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Resistance of Fortified Kaolin to Attack by Molten Frit

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Introduction: Low cost refractory mixes of adequate resistance to molten glass attack is required for frit furnace lining, but when the corrosion behaviour of alumino-silicate type refractories are studied, kaolin is often neglected. Meanwhile clay is cheap in the study area and studies had shown that clays that are comprised largely of kaolinite are refractory, and are applicable for various refractory purposes. In this study, the effect of addition of zirconia and alumina to selected kaolin on its physicomechanical properties and corrosion resistance were examined.
Aims: The study is aimed at developing a corrosion resistant refractory for lining frit furnaces used in studio practice by fortifying a locally available kaolin in Nigeria know refractory materials.
Study Design: The experimental design in which the effect of percentage addition of alumina and zircon on the sintering properties and corrosion resistance of base kaolin were measured against the desired properties of the resultant bodies.
Methodology: The clay mineralogical analysis was conducted using XRD. The refractoriness was measured by the pyrometric cone equivalence (PCE) method. The effects of varying percentage additive refractory material on the sintering properties of bodies formulated and sintered at 1300 ^{o}C were assessed using the ASTMC20 00 Standard test method. The corrosion resistance of the bodies was assessed using the crucible (slag cup) method.

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Results: Results indicated that the clay was predominantly kaolinite. The addition of alumina increases the porosity of the mix. The stabilized zircon increased the specific gravity the most. It increased the bulk density at both 5% and 10 % addition but decreased at 15% addition. The sample mix which contained 10% stabilized zircon and 5% alumina shows appreciable resistance to corrosion by the molten frit.

Conclusion: This study confirms that clay that is predominantly composed of kaolinite is a potential base material for composing refractory lining for a fritting furnace.

Keywords: Kaolinite; frit attack; corrosion resistance; zircon; refractory mix.

1. INTRODUCTION

In a developing country like Nigeria, low cost refractory mixes of adequate resistance to molten glass attack are needed for frit furnace lining. The frit furnace is important to the production of frit for constituting low temperature glazes that is compatible with the kind of bodies that most of the potters use. Alumina-Zirconia-Silica (AZS) refractory is a material often used in furnace part in contact with molten glass because of its high resistance to corrosive actions of molten glasses or slag [1]. Commercial AZS is composed of 43% Al_2O_3 37% ZrO_2 and 20% SiO_2 [2]. Unfortunately, pure alumina and zirconia are very expensive and this makes the application of AZS to be unaffordable at resource-disadvantaged places.

In many attempts at producing furnace lining, clay has always been used in little quantity as a bonding material [2]. However alumino-silicates are generally employed in frit kilns due to their low cost. Despite this kaolin is often neglected. Fatih and Sedat [3] studied the corrosion behaviour of alumino-silicate type refractories in frit but unfortunately kaolin was not considered in the study while kaynite, sillimanite and andalusite were investigated. The silica-alumina refractories are necessarily materials which are increasingly demanded for in the synthesis of mullite. The clay especially have the attributes of being relatively inexpensive compared to other aluminosislicate materials [2].

Fatai and Saliu [4] investigated locally sourced kaolin and potter's clay for the production of refractory lining for diesel fired rotary furnace. The work emphasize the effect of chamote content on the cold crushing strength, thermal shock resistance, shrinkages, bulk densities and specific gravity of the test samples. Yet there is the need to investigate resistance to corrosion, which is of cardinal importance to material for furnace lining. The resistance of the refractory to corrosion is important because it is used in parts that are always subjected to aggressive condition when in contact with molten liquid or gas. This property is rarely tested or specified [4].

In allusion to the conversion of kaolin to meta-kaolin: $2Al_2Si_2O_5\,(OH)_4 \rightarrow 2Al_2Si_2O_7 + 4\,H_2O$ [5], it could be deduced that if there could be kaolin of high purity, the addition of zircon and alumina in regulated quantities to it would yield a refractory of adequate resistance to corrosion at a lesser cost. This would fulfil the quest to balance cost and performance in refractory choice [6]. As earlier observed by Murray [7] clays that are comprised largely of kaolinite are refractory, and are used to make heat-resistant firebricks, insulating bricks, saggers, refractory mortars and mixes, monolithic and castable materials, ramming and air-gun mixes, and other heat-resistant products. Hence a choice of clay for refractory purpose must prima facia be kaolinite, which would only require a little quantity of alumina and zircon addition [6].

