Improving the Physical Properties of Iraqi Bauxite Refractory Bricks

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Abstract

In this study; physical and mineralogical test were carried out on the Iraqi bauxite mineral in order to assess its suitability for the production of refractory bricks. Two types of additives were used, Iraqi white kaolin as a binding material in ratio 10%, and (micro and nano) zirconia as additives, synthetic zirconia in ratios of (5, 10, 15, 20) % for the purpose of improving the general characteristics of the Iraqi bauxite bricks. The bricks were formed by semi-dry pressing, with added potassium silicate in ratio 10% as binder material.

The formed samples were of cylindrical shape (50×50) mm for diameter and height. The drying process of the samples was carried out at 110˚C for 24h, then firing at 1400˚C and soking time 2h. Physical properties such as microstructure by (SEM) and (XRD) analysis for bricks test were carried out.

Keywords: refractory bricks, Iraqi bauxite, physical properties.

Introduction

Bauxite is defined as a mixture of minerals which consists mainly of aluminum oxide bounded to one or more water molecules (hydrated aluminum oxide). They are diaspore, boehmite and gibbsite [1].

With Small amount of impurities such as SiO2, k_2O, Fe_2O_3, TiO_2, CaO, MgO and Na_2O [1].

Bauxite is the primary source For industrial aluminum and Alumina production by Bayer process [2].

Bauxite is also used to produced refractory bricks, During Firing of Bauxite below 1200°C, Its structure is transformed into dense granules contains mainly Corandom ($\propto$-Al_2O_3). At temperatures within the range (1250–1350)°C the mullite phase is formed as a result of the reaction between silica and alumina [2].

Gibbsite or hydrargillite losted its hydrate at (290–340)°C and transform to boehmite, and at less than(1200–1300)°C it is transform to corundum as shown in the following equation [1].

$$Al_2O_3.\,3H_2O \xrightarrow{290\text{-}340^\circ C} Al_2O_3.\,H_2O \xrightarrow{490\text{-}550^\circ C}$$

$$\gamma Al_2O_3 \xrightarrow{\text{below } 1200 - 1300^\circ C} Al_2O_3\,.$$

Mullite phase is Formed at temperature (1250–1350)°C, according to the following equation [1].

$$3\,Al_2O_3 + 2SiO_2 \xrightarrow{1250\text{-}1300^\circ C} 3Al_2O_3.\,2SiO_2$$

Mullite is considered as a binding phase in most of refractory brick and it has a high resistance to melting and minimum thermal expansion as well as low thermal conductivity. Mullite also characterized by its chemical and thermal stability as will be shown in the Table(1) [2].

Zirconia (ZrO_2) has an extremely high melting point of 2680°C, low thermal expansion, low thermal conductivity, a relative chemical inertness as shown in Table (1) [2].

Table (1)
Properties of mullite and zirconia [1,3].

Properties	*Mullite*	*Zirconia*
Melting Temp. (˚C)	1850	2680
Specific Gravity (g/cm^3)	3.03	5.7
Hardness	7.5 moh's	7 moh's
Thermal Conductivity (w m^{-1} k^{-1}) At 25˚C	6	2.3
Heat Capacity (J mol^{-1} k^{-1})	77.1	55.1

Zirconia is one of a special refractory materials, also it is an additive for refractory in order to increase the thermal shock, slag resistance, molten wetting and toughening [3].

Zirconia is usually obtained through a chemical process involving zircon ($ZrSiO_4$) or by fusing zircon with coke in an electric furnace.

Zirconia can occur in three polymorphs, monoclinic, tetragonal and cubic. The typical room temperature phase is monoclinic which is stable to about (1160–1190)˚C upon heating. Heating through the monoclinic-tetragonal transition causes a volume contraction, cooling through the transition causes a volume expansion [3].

The phase change transition through cooling is instantaneous and results in spontaneous failure of the zirconia crystal this failure is expressed in the cracking and/ or disintegration of the refractory shape [3].

The Fundamental cracking problem can be overcome using either of two contrasting approaches; one is to mill monoclinic zirconia to a fine size (less than one micron) and disperse it within a refractory body so that destructive micro–cracking is avoided. In fact, the dispersed phase works as a stress absorber as energy is absorbed by zirconia to convert from one phase to another.

In this way, the dispersed phase is said to produce a "toughening" effect [4, 5].

