DEVELOPMENT OF SLIP CAST ELECTRICAL PORCELAIN BODIES

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D E C L A R A T I O N

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2. this thesis has not been submitted in whatever form to any other institution, organisation or body for the award of any degree;

3. all inclusions from the work of others have been duly acknowledged and referenced.

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This thesis entitled *"Development of Slip Cast Electrical Porcelain Bodies"* by Henry Ehibhanre Okojie meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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D E D I C A T I O N

This work is dedicated to

my wife and children

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ABSTRACT

Electrical porcelains are glazed or unglazed vitreous ceramic whitewares used for electrical insulation. These materials which are widely used in the country as insulators in electrical power transmission and as insulator components in a number of electrical and electronic devices are currently being imported. The main raw materials for the manufacture of electrical porcelains are clays, feldspar and quartz and despite the availability of fuel and large deposits of these materials in the country, the porcelains are not being produced locally. The aim of this work was to investigate the optimal processing conditions and suitable body compositions for the production of electrical porcelains from local raw materials.

Kankara clay, Bukuru clay, Okene feldspar and Amper quartz were selected as the major raw materials. The mineralogical compositions of the materials were investigated by X-ray diffraction technique to ascertain their suitability for body formulation. The rheological properties of the clays and porcelain body slips were studied as a .function of deflocculants content to determine the appropriate amounts required in casting slip. Various bodies were formulated, wet ball milled, slip cast, dried and fired. The important green and fired properties of the casts were studied to determine their suitability for various applications.

The apparent viscosity of Kankara clay slip increased from 21.30 to 36.50 poises as the sodium carbonate concentration was increased from 0.001 to 0.005 percent. The unusual increase in apparent viscosity was attributed to a reduction of the electrical potential at the clay surfaces due to the presence of excess sodium ions in the medium resulting

from the hydrolysis of sodium carbonate. This reduction enhanced the aggregation of clay particles by the universal van der Waals forces and the development of inter-aggregate links between the floes. Only silicate ions of the two deflocculants, sodium carbonate and sodium silicate, appeared to have the greatest effect in deflocculating Kankara clay, Bukuru clay and Kankara clay-based porcelain body slips. The porcelain body slip exhibited considerable thixotropy as the sodium silicate concentration was increased from 0.017 to 0.052 percent. However, it was destroyed when the deflocculant concentration exceeded 0.061 percent.

The green and fired modulus of rupture increased with the clay content, and for a given clay content, the strength increased as the quartz content was increased from 20 to 25 percent and then decreased as the percentage of quartz was further increased to 30 percent.

The dry-to-fired shrinkage for all the bodies studied was about 12.5 percent while the differential shrinkage between diameter and length was about 1.25. The latter value indicated that the clay particles were preferentially aligned during the casting process.

The porosity and water absorption values for the high feldspar body C, and high clay bodies E and F were less than 1 percent which is well within the range of industrial vitrification. However, the values of these properties for the high quartz bodies, B and G were higher than 2 percent.

Microscopic'studies of thin sections of fired specimens showed that a significant proportion of quartz remained undissolved in the glass matrix. Some of the residual quartz showed extensive fracturing.

Comparisons of the properties of the porcelains developed with standard specifications for low and high voltage porcelain insulators clearly indicated that Bodies A, C, D and E are suitable for low voltage applications while Body F is suitable for both low and high voltage insulation.

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CHAPTER ONE

INTRODUCTION

Electrical porcelain is a glazed or unglazed vitreous ceramic whitware possessing electrical insulating properties (ASTM, 1983). They are used widely in electrical and electronic industries for electrical power transmission at low and high voltages and as insulator components in such devices as circuit breakers, switch boxes, fuse holders, lamp holders, transformers, etc. Porcelain has advantages over other insulating materials such as plastics, glass and wood because of its ability to retain its electrical and mechanical properties in atmospheric weather conditions.

Various types of electrical porcelains are being imported into the country to meet the needs of development and technology. In 1978, an estimated 12 million Naira worth of electrical porcelains were imported (Onaji, 1984). It is expected that the demand for electrical porcelains will increase as the country continues to expand the electrical power distribution networks.

The main raw materials for the production of electrical porcelains are clays, feldspathic rocks and quartz. Large deposits of these materials and fuel needed for the manufacture of electrical porcelains are available in the country. However, they are not being produced locally. Although the production of porcelain from foreign raw materials is well known, the processing conditions and body compositions vary for different raw materials due to variations in chemical and mineralogical compositions, and some physical properties. There is inadequate information on these conditions and compositions for local raw materials.

Electrical porcelains are currently being manufactured either by dry or wet methods. Wares produced by dry methods are generally porous and are not suitable for high voltage applications. Wares produced by wet methods may be formed in the plastic state by throwing, extrusion, jolleying, jiggering or lathe turning. They may also be formed by slip casting technique. This last method has some advantages over the others. It is conveniently used in research and industry for the production of small articles of intricate shapes and the process generally requires minimum machinery.

Recent attempts have been made by Umar (1985) and Okpanachi (1986) to develop slip cast electrical porcelain from Kankara clay, Bomo clay, Bukuru clay, Okene feldspar and Amper quartz. However, the body composition which the researchers developed was only suitable for low voltage applications. The objective of this work was to develop other bodies and optimise processing conditions especially for high voltage porcelain production.

Four main raw materials: Kankara clay, Bukuru clay, Okene feldspar and Amper quartz were studied. The mineralogical compositions of the raw materials were investigated by X-ray diffraction to ascertain their suitability for electrical porcelain production. The rheological properties of the clays and porcelain body slips were studied as a function of deflocculant content to determine the deflocculation treatment required in casting slip. Various porcelain bodies were formulated, wet ball milled, slip cast, dried and fired. The important green and fired properties of the casts were measured to determine their suitability for various applications and understand the effect of variation in body compositions on them.

CHAPTER TWO

SURVEY OF LITERATURE

In this chapter, the historical development of electrical porcelain is briefly reviewed. Types and composition of electrical porcelain in common use are described. A discussion of the chemical compositions and properties of raw materials and the various methods of production is presented. The important green and fired properties of porcelain are also discussed for the understanding of subsequent chapters.

2.1 Historical Development of Electrical Porcelain

Porcelain was first developed by the ancient Chinese at about the 16th century from a natural ceramic body which consisted of partially decomposed pegmatite (Norton, 1956). The decline in production in subsequent years was attributed to the depletion of these natural bodies. However, advances in the science and technology of materials have led to the development of porcelain from a blend of clays, feldspathic rocks and quartz.

Porcelain was first used for electrical insulation in the 19th century. It was developed along the same line as tableware and served as easy replacement for plastics and wood which were the predominant insulating materials before the development of porcelain.

The course of the development in body composition over the years has been necessitated by the continual requirement for higher mechanical strength as the voltages of power systems continued to increase.

2.2 Insulator Types

Electrical porcelain insulators are of three basic types: tension, post and hollow insulators.

The tension insulators are for overhead lines and they are designed to withstand tensile and compressive stresses. An example is the cap and pin insulator which is shaped such that the stress on it is predominantly compressive. Another example, the solid-core insulator, consists basically of porcelain which can be loaded in direct tension. Both units may be connected in series to give a length appropriate for the working voltages.

On the other hand, the post insulators are designed to withstand bending loads while hollow insulators are used as support insulator and are also subjected to bending loads. They are sometimes referred to as pressure vessels because they contain oil or gas often under pressure. Two examples of the post insulator type are the pedestal and the solid core insulators. Both units can be assembled to give a length appropriate to the working voltages.

2.3 Body Types

Porcelain bodies are classified as hard or soft according to their body compositions and firing conditions.

Hard porcelain bodies consist of about 40 to 50 percent clay, 35 to 45 percent quartz and 15 to 20 percent feldspar. These bodies are strong, white and translucent but the high firing temperature required (cone 16) necessitates special kiln equipment. The firing condition is characterised by a reducing atmosphere from 1050 to 1400°C. Hard porcelains seldom contain ball clays because they reduce

translucency and often impair color. Sufficient plasticity for working is, however, attained by fine grinding and aging.

Soft porcelain bodies consist of 40 to 50 percent clay while feldspar and quartz are present in almost equal proportions. Firing temperatures are within the range of 1170 to 1300°C and the kiln atmosphere may be oxidizing throughout the duration of firing.

2.4 Raw Materials

The three main raw materials for a triaxial porcelain are clays, feldspathic minerals and quartz. Water, deflocculants and plaster of Paris are also essential for ceramic processing. In this section, the composition and properties of clays, feldspathic minerals and quartz are discussed. An extensive discussion on the classification, composition and properties of clays is presented because of the tremendous effect the clays have on the physical properties of unfired and fired porcelain bodies.

2.4.1 Clays

Clays belong to the phyllosilicates in which the mineral lattice is layered, forming linked flat sheets. Clays may be defined as earthy mineral substances, composed largely of hydrous silicates of aluminium, which become plastic when wet and hard when fired. Clays occur in a great variety in nature and are found in commercial workable deposits all over the world. Most clay deposits have been formed by hydrothermal alteration of parent igneous rocks of suitable mineral composition. The feldspathic rocks and granites, according to Ryan (1978), are the most common rocks for clay formation.