Alumina belongs to the class of special refractory which increases the refractoriness of aluminosilicates with its degree of abundance [8]. Fatih and Sedat [3] studied the corrosion behaviour of aluminosilicate type refractories in frit melts in an isothermal corrosion test setup under both static and dynamic conditions. The experimental method of concomitant variation was used to measure the effect, (change in refractory properties) that occurs when percentage composition of alumina varies, and is correlated with the variations in the effect. The results indicate that mullite samples were more resistant to the corrosive frit and that temperature and exposure time are significant factors affecting corrosion of the refractories. The mullite type has higher alumina ratio (3:2) compared to andalusite (1:1). This shows that the corrosion resistance of kaolin may be improved with the addition of alumina.

The fortification of kaolin usually requires the introduction of zircon in addition to alumina. Zircon, otherwise called zirconium silicate with the chemical formula $ZrSiO_4$, falls into the category of neutral refractory. It is a source of zirconium oxide (ZrO_2) and silica (SiO_2) in body compositions. Qing-cai et al. [9] studied ZrO_2 corrosion resistance and the effect of its addition on the corrosion rate of the Al_2O_3-C based refractories. The test results show that the bricks containing ZrO_2 are of better corrosion resistance than the ZrO_2-free bricks. The ZrO_2 addition improved the oxidization resistance of the refractory and decreased the interaction rate between the melts and the refractory [9].

The cost of AZS may be too expensive for the kind of product for which the target furnace is to produce and the working temperature is lower than the capacity of AZS. This research therefore seeks to develop a low cost refractory formulation that will just be adequate for lining fritting furnaces with predominantly kaolin fortified with ZrO_2 and alumina [2].

2. MATERIALS AND METHODS

The kaolin used in this study was obtained from SOMAK Industries (NIG) Limited, Km 12 Auchi – Igara road, Ikpeshi, Edo State. It is white in colour and received in powdered form. The clay was reported to be composed predominantly of kaoilinite with traces of SnO_2, Fe_2O_3, ZnO and NiO [10]. It is white in colour appreciable purity and consequently be applicable for refractory purposes. It is found in commercial quantity which makes its supply sustainable. The alumina used was obtained from a chemical shop at Ile-Ife, Osun state. It is aluminium oxide of mole weight 101.98, pH value of 6.5 – 7.5; weight per mole of 0.9 and particle size 70 – 230 mesh. This is an imported material prepared by Loba Cheme Pvt. Mumbai India. The zircon used was obtained from a local dealer at Jos. It was from Azara-Lafia deposit in Nigeria. The zircon sand has chocolate cream colour. It came in particle size of 80 mesh. It was reported to be of high refractoriness and composed of 96% zircon, 1.6% kyanite, 0.8% rutile and 1.40% of other impurities [11].

2.1 Characterization of the Base Clay

Method of clay minerals investigation using X-ray diffraction (XRD) for the identification and quantification of aluminosilicates as explained by Al--Ani and Sarapää [12] was followed. The material was prepared for XRD analysis using a back loading preparation method. It was analyzed with a Malvern Panalytical Aeris diffractometer at XRD Analytical and Consulting cc, 75, Kafue Street Lynnwood Glen South Africa. A PIXcel detector and fixed slits with Fe filtered Co-Kα radiation were employed. From the XRD pattern, crystalline phases and the quantity of each phase in the mixture were determined.

