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Characterization of Clays from selected sites for Refractory Application

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Abstract- Clay is a stony or earthy mineral aggregate composed of fine-grained minerals, which are plastic at appropriate water content and hardens up when fired. Clay soils have various mineral groups such as kaolinite, smectites, illites and palygorskite-sepiolite with unique properties for industrial applications. Uses of clay include manufacture of cement, tiles, ceramics, bricks, drilling clays, lead pencils, printing inks and paints. This project determined elemental and mineralogical composition of clays from Githima (0º 46´ 40´´ S, 37º 6´ 31´´E), Kimathi (0º 40´ 0´´S, 37º 10´ 28´´E) and Ithanje (0º 36´ 30´´ S, 37º 6´ 46´´E). The elemental and mineralogical composition were determined using AAS and XRD techniques respectively. The results indicated that clays composed of SiO_2, Al_2O_3, and Fe_2O_3 as the major components in the following ranges of 40.80-55.40%, 16.27-30.33% and 3.90-20.53% for SiO_2, Al_2O_3, and Fe_2O_3 respectively. Mineralogical results showed that the main mineral present in the clays were kaolinite, illite and quartz. Apparent porosity, linear shrinkage, bulk density, refractoriness and thermal shock resistance were 26.31-31.33%, 1-3 %, 1.56-1.68 g/cm^3
1609-1686 ºC and 20-26 cycles, respectively

Index Terms- Clay; Minerals; Refractory.

I. Introduction

Refractory refers to the quality of materials to retain their strength at higher temperatures [1]. Refractories are composed of thermally stable mineral aggregates which are inorganic and nonmetallic. They have unique physical and chemical properties that promote resistance to physical wear, high temperature and corrosion [2,3,4]. They are used in constructing high temperature components of structures such as furnaces, kilns, heat exchangers, and incinerators. Refractories belong to the category of ceramic materials, that are utilized for prime temperature typically higher than 1100ºC [5]. Most refractories are made from naturally occurring high melting point oxides such as SiO_2, Al_2O_3, MgO, Cr_2O_3, ZrO [6]. The base material for refractory production is clay. Clays are naturally occurring sediments produced by chemical actions resulting from weathering of rocks [7]. Clay is a stony or earthy mineral aggregate composed of fine-grained minerals, which are plastic at appropriate water content and hardens up when fired, Clay has silica, alumina, and water as

primary constituents, other constituents are iron, alkaline, and alkaline earth metals [7]. Clay minerals are important industrial minerals and millions of tons are used yearly in various modern technology applications such as in ceramics, refractories, paper, foundry, rubber, paints, plastics, insecticides, pharmaceutical, textile, and adhesive industries [8]. Their applications are tightly dependent upon their structure, composition and physical attributes. The data of those characteristics will facilitate for best exploitation and eventually could open up new areas of applications. They conjointly contain non-clay minerals like quartz, feldspar, mica, calcite, dolomite etc. Deposits of clay are widely distributed in Kenya [9,10,11,12]. In order to determine their refractory applications, it is important to determine their mineralogical and elemental composition. In this project we report the mineralogical and elemental composition of selected Kenyan clays.

II. Materials and Method

Purposive non-probability sampling design was used to select sampling sites. Samples were obtained from sites whose clays were being used commercially for pottery. The clay deposits investigated were collected from Githima-clay (0º 46´ 40´´ S, 37º 6´ 31´´E), Kimathi-clay (0º 40´ 0´´S, 37º 10´ 28´´E) and Ithanje clay (0º 36´ 30´´ S, 37º 6´ 46´´E). The clay samples were collected at two depths that is 0.5 and 1.0 meter. In each site the clay samples were obtained from three (3) points that were at least 100 meters apart. From each sampling point/depth 10 kg samples were collected and packed in new cleaned plastic buckets which were then covered with their lids.

III. Elemental Analysis

Weighed 0.1g of clay sample was placed in a 125-mL plastic beaker, 1.0 mL of aqua-regia was added followed by 3.0 mL of hydrofluoric acid and left to digest for 8 hours. Further, 50 mL boric acid was added and the mixture allowed to digest for one hour. The solution was topped to 100 mL using distilled water. Samples were analyzed alongside the standards [9,11,13]. This was done using AAS SPECTRA AA10 Model, at department of Mines and Geology, Ministry of Environment and Mineral Resources, Kenya.

