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Study and Characterization of Heat Storage Materials Composed of Clay, Laterite, and Slag from the Maradi Region of Niger

Ouzeirou ALI OUMAROU[1,2], Boubou BAGRÉ[3], Mahamadou HAMIDINE[4], Makinta BOUKAR[1,*]

[1]Laboratoire d'Energétique et d'Electronique, d'Electrotechnique, d'Automatique, d'Informatique Industrielle (LAERT-LA2EI), Université Abdou Moumouni de Niamey, Niamey, Niger
[2]Université Privée Internationale Aboubacar Ibrahim, Maradi, Niger
[3]Laboratoire de Physique et de Chimie de l'Environnement (LPCE), Université Joseph KI-ZERBO, Ouagadougou, Burkina Faso
[4]Département de Physique, Faculté des Sciences et Techniques, Université Dan Dicko Dankoulodo de Maradi, Niger
*Corresponding author: makintag@gmail.com

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Abstract In this study, raw materials composed of clay, laterite, and clinker were characterized in order to analyse their thermal and thermogravimetric behaviour and validate their use as heat storage materials in thermodynamic power plants. The raw materials were first ground (to a particle size of 100µm) and characterized using various methods (X-ray fluorescence spectrometry, X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis) to better understand their different properties. This characterization made it possible to determine the various physicochemical properties of these raw materials. The aim is to make use of local materials such as clay, laterite from the Maradi region, and ash from the SONICHAR thermal power plant in order to develop new ceramic composite materials with good mechanical and thermal properties for use in thermodynamic power plants:

Keywords: *clay, clinker, laterite, power plants, thermal, X-ray*

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1. Introduction

Thermal storage is a key area of research for the development and optimization of CSP plants around the world [1]. It is a promising means of generating electricity while respecting the environment, and the current dynamic is favorable for the mass deployment of this technology [2]. It is a key element for CSP plants due to the intermittent nature of electricity distribution caused by variations in demand throughout the day and across seasons [3]. Under these conditions, heat storage therefore becomes a relevant solution.

However, even though the main storage materials currently available have shown interesting potential, their availability and cost do not allow for their long-term use, particularly in regions such as West Africa where the supply of materials remains difficult and expensive [8]. One alternative today is to develop heat storage materials from locally available natural materials in order to offer a realistic approach that takes into account the associated new environmental, social, and economic requirements. Thus, raw materials composed of clay, laterite, and ash (clinker) from the SONICHAR thermal power plant were studied in this work with the aim of determining their physicochemical properties in order to validate them as heat storage materials in thermodynamic power plants.

2. Materials and Experimental Methods

2.1. Materials

In this study, three (3) resources were used for characterization: clay, laterite, and ash. The clay and laterite were collected in the city of Maradi (location: 13° and 15°26' north latitude and 6°16' and 8°36' east longitude), and the slag was collected at the SONICHAR thermal power plant located in the Agadez region (Tchirozerine: coordinates 17° 15′ 50″ north, 7° 49′ 49″ east), as shown in Figure 1.

Figure 1. Location of study areas

2.2. Methodology

The clay, laterite, and clinker materials to be analyzed are first prepared by grinding them in an agate mortar to obtain fine particles (Figure 2 (a)). The elements constituting the materials were determined using X-ray fluorescence spectrometry. The samples were prepared by uniaxial pressing of the powders to be analyzed into pellets with a diameter of 25 mm and a thickness of 7 mm (Figure 2 (b)) The crystalline phases formed during heat treatment were identified using an X-ray diffractometer (XRD) in which the various samples were placed. This technique is based on the scattering of X-rays by matter. Once the diffractogram has been obtained, it must be processed. This involves subtracting the background noise and peaks due to the contribution of the Kα2 line, normalizing the main peaks of the two diagrams, and then identifying the main phases using Jad.6 software. A mass of 15 mg of each sample was taken for ATD/ATG analysis. These analyses were performed simultaneously between 30°C and 950°C under air scanning with a heating rate of 10°C/min. Alumina crucibles were used for the various experiments. For the DSC analyses, the following parameters were used for the different samples: the programmed heating and cooling rate was 10°C·min-1; the mass of the samples introduced was approximately 4.8, 5.3, and 6.7 mg for laterite, clay, and slag, respectively; the maximum temperature was 800°C; the experiments were carried out in air with an injection rate of 20 ml·min-1.