Advances made in the use of X-ray diffraction techniques and electron microscopy methods have facilitated the classification of clays according to their crystal structure.

Classification and chemical composition: The basic structural and compositional units in the layer silicates are the silicon-oxygen tetrahedral sheets and aluminium hydroxide or magnesium hydroxide octahedral sheets. The tetrahedral and octahedral sheets are superimposed in different ways to form the so-called 1:1, 2:1 and 2:1:1 layer types.

The 1:1 layer type consists of a combination of one silica tetrahedral sheet and one octahedral sheet and results in the kaolinite-serpentine group. In the kaolinite group only two-third of the octahedral cation positions are filled by aluminium (dioctahedral) while in the serpentine group, all the cation positions are occupied by magnesium ions (trioctahedral).

The kaolinite group consists of kaolinite, dickite, nacrite and metahalloysite. They all have the chemical composition $Al_2O_3.2SiO_2.2H_2O$ or $Al_2Si_2O_5(OH)_4$. The main difference between the various species, according to Keller (1985), is in the layer stacking geometry. In the better-ordered kaolinite crystals, these layers are stacked one above the other in triclinic symmetry. Each layer crystal is slightly more than 7 Å in thickness.

The 2:1 type of layer silicates refers to those in which one octahedral sheet is sandwiched between two tetrahedral sheets in the unit structure. The class includes the pyrophyllite, talc, smectite vermiculite and mica groups. According to Heystek (1978), the differences in the various groups are a result of varying relative surface-charge

densities ranging from zero electron charge per formula unit for pyrophyllite and talc to a charge of about 2.0 for the brittle mica.

Montmorillonite is an example of a dioctahedral smectite and is represented by the formula $Al_{2-x}\ Mg_x\ Si_4\ O_{10}\ (OH)_2$. This formula indicates that substitution of ions for the lattice ions is limited to the octahedral sheet. Frequently, the substitutions are by ions of lower valency thereby producing an excess of charge which causes the basal faces to be essentially electronegative. Beidellite, $Al_2\ Si_{4-y}\ Al_y\ O_{10}(OH)_2$, is another example of dioctahedral smectite with substitution in the tetrahedral sheet. Trioctahedral smectites are represented by the clay minerals, saponite $(Mg_{3-x}Al_x)(Si_{4-y}Aly)O_{10}(OH)_2$, hectorite $(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2$ and sauconite $(Zn_{3-x}Al_x)(Si_{4-y}Al_y)O_{10}(OH)_2$.

Another group of 2:1 layer clays often referred to as the non-expanding clay minerals is represented by the mica minerals (illites). Typical dioctahedral micas are muscovite $KAl_2Si_3Al\ O_{10}\ (OH)_2$ and paragonite $NaAl_2Si_3Al\ O_{10}\ (OH)_2$. The charge deficiency is typically concentrated in the tetrahedral sheet and the cations which compensate the charge deficiency are usually potassium ions which are held very strongly in the interlayer space resulting in characteristic 10Å basal spacing.

Chlorites are clays which are structurally related to the 2:1 layer clays. However, an additional interlayer of magnesium hydroxide sheet is present resulting in a 2:1:1 layer type. The characteristic basal spacing is 14·2Å and a typical chlorite, the penninite, is represented by the formula $(Mg_{3-x}Al_x)(Si_{4-y}Al_y)\ O_{10}\ (OH)_8$.

Because of the similarities in the crystalline structure and composition of various layer silicates, it is possible for layers of different types of clays to be stacked together (interstratification).

When this occurs in nature, it gives rise to mixed-layer clays.

The classification of clays according to their sources and functional uses is often preferred in industrial ceramic practice to classification according to their crystal structure. The clays are classified as white-burning (China clay and ball clays), refractory clays (fireclays, flint and high alumina clays), stoneware clays, slip clays, brick clays and heavy-clay product clays. Others are pottery clays, terra-cota clays and bentonite. Some of these clays are briefly described in this section.

China clay or kaolin, is composed entirely of kaolinite, in the form of well-ordered particles which may be sedimentary or residual in origin.

Ball clay consists of extremely fine-grained and relatively poorly organized kaolinite. Some ball clays also contain small amounts of mica and/or small amounts of montmorillonite, which may add to their desired properties. Also, many ball clays contain a small but appreciable amount of organic material, which appears to enhance their desired properties. The origin of ball clays is sedimentary and the clays are not widely distributed throughout the world. Non-clay constituents often associated with ball clays are fine-grained quartz and mica.

Flint clay is very hard and consists essentially of pure and extremely fine-grained kaolinite clays. Flint clay is slaking-resistant variety of the kaolins. Such resistance of flint clay to slaking in water makes its possible use in the raw (unfired) state as a processed material in the manufacture of refractories.

Fireclay is a material satisfactory for the manufacture of refractories, and is composed of kaolinite with the absence of iron, alkalies and alkaline earths. Usually, the term "fireclay" is applied to clays of sedimentary origin which can be heated to temperature above 1600°C without melting.

Stoneware clay is composed of a mixture of clays with relatively fine-grained unsorted quartz present in amounts ranging from 25 to 50 percent. Clay minerals present are illite and kaolinite. A small amount of chlorite may also be present.

Typical chemical composition of clays used in the manufacture of porcelain bodies is given in Table 2.1. The quality of clays is determined in part by the Fe_2O_3 and TiO_2 content. The total iron content, however, is not an accurate measure of fired color, since its coloring capacity depends to a large extent on the state in which it is present. Some of the iron are present as acid-soluble oxide, some in trace minerals, some in iron-bearing micas, and some probably are in the kaolinite lattice in place of aluminium. The proportion of the alkaline-earths has no significant effect on properties.

Table 2.1: Chemical analysis of some clays

Constituent	Kankara(1) clay	English(2) China clay	Low-grade clay	Georgia(3) clay	Kentucky(3) ball clay
SiO_2	48.46	46.62	47.10	45.70	49.90
Al_2O_3	34.49	38.31	37.80	38.70	31.40
Na_2O	0.19	0.30	0.06	-	1.20
K_2O	0.33	0.68	2.20	-	0.20
MgO	0.95	0.25	0.20	-	0.30
CaO	0.31	0.33	0.20	0.20	0.20
Fe_2O_3	1.17	0.38	1.20	0.30	0.60
TiO_2	0.45	0.07	0.15	1.40	1.50
Loss on ignition	13.19	13.20	11.80	13.70	14.70
Total	99.94	100.14	100.71	100.00	100.00

Source: (1) Robinson Research (1979)

(2) Oral et al. (1983)

(3) Norton (1956)

Properties: The physical properties of clays are controlled by factors relating to the particle size and size distribution, particle shape, particle orientation and packing, composition, and crystal structure. Some of the properties are discussed in this section.

Plasticity may be defined as that property of a material which permits deformation under the application of an external force with the deformed shape being retained when the force is removed. A theory of plasticity of clay proposed by Bloor (1959) attributes plasticity in clays to the fineness and platiness of clay minerals and the crystal surface structure in relation to water films around the plates. Clay particles carry a net negative charge due to the charge deficiency resulting from isomorphous substitution of low valence ions in the crystal lattice. The attraction of cations, especially H_3O^+ to the basal surfaces leads to the development of rigid water structure in the clay-water interface. The thickness of this oriented water structure depends on the surface charge density and on the exchangeable cations present.

Plasticity is highly desirable in ceramic processing since excellent workability is ensured during the process of forming. Although particle fineness and platiness will create small degree of plasticity it is, however, the chemical nature of clay surfaces and their ability to hold oriented water films that is responsible for much of the observed plasticity.

The relation of these features to the more common clays are briefly considered in this section.

Kaolinite is present in a wide range of China clays, ball clays and fireclays. Depending on the fineness and cation exchange capacity,

the plasticity may vary from medium to low.

The smectite group contains the finest minerals of the hydrated alumino-silicate group and is typified by the commercial bentonite. Very small proportion of bentonite contributes considerable plasticity to a clay body. This group is characterised by high cation exchange capacity, fine particle size, high water of plasticity and a property of swelling. Schofield and Samson (1954) provide evidence to suggest that high plastic ball clays may contain montmorillonite attached to the edges of the kaolinite clays. Dry strength of kaolin has also been shown by Bloor (1959) to increase with increasing amounts of plastic clay addition. This may be attributed to the increase in the fine particle fraction which favors good packing characteristics in the green state.

