

Journal of Science and Technology Research

Journal homepage: www.nipesjournals.org.ng



Assessing the Potential Application of Geophagic Materials as Refractory for Metallurgical Furnace Lining

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Article Info

Abstract

Received 11 June 2020 Revised 16 June 2020 Accepted 29 June 2020 Available online 31 August 2020

Keywords:

Geophagic material, Furnace, Anthill, Fireclay, Refractory



https://doi.org/10.37933/nipes/2.3.2020.13

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High temperature furnaces require the appropriate refractory materials as liners. Several of these refractory materials including fireclays have been employed in high temperature furnaces as refractories. Geophagic materials as a type of clay materials eaten by animals, including man have also been asserted to possess significant refractory properties but proper investigation and assessment of their thermal behavior have not well been studied. This work therefore investigated and assessed the potential utilization of these geophagic materials as refractories for furnace lining. The physical, chemical and thermal treatment properties of two common geophagic clay materials, anthill and pica, were explored. Bricks made from these clayed materials were fired in a locally manufactured furnace. Thermal shock resistance (13 cycles), linear shrinkage (1.3%) and loss on ignition (9.6%) as properties of these refractories were evaluated. The results indicated significant amount of Fe, Al, K, Ca and Mg as the predominant elements in these clay samples. The results also demonstrated that pica clav cannot withstand temperatures beyond 300 °C. Thermal treatment results show that anthill can withstand temperatures of 1500 °C without significant deformation. A blend between the two materials was able to withstand temperatures between 800 $^{\circ}C$ – 900 $^{\circ}C$ before cracking. These results indicate that anthill is a potential geophagic material which can be employed as a fireclay refractory in metallurgical furnace lining.

1. Introduction

Refractories are those materials which have high melting points and have properties which make them suitable to act as heat resisting barriers between high and low temperature zones [1]. Refractory materials can be divided into several classes based on: chemical composition (acid, basic and special), method of implementation (shaped and unshaped), method of manufacture (fused and sintered), and porosity content (porous and dense). These materials are supposed to be resistant to heat and are exposed to different degrees of mechanical stress and strain, corrosion from liquids and gases, and mechanical abrasion at high temperature [2]. Different types of refractory materials can be synthesized according to the nature of the raw materials and the process used. The application fields of refractory are multiple and depend on the properties of each type. In fact, the performance of a refractory (good resistance to heat and thermal shock) is directly related to texture and richness of the mineral refractories, such as mullite, corundum, periclase, doloma, spinel and alumina [3]. Refractories are mostly used in basic metal industries. The major characteristic requirement of these refractories is resistance to molten slag (basic) and to the high temperature generated in the process.

Saim A. K. et al. / NIPES Journal of Science and Technology Research 2(3) 2020 pp. 119-126

In the aluminum industry, the refractory property requirements are quite different from that of steel making. Although the temperature of aluminum refining and alloying process is much lower than for steel, it has the unique problem of penetration in the refractories. Hence, the refractory should be designed so that it has a nonwetting characteristic to molten aluminum [4]. In hydrocarbon industries, the refractories suffer from a high rate of abrasion due to the flow of high-velocity particles at a continuous rate. Hence, the refractory properties should be such that it should be capable of resisting the abrasion [2]. In the glass-making process, the refractories are in constant contact with the molten glass, and this poses different kinds of requirements for the refractory. Since glass in the molten state is quite fluid and tends to go through the refractories are used in molten glass contact areas [5].

Moreover, refractories are inorganic, non-metallic, porous, and heterogeneous materials consisting of thermally stable mineral aggregates, a binder phase, and additives. The general specifications of refractories include (i) the ability to withstand high temperatures and trap heat inside a restricted area such as a furnace, (ii) the ability to withstand action of liquid metal, hot gasses and liquid slag by resisting erosion and corrosion etc. (iii) ability to withstand load at service environment, (iv) ability to resist contamination of the material with which it comes into contact, (v) ability to maintain necessary dimensional stability at high temperatures and after/during repeated thermal cycling, and (vi) ability to conserve heat. Important properties of refractories include chemical composition, bulk density, apparent porosity, apparent specific gravity and strength at atmospheric temperatures. These properties are frequently among those which are used as 'control points' in the manufacturing and quality control process. The chemical composition serves as a basis for classification of refractories and the density, porosity and strength are influenced by many other factors. Among these are type and quality of the raw materials, the size and fit of the particles, moisture content at the time of pressing, pressure at mould, firing temperature, duration of firing, and the rate of cooling.

Fireclay refractories are widely used due to their ease of fabrication, resistance to chemical attack and low cost. Applications for fireclay refractory brick include insulation behind hot-face materials, furnace linings, and specialty applications such as laboratory crucibles and setters [6].

