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# Study of the mineralogical and mechanical evolution of the miocene marls in the region of fez (morocco) during firing

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**Abstract**

The present study aims to valorize and promote Miocene marls taken from the Fez region (Koudiat Ben Jaliik) in the ceramics industry as well as the optimization of the firing temperature. As part of this work, we have examined the mineralogical, ceramic and mechanical characteristics of these marls after being fired in order to understand certain mineralogical transformations during the firing process as regards to the mechanical character of these materials. Based on the technological, mechanical and mineralogical examination of the marl during the firing process, it has been proved that the mechanical resistance is remarkably improved at T = 900 ° C, especially for BJ3. BJ3 has shown, on the other hand, a very remarkable rate of shrinkage variation especially between 700 ° C and 750 ° C arising out of the departure of carbonates and the transformation of quartz α to quartz β, which subsequently has led to defects in the final product.

## 1. Introduction

The present study focuses on the valorization of the Miocene marl in the purpose of attaining a sustainable local development. In fact, this study aims to contribute broadly to the promotion of local building materials while improving the quality of the materials produced [1-2]. As it is known that traditional pottery, for example, is still widely used in the form of terracotta pottery in many Third World countries [3].

The sediments used in this study is retrieved from the region of Fez called [6], it is used locally in traditional pottery manufacturing and stone paving [4;5]. We have carried out in this study a mineralogical, ceramic and mechanical characterization of these marls during firing in order to understand certain mineralogical transformations that occurs during this process, to infer their

relation with mechanical character of these materials as well as their potential in the industry of bricks and ceramics.

## 2. geographical area of the study area

The study area Kodiat Ben Jallik (Fig. 1) is part of Sais Plaine, which is limited structurally between The Rif in the north, and Middle Atlas in th south. The lambert geographical coordinates are: latitude: 34°02'14,8"N and longitude:4°56'56,9" W.