IV. Mineralogical Analysis

About 3.0 g of the pulverized clay sample was poured into the well of a low background sample holder. The holder was tapped on a bench to help fill and properly pack the sample to avoid sample displacement which causes peak shifts. Using a sharp razor, the sample surface was slowly tapped into either direction pushing excess sample slowly to the end of the well and finally scrapping it off the holder. The sample was then loaded into the defractometer and measurements taken. This was done using a Bruker D2 Phaser defractometer at the Department of Mines and Geology, Ministry of Environment and Mineral Resources of Kenya.

Development of refractory brick

Test refractory bricks were made using wooden boxes molds having internal dimensions of 8.0 cm long, 4.0 cm wide, and 4.0 cm high. The test refractory bricks were air-dried then oven dried at 105^0C until the bricks attained a constant weight. Dried test bricks were then fired in a furnace at a temperature of 1000^0C for 6 hours [12].

Apparent porosity Tests

Test brick was dried in an oven set at 1050C until it achieved a constant mass. The brick was cooled then weighed and weight recorded as W1. The test brick was completely soaked in water for 24 hours, after which it was wiped then reweighed and the weight recorded as W2. Dimensions of the test brick were measured and used to calculate its volume. Percent apparent porosity was calculated using the following formula [14];
Apparent porosity, PA={(W2-W1)/V*100}
Where: W1= Weight of dry test brick, W2= Weight of test brick after soaking in water overnight, V= is the volume of the test brick cm3.

Bulk density

Air-dried test brick was oven dried at 1050C, cooled and weighed. Dimensions of the test brick was obtained and used to calculate test brick volume, bulk density was obtained by calculation using the equation [14,15]:
Bulk density, BD=DW/V g/cm3.

Where, DW=Weight of the dry brick, V= Volume of the dry test brick.

Firing shrinkage test

Firing shrinkage was determined by measuring dimensional changes that took place in a test brick after drying at 1050C and after firing it at 10000C. Firing shrinkage was calculated using the following formula [6, 14,16];
Firing shrinkage = (LD-LF)/LD
Where LD= Length of test brick dried at 1050C, LF=Length of test brick fired at 10000C.

Refractoriness

The refractoriness of a clay sample was calculated using equation below [17];
Refractoriness = {(360+%Al_2O_3)/0.228}-Ro
Where Ro is the sum of all other elements apart from alumina and silica in the composition.

Loss On Ignition (LOI)

Powdered clay samples (2.0 g) were weighed in a crucible. The crucible and its contents were fired at 1000ºC in a furnace for 3 hours after which it was allowed to cool in a desiccator before reweighing. Loss on Ignition was calculated using the equation below [16]:
Loss on ignition ={(W1-W2)/W1}100 where W1 = weight of the crucible + weight of the sample before firing and W2 = weight of the crucible + weight of the sample after firing.

V. RESULTS AND DISCUSSION

Elemental composition

Results of elemental analysis of clays from the selected sites are shown in **Table 1** below

Table 1: Elemental composition of clays

Composition	Githima	Kimathi	Ithanje	*Standard clay for refractory bricks
SiO_2 %	40.80±0.06	55.40±0.20	44.03±0.03	51-70
Al_2O_3 %	16.27±0.05	22.40±0.02	30.33±0.15	25-44
CaO %	0.56±0.04	0.67±0.05	0.53±0.03	0.1-2.0
MgO %	0.02±0.01	1.82±0.02	0.02±0.01	0.2-1.0
K_2O %	0.96±0.03	2.65±0.03	0.84±0.02	
TiO_2 %	7.62±0.03	0.62±0.03	3.49±0.03	
MnO %	0.08±0.02	0.06±0.02	0.23±0.15	
Fe_2O_3 %	20.53±0.15	3.90±0.02	10.40±0.20	0.5-2.4
LOI %	11.47	12.2	10.84	8-18.0

*Reference [18]

The major elements present in clay from the selected sites were silica SiO_2, alumina Al_2O_3, iron (III) oxide Fe_2O_3. The other elements present in appreciable levels were potassium oxide K_2O, titanium oxide TiO_2 and magnesium oxide MgO, while those present in trace amounts are calcium oxide, CaO and manganese oxide, MnO. The clays were found to have percentage range composition of 40.80-55.40% SiO_2, 16.27-30.33% Al_2O_3, 0.53-0.67% CaO, 0.02-1.82% MgO, 0.84-2.65% K_2O, 0.627.62% TiO_2, 0.06-0.23% MnO and 3.90-20.53% Fe2O3, while LOI was 10.84-12.20%. LOI for all the clays fall within the international acceptable limits for refractory application [18]. Based on SiO_2 content Kimathi clay was within the standard value for refractory application. Ithanje clay had the highest Al_2O_3 content compared to clays from other sites. The level lies within the standard value for refractory application. High levels of Fe_2O_3 is not desirable in refractory material, all clays from selected sites had higher levels of Fe_2O_3 above the standard value for Fe_2O_3 content for refractory materials [18]. Calcium oxide (CaO) of all selected clays were below the standard levels for refractory application. Magnesium oxide (MgO) content was found to be within the standard requirement except for Kimathi whose content was slightly higher than the recommended value.

