

Exploring the Use of Kenyan Diatomite As A Source Of Refractory Materials

Janet J. Kipsanai

Department of Mechanical & Production Engineering, Moi University

Abstract

The history of the developed and newly developed economies of the world shows that the establishment of material processing industries has had the greatest contribution to the growth of their national wealth. Refractories are essential for all industrial processes using elevated temperatures. The ability to withstand exposure to heat above 538 °C is the critical distinction separating refractory from other ceramics. The aim of this study therefore, is to find out the possibility of using Diatomite, mined in Kenya, as a major raw material in the production of refractory linings. Diatomite has been utilized in Kenya but majorly in the manufacture of products like industrial filters and fillers for local consumption and export. Diatomite were collected from Gilgil near Lake Elementaita, crushed, sieved and the chemical composition determined. The samples were moulded into rectangular shaped bricks of 40mm height, 40mm width and 80mm length, allowed to dry and later fired up to a temperature of 1000⁰C. Refractory properties like Compressive strength, Hardness, Linear shrinkage on firing, Apparent porosity and Density were determined. The result of chemical analysis indicated that the clay was composed of Silica (SiO₂), 74.8%; Alumina (Al₂O₃), 3.26%; Iron Oxide (Fe₂O₃), 2.19%; Calcium Oxide (CaO), 1.82%; Potassium Oxide (K₂O), 0.64%; Sodium Oxide (Na₂O), 2.77%; and other traces. The physical and mechanical tests show that the clay had Cold Crushing Strength of 1357kPa, Hardness of 10.03GPa, Linear shrinkage of 11.17%, Apparent Porosity of 64.55% and Bulk Density of 0.81g/cm³. Diatomite can make better local refractory raw materials.

Keywords: Refractory, Diatomite, cold crushing strength, hardness, density, porosity, shrinkage

1.0 INTRODUCTION

Any material can be described as a 'refractory', if it can withstand the action of abrasive or corrosive solids, liquids or gases at high temperatures. Refractory materials are used in linings for furnaces, kilns, incinerators and reactors. Depending on the operating environment, they need to be resistant to thermal shock and have specific ranges of thermal conductivity and coefficient of thermal expansion. The ability to withstand exposure to heat above 538 °C is the critical distinction separating refractory from other ceramics, fibres and coating applications at only lower temperature [1].

[2], reported in his work on refractory properties of termite hills under varied proportions of additives that over 80% of the total refractory materials are being consumed by the metallurgical industries for the construction and maintenance of furnaces, Kilns, Reactor Vessels and Boilers. The remaining 20% are being used in the non-metallurgical industries as cement, glass and hard ware.

The basic functions of refractory materials are given below [3];

1. To ensure the physical safety of personnel and installations between the hot material (the processed product) and the outer shell of the processing tool
2. To reduce heat loss.

Most refractory materials are made from naturally occurring high melting point oxides. They include silica (SiO_2), Alumina (Al_2O_3), Magnesia (MgO), Chromium oxide (Cr_2O_3), Zirconia (ZrO) and iron oxide (Fe_2O_3). They are either used in natural form without any formal processing or in roasted condition [4].

It is unfortunate that despite vast clay deposits in Kenya, the Country's metallurgical industries still depend on imported refractories to meet local consumption and as a result, a lot of hard earned foreign currencies are spent in the process.

[5], mentioned that the ceramic industry is basic to the successful operation of other industries and their properties are also critical for many applications.

The aim of this study is to research on the production of high temperature refractories from local materials. This research focuses on the use of Kenyan diatomite for the manufacture of refractory materials. High quality refractory at a cheaper cost is the main requirement because cost of refractory adds into the cost of products.

Diatomite also known as Diatomaceous earth is a naturally occurring, soft, siliceous sedimentary rock that is easily crumbled into a fine white powder. The powder has an abrasive feel similar to pumice powder, and is very light due to its porosity. Diatomite is a highly porous material that exhibits high absorption capabilities and has a good chemical inertness. Major applications are filtering aids, metal polishing, thermal insulation, and Portland cement [6].

