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Production of porous firebrick from mixtures of clay and recycled refractory waste with expanded perlite addition

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Abstract
Production of porous and lightweight bricks with acceptable flexural strength is accomplished. Expanded perlite was used as an additive to an earthenware brick to produce the pores. SEM-EDX, XRD and XRF analysis of the raw materials and the elaborated refractory were performed. Mixtures containing perlite were prepared at different proportions (up to 30% Vol.%). Apparent porosity at 1600°C was investigated with the bulk density, water absorption, firing shrinkage and flexural strength. Microstructural investigation was carried out by both natural light microscopy and polarized light microscopy. The results obtained showed that the samples tested here maintained their shape without undergoing any deformation up to 1600°C. The use of expanded perlite decreased the fired density of the bricks down to 1.55g/cm^3.

*Keywords***:** Porosity; Structural applications; Firebrick; Perlite

1. Introduction
Refractories could be classified into two categories depending on the porosity namely dense and porous refractories [1]. Dense refractories contain porosity in the range of 15-20%. These refractories were used in contact with hot liquid metal and gases. Porous firebricks constitute one of the refractory groups which are most commonly used today for heat insulation in industrial applications. They are lightweight refractories that have much lower thermal conductivity and heat capacity than other refractories [2]. Different types of porous firebricks are mainly manufactured by using the raw materials such as diatomite, perlite, expanded vermiculite, calcium silicate, fireclay, kaolin, silicon carbide, quartz, alumina and lightweight refractory aggregates by conventional methods [2-4]. Porosity is usually created by adding a combustible material to the raw material mixture. During firing, the combustible material burns out, and leaves a large fraction of pores within the fired body. Different types of pore-formers such as sawdust, foam polystyrene, fine coke, binders and organic foams, or granular materials such as hollow micro spheres and bubble alumina are commonly used to obtain decreased density or to produce porous bodies in the insulating material [2,3]. Insulating firebricks that have a highly porous structure (between 45% and 90% porosity) exhibit low thermal conductivity values [1]. The thermal conductivity not only depends on their total porosity, but also on their pore size and shape, chemical and mineralogical composition [2-4].
Many research studies have been conducted, until now, on mullite ($3Al_2O_3$-$2SiO_2$) as a mineral phase with many properties: low thermal expansion and conductivity, excellent creep resistance, high temperature strength, and good chemical stability. These studies have focused on the synthesis methods, the phase equilibrium, the microstructures and the thermo-mechanical properties. Different types of mullite can be synthesized according to the nature of the raw materials and the used process [5-9]. The application fields of mullite are multiple and depend on the properties of each type. In fact, the performance of a refractory (good resistance of heat and thermal shock) is directly related to its texture and its richness in mullite.
Perlite is a glassy volcanic rock of rhyolitic composition usually containing a small amount of combined water. Raw perlite when heated to an appropriate temperature (above 870°C) expands and transforms into a cellular

material of low bulk density (40 – 110 kg/m^3). This expansion process occurs due to the presence of 2–6% of combined water in the crude perlite rock. Upon rapid heating, the chemical water held within the perlite vaporizes and creates bubbles in the heat-softened rock. The formation of these bubbles allows perlite to expand even 15–20 times of its original volume and produces froth-like structure. This structure gives excellent insulation properties, low density and high porosity of materials [10]. Moreover, perlite shows chemical inertness, fire resistance and high absorption of sound. All these properties make perlite a useable material for many applications. The expanded perlite can be applied in the construction industry and horticulture market and as a filter aid and filler. This lightweight filler is used as insulating cover on the surface of the molten metal to prevent excessive heat loss during delays in pouring; to top of ingots, to reduce piping and decrease lamination; to produce refractory blocks and bricks or simply as fillers and in several important foundry applications [11].
In this study, porous firebricks have been developed by adding recycled refractory wastes and expanded perlite to mixture containing several types of Moroccan geomaterials (kaolin clay, red clay and silica sand).

