

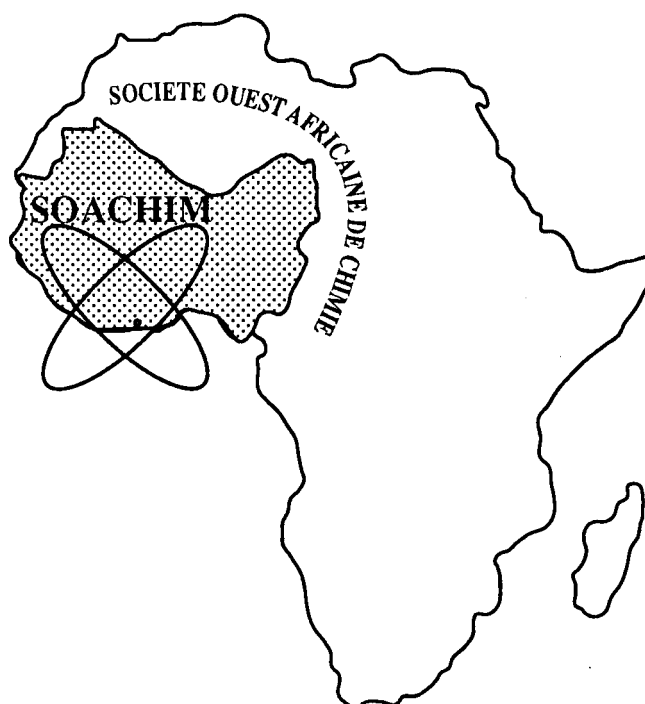
Densification behaviour of chamotte grog for refractory bricks: mineralogy and microstructure

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Journal de la Société Ouest-Africaine de Chimie

J. Soc. Ouest-Afr. Chim.(2016), 041 : 1 - 10

21^{ème} Année, Juin 2016



ISSN 0796-6687

Code Chemical Abstracts : JSOCF2

Cote INIST (CNRS France) : <27680>

Site Web: <http://www.soachim.org>

Densification behaviour of chamotte grog for refractory bricks: mineralogy and microstructure

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(Reçu le 21/05/2016 – Accepté après corrections le 10/10/ 2016)

Abstract : The paper deal with the densification behaviour of chamotte grog made with raw clay material at high temperature. The sintering conditions as temperature (1100, 1200, 1300 and 1400°C) temperature time (0.5; 1 and 2hours) have been varied to check the optimal condition to produce grog with better characteristics. The relationship between the mineralogy, microstructure of grog with its densification parameters have been studied using X-ray diffraction and scanning electron microscopy. From 1300°C with 1hour as temperature the obtained grogs are characterized by dense microstructure with some isolated pores. The mineralogy of these grog is composed essentially by mullite, cristobalite and residual quartz.

Keywords: Raw clay, Chamotte grog, densification, mullite, cristobalite, Refractory brick

Densification d'une chamotte pour l'élaboration des briques réfractaires : minéralogie et microstructure

Résumé : l'article est consacré à l'étude de la densification d'une chamotte produite à partir d'argile naturelle à température élevée. Cette argile a été extrudée puis frittée à différentes températures (1100, 1200, 1300 et 1400°C) avec des paliers variés (0,5 heure, 1 heure, et 2 heures) dans le but de déterminer les conditions optimales de production d'une chamotte de qualité. Le rapport entre la minéralogie, la microstructure de la chamotte avec ses paramètres de densification ont été étudiés en utilisant la de diffraction des rayons X et la microscopie électronique à balayage. A partir de 1300°C et de palier 1 heure on obtient de la chamotte dense avec des pores isolés. La minéralogie de ces chamottes est composée essentiellement de la mullite, la cristobalite et du quartz résiduel.

Mots clés : argile, chamotte, densification, mullite, cristobalite, brique réfractaire

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1. Introduction

Refractory materials are extensively used in most of production and treatment processes involving high temperatures [1-3]. The refractory materials are used as crucibles by mining and metallurgists for metal casting and as filter for liquid at high temperatures [4, 5]. In this important type of materials are used since they present specific thermal, chemical and physical stability. These exceptional properties are closely related to the specific elaboration processes (pressure, flow, temperature,) and to the type of used raw materials (clay, silica, alumina, carbon, magnesia).

Alumina silicate refractories are greatly used in the fields mentioned above [6]. They are generally produced with kaolin-quartz mixtures material using typical clay - chamotte process. The final product properties are depending to the densification performance such as density, porosity and water absorption of the grog [7]. The production of best refractory material using the grog needs the optimization of grog characteristics. The densification is governed by the mineralogy and microstructure change during the sintering process.

