 before the jury composed of:

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Academic Year : 2018/2019

Dedication

This work is dedicated to my mother more than anyone else, to my elder brother for the support that he gave me in every level of my life, to all my sisters and brothers, to the cute **AICHA** and **AHMED HABIB** the Joyce of my life

To all the little angels **HAROUN, ASMA, CHOUAIB, DJAWED, DJALEL, MOUHAMED** and **HIBA**.

In the end, this work is dedicated for me because only I had been through this experience; I made myself proud of me.

Acknowledgements

First thanks to ALLAH for his grace and for his help to let me completing my thesis

I would like to express my sincere gratitude to Prof. **Ouali Ameur** and **Sahnoune Foudil** for the continuous support for their patience, motivation, enthusiasm, and immense knowledge. Also, for their (really) unlimited kindness, helpfulness, for their guidance, for everything they did for me during memory time and for being able to create such a lovely environment to work in.

I address my thanks to Prof. **Sahnoune Foudil** and Prof**. Hraiz Menad** for their acceptance to judge this work.

Miss Djaida Redaoui and Ms. Smail Lamara was unfailingly cheerful and helpful and for that I am very grateful.

Thanks to my friends and colleagues at the University of M'SILA.

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General Introduction

Introduction

Clay is a raw material used since ancient times. The natural abundance and immediate availability of clays explain their great uses over time.

At the beginning of the 18^{th} century, the concept of clay was evaluated from the first chemical analyzes carried out on Kaolin; it was just in the 20^{th} century and thanks to the work carried out in X-ray diffraction and granulometry that the researchers were able to give the correct definition of the clay.

Nowadays the use of clays, especially those rich in SiO_2 and Al_2O_3, is experiencing a new boom in construction, in industrial and craft ceramics, in the pharmaceutical industry and in pottery.

Clay materials are often complex natural mixtures of minerals whose particle size and physicochemical properties are highly variable. User selection criteria are less related to the overall chemical composition of clay materials than to their behavior during the different stages of ceramic product manufacturing.

Clays and clay minerals are studied in many areas such as ceramics, agriculture...etc. For geologists, clays provide information on environmental conditions (source, formation condition, digenesis ...). Petroleum engineers deduce the thermal conditions of the deposits (degree of maturation), civil engineers, are interested in the properties of clays as an industrial material (refractory, building materials), while agronomists; analyze the properties of hydration and adsorption of clays to design fertilizers.

Whatever the discipline, the crystalline structure of clays is important because it is responsible for the specific properties of the mineral. It is often blamed drying or cooking to be at the origin of the waste observed at the exit of an oven and much more seldom at preparation. The causes of poor production are however numerous at the level of the preparation:

- Irregular mixing of the mixture results in a dispersion of the characteristics of the heterogeneous products.
- Irregular moisture dosing makes it impossible to balance the die, favoring cracks and deformations during drying.

- Poor homogenization of the mixture causes cracks on drying and gives heterogeneous products.

The work presented in this thesis aims at an analysis study for the local clay used in the local construction materials; all of my work is presented as follows: The first chapter is a bibliographic overview, which is divided into three parts, the first part is about the ceramics and the sintering as an essential step of fabricating it. The second is on the definition of silico-aluminous clays, the raw material, reminders on the structure and some of their properties. the third part talk about one of the most used construction material brick, a definition , types and the stages it goes through during its manufacture

The second chapter is devoted to the studied clay (clay of ouled dradj region (M'sila) and the experimental methods used in our work. The last chapter deals with the experimental stages of our work that consists of:

- The study the chemical and mineralogical composition of clays, by means of elemental analysis by XRF spectrometry, X-ray diffraction (XRD), and SEM analysis
- The study of dilatometric behavior of local clay.
- The thermal behavior was studied by DTA,TGA and DSC.
- The calculation of activation energy of the sintering, the quartz transformation and the various reaction that happens to the clay during the heating.

Chapter I:

Bibliographic study

PART 1: CERAMICS

I.1.1 Generalities

Ceramic products are those made of clay with or without additions of other products by molding, drying and baking.

Ceramic building materials are divided into two groups:

Porous materials and compact materials, the porous materials have a water absorption capacity of 5% and more, while the compact materials have a lower water absorption capacity.

For the manufacture of ceramics materials, clay is used with or without the addition. The clay materials are divided into the following classes: kaolin, clay, shale clay, shale,…etc. The clay minerals are kaolin Al_2O_3 $2SiO_2$ $2H_2O$, montmorillonite $Al_2O_3 4SiO_2 6H_2O$, galluisite $Al_2O_3 4SiO_2 2H_2O$, etc. The properties of raw materials influence the possibility of using ceramic materials [1].

I.1.2 Definition of Ceramics

Ceramics can be defined as solid compounds that are formed by the application of heat, and sometimes heat and pressure, comprising at least two elements provided one of them is a non-metal or a nonmetallic elemental solid. The other element(s) may be a metal(s) or another nonmetallic elemental solid(s). A somewhat simpler definition was given by Kingery, who defined ceramics as, "the art and science of making and using solid articles, which have, as their essential component, and are composed in large part of inorganic nonmetallic materials". In other words, what is neither a metal, a semiconductor or a polymer is a ceramic [2].

I.1.3 Sintering

I.1.3.1 Definition

Sintering is a processing technique used to produce density-controlled materials and components from metal or/and ceramic powders by applying thermal energy. Hence, sintering is categorized in the synthesis/processing element among the four basic elements of materials science and engineering. As material synthesis and processing have become crucial in recent

years for materials development, the importance of sintering is increasing as a material processing technology [3].

Sintering is, in fact, one of the oldest human technologies, originating in the prehistoric era with the firing of pottery. The production of tools from sponge iron was also made possible by sintering. Nevertheless, it was only after the 1940s that sintering was studied fundamentally and scientifically. Since then, remarkable developments in sintering science have been made. One of the most important and beneficial uses of sintering in the modern era is the fabrication of sintered parts of all kinds, including powder-metallurgical parts and bulk ceramic components.

Consequently, among the different physico-chemical characteristics, they usually chose porosity as a parameter for the description of the sintering process of ceramic bodies because the geometric variations of the material can be interpreted by the variations in pore size and shape that are related to the phenomena of growth of the crystalline phases [3].

I.1.3.2 Categories of Sintering

Sintering processes can be divided into two types: the first type is solid state sintering and the second type is liquid phase sintering. Solid state sintering occurs when the powder compact is densified wholly in a solid state at the sintering temperature, while liquid phase sintering occurs when a liquid phase is present in the powder compact during sintering [3].

I.1.3.3 The Geometric Variations of the Material during Sintering

The geometric variations of the material during sintering depend on the following factors:

- Nature of the sintered material (oxides, simple or mixed).
- Presence of liquid phase.
- Dimensions and shapes of the material grains.
- Temperature.
- Processing time.
- Atmosphere and applied pressure.

Despite the extreme complexity of the process and the difficulty of the researcher directly, the sintering mechanism requires that descriptions of the phenomenon be based on a defined and particularly simple models

Generally, the sintering is accompanied by:

- Decrease in the initial dimensions (shrinkage) of the treated part and increase in its density.
- Growth of the bonds between particles, therefore increase in the rigidity of the material.
- Reduction of the overall system energy caused by grain magnification.
- Improvement of the mechanical and thermal properties of the parts produced.

Note that the sintering temperature must always be lower than the melting temperature of the material but high enough to consolidate it. Even if there is a melting of one of the components,

I.1.3.4 the Sintering activation

The activation of sintering consists in accelerating sintering by reducing the temperature and cooking time by means of usual processes, which will be briefly mentioned in the following:

- Fineness of the grains by grinding or chemical preparation.
- Particule size distribution.
- Homogeneity of mixtures.
- High pressures and use of isostatic pressure.
- Use of glass phases (melting).
- Use of powders with a grain size distribution where the small grains fill the voids (pores) between the large grains, which increases the contact surface.

I.1.3.5 General Description of the Sintering Phenomenon

a) Starting Point

The starting point is the existence of a granular compact characterized in that each grain is in mechanical contact with at least one other grain of the same nature or different nature. The areas of grain-to-grain contact are at the start of the action of heat, the front of consolidation. Primary consolidation is favored by the addition of plastic or liquid binders more or less viscous. From the beginning of the action of the heat, the liquid products evaporate, the organic binders are carbonized which causes a variation of the dimensions of the compact [4].

b) Shrinkage

The crystalline reorganization, the increase of the areas of contact between grains and the reduction of the pore dimensions. All of these phenomena are summarized in Figure (I.1) and in the following points [4]:

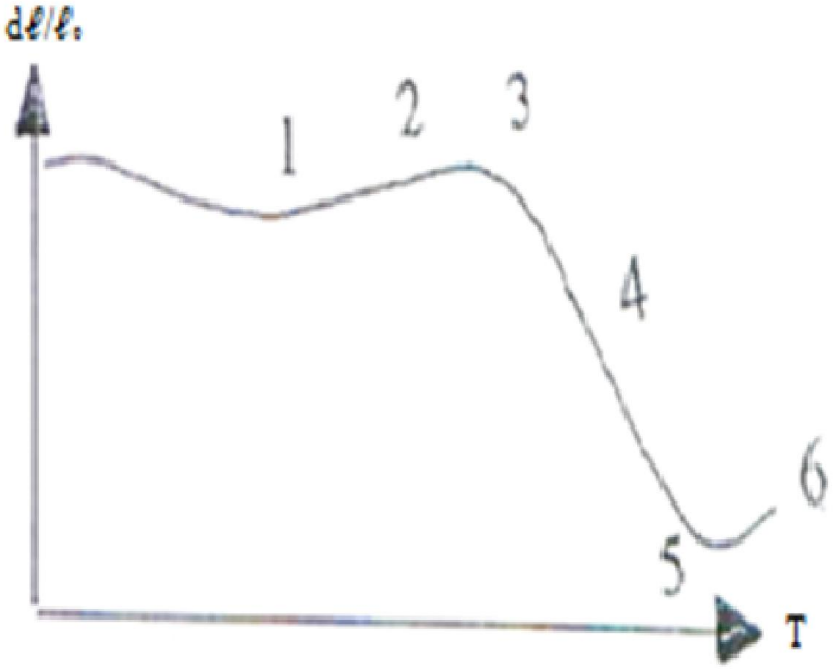

Figure I.1: Dilatometric curve of a compressed powder bar [4].

Zone 1

The expansion curve after the period of shrinkage due to drying, corresponding to the sum of the expansions of each grain. During the first hundreds of degrees, the organic liant and the absorbed vapour disappear in fact at 400 to 600 ° C, then there are only mineral grains.

Zone 2

As soon as the temperature is high enough, we assure an internal reorganization of the disorder of each grain. The amorphous zones crystallize, this stage is called primary re-crystallization.

Zone 3

In this zone, the contact area between the grains is growing, this is the beginning of sintering. This enlargement is accompanied by a reconciliation of their centers that annihilates the dilation and then prevails over the dilatation. it is the beginning of withdrawal and the disappearance of the open porosity.

Zone 4

The contact between the grains continues to grow, the star-shaped pores become spherical. Small pores disappear as a result of the escape of occluded (closed) gas bubbles. The large pores absorb the small ones and sometimes disappear by migration to the surface following the grain boundaries.

Zone 5

In this zone, the density of the product is the maximum. This is the optimum that can be achieved.

Zone 6

A new phenomenon appears (recrystallization) in this zone. Between adjacent grains of crystallized differently oriented, operates a rearrangement phenomenon such as the large grains grow at the expense of their smaller neighbors by progression and demise of the grain boundary. Macroscopically, the fight between large grains finally arriving at a contact results in the appearance of a porosity generally detrimental to the properties of the product Practically, this area should be avoided and sintering should be stopped at zone 5.

PART 2: CLAYS

I.2.1 Definition and Classification of Clays

The term clay comes from the Greek word "argilos", whose root argos means white, The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired. Associated phases in clay may include materials that do not impart plasticity and organic matter [4, 5]. There is no single definition

of the term "clay". This word includes two connotations, one linked to the size of the grains and the other to the mineralogy.

This definition depends on the discipline concerned: The geologist or soil scientist considers as "clay" any mineral of small particle size, containing particles with a grain size of less than 4 micrometres (μm). Engineers focus instead on the plasticity properties of clay materials regardless of their size. Ceramists group materials according to their heating behavior.

Clays are not a definite and unique material but are composed of complex mineral associations. The term "clay mineral" refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing.

Clay minerals have a sheet-like structure and are composed of mainly tetrahedrally arranged silicate and octahedrally arranged aluminate groups [5, 6].

I.2.2 Formation of Clay

Clay minerals typically form over long periods of time as a result of the gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and other diluted solvents. These solvents, usually acidic, migrate through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed through hydrothermal activity. There are two types of clay deposits: primary and secondary. Primary clays form as residual deposits in soil and remain at the site of formation. Secondary clays are clays that have been transported from their original location by water erosion and deposited in a new sedimentary deposit [7-9].

Clay minerals have a secondary geological origin; it was formed by the degradation of igneous (volcanic) rocks due to erosion and chemical alteration under the action of atmospheric agents. The nature of the clay products formed will depend on the nature of the source rock and the climatic and drainage conditions [6].

The diagram below (Figure (I.2)) shows the formation of clay materials.

I.2.3 The Structure of Clay Minerals

In order to avoid confusion or misunderstanding, it is necessary to define the major terms, which will be used in the following discussions. It is useful as a point of departure to

describe briefly the basic crystal lattice common to phyllosilicates (Figure (I.3)). The elementary character is the SiO tetrahedral linkage of an essentially two-dimensional, hexagonally symmetric, network. One side of this "sheet" network is coordinated with other cation-oxygen complexes joined by an important component of covalent bonding while essentially ionic bonding or van der Waals type bonds coordinate the other. The key to phyllosilicate structures is the oxygen network, which determines the shape and extent of the structure [8].

In other hand, the clay minerals are a complex mineralogical group; they are phyllosilicates or silicates in sheets smaller than 2µm. This means that layers sheet that constitute a layers sheet; one or two tetrahedral layers sheet, an octahedral layers sheet and an inter-ion space that often contains cations [7].