2. Experimental procedure

2.1. Materials

- Kaolin clay (ArgK) was selected as the clay raw material for its high refractoriness. This clay results from hydrothermal alteration of alkali granite of Oulmès, located in the center of the Moroccan Meseta [12,13].
- Red Clay (ArgS) is a very fine-grained silt of lower Cretaceous age, rich in clay minerals and poor in carbonates. Very large outcrops of these clay deposits exist in the region of Safi. Clays of this region are intensely exploited by the industrial ceramists for the manufacture of pottery, bricks and tiles [13,14].
- Silica Sand (SabM) used in this study comes from an artisanal quarry, located at 3 km SE of the Mechraa Hammadi Dam. The sands appear as a thin layer of a white-pink and friable rock, belonging to the limestone series of the upper Jurassic age [13].
- Many deposits of perlite occurs in the North-East of Morocco (Nador area) and show a relationship with other volcanic products (pozzolana, bentonite, tuffs, pyroclastics...) genetically related to Neogene volcanism activity of this region [15]. The largest deposits of perlite are located on the South - East of Tidiennit Mountain, where the rock is present as subhorizontal layers and shows variable structures. Our sample of perlite (PerN) comes from these large deposits in the region of Nador. Size of the used expanded perlite is between 1 and 2 mm.
- Brick raw material used in this study comes from a tiling manufacturer (Super Cerame) in Kenitra, Morocco. The contamination level of silica-alumina refractory materials used as coatings in kilns in the ceramics industry is low. It is for this reason that fire brick having undergone three years of use as a coating in a kiln was finely milled to obtain a white powder (AluR), and that contains 71.14% of alumina. Mineralogical analysis of this powder shows that it consists mainly of mullite [13]. The chemical compositions of the geomaterials, performed by X-Ray Fluorescence (XRF), are shown in Table 1.

Table 1: Chemical compositions by XRF of the geomaterials used in this study (wt %). (Chemical analysis was performed in laboratories of 'Unités d'Appui Technique à la Recherche Scientifique' UATRS, 'Morocco').

	SiO_2	TiO	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	CL	Total
ArgK	<u>57,20</u>	0,08	<u>29,40</u>	4,50	0,65	0,26	1,55	<u>3,08</u>	0,00	3,28	100,0
ArgS	<u>51,60</u>	1,06	<u>19,20</u>	<u>9,00</u>	5,36	0,90	0,58	3,89	0,23	8,16	99,98
SabM	<u>96,06</u>	0,15	2,22	0,51	0,17	0,09	0,06	0,20	0,02	0,49	99,97
PerN	74,00	0,00	11,71	0,72	0,21	0,73	3,37	4.00	0,00	4,34	99,08

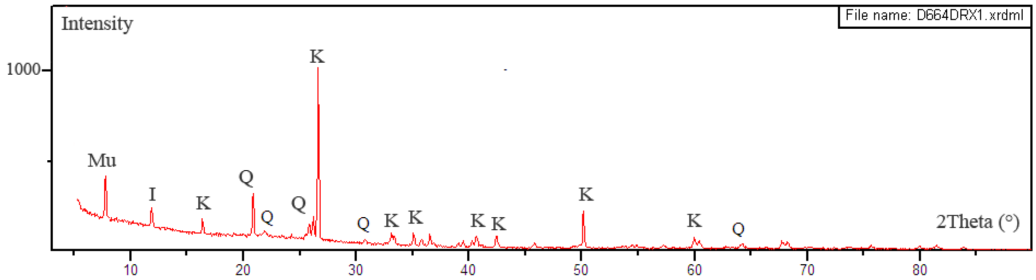


Figure 1: XRD patterns of Oulmès kaolinite-rich clay (ArgK). (K : Kaolinite, I : Illite, Q : Quartz, Mu : Muscovite).

The mineralogical composition of ArgK consists mainly on kaolinite and small quantities of quartz and illite (Fig.1). The following mineralogical phases were identified for the red clay (ArgS): illite as the main mineral, with kaolinite and quartz. Other secondary minerals phases found in this clay are hematite and dolomite [13].

2.2. Procedure for brick production

Initially, raw materials were dried at 100°C in oven. Then, they were powdered by a disc mill. The granulated powder mixtures were uniaxially compacted using hydraulic press under a pressure of 30 MPa for the rectangular-shaped specimens (10 cm × 5cm × 1cm). The pressed specimens were held overnight and then dried at 105°C for 24 h in an oven. Dried specimens were fired in a laboratory-type electrical furnace (Thermolyne 46200) at the rate of 5 °C/min up to 1600 °C (1h dwelling at 600°C). Technological parameters values were measured after firing steps.