In this context, this work is devoted to the optimization of grog obtained with a raw clay material from Burkina Faso. The first part describes the chemical, geotechnical and mineralogical characterization of the raw clay material. The second part is focused on the study of densification properties of chamotte according to mineralogy and microstructure evolution.

2. Materials and methods

2.1. Geological context of the raw material site

The raw material used in this work, referenced SAB, is from a deposit in Sabcé village, in the North Central (region) of Burkina Faso. The location of SAB on the map of Burkina Faso corresponds to 13.23 ° North and 1.54 ° West (**Figure 1-a**).

The geological environment (**Figure 1-b**) of the site consists mainly of granodiorite, basalt and volcano-sedimentary schist [8]. According to relative chronologies based on previous work [9-10] and airborne observation of images, the granodiorites are intrusive in volcano-sediments. The ground observations, especially at site levels, show a relatively abundant vein of quartz with a NE-SW average orientation.

The raw clay site is located essentially in eastern flank of volcano-sedimentary hills. The alteration profile is fairly important in respect of the presence of quartz veins, and probably results from an hydrothermal activity on one hand. As the explanation is from the location of the site in the side of Lake Bam, that induces a dense east draining system. These processes are probably favored by hydrothermal alteration but also from a contribution of a meteoric chemical alteration. The area of the clay site is around 350000 m².

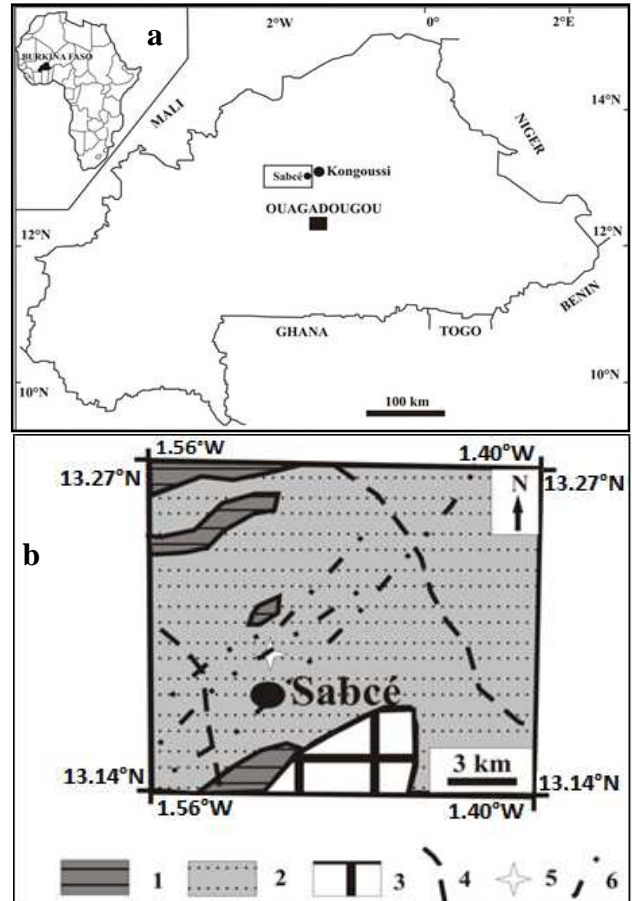


Figure 1: a- Localization of Sabcé site; b- Geological map of the argillaceous site
1- Basalt, 2- Schists volcano-sedimentary, 3- Granodiorite, 4- Rivers, 5- argillaceous Site, 6- quartz Seam

2.2. Characterization of raw material

The chemical composition of the raw material was determined using ICP-AES technique.

The mineralogical composition of SAB was performed using X-ray diffractometer (Bruker D5000) operating at 40kV and 40mA and using Cu K α radiation.

The thermal analyses of SAB have been recorded

with DTA / TG equipment SETARAM Setsys 24 with 10°C/min as heating rate.

The sintering behaviour of SAB is observed using a dilatometer MISURA 3.32 with 5°C/min as heating rate.

Atterberg limits (liquid limit, plastic limit and plastic index) have been determined according to NF P 94-051 standard [11]. The density and BET surface of raw particle are respectively determined with helium pycnometer and BET methods.