2.2.1. Measuring devices

The raw materials were characterized using various methods. To determine the chemical composition, a Genius – IF Xenemetrix XRF X-ray fluorescence spectrometer (Figure 3(a) and (b)) was used. The mineralogical composition was determined by XRD, using the powder method, performed with a PANalytical Pro X diffractometer (Figure 3 (c)), with a monochromatic wavelength λCu-Kα, in a 2Θ scanning range between 10° and 100°. Thermal behavior was studied using TGA/DSC methods with a thermogravimetric balance (Mettler Toledo TGA/DSC 3+ model, Netherlands, Figure 3 (d)). Thermogravimetry is a technique that consists of monitoring the mass loss of a sample as a function of the treatment temperature, and DSC (Figure 3(e) and (f)) when it allows the determination of the heat flow associated with the thermal transitions of a material, such as the glass transition, melting point, crystallization temperature, and reaction enthalpies [14].

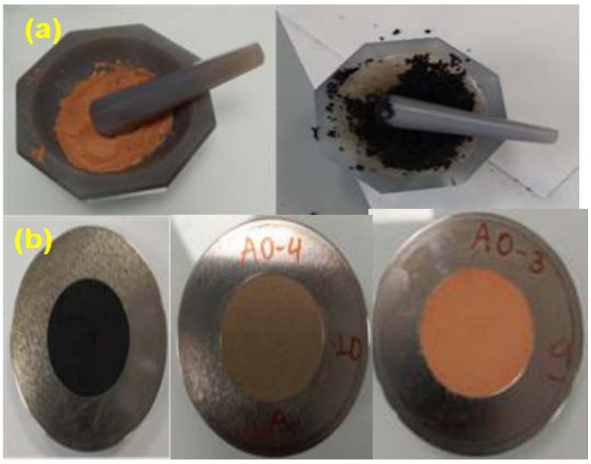


Figure 2. (a) Grinding materials in an agate mortar, (b) Preparation of samples for XRD analysis

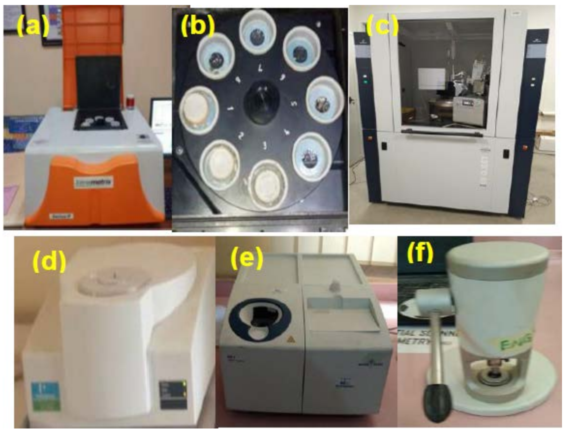


Figure 3. (a) Xenemetrix-Genius IF XRF, (b) Positioning of samples for XRF analysis, (c) PANalytical Pro X diffractogram, (d) ATG/ATD thermogravimetric balance, (e) Colorimetric Differential Scanning, (f) Pressing machine

3. Results and Discussions

3.1. Characterization of Raw Materials

3.1.1. Chemical Analysis of Raw Materials

The results of the chemical composition of raw materials obtained by X-ray fluorescence analysis are presented in the histograms below.

