DEVELOPMENT OF RAMMING MASS FROM INDIGENOUS REFRACTORY MATERIALS FOR LINING MELTING FURNACES

BY

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CERTIFICATION

We certify that this research work and the results obtained were carried out by Olasupo Olayode Adesola of the Department of Metallurgical and Materials Engineering, The Federal University of Technology, Akure and had been approved as meeting the requirement for the award of M. Eng. degree in Metallurgical and Materials Engineering of The Federal University of Technology Akure, Ondo State, Nigeria.

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DEDICATION

..... to all those interested in the advancement of the younger generation of materials Scientists and Engineers in Nigeria.

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ABSTRACT

Aluminosilicate refractory ramming masses for lining melting furnaces were developed from suitable indigenous raw materials. Chemical analyses of the raw materials were done using the Atomic Absorption Spectrophotometer (AAS). Rammed samples from several ratios of clay, silica, mica, bentonite and Durax were prepared using the American Foundrymen Society (AFS) standard rammer and thereafter tested for such properties as apparent porosity, volumetric firing shrinkage, cold compression strength, green compression strength, loss on ignition, thermal shock resistance and refractoriness. The effect of sintering temperature on the physical and the mechanical properties of the samples were studied and reported. Microstructural analyses of some samples were undertaken. Results indicated that 8 ramming cycles was just enough for production of the ramming masses. Two optimal ratios obtained from experiments have a refractoriness of 1500^{0}C, excellent thermal shock resistance and good cold compression strength over the sintering temperatures. They therefore qualify to serve as service lining in rotary and crucible furnaces for melting of cast iron and non-ferrous alloys and could serve as a viable alternative to imported ramming masses of the same service temperature.

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INTRODUCTION

1.1 INTRODUCTION

Refractory materials are materials that can withstand a high temperature and attack in the severe conditions of working. They are thermal insulators, and are therefore used for making furnace linings, kilns, nozzles for pouring molten metal, heat exchangers, driers, solar furnaces, aerobraking heat shields, e. t. c. (Prado, 1999). Generally, they are composed of large grog or refractory grains held together with a fine-grained bond. Both the bond materials and the refractory grains have a fine structure, and both are often multiphase. Many variations occur among bricks made from different raw materials and by different manufacturer.

Ramming masses as a class of refractory materials are used for obtaining monolithic working faces. Such refractory compounds have specific applications in the repairs and construction of various furnace parts where the refractory lining should have high strength at high working temperature, high resistance to abrasion and slag attack, and high volume stability.

The ramming masses set either chemically, by heat, or by the use of ceramic materials. The setting methods used depends on the chemical composition of the ramming masses. Chemical setting refractories are manufactured by processes in which mechanical strength is imparted by chemical bonding agents as against those by firing techniques. Air setting refractories develop a strong bond upon drying. Such include mortars, plastic refractories, ramming and gunning mixes. The dry compositions (ramming mixes) require tempering with water to develop the necessary consistency. Heat setting refractories require relatively high temperatures for the development of an adequate bond, commonly called the ceramic bond. In ceramic

setting refractories, the mechanical strength is developed by a heat treatment which causes the cohesion of adjacent particles.

There are several compositions of these ramming masses that have been developed in the past majority of which are imported and hence costly. The occurrence of large deposits of refractory materials especially in the southwestern part of the country therefore calls for the development of ramming masses for lining melting furnaces.

The present economic realities of the country calls for the local sourcing of raw materials used in the production of engineering materials. Refractories, been one of the materials largely used in metallurgical plants, cement industries and power generating plants, if sourced locally would go a long way in reducing the present level of importation of these materials. This will in no small measure conserve the foreign exchange earnings of the country.

The fortunes and the economy of a country are inextricably linked to its steel consumption. The steel industries on the other hand are the major users of refractory materials. The development of refractory materials therefore becomes something of importance if Nigerian economy is to develop. The completion of the primary steel producers in Nigeria: namely the Ajaokuta Steel Complex and the Delta Steel Complex will herald the establishment of downstream industries in the steel sector. A large inventory or quantity of refractory materials of different shapes, sizes and composition will be needed if and when these complexes are working full stream. Also, the development of foundry sector for the production of various spare parts will lead to the consumption of refractory lining and ramming mixes for the lining of melting furnaces. All these when put together will result into a high consumption of refractories which has to be sourced locally.

1.2 OBJECTIVE OF THE PROJECT

The project aims at producing an aluminosilicate–based ramming mass that could be used in producing monolithic working face for furnaces building and repairs.

In undertaking this project the thermo-physical characteristics and microstructural study of various ratios of ramming mass containing kaolinitic clay, silica, and mica with bentonite and Durax (calcium aluminate cement) as binders are studied. The optimal ratio from the various mixes is determined for applications in different parts of furnaces.

CHAPTER 2

LITERATURE REVIEW

2.1 REFRACTORY

The term refractory has its origin from the Latin word *refractarius*, meaning stubborn (Lorimer et at, 1995). It is often defined as resistant to elevated temperature. Therefore the term could be applied to any material, which can work in a high temperature environment. For the purpose of this project refractory materials shall be regarded as a class of materials used as a furnace lining for high temperature materials processing of metals, glasses and ceramics. It should be noted that the greatest user of refractories today is the iron and steel industry consuming about 80% of production (Hassan, 2001).

2.1 TYPES OF REFRACTORIES

Refractories can be classified into four groups according to their chemical compositions and behaviours:

(i) Acidic refractories

(ii) Basic refractories

(iii) Neutral refractories

(iv) Special refractories

(i) **Acidic Refractories:** This group of refractories contains an appreciable amount of SiO_2 (acidic oxide) which will react at high temperature with basic refractories, slags and fluxes. Included in this category are silica refractories and aluminosilicate refractories (fireclay and high alumina refractories).

(ii) **Basic Refractories**: These are mainly composed of CaO, MgO or both. They react with acidic refractories, slags and acids at high temperatures. Examples are magnesite (MgO), dolomite ($CaCO_3$. $MgCO_3$) and chromite.

(iii) **Neutral Refractories**: These are neither acidic nor basic. They resist attack from both acidic and basic materials at high temperature. Examples include carbon and mullite refractories.

(iv) **Special Refractories**: This term is used for more recently developed materials such as ZrO_2, SiC and Si_3N_4.

2.3 REFRACTORY FABRICATION

The general method of refractory fabrication involves the conventional methods of powder processing. The aim of processing is to form a body, which is generally as near to thermodynamic equilibrium as possible at a commercially viable cost. Refractories generally tend towards equilibrium in service.

Refractories may be fabricated in two major ways:

(i) **Shaped (Bricks)**: These are shaped refractory materials which differ in composition and shape depending on application. There are fire clay bricks, high alumina bricks, acid Proof firebricks, insulating firebricks, special insulating fire bricks, mica insulating fire-bricks e. t. c.

(ii) **Unshaped** (monolithics, castables, mouldables and rammables)

(a) **Castables Refractory**: This is a mixture of heat-resistant aggregate and heat-resistant hydraulic cement; for use, it is mixed with water and rammed, cast or gunned into place.

(b) Ramming Mix: A ground refractory material which is mixed with water and rammed into place for patching shapes or for forming monolithic furnace linings.

(c) Monolithic Lining: This is a furnace lining without joints and formed of material which is rammed, cast, gunned or sintered into place. Monolithic lining have the advantages of simple processing and simple construction of joint free linings, very good resistance to thermal shock and superior thermal insulating properties in comparison with the brick lining. The difference in monolithic lining when compared with the formed bricks is that some of the manufacturing operations are performed by the manufacturer, while the forming and the firing responsibilities are transferred to the consumers. Hence, the final consumer will require the same technological knowledge as the manufacturer of shaped materials. The second important difference lies in the addition of binders, which provides the adequate green strength of the lining. For this purpose, use is generally made of cement either Portland or Aluminate type possibly with an increased Al_2O_3 content up to 80% because the refractoriness of the binders increase with Al_2O_3 content (Hlavac, 1983). Materials containing hydraulic cement are also called refractory concretes. Monolithic linings using clay binders are called plastic refractories. They usually contain another inorganic binder as a strengthening component, usually the phosphate binder or sodium silicate (water glass). The inorganic binders employed have the purpose of providing green strength during drying and firing. Moreover, the binders usually take direct part in the sintering at the highest temperature when the material attains its final strength. During gradual heating up the original binder is subject to decomposition in a certain

temperature range, which may result in considerable loss in strength. This is usually encountered with Portland cement as binder and is almost non-existent with phosphate binders (Hlavac, 1983). Fig 2.1 is a typical study by Hlavac, (1983) on the dependence of cold compression strength of monolithic materials on firing temperature.

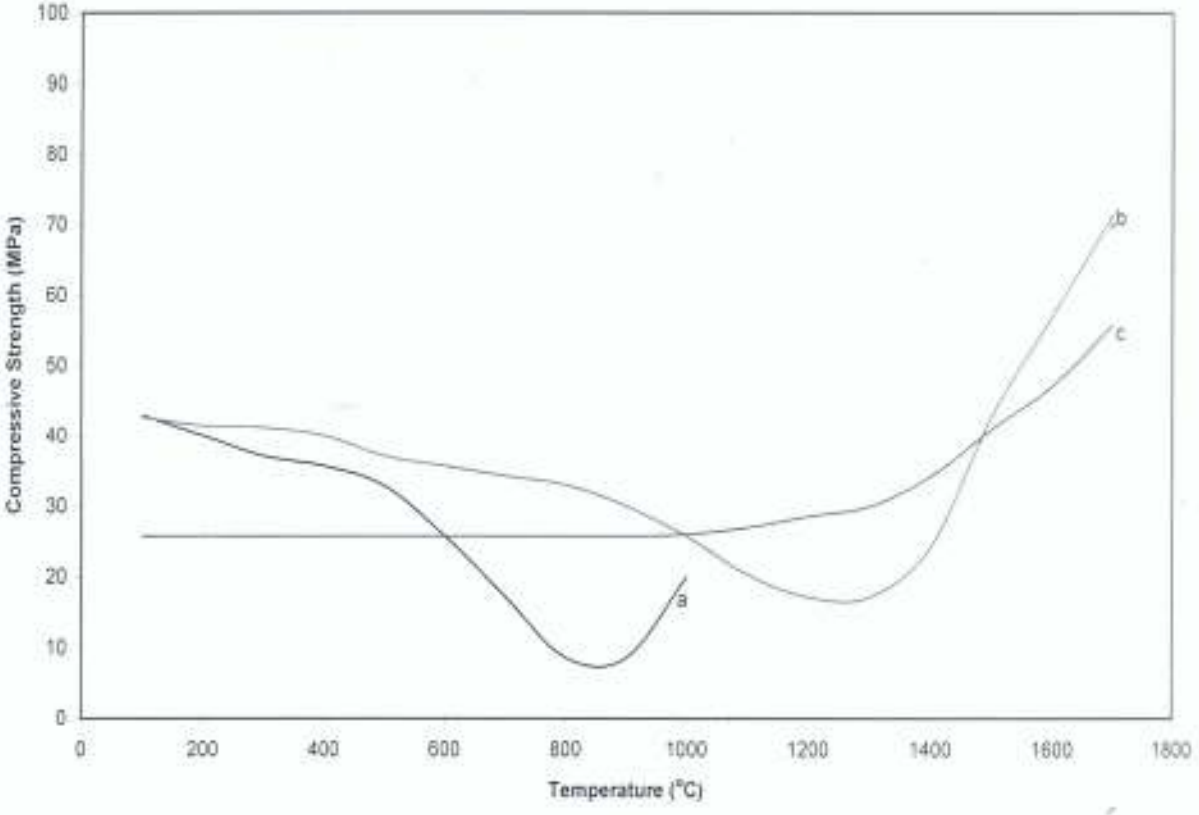


Fig. 2.1: The dependence of cold compression strength of monolithic materials containing various binders on firing temperature. (a) Portland cement, (b) aluminate cement, (c) phosphate binder. (Hlavac, 1983)

However, it should be noted that the strength of a rammed refractory is not uniform across the radial cross-section of a furnace / kiln. After heating up, the external (cooler) lining zone will exhibit a permanently lower strength because the material is sintered only on the hot side.

2.4 SILICA

Silica is very widespread in nature even in pure forms, so that it is utilized mostly as a natural raw material in the technology of silicates. Rock quartz is the purest natural form of silica. By washing in acids a content of more than 99.95% SiO_2 can be obtained. The raw materials of rock quartz include sand, sandstone and quartzite.

Natural silica sand may have up to 90-97% SiO_2, up to 8% foreign substances and not more than 2% clay (Asuquo, 1991), . When clay gets up to and beyond 50%, the material is essentially known as clay. Free silica, being non-plastic reduces plasticity and shrinkage in clays. Very small particles may act as flux whereas larger particles increase the refractoriness. Therefore, it may be necessary to use an optimum amount of silica in clay body so as to preserve plasticity to some extent and at the same time have enough to prevent severe or too much shrinkage. The particle size must not be too small and at the same time it should be noted that larger particle sizes reduces the crushing strength of the clay body. Therefore, a balance must be struck not only between the plasticity and shrinkage to determine the optimum amount of silica; a compromise also has to be reached in determining the most suitable particle size to be used.

Substances that may be present as impurities in silica are iron oxides, feldspar, mica and other minerals. Feldspar contains oxides of alkali and alkaline earth metals. These substances are harmful as they lower the refractoriness of quartz, combine chemically with it and melt in the furnace forming complex low – melting silicates of the type $nSiO_2$-$mFe_2O.Na_2O$. For this reason the concentration of the harmful impurities in refractories is limited especially in furnaces used for the melting of iron and other high melting temperature alloys (Hlavac, 1983).

2.4.1 POLYMORPHIC INVERSION OF SILICA

The phases in which quartz can exist depending on temperature are α-(low) quartz, β-(high) quartz, High β-tridymite, intermediate α-trydimite, low α-trydimite, β-crystobalite, α-crystobalite.

When α-(low) quartz is heated up to 573°C there is a rapid change to the high β- (high) quartz with a volume change of 3%. β-(High) quartz is stable between 896°C and 870°C it slowly converts to high or α-Tridymite. If α-Tridymite is cooled down there is a clear inclination to form intermediate phase known as β-Tridymite, the change occur at 163°C. On further cooling to 117°C β-Tridymite changes to low Tridymite with an accompanying volume change of 2.6%.

Crystobalite, the stable high temperature form of SiO_2 forms from Tridymite at 1470°C. If Crystobalite is heated to and above 1710°C, Silica will melt; this can revert to Crystobalite or form quartz glass, depending on the mode of cooling. However Crystobalite at 1470°C may invert at 180°C (low temperature) to yield Crystobalite in which case the inversion route is faster than the conversion route.

The inversion shown below (Fig. 2.2) by the horizontal arrows are relatively slow and are called reconstructive transformations in which the bonds in the secondary co-ordination sphere are broken and the SiO_4 tetrahedral are arranged. Meanwhile, the inversions shown by the vertical arrows take place at a relatively high rate and involve only minor structural changes without any bond breakage in the co-ordination numbers. The low temperature modifications are the distorted derivative structure of the basic high temperature forms.

The major problem that arises from the polymorphism of silica is the accompanying volume changes. The volume changes may lead to dimensional

instability during the firing process of a monolithic lining. Table 2.1 shows the volume changes accompanying polymorphic transformation of silica.