2.3. Formulation and characterization of chamotte grog

The chamotte grog formulation starts with the grounding of SAB. The material has been finely grounded into particle sizes finer than 280 µm. The obtained powder has been moistened up to 31 wt. % and mixed during 30 minutes. The resulting paste has been extruded using an extruder (SHIMPO NVA-04S) and cut in the form of cylinders. After drying at 110°C for 24 hours, the pellets have been sintered at different temperatures: 1100, 1200, 1300 and 1400°C using a Nabertherm furnace with 5°C/min as heating rate. For each sintering temperature, three temperature stages were used: 0.5; 1 and 2 hours. After sintering, the different chamotte have been characterized to determine their bulk density (BD), open porosity (OP) and water absorption (WA), according to the ISO 10545-3 standard [12].

The bulk density BD (g/cm³) is obtained using the equation (1):

$$BD(g/cm^3) = \frac{P_2}{P_3 - P_4} \quad (1)$$

The open porosity OP(%) is the relation between the volume of open pores to the exterior volume of the specimen. Its value is determined with the equation (2).

$$OP(\% vol) = \frac{P_3 - P_2}{P_3 - P_4} \times 100 \quad (2)$$

The water absorption is the relation of the mass of water absorbed to the mass of the fired specimen. It is calculated with the equation (3).

$$WA(\%) = \frac{P_3 - P_2}{P_2} \times 100 \quad (3)$$

In the last three different equations, P₂, P₃ and P₄ are respectively the mass of fired chamotte, saturated mass in water of fired chamotte and hydrostatic mass of fired chamotte.

The evolution of mineralogical composition of the fired chamotte has been determined using

X-ray diffraction with a Bruker D5000 operating at 40kV – 40mA and using a graphite monochromatic Cu Kα radiation. Each piece of grog has been finely grounded, finer than 80µm, before the test.

Microstructural evolution has been observed by scanning electron microscopy. For each piece of grog, experimented temperatures and temperature stages were examined by SEM.

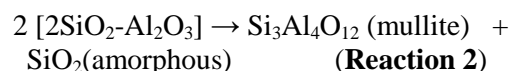
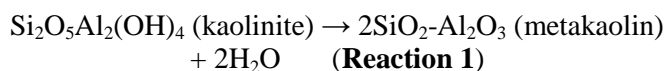
3. Results and discussion

3.1. Characterization of the raw material

The chemical composition of the raw material is shown in **Table I**. Alumina and silica are the major chemical components. The global chemical composition of clay – based refractory contains 20 - 45 wt.% Al₂O₃, 1 - 4 wt.% TiO₂, ≤ 2.5 wt.% Fe₂O₃ and ≤ 4 wt.% for the sum Na₂O + K₂O + CaO + MgO [1, 13]. The chemical composition of SAB agreed well with the required values for raw clay used in refractory elaboration.

The mineralogical composition of SAB shown by the **figure 2** indicated that quartz (SiO₂), kaolinite (Al₂Si₂O₅(OH)₄) and illite ((K, H₃O) Al₂Si₃AlO₁₀(OH)₂) are the main mineral phases. As the chemical composition, the mineralogical composition allows SAB to be used in refractory elaboration. Kaolinite and quartz are commonly used to produce silica – alumina refractory composed essentially by mullite and silica in amorphous or crystalline (quartz, cristobalite) form [14]. Kaolinite is the source of mullite formation and the quartz the source of crystalline or amorphous quartz.

The DTA /TG of SAB (**figure 3**) shows two main peaks and one shoulder. The two peaks at 535°C and 1000°C correspond to the successive transformations of kaolinite according to the typical reactions 1 and 2 [15]. The shoulder at 573°C shows the presence of quartz and is related its allotropic transformation from quartz α to quartz β.



By coupling the mineralogical and chemical results, a semi-quantitative estimation can be done. **Table II** presents this semi-quantification with 45 wt.% quartz, 40 wt.% kaolinite, and 13 wt.% of illite.

Geotechnical results of SAB are summarized in **Table III**. The different results corroborate those of mineralogy. The feeble value of specific surface is

related to the important amount of quartz. Atterberg limits indicate feeble plastic clay which was also predictable from the mineralogical composition in which quartz predominates. The dilatometric curve of SAB is presented in

figure 4. We note a shrinkage characteristic of kaolinite at 538°C and at 573°C for the quartz [16, 17]. The material densification begins at 960°C and up to 1115°C. The total shrinkage during the sintering is very limited that is an interesting property of the refractory used.