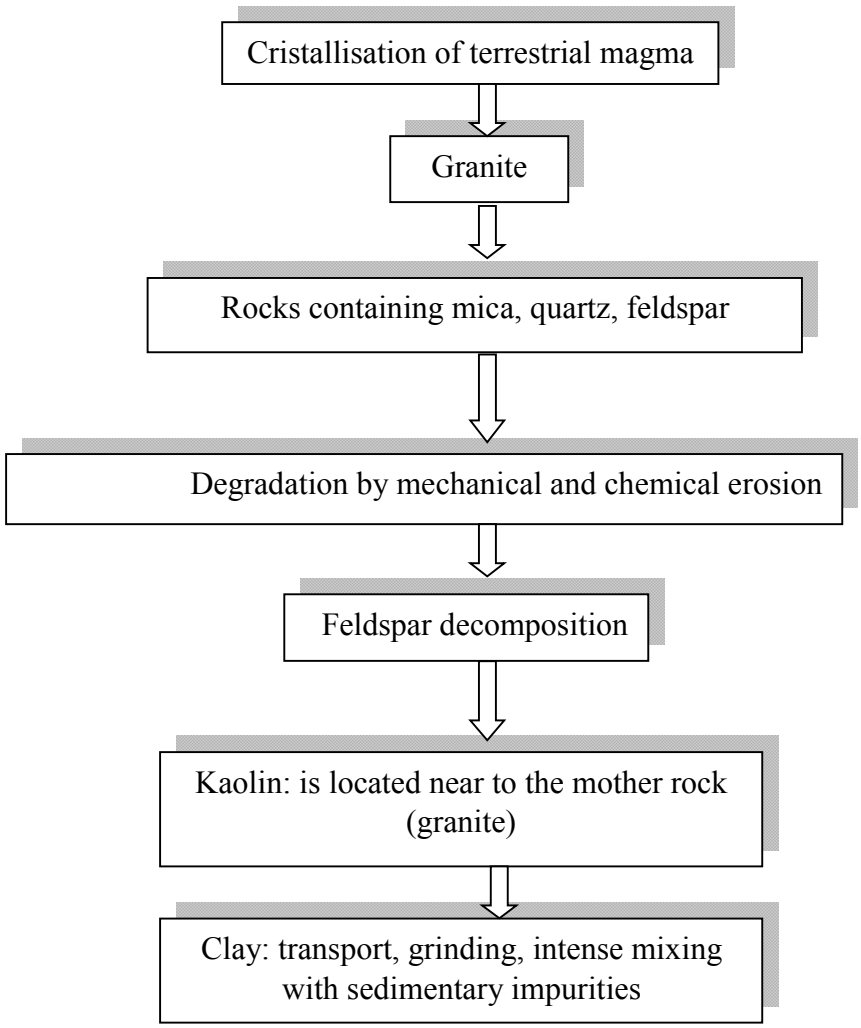

Figure I.2: The formation of clay materials

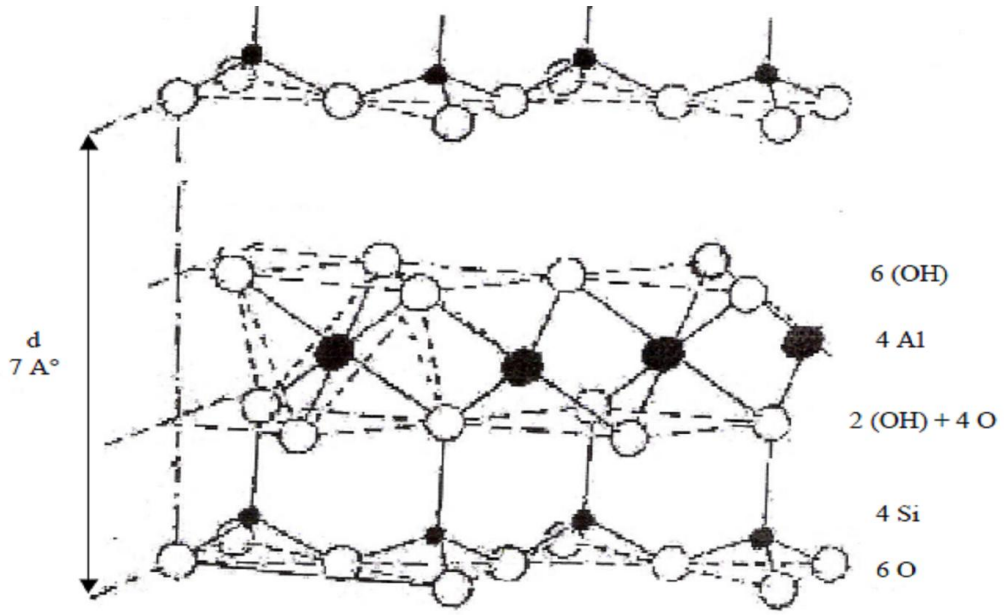

Figure I.3: Crystaline lattice of phyllosilicates [6].

I.2.4 Structural Types and Classification of Clays

Different classifications of phyllosilicates have been proposed. The first, established by AIPEA (International Association for the Study of Clays, 1966-1972), is based only on the charge of the sheet and on the number of metal atoms in octahedral layer. The second takes into account the location of substituent, their distributions and the type of compensating cations. The most classical classification is based on the thickness and structure of the leaflet. Based on their layered structure, clay minerals can be categorized as [5]:

Type 1:1 or T: O: The sheet consists of a tetrahedral layer and an octahedral layer. Its equidistance is about 7 Å. This type corresponds to the group of kaolinite (Figure (I.4))..

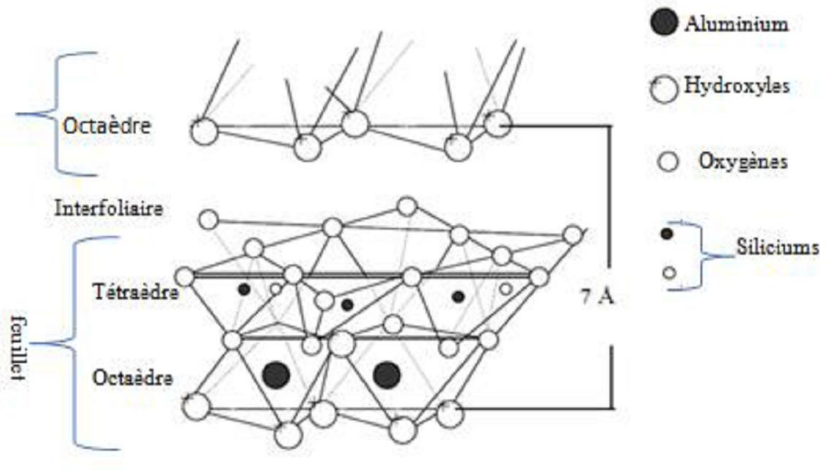

Figure I.4: Structure of kaolinite [6]

Type 2:1 or T: O:T: The sheet consists of two tetrahedral layers and an octahedral layer. Its equidistance is about 10 Å, corresponds to the groups of talc, smectites, vermiculites and micas…(Figure (I.5))..

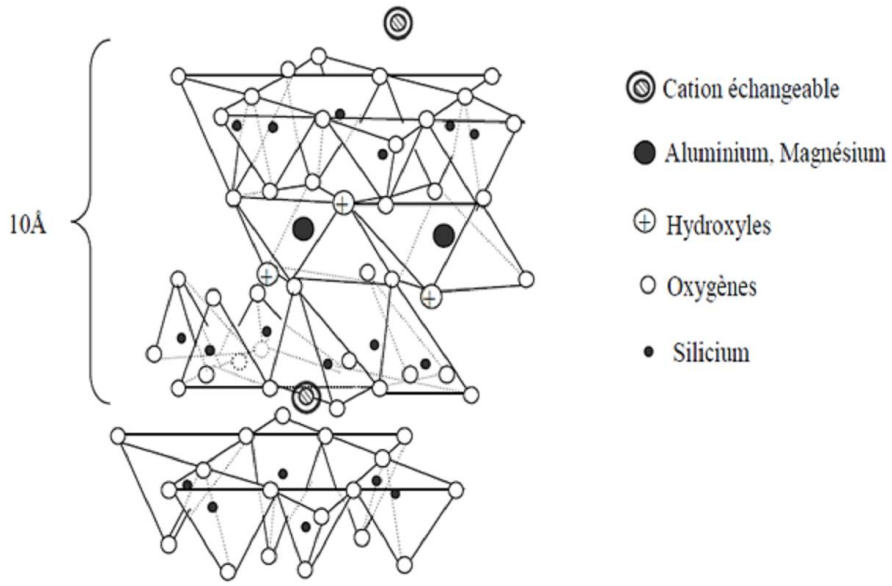

Figure I.5: Structure of Type 2:1 or T: O:T (structure of Illite (K,H_3O) $(Al, Mg, Fe)_2(Si, Al)_4O_{10}$ $[(OH)_2, (H_2O)]$) [7]

Type 2:1:1 or T:O:T:O: an octahedron layer framed by two tetrahedral layers, and an inter-layer of octahedra; the equidistance is about 14 Å; this type corresponds to the group of chlorite $(Mg, Al, Fe)_6$ $[(Si, Al)_4O_{10}](OH)_8$ [4].

I.2.5 Clay in Ceramics

Traditionally, the different sectors of ceramics fall into two groups:

- Structural ceramics that includes brick and tile sections, sandstone pipes, refractory products and expanded clay aggregates
- Fine and traditional ceramic and industrial ceramics, which includes the sectors of floor and wall tiles, ornamental ceramics, sanitary ware, technical ceramics and inorganic abrasives. However, the term terracotta is increasingly used to refer to bricks and clay tiles used as building materials. Most often, bricks and tiles have a name that denotes not the shaping technique used, but the use for which they are used. are intended for: facing bricks, paving bricks (solid, perforated or hollow), chimneys and tiles extruded or pressed.

I.2.6 Properties of Clays

Clay minerals are characterized by four main properties such as[6]:

- Specific shapes and surfaces.
- Clay-water relations **(**Water adsorption and swelling capabilities).
- Multiple possibilities of ion exchanges.
- clay activity.

I.2.7 Shape and Specific Surface

Clays come in three forms (Figure (I.6)) [9]:

- In flakes, characterized by the same dimension in both directions and a thickness equivalent to 1 / 20th of the length.
- In latte, with a longer dimension, thickness always equivalent to 1 / 20^{th} of the length.
- In needles, two identical dimensions and the 3rd much larger (enough rare).

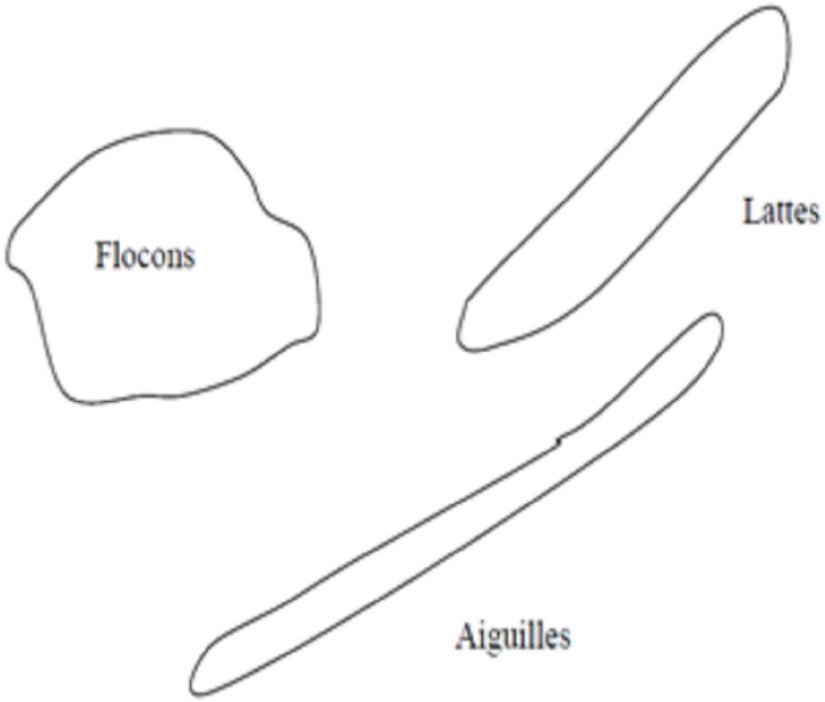

Figure I.6: Shape of clay particles [4].

PART 3: BRICKS

I.3.1 History of Brick

Human has used brick for building purpose for thousands of years. Bricks date back to 7000 BC, which makes them one of the oldest known building materials. They were discovered in southern Turkey at the site of an ancient settlement around the city of Jericho. They are one of the oldest types of building blocks. An ideal building material because they are relatively cheap to make, very durable, and require little maintenance. Bricks are usually made of baked mixtures of clay. In ancient times, bricks were made of mud and dried in the sun; modern bricks are made from concrete, sand and lime, and glass. The physical and chemical characteristics of the raw materials used to make bricks, along with the temperature at which they are baked, determine the color and hardness of the finished product. Bricks are made in standard sizes, are usually twice as long as they are wide and, since most bricklaying is done manually, are made small enough to fit in the hand. Bricklayers use a trowel to cover each brick with mortar a mixture of cement, sand, and water. The mortar hardens when dry

and keeps the bricks in place. Bricks are arranged in various patterns, called bonds, for strength.

I.3.2 Different Types of Bricks

I.3.2.1 Raw Brick

In the Middle East, mud bricks dating back to 50 centuries BC have been discovered. However, there is no guarantee that these cookies correspond to the oldest applications. Today, a large part of the world's population still lives in houses built using this technique, especially in rural areas, but also in cities. In dry climates, these dwellings offer quite satisfactory technical qualities [10].

I.3.2.2 Baked Brick:

There are few written sources on the baked brick manufacturing methods used locally in the past. This is a very old technology. They have adapted to the evolution of construction and its requirements, in the traditional industrial field. They are made from clay that often turns red when fired (except limestone clays, which range in color from pink to yellow and white [10, 11]

I.3.3 Manufacture of Bricks

The bricks are made from common clays, which constitute the basic material. The clays have fundamental differences, hence the need to modify their behavior by mixing different clays or by adding inert elements such as sand, quartz, chamotte etc. These blends facilitate the shaping, drying and firing of the brick and allow modifying its plasticity. The manufacture of a modern brick goes through the following major steps:

- Preparation of clay: The preparation consists of two main operations: grinding and mixing on the one hand, and dosing and mixing of raw materials on the other. The aim is to obtain a homogeneous paste, of constant quality, having the required plasticity for the molding of finished bricks. Additives can also be added in the mixture of the clay like shale, it is necessary to crush and grind it in successive stages. in a fine

powder that will be mixed with water to obtain a paste (clay) with the desired plasticity, or shade to obtain different colors ...[9, 10]

- Grinding the earth to obtain the desired particle size [11].
- Humidification and mixing of various types of land; addition of a small amount of lingo sulfite, a residue of the paper industry derived from lignin contained in trees; lingo sulfite facilitates extrusion [11].
- Extrusion through channeles corresponding to a given form of brick.
- Cutting**:** Figure (I.7) represents the brick during the cutting processes.