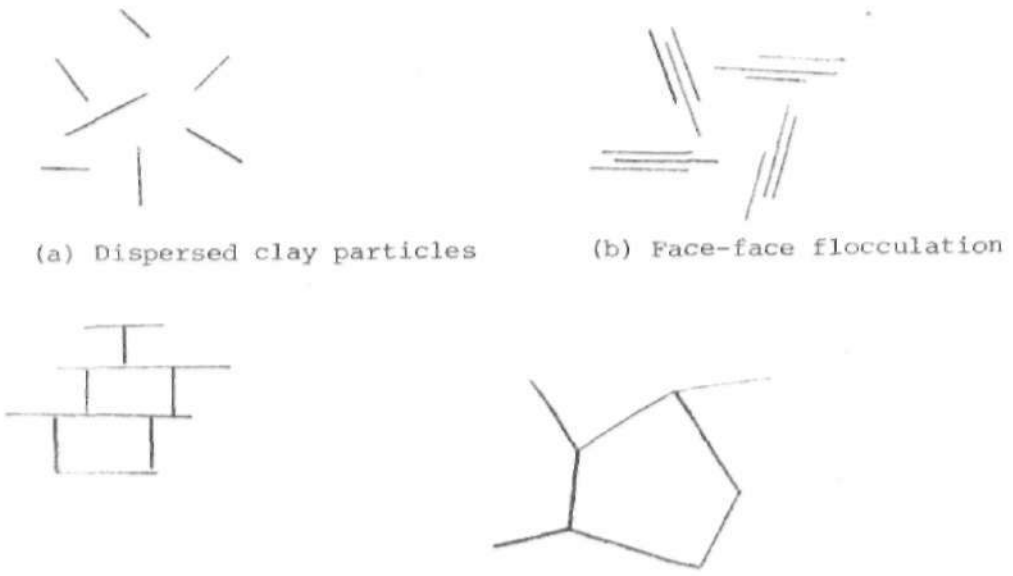
The illites or hydrous micas are coarser than the smectites and form a large portion of many natural plastic clays. As with smectites, the cation exchange capacity is high. Plasticity is high but water of plasticity and drying shrinkage are lower than for the smectites.

Clay particles carry charges which arise in two ways. The broken bonds at the edges of clay plates create positive and negative charge sites - $Al^{1.5+}$, Si^{2+}, O^{-} and $OH^{0.5-}$, etc. and secondly the negative charges at the basal surfaces can arise by isomorphous substitution in the crystal lattice of cations of similar size but lower valence. This charge deficit is compensated by cations which are attracted close to the clay surfaces by forces of electrostatic origin. In the presence of water, these cations tend to diffuse away from the clay surfaces to regions of lower concentration. A balance of the electrostatic force and diffusion results in the development of

a diffuse negative electrical double layer which is characteristic of the basal surfaces.

A different type of electrical double layer is developed at the clay particle edges. A concept of positive edge charge was proposed by Schofield and Samson (1954) and used by van Olphen (1977) to explain the type of electrical double layer in the clay edges. There is considerable evidence provided by Swartzen-Allen and Matijevic (1974), and van Olphen (1977) indicating that the potential at the edge surface of clay is a function of the pH value of the suspension fluid, whereas the surface potential at the basal surfaces is independent of the pH. Ferris and Jepson (1975) questioned the concept of pH-independent basal charge density on the basis of ion adsorption exchange experiments they performed with kaolinite suspensions. They reported that the pH slightly influenced the basal charge density. However, Rand and Melton (1977) did not believe that the evidence they provided was strong enough to raise doubt about the concept of pH-independent basal charge density.

The development of positive electrical double layer at the clay edges different from the negative electrical double layer at the basal surfaces is responsible for the different modes of particle aggregation in clay suspensions. A model proposed by Schofield and Samson (1954), and van Olphen (1977) has been used to explain the different aggregation patterns which van Olphen (1977) listed as edge-face (EF), edge-edge (EE) and face-face (FF). The different aggregation patterns result from the interplay of electrostatic and van der Waals forces on the clay particles. The different modes of particle aggregation in clay suspension is illustrated in Fig. 1.



(a) Dispersed clay particles (b) Face-face flocculation

(c) Edge-face flocculation (d) Edge-edge flocculation

Fig. 1. Different aggregation patterns of clay particles

The manner in which clay particles pack during casting, the density and permeability of the cast, and the kinetics of casting process were qualitatively explained by Celik et al. (1983) using the Schofield and Samson - van Olphen model.

In the presence of water, the compensating cations which constitute the outer layer of the diffuse electrical double layer at the basal surfaces may easily be replaced by other cations when available. Lawrence (1958b) pointed out that replacement of one cation by another depended on the bond energy between the cation and the negative crystal sites, and the mass action effect. The negative sites can attract such cations as Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Mg^{2+}, Ca^{2+}, Al^{3+} and H_3O^{+}, with bond strengths which increase in that order. Cation with high bond strength is preferentially adsorbed and can easily replace one with a lower bond strength. Hence sodium is easily replaced by calcium in clays with such replacement drastically affecting the properties of the

clay suspension. The deflocculation of clay suspension has been historically attributed to the improved stability resulting from the conversion of rather unstable natural clays into more stable and fluid sodium clays by cation exchange reaction. A complete or nearly complete conversion to sodium clays is cometimes achieved by adding controlled amounts of sodium carbonate.

Clay suspensions show a departure from the linear shear stress - shear rate relationship characteristic of Newtonian fluids and are therefore referred to as non-Newtonian fluids. The shear viscosity is dependent on the applied shear stress. However, the flow behaviour of non-Newtonian fluids may be described in terms of apparent viscosity η, which is defined as the ratio of shear stress and shear rate calculated from measurements of forces and velocities in a given experiment. The measured value depends on the type and dimensions of the apparatus used to measure it. Viscosity is a measure of the inter-particle forces in clays and may be regarded as a fundamental property of solid clay particles. Its measurement may be used to infer about the mode of particle aggregation in clay suspensions.

Some clay slips move easily at slower rates of shear but resist stirring at higher speeds. This phenomenon is termed dilatancy (shear thickening). Other kinds of slips which become progressively more fluid as shearing rate rises are said to exhibit pseudoplastic property (shear thinning). Fig. 2 gives illustrations of various types of flow.

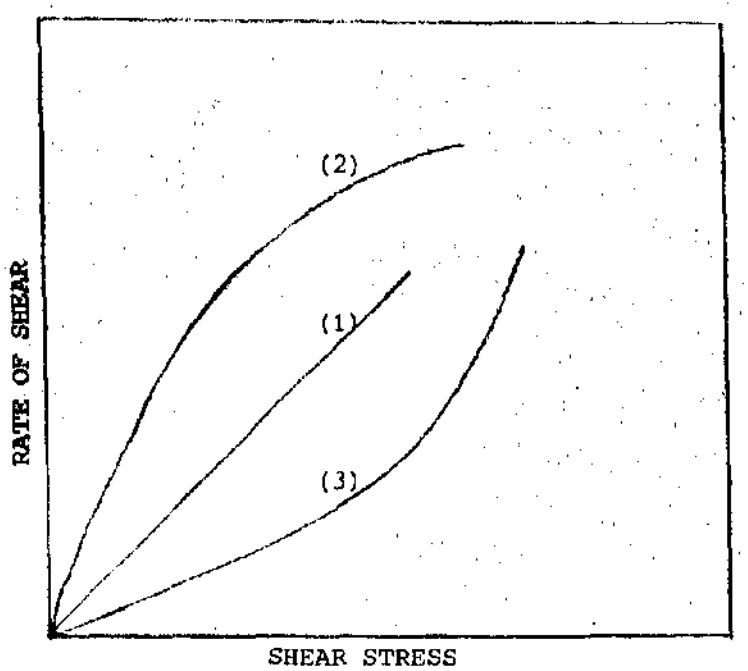


Fig. 2:- Relation between shear stress and rate of shear.
(1) Newtonian flow, (2) dilatancy, (3) pseudoplasticity.

Clay suspensions also show a tendency to thicken upon the cessation of stirring. This phenomenon is termed thixotropy. Various theories have been put forward to explain thixotropy. Goodeve (1939) after a review of the existing theories concluded that the phenomenon was far from being completely understood. However, the fact that the gel state of clay is converted to liquid on stirring and back into the gel state on standing corresponds to the breakdown and subsequent build-up of some form of structure. Clark (1957) attributes this property in clays to a manifestation of inter-particle forces resulting from incomplete deflocculation of the clay particles.

Thixotropy is a desirable property in slip casting as moderate thixotropic slips are stable and when cast they are easily handled in the green state.

Viscosity and thixotropy in clay suspensions are largely controlled

by electrolyte conditions of the clay mixture. At low pH values when the edges of clay particles are positively charged electrostatic attraction is promoted between the positive edges and the negatively charged basal surfaces resulting in a "card-house" type of structure which leads to high viscosity values. As the pH value increases beyond the isoelectric point the edges of the clays become negatively charged and the card-house structure collapses resulting in the lowering of viscosity. In addition, the electrical double layers in the basal and edge surfaces are progressively compressed to the extent that van der Waals forces begin to cause the particles to aggregate in the face-face pattern (cardpack structure). These aggregates may be linked up in the edge-face pattern or edge-edge fashion to produce a continuous network within the suspension resulting in slight increases in viscosity as the pH value increases beyond the isoelectric point.

The rate of cast of clay depends on permeability. Permeability is controlled mainly by the effective specific surface of the solid particles and depends on the extent to which inter-particle forces are removed by deflocculants. Increases in amount of deflocculants in clay suspension are followed by progressive reduction of viscosity and thixotropy decreasing rate of cast, decreasing void fractions, decreasing permeability and increasing effective specific surface. Under conditions of maximum deflocculation casting rate is a measure of permeability controlled by the effective specific surface, all expressed in a form determined by the square law of filtering (Adcock and McDowall, 1957).