3. Results and discussions

3.1. *Fired sample containing only clay and refractory waste mixture*

Refractory waste was used to increase the refractoriness of the product by reducing the amount of glassy phase in the structure. In a previous study by the same authors [13], a formula of composition M (40% ArgK + 15% ArgS + 5% SabM + 40% AluR) allowed obtaining a good quality of refractory at 1600°C. A detailed XRD showed the presence of Mullite, Quartz and Cristobalite (Figure 2). This sample presents very good dimensional stability and good mechanical characteristics (Table 2). The SEM micrograph of Fig. 3 clearly shows the mullite phase identified by its fine needle-like shape. The sample shows a homogeneous microstructure and especially richness of mullite.

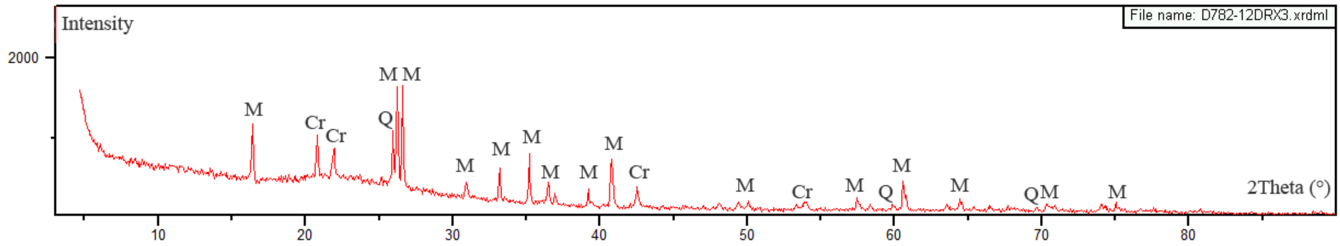


Figure 2: X-ray diffraction patterns of the brick manufactured from mixture and fired at 1600°C/1h (M: Mullite, Q: Quartz, Cr: Cristobalite) [13]

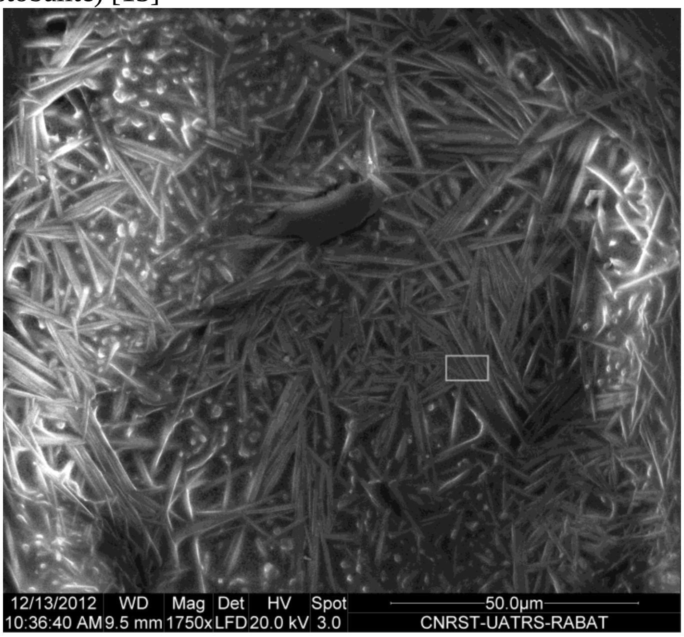


Figure 3: SEM microphotography of firebrick **[13]**

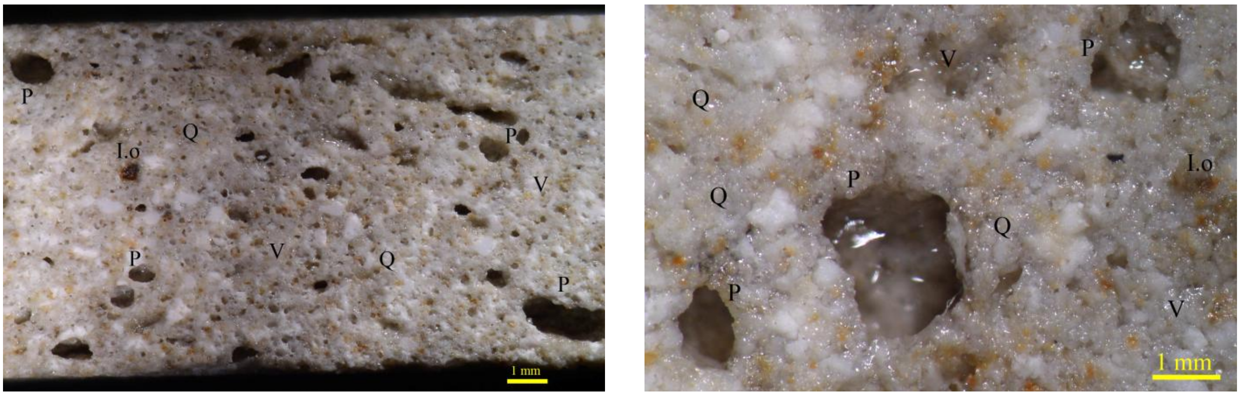
3.2. Fired samples containing clay and refractory waste mixtures with expanded perlite addition
3.2.1. Test results of the bricks
In the second stage for of this study we added 10%, 20% and 30% of expanded perlite at the mixture M. It was observed that the color of the fired brick does not change with increasing the amount of perlite addition. Experimental results of the sample with expanded perlite additive are given in Table 2. The tests were performed according to the procedures recommended by (ASTM) [16-18].