Aside the mineralogical composition, the physical properties of clay sample fired at 1200°C were measured. The Boiling Water method of the ASTM C20 was employed in assessing the porosity, water absorption, specific gravity, and bulk density of the clay. The test specimens were shaped into disks using a rammer with 6.4kg load falling from a height of 51mm. The mold used was cylindrical in shape with diameter 50.8mm and 120.6mm in height. Test specimens of approximately 16mm thick were dried and fired at 1200°C. The refractoriness of the sample was obtained by measuring the pyrometric cone equivalence as described in ASTM.C24. Test cones were prepared from representative sample of the clay. The test pieces with the standard cones were kept in the furnace on a refractory pedestal and the deformation end point of the test pieces was compared with that of a standard pyrometric cones.

2.2 Body Composition

The first set of samples were prepared by composing a line blend between kaolin coded Ka and alumina (A). Four samples containing 0wt%, 5wt%, 10wt%, and 15wt% of alumina were composed. The samples were subjected to analysis of the sintering properties and a choice for further fortification with zircon was made.

The second set of samples was composed of kaolin, alumina, and zircon. The zircon sand was milled to 75% < 100µm in particle size. The chosen batch with which zircon was mixed was the one with 5% Alumina. The samples were composed by blending the selected KaAb and Zircon dopped with10% MgO. Four samples containing 0wt%, 5wt%, 10wt%, and 15wt% of zircon (Z) were composed by calculating the weight fraction of each material in the composition thus:

For 5 % zircon = $\left\{\frac{95}{100}(95\mathrm{K}+5\mathrm{A})\right\}+\left\{\frac{5}{100}(90Z+10M\right.$

For 10% zircon = $\left\{\frac{90}{100}(95\mathrm{K}+5\mathrm{A})\right\}+\left\{\frac{10}{100}(90Z+10M\right.$

For 15% zircon $=\left\{\frac{85}{100}(95\mathrm{K}+5\mathrm{A})\right\}+\left\{\frac{15}{100}(90Z+10M\right.$ [12]

The resulting batch composition is as shown in table.

Each blend was intimately mixed together, formed into shape, dried, fired and assessed as the previous sample for sintering properties. In addition, the samples were assessed for corrosion resistance based on the varying percentages of zircon.

2.3 Corrosion Resistance of Bodies under Static Condition

The corrosion resistance of the bodies was assessed by adopting the crucible (slag cup test) method as used by Guzmán et al. [2]. The independent variables are the corrosive medium, refractory compositions, time and temperature. The response variable (effect) to be measured is the resistance to corrosion, where corrosion involves degree of wear and depth of penetration. The depth of penetration by the corroding agent (frit) was evaluated by measuring the dimensions shown in Fig. 2 for each refractory composition.

Glass line corrosion is calculated as follows:

$$G_c=\left[G-\frac{1}{2}(g_1+g_2)\right]/2$$

where;

G_c = glass line corrosion,

G = width of cross section specimen at glass line, before test, mm, and

g_1 and g_2 = width of the two halves of the cross section of the crucible at the glass line, after test, measured on cut face mm.

Half-down corrosion is calculated as follows:

$$H_c=\left[H-\frac{1}{2}(h_1+h_2)\right]/2$$

where;

H_c = half-down corrosion,

H = width of the cross section of the crucible, half way between glass line and the bottom crucible, before test, mm, and

h_1 and h_2 = width of the two halves of the sectioned test crucible at the half-down level, after test, measured on cut face in mm.

Table 1. Mix Proportions of Alumina, kaolin, zircon and magnesia

Samples	Kaolin	Alumina	Zircon	MgO
O	95	5.0	0	0
I	90.25	4.51	4.50	0.50
II	85.50	4.28	9.00	1.00
III	80.75	4.04	13.50	1.50