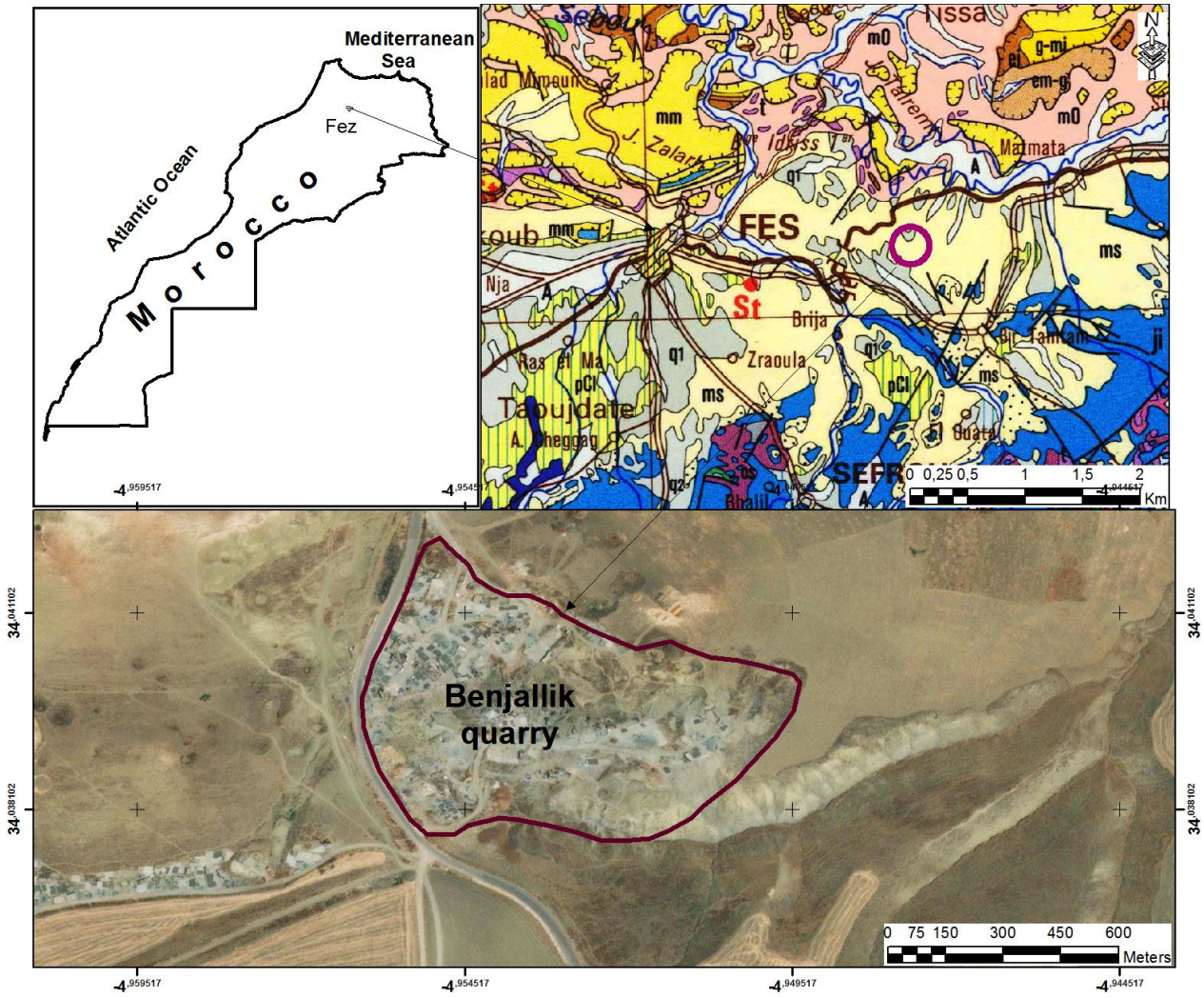


**Fig. 1.** Geographic map of the study area

## 3. Materials and methods

### *3.1. Sampling and Preparation of Sampling*

The basic raw material used in this study is a marl of the Miocene sequence that outcrops at the level of the quarry of Ben Jallik, in the region of Fez Morocco. We have taken three samples that require large quantities (more than 30 kg for each sample) to be studied. The table below contains the geographic coordinates of each sample with a brief description (Table. 1).

The samples are taken back afterwards to the laboratory, dried at ambient condition first, then in the laboratory oven, and finally sieved to 2 mm. The material obtained is, therefore, intended to be examined under different methods of characterization: ceramics, mineralogical and mechanical.

**TABLE 1.**The geographical coordinates of the three points of sampling.

| Sampling area | Coordinates (WGS84) | Samples | Lithostratigraphical level |
|---|---|---|---|
| **Quarry of Ben Jallik** | X:4°56'49,1"W<br>Y:34°02'18,2"N | BJ1:<br>Yellow | Upper Miocene |
| | X:4°56'53,2"W<br>34°02'16,9"N | BJ2:<br>Dark Blue | Upper Miocene |
| | X: 4°56'56,9"W<br>Y:34°02'14,8" N | BJ3:<br>Light Blue | Upper Miocene |

### *3.2. The Confection of Test Specimens and Technological Characterization*

For the fabrication of the briquettes (Fig.3) and cylinders (Fig.2), 2 kg of ground material for each sample was mixed with a quantity of water until achieving a malleable mixture, then this latter is left to remain in a desiccator for 24 hours, and then it is shaped in both tiles and cylindric forms using a metallic mold, we marked two diagonal segments on the upper side of the tiles , each 50 mm in length, and the sample references [6-7] .

After the molding process, we have weighted the test specimens and we have dried them in the ambient condition while constantly measuring (every 24 hours) their weight and length respectively using calipers till their weight and shrinkage are stabilized. Then we have dried the test specimens in the oven at 110°C and the same weighing and shrinkage measurement operation was repeated over at different temperatures, namely 700°C, 750°C, 800°C, 850°C, 900°C. C, 950°C in a programmable oven with a 30-minute level and a firing temperature degree of 10°C/ min.