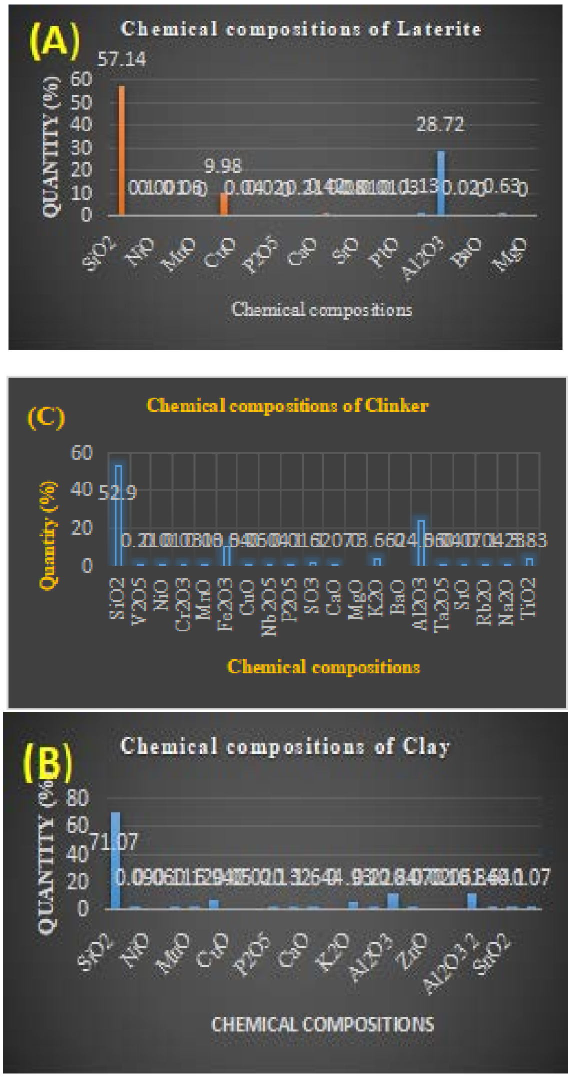
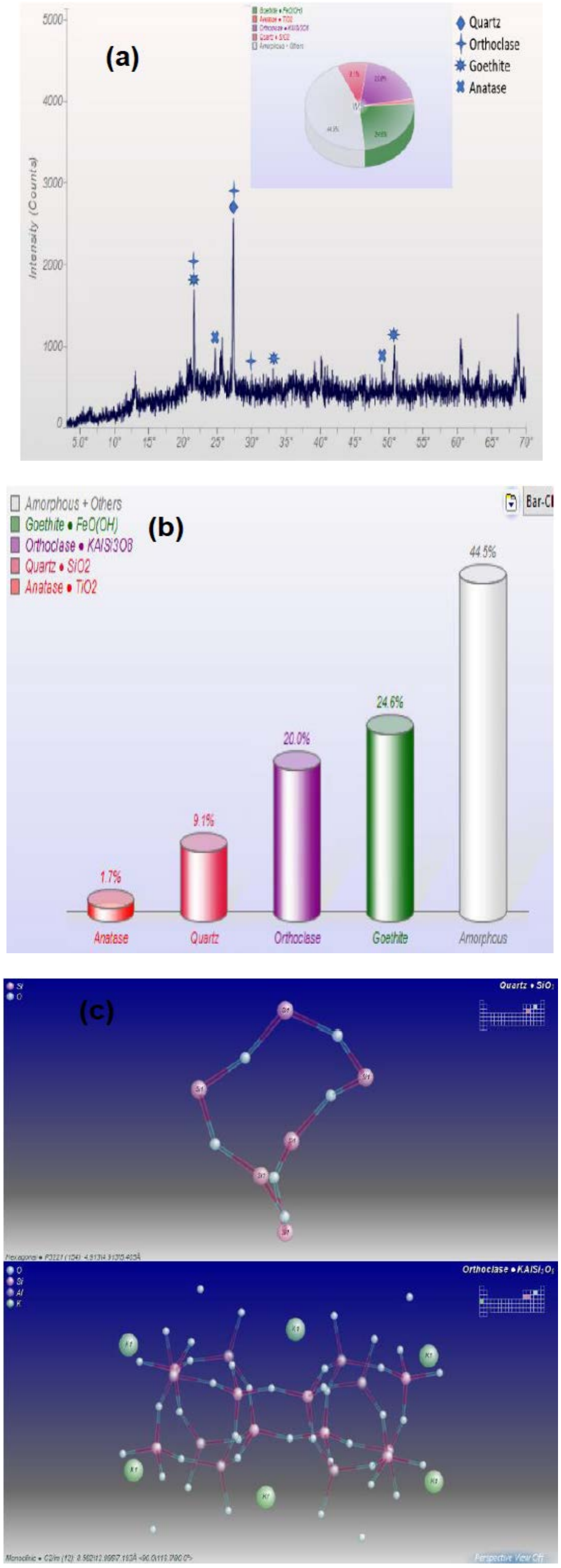


Figure 4. Chemical compositions: A) Laterite, B) Clay, C) Clinker

These analyses show that silica, alumina, and iron oxide are the most abundant elements in these three (3) materials. The data indicate that silica (SiO_2) is the most dominant element in clay (71%), laterite (57.14%), and clinker (52.9%), respectively. This dominance is important for the refractoriness and thermal and mechanical stability of the material. Alumina (Al_2O_3) is the second most abundant component in laterite (28.72%) and clinker (24.56%), improving the thermomechanical properties of the material. It should also be noted that, despite its low proportion, the presence of iron oxide will increase the density and thermal conductivity within the materials. This shows that they are particularly suitable for thermal storage. These results can be confirmed by the X-ray diffraction spectra (Figure 5(a) and Figure 6(a), Figure 7(a)).