The other approach is to stabilize the cubic structure with lime, magnesia or yttria by heating zirconia with one of these oxides within the temperature range (1500-1700)˚C [4,5].

Experimental Work

Materials and Method

Iraqi bauxite rocks were washing, crushing, firing at 1400˚C, grinding and sieving. Also, Iraqi kaolin rocks were crushing, grinding and sieving. Iraqi kaolin clay used as a binder, which characterized with its good plasticity. Iraqi bauxite and kaolin were produced from Iraqi state Co. of Mining Industry.

The chemical composition of bauxite and kaolin raw materials were taken by chemical analysis and shown in Table (2).

Table (2)
The chemical analysis of the raw materials used for the production of the refractory bricks.

Component	*Bauxite Wt%*	*Firing Bauxite Wt%*	*Kaolin Wt%*
SiO_2	18.98	17.09	49.38
Al_2O	61.90	74.91	32.72
Fe_2O_3	1.30	1.36	2.07
TiO_2	1.80	3.65	1.08
CaO	1.20	0.28	1.19
MgO	1.07	0.02	0.18
Na_2O	-	0.02	0.22
K_2O	-	0.02	0.44
SO_3	-	0.03	0.05

In order to improve the quality of produced bricks, different amounts of (micro and nano) zirconia were added. Zirconia which is used; micro zirconia (fixanal, hannover- Germany), and Nano zirconia (SIGMA-China). The refractory bricks were produced with different mass ratios listed in Table (3).

Table (3)
Mass ratios of raw materials used to prepare the improved bauxite bricks through the addition of zirconia.

No. of Samples	*Refractory bricks Mixture %*	*Zirconia (45 μm)*
1	100	0
2	95	5
3	90	10
4	85	15
5	80	20
	Zirconia (40-50) nm	
6	95	5
7	90	10
8	85	15
9	80	20

Cylindrical shape of bauxite bricks were formed by implementing the semi-dry pressing method. The size of the prepared samples was (50×50) mm and the amount of potassium silicate as a binder of ratio (10%). The forming pressure was (15) ton. After the shapes has been formed. The sample were left under atmospheric conditions for 24h, Then put in electrical dryer at 110˚C for 24h. The samples were heated from room temperature to 1400˚C by a program as shown in Fig.(1).

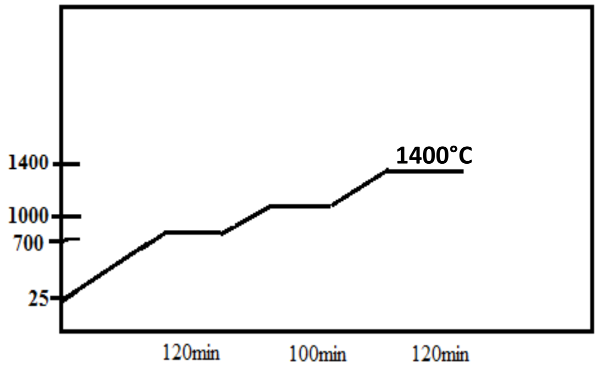


Fig. (1) Firing program.

After fining of the samples of bauxite bricks, the physical properties of the samples were tested to determine physical properties such as:- apparent density, apparent porosity, water absorption, linear expansion, (XRD) analysis and microstructure.

Results and Discussion

Characterization of the Raw Materials

As can be noticed from the data of Table (2), the bauxite fired at 1400˚C contains an amount of 74.91% alumina which makes it possible to classify it as intermediate level alumina content refractory materials which contains up to 65.60% alumina [4]. This means that the produced refractory bricks will have a higher softening and fusion temperatures. The silica content of 17.09% and the presence of 1.63% of Fe_2O_3 will result in improvement of specific gravity and density as well as improvement it is resistance against sudden thermal changes [6].

The kaolin used as a softening and binding material, which has the chemical analysis listed in Table (2) has a composition lies within the accepted limits of fire clays suitable as raw material for the production of bauxite bricks.

XRD Analysis

Mineral analysis of bauxite using XRD method, Fig.(2) shown that Iraqi bauxite consist of Boehmite, kaolinite. Firing Iraqi Bauxite consist of mullite and a small amount of cristobaliteas shown in Fig.(3).