The green strength of clays is associated with the shape of the clay particles. The greater the proportion of platelets and the greater their area to thickness ratio the greater is the green strength, Dale (1964). When surfaces of clay platelets draw close together as is

the case during drying, they are held by bonds of some kind. The nature of these bonds has been investigated by Williamson (1971) who concluded that the bonds are of several types with strong ionic character.

The particle size is undoubtedly a significant factor in vitrification since reactions during the sintering of clay bodies are controlled by surface area. The alkali content also determines the vitrification temperature as it acts as the fluxing agent. The firing shrinkage and porosity are determined from the vitrification pattern which, in turn, is influenced by the particle size and alkali content of the clay numerals.

2.4.2 Nonplastics

The nonplastic components of clay bodies include the fluxing agents such as feldspars, nepheline syenite, pegmatites and other feldspar bearing rocks, and body fillers such as quartz, alumina and zirconia. In this section the various forms and properties of the more commonly used nonplastics-feldspar, nepheline syenite and quartz are discussed.

Feldspar and nepheline syenite: Feldspar is the most important fluxing agent used in ceramic bodies and glazes. It is an alkali aluminium silicate and occurs in the form; potash feldspar ($K_2O.Al_2O_3.6SiO_2$), soda feldspar ($Na_2O.Al_2O_3.6SiO_2$) and lime feldspar ($CaO.Al_2O_3.2SiO_2$). Potash feldspar exists as orthoclase or microcline while soda and lime feldspars are known as albite and anorthite respectively. The individual varieties are rarely encountered in pure form as they commonly form solid solutions of orthoclase and albite or albite and anorthite. Natural feldspars also contain traces of other minerals such

as Fe_2O_3 and MgO. Table 2.2 provides the theoretical mineral composition of the various feldspars. Budnikov (1964) suggested that suitable feldspars used in porcelain insulator bodies are those with low iron oxide content (less than 0.2 percent) and 18 percent of Al_2O_3 and at least 14 percent of alkali-metal oxides.

Table 2.2: **Theoretical Composition of Feldspar Minerals**

Constituent	Microcline or Orthoclase	Albite	Anorthite
K_2O	16.90	-	-
Na_2O	-	11.80	-
CaO	-	-	20.10
Al_2O_3	18.40	19.40	36.62
SiO_2	64.70	68.80	43.28

Nepheline syenite is another commonly used fluxing agent in whiteware bodies. It consists of the mineral nepheline ($K_2O.3Na_2O.4Al_2O_3.9SiO_2$), microcline, albite, mica and traces of other minerals.

The crystal structure of potash feldspar is monoclinic or pseudo-monoclinic while albite and anorthite are of triclinic symmetry. Potash feldspar appears red or pink and anorthite is white or greyish. The specific gravity of feldspar minerals lies in the range of 2.5 to 2.7. Nepheline syenite has hexagonal crystals and may be colorless, white, yellow, dark green or brownish. Its specific gravity lies in the range of 2.5 to 2.6.

When potash feldspar is heated, it melts incongruently at 1150°C yielding leucite ($K_2O.Al_2O_3.4SiO_2$) and a liquid richer in silica than potash feldspar. Melting is completed at 1530°C. Potash feldspar and silica melt at a eutectic temperature of 990°C and a mixture of potash feldspar, kaolin and silica melts at a ternary eutectic temperature of 985°C. The molten feldspar wets the solid particles and the surface tension causes the particles to pull together while the feldspar liquid fills the pores. A glass phase richer in silica is developed from the dissolved silica in the feldspar melt. This glass phase forms solution rims around the residual silica grains.

Nepheline syenite has a greater fluxing power than feldspar. The lower firing temperature for whiteware bodies containing nepheline syenite saves timeand energy. It is widely used in sanitary bodies, floor and wall tiles, and vitreous China. It is, however, not used in electrical porcelain bodies since, according to Johnson and Robinson (1975), the loss of electrical resistance due to the greater mobility of the sodium ions facilitates dielectric breakdown at high operating voltages or elevated temperatures.

Quartz: Quartz which is the most common crystalline form of silica (SiO_2) occurs in nature in various forms and degree of purity. The structure is composed of silicon-oxygen tetrahedra linked in spiral fashion. The crystallized varieties of quartz obeying trigonal symmetry are known by mineralogists as alpha-quartz or low quartz. The various forms of trigonal quartz are described by King (1985). The varieties controlled by color are formed from pure silica by elemental or mineralogical contaminations which give rise to color modifications. Some of these varieties are milky quartz - a variety named to describe its color and lack of transparency, rock quartz -

colorless and perfectly transparent quartz, smokey quartz - a variety named to describe its color which is due to the presence of aluminium in the crystal lattice. A poorly crystallized form of quartz commonly used as a source of silica is flint.

Quartz in all its forms, is one of the most abundant minerals in the earth's crust. It is present in silica-rich igneous and metamorphic rocks, such as granites and granite pegmatites where large crystals may be formed.

Quartz is used in whiteware bodies as a filler to provide the skeletal framework to minimise shrinkage during firing and to enhance the mechanical strength of the fired body. Flint pebbles are also used in ball mills if the silica lost from them by abrasion is not deleterious to the materials being ground.

The melting point of quartz is about 1600°C and its specific gravity is 2.65. There are high temperature modifications of quartz of which the most important are tridymite and cristobalite. Tridymite crystallizes in the hexagonal system and has a specific gravity of 2.27. It is stable in the range of 870 to 1470°C and melts at 1670°C. Cristobalite crystallizes in the cubic system and has a specific gravity of 2.21. It is stable above 1470°C and melts into a vitreous solution at 1710°C. Tridymite and cristobalite may occur at ordinary temperatures as the speed of transformation at room temperature is far too sluggish to convert these modifications into alpha-quartz. The conversion of quartz to tridymite or cristobalite is accompanied by a marked volume change since the products have lower specific gravity. This phenomenon affects ceramic processing and the quality of the final product significantly.

Apart from the conversion reactions each of the three forms of quartz can also undergo structural changes known as inversions. These inversions which occur are represented by these equations;

$$\alpha \text{ - quartz} \underset{\rightleftharpoons}{573^{\circ}C} \beta \text{ - quartz}$$

$$\alpha \text{ - tridymite} \underset{\rightleftharpoons}{117^{\circ}C} \beta_1 \text{- tridymite}$$

$$\beta_1 \text{ - tridymite} \underset{\rightleftharpoons}{163^{\circ}C} \beta_2 \text{- tridymite}$$

$$\alpha \text{ - cristobalite} \underset{\rightleftharpoons}{220\text{-}280^{\circ}C} \beta \text{ - cristobalite}$$

Although the changes in structure involved in inversions are slight, the various forms possess different physical properties. Ryan (1978) considered thermal expansion as the most important property which is different for the various forms. Unlike conversions, inversions occur almost spontaneously leading to a corresponding change in volume. The rapid change in volume can result in cracking during firing if the rate of heating or cooling through the inversion temperatures is too high.

2.4.3 Deflocculants

Deflocculants are chemicals used to disperse clay particles to form stable suspension. They are sodium and lithium salts of weak acids which give alkaline reactions. The carbonates, silicates and phosphates of alkali ions are commonly used as deflocculants. A list of chemicals used as deflocculants is contained in a text by Singer and Singer (1963).

Sodium carbonate (Na_2CO_3) and sodium silicate ($Na_2O.3.3SiO_2$) are widely used to improve the flow properties of clay suspensions. On hydrolysis, both deflocculants yield sodium ions which are exchanged

for the strongly adsorbed cations present in clays. This process is made possible by removing the strongly adsorbed cations as insoluble carbonates or silicates. Sodium silicate also yields complex silicate ions on hydrolysis and when these are adsorbed at the clay particle edges they alter the chemistry of the surfaces by making them electrically negative.

Sodium silicate tends to remove all the inter-particle forces in clays thereby destroying thixotropy. Sodium carbonate is also a good dispersant but, if used alone, induces considerable thixotropy due to the overcrowding of sodium ions at the clay surfaces which results in the compression of the diffuse electrical double layers developed and a subsequent reduction in their electrical effects.

The correct balance of high slip density, flowability and the correct degree of thixotropy is attained in industrial practice by using a mixture of sodium silicate and sodium carbonate. The correct amounts of these chemicals can only be deduced by experimentation with clay or clays being used.

2.4.4 Water

Water (H_2O) is of prime importance to ceramic industry. It is used at various stages of ceramic processing. Water is used as a suspension and washing medium in a number of preliminary processes such as the washing of clay and parent rocks, and numerous sedimentation methods of purification.

The rheology of ceramic slips is affected by the ions present in water. As Merwin (1955) pointed out, the minerals present in water must be determined if the physico-chemical interactions of clay and water are to be controlled. Water from many sources often contains

calcium, magnesium and sulfate ions. Since these ions act as flocculants their presence could be very disturbing during slip preparation.