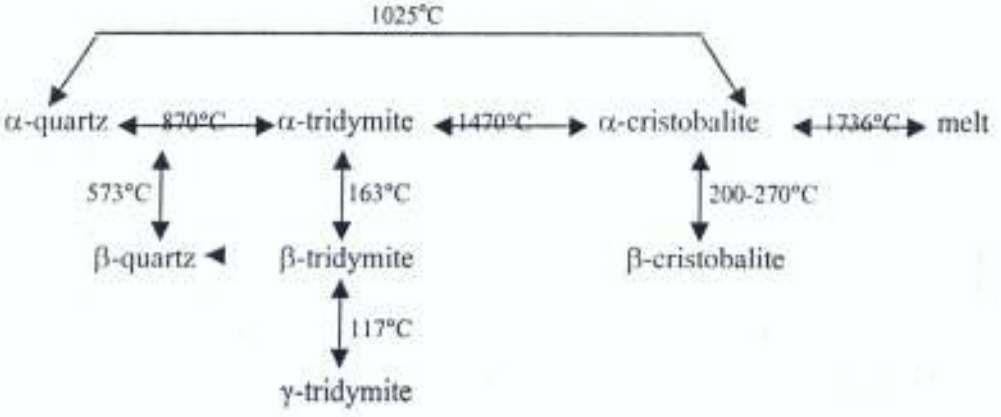


Fig.2.2: Polymorphic Inversion of Silica (Hlavac, 1983)

Table 2.1 Volume Changes Accompanying Polymorphic Transformation of Silica

Transformation	Volume Change (%)
(low) α–quartz → (high) β-quartz	0.82 – 1.3
(low) α-trydimite → (high) β–trydimite	14.4 – 16.0
β-quartz → β-crystobalite	15.4 – 17.4
α-trydimite → β-trydimite	0.4 – 0.5
α-crystobalite → β-crystobalite	2.0 – 2.8

***(Hlavac, 1983)**

2.5 CLAYS

Clays can be defined as the weathered products of silicate rocks, containing sufficient hydrosilicate of alumina in the softened condition to produce a plastic or semi-plastic mass when tempered with water. The clays are thus hydrous aluminosilicates with extreme minute crystalline or flake shaped particles that can be classified on the basis of the structure and composition in the few groups, which are known as clay minerals.

The characteristic properties of the clays are imparted by their main functional hydroxyl groups. The common feature of clay minerals is their layered structure and their occurrence as very fine particles. The physical and technological properties of clays depend not only on the composition and structure of their respective clay minerals, but also on the particle size and shape. The finer the clay particles, the higher the plasticity.

The excellent bonding properties of clays make them to become the principal source of strength and plasticity in refractory making, when the appropriate portion of water is added to the mixture.

2.5.1 The Clay Minerals

The clay mineral consists of hydrated Aluminium silicates that are fine-grained and are usually have a plaity habit. (Mikhailov, 1987).

The characteristic properties exhibited by clays are largely dictated by their main functional components known as the clay minerals which are aluminosilicates containing hydroxyl groups. Clay minerals exhibit layered structures and occur as very fine particles.

The common clay minerals are the followings:

Kaolinite, the most common type of clay, has structural formula $Al_2O_3.2SiO_2.2H_2O$. Kaolinite forms plates 0.1 to 3μm in size and about 0.005μm thickness.

Montmorilonites which is another type of clay mineral have the structural formula $Al_{12}.(SiO_5)_2.(OH)_2$. It has a three–layered structure. The particles are finer than that of kaolinite (up to 60% are below 0.1μm). Easy penetration of water through the gaps in the layered structure occurs. This leads to swelling of the clay when wetted and shrinkage when dried. Montmorilonite is strong bonding clay than kaolinite. When clay contains more than 80% Montmorilonite it is referred to as bentonite.

Illites are characterised also by a 3–layered structure exactly like the montmorilonites. The general formula of the illites is $KxAl_4\ (Si_8\text{-}xAlx)\ O_{20}\ (OH)_4$.

x ranges between 1.0 and 1.5.

2.5.2 Chemical Analysis of Clay

An estimate of the degree of contamination of the basic clay mineral can be determined by the chemical analysis of clay. Clays having a high alumina content approaching the theoretical value in the clay minerals possess a high grade of clay. Higher silica content than the corresponding proportion in the clay minerals indicates contamination with quartz. The presence of alkalis implies the presence of feldspar and mica, which together with bivalent oxides and Fe_2O_3 reduces refractoriness considerably by facilitating the formation of flux.

2.6 MICA

The mica minerals as a whole show considerable variation in chemical and physical properties, but all are characterized by a plaity morphology and perfect basal cleavage, which is a consequence of their layered atomic structure.

Among the most common micas are muscovite, aragonite, glauconite, lepidolite, phlogophite, biotite, and xanthophyllite. For the most part each of these is a distinct mineral, which does not form a complete solid solution series with any of the others. But phlogophite and biotite are separated merely for convenience in dealing with otherwise so large a group.

2.6.1 CHEMISTRY OF MICA

The general formula which describes the chemical composition of micas is

$X_2Y_{4-6}Z_8O_{20}(OH.F)_4$

where

X is mainly K, Na or Ca but also B, Rb, Cs, etc

Y is mainly Al, Mg or Fe but also Mn, Cr, Ti, Li, etc

Z is mainly Si or Al but also perhaps Fe^{+3} and Ti. (Deer, 1978)

The micas can be subtitled into di-octahedral and tri-octahedral classes in which the numbers of Y ions is 4 and 6 respectively. A further sub-division can be made according to the nature of the principal X constituents. In the common mica X is largely Ca: further subdivision of the common micas are made according to the principal constituents in the categories X, Y and Z and these are depicted with appropriate formulae in Table 2.2 and 2.3.

Table 2.2 Di-Octahedral Micas*

Common Micas	muscovite paragonite glauconite	K_2 Na $(K, Na)_{1.2\text{-}2.0}$	Al_4 Al_4	Si_6Al_2 Si_6Al_2
Brittle Micas	marganite	Ca_2	Al_4	Si_4Al

***(Deer, 1978)**

Table 2.3 Tri-Octahedral Micas*

Common Micas	phlogopite	K_2	$(Mg,Fe^{+2})_6$	Si_6Al_2
	biotite	K_2	$Mg, Fe, Al)_6$	$Si_{5\text{-}6}Al_{2\text{-}3}$
	zinnwaldite	K_2	$(Fe, Li, Al)_6$	$Si_{6\text{-}7}Al_{2\text{-}3}$
	lepidolite	K_2	$(Li, Al)_{5\text{-}6(x)}$	$Si_{6\text{-}5}Al_{2\text{-}3}$
Brittle Micas	cicutonite and xanthophilite	Ca_2	$(Mg, Al)_6$	$Si_{2.5}Al_{5.5}$

***(Deer, 1978)**

2.7 BINDERS

Binders are necessary in refractory ramming mix so that the monolithic working face can be given a good green strength before firing. There are two main divisions of binders.

(i) **Inorganic binders** e. g. clays, cement, water glass, Plaster of Paris e. t. c.

(ii) **Organic binders** e.g. emulsion, methylcellulose, hydroxypropyl, methyl cellulose, starches and dextrin.

Some of these binders could lower the refractoriness of the ramming mass. For example water glass (sodium silicate), a common inorganic binder, will lower the sintering point of aluminosilicate refractories.

2.7.1 Calcium Aluminate Cement

This is hydraulic cement that can be used either individually or in combination with other binders for various construction and refractory application. It is typically used as the principal or secondary binding portion of a concrete at addition levels of 1-40 wt.%. When mixed with water, it hydraulically sets and binds any aggregates or other fine materials present in the concrete. When used in refractory castable (concrete) applications, the purity level of the cement can be one of the properties that determine the end refractoriness of the concrete. Purity levels of commercially available calcium aluminate cements range from 38-90% Al_2O_3. High-purity calcium aluminate cements contain 70-80% Al_2O_3 and 18-25% CaO, with 2% or less impurities. In all of the varieties of calcium aluminate cement, the principal hydraulic phase is $CaAl_2O_4$ (monocalcium aluminate)

2.8 WATER

This is one of the most important materials in the manufacturing process of refractories. The materials are bonded together by water in such a way that we have an aluminosilicate-silica-water system. Bonding of the refractory materials can as well be achieved using other polar compounds such as sodium silicate, alcohol, glycol, acetic acid e. t. c. clays only become plastic and exhibit bonding capacities in the presence of these polar liquids having the OH^- and the H^+ ions.

The development of plasticity by clay can be visualised thus: when clay is very stiff, then water films are so thin that all the molecules are arranged in layers and water is said to be viscous. As the moisture content increases, the water films become thicker and the layers midway between the flakes become more plastic. When the thickness of the water layer is about 10^4A° water will be randomly oriented and the

sticky point of the clay is reached. Beyond the sticky point of the clay excess water is of no advantage to the bonding it even weakens the bonded sand. At the sticky point, the surfaces of the flakes are 10^3 to 10^4 A° apart i. e. the flakes are separated by films of liquid which are assumed to be highly viscous. The water requirement for ramming mass depends on composition. For example for alumina-spinel castables water requirement is 5-5.5% w/w. Aluminosilicate based ramming mass requires a water content of 6-10% (Rashdi, 1986)

2.9 MANUFACTURING TECHNOLOGY OF GRANULAR REFRACTORIES

2.9.1 Drying

The production of granular refractories involves a good understanding of the ceramic production on the part of the user, which includes a proper understanding of the drying procedure.

Drying can be defined as the removal of water from a granular material by evaporation (Ford, 1986). This process involves both the transfer of heat from the surrounding (the drier) to the solid water system and the simultaneous transfer of water vapor in the reverse direction.

There are two broad factors governing the drying rate of refractory materials. These according to Ford, R. W. (1986) are:

(i) **External conditions** the heat transfer methods such as convection, radiation, and conduction.

The Effect of External Conditions on the Rate of Drying of Refractory Materials

Convective heat transfer: When a free water surface, thermally insulated except for the air stream in contact with it, is subjected to a stream of air at constant velocity,

temperature and humidity a constant rate of evaporation is rapidly attained, indicating a state of equilibrium has been reached between the flow of heat to the surface and the latent heat requirements of the evaporated water. At the commencement of evaporation the temperature falls because of loss of latent heat of water evaporated. As the difference in temperature increases, the rate of heat transfer increases until it exactly equals the latent heat in the water vapour being removed from the surface making the temperature at the surface steady.

Increasing the velocity of air stream passing over a wet surface increases the rate of evaporation from it. But an increase in the velocity of air is associated with a proportionately smaller increase in the rate of evaporation e. g. doubling the air velocity results in less than a two-fold increase in the rate of drying. The greater degree of turbulence at the surface resulting from perpendicular flow gives higher coefficient of mass transfer and heat transfer than with parallel flow and results in faster drying. However the difference in effect of the two types of flow is less marked at high velocities.

Radiative Heat Transfer: Drying is also accomplished by radiation. Heat is transferred more quickly by radiation than by convections. The rate at which drying takes place via radiation is higher than by convection. The humidity of the surrounding atmosphere has little effect on the evaporation rate from the irradiated surface because of the amount of heat being transferred.

(ii) Internal conditions of the bulk of the particles.

Drying can be divided into two stages: to begin with, evaporation occurs only at the surface of the article, the evaporated water being replaced to some extent by

liquid water that migrates to the surface. As drying progresses eventually liquid water can no longer move to the surface and it has to evaporate within the pore system, the resulting vapour diffusing to the surface before it can be removed.

There are two categories of granular materials: those, whose surface does not interact to any extent with water (mica & quartz) and those whose surface reacts physically or electrochemically at the grain surface. The clay–water system belongs to the second category. Clay minerals are diluted by inert materials such as quartz and micas. Water molecules are taken up by solids in a process of adsorption and capillary condensation.

2.9.2 Sintering

Sintering which consists of heating the components to elevated temperatures (typically 0.7 times the liquidus temperatures) densifies the refractory material (Kumar, 2000). The firing process may also involve the removal of any remaining water and / or polymers added to assist the forming process and formation of new phases by chemical reactions. During sintering, densification is achieved by decreasing the porosity to low levels (100% density is impossible to achieve). Driving force for sintering is derived from reduction in surface energy through the removal of solid-vapour interfaces in powder compacts and replacing them with lower energy solid-solid interfaces. When particles remain solid during sintering, reduction in porosity can only take place by diffusion. The local vacancy concentration is higher near small pores than near large pores determined by the thermodynamic equilibrium at the pore / solid interface. Thus vacancies will tend to flow from smaller pores to larger ones which is equivalent to matter flowing from larger pores to smaller pores and therefore small pores will close down and sharply curved neck surfaces will grow.

The density will increase as long as the sites for vacancies are found in dislocations, grain boundaries and surfaces. When sintering is mainly achieved by solid state diffusion, it is a relatively slow process, especially for covalent ceramics such as Si_3N_4, because of the lower atomic mobility. It is important to decrease the diffusion distances by using very fine powders and if possible increase the mobility by sintering at higher temperatures and by incorporating liquid phases during sintering. Liquid phase sintering is very common in conventional pottery, where feldspar or bone is added to clay as flux. Hot Pressing is a process in which both shaping and sintering are carried out simultaneously by die pressing at high temperatures and are particularly suitable for materials that form no liquid phases or have low atomic mobility during sintering. Use of pressure during sintering can help achieve densification in carbides and nitrides. Graphite is the most commonly used die material. Hot Isostatic Pressing (HIP) is used only for high value products such as ceramic cutting tools or turbocharger rotors. Pressure is transmitted at sintering temperatures to a pre-shaped partially densified component in a chamber through a high-pressure gas such as nitrogen.

2.9.3 Firing of Refractories

Firing of fireclay refractories takes place in five stages: (Rashdi, 1986).

The first stage in the firing process is steaming. At this stage, expulsion of moisture takes place as the temperature is raised from room temperature to about 120°C. All molecular water is also expelled until a temperature of 350°C is attained. The second stage starts at about 350°C when there is a breakdown of impurities in the clay. All molecular water, combustible materials and volatile materials are expelled. Some of the chemical reactions that take place at different temperatures are as follows: (Rashdi, 1986).

Reaction	Temperature (^{0}C)
$S + O_2 \longrightarrow SO_2$	250 – 920
$C + O_2 \longrightarrow CO_2$	350
$FeS_2 + O_2 \longrightarrow FeS + SO_2$	350 –450
$MgCO_3 \longrightarrow MgO + CO_2$	400 –900
$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 3SO_3$	560 – 775
$CaCO_3 \longrightarrow CaO + CO_2$	600 – 1050
$4FeCO_3 + O_2 \longrightarrow 2Fe_2O_3 + 4CO_3$	800
$CaSO_4 \longrightarrow CaO + SO_3$	1250 – 1300

The third stage, known as oxidation stage or full-firing stage extends up to a temperature of 1350^{0}C permitting various mineral transformation in both alumina and silica. At a temperature of 950^{0}C, alumina combines with silica to form mullite ($3Al_2O_3.2SiO_2$). This is an exothermic reaction. The clay shrinks and gets hardened. No shrinkage of the refractories takes place on further heating when in use.

The fourth stage is referred to as the incipient fusion stage. This extends up to 1500^{0}C. This involves the fusion of the impurities and the filling up of the interstices between the solid particles by the fused mass. Porosity gets reduced, bonding of the clay and the grog particles takes place and a compact hard mass results. The refractory is already in a thermodynamically stable state where when in use at this temperature no further transformation takes place. The material is soaked at this temperature to attain a uniform property

The final stage is known as the annealing and cooling stage. This involves a very slow cooling of the fired refractory.

Firing temperature of aluminosilicates depends on the alumina content of the mass, and the percentage of grog. The higher the alumina content, the higher is the

firing temperature. Low rates of firing are maintained for low grog refractories as they undergo higher shrinkages. High grog refractories on the other hand involve low shrinkage and can therefore allow higher firing rates. (Lee and Rainforth, 1994).