Diatomite in its natural state is a soft rocklike material consisting of the skeletal remains of a variety of single celled microscopic plants known as diatoms. They are generally amorphous, hydrated or opaline silica, $\text{SiO}_2 \times n \cdot \text{H}_2\text{O}$, with various amounts of impurities such as silica sand, clay minerals, metal salts and organic matter. Because of these contaminants, silica content may range from 58 to 90% of the dry product [7].

Since its establishment in 1942, Africa Diatomite Industries Limited (ADIL) has been exploiting diatomite in Gilgil, a town north west of Nairobi (Kenya), for export. ADIL has access to good quality diatomite deposits estimated at over 6 million tons and currently boasts having the only known viable quality deposits of Diatomite in Kenya [8].

In addition to diatomite deposits in Gilgil, the mineral has also been discovered in Baringo. Currently, according to [9], diatomite mining in the area is carried out by artisans in an open-cast method. The amount is yet to be quantified but it is estimated to be of substantial quantity. [9] also reports that, a Chinese company holding 202 square kilometers-rich in diatomite and non-metallic gem minerals in Baringo is looking to setting up a KSh200 million diatomite mine.

According to [10], the Physical properties of the diatom and of processed diatomite that provide unique commercial value in a broad spectrum of market end users include ornate fine structure, low bulk density, high porosity, and high surface area. Properties of equal importance are mild abrasiveness, high absorptive capacity, insulating ability, relative inertness, high silica content and high brightness.

Processed diatomite possesses an unusual particulate structure and chemical stability that lends itself to applications not filled by any other form of silica. Foremost among these applications is its use as a filter aid, which accounts for over half of its current consumption. Its unique diatom structure, low bulk density, high absorptive capacity, high surface area and relatively low abrasion are attributes responsible for its utility as a functional filler and as an extender in paint, It is actively exploited and used as raw material for filtration of fluids, pesticides, thermal treatment, paper and rubber filling and natural water purification [7].

2.0 THE OBJECTIVES OF THE RESEARCH

General Objective

To investigate the potential of Kenyan diatomite for use in the production refractories.

Specific Objectives

1. To carry out chemical analysis of the clay under study.
2. To prepare brick samples out of the diatomaceous earth.
3. To determine the physical and mechanical properties of the prepared samples.

3.0 MATERIALS AND METHODS

3.1 Raw material and Sample Preparation

The production of refractories begins with processing of raw materials. Raw material processing involves drying, crushing and grinding and determination of the Chemical Composition.

The raw materials (clays) were initially air dried and then later oven dried at 105⁰C to ensure that all the moisture had been removed.

The raw materials were then crushed using a pestle and mortar until a suitable ratio for coarse particles to fine particles was achieved.

The chemical composition of the raw clay sample in percentage weight (wt %) of (SiO₂, Al₂O₃, Fe₂O₃,etc) was examined using Atomic Absorption Spectrophotometer (AAS), which was carried out at Ministry of Mining Research Laboratories Center, Nairobi, Kenya.

3.2 Development of the refractory from the raw materials

This involved the actual production of refractory from the collected raw materials to the final shaped (formed) product.

1. Mixing

The ground particles were thoroughly mixed. This was done for two purposes;

- i) For even distribution of the coarse and fine particles
- ii) For making moulding easy

2. Moulding

The brick samples were formed into the required shape and size with the aid of a wooden box type of mold which could produce three samples at one go. The test pieces of the refractory materials were made into rectangular shapes of dimensions 80 x 40 x 40 mm in a mold and compacted under a hydraulic pressure of 350kN/m². 350kN/m² was determined as the optimum hydraulic pressure necessary from the work of [11].

3. Drying

The molded refractory was dried to remove its moisture. This was carried out very slowly and under particular set of conditions of humidity and temperature.