The quality of water may be controlled by distillation or di-ionisation. This inevitably results in a drop in the amount of deflocculant required to bring a slip to the desired degree of dispersion.

2.4.5 Plaster of Paris

Plaster of Paris is essentially calcium sulfate hemihydrate ($CaSO_4.\frac{1}{2}H_2O$). It is produced from the mineral gypsum ($CaSO_4.2H_2O$). When mixed with water, the hemihydrate rehydrates to the dihydrate. This reaction is exothermic and is accompanied by expansion and stiffening of the mass to rigidity.

Plaster of Paris is used in the ceramic industry for making molds used in slip casting. The ratio in which plaster is mixed with water is most important as it affects the setting time, the hardness and porosity of the set plaster. A common water: plaster consistency ratio for molds suggested by Whitemore (1978) for slip casting is 75 : 100 by weight.

2.5 Body Formulation

There are several reasons for the great variety of body compositions for triaxial whitewares. There is the need for a body to possess good working properties in the plastic state to facilitate shaping. It must dry reasonably fast without warping or cracking and it must fire to a strong, dense structure without excessive shrinkage or pyroplastic deformation. The final product must possess the desired properties,

color and translucency at the firing temperature.

Improvement of any one of the above properties may occur at the expense of other properties. It is, therefore, a matter of compromise to obtain the best over-all body composition for a product of desired characteristics and properties.

Primary clays, by themselves, are not practical for making porcelain bodies because of the high temperature required to bring about fusibility. The fusion temperature of most clays is aout 1500°C. To bring about fusion and translucency at a much lower temperature, fluxing agents such as feldspars, nepheline syenite and pegmatites are added to the clays. Quartz is also added to the clay body as a filler to improve the resistance of the body to warping and excessive shrinkage and to give hardness and stability when sufficiently fired. A blend of natural clays is preferred to a single clay in ceramic bodies since, according to Cox (1948), many natural clays do not possess good working and firing properties and almost none combines these two properties. He suggested the use of several clays in bodies as each would contribute to some specific desirable property.

Bodies with 40 percent clay mineral content have reasonable amount of plasticity and 50 percent clay gives excellent workability. Feldspar content for electrical porcelain bodies may be as high as 35 percent for soft porcelains while hard porcelains may need as little as 20 percent. Quartz content may be as low as 20 percent for soft porcelains and up to 30 percent for hard porcelains. Rhodes (1973) suggested a practical porcelain recipe consisting of 40 percent kaolin, 10 percent ball clay, 30 percent feldspar and 20 percent quartz and added that adjustments of these proportions may be necessary to reflect

the influence of the maturing temperature, the kinds of clays and the fusibility of the feldspar.

The search for electrical porcelain with improved mechanical strength has resulted in the introduction of alternative body fillers such as alumina and zirconia as replacements for quartz which is generally believed to be detrimental to the mechanical strength of fired bodies. A list of quartz alternatives considered relevant for electrical porcelain bodies has been published by Bruce and Wilkinson (1966). Mineralisers are also being used to improve the microstructure of porcelain. A description of the influence of ZnO, TiO_2 and Fe_2O_3 on the microstructure of hard porcelain was given by Chandhuri (1974).

Fig. 3 shows the triaxial diagram of whiteware bodies indicating compositions of the various commercial wares.

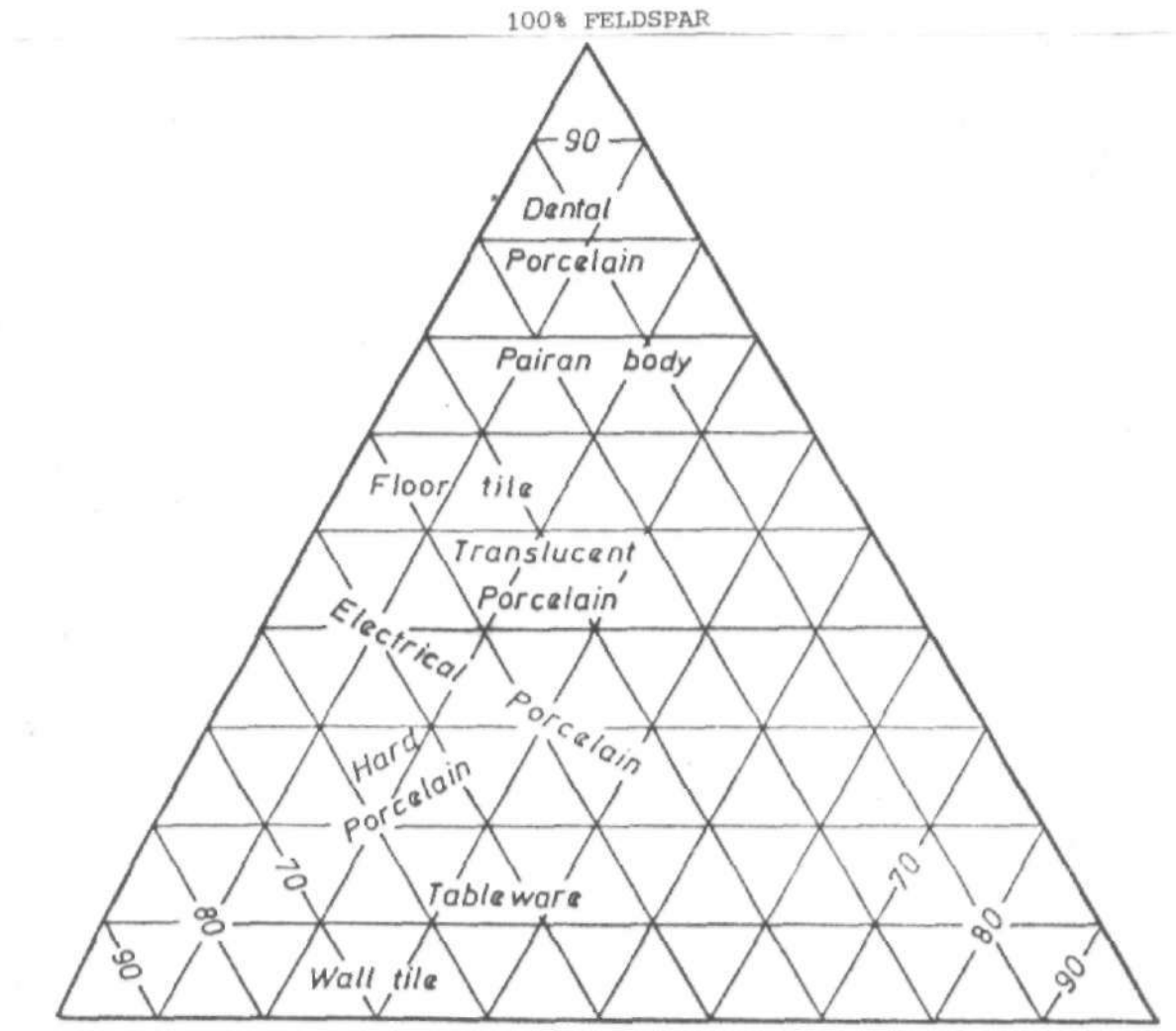


Fig. 3:- Triaxial diagram of various porcelain wares

26. Forming Methods

Preparation of a ceramic body is an important step in the fabrication of a ceramic ware. Bodies are prepared by intimate mixing of the various raw materials in the right proportions and in the right degree of fineness to produce a homogeneous mixture which has the appropriate water content and consistency required for the method of shaping. Various methods of body preparation are briefly described by Ryan (1978). The methods of dry mixing, plastic mixing and slip mixing are commonly employed in industrial practice.

2.6.1 Plastic forming

This covers a wide range of shaping methods all of which depend on the development of plasticity in the body. Bodies containing a high proportion of clay readily develop plasticity when water is added. However, plasticity may be improved for bodies of low clay content by the addition of small amount of bentonite or certain organic materials known as binders.

A plastic body may be prepared by mixing the proportioned raw materials with just enough water to bring the mixture to the plastic consistency desired. As water is being added the mixture is gently kneaded. The mass may be pugged in a pug mill during which the mass is further mixed and consolidated into a homogeneous mixture and extruded as a blank for the next stage of processing. A de-airing pug mill may be used instead. This has the advantage of removing the entrapped air in addition to the homogenization of the mass. The removal of the entrapped air in the mass results in higher plasticity and improved green strength.

Another method of preparation of a plastic body involves the blunging of the proportioned raw materials with excess water in a mixer. The mixture is thoroughly blended as a result of the greater dispersion and homogenization. The resulting slurry is screened, passed through a magnetic separator and filter pressed to remove as much water as required to bring it to the plastic consistency desired. Plasticity may also be controlled by use of flocculating and deflocculating agents. The plastic mass may be shaped by throwing on the wheel, jolleying, jiggering, lathe turning or extrusion.

In the jolleying process, de-aired pug or blank is shaped by introducing it into the inner surface of a rotating plaster mold. The outside shape is formed in the plaster and the inner contour is formed by a metal profile which may be controlled manually or mechanically. This method is used extensively in the fabrication of porcelain insulators. Large insulator types such as post and pedestal insulators are fabricated in parts and then cemented together with a special binder made from alumina cement.