2.10 Microstructural Evolution of Firing Clay

The combined water in the clay is driven off at about 500°C (dehydroxylation) and metakaolin is formed according to the reaction (Lee and Rainforth, 1994).

$$Al_2SiO_5(OH)_4 \xrightarrow{500^\circ C} \text{metakaolin} + 2H_2O$$

Decomposition of the metakaolin by removal of the final residual hydroxyl radicals at 970°C triggers the separation of a considerable amount of amorphous free silica and formation of poorly crystalline mullite and a phase with a cubic, defect-spinel, crystal structure similar to γ–Al_2O_3. The mullite and spinel form in tandem, the former originating in the vicinity of Al-O units of regular octahedral and tetrahedral symmetry. At 970°C, the metakaolin formed changes to alumina-rich mullite, defect spinel and glass according to the reaction.

$$\text{Metakaolin} \xrightarrow{970^\circ C} \underset{\text{Defect spinel}}{3Al_2O_3} + \underset{\text{Alumina-rich mullite}}{Al_6SiO_{13}} + \underset{\text{Glass}}{3SiO_2}$$

On further heating above 1125°C the spinel phase is converted to mullite by reaction with some of the amorphous silica, the balance of which eventually becomes crystobalite. Hence the end products of firing kaolinitic clay are mullite and silica (crystobalite).

2.11 PROPERTIES OF REFRACTORIES

From the definition of refractory materials given in section 2.0, the important requirements of the material to the user are:

(i) **Ability to maintain shape and strength** at the operating temperature. This is measured by

(a) The volume shrinkage after drying and the volume shrinkage after firing and

(b) Cold compression strength

(ii) **Ability to withstand thermal shock** due to fluctuation usually experienced during charging and shutting down operations or enduring normal furnace operations. The result of thermal shock resistance must depend on at least four properties of the material- (1) its thermal conductivity which determines the temperature gradient set up under the test condition; (2) the coefficient of thermal expansion which determines the strain induced by this thermal gradients; (3) the modulus of elasticity and; (4) the shear strength of the brick, which together determines the stresses set up and whether or not they will be relieved by crack formation or propagation. (Gilchrist, 1977).

(iii) **Resistance to chemical attack** by whatever gasses slag or metal is likely to be encountered.

(iv) **Thermal conductivity**: This has to be low if the material has to be actually refractory. Thermal conductivity increases with the decreases of porosity. Porous refractories have air entrapped in their pores this acts as a non-heat conducting material. The amount of the entrapped

air increases with the porosity of the refractories and hence its thermal conductivity decreases. Refractories used in melting furnaces should have low thermal conductivity to ensure least heat losses and maximum heat efficiencies whereas in recuperators where maximum heat transfer is desirable, refractories with high thermal conductivity are required. Table 2.4 gives thermal conductivity of some refractory raw materials.

Table 2.4: Thermal Conductivities of Refractory Raw Materials*

Refractory Raw Material	Thermal Conductivity (W/cm.K)
Silicon Dioxide	0.014
Silicon nitride	0.16-0.333
Alumina (pure)	0.276
Alumina (85%)	0.118
Berylia(99.5%)	1.969
Mica	0.07

***Thermal Conductivity of Materials, (2002)**

(v) **Electrical conductivity:** This is important when the refractories are used in electrical furnaces. Graphite and metals are good electrical conductors among the refractories. Others are all electrical insulators. Refractories used for lining electric furnaces should have very low electrical conductivity. Electrical conductivity also depends on the refractories as porous bodies are less conductive.

(vi) **Porosity:** This is essential to the control of the thermal conductivity and slag abrasion. Low porosity achieved by grading and moulding pressure is available in conferring high resistance to abrasion, to slaging and to attack by gases such as occurs in the iron blast furnaces. Low porosity due to a high flux content and over-firing would not enhance the slag resistance but would probably give a very poor spalling resistance. Porosity values are usually about 20-25% with their values down to 12-15% obtainable with some difficulty when thought to be desirable.

(vii) **Refractoriness**: Generally it is not practicable to measure the melting temperature of a refractory material since it extends over a range of temperature - perhaps over several hundreds of Celsius. The determination of solidus and liquidus temperatures would not be easy and might not be very useful. Therefore, working temperatures or the service temperature is always quoted for these materials. Refractoriness is usually measured by 'pyrometric Cone Equivalent' (PCE). This is the 'number' of the standard pyrometric cone that begins to melt at the same temperature as the material under test.

If the chemical analysis of a clay is available, then clays with over 30% Al_2O_3 and less than 5% in total of Fe_2O_3, CaO, MgO, Na_2O and K_2O would probably have a PCE of at least cone 26 (1570°C) (Gilchrist, 1977). The PCE increases in proportion to the amount of Al_2O_3. 40% Al_2O_3 would probably give a PCE of Cone 33 or 34. There are few raw materials that have a very high Al_2O_3 content and these can be added, suitably ground, to the clay mixture to greatly improve the

refractoriness. White or grey bauxite, sillimanite and kyanite are the ones most likely to be found. Addition of quartz sand, which is often more easily found than the above raw materials will also increase the refractoriness of clay. However due to the large expansion of free silica at about 600°C, it is best avoided as the bricks are more likely to crack on heating and cooling. There is also an additional problem with free silica as mentioned below:

When two or more ingredients which each individually have very high melting point, are combined in certain proportions the resulting product melt at a much lower temperature. Of particular concern are the following:

Silica	m. p. 1620°C
Al_2O_3	m. p. 2050°C
CaO	m. P. 2580°C

Yet, these three oxides (all present in a furnace) can melt at a temperature as low as 1170°C. The dangerous combination is a high silica and low alumina one. So this is an additional reason for increasing the alumina and not the silica content of bricks. (Nobbusch and Mitchell, 1988)

(viii) **Cold strength**: this is a measure of simple compression. It is needed to assure the user of the material that it will not fail in compression during service. In case of bricks it also shows whether they have been properly fired or not: and indicate whether the brick would transport readily without damage to corners and edges. Strength depends on

porosity and the thoroughness of firing and where appropriate on the distribution of "grog" particles, which help to arrest cracks.

2.12 TESTING OF REFRACTORIES

It is important to ensure the suitability of a refractory material for service condition. This could only be guaranteed by a number of tests carried out on the samples of the refractories. Among the essential tests carried out on refractories are described below:

(a) **Refractoriness Test**: Refractoriness of a refractory material is determined by the use of a set of standard pyrometric cones. These are elongated trigonal pyramids 30 or 62mm in height, whose composition is graduate to ensure their deformation at various temperatures. The main components are kaolin, quartz, feldspar, Al_2O_3, $CaCO_3$, B_2O_3, and PbO. The temperature of pyrometric deformation (softening) is indicated by the top of the cone bending over the tip touching the support (the end point) at a heating rate of 3–5^{o}Cmin^{-1}. To determine the refractoriness of a material, it is cut or shaped into a cone of the same shape as the pyrometric cone and is then heated at the specified rate together with the several standard cones. The refractoriness is then specified by the number of that standard pyrometric cone whose tip would touch the supporting plaque simultaneously with a cone of the refractory material under investigation. Table 2.5 gives the temperature equivalents for the pyrometric cones on the Seger and Orton standards.

Table 2.5 Temperature Equivalent for Pyrometric Cones *

Cone Number	End Point °C	
	Seger Cone	Orton Cone
12	1350	1337
14	1410	1398
16	1460	1491
18	1500	1522
20	1530	1564
26	1580	1621
28	1630	1646
30	1670	1665
32	1710	1717
34	1750	1763
36	1790	1804
38	1850	1835
40	1920	1885
42	1980	2015

***(Hlavac, 1983)**

(b) **Thermal Shock Resistance (Spalling Resistance)**: There are two methods for carrying out this test

(i) Panel Test: 12 to 14 test specimens are cut from the original refractories to a size 65 – 75mm thick, 230mm long and 113mm wide. The test specimens are labelled with ceramic paint on the inner face which is not exposed to heating. Each specimen is dried at 105°C and

weighed to the nearest 0.005Kg. The test specimens are then laid in the panel frame by kaolin or any other suitable material having a PCE value corresponding to not less than that of the test specimen and which does not react with the test specimens. Joints made should not be more than 2mm thick. The test panels are backed with suitable insulation. Its mean temperature should about 700^{0}C. The panel assembly is heated in a gas or oil fired furnace (preheating furnace) to attain a face temperature of 1600^{0}C in 5–8hrs. This temperature is maintained for 24hrs. The condition of the test specimens is reached after completing preheating. Photographs of the panel surface are also taken for record. The insulation is removed from preheated bricks and the panels are transferred, by means of a track or trolley, into another gas or oil-fired furnace called spalling furnace to heat the test specimens up to 1400^{0}C. The position of the panels is changed at 1000^{0}C, 1200^{0}C, and 1300^{0}C to ensure uniform heating. Heating at 1400^{0}C is allowed for 10mins and the panel is cooled in another 10min by means of a blast of air water mist delivered through a vertical manifold having an aperture of 90mm x 60mm. Air is admitted at a rate of 11liters/minute during the first 8mins of cooling. No water is admitted during the last 2mins.

The cooling unit has a means of reciprocating motion to facilitate its to and fro movement (about 125 times in 10 minutes) over the entire surface of the panel including the dummy guard refractories. The test specimens are subjected to 12 such heating and cooling cycles and the furnace is then shut off. The panel is given two additional cooling

cycles without using any water-mist. Subsequent cooling is allowed to take place overnight after spacing the panels 25mm face to face. The refractories are then removed from the panel very carefully, each of them reweighed, rearranged in the order they were placed in the test panel and photographed for comparison with the first photograph giving the original condition of the refractories. Average loss of the refractories for the whole panel is reported. The extent of the loss of weight of refractories gives an indication of the spalling resistance of the refractories.

(ii) Small Prism Test: Three test pieces dimensioning 50 x 50 x 75mm is placed in a furnace to attain test temperature of 1100°C. Each test sample is then withdrawn from the furnace using a preheated tong and cooled for 10 min and then returned to the furnace to attain the 1100°C temperature and hold for another 10min. The procedure is repeated until an appearance of a crack is visible. The number of cycles necessary to cause crack is recorded for each brick. The number of cycles each test piece withstands before failure is taken as a measure of its thermal shock resistance.

(c) **Cold Crushing Strength**: This is to determine the compression strength to failure, which is an indication of probable performance in service of each brick. The test is carried out as follows:

Test pieces dimensioning 50 x 50 x 75mm is placed between the two plates of the compression tester. This is followed by the application of

a uniform load to it. The load at which cracks appear in the refractory sample represents the cold crushing strength of the sample.

(d) **Shrinkage Test**: This will determine the average shrinkage after firing. The test is carried out as follows:

Measurement of the dimensions of the test pieces before and after firing is taken. The change resulting determines the linear shrinkage. This is calculated from the formula given below:

$$\%\ Shrinkage = \left[\frac{Initial\ Length - Final\ Length}{Initial\ Length}\right] x\ 100\% \qquad \textbf{2.1}$$

(e) **Porosity**: This is used to determine the permeability of each brick. There are two standard methods for the determination of the apparent porosity of refractory materials.

(i) **Evacuation method**: The test specimen is dried at 110^0C in an oven to dry weight D. The dry specimen is immersed in water for 5 – 6hrs to soak and weighed while still suspended in water. The weight is recorded as S. The soaked specimen is also weighed while keeping it suspended in air. The weight is recorded as W. the apparent porosity P is then calculated from the formula:

$$P = \left(\frac{W - D}{W - S}\right) x\ 100\% \qquad \textbf{2.2}$$

(ii) **Boiling Point Method:** The test specimen cut from a burnt refractory brick is dried in an oven at 110^0C to a constant weight D with an accuracy of 0.1g. The dried specimen which is suspended in

water is not allowed to touch the bottom or sides of the container. It is then boiled for two hours while still being suspend in water, after boiling it is allowed to cool to room temperature. And its weight is recorded as S. the specimen is removed from water and extra water is wiped off from its surface by lightly blotting with a wet towel. Its weight in air is recorded as W. The apparent porosity P can then be calculated from the formula:

$$P = \left(\frac{V_1}{V}\right) x\ 100\% \qquad \textbf{2.3}$$

Where V_1 = Actual volume of the open pores of the specimen

$= W - D$

And V = External volume of the specimen

$= W - S$

(f) **Loss on Ignition**: This is done to determine the percentage weight reduction to the total weight of the rammed mass. It is calculated from the formula:

$$LOI = \left(\frac{W_i - W_f}{W_i}\right) x\ 100\% \qquad \textbf{2.4}$$

Where LOI = Loss on ignition

W_i = Weight of sample before firing

W_f = Weight of sample after firing

(g) **Resistance to slag attack:** There are several ways of testing the resistance of a refractory material to slag attack. There are running slag test and the spray test.

(i) **Running Slag Test**: the resistance to slag attack is tested by heating the refractory to be tested to a uniform temperature near to the service temperature of the refractory. Powdered slag is then dropped regularly on the top of the refractory from where it runs down through a groove provided for that purpose. The depth to which the groove has been enlarged at the close of the test is taken as a measure of the resistance of the refractory to slag attack.

(ii) **Spray Test**: this is similar to the running slag test in which powdered slag is sprayed on a heated refractory surface uniformly and under standard temperature and other working conditions over the entire surface of the refractory under test. The extent of slag penetration is taken as a measure of the resistance of the refractory to slag attack.

2.13 MICROSTRUCTURES OF REFRACTORIES

Microstructure can be defined as the structure of a material as determined by any of the available microscopic techniques, including reflected light metallography, thin sections, electron microprobe analysis (EMPA), Scanning Electron Microscope (SEM), Scanning / Transmission Electron Microscopic Analysis (STEM), Transmission Electron Microscopy (TEM) and others. Microscopic analysis of refractories is valuable for many applications, such as refractories development and improvement, quality control, evaluation of refractories performance in service and research.

The analysis and understanding of microstructure has played a vital role in the advancement of refractories technology with a direct contribution to the increased service life of refractories leading to a longer lining life for effective lower cost.

The manufacturing procedure for refractories usually involves the mixing of powders of many different materials types such as the oxide powders, graphite flakes and polymer resins to form the final product. The powder usually have a large size distribution enabling small sub-micron particles to pack in the gaps between large ones (up to several mm) so that most of the densification occurs during the shape forming operation. Usually densification occurs as a result of firing whereby one component must form a bond to glue the large grains together either by reaction of the clay to give a small amount of liquid which cools to a glass or by decomposition of a carbonaceous binder to form a carbon bond. The attendance shrinkage from the sintering operation must be minimized so that stresses set up by the shrinkage could be accommodated. Fig 2.3 gives the basic components of a refractories microstructure (Semler, 2002).

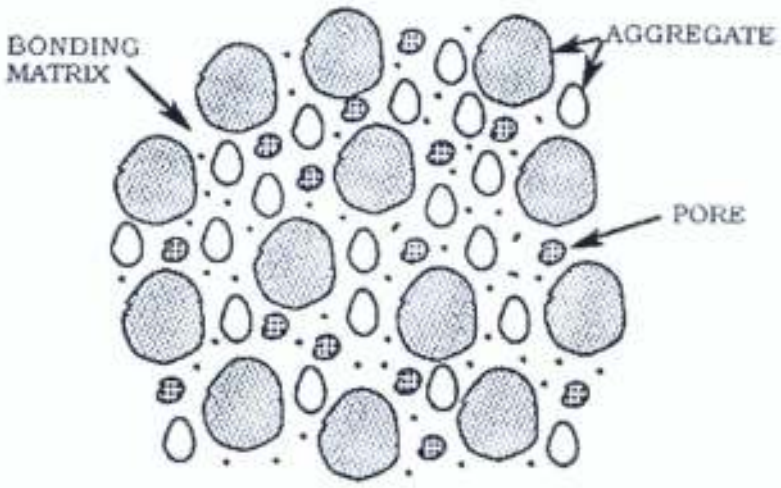


Fig. 2.3: Refractories Microstructure

Refractories are never fired to 100% density because of the long time and high temperature involved and because the presence of porosity may be required. The difference between a ceramic material and refractories is, therefore, seen to be solely

one of texture with refractories having a much coarser grain size and higher porosity than engineering ceramic.

A common feature in a ceramic microstructure is the presence of the micro-cracks arising from thermal mismatch of the different phases and from sintering of the fine particles, which do not sinter rapidly. If not larger than the critical flaw size, these micro-cracks can provide useful toughening to the body, increasing resistance to crack propagation and improving thermal shock resistance (Lee and Rainforth, 1994).