**Fig. 2.** photo of cylinders after the firing process

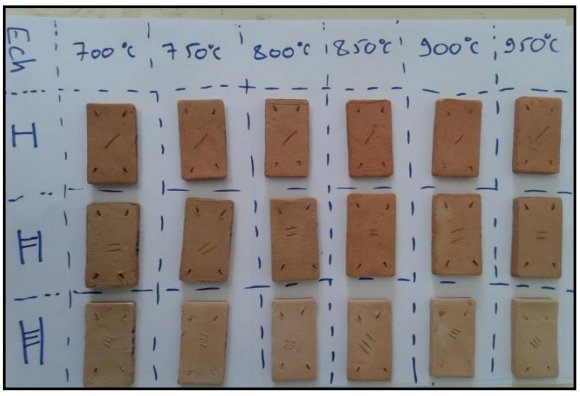


**Fig. 3.** picture of briquettes after the firing process

### *3.3. Structural Characterization Method: X-Ray Diffraction*

The mineralogy of the marls is determined for the raw samples at different firing temperatures by X-ray diffraction analysis (XRD) at the Technical Support Units for Scientific Research (UATRS) under the National Center for Scientific and Technical Research (CNRST) in Rabat (October 2015).

After, milling the dried and the fired samples till obtaining a smaller size than 100 µm, using the mortar grinder. These disoriented powder samples are exposed to X-ray diffraction between 0° and 90° 2 theta using a Philips XPERT-PRO "PW 3064-type apparatus, with copper Kα1,2 radiation [8;9].

### *3.4 Mechanical Characterization Methods*

The mechanical characterization is determined by two tests: the first is the three-point bending test (Fig.5) and the second is the compression test (Fig.6). These tests are executed using an electromechanical test machine EM550, with a capacity of 50 KN at the Materials Resistance Laboratory at the FST Fes (Fig.4).

**Figure 4.** Electromechanical testing machine em 550, 50 KN

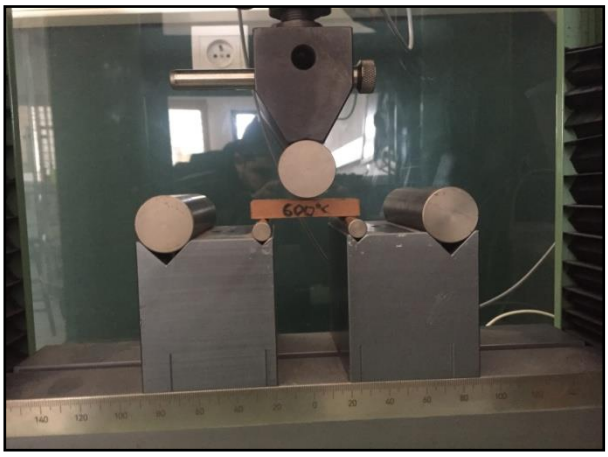


**Figure 5.** Three-point bending test

**Fig. 6.** Compression test

## 4. Results and discussion

### *4.1. Technological Characterization*

#### *4.1.1.* Shrinkage and Weight loss in the ambient condition

The curves of the evolution of shrinkage resulting from drying the three samples (Fig.7) are not perfectly stackable due to the incertitude coming from the random placement of the briquettes during the drying process. We found that the briquettes that are well exposed to air likely dry much faster by the evaporation of maximum quantity of water; this process is also facilitated by the weak structure of the elementary particles, consequently these briquettes show a greater shrinkage from the first day [10]. Add on to that the incertitude resulting from the placement of the marks that are used to take measurements of shrinkage during drying process as well as the air conditions.

It can be further stated that the evolution of shrinkage that results from the drying process and time that is restrictively conditioned by the amount of water as well as the arrangement of the briquettes.

We have noticed that the curves of the three samples have a steep slope during the first days. This is the first phase of the water loss where the three samples reach between 4% and 10%. The mineral particles tend, during this phase, to agglomerate and occupy the space left by evaporated gravitational water, after this process the curves become even. In this phase, the rest of the water is also removed, the evaporation affects the capillary water. The points of the contact between the solid particles are sufficient to ensure that the briquette stay in shape during the drying process which results in a slow-down of the shrinkage process. Hence, the slope becomes sub horizontal thing during the last days in the open air which signals the end of the shrinkage process. The end of this process is linked to the appearance of a number of sufficient points of contact between the particles in the sample due to the depletion of the imbibition water. As a result, the sample BJ3 constantly shows more or less a significant shrinkage compared to the rest.