3.1.2. Mineralogical Characterization of Raw Materials

X-ray diffraction (XRD) analysis identified the mineral phases present in the three samples analyzed. The diffractograms obtained (Figure 5(a) and Figure 6(a), Figure 7(a)) were analyzed using Jade.6 software [4] and revealed several peaks of varying intensities, corresponding to well-defined crystalline compounds. The peaks were attributed by comparison with standard crystallographic databases [5].



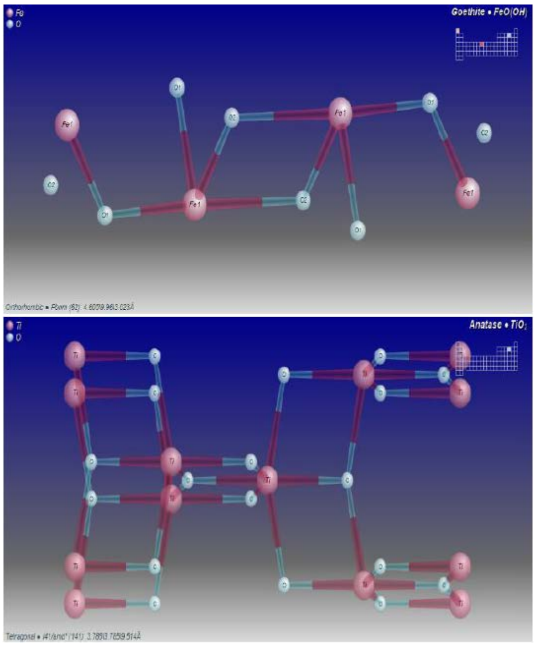
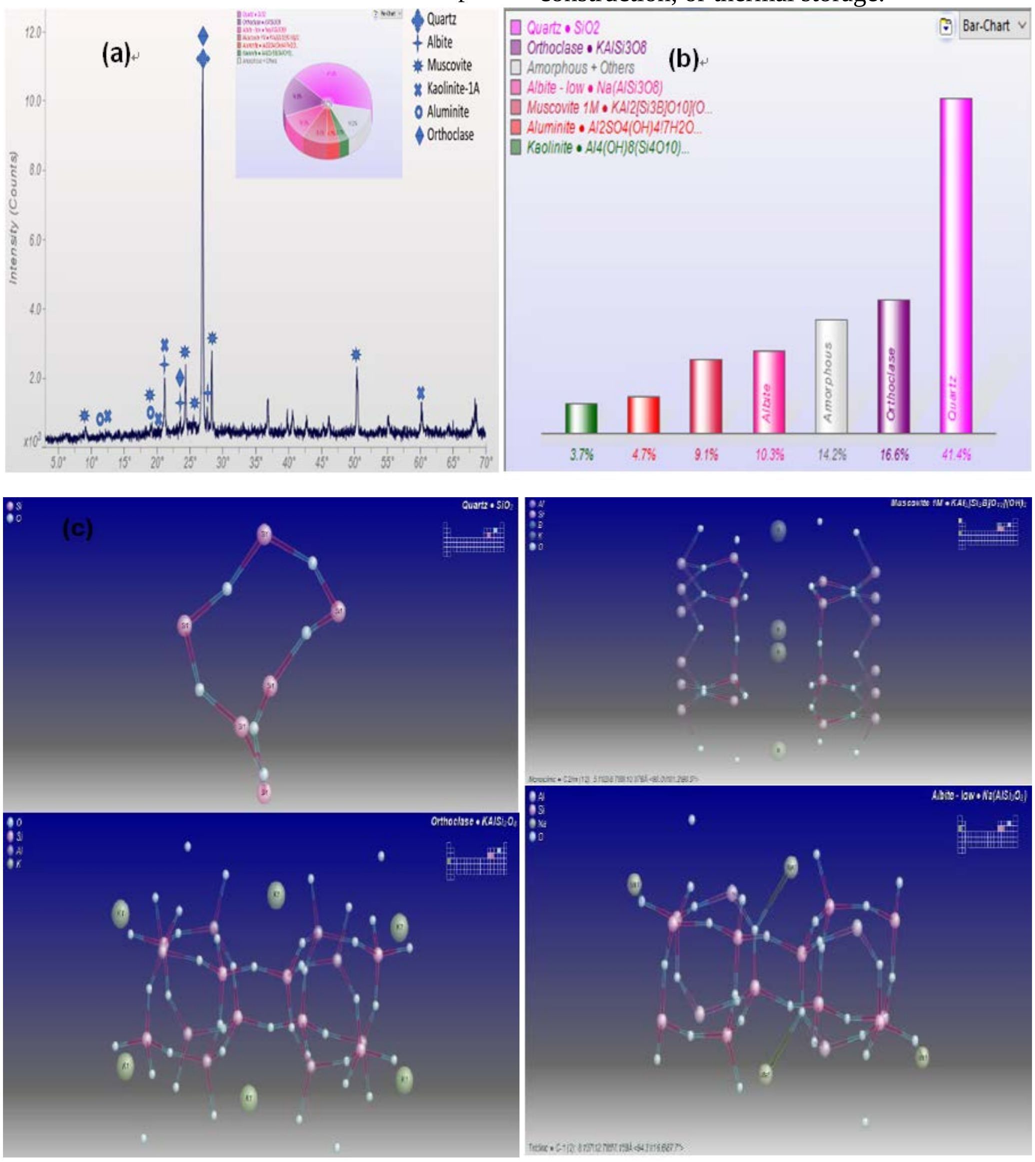