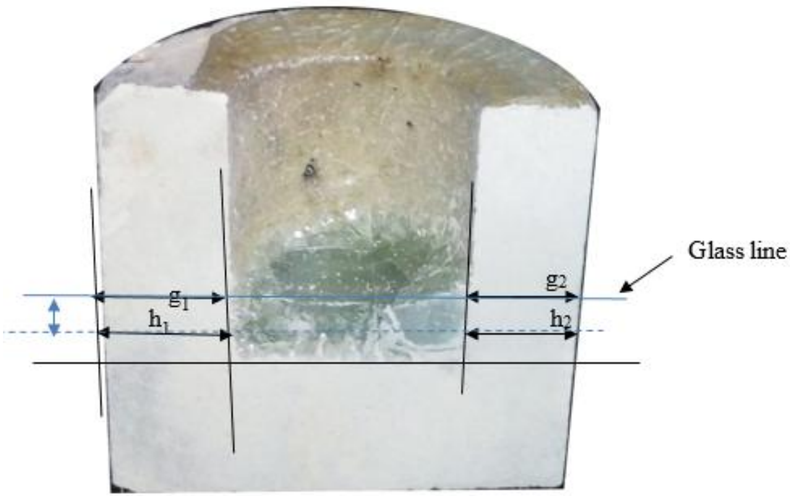

Fig. 1. Corrosion resistance model

Further, thin sections of samples were prepared using the method described by Hirsch [13]. The slides of the thin sections were analyzed, using the method as explained by Michael et al. [14]. The deterioration layer and interface zone between the melt and the refractory were examined using a polarizing petrographic microscope. The micro-textural and morphological features in the thin sections were used as a measure of degradation. The samples were viewed under both plane-polarized and crossed polarized lights. The boundary between the refractory and the molten frit was examined for reaction, penetration and erosion. The photomicrographs of the images were then taken and the least affected sample was identified.

3. RESULTS AND DISCUSSION

3.1 Mineralogical Composition of Kaolin Samples

The X-ray diffraction (XRD) patterns of oriented powder mount of the <2μm fraction samples are as contained on Fig. 2, showing the appearance of hkl peaks kaolinite, and other silicates. The kaolinite phase is represented by blue sticks, quartz green, muscovite brown and albite pink. It could be observed that the positions and intensities of the reference sticks match the sample data. The phases present were kaolinite, quartz, anatase, muscovite and plagioclase. This result was in agreement with the findings of Omang [10] about the sample of okpella clay collected from Ajego 2.

The clay was predominantly kaolinite as shown in Table 2. It belongs to high kaolinite group according to the classification proposed by Dondi [15] which is characterized by high to very high amount of kaolinite and may be containing low amounts of illite-mica, Al-oxyhydroxides and non-plastic components (quartz, feldspars, rock fragments, titanium dioxide) each below 15%. This means that the clay is fit for refractory purpose.

The sintering property of the base clay is as shown on Table 3. The clay has the refractoriness typical of kaolinites and many fireclay refractories in agreement with ASTM classification for refractory fireclays. It falls into the class of High Duty Slag resistant refractory brick having the refractoriness of 31.5 PCE, bulk density of min. 2.19g/cm^3. However, the apparent porosity is higher and the bulk density is about 14% lower than expected minimum. This degree of porosity in an indication that the clay is yet to be thoroughly vitrified at the temperature of 1200^{o}C. That is, it can still be fired to much higher temperatures safely.

Table 2. Mineral composition of the Raw Clay sample

Kaolinite	Quartz	Anatase	Muscovite	Plagioclase	Class
94.06	4.12	0.83	0.96	0.03	HK