Figure 8 (Fig. 8) shows the curves of the weight loss compared to time of our samples. According to the shape of the graph, there are 3 phases for each sample.
For BJ2 and BJ3:

- [J0, J1]: the curves show a declining trend from the first moment of their confection. This weight decrease apparently results from the evaporation of the gravitational water absorbed by our samples during the confection process. In addition, it is observed that the briquettes lose between 4% and 7% of the weight from the first day.
- [J5, J7]: The curves become gradually smooth and ascending since the rate of weight loss begins to decrease in this second phase as the stock of gravitational water almost run out.
- [J7, J9]: the rate of weight loss stabilizes from the seventh day because the gravitational water has run out.

For BJ1: we have the same observations except for the period of each phase which is offset by one day.

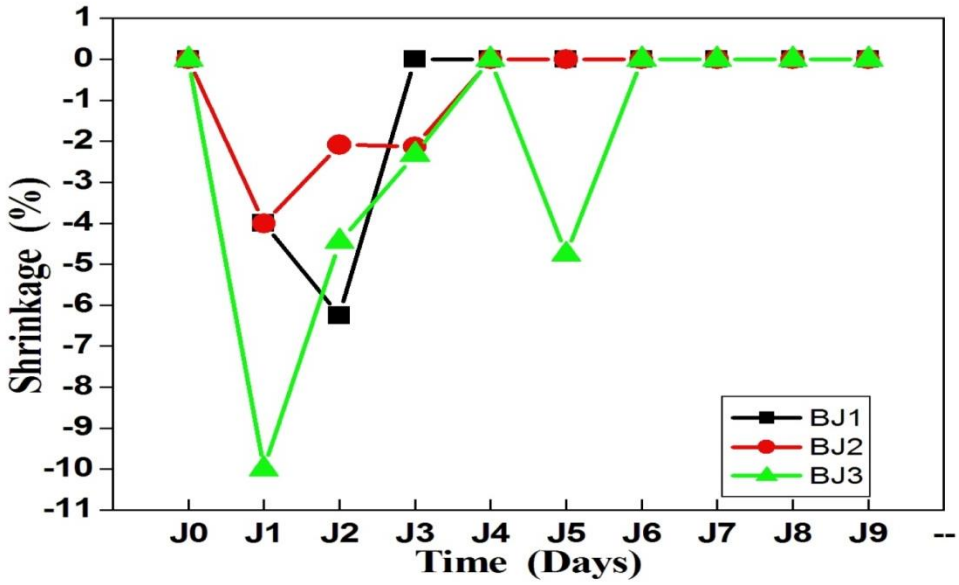


**Fig. 7.** Evolution of shrinkage in function of time (days)

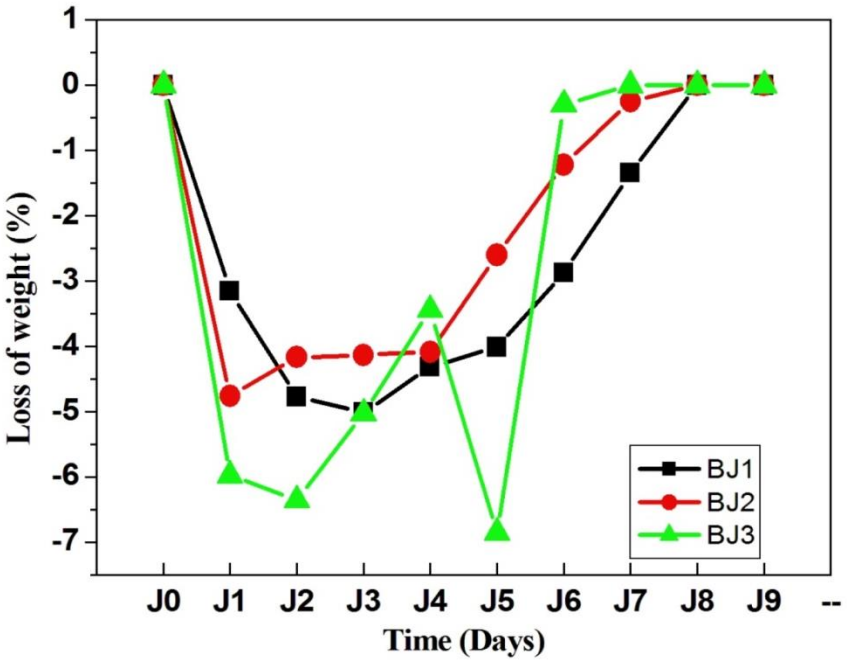


**Fig. 8.** Evolution of weight loss in the ambient conditons

### *4.1.2. Shrinkage and Weight loss During Firing process*

The observation of the graph below (Fig 9) indicates that the variation of shrinkage is low for BJ1 and BJ2. On the contrary, the sample BJ3 shows a very remarkable rate of change of shrinkage especially at temperature level 700 ° C and 750 ° C. This shrinkage is due to the loss of carbonates and the transformation of quartz α to quartz β [11].

In fact, the loss of weight (Fig 10) is generally attributed to the dehydration that is caused by the firing process. It also occurs because of the presence and the nature of the mineral species regarding their respective proportions and their alteration states. The quantification of the proportion of weight loss of each mineral species is, therefore, not feasible if not impossible in a mixture with several mineralogical components [12]. Indeed, in a oxidizing firing atmosphere, the weight losses are blurred due to the dehydration reactions.