Figure 5. a) Diffractogram of laterite, b) XRD diagram of laterite, c) Molecular structures

The main minerals detected in the laterite sample (Figure 5(b)) are quartz (SiO_2), orthoclase ($KAlSi_3O_8$), goethite (FeO(OH)), and anatase (TiO_2). This composition suggests that the material has interesting potential for thermal or refractory applications, particularly as a heat storage medium or high-temperature ceramic material [6] [7]. The moderate content of amorphous phases may also have a positive influence on the material's thermal absorption capacity or bulk density [8]. The arrangements of the main elements in each material are shown schematically, illustrating the different positions of the atoms and their main bonds (Figure 5(c)).

The identified mineralogical composition of the other two raw materials (clay and slag) consists mainly of quartz (SiO_2), orthoclase ($KAlSi_3O$), muscovite (($KAl_2(AlSi_3O_{10})(OH)_2$) traces of kaolinite, calcite, iron oxide, and illite. The presence of quartz promotes thermal and dimensional stability due to its high melting point [9]. In addition, the presence of iron oxide increases the density and thermal conductivity of the material [10]. The presence of kaolinite, muscovite, and albite indicates a high content of phyllosilicates and feldspars, which are useful for plasticity, thermal reactivity, and mechanical properties [13]. This type of composition in a material is typical for applications in refractory ceramics, construction, or thermal storage.



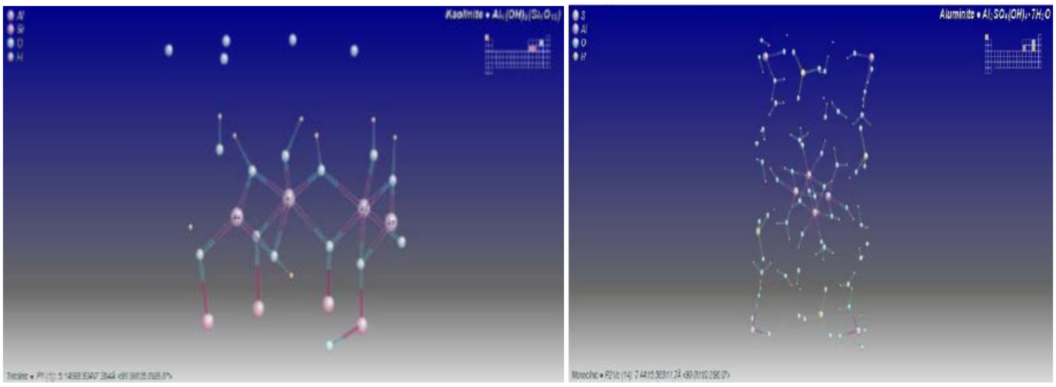


Figure 6. a) Diffractogram of clay b) XRD diagram of clay, c) Molecular structures

