

Improvement of Iraqi Red Kaolin as a Refractory Material

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ABSTRACT

In this work refractory material was prepared from Iraqi red kaolin with the addition of different proportions of silica and alumina (10, 15, 20 %) for each one and the red kaolin 70%. The powders were mixed in a ball mill, sieved, formed, dried at 110 °C for 8 hrs and then fired at different temperatures 800, 900, 1000 and 1100°C for 2 hrs. The physical properties (linear and volumetric shrinkage, apparent density and porosity) were calculated from the measured data. It was found that the higher the firing temperature the better the properties of the prepared samples for a given mixture, the best properties obtained in this work was 70% red kaolin, 10% silica and 20% alumina).

Keyword: Kaolin, Refractory material.

تحسين خصائص الكاولين الاحمر العراقي كمادة حرارية

الخلاصة

في هذا البحث تم تحضير مادة حرارية من الكاولين الاحمر العراقي مع اضافة نسب مختلفة من السليكا والالومينا (10 و 15 و 20%) لكل منهما و 70 % كاولين احمر. تم مزج المساحيق حسب النسب المذكورة بواسطة طاحونة ذات الكرات ونخلت، شكلت، جففت بدرجة 110 درجة مئوية لمدة 8 ساعات ثم حرقت بدرجات حرارية مختلفة 800, 900, 1000 و 1100 درجة مئوية لمدة ساعتان. تم حساب الخصائص الفيزيائية (الانكماش الخطي والحجمي والكثافة الظاهرية والمسامية) للنماذج المحروقة من القيم المقاسة. وجد انه كلما زادت درجة حرارة الحرق حصلنا على خواص افضل ولقد وجد بأن افضل نتائج تم الحصول عليها للنموذج ذو المحتوى (70% كاولين و 10% سليكا و 20% الومينا).

INTRODUCTION

Kaolinite are natural components of the soil and occur widely in ambient air as floating dust with chemical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Kaolinite is formed mainly by decomposition of feldspars (potassium feldspars), granite, and aluminum silicates. Red Kaolin has a considerably stronger drawing power than other Kaolin Clays. There are many technical characteristics that define a material as a clay

but, for ceramics, the primary characteristic beyond the alumina and silica content is the fact that they are composed of very small flat plate lids with a resulting very large surface area with microscopic water between them so they slide on one another and additionally tend to hold their shape. Additional properties of clays are 1) harden when dried and become permanent when fired, 2) shrink during drying and firing, 3) refractory (resist softening at high temperature), 4) heat, sound and electrical insulation [1].

Refractories are heat resistant materials used in almost all processes involving high temperatures and/or corrosive environment. These are typically used to insulate and protect industrial furnaces and vessels due to their excellent resistance to heat, mechanical damage [1]

Alumina is one of the most chemically stable oxides known, which offers excellent hardness, strength and spalling resistance. It is insoluble in water and super heated steam, and in most inorganic acids and alkalis. Alumina refractory have the characteristics of fire –clay brick which carry high temperature ranges that makes it suitable for lining furnace [2]. Silica as quartz raw material was taken from Al-Ruatba in the western desert of Iraq contains 98.2%SiO₂ (Stat Company for Geological Survey and Mining). There are several parameters that may determine the type of raw material to use in a refractory product.

No single refractory material has ideal properties e.g. sintered alumina may have excellent corrosion resistance but poor thermal shock properties. This means a wide range of alumina raw materials need to be made available to refractory organizations.

In general alumina based materials are defined by their Al₂O₃ content, other elements such as Fe₂O₃, SiO₂, CaO, K₂O and Na₂O are important factors during the selection process. Also, bulk density, porosity and high temperature volume stability of a raw material have a significant effect on the properties of the final product [3]

Abundant clay deposits are found in Iraq, unfortunately many of these reserved are considered unsuitable for brick industry. The clays are full of calcium in the form of carbonate, soluble salts, and contain almost the most difficult clay mineral there is from a processing point of view montmorillonite[4].