The sample bricks were air dried until when they were physically seen to be dry. From the drying floor the samples were then put in an oven operating at 105°C for twelve hours to remove all the remaining moisture.

4. Firing

The dried refractory was burnt for vitrification and development of stable mineral forms. In this step the already dried bricks were passed through a furnace at a controlled temperature over a certain fixed duration. The samples were fired at a temperature of 1000°C. At this temperature, the soaking time was six hours (6hrs). This is according to [12].

3.3 Testing of the brick samples to establish their stability characteristic properties.

3.3.1 Apparent porosity Test

Porosity of a material is defined as the ratio of its pores volume to the bulk volume. Thus porosity is an important property of refractories because it affects several other characteristics like strength, abrasion resistance, thermal conductivity and chemical stability. Porosity decreases the strength, thermal conductivity, resistance to abrasion and resistance to corrosion. On the other hand, it increases the penetration of slags, molten charge and/or gases into the refractory material and resistance to thermal spalling (thermal shock resistance). Therefore, in general, a good refractory should have lower porosity.

The apparent porosity, sometimes referred to as open porosity, is a measure of the open or interconnected pores in a refractory. The apparent porosity is determined by the volume of liquid which was absorbed by the pores when the specimen is boiled in vacuum conditions, and when the material is saturated in water.

According to [13], the porosity of a refractory has an effect upon its ability to resist penetration by metals, slags and fluxes and, in general, the higher the porosity, the greater the insulating effect of the refractory.

[14], also states that porosity and pore size distribution of a refractory will influence its thermal conductivity, in that, more porous refractory translates to a more insulating refractory.

This experiment was performed according to [15], whereby dry specimens were put in an oven maintained at a temperature of 110⁰C till it attained a substantially constant mass (with an accuracy of 0.01grams). The weight of the specimen (W_1) was recorded after cooling it to room temperature. The dry specimens were then immersed completely in water at atmospheric temperature for 24 hours. The specimens were taken out of water and wiped out with a cloth before being weight. The weight after removal from water was let to be, W_2 .

The respective dimensions of the samples were measured using a vernier caliper. The dimensions were then used to calculate the sample volume (V).

The apparent porosity per cent, after 24 hours immersion in cold water is given by the relation;

$$\text{Apparent porosity, } P_A = \frac{W_2 - W_1}{V} \times 100$$

Where: W_1 and W_2 is the weight of the absolutely dry specimen and the weight of the same specimen saturated in water [g], and V is the volume of the specimen [cm^3] [16]

$$\text{Volume} = \text{length} \times \text{width} \times \text{height}$$

3.3.2 Bulk density

The bulk density (BD) is the amount of refractory material within a volume (kg/m^3). An increase in bulk density of a given refractory increases its volume stability, heat capacity and resistance to slag penetration. Bulk density is the ratio weight or mass to volume and it is expressed in pounds per cubic foot or kilograms per cubic meter [17].

[13], also defines bulk density as a measure of the ratio of the weight of a refractory to the volume it occupies.

According to [14] report, the simplest way of measuring Bulk Density for uniform rectangular refractory shapes is by dividing Dry Weight by Bulk Volume which is calculated from measured dimensions. Density, porosity and permeability measurements show whether a body is fully dense, and whether therefore it can be expected to stand up to aggressive slag attack and/or penetration by process gases.

The air dried specimens were further oven dried at 110 °C, cooled and weighed to the accuracy of 0.01 in order to determine their dried weight (DW). The respective dimensions of the samples were measured using a vernier caliper. The dimensions were then used to calculate the sample volume (V).

The bulk density was calculated from the equation proposed by [18].

$$\text{Bulk density, } BD = \frac{DW}{V} \text{ g}/\text{cm}^3$$

Where, DW = Dried Weight V = Volume

$$\text{Volume} = \text{length} \times \text{width} \times \text{height}$$

3.3.3 Cold crushing strength

Cold crushing strength is the resistance of the refractory to compressive loads. As per [19], a cold crushing strength test is used to measure the cold strength of a brick. It is used to show whether or not the brick has been properly fired. This test, generally a quality control check, also indicates whether the brick will damage to corners and edges in transport. Cold crushing strength is the maximum load at failure per unit of cross-sectional area when compressed at ambient temperature.