Over the years, there have been several works towards developing refractory products from local clay deposits. Various research works have found that refractory clays are suitable for use in furnace lining and steel industries. Andrews et al., [6], have studied the production of refractory material from lithomargic clay deposit. Lithomargic clay underlying bauxite deposits in Ghana result from incomplete bauxitisation process. The lithomargic clay consists mainly of kaolinite and gibbsite (42.2% of Al₂O₃; 50.3% of SiO₂). The results show that the linear firing shrinkage values were within limits acceptable for refractory clays. The cold crushing strength increases as temperature increased to 1400°C and with increasing binder content. This study indicates that lithomargic clay under lying bauxite deposits could be used to produce fire clay aluminosilicate refractories. Different forms and wares were fabricated with the clay materials from the anthill. It unveiled anthill as an insulative structure that retains heat in the semblance of an insulation brick kiln [7]. Nnuka and Agbo [8] studied the characteristics of Nigerian clays and discovered that the Otukpo clay has refractoriness of 1710 °C, which compares well with imported refractories. Recently, Asante-Kyei, [9] designed and produced a large gas kiln utilizing a mixture of kaolin and anthill as the refractory bricks.

Geophagic materials are soil and clay deposits which are deliberately eaten by animals including man; mostly among children and pregnant women [10]. It is a special type of pica, which is defined as the craving and subsequent consumption of non-food substances. Thin sections of some

geophagic materials in Ghana revealed the presence of large amounts clay and some quartz, feldspars and sericite [11]. In this work, two geophagic materials namely, pica and anthill were evaluated to ascertain their potential utilization as a refractory material for furnace lining. Important properties such as thermal shock resistance, linear shrinkage and loss on ignition were also evaluated.

2. Methodology

2.1 Materials

Anthill clay samples were taken from a village farm near Tarkwa in the Western Region. The pica samples were also obtained directly from the mine site of Anfoega in the Volta Region of Ghana. The furnace, "*sikabukyia*" used for firing the bricks was a high temperature gas fired furnace at the Minerals Engineering Laboratory of University of Mines and Technology, UMaT. Infrared thermometer, thermocouple, screens, pair of tongs, water and all other materials used for the experiment were obtained from the Minerals Engineering Laboratory, UMaT.

2.2 Sample Preparation

The geophagic clay samples (Figure 1) were sun dried for 24 h. The samples were crushed and pulverized in a ball mill for 30 min. The pulverized samples were screened and a particle size of $-150 \,\mu\text{m}$ was used to mould the bricks.

2.3 Experimental Procedure

Three different bricks $(10 \text{ cm} \times 6 \text{ cm} \times 2 \text{ cm})$ were formed from the clay samples as shown in Figure 2. The bricks slabs (100 g each) were air dried and allowed to cure for 24 h.



Figure 1. Geophagic Clay Samples (a) Pica, (b) Anthill



Saim A. K. et al. / NIPES Journal of Science and Technology Research 2(3) 2020 pp. 119-126

Figure 2. Moulded bricks (a) 100% anthill, (b) 50% anthill and 50% pica material, and (c) 100% pica

2.3.1 Firing of Bricks

After curing of the bricks, each block was fired in a locally manufactured furnace to maximum temperatures of 1400 $^{\circ}$ C – 1550 $^{\circ}$ C for 1 h. Both the infrared thermometer and the thermocouple were used to monitor the temperature changes within the furnace. The bricks were allowed to cool for 30 min after the first firing and they were subsequently subjected to another firing in the furnace.

2.4 Elemental Analysis

50 g of the pulverized pica samples was weighed into a conical flask and it was acid digested using aqua regia of 25 mL nitric acid and 75 mL HCl. After the digestion, the mixture was filtered. A 32-Element Test was conducted on the filtrate using the ICP-OES at an externally certified lab, Crystal Scientific Laboratories, Tarkwa, Ghana.

2.5 Thermal Shock Resistance

Two prepared brick slabs of anthill were inserted in the furnace which has temperatures between 1300 $^{\circ}$ C – 1500 $^{\circ}$ C. This temperature was maintained for 10 min. The slabs were removed with a pair of tongs from the furnace one after the other and then cooled for 10 min. The slabs were returned to the furnace for further 10 min. The process was continued until the test bricks were cracked. The number of cycles of heating and cooling before cracking of the slabs was recorded as its thermal shock resistance.

2.6 Linear Shrinkage

Rectangular test pieces were marked along a line in order to maintain the same position after heat treatment. The distance between the two ends of the slabs was measured with vernier calliper. The slabs were air dried for 24 h and oven dried at 110 °C for another 24 h. They were then fired for 1 h at 1500 °C. The test pieces were cooled to room temperature and measurements taken. The fired linear shrinkage was calculated from Equation (1) [13].