Calcium carbonate is commonly associated with most of the Iraqi soils and especially with that of the northern part of the country. During CaCO₃ decomposes to lime when carbonate-contained soil is fired and if not very finely ground, "lime blowing" occurs causing cracking or even complete disruption of the bricks. On the other hand, finely divided lime acts as a powerful flux which accelerates vitrification and shortens its temperature range. It has also been observed that decomposition of CaCO₃ creates cellular structures and affects efflorescence formation [5].

The formation of glassy matrix was responsible for the densification and shrinkage of bricks, and consequently the reduction of the porosity. The higher the glassy matrix, the higher is the development of densification [6].

Materials and Methods

The materials used are red kaolin, alumina and silica with the distilled water as a binder. The chemical analysis of red kaolin as shown in Table (1):

Table (1) the chemical analysis of Iraqi red kaolin.

Oxides composition	Wt%
SiO ₂	40.54
Al ₂ O ₃	07.55
Fe ₂ O ₃	05.73
TiO ₂	00.53
Na ₂ O	01.03
K ₂ O	01.50
CaO	21.87
MgO	04.65
SO ₃	00.25
L.O.I	16.35

*Chemical analysis was made by (State Company of Geological Survey and Mining

The equipments and tools used were include ball mill for mixing, sieve shaker, steel moulds, electrical furnace, Vernier, sensitive balance, and electrical dryer. The red kaolin is the main raw material was mixed with alumina and silica in different proportions as in Table (2) below:

Table (2) The percentages of materials in each batch.

Material	Batch 1	2	3	4
Red kaolin	100%	70%	70%	70%
Silica	0	10%	15%	20%
Alumina	0	20%	15%	10%

Shrinkage test

Test specimens from each composition were dried at 110°C for 8 hours to ensure water losses. The test specimens were then measured (in terms of dimension) and their values were noted as dry lengths.

The test specimens were also fired in an electric furnace to temperatures of 800, 900, 1000 and 1100°C. They were allowed to cool. The specimens were weighed and measured. And the fired weight and fired length were recorded. For each sample, different specimens were tested and the averages of the above parameters were calculated and recorded.

The linear shrinkage and volumetric shrinkage were calculated for each test specimen using the following formula [7]:

$$\text{Linear Shrinkage} = \frac{L_1 - L_2}{L_1} * 100\% \quad \dots (1)$$

$$\text{Volume Shrinkage} = \frac{V_1 - V_2}{V_1} * 100\% \quad \dots (2)$$

Where: L₁ means initial length; L₂ is fired length V₁, V₂ is the initial volume and fired volume respectively.

Apparent density and apparent porosity,

The test specimens after drying and firing in an electric furnace were weight measured and recorded. They were allowed to cool and then immersed in a beaker of

water. Bubbles were observed as the pores in the specimens were filled with water. Their soaked weights were measured and recorded. They were then suspended in a beaker one after the other using a sling and their respective suspended weights were measured and recorded.

Their respective apparent densities, apparent porosity, were calculated using the Archimedes method as in the formulae below [7]:

$$\text{Apparent Density} = W_f / (W_f - W_s) \quad \dots (3)$$

$$\text{Apparent Porosity} = (W - W_f) / (W - W_s) * 100 \quad \dots (4)$$

Where: W_f = Weight of fired specimen, W_s = Weight of fired specimen suspended in water, and W = Weight of soaked specimen suspended in air

RESULTS AND DISCUSSION

Linear Shrinkage

From Figure (1) the percentage linear shrinkage values of the samples prepared with varying Silica and Alumina content as in Table (2) and fired at different temperatures 800, 900, 1000 and 1100°C varied from 14% for sample prepared from batches 1 and fired at 800 °C to 5.5% for sample prepared from batch 2 fired at 1100 °C which is differs from that for batch 3 and 4 fired at the same temperature 1100 °C. It does appear that alumina reduce shrinkage. The higher the kaolin content, the higher the shrinkage. The drying shrinkage indicates to some degree the plasticity of the mixture. A large drying shrinkage means that mixture could absorb much water, which in turn indicates fine mixture particles. The firing shrinkage indicates how fusible the mixture is and the shrinkage of samples increases with kaolin quantity increasing [8].