Jolleying, though widely used in insulator fabrication, is a rather slow process. Small ceramic wares such as pin and cap insulators may be shaped much faster by semi-automatic lathe-turning. The plastic body is extruded from a de-aired pug mill and cut into blanks of suitable sizes. Each such blank is allowed to dry to a leatherhard state and is turned on a lathe where cutting tools are guided by accurate profile plates. Introduction of vertical lathes in recent years has made it possible to extend this process to much bigger insulators.

2.6.2 Dry and semi-dry forming

A ceramic body may be dry-mixed. This preparation method involves the proportioning of the raw materials which have been processed into powders and followed by pulverisation of the mixture to ensure homogeneity and further particle size reduction.

Plastic body which may be prepared by any of the methods previously described, may be formed into a powdered mixture by drying the plastic mass into cakes which are then ground into a fine powder. Bodies may also be prepared by wet-ball milling after which the slurry is formed into a powdered mixture by a process known as spray-drying.

Dry pressing is accomplished by compacting the dry powder under very high pressure in steel or other suitable dies. This method of shaping is particularly well suited for rapid production of a variety of ceramic parts. When the moisture content of the dry powder is as high as 4 percent the method is often referred to as dust pressing or semi-dry pressing. Small insulators such as switch bases, fuse holders, and other small porcelain articles are easily produced by this method. However, the properties of dust-pressed porcelain are such that they are only suitable for low voltage applications.

2.6.3 Slip casting

Slip casting is a ceramic shaping method often preferred in industry and research in the fabrication of sanitary wares, electrical porcelain components, tablewares and others of intricate shapes for its relative low cost in comparison to other shaping methods which require costly facilities. Phelps (1978) defines slip casting as a consolidation of slip particles into a plastic mass through removal of

part of the liquid by an absorbent plaster mold. The plaster mold provides the driving force for the removal of water from the slip and also acts as a reservoir for the water absorbed. Slip casting is an unsteady-state phenomenon and the resistance to the flow of liquid through the cast layer is related to a property known as permeability. If a hollow cast is desired, the excess slip is poured out of the mold after the required wall thickness has developed. This process is sometimes called drain casting. Solid objects may also be produced by providing enough slip in the mold for a solid cast to develop. This is referred to as solid casting.

Casting slip: This is a suspension of polydisperse lyophobic particles in a liquid, with the particles ranging from more or less continuously from an upper to some lower size limit. When natural clay is a major component of a slip, clay particles readily agglomerate into flocs as a result of Brownian motion, attractive van der Waals forces and attractive forces developed at the clay surfaces which, according to van Olphen (1977), are of electrical origin.

Originally casting slips were prepared from simple mixtures of body constituents and water. However, the tendency of the slips toward flocculation was minimised by using a high proportion of water as the suspension medium. The disadvantages of very low slip density (1.35 kilograms per liter) are that the slips tend to give unmanageable casts and the molds used get easily saturated and deteriorate rapidly. Most modern slips are deflocculated using alkaline dispersants in order to achieve high slip densities of the order of 1.8 kilograms per liter while maintaining reasonable fluidity.

Slip preparation methods: Slips may be prepared by blunging the body constituents with water in a blunger. The mixing procedure, the sequence of body preparation, slip blunging time and aging period are significant factors in determining the properties of the slip. Slip may also be prepared by dry ball-milling. This process involves the grinding of the body constituents in a ball mill for several hours after which the ground powder is blunged with the appropriate amounts of water and dispersants to produce a homogeneous slip. The technique of grinding body constituents with water and dispersants is known as wet ball-milling. It is accomplished by charging the body constituents, water and dispersants into a ball mill and grinding for several hours. The properties of slip and cast ware are significantly controlled by the ball milling time.

Russel et al. (1949) investigated the influence of slip preparation methods on the properties of cast ware and provided data to indicate that wet ball-milled slips yielded ware with better properties than blunged slips. They also found that wet ball-milling of all the constituents yielded better properties than selective ball milling since, according to the authors, optimum homogeneity attained was due to thorough dispersion of the clay materials and to a reduction of the particulate sizes of all the constituents. The study by Russel et al. (1949) demonstrated very clearly the importance of body preparation methods in ceramic processing.

Deflocculation: This is the process of dispersing particles in a suspension to produce stability, homogeneity and fluidity in the suspension by the use of certain chemical agents known as deflocculants. In a deflocculant-free clay suspension both electrical double layers at the clay basal and edge surfaces are sufficiently developed for the

clay particles to aggregate in the edge-face pattern (internal mutual flocculation) causing a relatively high apparent viscosity and yield stress in dilute and concentrated suspensions.

There is little doubt that the effect of deflocculants in clay suspensions is to alter the chemistry of clay surfaces and reduce the attractive forces causing the clay particles to agglomerate into flocs. The reduction of apparent viscosity with increase in deflocculant concentration is apparently a manifestation of the disruption of these attractive forces. Apparent viscosity remains the most significant parameter in describing the rheological properties of slips. A deflocculation curve is a plot of apparent viscosity against deflocculant concentration and can be interpreted in terms of the mode of particle interactions in the clay suspensions. Fig. 4 shows the regions in which edge-face, edge-edge and face-face structures are expected to be dominant according to the predictions of van Olphen (1977), and Rand and Melton (1977).

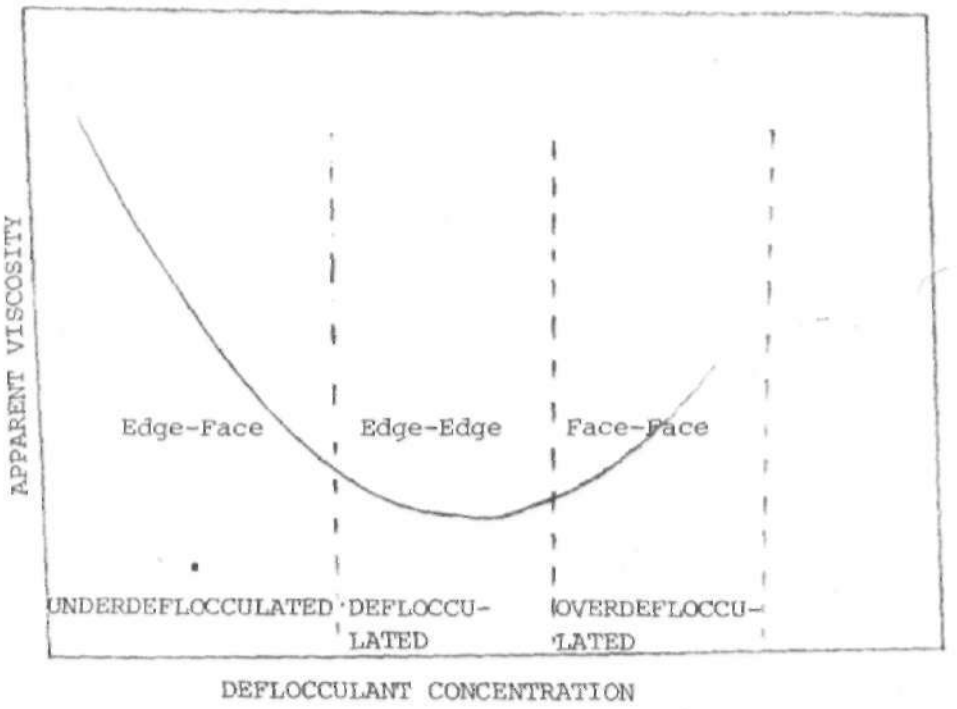


Fig. 4. Interpretation of the effect of deflocculant on the apparent viscosity of clay suspensions, in terms of the mode of particle interactions.

Several mechanisms of deflocculation have been proposed. Johnson and Norton (1941), and Grimshaw (1958) attributed deflocculation in clay suspensions to a replacement of flocculating polyvalent cations by monovalent cations. However, Schofield and Samson (1954), and van Olphen (1977) believed that edge charge reversal by anion adsorption is the principal mechanism of deflocculation of clay suspensions. These two mechanisms are briefly discussed in this section.

The first concept of mechanism of deflocculation of clays is their conversion to sodium clays by cation exchange reactions (Grimshaw, 1958). There is little doubt that the active clay surfaces adsorb H_3O^+ and OH^- to form rigid water structure extending some distance from the crystal-water interface. Ability of two clays to slip past each other is governed by the ease with which the rigid water structure is deformed under an applied external force. The configuration of this water structure and the factors controlling them largely determine the plastic, bonding, suspension and other properties of clays which also govern their economic use.

According to Grimshaw (1958), large cations of small charge (e.g. Na^+, K^+) are effective in producing stable and fluid clay suspension because of their tendency to reduce the demand for oriented water. Once the thickness of the oriented water structure is reduced, the clay particles are easily dispersed in slips containing a high proportion of clays. However, small cations of large charge (e.g. Al^{3+}, Mg^{2+}, Ca^{2+}, etc.) cause agglomeration because they increase the demand for oriented water structure. These ions according to Lawrence (1958a), would not promote disorder in the water structure but would increase the long-range order in the system.