Table I : Chemical composition of SAB

Oxydes	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	PF	Total
%	69.09	20.55	0.85	0.00	0.12	< LD	0.49	1.45	0.95	< LD	6.10	99.60

LD = Limit of Detection

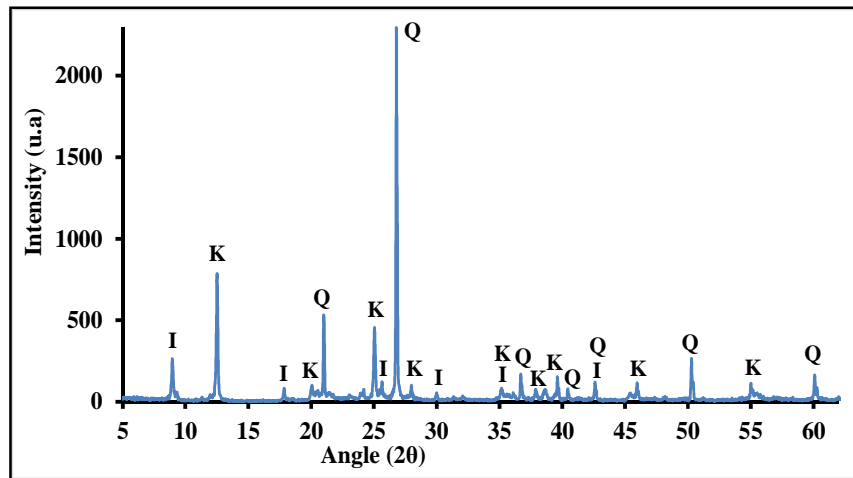


Figure 2: X-ray Diffraction of SAB; K = kaolinite, Q = quartz, I = illite.

Table II: Mineralogical composition of SAB

Phases	Kaolinite	Quartz	Illite	Total	Balance
%	40	45	13	98	2

Table III: Some geotechnical properties of SAB

Properties	SAB
Density (g/cm ³)	2.66
BET Surface (m ² /g)	3.16
Water content (%)	0.29
Loss on ignition (at 1000 °C) (%)	6.43
d ₁₀ (μm)	2.24
d ₅₀ (μm)	6.32
d ₉₀ (μm)	21.67
Liquid limit, W _L (%)	32
Plastic limit, W _P (%)	16
Plasticity index, I _P (%)	16