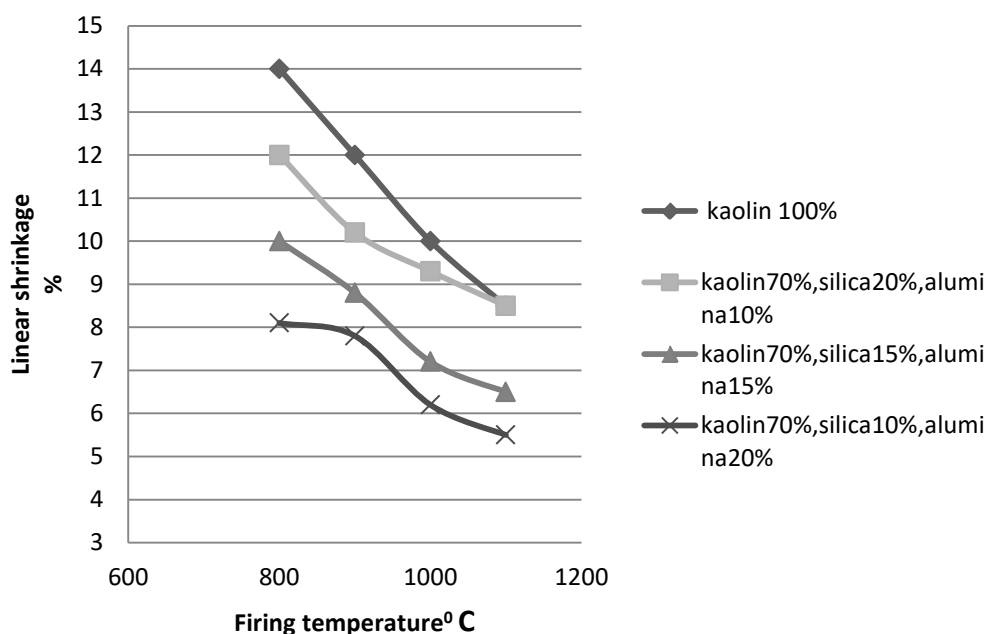


Figure (1) the linear shrinkage of red kaolin with different alumina

and silica contained, as a function of firing temperature.

Volumetric Shrinkage

The volumetric shrinkage as in Figure (2) shows the same behavior as that in linear shrinkage with maximum value 16% also for sample prepared from batch 1 without addition of Silica and Alumina ,fired at 800 °C, and a minimum value 5.3% for sample prepared from batches 2 , fired at 1100 °C . This indicates a stability and homogeneity in shrinkage happened after firing due to the good distribution of water molecules through the bulk of prepared samples with the given ratios of added alumina and silica.

The increasing amount of kaolin and firing at the highest temperature raised the quantity of mullite phase. It begins to dominate over the corundum phase. This is observed with decomposition of kaolin to mixed oxides and the formation of mullite in the reaction with additional alumina and silica oxides during firing process.