Mineralogical Composition

The minerals present in the clays were determined using XRD and the results are as given in Figure 1 and Table 2 below.

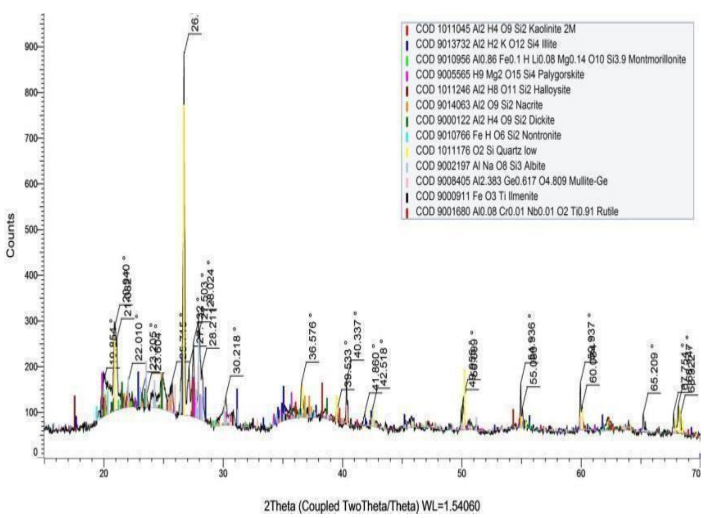

Figure 1: XRD spectrum for Ithanje clay

Table 2: Mineralogical composition of selected clays

% Mineral	Githima	Kimathi	Ithanje
Kaolinite	15.0	8.3	17.0
Quartz	17.6	11.6	4.8
Illite	37.9	15	13.9
Nacrite	6.2	10.3	16.8
Dickite	5.8	7.4	16.4
Montmorillonite	2.8	4.8	3.7
Ilmenite	1.8	0.5	2.3

XRD results showed that kaolinite, quartz and illite were the major mineral components in selected clays. Kaolinite levels ranged between 8.3 and 17.0% while illite concentration ranged between 13.9 and 37.9%. Kaolinite and illite are important clay minerals and due to their high levels, these clays may be used for refractory purposes with some enhancement. Quartz had a concentration in the range of 4.8-17.6%. The selected clays also contained nacrite and dickite which belong to kaolin group clay mineral.

Physical and thermal properties

Physical and thermal properties of selected clays compared with standard properties for refractory bricks are shown in Table 3 below.

Table 3: Physical and thermal properties of selected clays

Property	Githima	Kimathi	Ithanje	*Standard clay for refractory bricks
Fried Linear Shrinkage (%)	1	3	3	2-10
Permeability to air	37	45	53	25-90
Apparent porosity %	26.31	26.72	31.33	20-30
Bulk density g/cm3	1.56	1.68	1.56	2.2-2.8
Thermal Shock Resistance (cycles)	20	24	26	20-30
Refractoriness, 0C	1609	1655	1686	1500-1750
Loss On Ignition	11.47	12.20	10.84	

*Thermal properties international standard [19]

The clays had a range of 26.31-31.33% apparent porosity, 1-3 linear shrinkage, 1.56-1.68g/cm^3 bulk density, 1609-1686 ºC refractoriness. Refractoriness of clays from selected sites were within the standard limits. Permeability to air values were within the recommended range [19]. Ithanje clay apparent porosity was slightly above the standard limit whereas Githima and Kimathi clay apparent porosity are within the acceptable range. Thermal shock resistance of these clays were within the standard range of 20-30 cycles. However, bulk densities of the clays were below the standard values for refractory materials.

VI. Conclusion

Githima, Kimathi and Ithanje clays are composed of SiO_2 and Al_2O_3 as major constituents hence are fit for use as a source of alumino-silicate refractories. However, further research should the carried out to improve their properties for refractory application.

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