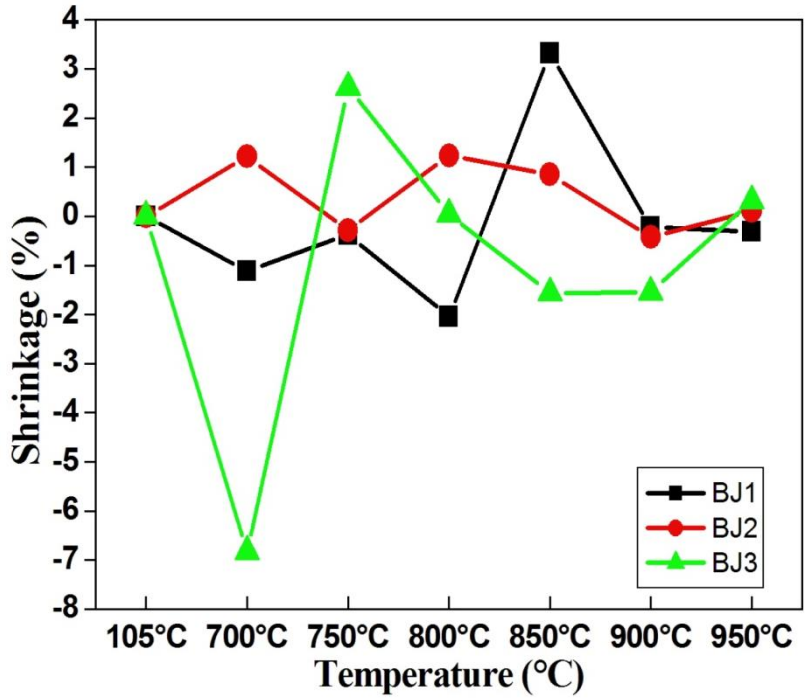


**Fig. 9.** Evolution of the shrinkage according to the firing temperature.

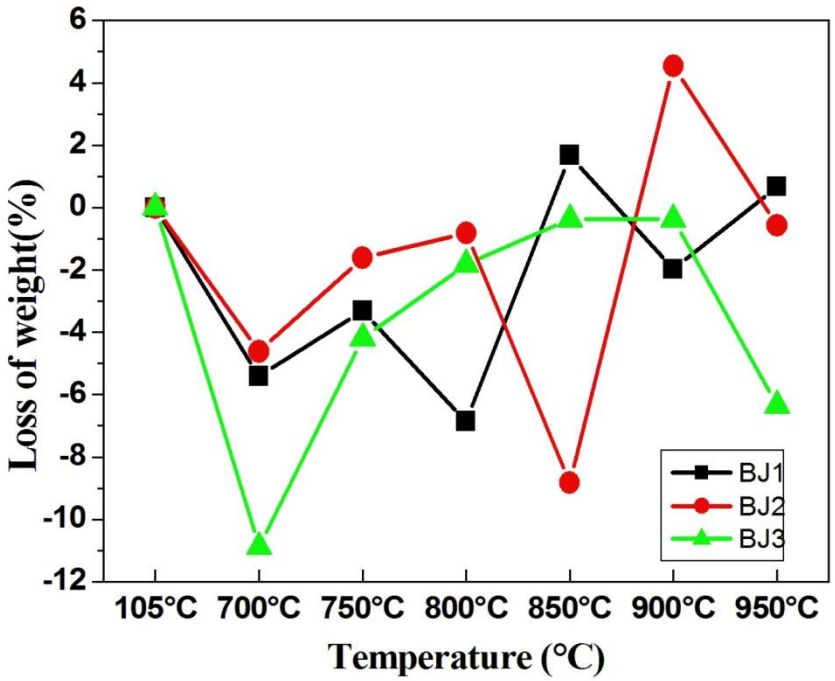


**Fig. 10.** Evolution of the weight loss according to the firing temperature.

### *4.2. Mechanical Characterization*

Both figures 11 and 12 illustrate respectively the variation of compressive strength and bending comparatively to the firing temperature. The analysis of BJ1, BJ2 and BJ3, indicates that the mechanical strength is most likely improved by the increased firing process.

The results obtained by the bending test are highly compatible with those of compressions. Based on this, we can significantly deduce that 900 °C is the typical baking temperature for marl, in

particular BJ3 shows a high mechanical strength that can go up to 725 N for bending and 13.8KN for the compression test.