Many natural clays contain Al^{3+}, Ca^{2+}, Mg^{2+}, H^{+} etc. as the exchangeable cations at the clay surfaces. Clays are often identified by the exchangeable cation that is dominant in the clay-water system. For example, Ca-clays refer to clays in which the exchangeable cations are essentially calcium ions. Although hydrogen ion (H^{+}) has a unit charge, it is extremely small in size and it is the most powerful counter-balancing cation. As a result, H-clays have poor fluid properties although they usually possess high plasticity.

In the light of the above discussion, it is obvious that, in order to control the properties of clay suspension, the types of exchangeable cation must be chosen carefully. The Hofmeister series gives an indication of the preferential adsorption of principal cations associated with clays as follows;

$$H^{+}>Al^{3+}>Ba^{2+}>Ca^{2+}>Mg^{2+}>NH_4^{+}>Na^{+}>L_i^{+}.$$

A change from cation-type clay to another involves a cation exchange reaction which may be represented by an equilibrium condition;

$$\text{Clay-}A^{+}+B^{+} \rightleftharpoons \text{Clay-}B^{+} + A^{+} \qquad \ldots\ldots\ (1)$$

The reaction is in the direction of the clay containing the strongly adsorbed ion as predicted by the Hofmeister series. Na-clays would be difficult to produce from one containing other cations as their bond strengths are considerably higher than that of sodium. If, however, the strongly adsorbed cations can be precipitated as insoluble salts, Na-clays may readily be formed by cation exchange reaction. If a clay type is predominantly Ca-clay, a more fluid and stable Na-clay is readily formed by treating the clay with sodium carbonate or sodium silicate.

$$\text{Clay-}Ca^{2+} + Na_2CO_3 \rightleftharpoons \text{Clay}\begin{matrix}Na^{+}\\Na^{+}\end{matrix} + \underset{\text{(Insoluble)}}{Ca(CO_3)_2} \qquad \ldots\ldots\ (2A)$$

$$\text{Clay-Ca}^{2+} + \text{Na}_2\text{SiO}_3 \rightleftharpoons \text{Clay} \begin{matrix} \text{Na}^+ \\ \text{Na}^+ \end{matrix} + \underset{\text{(Insoluble)}}{\text{CaSiO}_3} \qquad \ldots\ldots \quad (2B)$$

However, sodium carbonate will not be effective in deflocculating H^+-clay because hydrogen cannot be removed from solution.

$$\text{Clay-H}^+ + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{Clay} \begin{matrix} \text{Na}^+ \\ \text{Na}^+ \end{matrix} + \text{H}^+ + \text{CO}_3^{2-} \qquad \ldots\ldots \quad (2C)$$

The above equilibrium condition indicates that the hydrogen ions which are produced would easily replace the sodium ions thereby forcing the reaction to the left of the equilibrium. The addition of Na_2Co_3 only produces excess sodium ions which migrate close to the clay surface and reduce the effective potential of the electrical double layers with undesirable effects on the flow properties of the suspension.

Clay suspension may be made more fluid and stable by the addition of dispersants which reverse the positive edge charge by anion adsorption. According to van Olphen (1977), the edge charge reversal creates a well-developed negative edge double layer which results in the breakdown of the cardhouse structure of the edge-face aggregation pattern of the clay particles. Instead, the clay particles develop repulsive forces of interaction and are well dispersed.

Sodium silicate and sodium phosphate are frequently used as deflocculants to promote edge charge reversal since the silicate and the phosphate anions are readily adsorbed at the clay particle edges. In addition, the sodium ions are also available for cation exchange reaction. Organic content of most clays appears to contribute to the desired flow properties because it is thought that its reaction with deflocculants such as sodium carbonate yields protective colloids which tend to enhance the stability of slip. The protective colloids apparently contain organic compounds which hydrolyse in solution to

yield complex anions which would participate in reversing the edge charge. Protective colloids also increase the tolerance limit of most clays to excess deflocculants.

The suggestions by Webb (1934) on the use of sodium carbonate and sodium silicate for various types of clay are in agreement with the concepts of cation exchange and edge charge reversal as the mechanisms of deflocculation. There is evidence to support the fact that deflocculation may infact be due to a combination of factors instead of a single one. The failure to produce good and manageable slips from some clays may be due in part to the difficulty in achieving deflocculation by one of the two possible mechanisms.

Slip properties: A good casting slip has a number of well defined characteristics which affect the properties of the cast ware. It must be stable at high solid concentrations and must possess good casting properties consistent with a good drain. The cast ware must have the habit of easy release from the mold surface and be strong enough to be handled in the green state.

A number of studies aimed at investigating the factors affecting the properties of casting slips had been carried out by Hind (1923), Loomis (1940), Kocatopcu (1946), and Adcock and McDowall (1957). The various studies provided evidence which showed that the flow and casting properties of slip are largely controlled by such factors as particle size, specific gravity, viscosity, thixotropy and casting rate.

The clay particles generally provide the fine particle fraction of a slip. The nonplastic additions are well ground to reduce the average

particle size. If coarse particles are present in the slip they tend to settle out of suspension resulting in a nonuniform cast and leading to unacceptably high casting rate. The best properties of a casting slip may be obtained at a size distribution corresponding to a closed-packed system rather than mono-sized particle system. There is also a good agreement between casting rate and the percent of body finer than 1 micron (Loomis, 1940).

Slips of high solid concentration are more manageable than dilute suspensions. Modern slips are deflocculated in order to achieve high slip densities in the range of 1.70 to 1.80 kilograms per liter. Such slips drain very cleanly and they form uniform casts. The molds are also less saturated and hence can be used over a number of casting cycles.

Viscosity is a measure of the forces of attraction between the clay particles and their aggregates. At high solid concentrations the clay particles in the slip are close enough for van der Waals forces, attractive electrical forces and surface tension forces to cause them to form flocs resulting in a viscous suspension which does not pour easily. Deflocculants are used to reduce these attractive forces so as to promote flowability at high slip densities. At maximum deflocculation the slip particles are sufficiently dispersed to promote stability and homogeneity. Industrial porcelain slips usually have apparent viscosity values in the range of 200 to 1700 centipoises (Barta, 1960).

Thixotropy is a measure of the inter-particle forces of attraction between clay particles in a suspension resulting from under-deflocculation. The slip becomes more viscous with time when left undisturbed and the

force provided during pouring is usually sufficient to break the links between the particles. Moderate thixotropy is highly desirable since the links between the clay particles enhance the ability of the suspension to keep the nonclay components well dispersed. This promotes stability and homogeneity of the slip and also leads to better casting properties than fully deflocculated slip. The green ware produced from a moderately thixotropic slip can easily be trimmed with minimum risk of damage.

Under conditions of maximum deflocculation casting rate is a measure of permeability controlled by ultimate effective specific surface. The effect of degree of deflocculation, colloid content and size distribution on the ultimate effective specific surface and hence permeability had been investigated by Phelps (1978). He observed that progressive increase in deflocculant concentrations was accompanied by decreasing rate of cast. Slip which cast too rapidly resulted in a flabby cake while slip which cast very slowly resulted in a dense and brittle cake.

Adcock and McDowall (1957) formulated equations based on the modified Kozeny equation relating the properties of slip to the rate of cast. They related the rate of cast to the surface area of the solid phase, the percentage of voids, the density and temperature of the slip and the applied pressure to the cast wall thickness.

$$L^2/_T = 2PgE^3/5So^2\ \eta(y-1)(1-E)^2 \qquad \ldots\ldots \quad (3)$$

where L is the cast wall thickness in time T, P is the suction pressure of the absorbent mold, E is the void fraction of the moist cast, η is the viscosity of the liquid medium, So is the effective specific surface, g is the gravity constant

and y is the volume of the slip containing (1-E) volume of solids. The effective specific surface So, is related to permeability K, by the Kozeny equation

$$So^2 = gE^3/5K(1-E)^2 \quad \ldots\ldots (4)$$

The above Equations (3) and (4) clearly show the overiding importance of the effect of surface area of the slip solids on the rate of cast.

2.7 Drying and Firing of Slip Cast Porcelain Bodies

Porcelain bodies are dried very slowly to prevent warping and cracking, and thoroughly to prevent explosions during firing. During the first stage of drying water is removed in between the platelets. As drying proceeds the clay platelets draw closer together and the whole mass shrinks until all the water films have disappeared. As platelets touch each other a little more shrinkage occurs and the body is said to be leatherhard. The remaining water occupying the irregular spaces between the grains are removed very slowly because of the interruption of the capillary channels.

The rate at which drying takes place during the shrinkage period depends on three factors: (i) the temperature of the surrounding air, (ii) the moisture content of air and (iii) the velocity of air. In addition to controlling the rate of drying, the overall shrinkage can also be reduced by controlling the initial water content of the casting slip.