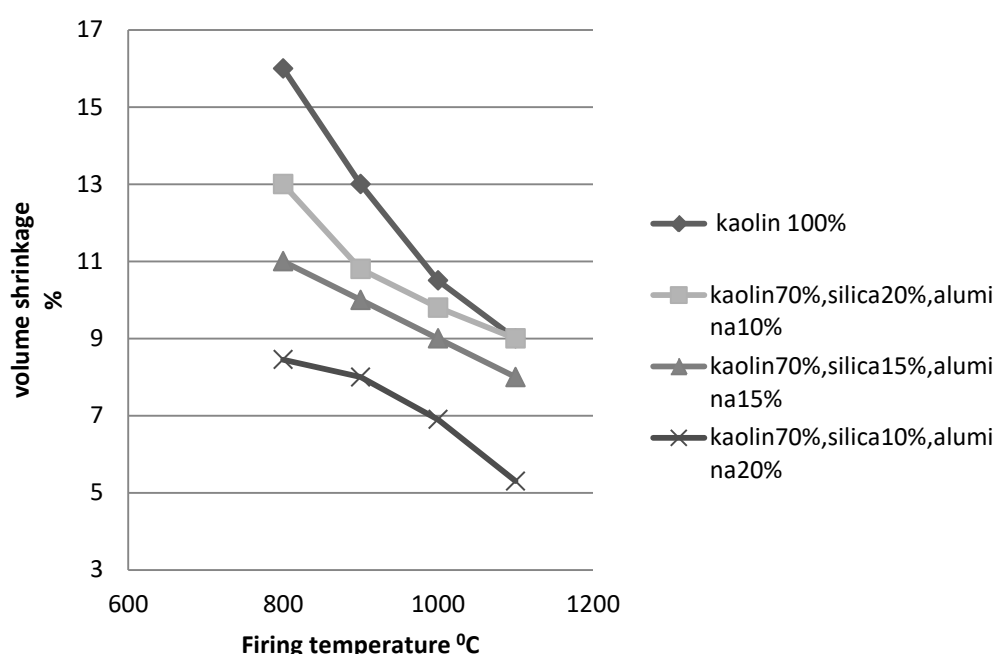


Figure (2) the volumetric shrinkage of red kaolin with different Alumina and silica contained, as a function of firing temperature.

Apparent Density

From Figure (3) it is appeared that the apparent density increased by increasing the firing temperature and with increasing alumina content and reach a maximum apparent density for batch 2 (70% red kaolin, 10% silica and 20% alumina). This indicates the formation of glassy matrix which was responsible for the densification and shrinkage of the investigated samples, and consequently the increase in density. The higher the amount of glassy matrix, the higher is the development of densification. Therefore the sample prepared with 10% silica and contain relatively high amount of alumina showed relatively higher density, and lower porosity. It has

been reported that the density reaches its maximum at the temperature where there is enough liquid phase to block the open porosity (9).

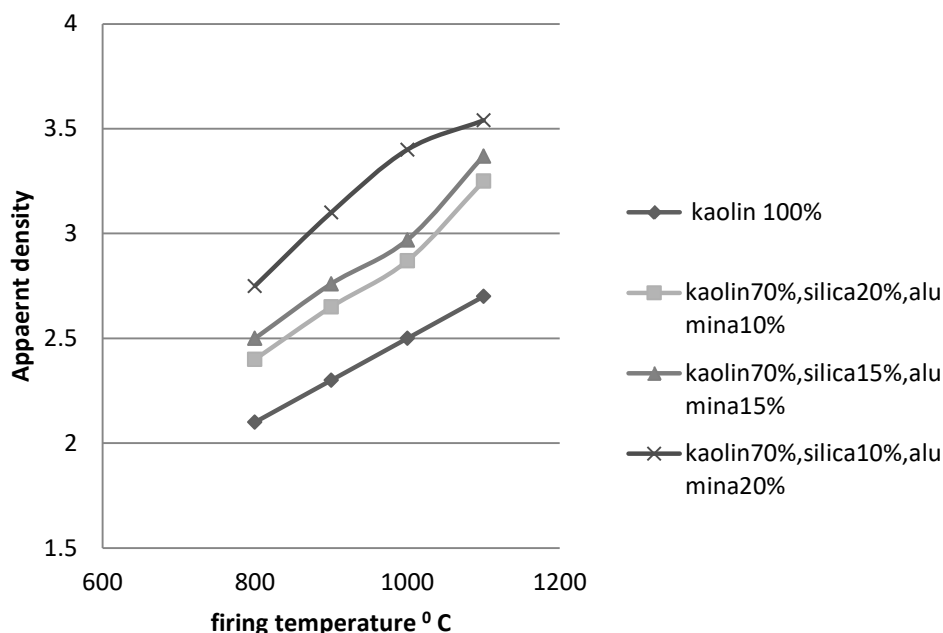


Figure (3) the apparent density of red kaolin with different alumina and silica contained, as a function of firing temperature.

Apparent Porosity

From Figure (4), sample prepared from batch 1 fired at 800 °C shows the highest porosity, 8.2% while sample prepared from batches 2 and 3 which fired at 1100 °C showed the lowest, 4.1 % . This indicates that high percentage of silica in a sample leads to high porosity of that sample at high temperature but further increase in temperature led to a reduction in porosity because the resulted silica liquid formed during firing helps to bind the different particles together by occupying of the spaces or voids present between ceramics particles leading to decrease in the porosity.