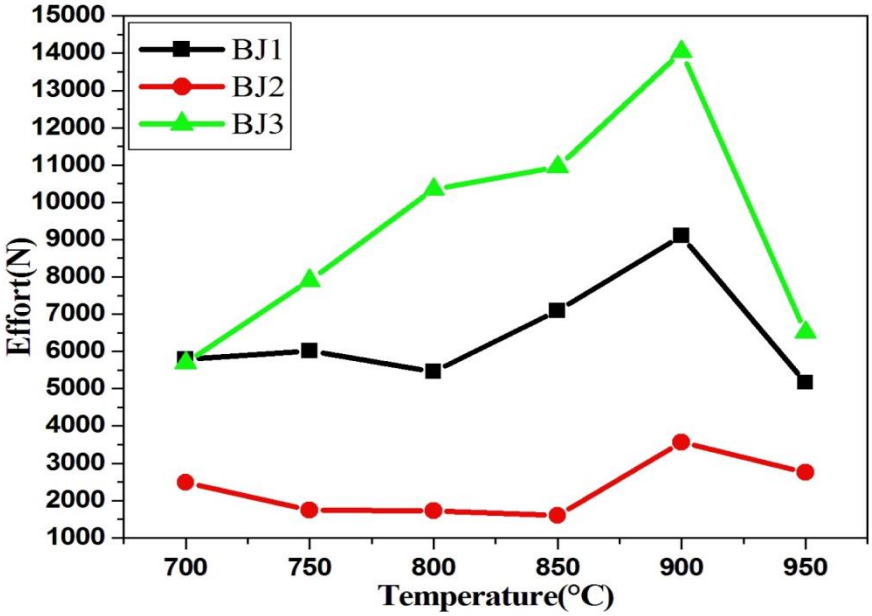


**Fig. 11.** Variation of resistance to compression according to cooking temperature

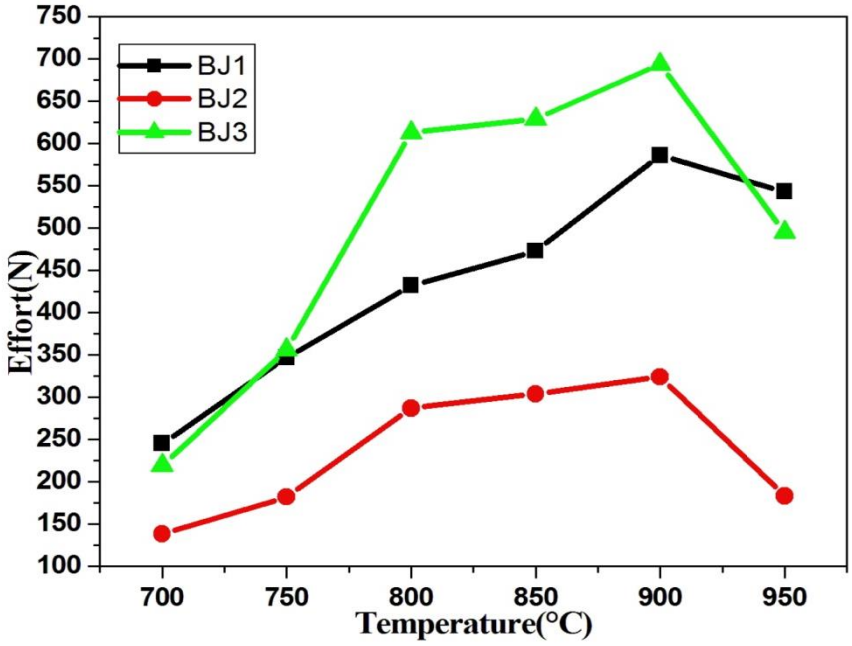


**Fig. 12.** Variation of resistance to bending according to cooking temperature

### *4.3. Mineralogical Characterization*

The X-ray diffraction of the different samples under study shows that they are mainly formed of calcite ($CaCO_3$), along with quartz ($SiO_2$). Hence, the presence of calcite and the absence of portlandite indicates that the binders are entirely carbonated [13].

We have further noticed through the analysis of the graphs that several mineralogical transformations have occurred such as:

– 750 °C to 850 °C, the carbonate $CaCO_3$ decomposes into quicklime (Calcium oxide) with release of $CO_2$ [6].

$$CaCO_3 \longrightarrow CO_2+CaO$$

– Beyond 850 ° C, the CaO disappears and new phases begin to form such as calcium silicates and calcium aluminosilicates (gehlenite) [18; 20]

– As an example, to illustrate this, CaO reacts with metakaolin at about 900 °C in accordance with the following reaction:

$$SiO_2,\ Al_2O_3+2CaCO_2 \longrightarrow SiO_2,\ Al_2O_3,2CaO+SiO_2+2CO_2$$

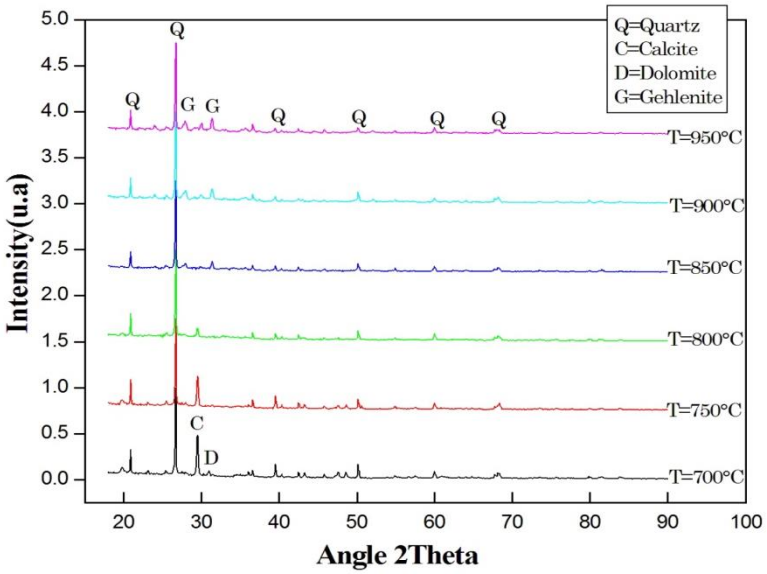


**Fig. 13.** Diffractogram of BJ1

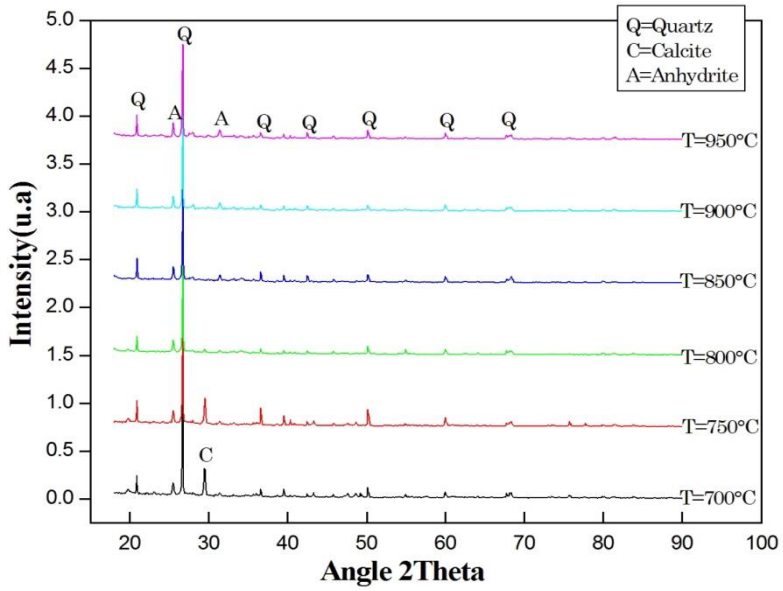


**Fig. 14**. Diffractogram of BJ2

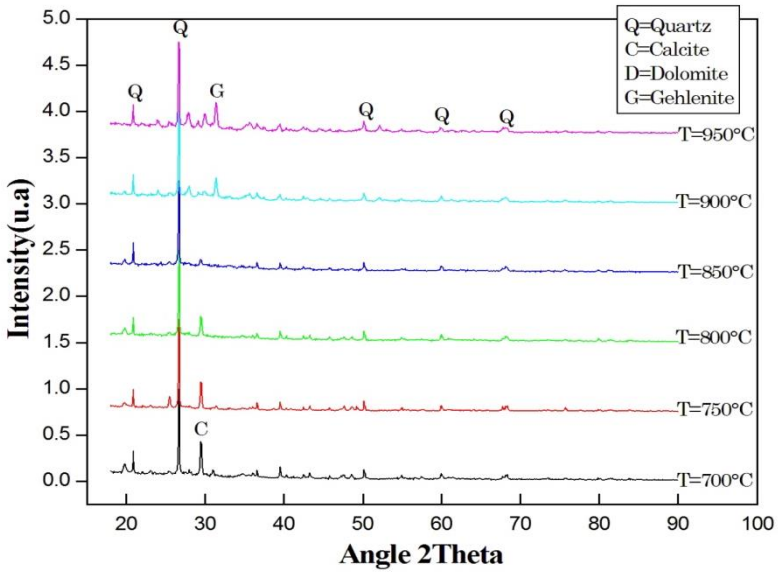


**Fig. 15**. Diffractogram of BJ3

## Conclusion

The analysis of the ceramic results has allowed us to deduce from the Bigot curve that the rate of variation of the shrinkage of briquettes in the open air of the three samples is moderately high, in particular for Sample 3 (BJ3). The three samples have reached the rate 4% and 10% of the shrinkage since the first days. It has been found during the firing process that the shrinkage variation is low for Sample 1 (BJ1), and Sample 2 (BJ2), unlike the sample 3 (BJ3) shows a very remarkable shrinkage variation rate especially at a temperature of 700 °C and 750°C.

The tests of compression and bending have shown, on the one hand, that the mechanical resistance of marls is greatly improved by firing, on the other hand, it has been deduced that the ideal temperature for firing is 900 °C.

The X-ray diffraction of the different samples shows that they are mainly formed of calcite ($CaCO_3$), quartz (SiO2), but during the firing process, we have noted the disappearance of calcite and the appearance of a new phase (Gehlenite).

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