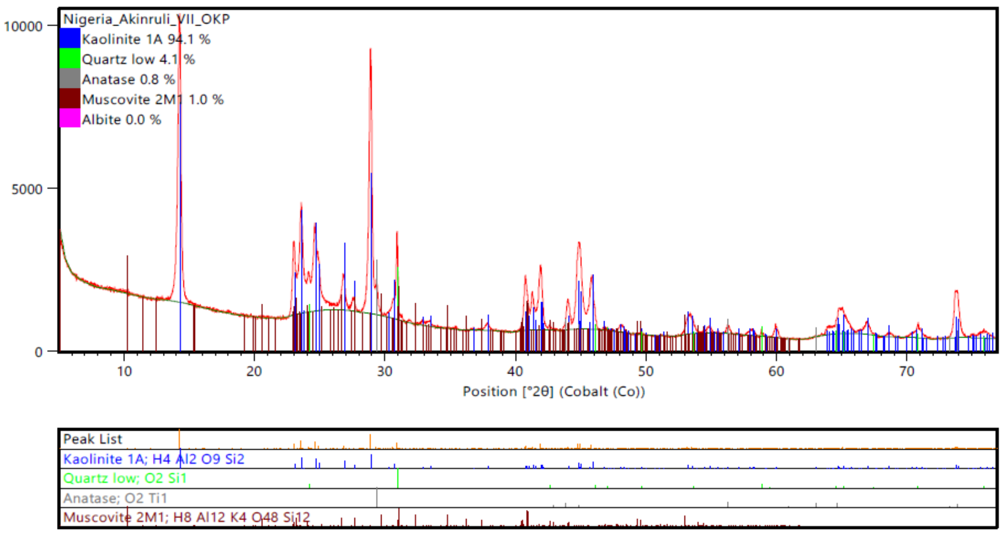

Fig. 2. X-ray diffraction (XRD) patterns of clay sample

Table 3. Property of the clay after sintering

Properties	Values
Refractoriness (PCE)	≥32 (1738.33 °C)
Apparent specific gravity	2.686
Bulk Density at 1200°C	1.877±0.00
Apparent Porosity(%) at 1200°C	30.11±0.77
Water Absorption (%)	16.044
Strength(Mpa)	34.73

On the table, the strength shown is within the acceptable value for refractory. The cold crushing strength is the resistance of the refractory to crushing, which mostly happens during handling. This property has an indirect relevance to refractory performance, and is used as one of the indicators of abrasion resistance.

It is shown in Fig. 3 that addition of alumina increases the porosity of the mix, which is detrimental to a refractory. These effects could be attributed to the fact that alumina is refractory and the temperature at which it was fired was relatively low for it to react with other materials in the mixture. This is in agreement with the explanation offered by Jim [16] on Arrhenius theory about the influence of temperature on rate of reaction. This shows that a substance must be heated to overcome its activation energy before reaction progresses with time. Since alumina is required in the mix, the sample with 5% alumina and of the highest bulk density among the samples of which alumina content is >0 was selected for zircon addition.

Also zircon addition increases porosity but not as much as that of alumina. It imparts slight increase on the apparent specific gravity with no difference with increasing percentage addition. In Fig. 4, it is shown that the stabilized zircon increased the bulk density at both 5% and 10 % addition but decreased at 15% addition. This increase in bulk density desirable for the refractory. Bulk density, apparent porosity, apparent specific gravity and strength at atmospheric temperatures are among those properties which are used as control points in the manufacturing and quality control process for a refractory [17].

The bulk density is generally considered in conjunction with apparent porosity. For many refractories, the bulk density provides a general indication of the product quality; it is considered that the refractory with higher bulk density (low porosity) is of better in quality. increase in bulk density of a given refractory increases its volume stability; heat capacity and resistance to slag penetration.

Fig. 5 shows the XRD pattern of the sintered mixes. The pattern indicates that new phases developed after sintering. The new phases include mullite, cristobalite, cordierite and amorphous phases. These phases are more stable at high temperature than their other polymorphs. Table 4 indicates the relative abundance of these phases in the mixes. The amount of amorphous phase is least where the zircon addition is the highest. Cordierite develops due to the addition of MgO to stabilize zirconia during heating and cooling. There may be need to increase the sintering temperature of the mixes so as to convert all the quartz to cristobalite. This will make the composition more stable such that the reheat change due to quartz inversion and conversion will be eliminated.