The characteristics of the sintering powder such as particle size, shape, size distribution, degree of aggregation and agglomeration exert a profound influence on densification and development of the microstructure.

The effect of some of these parameters on the microstructure is described below.

Porosity: This is defined as the total volume fraction (or volume %) of pores in a porous material. These different porosities exist for refractory materials:

(i) **Apparent Porosity (or open porosity):** This is given by the volume of the open pores in a material divided by the bulk volume.

(ii) **Closed Porosity**: This is the volume of the closed pores the material contains divided by its bulk volume.

(iii) **True Porosity (Total Porosity)**: This is the volume fraction of the open pores to the closed pores. It is directly related to density by (1- relative density).

Prior to sintering, almost the entire porosity in refractories is open but upon firing the volume fraction of porosity decrease and many pores become closed. The total pore content (open or closed, inter-granular or intra-granular,) between and within grains respectively, the pores coordination number (the number of grains in contact with it)

and the pore shape, size and distribution all influences properties. Pores are stress raisers in refractories and lower their strengths.

The porosity of non-insulating industrial refractories typically falls in the broad range of 2-30 % (Semler, 2002). Porosity provides the openings for the penetration and reaction of working face refractories that are directly exposed to service conditions such as molten metal and slag or dross, cement clinker, and molten glass, Therefore, mix changes that results in lower porosity will, in general, reduce or slow the reactivity in service and extend the service life of the refractories.

Grain Sizes and Shape: The grain size of a ceramic is a critical microstructural variable. The particle size has an effect on the grain boundaries. The smaller the grain size, the greater the grain boundary area. Grain boundaries are regions of open crystal structure and usually contains second phase so that diffusion is more rapid at them. The grain size required depends on the application temperature. The final grain size of the dense product is governed by many processing variables in particular the starting powder, size and sintering temperature.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Materials

The materials used for the various mixes of the tested refractory materials are as follows:

(i) clay from Ikere-Ekiti , Ekiti state

(ii) silica (coarse grained)

(iii) mica from Ijero- Ekiti, Ekiti State

(iv) Durax, calcium aluminate cement from Premier Vesuvius Inc., U. S. A.

(v) Bentonite

3.2 Materials Preparation

The as–received clay form Ikere-Ekiti was dried, crushed in a laboratory pulveriser and ground in a ball mill. It was later sieved through a 300μm sieve and the oversized that is predominantly silica was rejected.

The silica was washed and dried to remove impurities that may lower the refractoriness of the final mixes.

The mica was washed and dried to remove organic materials and clay. This was followed by milling in a ball mill. It was later sieved through a 300μm sieve.

3.3 Chemical Analysis of the Raw Materials

Chemical analysis of the sampled raw materials was carried out using the Atomic Absorption Spectrophotometer (AAS) and the result is presented in Table 4.1.

3.4 Particle Size Analysis

Particle size analysis of the silica was carried out using the American Foundry Society (AFS) Standard. 100g of the sample was weighed and sieved through the set of sieves placed on the laboratory sieve shaker vibrated continuously at an amplitude of 7mm for 15min. The result of the analysis is presented in Table 4.2

The particle size of the clay, mica, durax and bentonite were carried out using the same equipment and the results obtained are presented in Table 4.3.

3.5 Test Samples Preparation

3.5.1 Mixing

The various mixes prepared were mixed using a laboratory sand mixer. Each composition is first mixed in the dry state for a period of 10 minutes to facilitate thorough mixing. Water was then gradually added to the dry powder while mixing is on and then subjected to further mixing for another 20 minutes. At this point no dry powder is left. The mixed sample was then withdrawn from the machine.

3.5.2 Ramming

The ramming of the samples were done using an AFS Ramming machine to produce samples of dimensions φ50mm ±0.5mm and 50mm ±0.5mm in height. The rammer applied a load of 6,666g from a height of 50mm on the sample at each cycle of ramming.

3.5.3 Drying

Samples were left to air-dry overnight before drying in the laboratory oven at a temperature of 120°C for 130mins and then allowed to cool to room temperature

3.5.4 Firing of Samples

Firing of samples was done at a rate of 5°C/min to different temperatures of 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C, 1200°C 1300°C and 1400°C for the various tests described in the experimental procedure in section 3.6.

3.6 Testing of Samples

The following tests were carried out on the materials

(a) **Shrinkage Test**: This was done to determine the volumetric shrinkage after firing the samples. The procedure involved taking the dimension of the test pieces before and after firing. The difference in the dimensions gave the volume shrinkage estimated from the expression:

$$\%\ Volumetric\ Shrinkage = \left(\frac{Initial\ Volume - Final\ Volume}{Initial\ Volume} \right) x\ 100\% \qquad \mathbf{3.1}$$

(b) **Apparent Porosity**: There are two standard methods for the determination of the apparent porosity of refractories described in literature.

(i) Boiling point method and

(ii) Evacuation method

The evacuation method described below was used in this work:

The test samples were first dried at 110°C in an oven, and sintered at various temperatures such as 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C, 1200°C 1300°C 1400°C and then weighed. The weight was recorded as *D*. The sintered specimen was immersed in

water for 5 – 6 hrs to soak and weighed thereafter and the weight was recorded as W. Finally, the specimen was weighed when suspended in water. This was recorded as S the apparent porosity P was then calculated from the expression:

$$P = \left(\frac{W - D}{W - S} \right) x100\% \qquad \textbf{3.2}$$

(c) Loss on Ignition (LOI): This determines the percentage weight reduction of the total weight of the rammed samples. Different samples were made and fired at the desired temperatures. The percentage loss in weight was determined by the difference between the weight before firing and after. This represents the loss on ignition at that temperature. The loss on ignition was calculated from the expression:

$$LOI = \left(\frac{m_1 - m_2}{m_1} \right) x\,100\% \qquad \textbf{3.3}$$

Where LOI = Loss on ignition

m_1 = Weight of sample before firing

m_2 = Weight of sample after firing

(d) Cold Crushing Strength: This was done to determine the compression strength to failure of a sample, which is an indication of its probable performance in service. The test was carried out as follows:

Each test piece was placed between the two plates of the compression tester. This was followed by the application of a uniform load to it. The

load at which cracks appear on the test sample is noted and the cold compression strength (*CCS*) is calculated from the expression:

$$CCS = \left(\frac{Load\ to\ Fracture}{Surface\ Area\ of\ Sample} \right) Kg/cm^2 \qquad 3.4$$

(e) **Thermal Shock Resistance (Spalling Resistance)**: Each test piece dimensioning φ50mm ±0.5mm and 50mm ±0.5mm in height was placed in an electrically heated furnace to attain test temperature of 1100^{0}C. Each test sample was then withdrawn from the furnace using a preheated tong and cooled in air for 10 minutes and then returned to the furnace to attain the 1100^{0}C temperature and held for another 10min. The procedure was repeated until an appearance of a crack was visible. The number of cycles necessary to cause crack was recorded for each sample. The number of cycles each test piece withstood before failure was taken as a measure of its thermal shock resistance.

(f) **Sintering Test**: This was done to determine the temperature at which each test sample would fuse. The sintering test was carried out as follows:

The test sample was placed in the furnace and the temperature was raised to 1000^{0}C. The sample was then observed to check for fusion. The process is repeated several times raising the temperature by 50°C until fusion is observed.

3.7 Experimental Procedure

The procedure for the experiments is described below:

Test samples containing 10% water were prepared from the Ikere-Ekiti clay to the specification of φ50mm diameter and 50mm height using an AFS standard rammer. The test pieces were dried in an oven at 120^{0}C for 130mins to determine the drying rate of the samples. The weight of the samples was taken after 10 consecutive minutes. It was observed that fine cracks developed on the samples after 60min due to the shrinkage experienced by the samples.

Consequently, samples with varying percentage of silica were prepared and the drying behaviour was observed. The results obtained are presented in Table 4.5.

The 10% quartzite composition was picked for further studies due to the formation of no cracks. This composition was therefore worked upon to determine the effect of mica addition on the clay–silica system. The results obtained are presented in Table 4.6. AFS standard samples were prepared from 10% Silica + 90% clay (hereafter called sample **B**) with addition of varying percentage of mica. The green compression was tested and the effect of heat (drying behaviour) was observed. The results obtained are presented in Table 4.6.

The clay–silica-system sample with composition **B** + 20% mica (now called sample **C**) was selected for further investigations.

Samples were prepared from **C**. These samples were rammed at different ramming pressure to determine the effect of ramming pressure on the apparent porosity of the mixtures. The samples prepared were dried at 120°C in an oven and the drying rate measured. Table 4.7 presents the result. The dried samples were fired at 1200°C. The apparent porosity was measured.

Samples of **C** were made and fired at different temperatures. The percentage loss in weight was determined at different temperatures. This was done to determine the rate of loss of combustible materials during sintering. Table 4.9 presents the result.

The effect of additives such as bentonite and durax on the properties of rammed sample **C** was carried out. Varying proportions of these additives were made to AFS specimen and then subjected to various tests to determine their properties such as volumetric firing shrinkage, green compression, loss on ignition and apparent porosity, as earlier described in section 3.5. The results obtained are presented in Tables 4.8, 4.9, and 4.10.

Two samples of C to which has been added 4% bentonite and 4% Durax, now referred to as **D** and **E** respectively was further investigated upon. Samples made to AFS dimension and rammed with eight ramming cycles were prepared and subjected to various tests to determine the effect of sintering temperature on their properties, which include volumetric firing shrinkage, loss on ignition and apparent porosity. The results obtained are presented in Tables 4.11, 4.12 and 4.13. Samples of **D** an **E** were subjected to thermal shock resistance and refractoriness tests as described in sections 3.5e and f. The results obtained are presented in Tables 4.14 and 4.15.

Samples to be investigated for microscopy were cut from rammed samples. Microscopic examination of samples was done using optical microscopy at a magnification of 100x. Photomicrographs of the various samples are presented in plates 4.1 to 4.6.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 EXPERIMENTAL RESULTS

Table 4.1: Chemical Analysis of the Raw Materials

Chemical Compound	Composition (%)				
	Ikere-Ekiti Clay	Silica	Ijero-Ekiti Mica	Durax	Bentonite
SiO_2	46.28	95.26	50.87	15.43	55.4
Al_2O_3	27.71	1.22	33.50	34.13	23.1
Fe_2O_3	5.84	0.64	0.184	5.64	4.4
CaO	1.81	0.01	1.57	21.82	0.2
K_2O	0.85	0.004	0.85	0.85	3.0
MgO	3.65	1.22	1.30	2.18	2.5
Na_2O	0.5	0.69	0.95	0.13	3.0
MnO	0.74	0.35	0.57	1.87	0.02
LoI	12.6	0.56	10.20	17.67	7.8
Others	0.02	0.046	0.006	0.28	0.58
Total	**100**	**100**	**100**	**100**	**100**

Table 4.2: Particle Size Distribution of Silica

Sieve Size	Mesh No.	Weight of Pan (g)	Weight of Pan (g)	Weight of Sand Retained (g)	Product
1.4mm	12	311.5	388	76.5	0
1.0mm	16	298.5	314.5	16	192
710μ	22	286.0	292.5	6.5	104
500μ	30	258.5	258.5	0	0
355μ	44	240.5	240.5	0	0
250μ	60	232.5	232.5	0	0
180μ	85	224.5	224.5	0	0
125μ	120	212.5	212.5	0	0
90μ	170	207.5	207.5	0	0
63μ	240	207.5	207.5	0	0
45μ	350	209.0	209.0	0	0
Pan	Thru 350	195.0	195.0	0	0
Total				**100**	**381**

AFS GFN = 381/100

= 3.81

Table 4.3: Particle Sizes of Materials

Raw material	Particle size
Ikere Ekiti Clay	<300μm
Ijero mica	<300μm
Durax	<300μm
Bentonite	<300μm
Silica	AFS GFN 3.81

Table 4.4 Effect of Addition of Silica on the Drying Properties of Ikere–Ekiti clay

Silica (%)	Clay (%)	Volumetric Drying Shrinkage (%)	Green Compression Strength (KN/m2)	Drying Behaviour
0	100	11.53	>135	cracked
2	98	10.58	>135	cracked
4	96	9.54	>135	No rack
6	94	6.94	>135	No rack
8	92	5.49	>135	No rack
10	90	5.49	>135	No rack

Table 4.5: Effect of Addition of Mica on the Green Compression Strength of Clay-Silica (90:10) System

Sample No.	Mica (%)	B (%)	Green Compression Strength KN/m^2	Effect of Heat (Drying Behaviour)
1	2	98	>135	**No Crack**
2	4	96	>135	No Crack
3	6	94	>135	No Crack
4	8	92	>135	No Crack
5	10	90	>135	No Crack
6	12	88	120	No Crack
7	14	86	102	No Crack
8	16	84	97	No Crack
9	18	82	90	No Crack
C 10	20	80	82	No Crack
11	22	78	65	cracked on Heating
12	24	76	45	cracked on Heating

Table 4.6: Effect of Ramming Pressure on the Apparent Porosity of Clay-Silica-Mica System

S/N	No. of Cycles of Ramming	Apparent Porosity (%)
1	3	38.33
2	4	33.33
3	6	26.98
4	8	23.50
5	10	23.20

Table 4.7: Drying Rates of Clay-Silica-Mica System at 120°C

Time (min)	Mass (g)	Water loss(g)	Cumulative Water Loss	
			(g)	(%)
0	150	0	0	0.00
10	147.5	2.5	2.5	16.67
20	145.5	2.0	4.5	30.00
30	143.5	2.0	6.5	43.33
40	142.0	1.5	8.0	53.33
50	141.0	1.0	9.0	60.00
60	140.0	1.0	10.0	66.67
70	139.0	1.0	11.0	73.33
80	138.0	1.0	12.0	80.00
90	137.0	1.0	13.0	86.67
100	136.0	1.0	14.0	93.33
110	135.5	0.5	14.5	96.67
120	135.5	0.5	15.0	100.00
130	135.5	0.00	15.0	100.00

Table 4.8: Loss on Ignition of Clay-Silica-Mica System at Different Firing Temperatures

Initial weight of samples = 135g

Temperature (°C)	Weight After Firing (g)	Weight Loss (g)	L O I (%)
600	130.0	5.0	3.70
700	127.5	7.5	5.50
800	127.0	8.0	5.90
900	125.5	9.5	7.03
1000	124.0	11.0	8.15
1100	121.5	13.5	10.0
1200	121.5	13.5	10.0

Table 4.9: Effect of Addition of Bentonite to Clay-Silica-Mica System

Bentonite (%)	Green Compression Strength (KN/m^2)	Volumetric Firing Shrinkage (%)	L O I (%)	Apparent Porosity (%)
2	>135	3.72	16.6	23.0
D 4	>135	3.66	16.3	22.5
6	>135	3.67	16.6	20.33
8	>135	3.05	16.4	21.23
10	>135	2.95	16.6	20.4
12	>135	2.85	16.5	19.2

Table 4.10: Effect of Addition of Durax to Clay-Silica-Mica System

Durax %	Green Compression Strength (KN/m^2)	Firing Shrinkage (Volumetric) (%)	L O I (%)	Apparent Porosity (%)
2	>135	3.83	13.3	20.5
E 4	>135	3.56	13.3	20.1
6	>135	3.01	12.6	19.4
8	>135	2.91	13.3	19.1
10	>135	2.91	13.2	18.5
12	>135	3.05	12.5	18.0

Table 4.11: The Effect of Sintering Temperature on the Cold Compression Strength of Clay- Silica-Mica-Bentonite and Clay-Silica-Mica-Durax System (Samples D and E)

Temperature (°C)	Cold Compression Strength ($Kgcm^{-2}$)	
	D	E
1000	40.89	47.85
1100	46.35	60.75
1200	47.71	80.56
1300	54.52	100.48
1400	40.89	80.89