Figure I.7: represents the brick during the cutting processes

- Drying: The products are shaped with a water content of 15 to 30%. It is necessary, before submitting them to cooking, to eliminate most of this water, this is the drying operation. It is about a Delicate and important phase of manufacturing that must be conducted wisely if you want get quality products. After passing through the dryer, they only contain 1 to 2% residual water sometimes less (in a gas dryer duration between 20h and 50) [9, 10].
- Firing: At about 900 ° C, up to 30 hours firing this is the last step that the shaped and dried clay brick must undergo (figure (I.8)), before it can become a clay brick properly speaking. This very important phase must take place very gradually. The temperature is gradually increased until the firing temperature (between 850 and 1200 ° C,

depending on the type of clay) is obtained, then the temperature is gradually decreased to complete cooling. Each clay mixture is characterized by its own " firing curve"[9, 10].

Figure I.8: Brick at the beginning of the firing.

I.3.3 The Firing Steps

Concern the reaction of the raw materials to cooking, the heat causes modifications of density, porosity, hardness, and dimensions. It also causes dehydrations, decompositions and de-combinations that modify the properties as follows:

- Up to about 200 °C, evacuation of residual drying water.
- From 200 to 450 °C, decomposition of organic matter.
- From 450 to 650 °C, destruction of the clay minerals with departure of the water of constitution.

- From 650 to 750 °C, decomposition of carbonate of calcite (case of limestone clays) (Figure (I.9)).

Figure I.9: brick after the firing.

PART 4: KINETICS OF REACTIONS

I.4.1 Kinetics of Thermally Stimulated Solid Reactions

Thermal activation is, probably, the most common means to stimulate solid-state reactions, although the applications of photo activation, magnetic field, pressure, and electrochemical potentials are also possible. By activating by external heating or cooling stimuli, the structure, phase state, and chemical properties of solids are changeable; thermal analysis techniques measure the physical and chemical changes of solids as a function of temperature in controlled thermal conditions. Thermal analysis techniques have been employed since the early 20th century and are increasingly important as an analytical tool in the fields of chemistry, physics, materials, geology, metallurgy, medicine, and combustion. The development of thermal analytical instruments and thermal analysis methods have provided a useful tool to obtain the kinetic parameters of solid state reactions with a small

amount of solid sample. The most common and widely used thermal analysis techniques are Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

TGA is a method commonly used to measure selected characteristics of materials' mass changes due to decomposition, oxidation, or loss of volatiles (e.g., moisture and combustibles) and to record information digitally as a function of increasing temperature and/or of time (Figure (1.10)). Most typical TGA applications are studies of reaction kinetics and degradation mechanisms, materials characterization by analysis of characteristic decomposition patterns, and determination of organic or inorganic contents in samples.

DSC is a thermoanalytical technique that measures the difference in the amount of heat needed to increase the temperature of a sample and a reference as a function of temperature. The fundamental mechanism underlying this technique is that, more or less, the reactions will be exothermic or endothermic, and heat will need to flow to or from the sample and reference to keep them at the same temperature when the sample experiences a physical transformation. For instance, a phase transition from solid to liquid absorbs heat; when a solid sample melts, it will take more heat to increase its temperature at the same rate as the reference, and DSC is able to measure the amount of heat absorbed or released during the reaction (Figure (1.10)). DSC is also applied to observe more subtle physical changes (e.g., glass transitions and polymer curing).

A similar technique is differential thermal analysis (DTA) in which heat flows to the reference and the sample and is kept the same rather than the temperature. Hence, DSC and DTA provide similar information. Solid state kinetic data obtained by TGA and DSC are of an increasing practical interest because a growing number of technologically important processes like thermal energetic materials and crystalline solids, thermal oxidation and pyrolysis of fuels and polymers, crystallization of glasses and polymers, and the solidification of metallic alloys are fruitfully studied using these techniques [12].

Thermal Analysis Kinetics (TAK) seeks to quantitatively analyze the relationships between Temperature and physical properties (e.g., the mass change as a function of time) measured by the thermal analysis techniques.

The development of TAK is based on chemical thermodynamics, chemical kinetics and thermal analysis techniques. By analyzing data obtained by thermal analysis techniques, TAK is able to:

- provide kinetic parameters,
- estimate the thermal stability and life span of materials,

- and the best operation conditions of polymers,
- quantitatively describe the reaction rate and reaction mechanisms,
- Provide supporting information for estimating properties of energetic materials and combustibles [13].

Interests in TAK were awakened in the early 20th century, and tremendous developments occurred during the recent decades. TAK has been developed for no less than one hundred analytical methods and applied in various fields. It is capable of quantitatively characterizing reactions and phase change processes, determining the most probable reaction mechanisms, and extracting activation energies and pre-exponential factors of solid-state reactions.

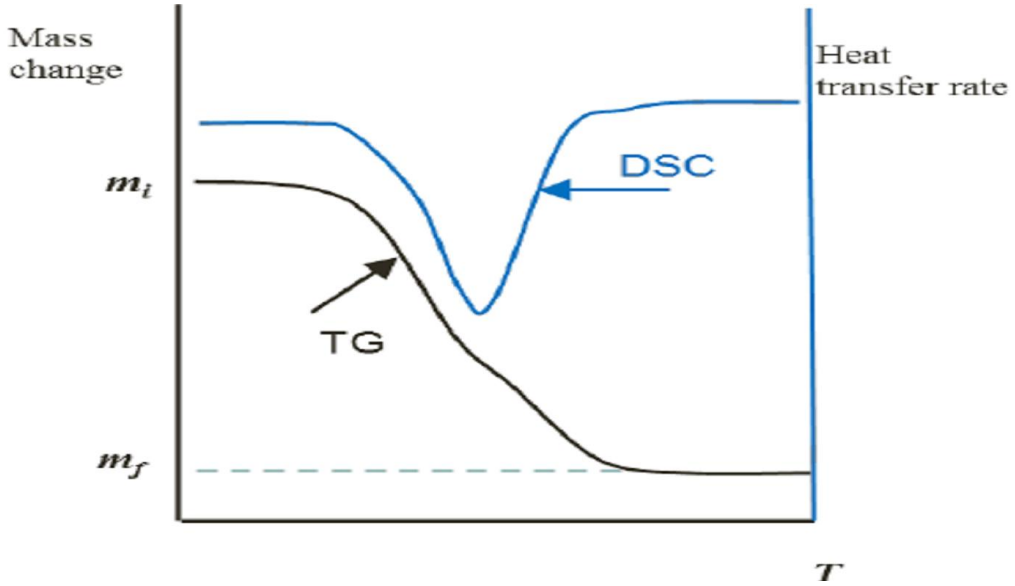

Figure 1.10: Schematic of TG and DSC plots.

I.4.2 Kinetic Triplets and Equations

Non-isothermal, heterogeneous thermal analysis kinetics originated from the theory of isothermal and homogenous gas or liquid phase kinetics, the basis of which had been established by the end of 19th century. Its description equation is:

$$\frac{dc}{dt} = k(T)f(c)$$

where c is the concentration, t is the time, T is temperature, $k(T)$ is the rate constant that dependent on temperature, and $f(c)$ is the reaction mechanism.

Early solid state kinetic studies were carried out under isothermal conditions [14-16], and used the following kinetic equation

$$\frac{d\alpha}{dt} = k(T) f(\alpha)$$

The temperature dependence of the rate of solid-state reactions is typically parameterized through the Arrhenius equation

$$k(T) = Ae^{\left(-\frac{E}{Rt}\right)}$$

where *A* is the pre-exponential factor, *E* is the activation energy, and *R* is the universal gas constant.

As pointed out in Ref. [17], Vallet studied the first kinetic evaluations of non-isothermal data that were carried out at a constant heating rate, β = dT / dt. To extract values of the kinetic parameters, Vallet suggested replacing the temporal differential by

$$dt = dT / \beta$$

Note the transformation of previous Eq. implicitly contains an assumption that the change in experimental conditions from isothermal to non-isothermal does not affect reaction kinetics; this assumption may have serious implications for multi-step reaction kinetics [17]. Based on the aforementioned theories, the equation of heterogeneous solid state reaction rate under isothermal condition can be described as

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) f(\alpha)$$

Which under non-isothermal conditions with a constant heating rate leads to

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right) f(\alpha)$$

The parameters of *E*, *A*, and *f* (α) are often called the kinetic triplet, which are to be determined during the kinetic analyses of solid state reactions.

Currently, the core of TAK is to study the kinetics of non-isothermal solid state reactions (including physical effects). The reason for using non-isothermal conditions is because of the difficulty to attain strict isothermal conditions, especially during the initial stage of a reaction process; using isothermal conditions is also more time consuming. Moreover, theoretically, a thermal experimental curve obtained under non-isothermal conditions could carry information equivalent to that in multiple data curves obtained from isothermal conditions.

I.4.3 Activation Energy (E_A) in The Case of The Non-Isothermal Method

Many methods have been introduced by many researchers to calculate the activation energy (E_A) in the case of the non-isothermal method. In this study will using just three of them whose Ozawa–Flynn–Wall (OFW) [18, 19], Boswell [20] and Kissinger–Akahira–Sunose (KAS) methods [21-23]. The principle basics were listed by these three formulas below:

$$\ln(\varphi) = -1{,}0518\frac{E_A}{RT_p} + C_1 \quad (1)$$

$$\ln\left(\frac{\varphi}{T_p}\right) = -\frac{E_A}{RT_p} + C_2 \quad (2)$$

$$\ln\left(\frac{\varphi}{T_p^2}\right) = -\frac{E_A}{RT_p} + C_3 \quad (3)$$

Where C_i (i=1,2 and 3) is a constant, φ is the heating rate in the DTG analysis, E_A is the activation energy, T_p is the absolute peak temperature in DTG curves and R is the ideal gas constant. The activation energy can be calculated by the slope obtained. The value of Avrami exponent, n was determined from the shape of DTG curves at any heating rates as [24, 25]:

$$n = -\frac{2{,}5T_p^2 R}{\Delta T_p E_A} \quad (4)$$

Where ΔT_p: is the width of crystallization peak at half maximum.

Matusita and co-workers have proposed to change Kissinger method as follows [26]:

$$\ln\left(\frac{\varphi^n}{T_p^2}\right) = C_3 - \frac{mE_A}{RT_p} \quad (5)$$

Where m is a numerical factor depends on to the dimensionality of crystal growth and n is the Avrami parameter which indicates the crystallization mode.

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Chapter II:

Materials and Methods

II.1 The Used Materials

The raw materials used in our study are: the yellow clay and the red clay from the region of ouled dradj (M'sila, Algeria), in addition to the mixture between the tow types of clay.The mixture is consist 14% of quartz, the rest is 90% of the red clay and 10% of yellow one with the addition of the mixture mentioned above was done in a brick manifacturing facility with the apropriate proportion.

II.2 Experimental Methods

II.2.1 Thermal Treatment

The four samples wastaken in gross state then manualy grinded until get a fine powder, after that it was treated according to the table bellow (Table II.1).

Figure II.1 represent sample of clay treated at 900 °C.

Table II.1: Heat treatment

Number of treatement	Treatement temperature(°C)	The maintenance (min)
01	25	---
02	300	120
03	400	
04	500	
05	600	
06	700	
07	900	
08	1000	
09	1100	

II.2.2 XRD Analysis

After each heating treatment, the clay are analysed by X-ray diffraction analysis, using a high-temperature diffractometer MRD, PANalytical (ISM), with CuKα radiation of a wavelength 0.15418 nm, this technique was used to characterize the raw powders as well as sintered samples,and to characterize the formation of phases and their transformations during the heat treatment using the information recorded on the diffraction spectrum,.

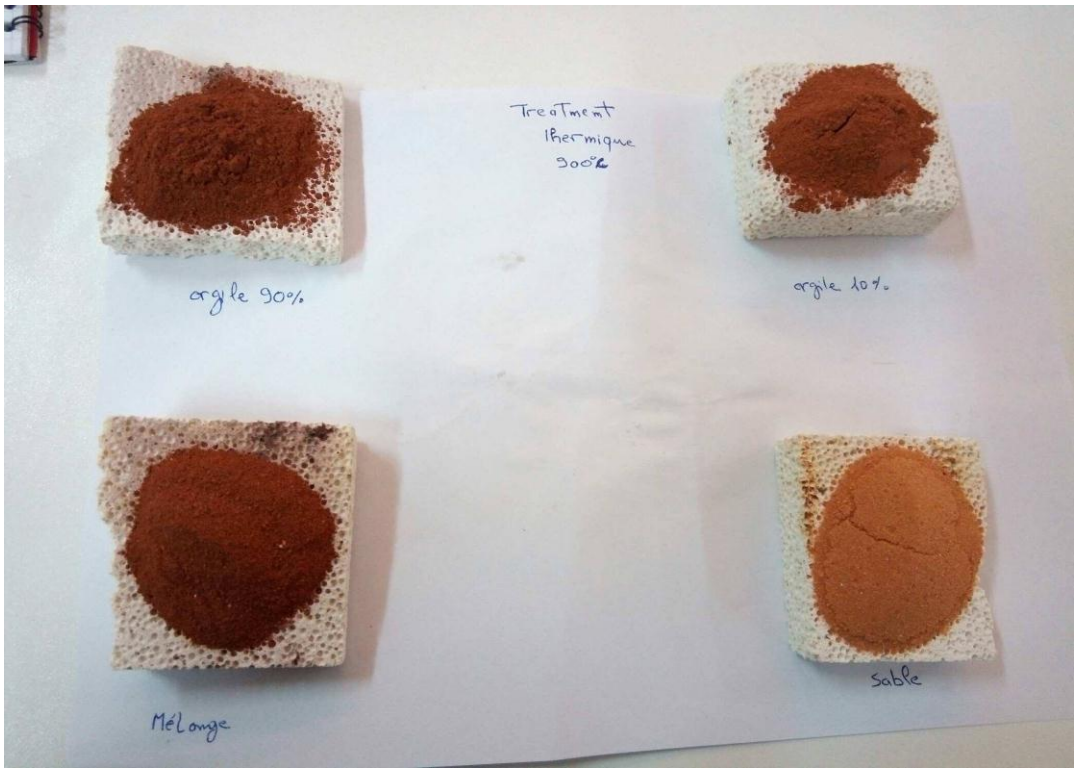

Figure II.1: Sample of clay treated at 900 °C

II.2.3 XRF Analysis

The chemical composition of the clay used in this work was determined by XRF.