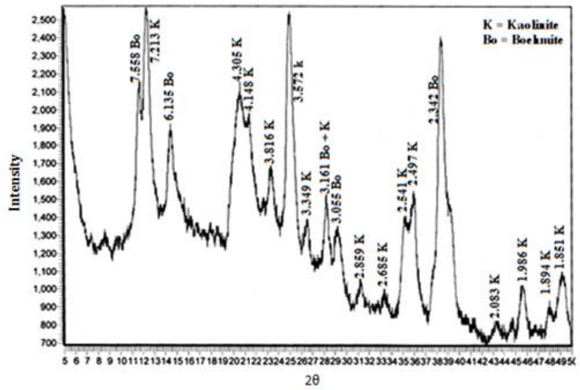


Fig.(2) The mineral composition of the raw bauxite using XRD analysis.

The mineral analysis of kaolin, will be shown in Fig.(4) exhibits a higher ratio of kaolinite and small amount of quarts minerals.

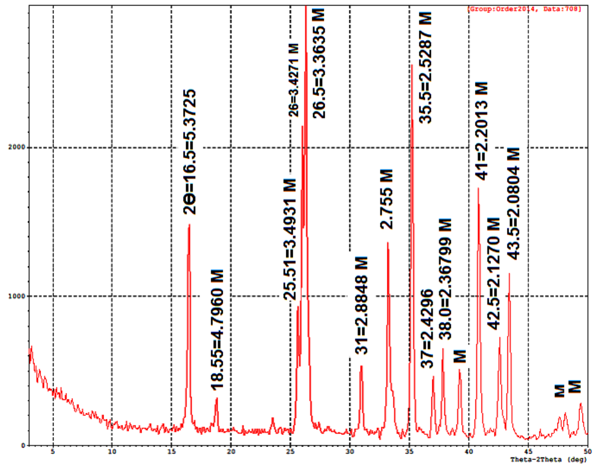


Fig. (3) The mineral composition of the firing bauxite at 1400˚C using XRD analysis.

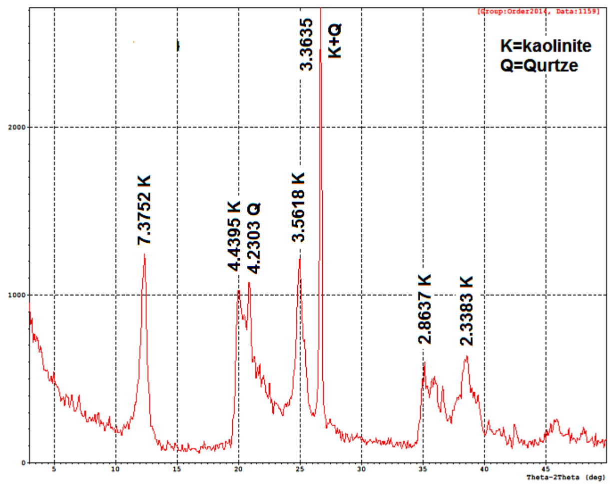


Fig.(4) The mineral composition of the white kaolin using XRD.

The mineral analysis of refractory bricks after adding zirconia was shown in Fig. (5). It consists of mullite and small amount of cristobalite and zirconia.

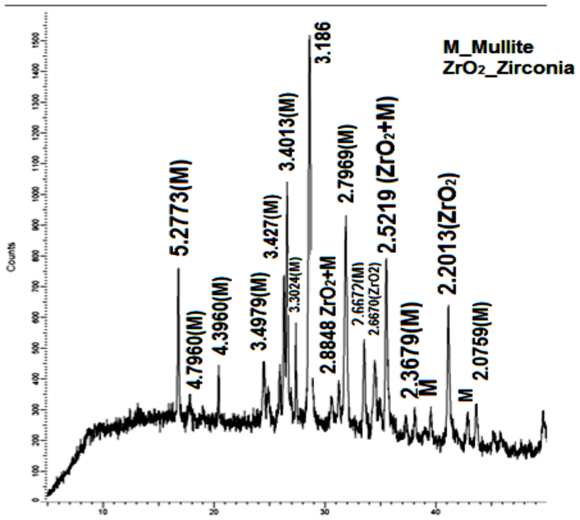


Fig.(5) XRD for the refractory bricks.

Apparent density

Apparent density such as the non bounded materials, the firing temperature, granular size, additives and the forming pressure.

Fig.(6) presents that the density of the bauxite fire bricks increases with the amount of the added zirconia.