Table 4.12: The Effect of Sintering Temperature on the Volumetric Shrinkage after Firing of Clay- Silica-Mica-Bentonite and Clay-Silica-Mica-Durax System (Samples D and E)

Temperature (°C)	Volumetric Shrinkage (%)	
	D	E
1000	3.66	3.56
1100	3.92	3.82
1200	4.52	4.32
1300	5.88	5.56
1400	7.79	6.3

Table 4.13: The Effect of Sintering Temperature on the Apparent Porosity of Clay-Silica-Mica-Bentonite and Clay-Silica-Mica-Durax System (Samples D and E)

Temperature (°C)	Apparent Porosity (%)	
	D	E
1000	22.5	20.1
1100	15.4	16.3
1200	12.52	13.3
1300	5.5	5.76
1400	2.77	3.85

Table 4.14: Thermal Shock Resistance of D and E

Sample	No of Cycles Withstood	Comment*
D	>30	Good
E	>30	Good

* Gilchrist, 1977

Table 4.15 : Refractoriness of D and E

Sample	Refractoriness (°C)
D	1500
E	1500

4.2 DISCUSSION OF RESULTS

4.2.1 The Effect of Addition of Silica on Ikere-Ekiti Clay

It was observed that the Ikere-Ekiti clay mixed with 10% water cracked during the drying and firing operations at a temperature of 120°C and 1000°C respectively. This is due to the volumetric shrinkage which followed the drying and firing operations. Therefore, to reduce the shrinkage and avoid cracks, free silica of AFS GFN 3.81 and particle size distribution as indicated in Fig. 1 was added in steps of 2% w/w of silica, keeping the water content constant at 10%. The choice of this grain size is due to the fact that it has been established that free silica of finer grain size lowers the refractoriness of clay by reacting with the alkali and alkaline earth oxides in clay. Larger surface area will however increase the tendency for softening (Adeoye, 1985). It could be observed from Table 4.4 that compositions with 10% Silica and above showed no crack. This is due to the low volumetric shrinkage after firing. The shrinkage has been reduced from 11.5% in 100% Ikere-Ekiti clay to 5.9% in 90% clay-10% silica mix as could be seen in Fig. 4.2. Since the 5.9% value is acceptable for ramming purposes (Kundan refractories, 2000), the 10% Silica-90% clay mix was chosen for further investigations. The choice was arrived at based on its low volumetric change after firing and because of the fact that higher silica content will lower the cold compression strength of the mix and present rough surface to the rammed mass. It has been established that rough surfaces usually lower the abrasion resistance of monolithic working surfaces (Semler, 2001). Furthermore, the thermal conductivity of the refractory will increase with increasing silica content into a clay-mica aggregate. (Thermal conductivity of materials, 20002).

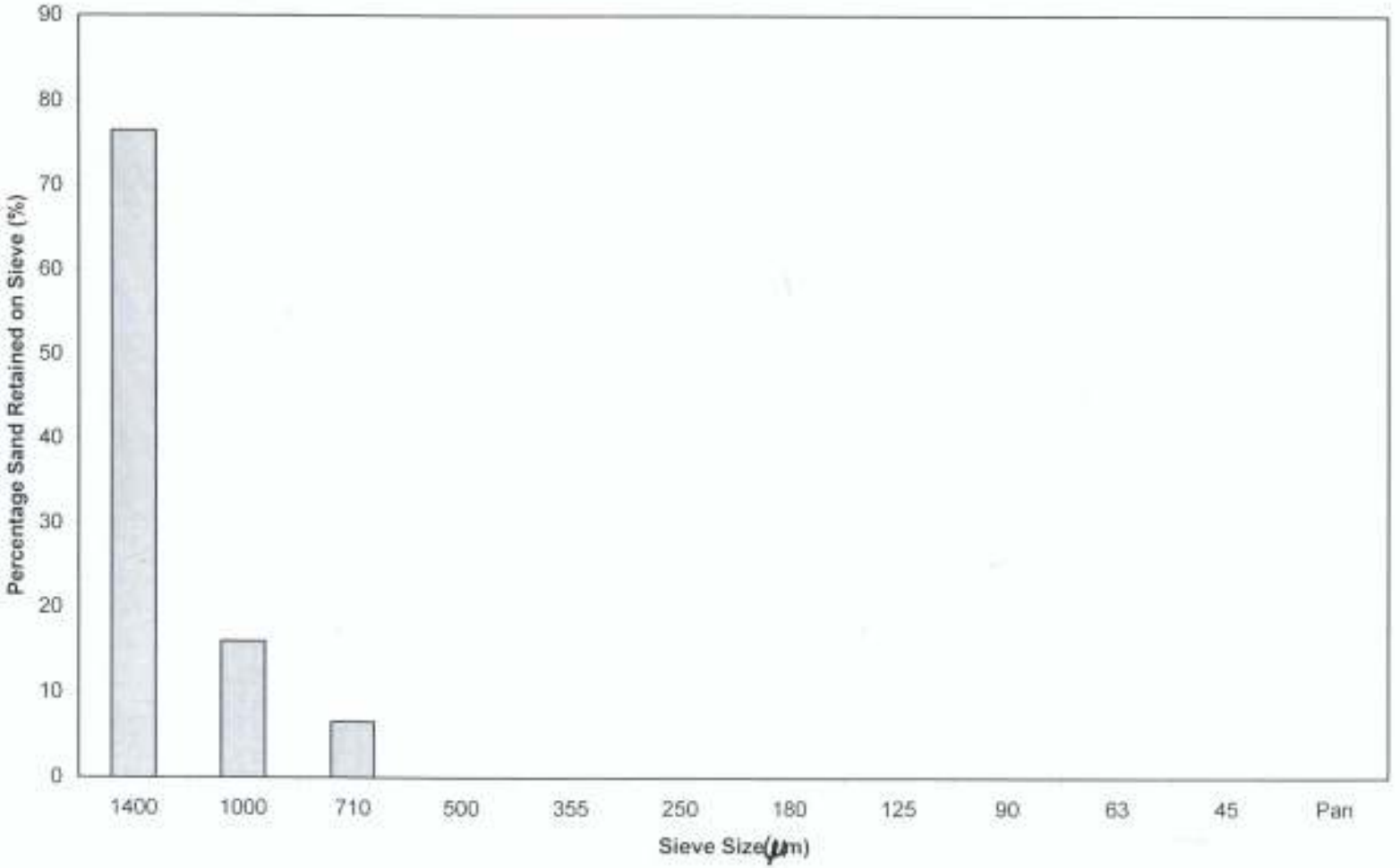


Fig. 4.1 Particle Size Distribution of Silica

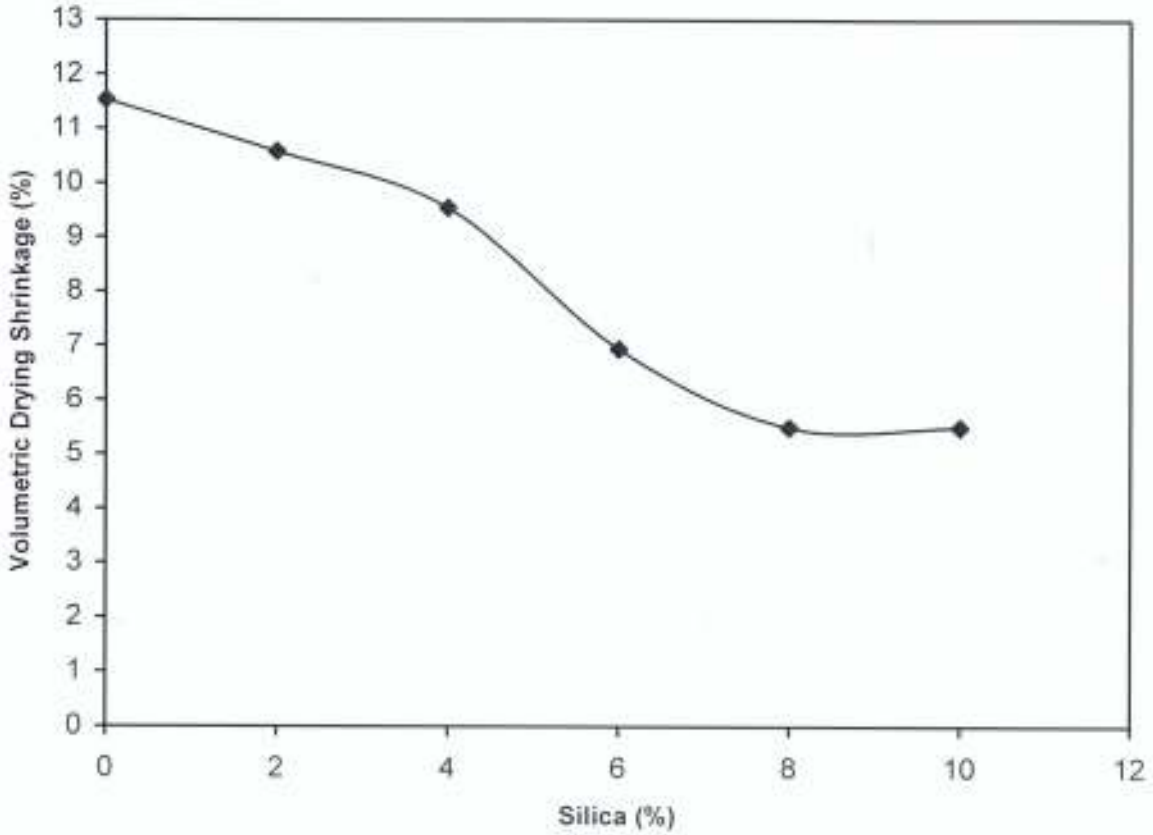


Fig 4.2 The Effect of Addition of Silica on Volumetric Drying Shrinkage of Ikere-Ekiti Clay

4.2.2 Effect of Addition of Mica on the Green Compression Strength and Drying Behaviour of Clay-Silica System

The effect of mica addition on the green compression of clay-silica system was studied and the result is presented graphically in Fig. 4.3. The compression strength decreases with increase in mica content. This is due to the non-plastic nature of mica and the inertness of its surface to water films. Fine cracks appeared on the surface of samples with mica content exceeding 20%. This is as a result of the inert surface of mica to water film, which tends to cause cleavage between the mica particles, silica and clay.

The choice of the sample containing 20% mica (sample **C**) for further investigations is due to the fact that this composition contains the maximum mica content with which sample **B** can be bonded without noticeable cracks on drying.

4.2.3 Effect of Ramming Pressure on the Apparent Porosity of Clay-Silica-Mica System

The effect of ramming pressure on the porosity of clay-silica-mica System (sample **C**) is given in Fig. 4.4. A decrease in the apparent porosity was observed with the increase in the no of cycles of ramming. This is due to the close packing of the aggregates at higher ramming pressures. The apparent porosity became fairly constant after six cycles of ramming. Eight ramming cycles was therefore chosen as the optimum for production of samples for further investigations.

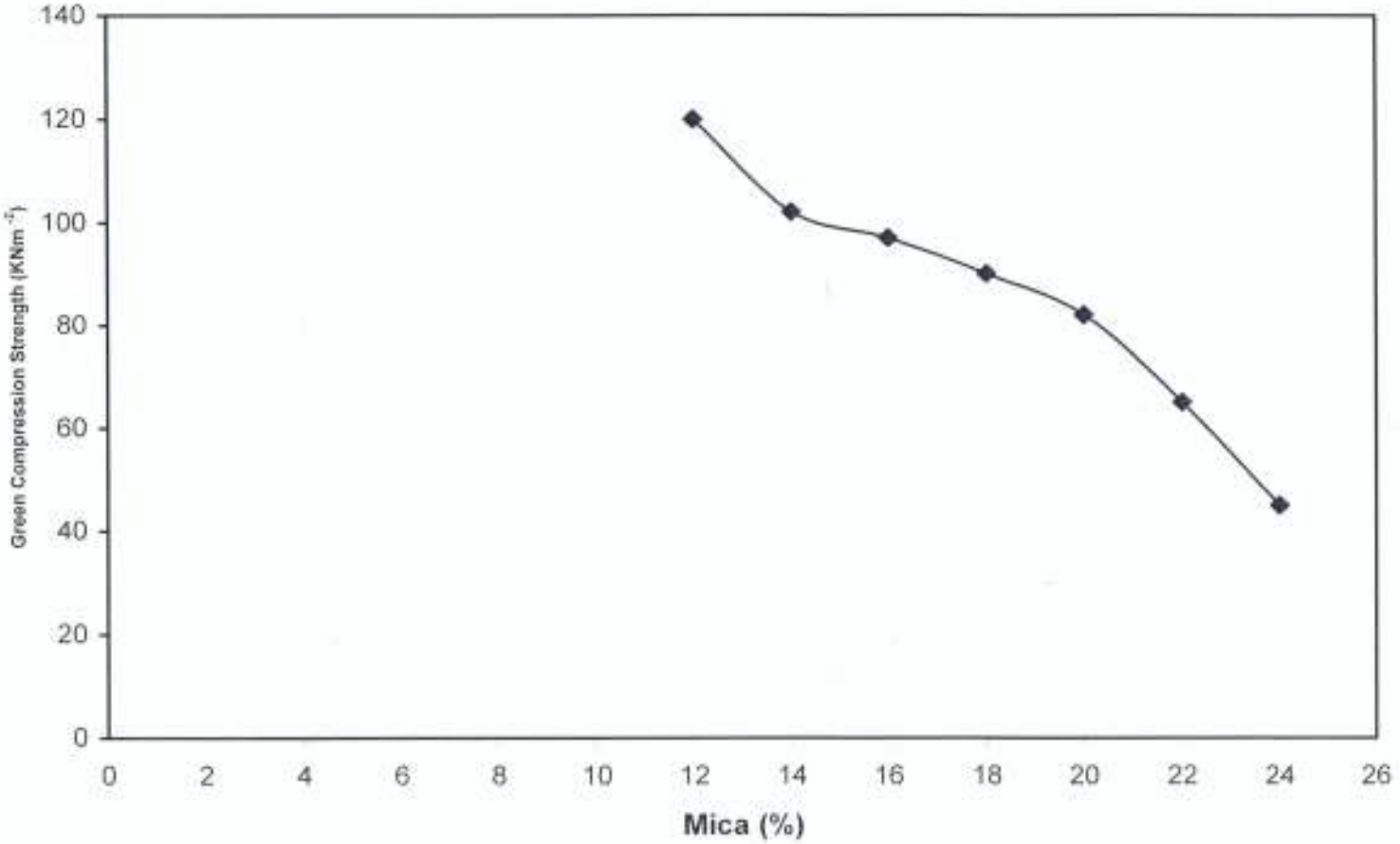
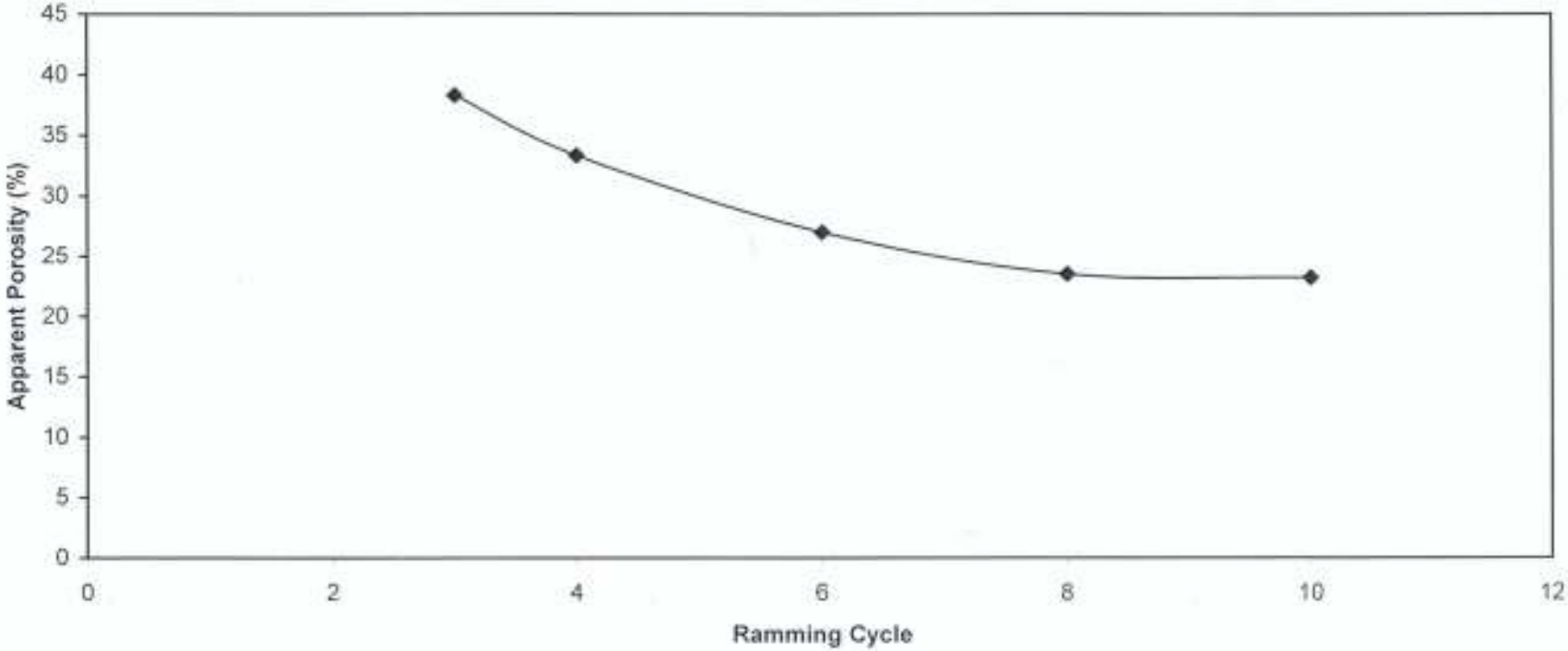