II.2.4 Differential Thermal Analysis DTA, Differential Scanning Calorimet DSC and Thermogravimetric AnalysisTGA

The differential thermal analysis DTA is based on the amount of heat absorbed or emitted from the sample when physical or chemical transformations occur during heat treatment. Any phase shift, crystallization, chemical reaction, water or carbon exodus or other changes in the sample, is the source of the emission or absorption of the temperature. The difference between the studied sample and the other sample that is used as a witness gets recorded . In this sense, the heat treatment of some ceramics leads to a decrease in its mass. This decrease is due to the combustion of organic matter, the disintegration of some carbon compounds, water humidityor water inside the installation of these ceramic materials.

On the other hand, Thermogravimetric AnalysisTGAallows for the determination of mass lost during thermal treatment. Temperature values corresponding to mass loss zones are complementary to those obtained by differential thermal analysis can be drawn to be more

useful because the latter represents the speed of mass loss in terms of temperature and this allows the identification of sensitive areas, which should be taken some reserves during the heat treatment of the sample.

II.2.5 Scanning Electron Microscopy SEM

The scanning electron microscopy provides the surface images of virtually all solid materials at scales ranging from magnification (x10) to transmission electron microscopy (x500,000 or more). These images strike first by the very pronounced rendering of the relief and the great depth of field. Conventional SEM operates in an ordinary vacuum (10-5 to 10-6 mbar); samples can be massive, ranging in size from a few 1mm (particles) to atens of cm in diameter, they must withstand the vacuum without polluting and be drivers. The preparation is usually simple. Equipped with appropriate detectors.

Morphology of the clay powder and the microstructure of sintered samples were characterized using a JEOL scanning electron microscope (SEM) model JSM-7001F.

II.2.6 Dilatometric Study

Dilatometry experiments were carried out using NETZSCH (Dil 402 C) equipment and were performed from 20 ° C to 1100 °C at a heating rate between 1 and 9 °C/min.

II.3 The Used Equipment

II.3.1 Heat Treatment Furnace

Heat Treatment experiments were carried out using a nabertherm type furnace as shown in figure II.2, where its maximum tempertaure could reatch 1400 °C and more.

II.3.2 Dilatometer

The linear shrinkage of material was followed using a NETZSCH (Dil 402 C) equipment, its maximum temperature is 1600 ° C as shown in figure II.3. The sample is placed in a special holder containing a thermocouple which measures the temperature of the sample inside an electric oven. When the sample is heated by gradual change in temperature, the latter responds to the heating process and its dimensions change. These changes are detected by a very sensitive spring, A subject against the sample and connected to a picker that converts these changes in dimensions to signals recorded in the computer according to a special program gives the curves of the change in length in terms of temperature.

Figure II.2: "Naberthem" type furnace.

Figure II.3: Dilatometer type "NETZSCH DIL402C".

II.3.3 The Diffractometer

a high-temperature diffractometer MRD, PANalytical (ISM), with CuKα radiation of a wavelength 0.15418 nm as shown in figure II.4 was used in this study based on the extrusion of samples with a monochromatic x-ray packet,

$2d_{hkl}\sin\alpha = n\lambda$

n : diffraction range,

α: diffraction angle.

λ: wavelength of X-rays,

d_{hkl}: the dimension between crystalline levels

II.3.4 Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis DTA

TGA and DSC experiments were carried out using a LABSYS EVO DTA/DSC-TG SETARAM equipment (figure II.5), under flow of argon gas (40 $cm^3.min^{-1}$), from room temperature to 1100 °C using different heating rates, in order to know the phases transitions and to analyze the kinetics and the mechanisms of the reaction that occurs during the treatment. The thermal analysis technique depends on the successive measurement of the sample mass with the evolution of temperature.The variation of sample mass gets recorded by a program related to the method, so it be exported as a curve which represents the variation of mass in term of temperature. Whereas, the differential thermal analysis DTA depends on the measurement of the deference in temperature between the sample and the reference sample this deference gets recorded as a function of temperature.

Figure II.4: a diffractometer MRD, PANalytical (ISM).

Figure II.5: LABSYS EVO DTA/DSC-TG SETARAM equipment.

Chapter III:

Results And Discussion

III.1 An Analysis Study of The Raw Materials

III.1.1 Chemical Analysis

Table III.1 below represents the elementary analysis using XRF spectrometry that was affected on a sample of clay, in order to determine the chemical composition.

Table III.1: the results of the chemical analysis of local clay.

Clay component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Percentage (%wt)	53.3	17.1	9.46	10.9	3.39	0.369	2.45	0.924

III.1.2 Mineralogical Study using XRD of Clay in Gross State

The test was done on three different samples red clay, yellow clay and the mixture between 90% of red clay, 10% of green one and a certain percentage of sand obtained from the region of Ouled Drradj. The mixture was done in facility for brick manufactory using the previous conditions. The X-ray diffraction pattern of the raw material (figure III.1) confirmed that quartz is the most important non-clay mineral associated with phyllosilicates belonging to the T–O and/or T–O–T groups (XRD), also proofed in the amount of SiO_2 in the XRF results.

The XRD diffractometer also shows the presence of calcite $CaCO_3$, Calcium, Magnesium and Carbonate exists as well which were reported in dolomite ($CaMg(CO_3)_2$) peaks. The presence of some alumino-sillicates was shown in both mixture and clay (90% and 10%).

III.2 Thermal Study

III.2.1. Thermogravimetric Analysis (TGA) and differential Scanning Calorimetric (DSC)

Thermal methods enable to study the different steps of weight loss due to release of OH (dehydroxylation reactions), adsorbed water and CO_2 (decarbonation reactions).
TG/DTG curves of the clay minerals measured under heating rate of 20 °C min^{-1} as shown in Figure III.2 reveal that:

- The first weight loss occurs in the 60°C-250°C range and probably it is associated with the release of adsorbed or weak bonded water molecules [1-3]. Mass loss of sample was reduced about 12.8±0.1 wt. % during this process [4].

- Followed by dehydroxylation of clay minerals initiated at almost similar temperature, 580 °C. In this step of heat treatment kaolinite transforms to metakaolinite as reported by other researches [5, 6], the amount of mass loss is equal to 2.5%wt.
- Another weight loss at about 800 °C refers to the decomposition of carbonates of the calcite and dolomite.

The DSC curve for clay sample with a heating rate of 20°C/min is shown in figure III.3. The endothermic peaks at 180 °C, 570 °C and 800 °C are due to the evaporation of the adsorbed water, dehyroxylation of clay minerals and the decomposition of carbonates respectively.

The endothermic peak observed in DSC curve near to 571°C, is associated with the allotropic transformation of quartz. The exothermic peak at 982 °C are due to the transformation of metakaolinite to a spinel-type structure, this structural reorganization of the metakaolinite between 980 and 1000 °C yielded an amorphous phase rich in SiO_2 and a spinel phase at 1100 °C, the spinel phase was transformed in mullite [6] [4] which is a ɤ-Al_2O_3 and alumino-silicate spinel [6]. This process isn't accompanied by change of mass of the sampl

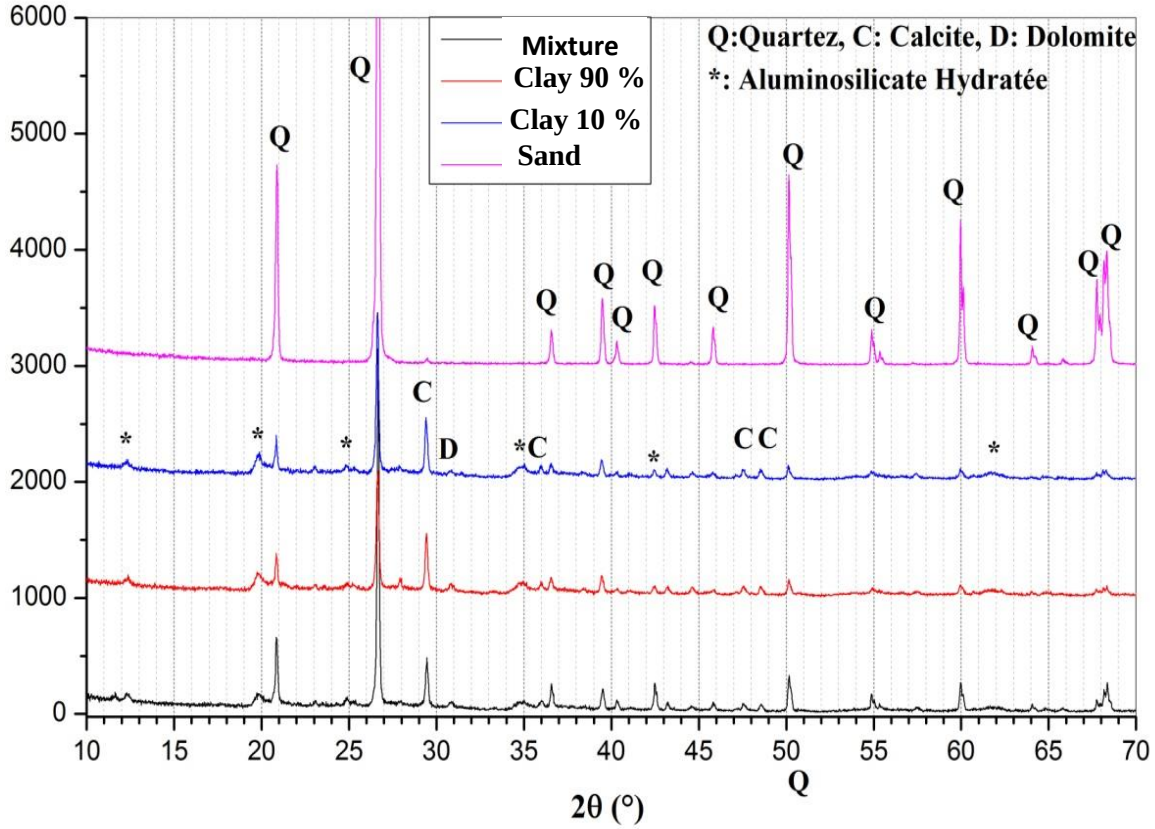

Figure III.1 Mineralogical study using XRD of clay in gross state.

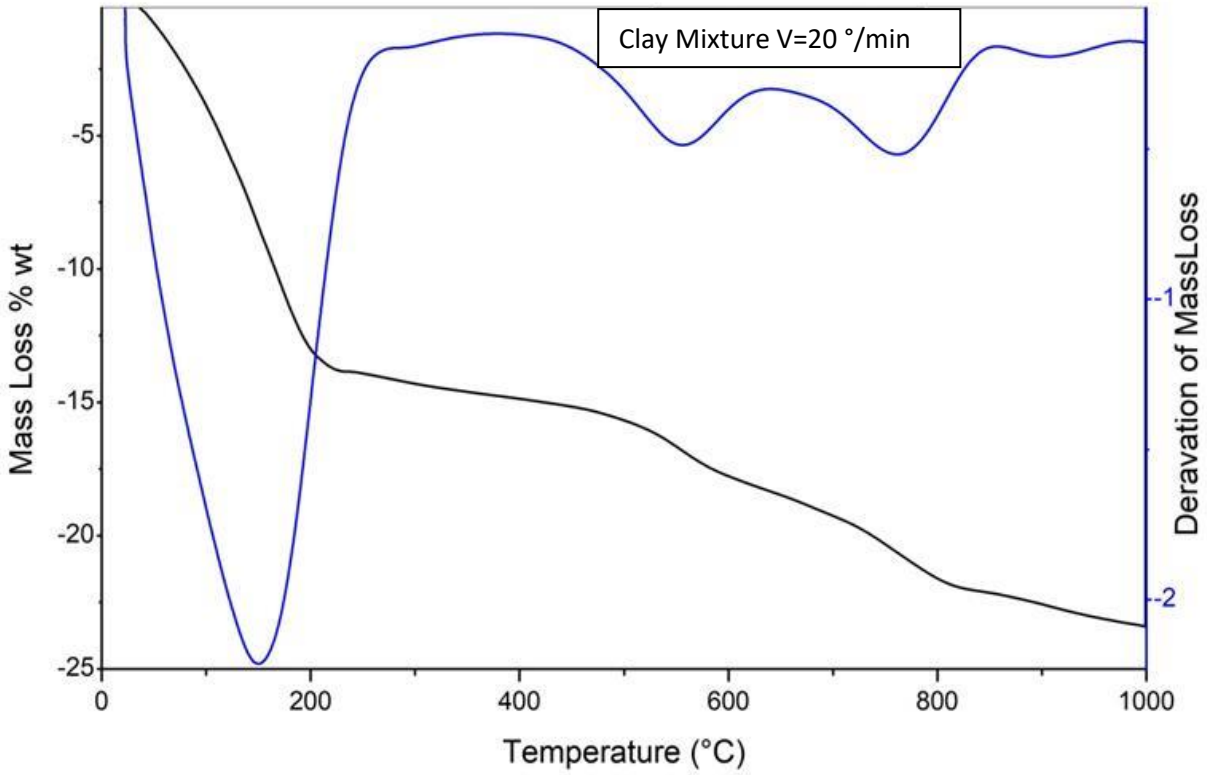

Figure III. 2**:** TGA/DTG curves of the clay mixture.