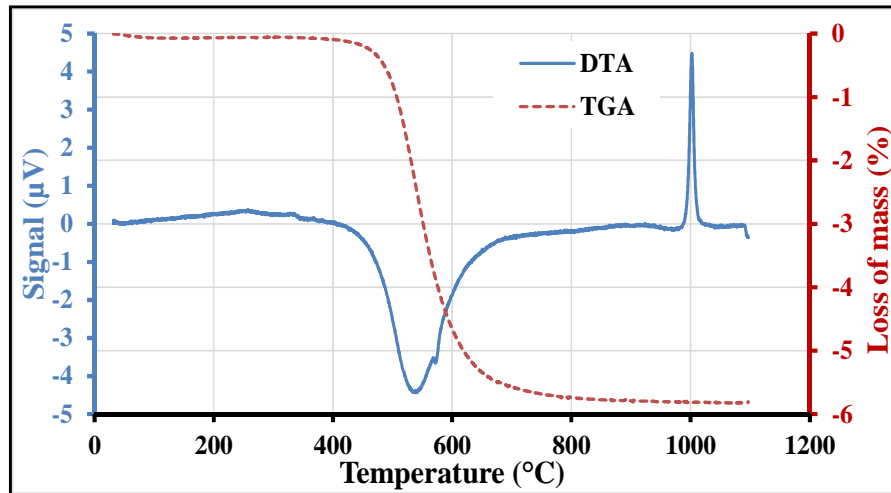


Figure 3: DTA/TGA curves of SAB

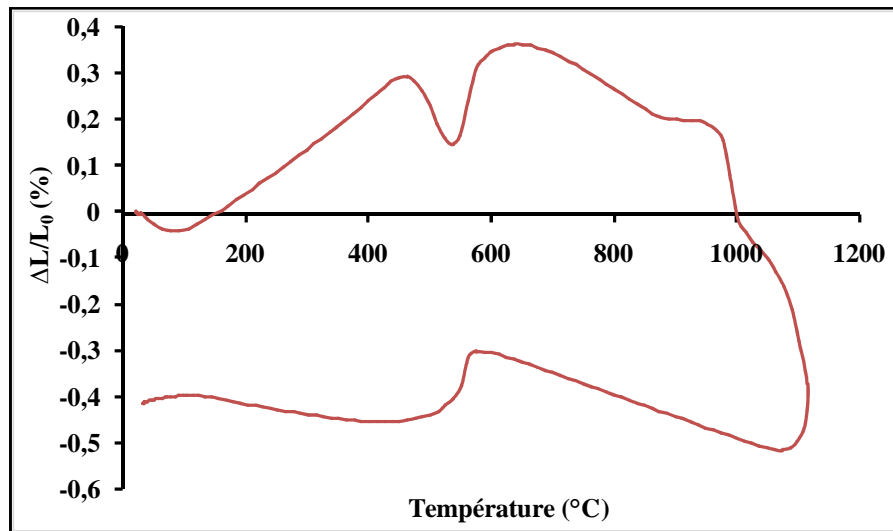


Figure 4: Dilatometric analysis of SAB

3.2. Densification parameters of the chamotte grog

The bulk density of chamotte according to sintering temperature and bearing is shown by **figure 5**. The bulk density increases with temperature. In general, long temperature stage improves the density of chamotte. Between the temperature stage of 0.5 and 1 hour, the density is significantly increased. With the feeble temperature stage, the temperature effect is more pronounced. Beyond temperature stage of 1 hour, the change in density is very small.

Figure 6 presents the evolution of open porosity following the sintering temperature and its temperature stage. The porosity decreases with increasing the firing temperature. This decrease of

the porosity is more pronounced above the temperature of 1200°C. In this temperature area, the temperature stage also contributes to porosity reduction. However, the effect of temperature stage in the open porosity variation is less important than that of density. Only at temperature of 1300°C, a slight difference is observed for 2 hours temperature stage.

The water absorption according to sintering temperature and temperature stage is shown in **figure 7**. The evolution of water absorption is similar to that of open porosity. We note a greater decrease of the water absorption above 1200°C. The effect of temperature stage on the water absorption is slightly more pronounced than that of open porosity.

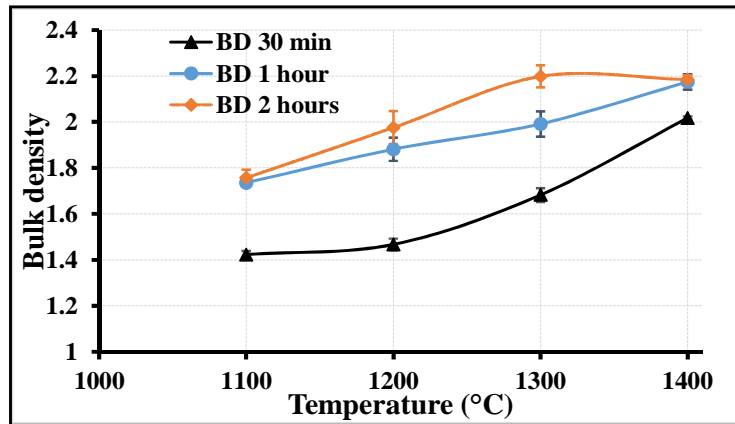


Figure 5: Evolution of the bulk density according to the temperature and the temperature stage

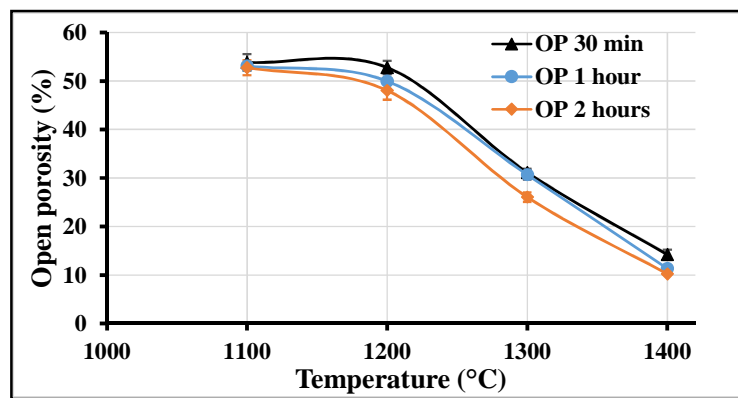


Figure 6: Evolution of the open porosity according to the temperature and the temperature stage

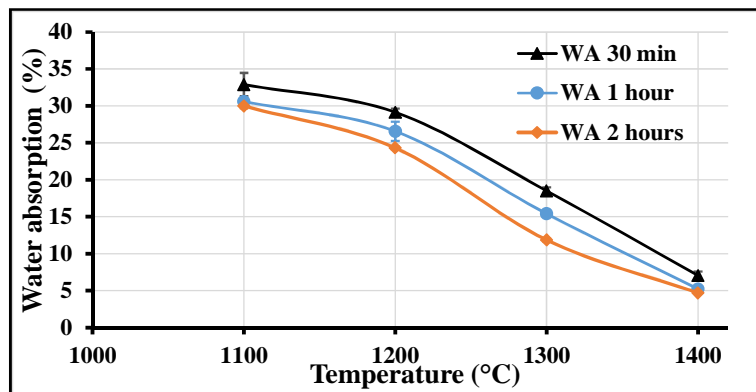


Figure 7: Evolution of the water absorption according to the temperature and the temperature stage