Fig 4.3 The Effect of Addition of Mica on the Green Compression Strength of Clay-Silica System



Flg 4.4 The Effect of Ramming Pressure on the Apparent Porosity of clay-silica-mica System

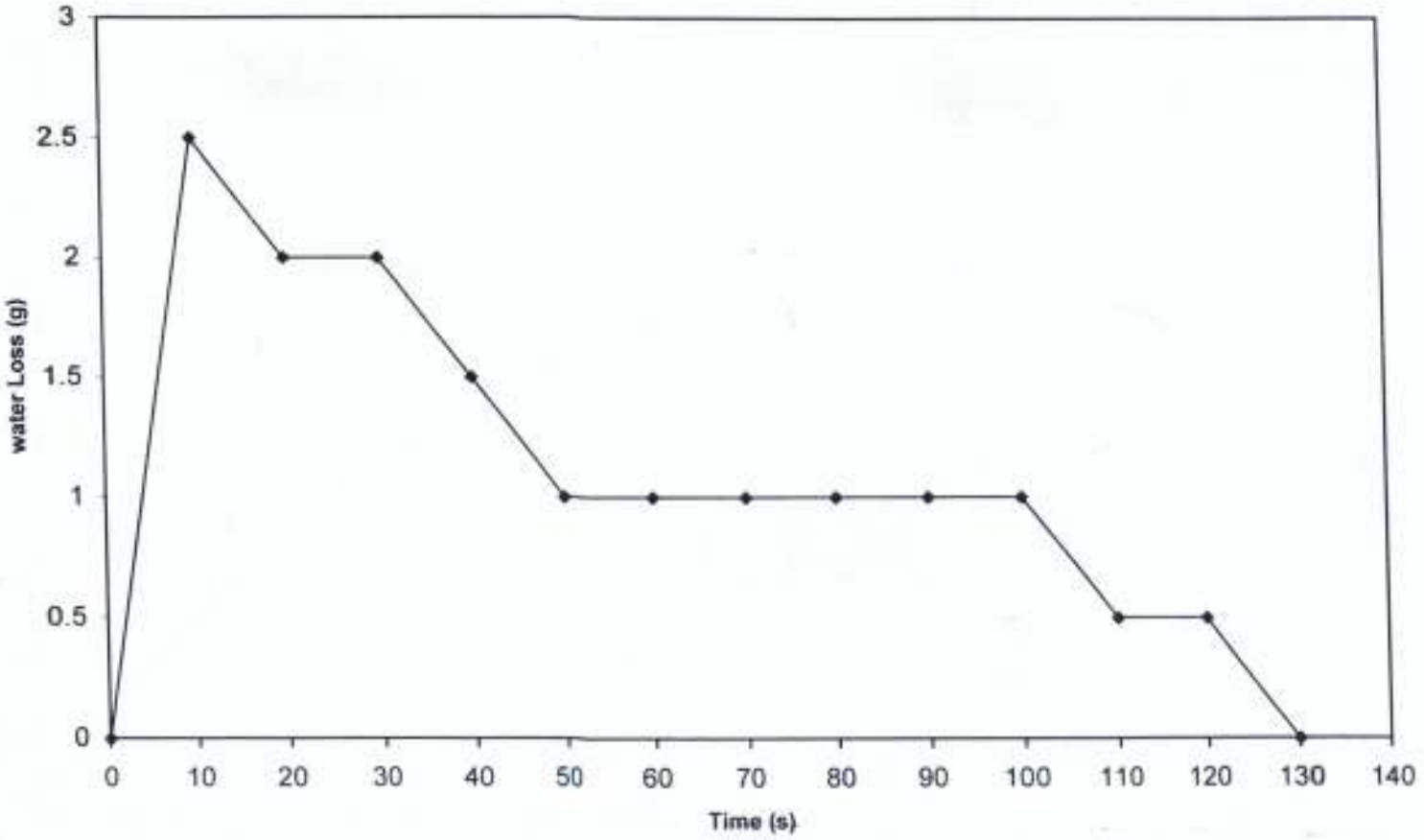


Fig. 4.5 Drying Rate of clay-silica-mica System

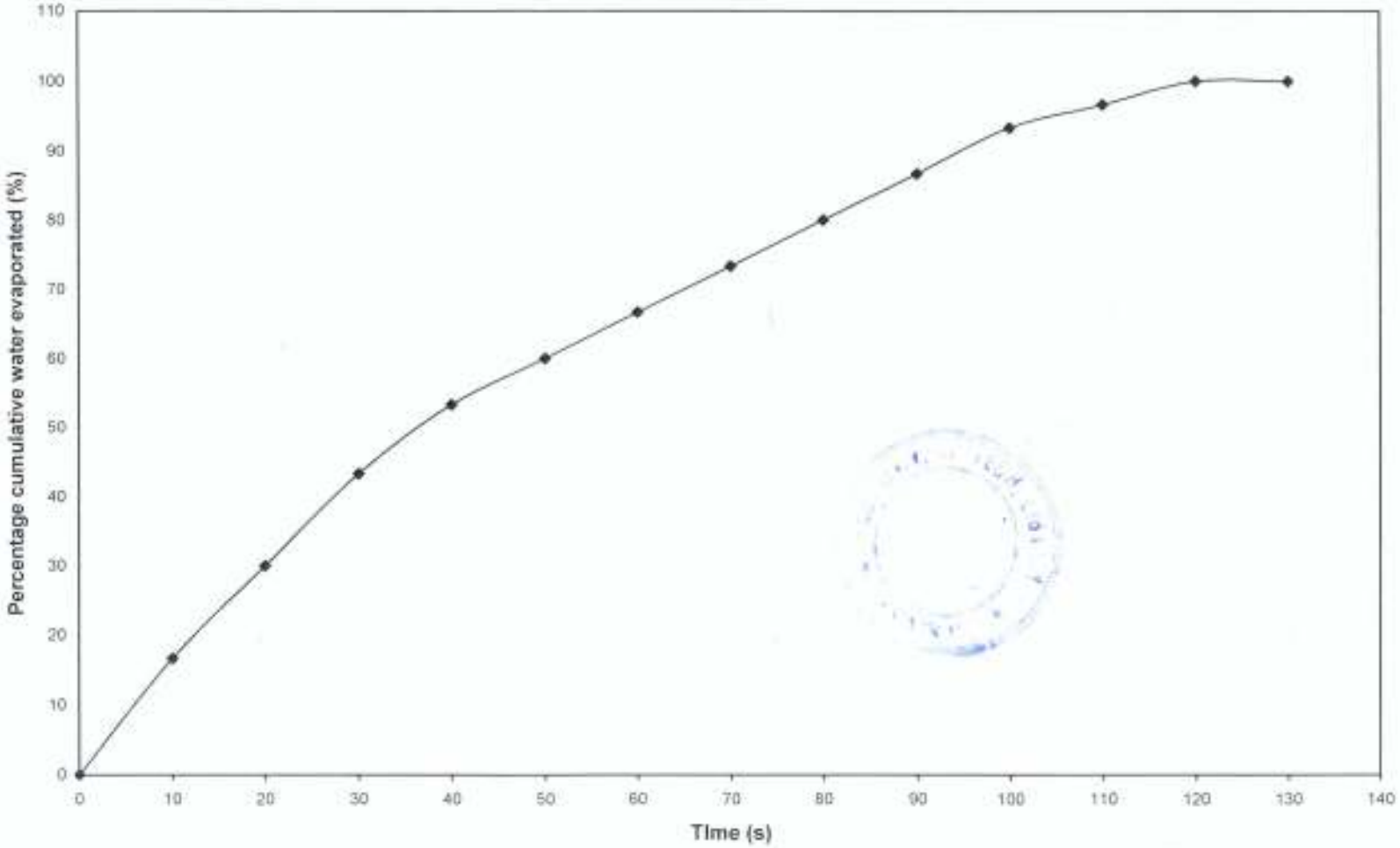


Fig. 4.6 Cummulative Water Loss in clay-silica-mica System During Drying

4.2.4 Drying Rate of sample Clay-Silica-Mica System at 120°C

Studies were carried out to determine the drying rate of clay-silica-mica system (sample C) at 120°C. The results obtained are presented in Figs. 4.5 and 4.6. It was observed that the drying rate of the sample was highest in the first 10minutes of drying. This is because; there is a faster removal of water from the surface of the material with the attendant replenishment by water molecules migrating from the pores within the samples. Drying was by convection and conduction. The rate became reduced until after 50min of operation, before becoming constant at the rate of 0.1g/min between 50 and 100mins. The constancy of the drying rate over this long period signifies that the rate of water removal from the surface equates the rate at which water molecules migrates to the surface. Drying was however completed after 120mins of heating. The significance of the study of the drying rate is in the adoption of the technique to the manufacturing process of the final product.

4.2.5 Loss on Ignition of Clay-Silica-Mica System at Different Firing Temperature

The study of the effect of temperature on the loss of ignition of Clay-Silica-Mica System (sample C) was presented in Fig. 4.8. Measurement of loss on ignition of sample C at different firing temperatures shows that there is a progressive loss in weight of samples as the temperature increases. Loss of combustible materials occurred at this temperature range. Also, chemical reactions: oxidation of sulphides and carbonates and volatilization reactions occurred. The loss on ignition became consistent after 1100°C. This shows that there are no further reactions that could bring about weight reduction.

4.2.6 Effect of Additives on Some Properties of Clay-Silica-Mica System

Measurements were taken to determine the effect of some additives such as bentonite and Durax on some properties of clay-silica-mica system (sample C). The samples were subjected to eight ramming cycles to achieve apparent porosity of 23.1% which is comparable to the values for aluminosilicate bricks (Gilchrist, 1977). Properties such as volumetric firing shrinkage, loss on ignition and apparent porosity were then determined using the methods earlier described in section 3.5. The results obtained are presented in Figs. 4.8, 4.9, and 4.10 respectively. It can be seen from Fig. 4.8 that the increase in bentonite content caused a slight decrease in volumetric firing shrinkage. This is due to the small sizes of bentonite which causes a closely packed aggregate resulting in reduction of firing shrinkage as bentonite content increases. On the other hand, increase in volumetric firing shrinkage and thereafter remains fairly constant. Fig. 4.9 presents the effect of additives on the loss on ignition of the clay-silica-mica system. As it can be seen from the curves, the loss on ignition remains fairly constant with increase in additive. For the same percentage addition of durax and bentonite, bentonite addition gave a higher value of loss on ignition. From Fig. 4.10 increase in durax and bentonite results in a decrease in the apparent porosity values of samples. This is due to the small particle size of these additives which caused a close packed aggregate in the structure of the rammed samples.

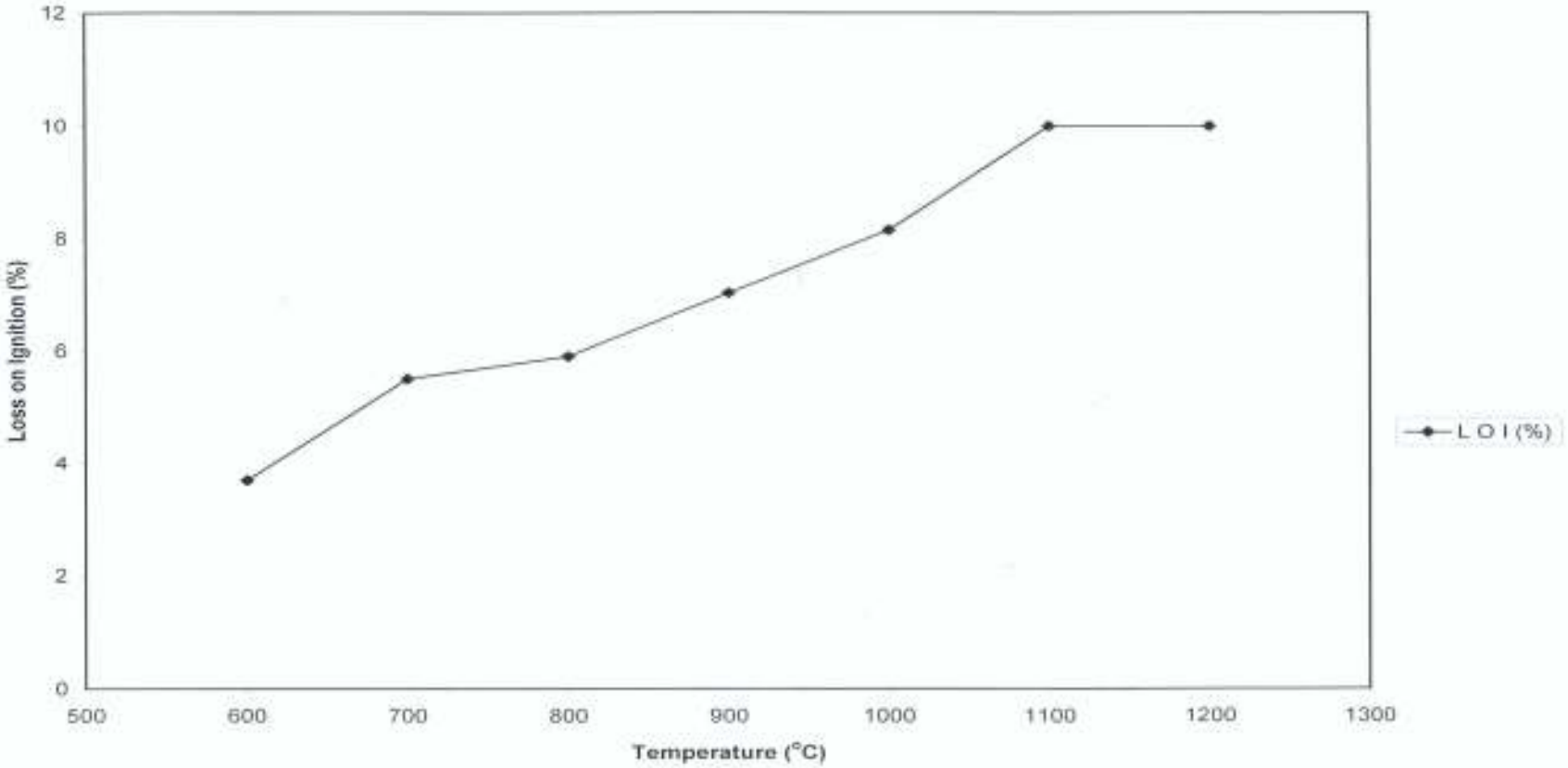


Fig. 4.7 Loss on Ignition of clay-silica-mica System at Different Firing Temperatures