Porosity is a measure of the effective open pore space in the refractory into which the molten metal, slag, fluxes, vapors etc can penetrate and thereby contribute to eventual degradation of the structure. The porosity of refractory is expressed as the average percentage of open pore space in the overall refractory volume.

High porosity materials tend to be highly insulating as a result of high volume of air they trap, because air is a very poor thermal conductor. As a result, low porosity materials are generally used in hotter zones, while the more porous materials are usually used for thermal backup. Such materials, however, do not work with higher temperatures and direct flame impingement, and are likely to shrink when subjected to such conditions. Refractory materials with high porosity are usually NOT chosen when they will be in contact with molten slag because they cannot be penetrated as easily.

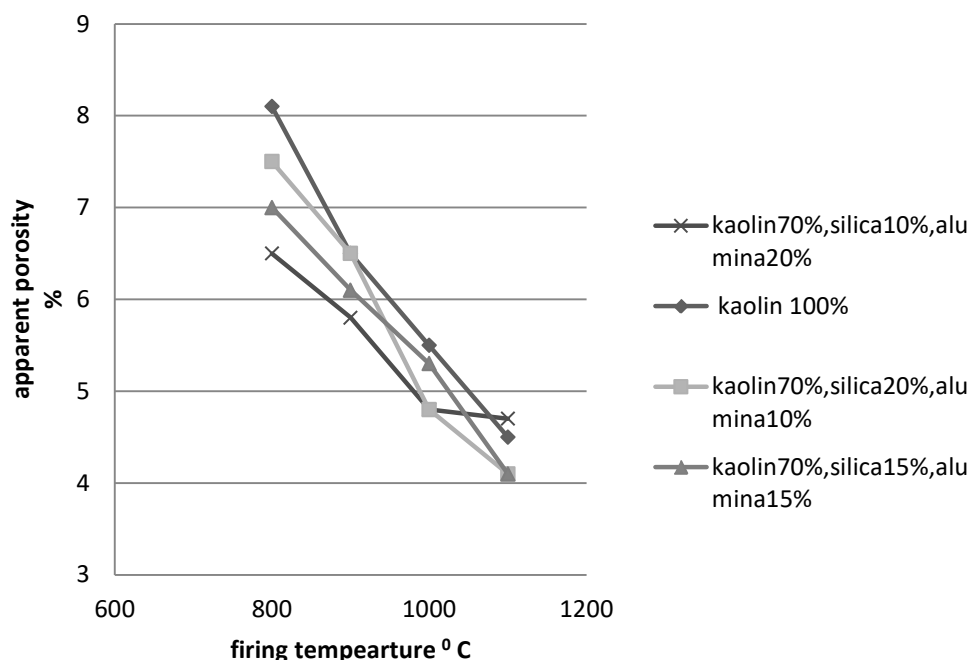


Figure (4) the apparent porosity of red kaolin with different alumina and silica contained, as a function of firing temperature.

CONCLUSIONS

- 1- Red kaolin is suitable for the industrial production of ceramic roofing tiles with the addition of silica and alumina in amount up to 30% by weight for both. The recommended method for molding is the semi-dry pressing process, and firing at 1100 °C.
- 2- All properties of the Iraqi fire bricks can successfully improved using red kaolin, silica and alumina with different amounts. The degree of improvement depends on the replacement of red kaolin with SiO_2 and Al_2O_3 and the firing temperature,
- 3- The local raw materials – red kaolin is suitable for the production of building firebricks with small added materials SiO_2 and Al_2O_3 with good properties.
- 4- The best batch is that with 70% red kaolin, 10% silica and 20% alumina which gives the best combination of properties such as linear, volume shrinkage, density and porosity.
- 5- Red kaolin can be used as a matrix and reinforced with Silica and Alumina to make suitable brick for lining furnaces which effectively reduces the cost of refractory in Iraq.

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