3.3. Mineralogy of chamotte grog

The evolution of the mineralogical composition of chamotte grog depending to sintering temperature and temperature stage is observed in the diffraction patterns of **figures 8, 9** and **10**. For all the diffraction patterns, the peaks of kaolinite

and illite completely disappeared leaving only the peaks of quartz. New phases were formed namely cristobalite and mullite. Whatever the used sintering temperature stage, the mullite formation starts at 1100°C. Its quantity increases with temperature and temperature stage. The amount of quartz decreases with temperature and is more pronounced above

1300°C. At 1400°C, the peak of quartz is greatly reduced into a small peak. Contrary to quartz, the peak of cristobalite appears above 1300°C and becomes important at 1400°C. Here, the effect of sintering temperature stage is clearly shown. It

means that long time temperature stage favors the disappearance of quartz to form cristobalite. The quantity of mullite seems to not be affected by the temperature stage but mostly by temperature.

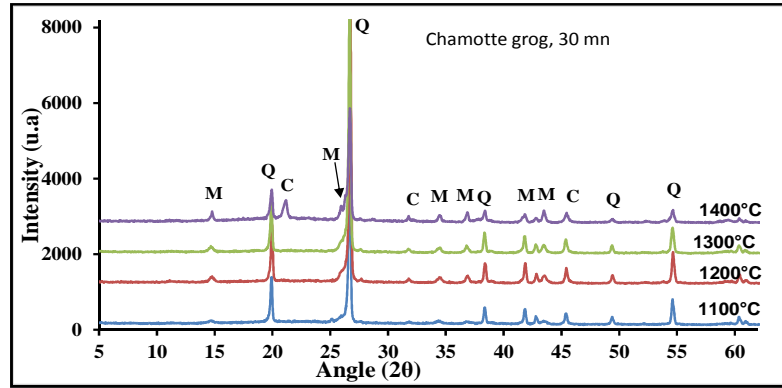


Figure 8: diffractograms of chamotte grog at various temperatures and temperature stage of 30 min

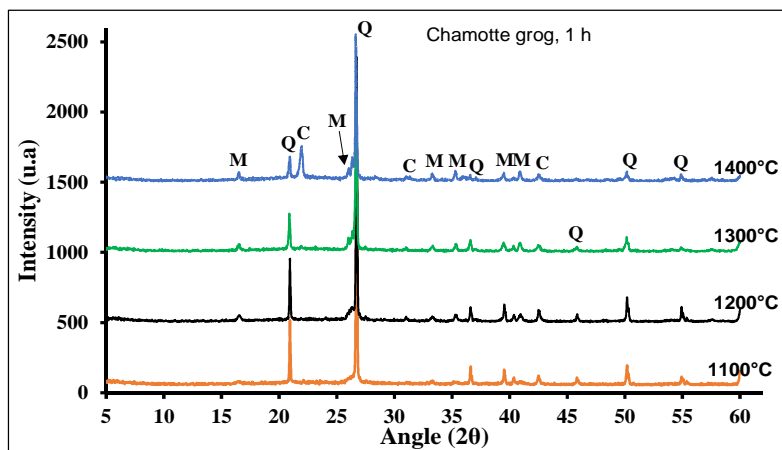


Figure 9: diffractograms of chamotte grog at various temperatures and temperature stage of 1 hour

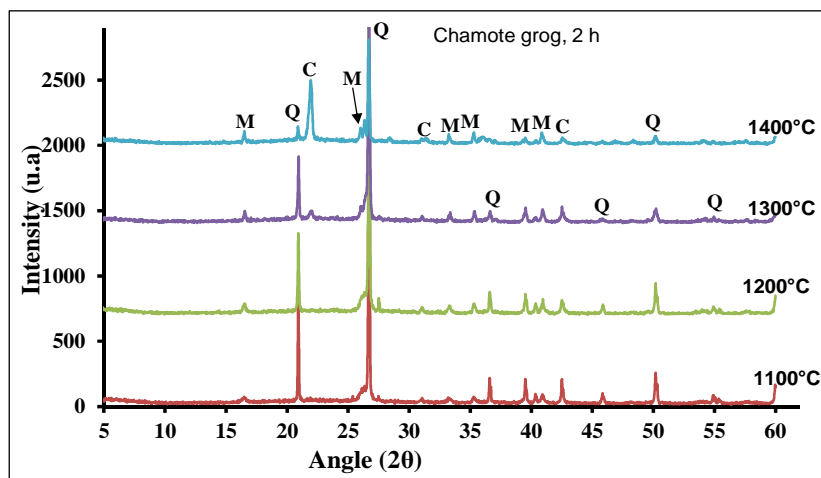


Figure 10: diffractograms of chamotte grog at various temperatures and temperature stage of 2 hours