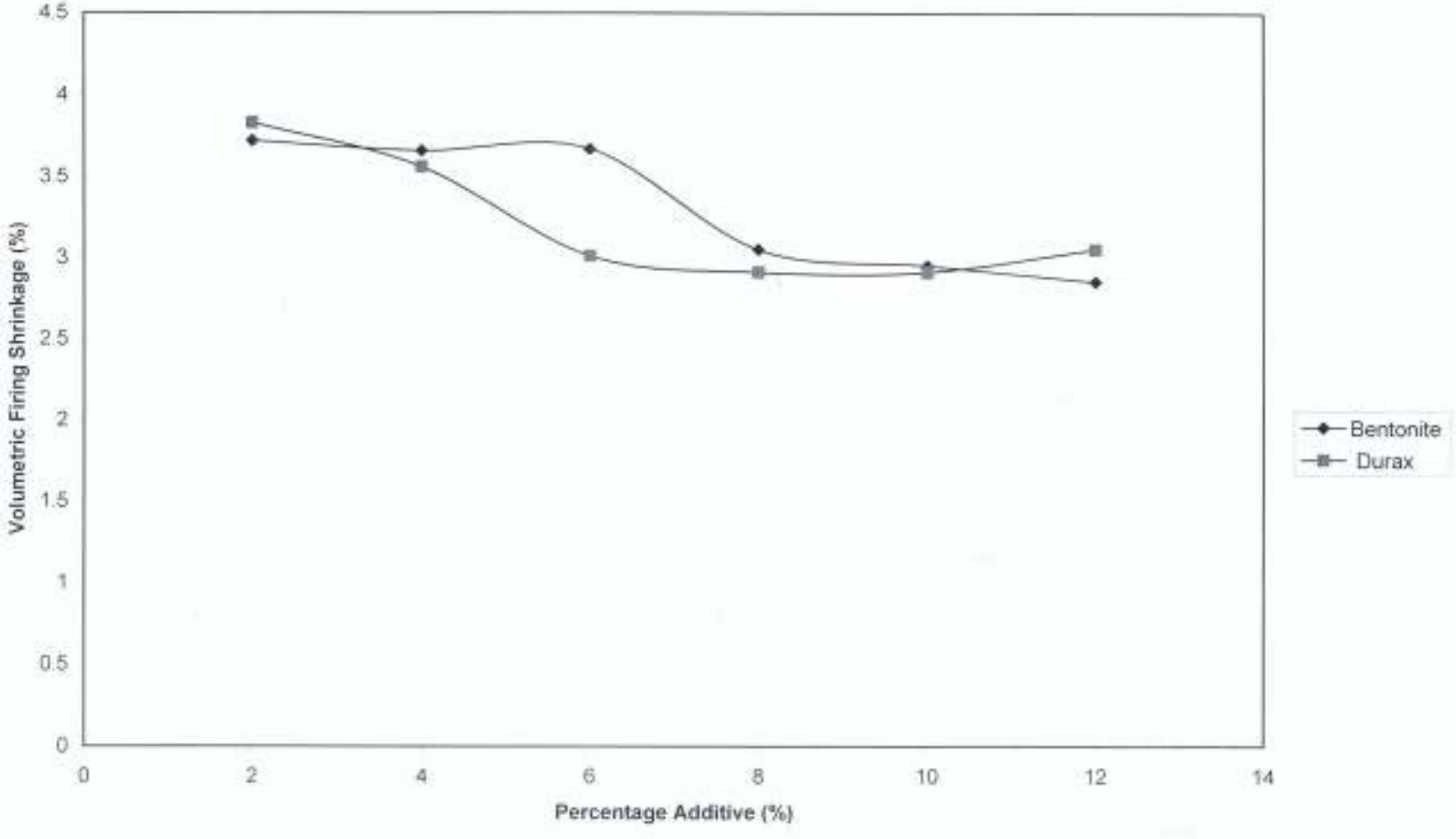


Fig. 4.8 The Effect of Additives on The Volumetric Firing Shrinkage of clay-silica-mica System

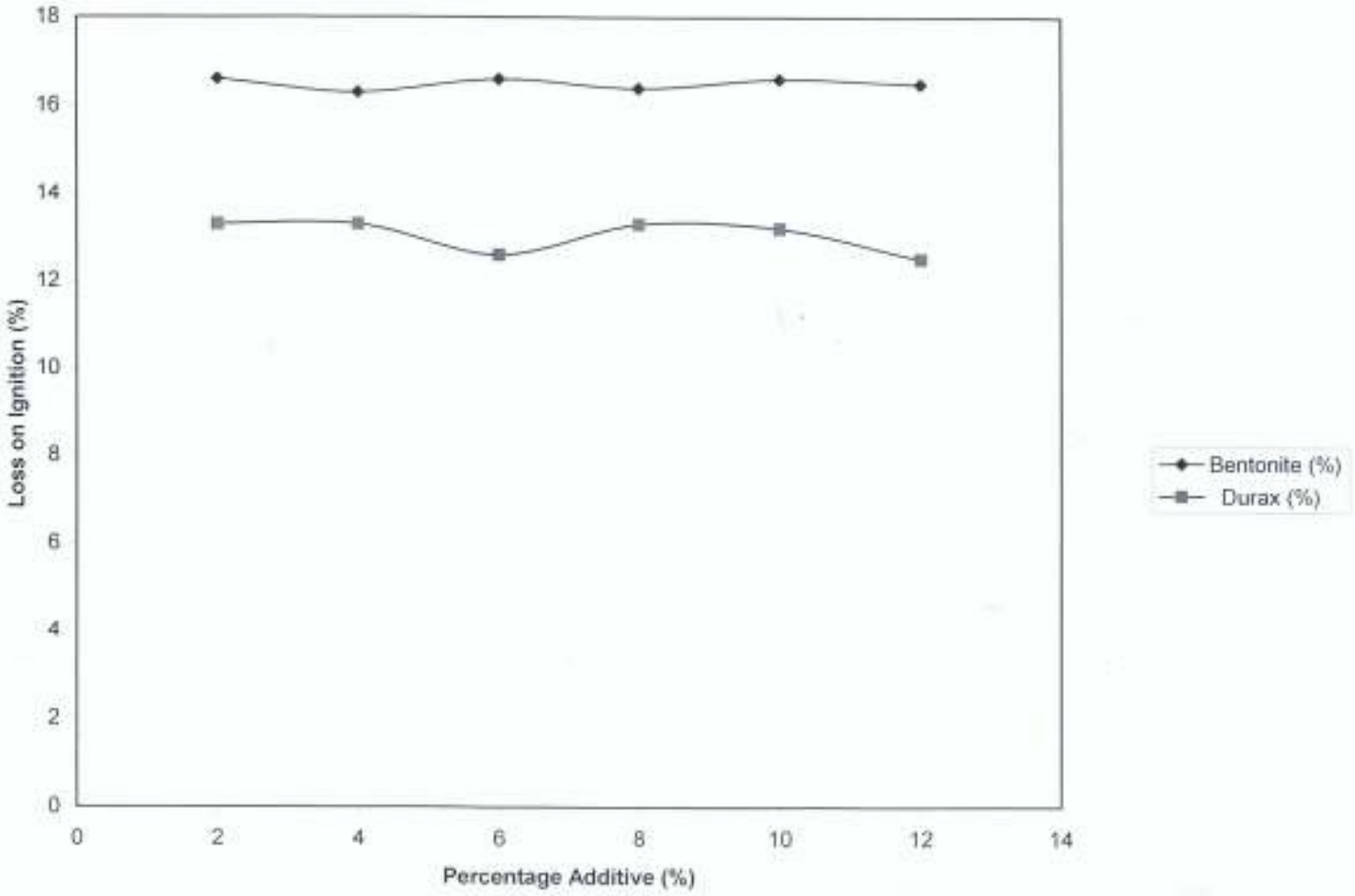


Fig 4. 9 The Effect of Additives on the Loss on Ignition of clay-silica-mica System

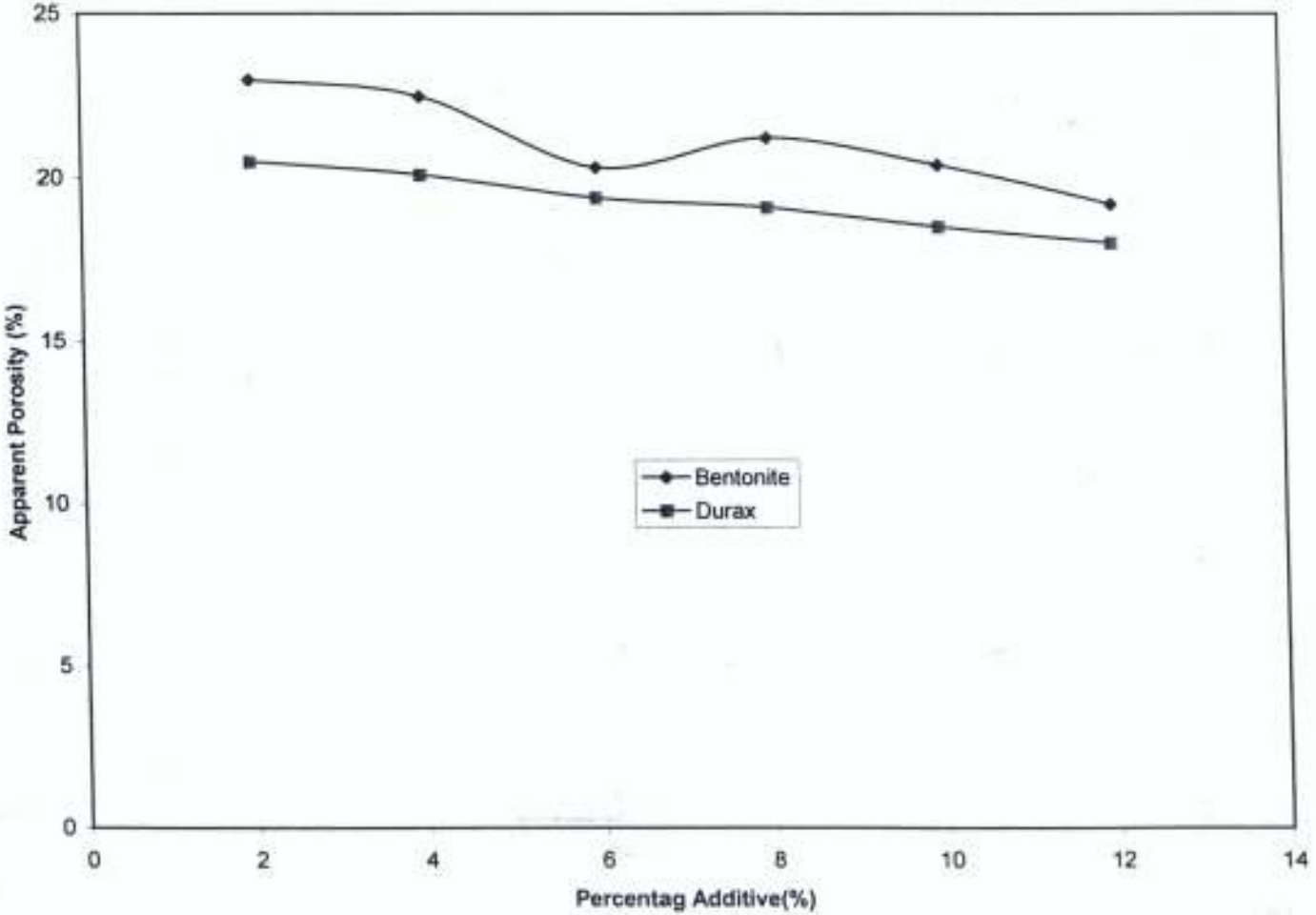


Fig 4.10 The Effect of Additives on the Apparent Porosity of clay-silica-mica System

4.2.7 Effect of Sintering Temperature on the Mechanical and Thermal Properties of Clay-Silica-Mica-Bentonite and Clay-Silica-Mica-Durax System

Experiments were performed to determine the effect sintering temperature on such properties of clay-silica-mica-bentonite and clay-silica-mica-durax (samples **D** and **E** respectively). The properties include cold compression strength, volumetric firing shrinkage and apparent porosity. Samples made to AFS specification were rammed and the properties as mentioned above were measured at different sintering temperatures. This was done so as to determine the variation of these properties with temperature as sintering temperature and hence to study the properties of a monolithic lining which are not uniform across the radial cross-section of the furnace. The results obtained are presented in Figs. 4.11, 4.12 and 4.13.

From fig. 4.11, the cold compression strength of the samples increases with sintering temperature; reaching a maximum at 1300^{0}C and falls thereafter before fusion at 1500^{0}C. The increase in *CCS* between 1000^{0}C and 1300^{0}C is due the bonding together of the particles by a liquid phase (which solidified as glass) formed by some of the clay particles surrounding the silica and mica aggregates. Loss of strength noticed at 1400^{0}C is due to an increase in the liquid phase which led to the weakening of the structure and consequently fusion at 1500^{0}C.