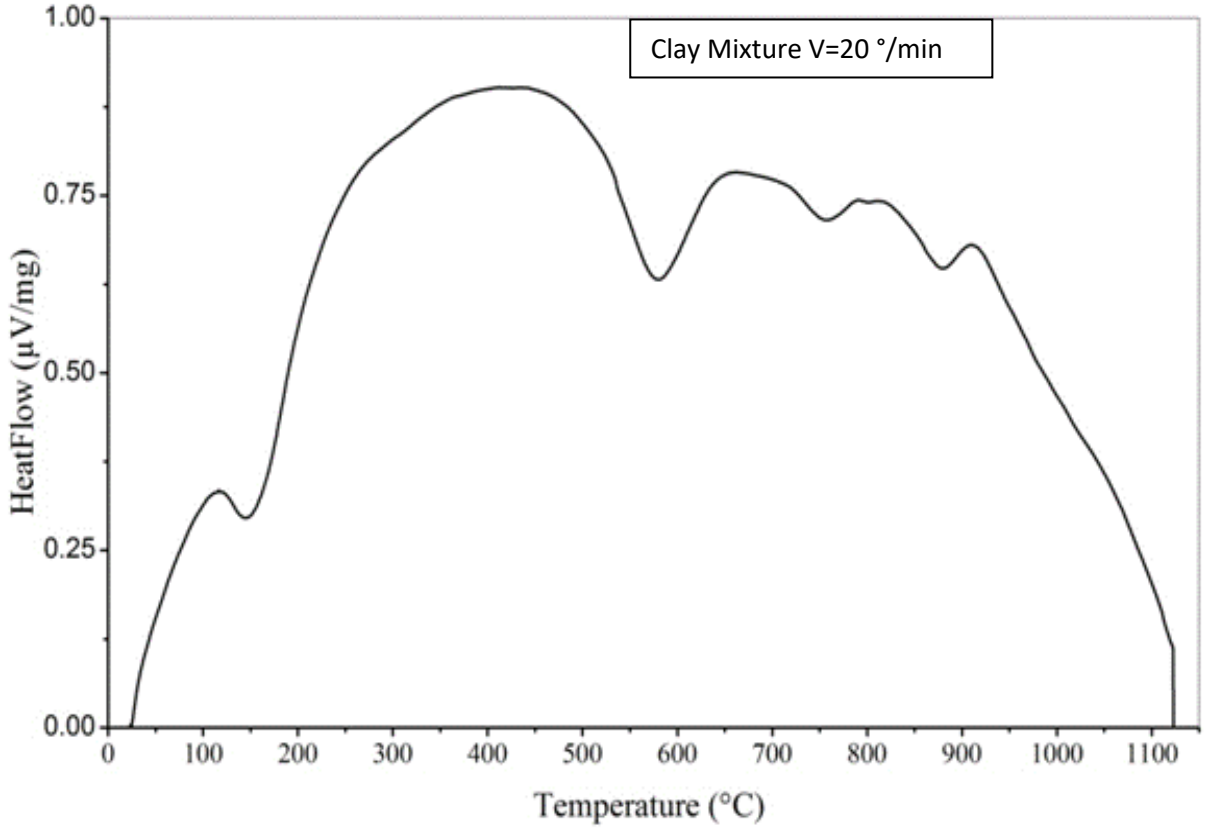

Figure III.3. DSC curve of clay sample at 20 °C/min

III.2.2. Dilatometric Study

The dilatometric analysis of the compact clay materials presents generally an important shrinkage correspondent to a sintering densification, with the elimination of porosities [7]. Figure III.4 shows linear shrinkage curve a function of T (°C) for clay materials heated from room temperature to 1100 °C using a heating rate of 5°C/min, also the cooling curve is plotted. The results show:

- An important diminution in sample length that refers to the evaporation of the adsorbed water or the drying processes, at about 200°C, the first derivative of linear shrinkage curve in figure III.5 shows tow peaks one at 150°C and another at 180 °C this confirms that the evaporation does happen in two materials which are the components of the mixture analyzed (clay and SiO_2).
- A small relative linear shrinkage where the rate of shrinkage is maximum at 555 °C; this shrinkage associated with an increase in volume caused by the allotropic transformation of quartz from α-quartz to β-quartz leading to a linear elongation about 0.5 % this transformation is reversible during the cooling, appeared at 551°C.
- From 650°Cto 750°C, the destruction of clay with the departure of the combined water.
- An important shrinkage observed from 810 °C to 860 °C corresponding to the sintering.

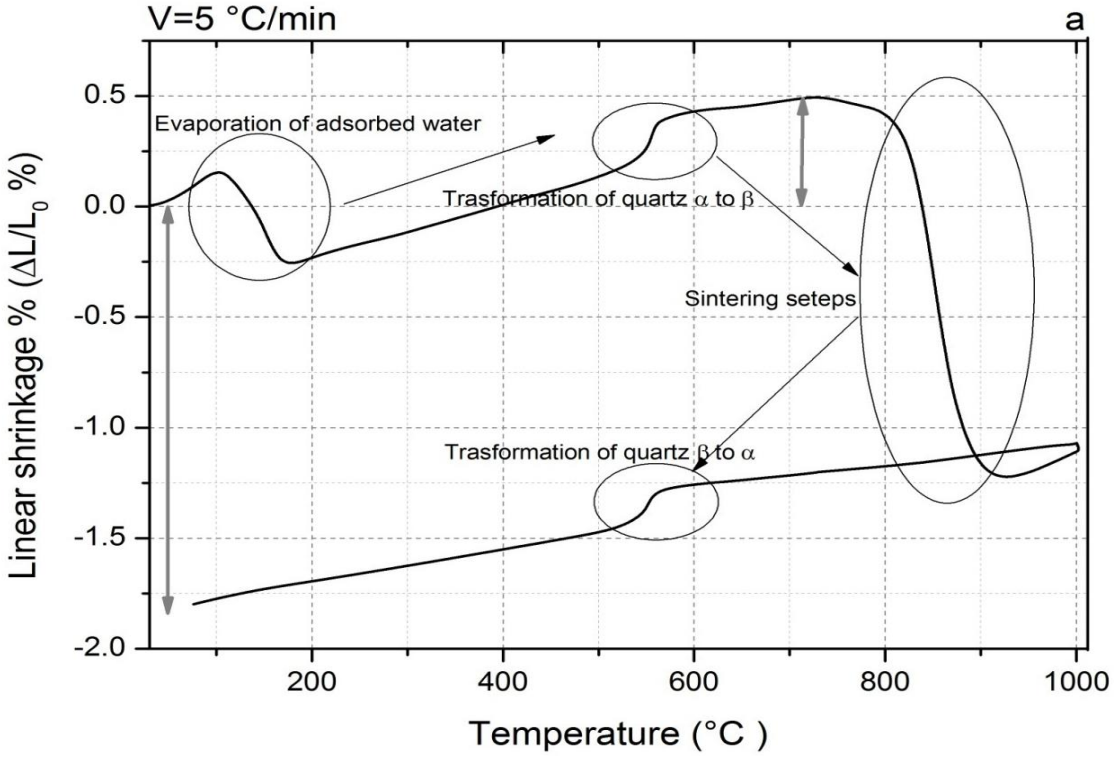

Figure III.4: Dilatometric curve of the mixture of clay (V=5°C/min).

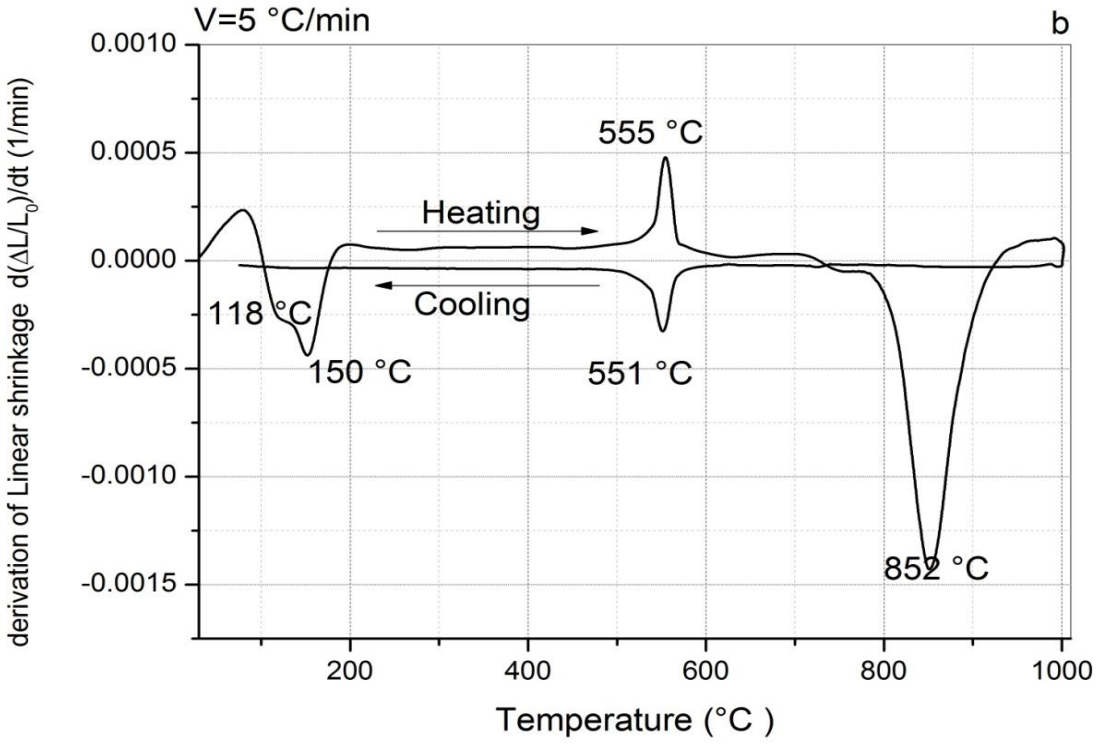

Figure III.5: Derivation of linear shrinkage curve.

III.2.3 Analysis by XRD for Treated Clay

In order to determine and characterize the formation of phases and their transformations, the samples (clay 90, 10% clay and the mixture) were treated in various temperatures from 25 °C to 1200 °C for 2 h. The samples have been studied by X-ray diffraction.

In order to determine the effect of heating on the phases that occurs on the samples treated less than 600 °C, the correspondent curves were compared as shown in figure III.6. As a result of the comparison we conclude that:

The phases present in the sample sintered between room temperature and 400 ºC were alumino-sillicates hydrated, quartz, calcite and dolomite. The alumino-silicates hydrated phase disappeared and alumino-sillicates phase appeared in the sample sintered at 500 ºC, because the dehydroxylation of clay minerals, while quartz phase is still present in a small fractions. In the sample sintered at 600 °C, just two phases present and refer to quartz and calcite.

It is very important to mention that when the sintering temperature increase, the crystallization of annite phase increased too. With further heating degrees over 600 °C, its cristallinity reduces (as shown in Figure III.7). The calcite peaks disappeared at 700 °C,

because of the decomposition of calcium carbonates, the occurrence of lime (CaO) , a new spinel phases at 900 °C, and iron oxide over 900 °C. Noting that quartz peaks remains in all the sintering temperatures.

Figure.III.8, Figure.III.9 and Figure.III.10 shows no deference in XRD patterns between the three clay powders treated at different temperatures.

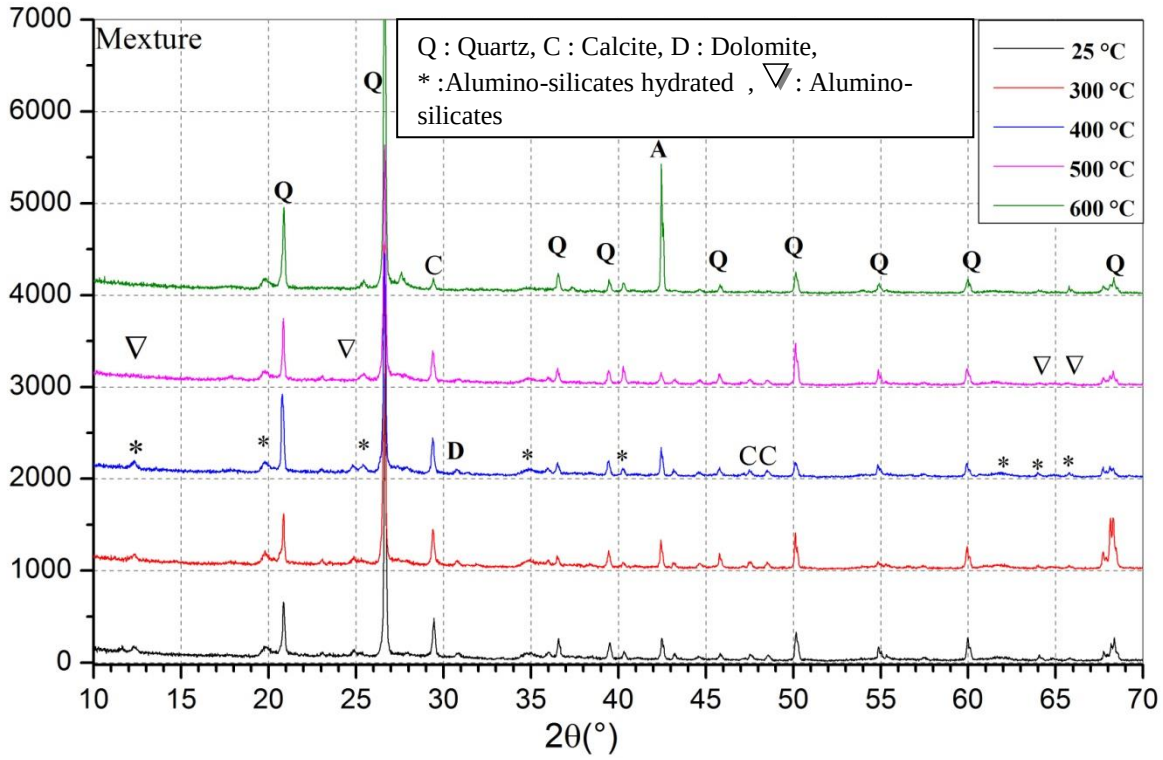

Figure III.6. XRD patterns of clay powders treated at different temperatures for 2 h. A: annite, Q: quartz, D: dolomite, C: calcite, *: alumino-sillicates hydrated and ∇: alumino-sillicates.