3.4. Microstructure of chamotte grog

The SEM images of chamotte at different temperatures with different temperature stages are given in **figures 11** and **12**. At 1100°C, images are characterized by large numbers of sheet platelets. The edges of most of sheets are broken. At 1200°C, platelets disappear and the densification of the

chamotte starts. At 1300°C, the densification increases with the formation of a liquid phase and of mullite. At this temperature, the porosity remains interconnected. The amount of liquid phase and mullite increases at 1400°C and interconnected pores disappear to form a few isolated pores. The quantity of liquid phase is more important with temperature stage of 2 hours.

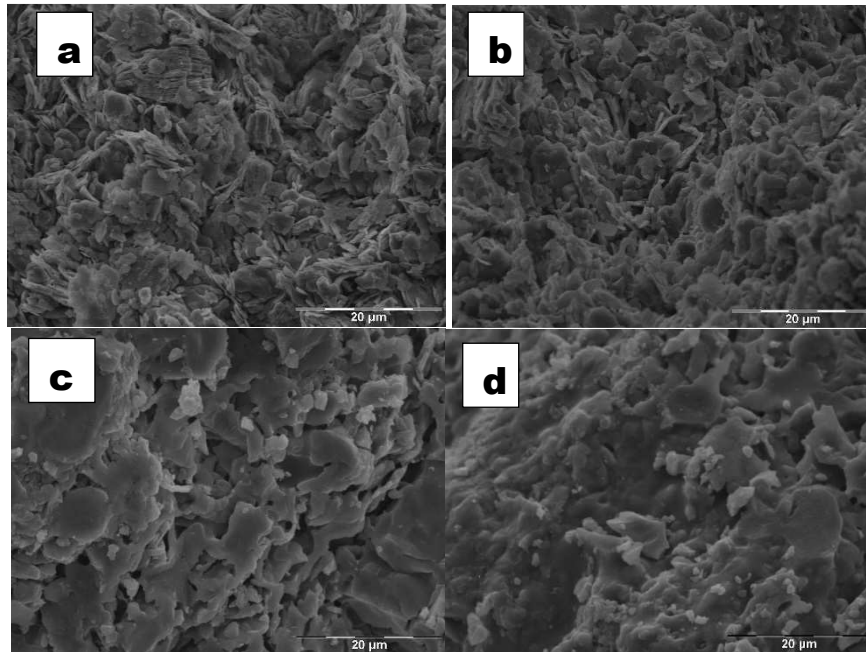


Figure 11: SEM images of chamotte grog at various temperatures and temperature stage of 1 hour: a = 1100°C. b = 1200°C. c = 1300°C. d = 1400°C

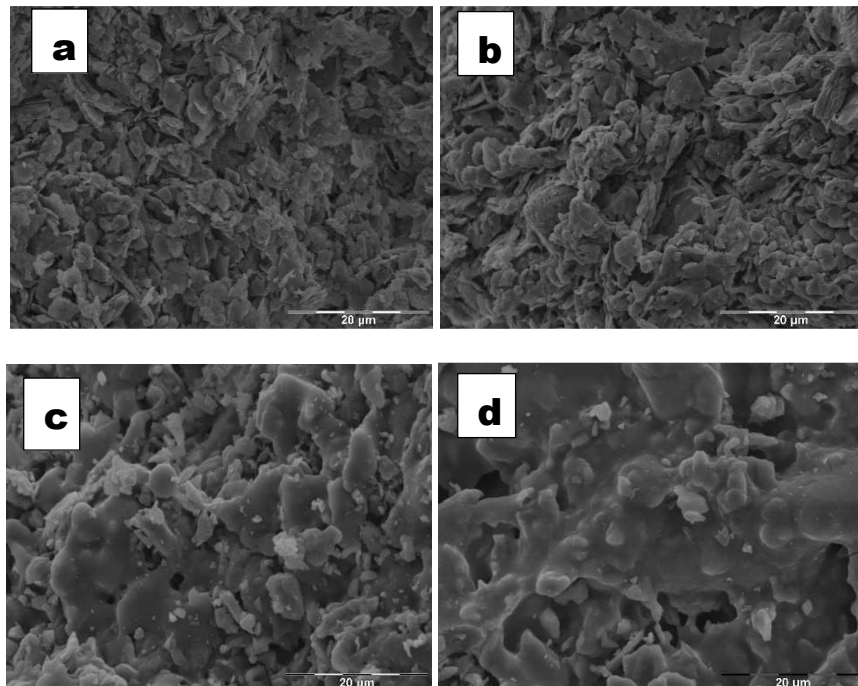


Figure 12: SEM images of chamotte grog at various temperatures and temperature stage of 2 hours: a = 1100°C. b = 1200°C. c = 1300°C. d = 1400°C