Table 2: Technological test results of the brick without and with expanded perlite added to the mixture and fired at 1600°C/1h

Physical properties	Mass ratio of expanded perlite addition			
	0%	10%	20%	30%
Bulk density (g/cm^3) ASTM C373-88	2.15	1.95	1.72	1.55
Apparent porosity (%) ASTM C373-88	9.8	51.5	57.5	65.8
Water absorption (%) ASTM C373-88	6.2	28.7	31.8	35.1
Shrinkage (%) ASTM C326-03	5.5	5.6	5.8	6.1
Flexural strength (MPa)	71.41	65.8	53.6	42.7

The apparent porosity values of fired samples ranged from 9.8 to 65.8%. Bulk density of the product with 0% and 30% of expanded perlite showed a reduction of 27.9 %. Shaping (pressing) direction of the brick and the shape of the pores affect the mechanical strength. Depending on the increase in the perlite addition and porosity content, the resistance values of the samples progressively decreased from 71.4 to 42.7MPa.

3.2.2. Microstructural analysis of the bricks
The observation of refractory sample under a binocular microscope identifies some traces related to the manufacturing technique, the characteristics of the briquette, and the size and color of inclusions and pores. The observation of the samples was performed using a binocular microscope OLYMPUS-SZX9 with a camera (DS Camera Head DS-5M). The microstructural analysis revealed a higher porosity in the briquettes containing expanded perlite. As it can be seen in Fig. 4, largest pores about 1-2 mm, co-exist with micro-pores less than 0.1 mm. The pores are often isolated and have globular shape. In addition, the inner walls of pores are covered by vitreous materials which would correspond to a melting product of perlite (Fig.4.b). So, the effect of expanded perlite addition was obviously observed from the microstructure.

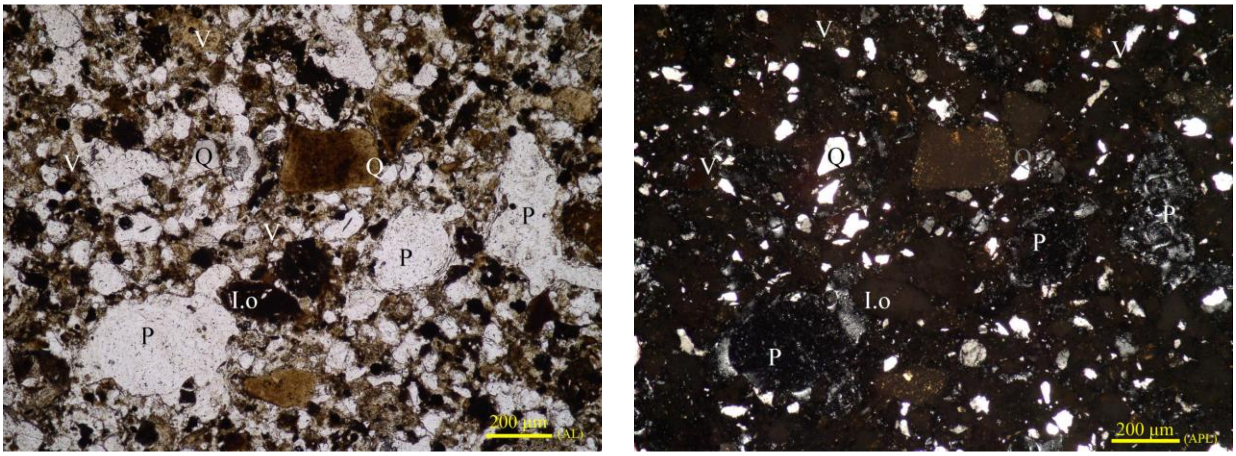


a) b)

Figure 4: a) Optical micrographs showing the highly porous structure of the firebrick with 30% of expanded perlite. b) Detailed observation of pores systematically covered by glass products.