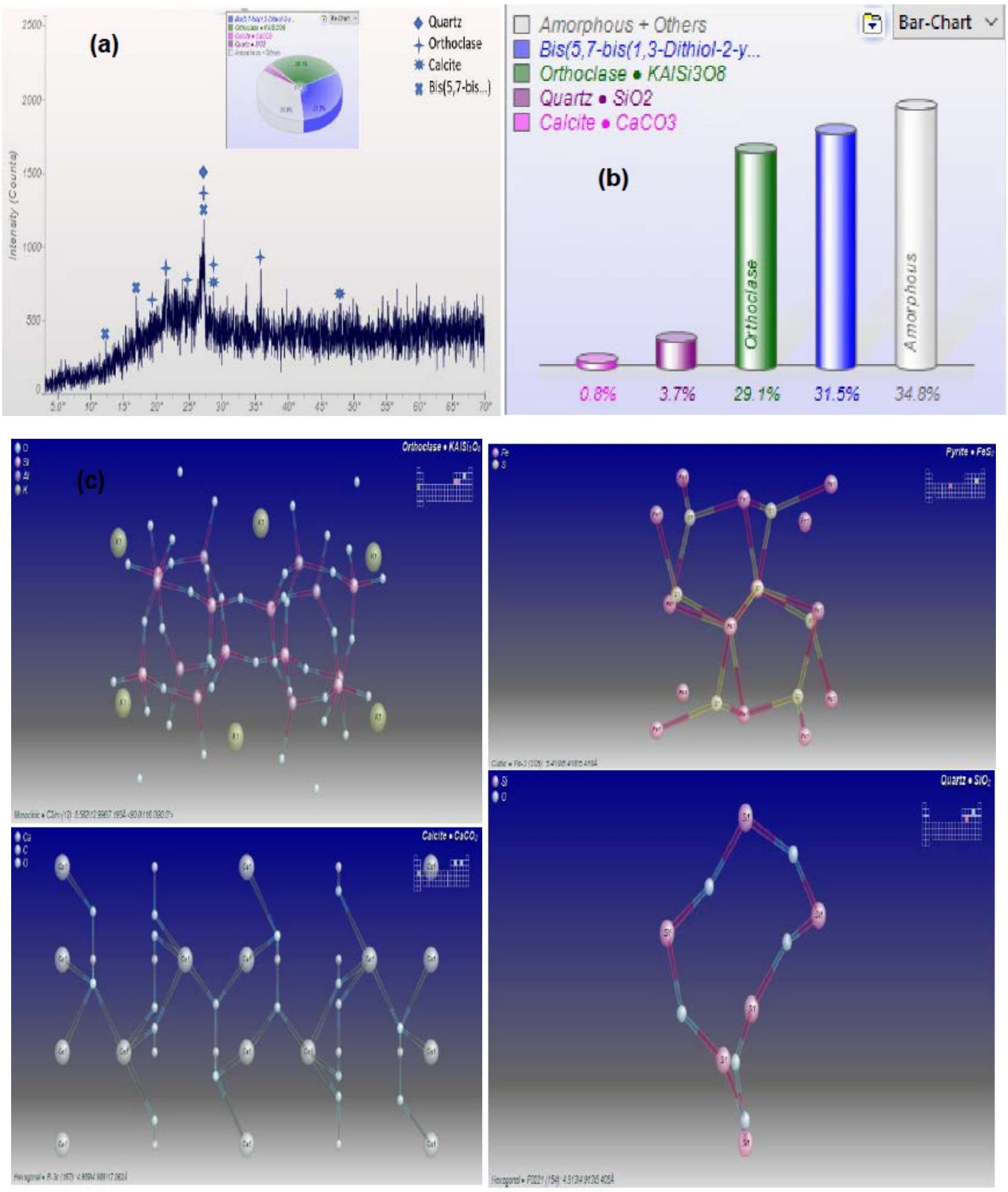
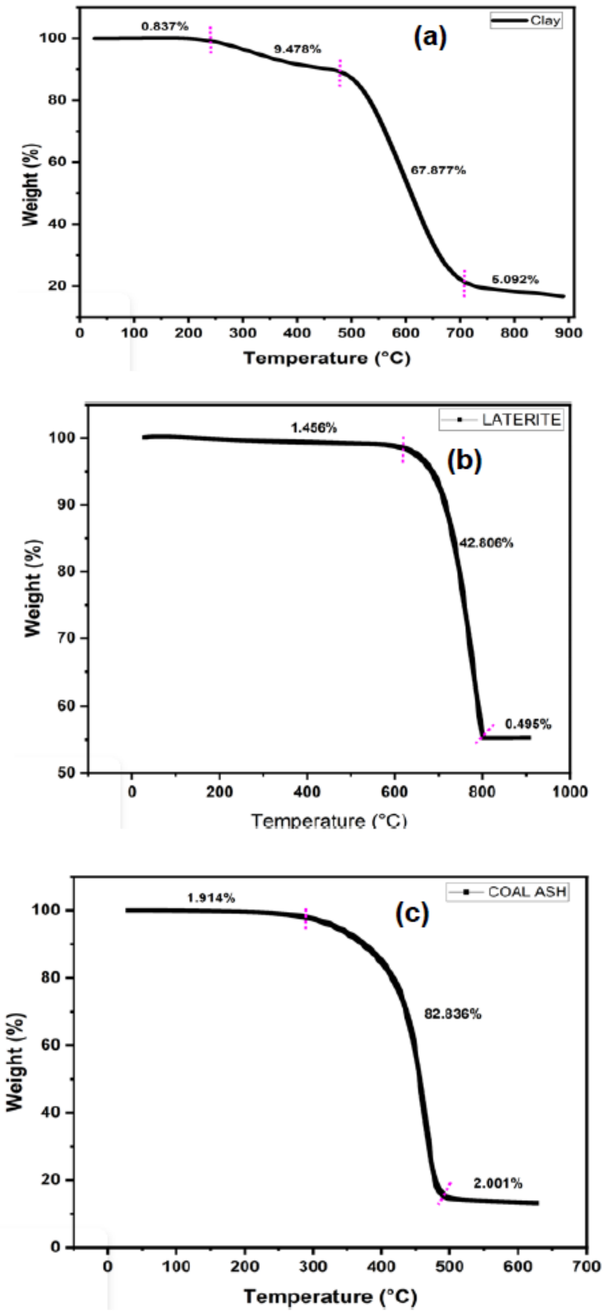