3.5. Discussion

Kaolinite and quartz are the main phases in the initial material mixture. During the sintering, the kaolinite is transformed successively and progressively into metakaolinite and mullite. The quartz participates in the formation of a liquid phase in the presence of alumina and alkali. Free silica obtained from the mullite formation and the remaining quartz after dissolution gives a liquid phase. It participates together with temperature in the formation of cristobalite^[18].

Indeed, at 1100°C, the mullite recrystallization begins from only metakaolinite transformation. Its initial quantity is very low at this temperature according to the important presence of broken platelets of metakaolinite (figure 11, 12). The densification of chamotte is therefore not possible since the significant presence of metakaolin platelets. This behaviour corroborates the results of density, porosity and water absorption (figure 5, 6, 7). With increasing temperature, the amount of formed mullite increases when temperature attains 1200°C, but an important quantity of quartz is remaining in chamotte (figure 8, 9, 10). The remaining presence of quartz indicates that its dissolution has not started and that its presence is responsible in the lack of a significant improvement of properties despite the increase in the amount of mullite. Quartz dissolution becomes effective above 1300°C by the combined action of alkaline oxides K₂O and temperature. The dissolution of quartz is responsible in the formation of a silicate liquid phase, which induces the decreases of open porosity and water absorption. At 1400°C, the quantity of glassy phase is very important and improves greatly the properties by reducing the open porosity of the chamotte. The amount of mullite is also improved significantly in the temperature range of 1300 - 1400°C inducing the dissolution of alumina, to give a secondary mullite phase. The combined action of the secondary mullite and the liquid phase consolidates the chamotte properties. Thus, with the temperature we have the densification of the chamotte by agglomeration or by reaction between the particles of the raw material. These reactions are fusion-reaction of particles from the formation of a liquid phase. This densification corroborates the values of bulk density and open porosity of the chamotte. An increase of temperature increases densification by reducing the pores volume; which reduces the water absorption. During sintering, cristobalite is formed from 1300°C. It results from the conversion of free silica that has not participated in the formation of the liquid phase. At 1400°C, the

obtained chamotte is mainly composed of mullite and cristobalite with small proportions of quartz. Sintering temperature time influence the amount of formed mullite and liquid phase and this is more pronounced at elevated temperatures of 1300 and 1400°C. With long temperature stages, the amount of liquid phase and cristobalite quantity is higher and thus contributes to improve physical properties. The bulk density and open porosity of chamottes are very interesting compared to the literature data on refractory bricks. Indeed, the obtained values density and porosity of the chamotte are better than those found by Seynou and al^[19] during the refractory brick elaboration. At 1400°C and for a 2 hours bearing time, Seynou and al have obtained values of 1.87 g/cm³ as bulk density and 23.92% as open porosity. With a firing temperature of 1300°C and for a 2 hours as temperature stage, our grog chamotte density attains 2,1g/cm³ and its open porosity is 25%.

The results of the technological properties of chamotte are better above 1300°C and for a 1 hour temperature stage. Mineralogy and microstructure also show the presence of recrystallized phases in large quantities.

4. Conclusion

Chamotte grog obtained with Sabcé raw clay presents physico-chemical, mineralogical and microstructural properties related to processing conditions such as temperature and temperature stage. The densification parameters namely density, porosity and water absorption change positively with the temperature and the temperature stage. This result is closely related to the mineralogical evolution of grog. With the increase of the firing temperature, kaolinite and illite disappear and favour the reduction of mullite and quartz to form cristobalite. Both a temperature increasing and the fluxing action of alkaline caused the dissolution of quartz into a glass phase. The new formed phases and the liquid phase transform the microstructure of the chamotte, inducing a consolidation and the disappearance of connected open pores. These transformations are more significant from 1300°C with 1 hour temperature stage. From this temperature and temperature stage until 1400°C, the evolution of different properties is low. Thus, for energy issues, we believe that the temperature of 1300°C and temperature stage of 1 hour must be used to obtain a dense grog for the development of refractory bricks.

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