For more details on the nature of the mineral phases and microstructure of briquettes fired at 1600°C, we use the polarized microscope, generally used for petrographic study of natural rocks. For this, we started by making thin slices approximately 30 µm thick in brick fragments. These thin sections have been observed under a microscope Olympus BX 51TF.
Fig. 5 illustrates the microscopic observations of fired brick with 30% of expanded perlite using both natural and polarized light (AL and APL). The studied material appears heterogeneous with some anisotropic crystals, opaque phases, amorphous areas and porosity. The anisotropic minerals correspond to quartz crystals which are xenomorphic, show a rolling extinction and are often cracked. The opaque phases are frequently iron oxides.

The porosity shows a random distribution and the pore have a size less than 400 µm (Fig. 5). The bottom of the firebrick, mainly composed of amorphous phases, is invaded by microscopic needles of mullite (Fig.6).



a) b)

Figure 5: Microstructural analysis of the bricks taken with. a) Natural microscopy light (AL). b) Polarized microscopy light (APL). P: Porosity, I.o: Iron oxide, Q: Quartz, V: Vitreous phase.

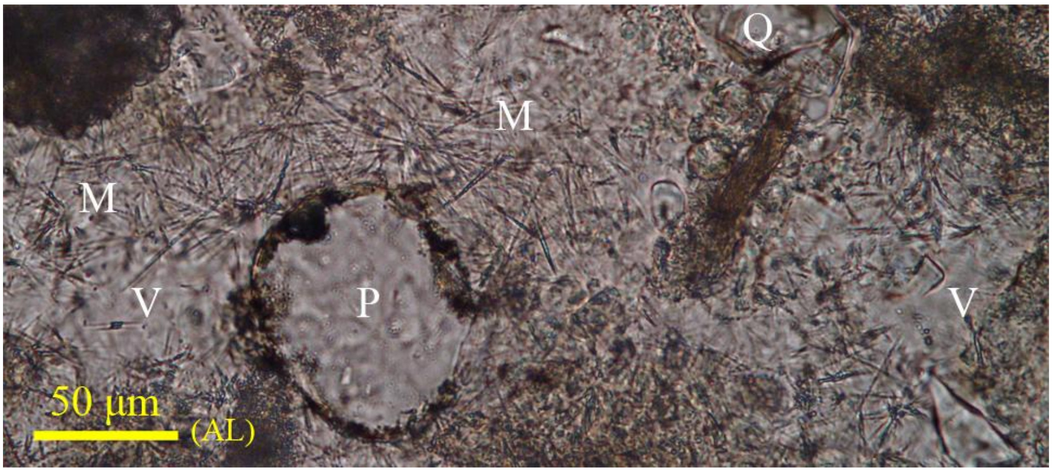


Figure 6: Micrograph showing the shape and abundance of mullite crystals invading the vitreous bottom of the firebrick (PL)

Conclusion

The present study shows the possibility to produce refractory with high mechanical performance from a mixture of Moroccan silica-alumina geomaterials (M = 40% ArgK + 15% ArgS+ 5 % SabM + 40% AluR). In fact, the thermal treatment at 1600°C gives briquettes having the following technological characteristics: P = 9.8 %, d = 2.15 g/cm^3 and F.S = 71.41 MPa. Subsequently, we have tried to synthesize lightweight refractory from the same mixture of geomaterials (M) with the addition of varying amounts of expanded perlite (PerN).

The combination of techniques XRD, SEM-EDX and polarized microscope, allowed a better analysis of the structural and mineralogical evolution after sintering at 1600°C. The addition of AluR has strengthened the mullite crystallization that appears under the SEM and optical microscope like fine needles invading the vitreous bottom of the brick. The addition of the expanded perlite at variable rates (10, 20 and 30 %) allowed the gradual increase of the porosity of the brick. The rate of 30% seems to be optimal because it provides a highly porous briquette (P = 65.8 %, d = 1.55 g/cm^3). The addition of more than 30 % of expanded perlite to the mixture gives, after firing, refractories characterized by a low flexural strength.

In addition, optical observations indicate that the inner walls of the pores are systematically covered with glassy products resulting from the fusion of perlite at high temperature. This indicates that the synthesized porous refractory bricks will have a good capacity of thermal and sound insulation. This aspect of isolation is still to be developed in a later study.

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