Also the occurrence of the liquid phase at high temperatures. There are several parameters influencing the resulted from the chemical reactions taking place between the components of the bricks among them MgO, CaO, Fe_2O_3, Al_2O_3 and SiO_2. These components contribute in formation of chemical components of low fusion temperature which flow easily into the pores resulted in an increase in the density of the bricks [7,8]. Moreover, the surface tension of this liquid phase cause a compacting of the grains together causing a reduction in the dimensions of the from, as shown in the Fig.(7).

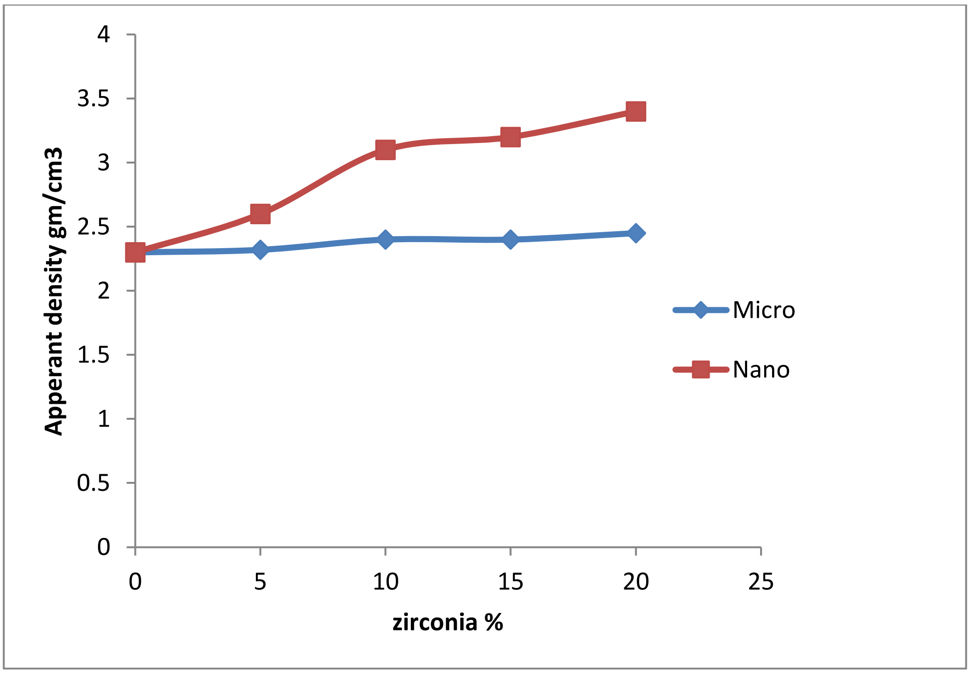


Fig. (6) The influence of the added amount of zirconia on apparent density.

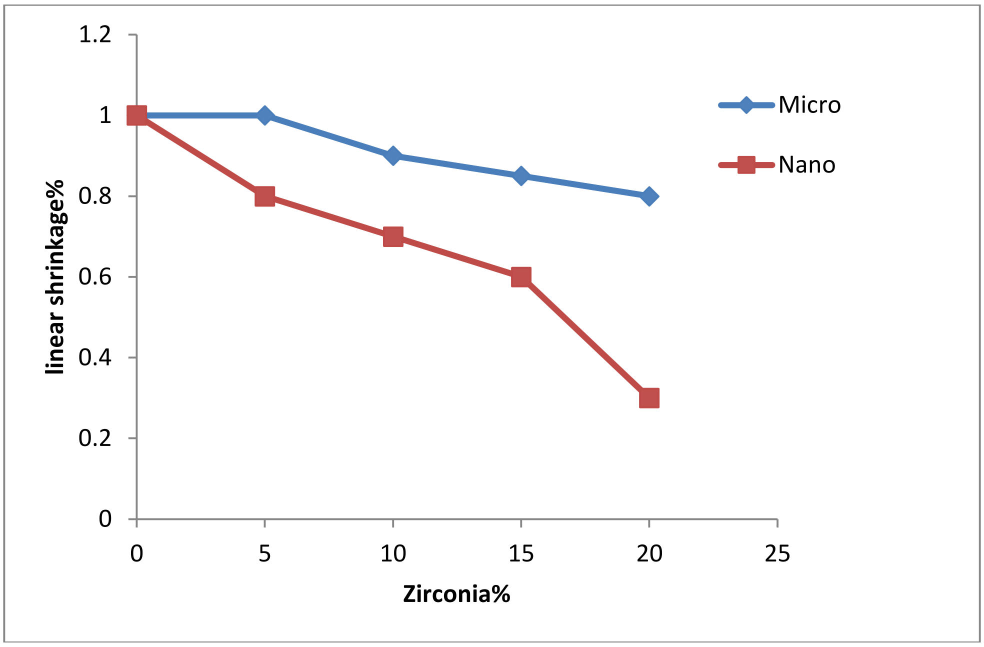


Fig. (7) The influences of the added amount of zircon on linear shrinkage.