Fig. 4.12 shows the effect of sintering temperature on the volumetric firing shrinkage of samples **D** and **E**. It was observed that volumetric firing shrinkage decreases with temperature. This is due to the densification of the samples occasioned by the filling up of the pores by the liquid phase. From Fig. 4.13, the apparent porosity decreases in the

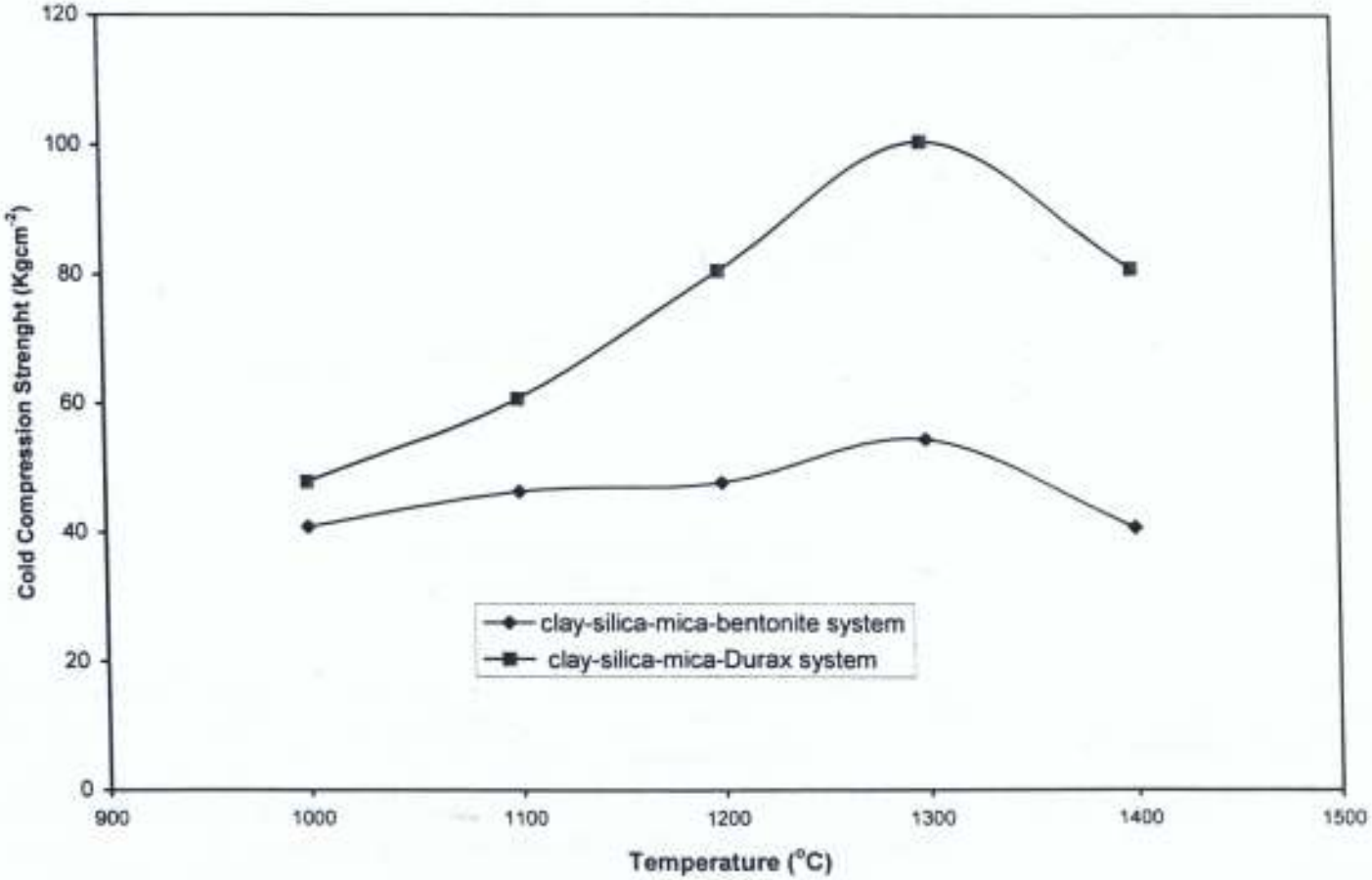


Fig 4. 11 The Effect of Sintering Temperature on the Cold Compression Strength of clay-silica-mica-bentonite and clay-silica-mica-Durax System

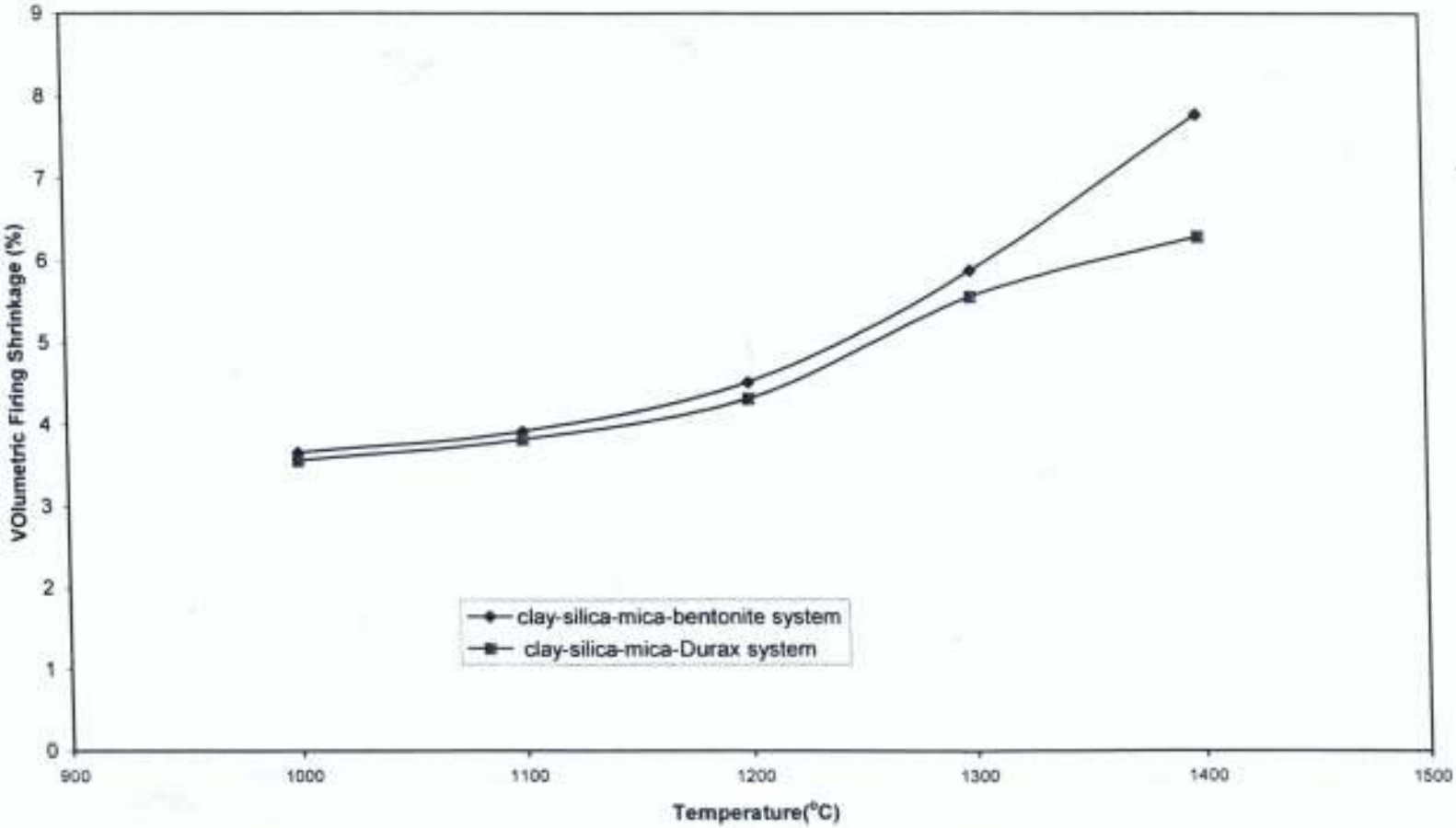


Fig 4.12 The Effect of Sintering Temperature on the Volumetric Firing Shrinkage of clay-silica-mica-bentonite and clay-silica-mica-Durax System

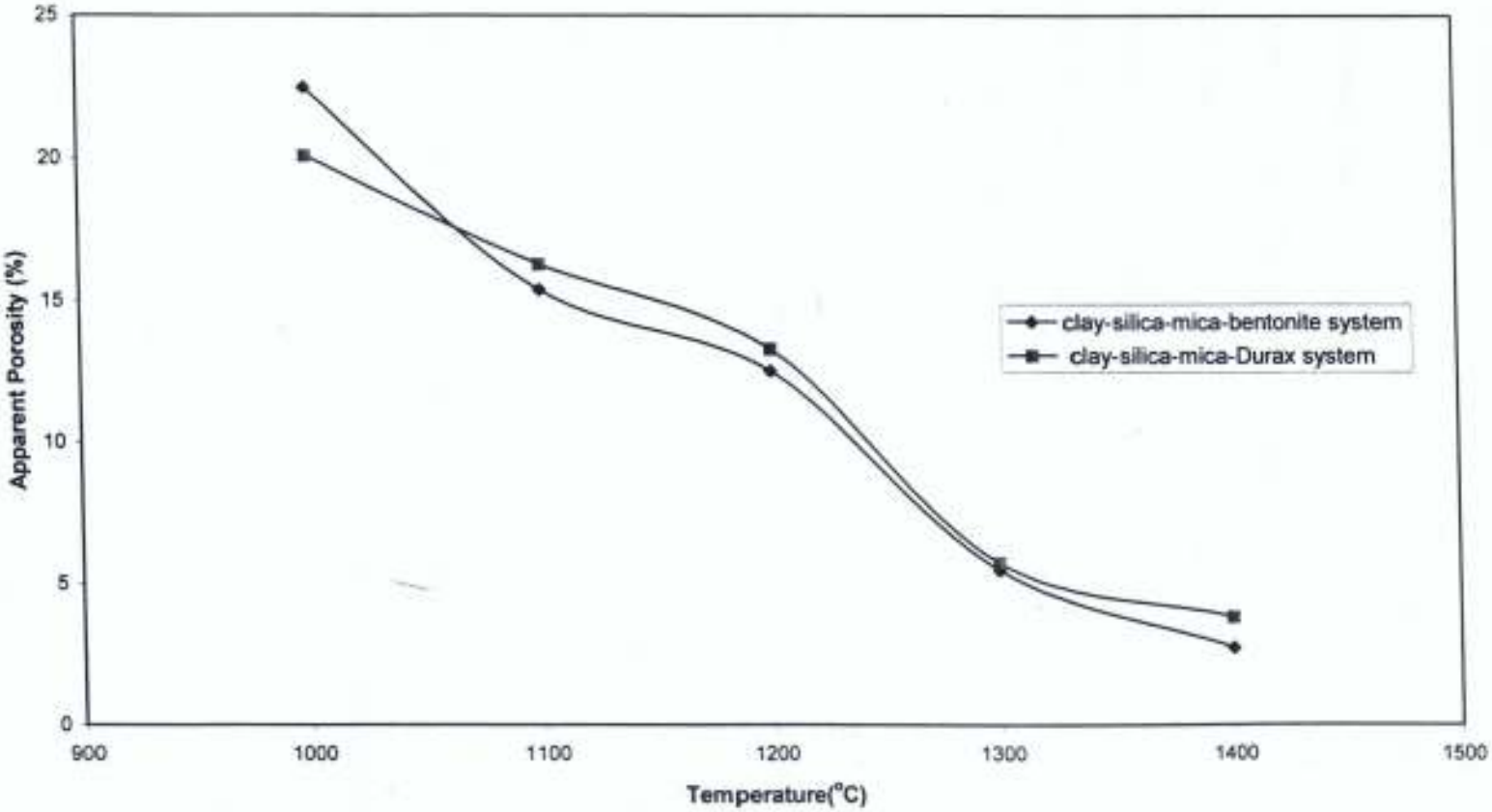


Fig. 4.13 The Effect of sintering Temperature on the Apparent Porosity of clay-silica-mica-bentonite and clay-silica-mica-Durax System

sintering temperature range due to densification of samples causing an increase in the numbers of closed pores.

4.2.8 Thermal shock resistance

The two samples **D** and **E** were used for these tests. These samples withstood more than 30cycles during the thermal shock resistance tests. This was reported in Table 4.14. The values reflect a good thermal shock resistance for the samples as these values are comparable to the values for the aluminosilicate bricks having excellent thermal shock resistance (Gilchrist, 1977).

4.2.9 Refractoriness

Samples of **D** an **E** prepared to AFS dimension were used for the refractoriness tests as described in section 3.5f. The fusion of the samples took place at 1500°C. This is the highest temperature the samples can withstand and hence their use should be below this temperature.

4.2.10 MICROSTRUCTURAL STUDIES OF SAMPLES

Studies were made on three samples each of clay–silica-mica-bentonite and clay-silica-mica-durax systems. Samples were fired at 1200°C, 1300°C and 1400°C.

Plates 4.1, 4.2 and 4.3 indicate the clay-silica-bentonite system fired at 1200°C, 1300°C and 1400°C respectively. The two samples fired at 1200°C showed the aggregate particles as separate phases without a distinct grain boundary. The clay is in red and the mica in white. At 1300°C, grain boundaries have appeared showing the liquid phase

surrounding the grains as the bonding matrix. This accounts for the maximum cold compression strength observed at this temperature. On firing at 1400°C, the grain boundaries have virtually disappeared except in some minute places the disappearance of grain boundaries is due to the densification upon firing and the formation of a thermodynamically stable phase.

Plates 4.4, 4.5 and 4.6 indicate the clay-silica-mica Durax system fired at 1200°C, 1300°C and 1400°C respectively. At 1200°C, the sample shows the individual aggregates of clay, silica and Durax. The bonding here consists of the solid state sintering of the particles and the strength is imparted by the stable $CaAlO_3$ phase. The sintering operation at 1300°C shown in plate 5 showed the transformation of the aggregates whereby a liquid phase is formed within the matrix of the structure which latter solidified into glass. There is no clearly defined grain boundary here as in the **D** samples fired at the same temperature. At 1400°C densification of the samples occurred with an increase in the amount of the liquid phase.

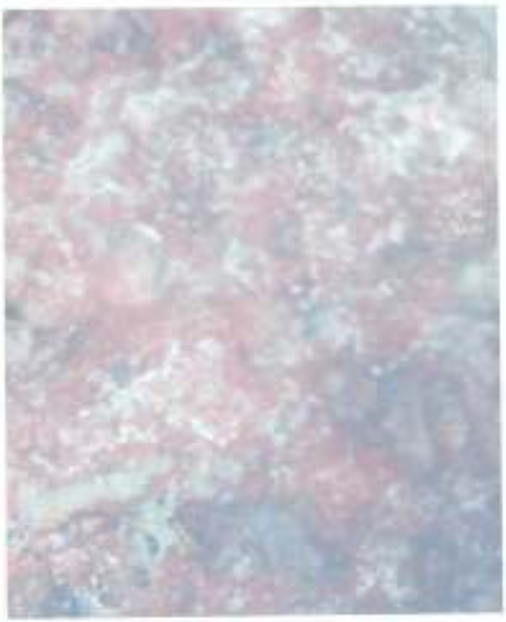


PLATE 4.1: SAMPLE D FIRED AT 1200°C 100x

PLATE 4.2: SAMPLE D FIRED AT 1300°C 100x

PLATE 4,3: SAMPLE D FIRED AT 1400°C 100x

PLATE 4,4: SAMPLE E FIRED AT 1200°C 100x

PLATE 4,5: SAMPLE E FIRED AT 1300°C 100x

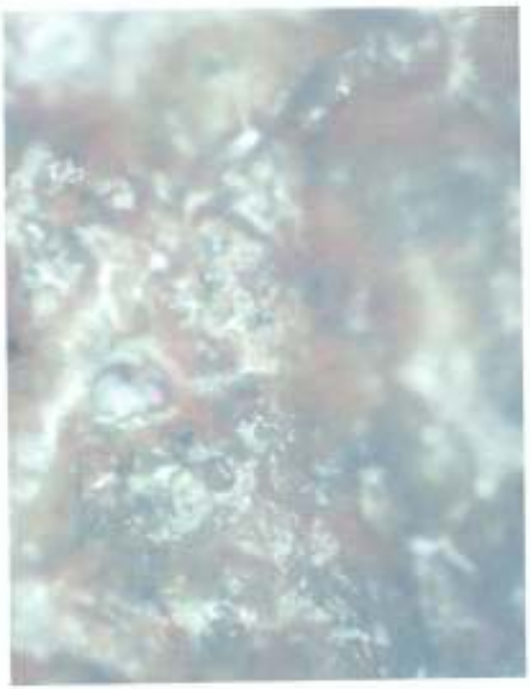


PLATE 4,6: SAMPLE E FIRED AT 1400°C 100x

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The research work had centred on the development of Aluminosilicate ramming mass. From experiments it was shown that samples **D** and **E** having the ratio clay:silica:mica: bentonite 90:10:20:4 and clay:silica:mica: Durax 90:10:20:4 respectively possesses good thermo-physical and thermo-mechanical properties for the lining of rotary, cupola and crucible furnaces. They could serve as very good ramming mass for lining of furnaces for melting of ferrous and non- ferrous alloys which pouring temperature does not exceeds 1475°C. These include aluminium (660°C), brasses (1050°C for 60 – 40 brass and 1185°C for 10-90 brasses), cast iron (1150°C - 1350°C) (Higgins, 1991). There thermo-physical and thermo-mechanical properties are good enough to serve as alternative to imported ones and hence lead to an increase in the local input of engineering materials production in Nigeria.

5.1 RECOMMENDATION

Due to the large deposits of refractory materials scattered all over the country, refractory materials from other parts of the country should be investigated for production of ramming mass so that a wide range of products could be made available for the lining of metal melting furnaces and thereby enhancing the growth of the foundry industry in Nigeria.

As much as this work covered the aspects of thermo-physical and thermo-mechanical and microstructural studies of ramming mass, other research areas on monolithic lining production should be investigated.

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