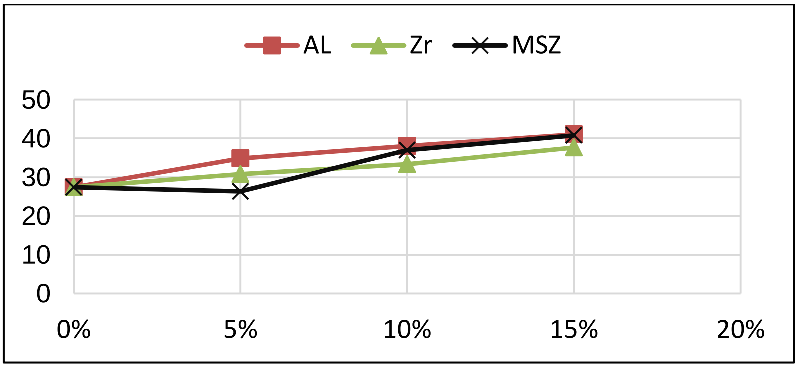

Fig. 3. Effect of Additives on porosity of the mix

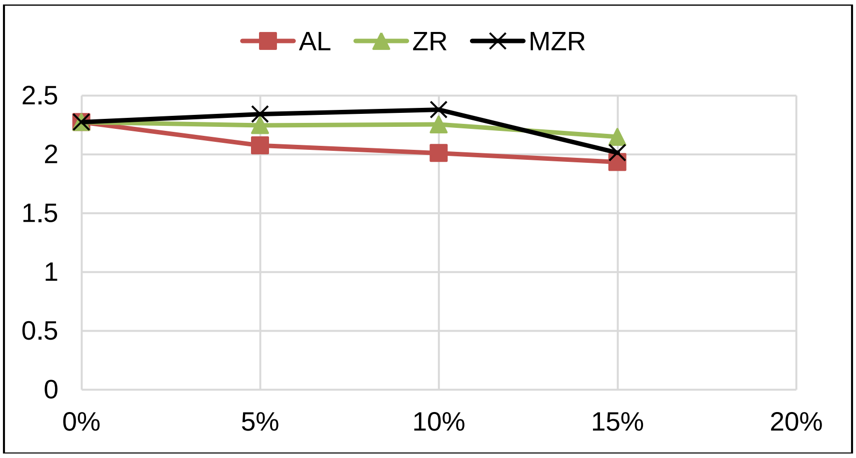

Fig. 4. Effect of Additives on Bulk Density of the mix

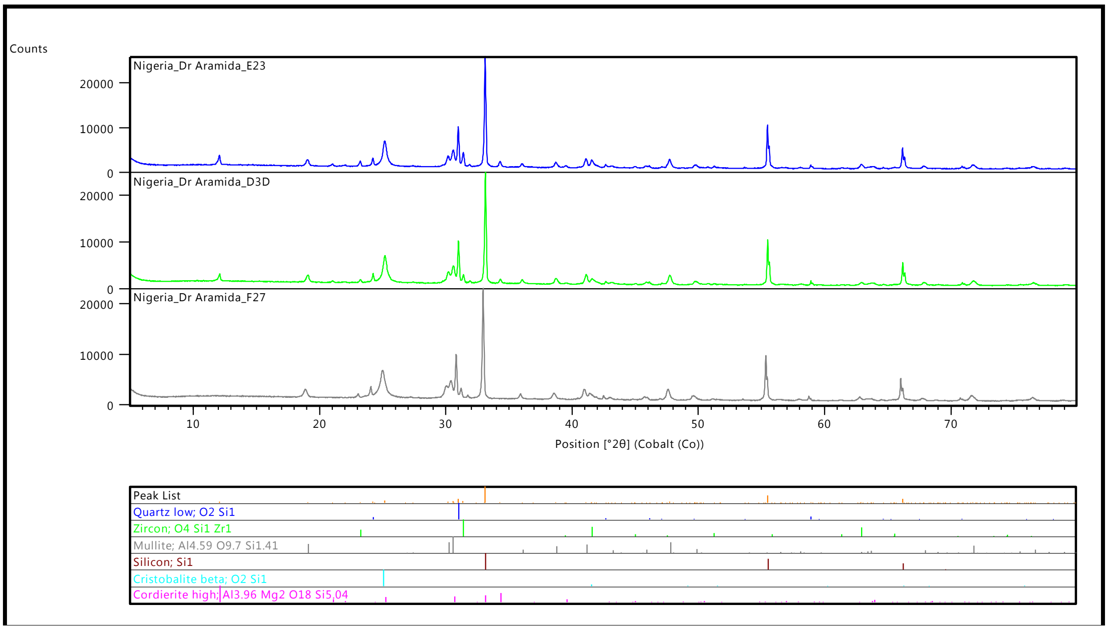

Fig. 5. XRD Pattern of Sintered Mix