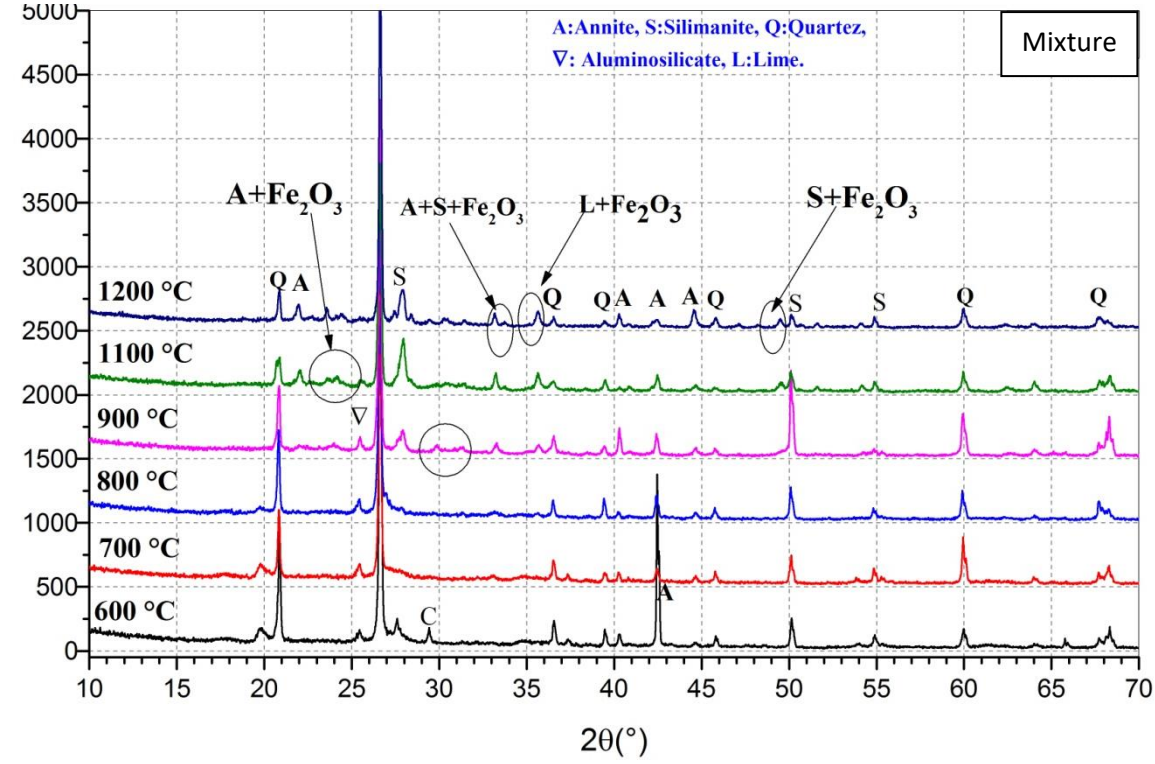

Figure III.7: XRD patterns of clay powders treated between (600°C-1200°C).

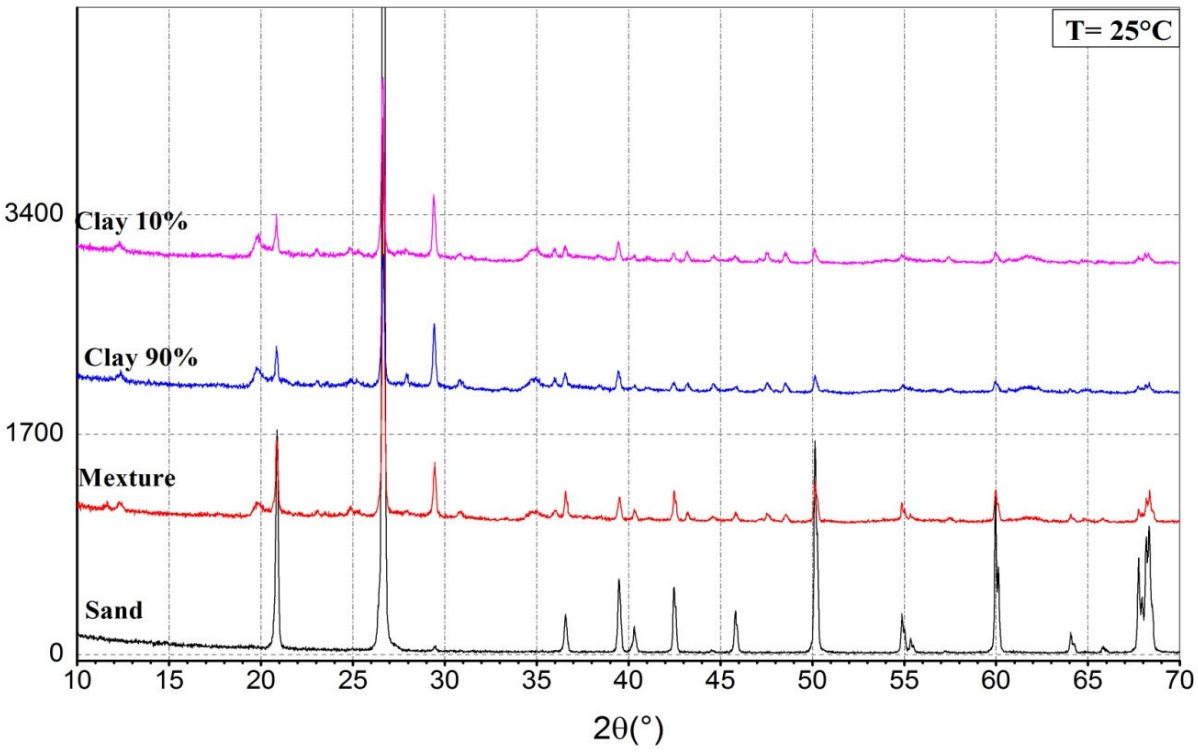

Figure III.8: XRD patterns of raw clay samples (90%, 10% and mixture) at 25°C

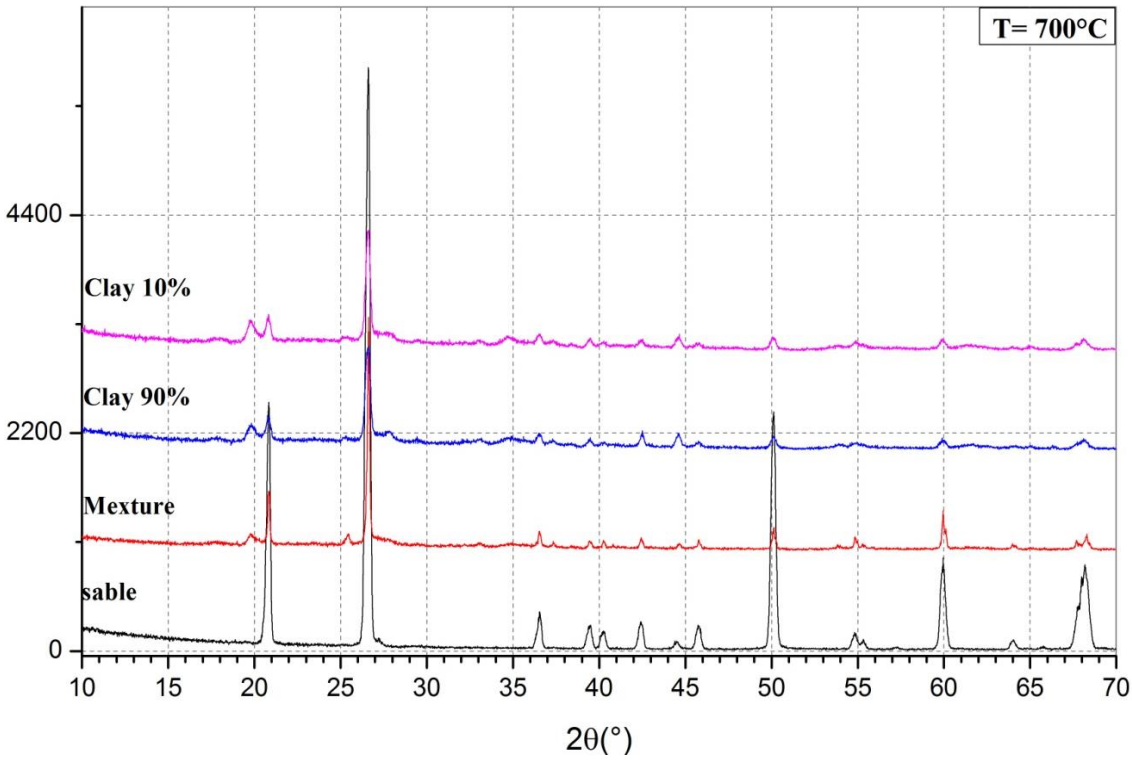

Figure III.9: XRD patterns of fired clay samples (90%, 10% and mixture)

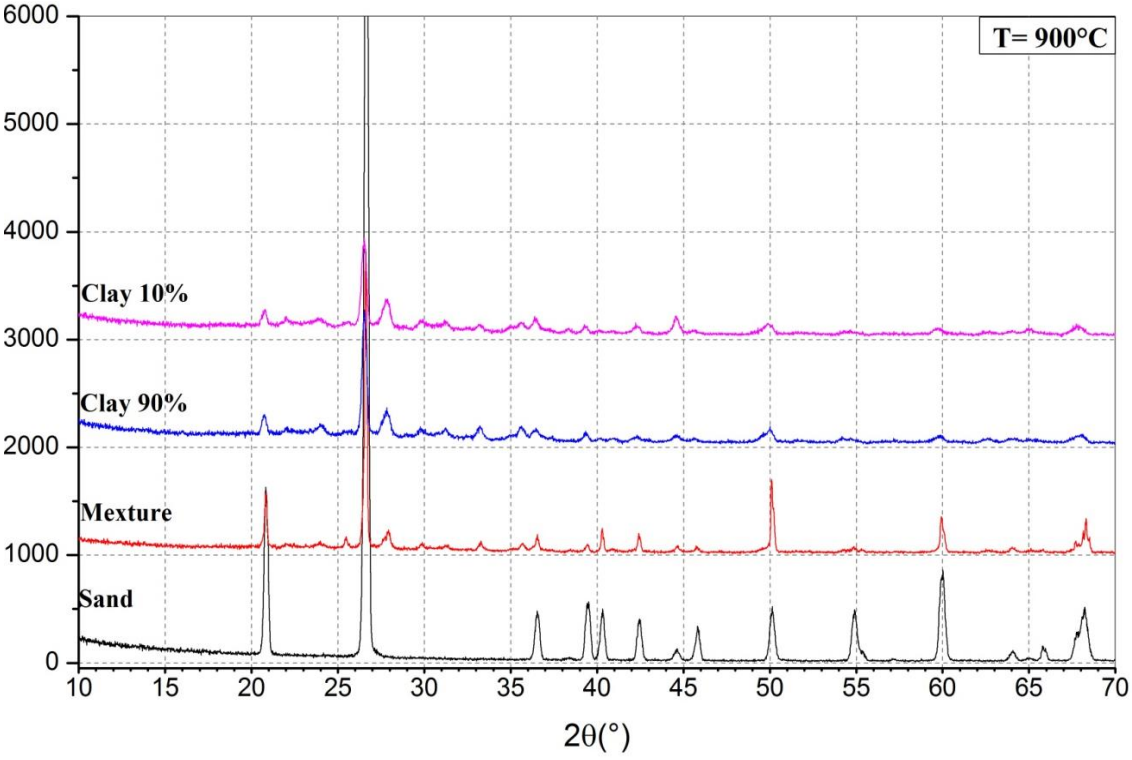

Figure III.10: XRD patterns of fired clay samples (90%, 10% and mixture)

III.2.4 Analysis by scanning electronic microscope of treated clay

Typical SEM micrographs of surfaces of a fractured sample sintered at 900 °C for 2 h are shown in (Figure III.11) Sintering led to the formation of a homogeneous microstructure, with uniform distribution of small pores (smaller than 3 µm). The aggregation of quartz with the structure leads to empty spaces. At this scale of observation, there does not seem to be other minerals present in the matrix. Separate grains of variable size are also observed, probably corresponding to quartz and a mass that is probably amorphous. The SEM image reveals a larger number of distinct grains while the density of pores with diameters considerably smaller (sintering step). The matrix always contains quartz and the spherical pores seem big with the cooking temperature. The previous observation scale does not allow seeing the reactions located at the heart of particulate assemblies.

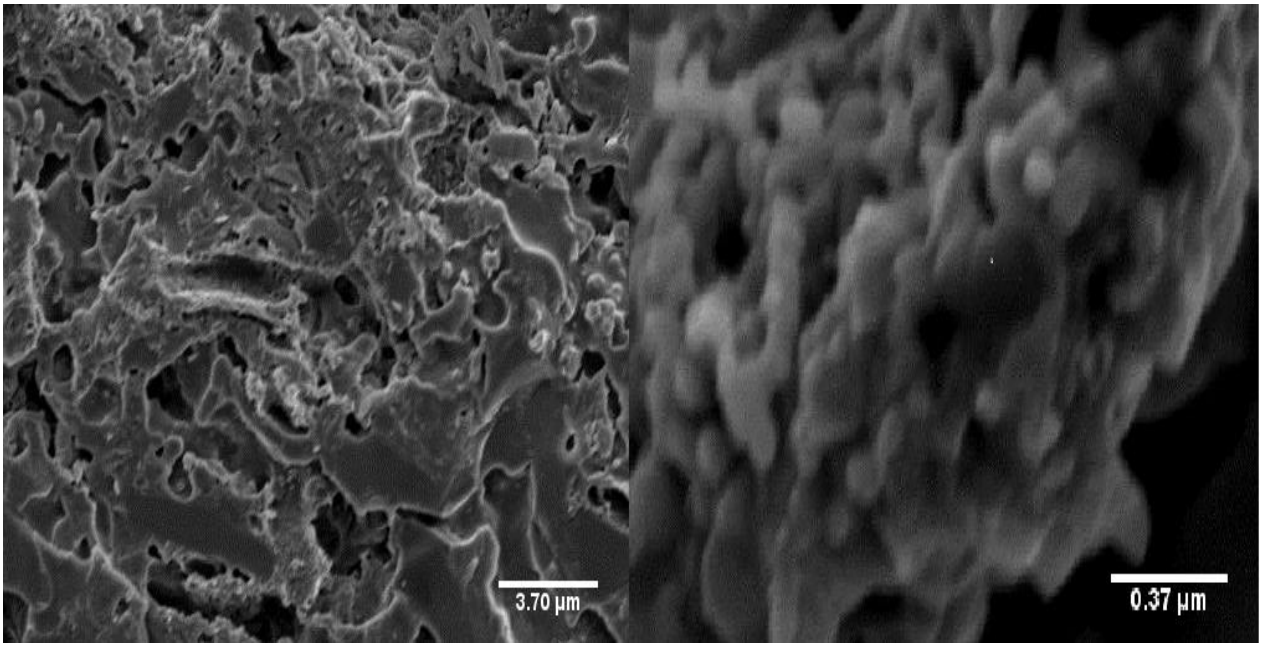

Figure III.11: Micrographs (SEM) of fractured surface of sample sintered at 900 °C.