Apparent porosity and water absorption

This property is dependent on two important factors. The first factor is the influence of the sintering process while the second factor is the formation of the channels and pores within the body of the bricks due to due to the liberation of gases. The two factors have a counter effect because the reaction products resulted from the firing of the days form a glass phase which fills the pores inside the body of the bricks, as shown in Fig. (8).

The obtained experimental results indicate that the reduction of the apparent porosity accompanies with a reduction in the water absorption, as shown in Fig. (9).

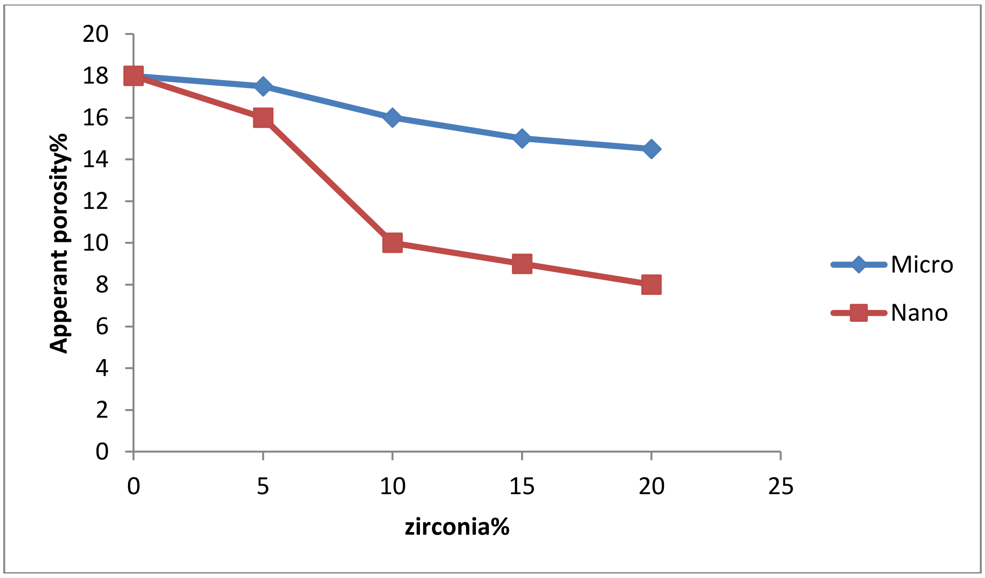


Fig. (8) The influence of the added amount of Zirconia on an apparent porosity.