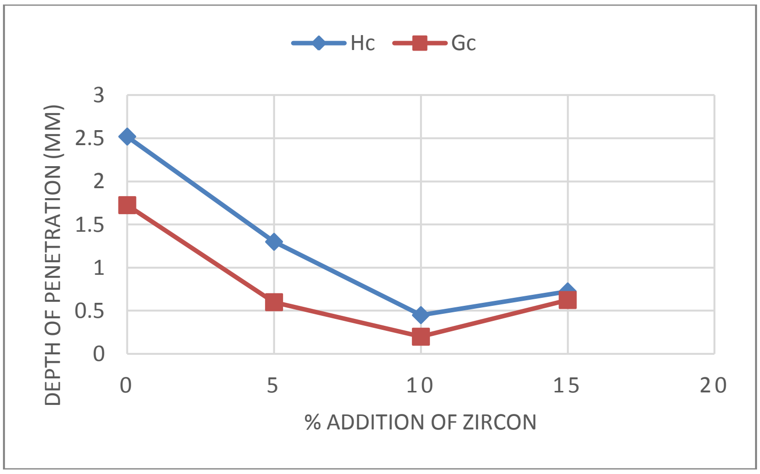

Fig. 6. The images produced from the thin-section

Table 4. Relative Abundance of Phases Present in the Sintered Mix

	Quartz	Zircon	Mullite	Cristobalite	Cordierite	Amorphous
I	13.3	3.4	49.1	18.1	9.6	6.6
II	13.2	1.6	53.7	20.0	6.4	5.0
III	13.8	1.8	59.4	24.5	0.0	0.5