Fired Shrinkage =
$$\frac{D_L - F_L}{D_L}$$
 (1)

Where, D_L is the dried length and F_L is the fired length.

3. Results and Discussion

3.1 Chemical Composition

The behavior of the refractories during their use depends also on the type of raw materials used and the reactions achieved during the firing. The result of the 32-Element test is shown in Table 1. It can be seen that the predominant elements in pica clay are Fe, Al, K, Ca and Mg. The silica content is very low in pica. For anthill, the silica content is reported to be as high as 59.83% [12].

3.2 Heat Treatment Studies

Good refractory materials show very high resistance to heat. Firing of the pica materials in the furnace beyond 300 °C resulted in the cracking and disintegration of the slab indicating that pica cannot withstand very high temperatures. Figure 3 shows the disintegrated fired pica. Brick (b),

Element	Concentration (mg/50g)
Iron	4631
Aluminium	2516
Potassium	652.9
Calcium	93.29
Magnesium	81.38
Sulphur	28.01
Copper	24.69
Sodium	22.96
Barium	17.38
Phosphorus	15.64
Vanadium	13.31
Chromium	9.511
Silica	7.311
Lead	4.054
Manganese	3.386
Arsenic	3.349
Nickel	1.58
Strontium	1.56
Zinc	1.424
Titanium	0.894
Antimony	0.344
Molybdenum	0.313
Tin	0.299
Boron	0.231
Silver	0.219
Lithium	0.157
Cobalt	0.144
Beryllium	0.099
Cadmium	0.041
Thallium	<0.0044
Selenium	<0.0031
Mercury	< 0.00014

Table 1. 32-Element Test Results from Pica Sample

Saim A. K. et al. / NIPES Journal of Science and Technology Research 2(3) 2020 pp. 119-126

which contains 50% pica and 50% anthill also withstood temperatures of 800 °C – 900 °C before cracking and decoloring into dark-brown as depicted in Figure 4. The anthill showed very good resistance to heat because it was able to withstand temperatures between 1400 °C to 1550 °C without any significant deformation (Figure 5). To confirm this observation, the anthill brick was allowed to cool and it was re-fired at that same temperature range for 2 h. This observation established the refractoriness of anthill for furnace lining at 1550 °C. Hence, subsequent experiments were conducted using anthill clay. These results show that a blend ratio of pica with anthill reduces the refractory properties of anthill whereas the refractory properties of pica improves with the addition of anthill.



Figure 3. Disintegrated pica at a firing temperature of 300 °C.



Figure 4. 50% blend ratio of pica and anthill brick after firing at 800 °C to 900 °C for 1 h.



Figure 5. Anthill after firing at 1400 °C – 1550 °C for 1 h

3.3 Linear Shrinkage

The average linear shrinkage (1.3%) for anthill bricks are lower than the recommended range of 4-10% for fireclay as reported by [13]. This is more desirable. Higher shrinkage values may result in warping and cracking of the brick and this may cause loss of heat in the furnace.

3.4 Thermal Shock Resistance

The thermal shock (13 cycles) of the anthill brick sample was below the acceptable values of 25-30 cycles as established [14]. The practical implication of this is that their use is restricted to lining of ladles and slag pots which are early mended at shock intervals.

3.5 Loss on Ignition

This is the combustion of volatile matter present in the clay. 50 g of the dried anthill pulverized sample contained in a crucible was fired in the furnace at 1200 °C to 1500 °C for 1 h. The final weight (45.2) after heating showed 9.6% loss on ignition. This value was lower than 18% specified upper limit for refractory clays.

4. Conclusion

This work assessed the potential utilization of geophagic materials as refractory for furnace lining. The refractory properties of two geophagic materials namely, anthill and pica were studied and compared. It has been shown that pica cannot withstand temperatures over 300 °C whereas anthill demonstrated a refractoriness of 1550 °C. Physical observations and other refractory properties such as linear shrinkage (1.3%), thermal shock resistance (13 cycles) and loss on ignition (9.6%) of anthill bricks has shown the possibility of employing it as a furnace lining. This also means that this anthill cannot be used as a refractory when treating materials with melting points beyond 1500 °C. These anthills or termite moulds are ubiquitous in natural landforms, forming part of their landscape. This work has ascertained the possibility of harnessing these anthills as refractory materials.

Further work can be done to explore several other refractory properties of these geophagic materials. Moreover, it is recommended to adequately investigate the use of other additives or binders to improve the fireclay refractoriness of these materials.

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