Figure 7. a) Diffractogram of clinker b) XRD diagram of clinker, c) Molecular structures

3.1.3. Thermal Behavior of Materials

3.1.3.1. Thermogravimetric Analysis

(TGA) TGA measures mass loss as a function of temperature, revealing thermal reactions such as evaporation, dehydroxylation, and chemical decomposition [14]. The thermograms (Figure 8) show the weight loss as a function of temperature for the three materials (clay, laterite, and slag). This analysis made it possible to observe the variation in mass as a function of temperature and to learn about the chemical composition, thermal stability, and decomposition reactions of these materials. The ATG thermogravimetric curve for clay indicates a major loss of mass (83.28%) between 400 and 700°C. This corresponds to mineralogical transformation (dehydroxylation of phyllosilicates). Laterite shows good thermal stability, with the main mass loss (44.75%) occurring above 400°C due to dehydroxylation. On the other hand, ash exhibits the highest thermal instability, accompanied by a significant loss (86.75%) at around 500°C, while laterite is the most stable of the three (Figure 8 (d)). These results are essential for the choice of materials in thermal storage applications or in the formulation of refractory bricks [11].



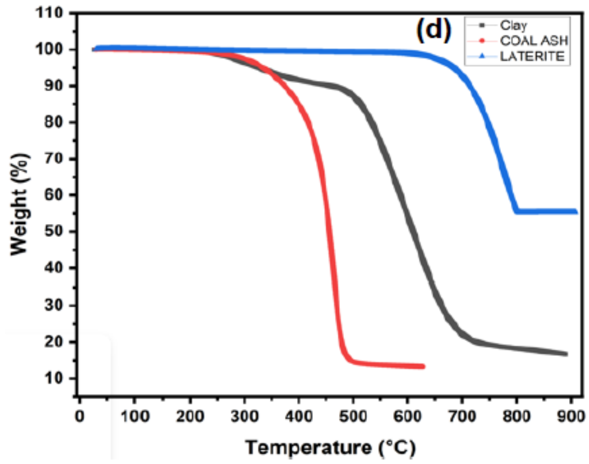
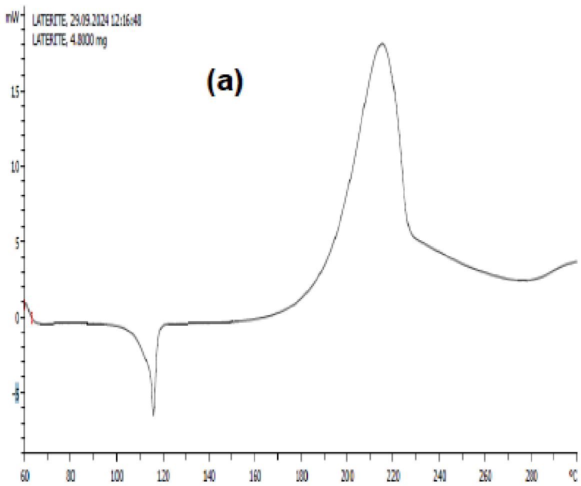