The dried test bricks produced from the anthill clay, were oven dried at a temperature of 110 °C for 12 hours. It was then cooled to room temperature. The specimen was then taken to the compressing test machine where load was applied until cracks were noticed. The load at which the specimen cracked was noted, which represents the load required for determining cold crushing strength of the test specimen.

The test was carried out in accordance with [20]. Cold Crushing Strength was then calculated using Equation;

$$CCS = \frac{\text{Maximum load (kN)}}{\text{Cross-sectional area (m}^2\text{)}} = \frac{P}{A}$$

Where, CCS = Cold Crushing Strength P = Applied Load A = Area of Load Applied

A good refractory material must possess high mechanical strength to bear the maximum possible load without breaking.

3.3.4 Linear shrinkage

Linear shrinkage represents the permanent change that the refractory shapes undergo on heating or after reheating under a given set of conditions. The drying of clay is always accompanied by shrinkage. As the film of water between the clay particles is drawn off by evaporation the particles draw closer together to close up the interstices. The effect of this action is the shrinkage of the entire mass of clay.

To determine the fitness of a particular brick for service, it is often tested for shrinkage under temperature conditions equivalent to those which it would receive in use. This is done by first determining the length or volume of the brick by measurement and then subjecting it to a prolonged heating at the desired temperature. After the brick has cooled, it is again measured and the length, volume and shrinkage determined.

A slanted line of length 6cm was inserted horizontally on each piece and recorded as (L_1). The test pieces were then placed inside the furnace and fired up to 1000°C and the line drawn across the horizontal axis of the pieces was measured to determine its final length (L_2) after firing. The linear shrinkage of the materials was determined with equation;

$$\text{Linear shrinkage (\%)} = \frac{L_1 - L_2}{L_1} \times 100$$

The test was carried out in accordance with [21].

3.3.5 Hardness test

Hardness is a characteristic of a material, which can be defined as the resistance to indentation, and it is determined by measuring the permanent depth of the indentation. Measuring the hardness of a ceramic is important and this is usually done using an indentation test. The basic idea is that a permanent surface impression is formed in the material by an indenter. The actual or projected area of the impression is then measured. The hardness is then determined by dividing the applied force, F , by this area [22].

In this study, hardness will be determined using the Brinell method. The Brinell method applies a predetermined test load (F) to a carbide ball of fixed diameter (D) which is held for a predetermined time period and then removed. The resulting impression is measured across at least two diameters – usually at right angles to each other and these result averaged (d).

In this experiment, the indenter diameter (D) used was 5mm and the test force (F) was 1kN.

Typically, an indentation is made with a Brinell hardness testing machine and then measured for indentation diameter in a second step with a specially designed Brinell microscope or optical system. The resulting measurement is converted to a Brinell value using the Brinell formula or a conversion chart based on the formula.

Equation below illustrates the formula used to obtain the Brinell value.

$$HB = \frac{0.102F}{0.5\pi D(D - \sqrt{D^2 - d^2})} \text{ N/m}^2$$

Where F = Force, D =Ball Diameter, d = diameter of indentation.

at a constant force of 1kN, and a ball diameter of 5mm

4.0 RESULTS AND DISCUSSION

The results from the experimental work are given in tables 1 and 2. From table 1, it is evident that diatomite clay has silica as the predominant substance and it could be concluded that it is siliceous in nature.

The sample has high silica content well above the ideal 46.51% for clay which makes it be able to withstand fairly high temperatures [23]. From [24] report, the silica content of diatomite satisfies the standards for the manufacture of high melting clay.

The sample clay has a fairly high iron content (Fe_2O_3) which makes it fire terracotta red (brick red) color on firing [11].