III.3 Analytical Thermal Study

III.3.1 Influence of the Heating Rate on the Peak of Dehydroxylation, Decomposition of Carbonates and on the Formation of Spinel Phases using DTA

Various changes happening during different heating rates (V=20, 30, 40, 50°C/min) are shown in figure (III.12) as observed, the maximum temperature of each peak increases as the heating rate increases for the evaporation of the adsorbed water, the dehydroxolation of clay minerals and also for the formation of spinel phase.

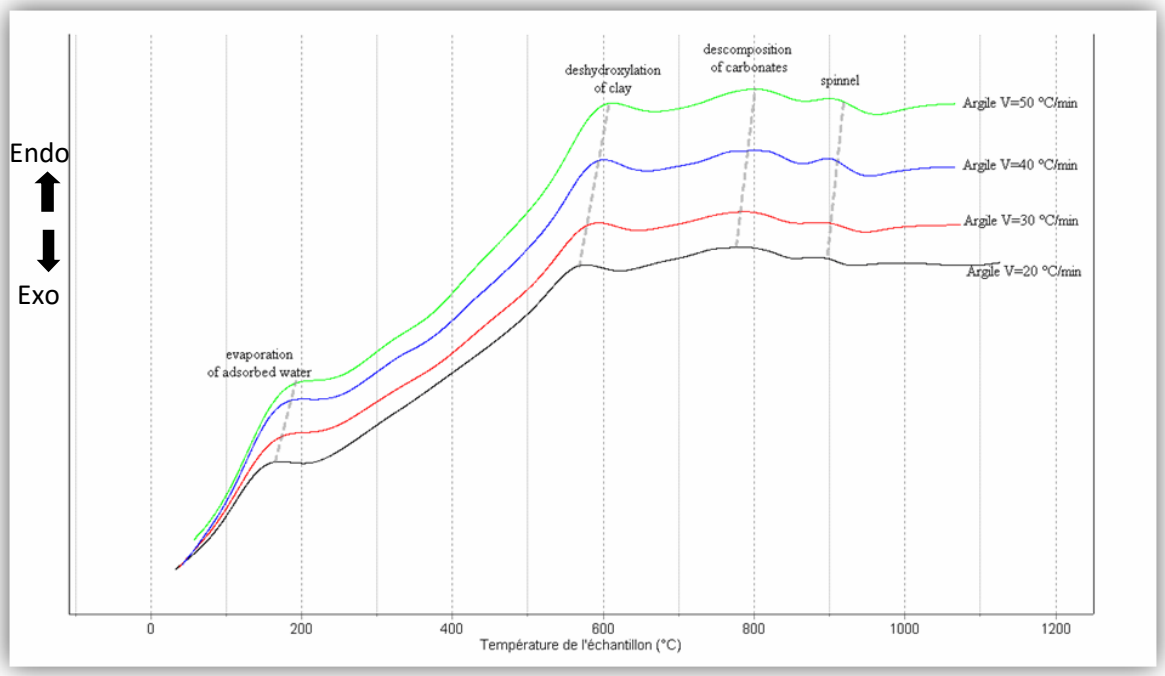

Figure III.12: DTA curves of mixture of clay treated at different heating rates

III.3.2 Influence of the Heating Rate on the Peaks of Quartz Transformation using DL

Figure III.13 shows the influence of heating rates on the appearance of quartz transformation peaks during the heating and cooling. There is an increase in the area of the peaks with the heating rate. Similarly, the maximum temperature of each peak increases as the heating rate increased, for both heating and cooling processes. As it is for sintering peaks figure III.14.

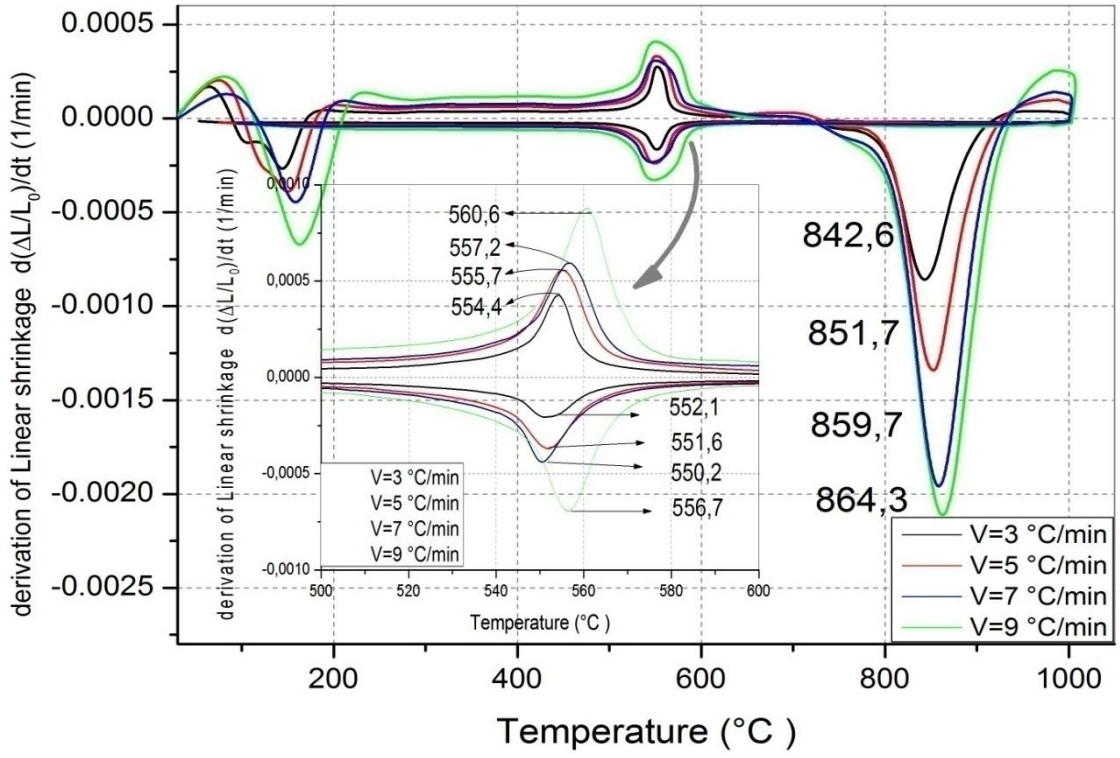

Figure III.13: Derivation of linear shrinkage of clay mixture treated at different heating rates.

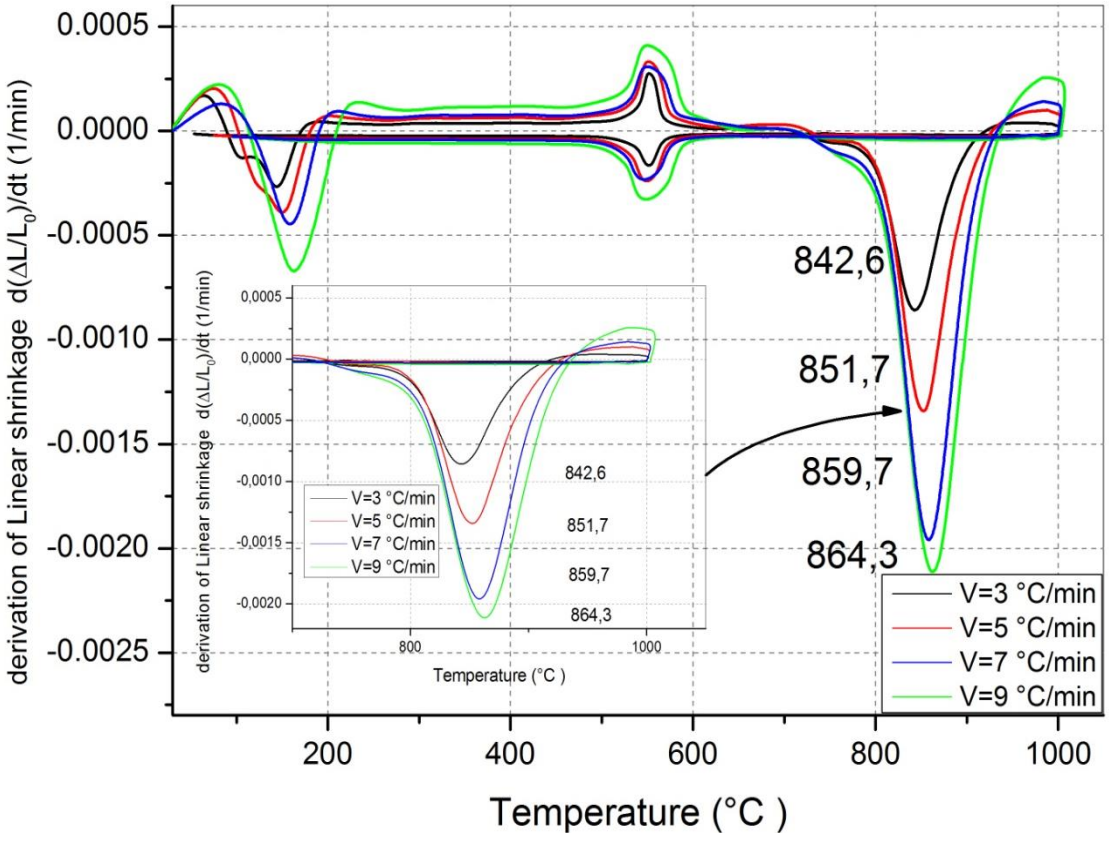

Figure III.14: Derivation of linear shrinkage of clay mixture treated at different heating rates.

III.3.3 Activation Energies

III.3.3.a Activation Energy of Quartz Transformation using DL

We can calculate the activation energy for the allotropic transformation of quartz (α → β) by Kissinger, Ozawa and Boswell methods, from equations (1, 2, and 3).

Kissinger $$\ln\left(\frac{\emptyset}{T^2}\right) = \frac{E}{RT^2} + C \text{..... (1)}$$

Ozawa: $$\ln(\emptyset) = -1.0518\,\frac{E}{RT_p} + C \text{ ..... (2)}$$

Boswell: $$\ln\left(\frac{\emptyset}{T_p}\right) = -\frac{E}{RT_p} + C \text{ ..... (3)}$$

From figure III.12 which depicts the first derivation of shrinkage curves for transformation of quartz (α → β) in the clay mineral at different heating rates. The temperature of the maximum of the exothermic peak Tp, shifts to a higher temperature as the heating rate increases V=3, 5, 7, 9 °C/min. The values of the activation energy calculated from the slope of the function $Y = f(1/T_p)$ (Figure III.15) and listed in Table III.2 below:

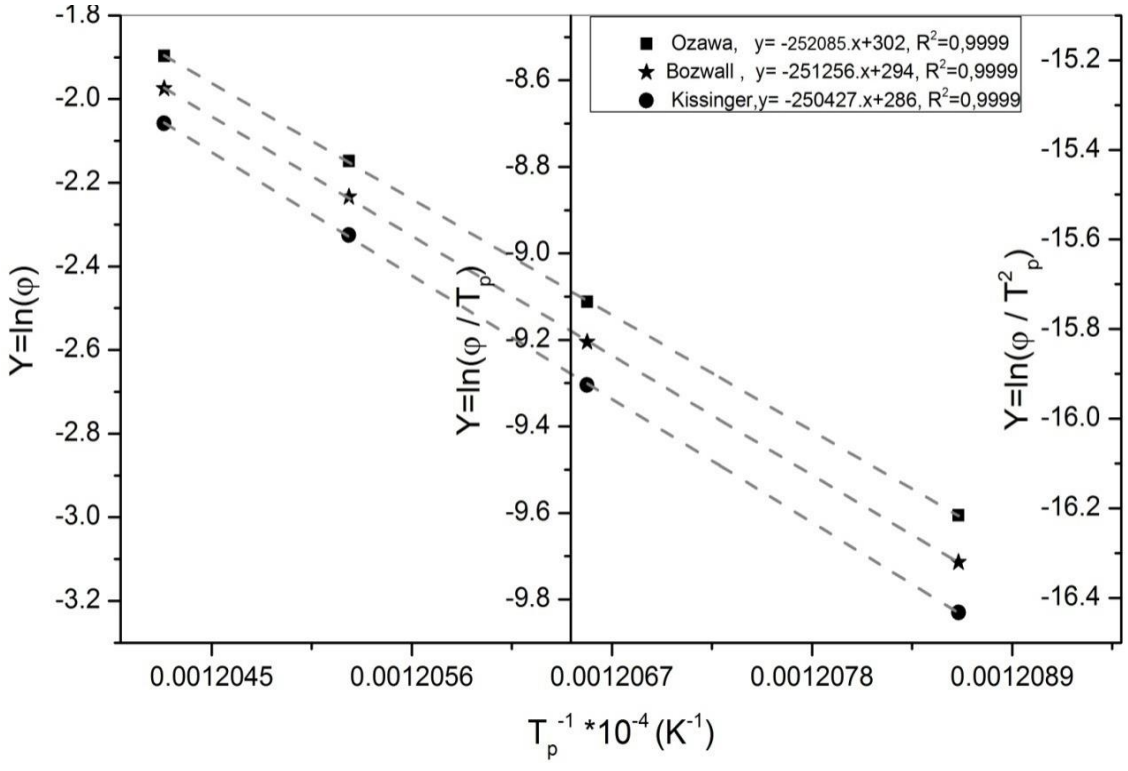

Figure III.15: Plots of Y versus ($1/T_p$) of the allotropic transformation of quartz (α → β) at various heating rates.