Figure 8. TGA curves: (a) Clay, (b) Laterite, (c) Clinker, (d) Three raw materials

3.1.3.2. Differential Scanning Calorimetry (DSC)

DSC (Differential Scanning Calorimetry) measures the difference in heat flow between a sample and a reference as a function of temperature [12]. The DSC of laterite (Figure 9(a)) shows a slight endothermic peak around 100-130°C, which probably corresponds to the loss of free water and adsorption. Significant thermal activity accompanied by an exothermic peak is visible between 130-220°C, which could correspond to the dehydroxylation of iron and aluminum hydroxides (goethite, gibbsite) present in laterite. After 220°C, thermal stabilization is observed, indicating the end of major transformations. The clay exhibits typical behavior with physical water loss <150°C, dehydroxylation of clay minerals (kaolinite, illite, etc.) around 180°C, and the onset of structural reorganization >250°C. Slag shows few clear peaks but a gradual exothermic behavior. This may correspond to the oxidation of residual carbonaceous or metallic materials (Fe, C) and amorphous (crystalline) recrystallization [10].



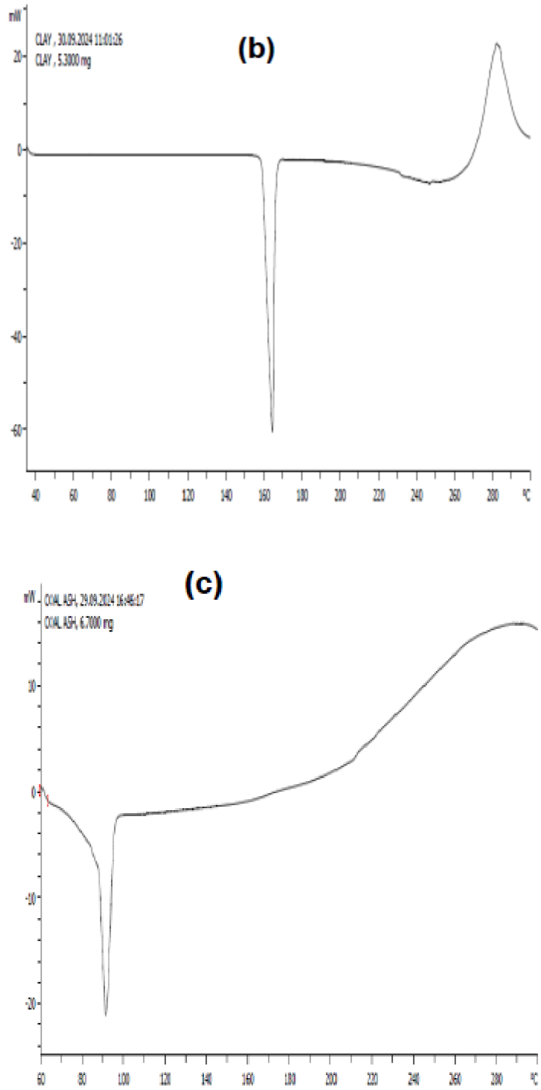


Figure 9. DCS of the sample of: (a) Laterite, (b) Clay, (c) Clinker

4. Conclusion

The use of solid materials suitable for high-temperature energy storage is part of the search for alternatives to more conventional options, with a view to reducing storage costs.

This work has characterized clay, laterite, and clinker raw materials using various characterization techniques to determine their storage potential for use as TESM in solar thermal power plants. The results obtained from the various analyses (X-ray fluorescence, XRD, ATG/ATD, DCS) confirm the possibility of developing refractory composite ceramics based on these solid materials (clay, laterite, and slag) for use in heat storage systems.

In our further research, we plan to optimize the proportions and particle size of the powders in the mixture of clay, laterite, and clinker raw materials to formulate a single terracotta composite material for use as a TESM (thermal energy storage material) in solar thermal power plants.

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