The Loss on Ignition of the diatomite clay (LOI) was determined as the percentage of moisture loss to ignition on firing. This represents the amount of moisture the clay material could hold or percentage weight reduction of the soil sample which may probably be a reflection of its grain structure and fineness. Following the report by [24], the loss on ignition of the sample falls within the standard range for the production of ceramics, refractory bricks and high melting clay. [25], suggests that the loss on ignition values, are required to be low in order to reduce on the effect of porosity on the final products.

Table 1: Chemical composition analyses of Anthill clay compared with standard clay for industrial applications [24].

Composition	Diatomite Clay	Ceramics	Refractory Brick	High melting clay	Glass	Paper	Paint
SiO ₂	74.8	60.5	51.7	53-75	80-95	45-45.8	45.3-47.9
Al ₂ O ₃	3.26	26.5	25-44	16-29.0	12-17.0	33.5-36.1	37.9-38.4
Fe ₂ O ₃	2.19	0.5-1.2	0.5-2.4	1-9.0	2-3.0	0.3-0.6	13.4-13.7
CaO	1.82	0.8-3.0	0.1-2.0	0.5-2.6	4-5.0	0.03-0.6	0.03-0.6
K ₂ O	0.64	-	-	-	-	-	-
TiO ₂	0.22	-	-	-	-	-	-
CuO	-	-	-	-	-	-	-
V ₂ O	-	-	-	-	-	-	-
LOI	13.78	8-18.0	8-18.0	5-14.0	-	-	-

The physical test results of diatomite clay showed an apparent porosity of 64.5% which according to [26], qualify to be used as insulating firebricks. The samples with the values ranging between 40-70%, are likely to be poor heat conductors, and of low strength. They can be used for insulating purposes. The low strength can be improved upon by increasing the firing intensity.

The bulk density of 0.8 g/cm³ was obtained which according to [27] makes them qualify to be used as insulating refractories.

The Cold crushing strength of the diatomite bricks obtained was 1357 Kpa. This value falls within the standard range for the manufacture of thermal insulators as given by [28]. According to Kumar, the standard range is 981-6867kPa.

According to [25], the total percentage shrinkage for standard fireclay and siliceous refractories are supposed to be ranging between 4-10%. The total percentage shrinkage value obtained from the brick samples was 11% which fall slightly above the acceptable range.

The hardness value obtained from the fired diatomite bricks was 10.03GPa which falls between the highest and least hardness values for ceramics as given by [22]. It is reported that MgO has the least hardness value of 3.63GPa while Diamond is the hardest with a value of 78.48 GPa.

Table 2: Physical and Mechanical test results

Sample description	Tested properties				
	Apparent Porosity (%)	Bulk Density (g/cm ³)	Cold Crushing Strength (kPa)	Linear Shrinkage (%)	Hardness (GPa)
Anthill Brick	64.5	0.8	1357	11	10.03

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

An experimental study was conducted to investigate the suitability of diatomaceous earth as industrial raw material for making refractories in view of their chemical, mechanical and physical properties.

The results of the chemical analysis showed that the clay contain silica (SiO₂) as major constituent making it suitable as siliceous refractory material.

The batch samples passed through the experimental tests to determine their refractory properties in terms of mechanical and physical behaviors showed that the selected raw material (clay) can substitute for the imported refractories as thermal insulators. The cost of refractories will also reduce since they can be obtained locally.

The chemical composition results also suggested that the clay is found to be a source of local raw materials for the production of thermal insulators.

The results of the investigation will be very useful and serve as a database for prospective investors and managers of metallurgical industries.

It can therefore be concluded that diatomite can substitute for the imported refractory raw materials.

5.2 Recommendation

The clay under study, that is, diatomite, has not been exploited in Kenya for the production of refractories. Thus if this clay is exploited and harnessed, it will no doubt provide an internal source of raw materials.

There is also the need for geological survey to determine the extent of the deposits.

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