0 = n.d. – not detected above the detection limit of 0.5-3 weight per cent

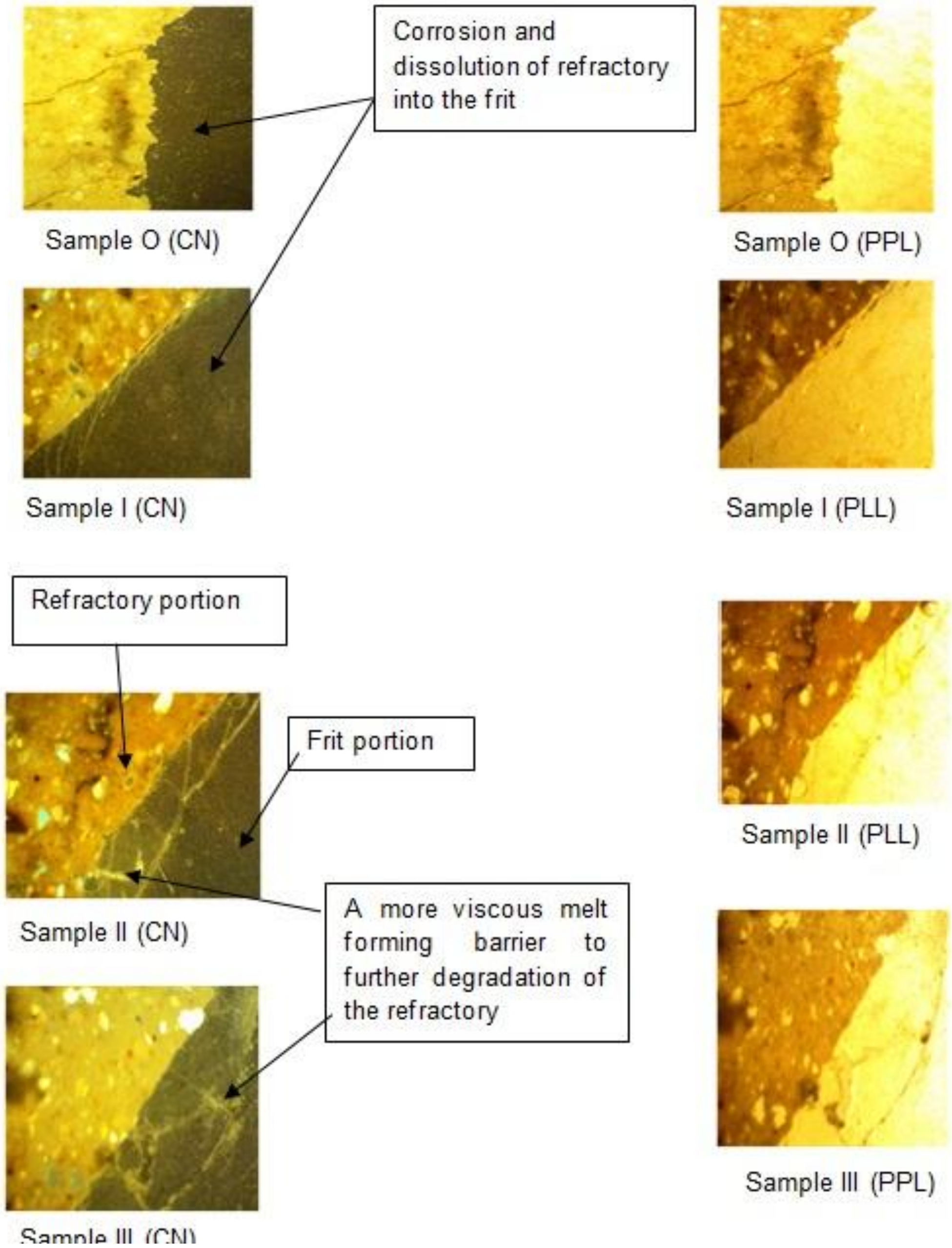

Fig. 7. Polarized Light Microscopy Images of Thin Sections

A measure of corrosion the involves degree of wear and the depth of penetration. Fig. 6 shows the effect of zircon addition on the corrosion resistance of the mix. It could be observed that the depth of penetration decreases with the addition of zircon. This effect was observed at two region of the crucible -that is, the half-down corrosion and the glass line corrosion. The depth of penetration by the corroding agent is grater at the glass line area than the half down the crucible from the top of the glass to the base of the crucible. However, the corrosion at both areas follows the same trend and the addition of zircon is best at 10%.

Fig. 7 shows the images produced from the thin-section of the sample test crucibles after heat campaign. There is a distinct boundary between the crystalline (refractory crucible) and amorphous (frit) portions. Sample O that is 100% kaolin presents a jagged boundary arising from erosion of the boundaries into the frit. The corrosion here is more intense as it involves both chemical and mechanical wear. The glassy portion of Samples O and I are cloudy under plain polarized light, indicating the presence of fugitives. Of course this would have happened if clay is added to the frit when reconstituting it into glaze. Sample II shows straight edge at the boundary between the glass and the refractory. The glass portion is clear indicating that the corrosion was passive and no contamination of the frit.

4. CONCLUSION AND RECOMMENDATIONS

Results obtained from this study confirm that clay that is predominantly composed of kaolinite is a potential base material for composing refractory lining for fritting furnace. However, the clay alone is not adequate for the purpose of lining the furnace. It has to be fortified by the addition of alumina and most importantly stabilized zircon. Even so, zircon addition should be limited to 10 % if the temperature of firing is not more than 1300^oC. In order to produce a dense mix that is rich in alumina and zircon, the sintering temperature must be increased with increasing percentage addition of these refractory materials. Also it is important to add a stabilizer to zircon not only to prevent cracks but also to improve upon the density of the refractory. The type of processes that are in operation during corrosion must be taken into consideration for proper analysis of corrosion resistance of a refractory. The process can take any one or a combination of direct dissolution, indirect dissolution, or selective dissolution.

The concentration of efforts on glaze materials or glaze calculation is inadequate for solving glaze production problem. Research efforts should be geared towards improving and producing refractory for the purpose of frit making as a way of resolving the problem of glaze production. In particular, priority should be given to issues of cost and corrosion resistance.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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