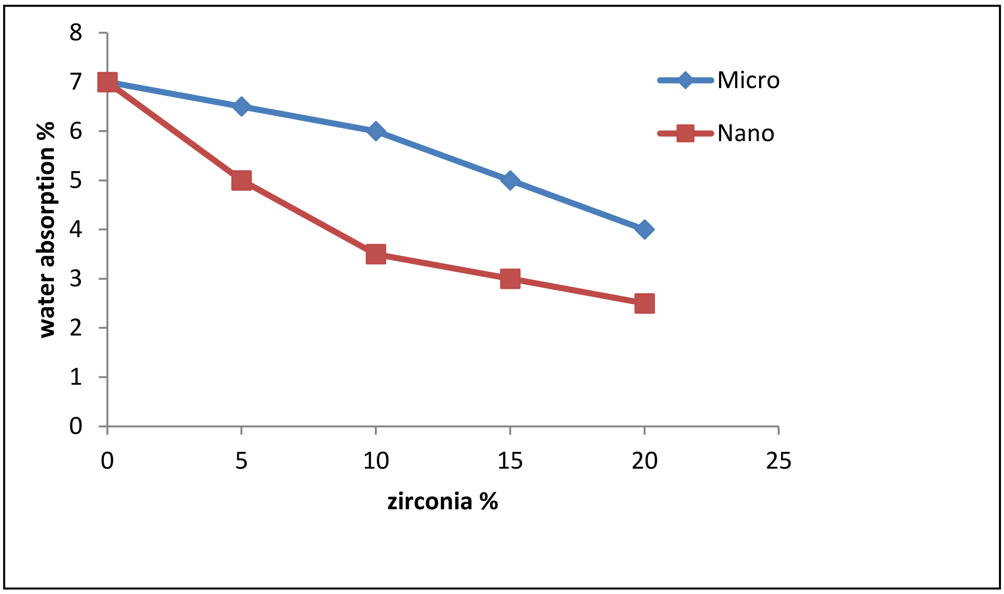


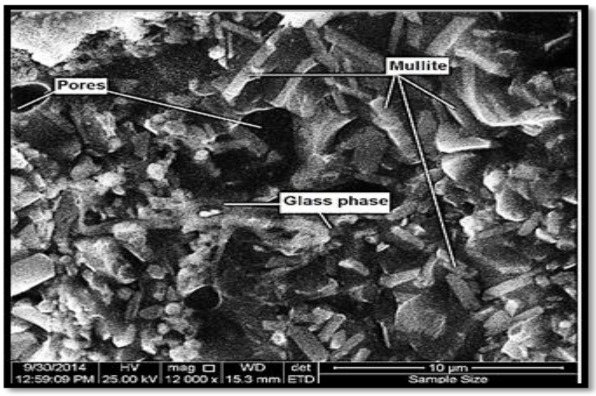
Fig. (9) The influence of the added amount of zirconia water absorption.

It was experimentally found that the amount of zirconia added to the raw materials mixture influences on the properties of the refractory bricks. When the zirconia is added within the range (5-20%) the ratio of the liquid phase formed during firing is reduced as the amount of zirconia increases. This is resulted from the decrease in the amount of melted materials in one side and the high fusion temperature of zirconia on the other side.

Nano zirconia decreased formed of the liquid phase amounts, and increased formed of the mullite phase because of nano size particle enhance the appearance the reaction between alumina and silica, The refractory bricks which has nano zirconia has the highest density because of the high density because of the high density of material in nano size compared with the micro size.

Microstructure

Scanning electron microscope (SEM) used to study the microstructure of the fractured surface of the refractory brick, as will be shown in the Fig.(10). The SEM photographs shown increased in mullite phase amount with added nano zirconia, on the other side decreased in liquid phase.



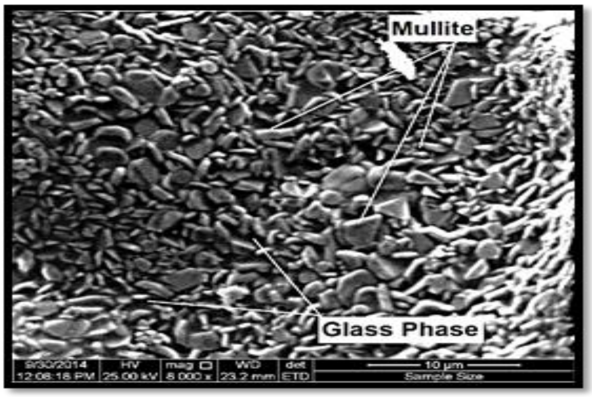


Fig.(10) SEM of the refractory bricks, (a).bauxite brick (b) bauxite brick (6).

Conclusions

From the rustles, it was found out that the properties of the refractory bricks produced are suitable to be used for high temperature application.

On the other hand the firing bauxite which was used has a high mullite phase amount which makes it more suitable for the production of refractory bricks with improved its properties.

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الخلاصة

في هذه الدراسة اجريت الاختبارات المعدنية والفيزيائية لخام البوكسايت العراقي من اجل تقيم ثباته الحراري لانتاج الطابوق الحراري. تم اضافة نوعين من المواد الكاؤلين العراقي الابيض كمادة رابطة بنسبة (10%)، والزركونيا المايكروية والنانوية كمواد مضافة، بالنسب %(5,10,15,20) لتحسين الخصائص العامة لطابوق البوكسايت العراقي. شكل الطابوق بطريقة الكبس شبه الجاف مع اضافة سليكات البوتاسيوم بنسبة %(10) كمادة رابطة.

شكلت النماذج بشكل اسطوانات (50×50)mm للقطر والارتفاع. جففت النماذج عند (110 ℃) لمدة 24h، ثم حرقت عند 1400℃ ولزمن انضاج 2h. الخصائص الفيزيائية والبنية المجهرية وفحص حيود الاشعة السينية اجريت للطابوق.