Table III.2: the activation energies of sintering

Method	Kissinger	Boswell	Ozawa
Activation energy(kJ/mol)	2081	2087,9	1991,6

III.3.3.b Activation Energies of the Sintering using DL:

The activation energy for the sintering zone can be calculated by the Kissinger, Ozawa, and Boswell methods of clay samples, based on the previous equations (1, 2 and 3) and its plots is shown in Figure III.16. The activation energies of sintering calculated from the slope of the function *Yi=f* (1/*T*p) are listed in Table III.3. These values are comparable with the value reported by (el-maadid) clay study [8]

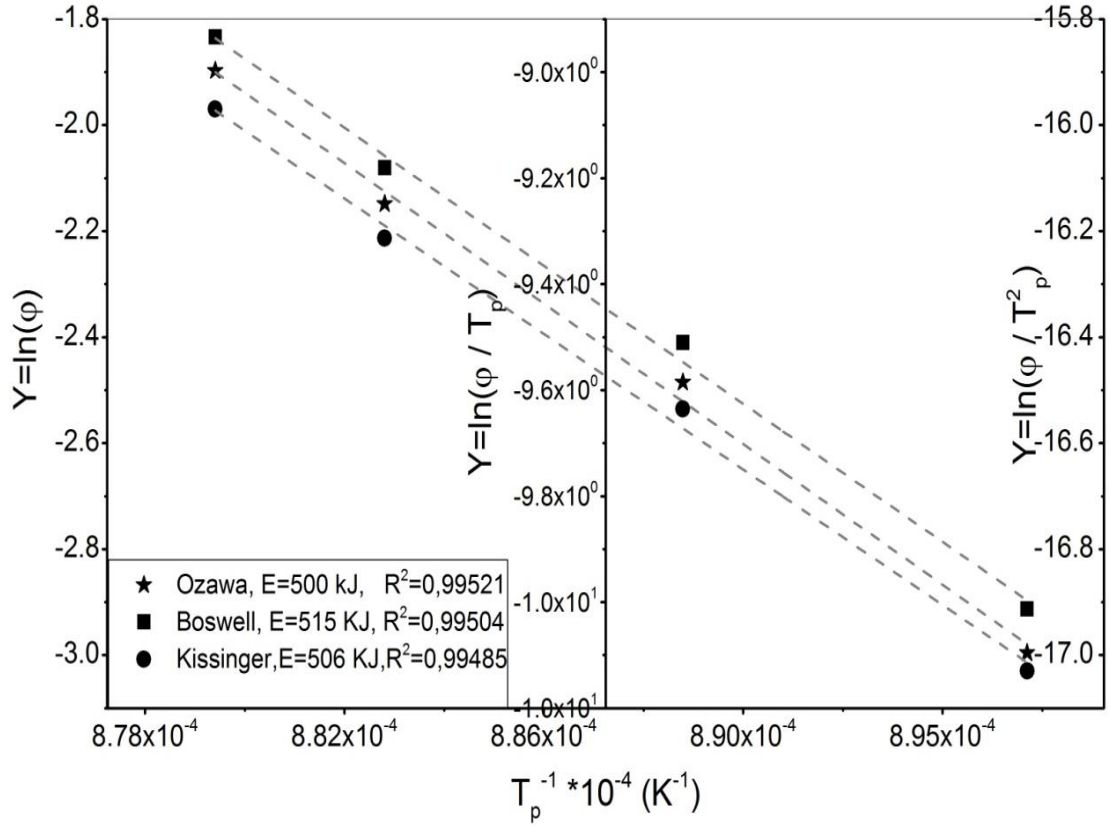

Figure III.16 Plots of Y versus ($1/T_p$) of sintering at various heating rates

Table III.3: the activation energies of sintering

Method	Kissinger	Boswell	Ozawa
Activation energy (KJ/mol)	506	515	500

III.3.3.c Activation Energies of the Dehydroxylation of Clay Minerals by DTA

Thermal analysis techniques remain important tools among the large variety of methods used for analysis of the dehydroxylation of clay minerals. In the present study, the kinetics of dehydroxylation of the obtained clay from the region of Ouled Dradj, was investigated using differential thermal analysis (DTA) experiments that carried out between room temperature and 1100 °C at heating rates of 20, 30, 40 and 50 °C min^{-1}. The dehydroxylation temperature was found around 570 °C. The activation energy evaluated through isothermal DTA treatment was about 150 kJ mol^{-1} close to the value obtained by Algerian kaolinite [9-10]. The values of the activation energy calculated from the slope of the function $Y = f(1/T_p)$ (Figure III.17) and listed in Table III.4.

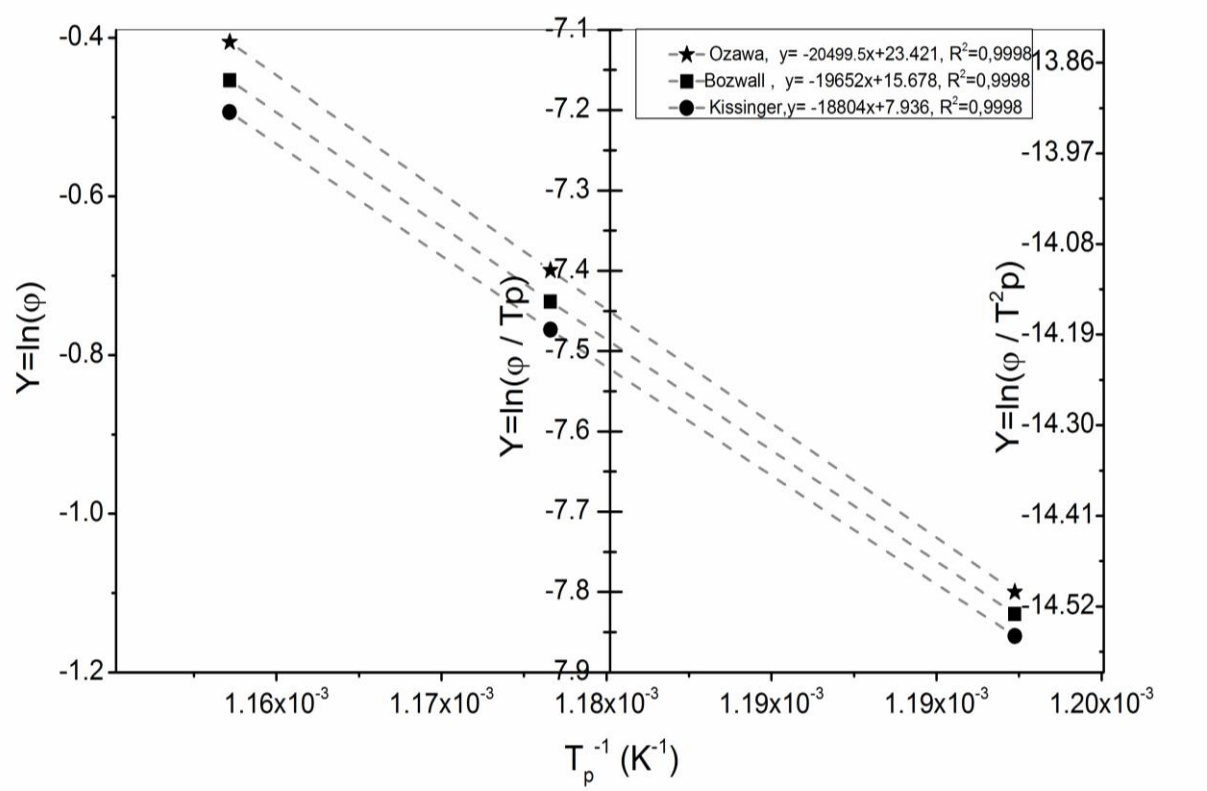

Figure III.17**:** Plots of Y versus ($1/T_p$) of the dehydroxylation at various heating rates

Table III.4**:** The activation energies of the dehydroxylation

Method	**Kissinger**	**Boswell**	**Ozawa**
Activation energy (kJ/mol)	156.2	163.3	154

III.3.3.d Activation Energies of the Spinel Phase Formation by DTA

The values of the activation energy for the formation of spinel are 556 kJ/mol , 566 kJ/mol and 564 kJ/ mol according the Kissinger , Boswell and Ozawa equations, respectively (Table III.5). Figure III.18 shows change of $\ln(\varphi/T^2)$, $\ln(\varphi/T)$ and $\ln(\varphi)$ as function of the inverse of temperature $1/T_p$ for the formation of spinel phase. This activation energy was studied by the others researchers [11] working on the Algerian kaolin DD1, and they were found value about 1000 kJ/mol. The deference in the activation energy values is due to the deference in the source of clay.

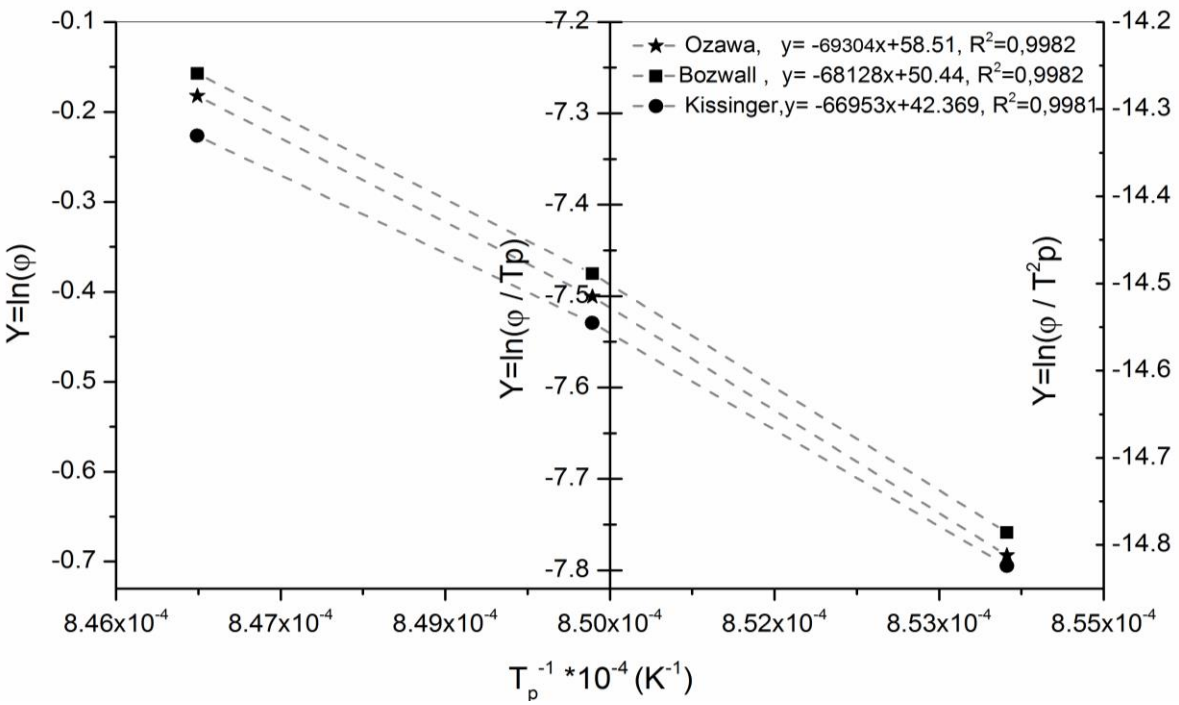

Figure III.18: **:** Plots of Y versus $(1/T_p)$ of spinel phase formation at various heating rates

Table III.5: The activation energies of the spinel phase formation.

Method	**Kissinger**	**Boswell**	**Ozawa**
Activation energy (kJ/mol)	556	566	564

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Conclusion

CONCLUSION

The aim of this work is to study sintering and their mechanisms for local clay, as well as the chemical properties obtained by elemental chemical analysis (XRF), X-ray diffraction (XRD), and scanning electron microscopic analysis (SEM). And these analyzes make it possible to give silico-aluminous compounds and clay minerals for the clay studied. This work also contains the study of the thermal behavior in order to measure the activation energy value of the sintering zone. The results of this study showed that:

- ✓ The mineralogical analysis reveals that the local clay (of M'sila) is mainly composed of: kaolinite and quartz. These two types of raw materials are the most compound used in the ceramics industry.
- ✓ Clay chemistry indicates that at the base of the constituents are alumino-silicates.
- ✓ The mechanical strength due to the porosity of clay.
- ✓ Evaluation of the value of the activation energy of the sintering.
- ✓ Determination of the effect of heating rates on the deferent changes occurring during this last.

ملخص

الغرض من هذا العمل هو إجراء دراسة تحليلية للطين المحلي المستخدم في تصنيع مواد البناء المحلية. تم أخذ العينات المدروسة من منطقة أولاد دراج مسيلة وخلطها في مصنع للطوب. في هذا العمل ، تمت معالجة العينات بدرجات حرارة متفاوتة ؛ تمت دراسة سلوك التقلص باستخدام مقياس التمدد الطولي ؛ تم اختبار السلوك الحراري أيضًا ATD، ATG، DSC ؛ تم تحديد التركيب الكيميائي بواسطة XRF و XRD ؛ كمت تم حساب طاقة التنشيط بواسطة طرق كل من Ozawa و Kissinger و Boswell

الكلمات المفتاحية: الطين ,السلوك الحراري ,التقلص , طاقة التنشيط.

Abstract

The purpose of this work is to make an analytical study for the local clay used in the manufacture of constructions local matter the studied samples were taken from the region of Ouled Derradj Msila and mixed at a brick manufacturing facility in this work the samples were treated at deferent heat degrees the shrinkage behavior was studied by dilatometer; also the thermal behavior was tested ; the chemical composition was determined by XRF, AND and XRD diffraction ; and an interpretation of the energy of activation by the Ozawa; Kissinger and Boswell methods

Keywords: clay, thermal behavior, shrinkage, activation energy

Résume

Le but de ce travaill est de faire une étude analytique pour l'argile locale utilise dans la fabrication des materiaux de constructions locauax. Les échantillons étudiés ont été prélevés dans la région d'ouled Derradj Msila et mélangés dans l'usine de fabrication de briques. Dans ce travail, les échantillons ont été traités à des différente température ; le comportement au retrait a été étudié au dilatomètre ; le comportement thermique (ATD ; ATG ; DSC) a également été testé; la composition chimique a été déterminée par diffraction XRF et XRD; et une interprétation de l'énergie d'activation par l'Ozawa méthodes Kissinger et Boswell

Mots clés: Argile, comportement thermique, retrait, Energie d'activation

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