The firing process is the most important production process because the final properties of the ware are consolidated during this process and variations in processing prior to firing are amplified so that inspection of fired product often serves as a test for successful processing. Ceramic body approaches physical and chemical equilibrium

during the period of heat treatment. The physical and chemical changes that occur may involve complete or incomplete reactions. Many of the fired properties of ceramic ware depend, to a large extent, on the incompleteness of the reactions which Foster (1951) acknowledged to be responsible for the difficulty in using the phase diagrams to predict equilibrium reactions and products during firing.

Firing time is dictated by diffusion reactions which, according to Kingery (1978), are usually the rate limiting process. However, maximum reasonable time allowed in the firing schedule is limited by economic consideration and the boundaries of normal human patience. A postulated outline of the changes which take place in porcelain body during firing is described by Norton (1956), Williams et al. (1963), Budnikov (1964) and Kingery et al. (1976). Fig. 5 shows a flow scheme of the physical and chemical changes that take place during firing at various temperature ranges.

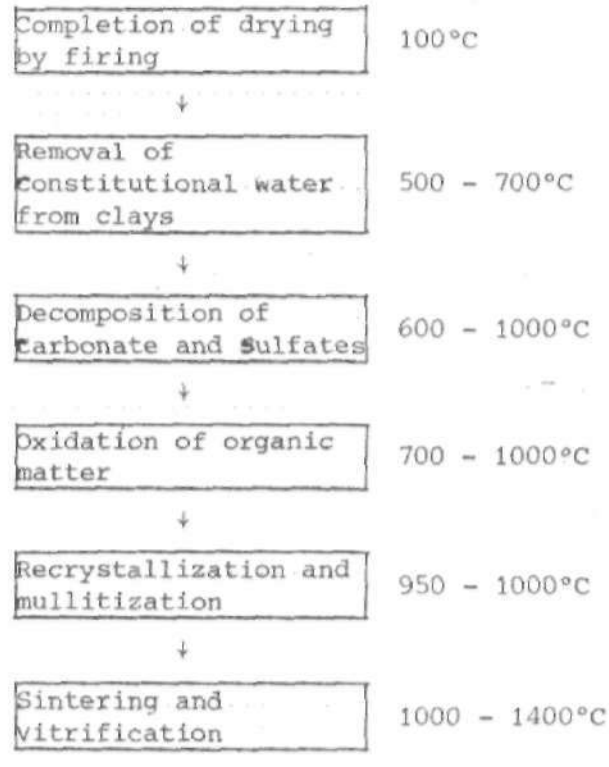


Fig. 5: Flow scheme of the changes in porcelain during the process of firing.

In deriving the firing schedule (rate of heating, rate of cooling and the soaking temperature) such factors as volume changes, types and extent of reactions are taken into consideration to minimise the dangers of excessive shrinkage and warpage and to ensure reproducibility of product.

2.7.1 Sinterability and vitrification of porcelain bodies

Sintering is defined by Walker (1955) as the extension of the contact area between powder particles in the solid state by the transport of material across or around pores under appropriate conditions of time, temperature, pressure and atmosphere. The proper sintering of porcelain bodies depends, to a large extent, on the firing schedule. Although certain reactions require a given amount of heat input and would theoretically be brought about by heating at a higher temperature for a short time or a longer heating time at a lower temperature, Singer and Singer (1963) pointed out that the properties of the bodies produced are not generally the same.

Several sintering mechanisms have been proposed. Johnson (1978) gave a brief description of the various sintering models. The author believed that the fluxes that arise from the chemical potential gradients between the curved surfaces provide the driving force which moves atoms in such a way as to reduce the chemical potential gradient. The fluxes can occur within the vapour phase, along the surfaces, through the bulk of the particles, or along grain boundaries. The material transport in real particle compact can be achieved by one or a combination of the various sintering mechanisms. Material transport by viscous flow is perhaps one of the most significant sintering mechanisms in porcelains. According to White (1983), little attention appeared to have been paid

by researchers to this mechanism. The only kinetic model available is that proposed by Kingery (1959). This model proposes that the liquid phase which develops from the fluxing agent aids densification process by providing the surface tension forces. The liquid phase also readily enhances material transfer to the voids in the solid structure.

The various sintering models suggest very strongly that particle size is a very important variable in sintering and that factors which determine the vitrification rate are the pore size, the viscosity of the liquid phase, surface tension, temperature and time. Changes in body composition affect the vitrification rate as some of these factors are influenced by such changes.

2.8 Properties of Electrical Porcelain

The unfired and fired properties which are critical for successful processing of electrical porcelains are discussed in this section. The close correlation between mechanical, thermal and electrical properties limits the number of tests sufficient for research, quality control, and comparison of body compositions. The selected properties which are tested in this study are the drying and firing shrinkage, dry strength, vitrification as determined from porosity and water absorption tests, bulk density, specific gravity, mechanical and dielectric strengths.

2.8.1 Linear drying shrinkage

The linear reduction in size which accompanies the drying of a piece of ceramic ware is the result of the elimination of water between the clay platelets. The finer the clay particles, the more water films are present, and the higher the drying shrinkage. Coarse-grained nonplastic additions such as quartz and feldspar in clay bodies lead to a reduction of shrinkage.

In the first stage of drying during which shrinkage occurs, the clay body dries into a leatherhard structure after which little additional shrinkage occurs. Non-uniform shrinkage in clay bodies results from preferred orientation of clay particles during the process of forming. In slip cast ware, clay particles align parallel to the mold surface as well as to themselves. During drying there is more shrinkage in the direction perpendicular to the plane of the clay platelets than within it. Excessive shrinkage and non-uniform shrinkage are principal causes of warping and cracking during drying. Drying behaviour of clay bodies is well described by Norton (1956) and Packard (1967). The control of linear drying shrinkage enables designers to determine the proper size of mold so as to produce a fired body of predetermined size.

2.8.2 Dry strength

The dry strength of clay bodies as usually determined from modulus of rupture tests depends on the bonds existing between clay platelets, their aggregates and nonplastic grains. The nature of these bonds had been investigated by Williamson (1971) who described some of them as ionic in character. Williamson (1978) also pointed out that dry strength increases with the number of these bonds per unit volume. Large area to thickness ratio of clay particles permits the development of a high concentration of bonds. The observed increases in dry strength with higher proportion of clay in bodies are attributed to the increased number of bonds per unit volume.

Increases in dry strength with progressive increase in the proportion of nonplastic grains in clay bodies had also been reported

by Williamson (1978). It is believed that the nonplastic grains lie across fracture paths thereby inhibiting crack propagation during loading. However, strength increases are only obtained within a limited range of nonplastic proportions since stresses developed in the grain boundaries of these nonplastics give rise to cracks which act as dangerous flaws.

Dry strength is also influenced by the effectiveness of flaws in concentrating the applied stress and thus breaking the bonds. The lack of a quantitative relationship between dry strength and porosity has been attributed by Kennard and Williamson (1971) to the neglect of pore structure which determines whether a pore will operate as a dangerous flaw or not.

Modulus of rupture tests are usually determined by three point loading on a suitable testing machine or hand operated loading device. The modulus of rupture for cylindrical test pieces is calculated by using the formula:

$$MOR = \frac{8Pl}{\pi d^3} \quad \text{(Newtons per meter}^2\text{)} \qquad \ldots\ldots (5)$$

where MOR = modulus of rupture (Newtons per meter^2)

P = load at Rupture (Newtons)

l = distance between supports (meters)

d = diameter at fracture point (meters)

2.8.3 Dry-to-fired shrinkage

Shrinkage during firing occurs significantly during initial and intermediate stages of sintering. Firing shrinkage varies considerably among the different clays. It is calculated as a percentage of the dry size and varies from 10 to 14 percent on a linear basis for vitreous

bodies. Firing shrinkage is influenced by the method of forming. It is lowest for bodies formed under pressure while bodies shaped by pressureless forming methods have higher values.

Large differential shrinkage between length and diameter of fired bodies had been reported by Waye et al. (1963). It is believed that the orientation of clay particles during shaping is responsible for the non-uniform shrinkage which appears to persist well above the vitrification temperature.

Monitoring and control of firing shrinkage is important in processing if the body must be fired to meet close dimensional tolerance.

2.8.4 Porosity

Porosity is a phase that is almost always present in ceramics and is characterised by the volume fraction of pores present. Apparent porosity is defined as the ratio of the volume of open pores to the bulk volume of the material expressed as a percentage. Apparent porosity is determined by liquid immersion methods.

In contrast to apparent porosity, the true porosity is the ratio of the volume of the pore phase (open and closed pores) to the bulk volume. It may be expressed in terms of the bulk density B, and the true specific gravity G, of the fired body.

$$P_t = 100\left(1 - \frac{B}{G}\right) \qquad \ldots\ldots \quad (6)$$

where P_t is the true porosity of the body.

Before firing, almost the entire porosity phase is present as open pores. During firing the volume fraction of pores decreases as a result of sintering and densification processes. At vitrification,

open pores are virtually eliminated and densification processes cause closed pores to reduce to less than 5 percent. Pores show a ndency to increase in size when a body is overfired. This is due to the increased amounts of gases (residual gases and those released from decomposition reactions) and increased pressure in the void spaces which cause the pores to increase in size. Because of this tendency of bloating, closed porosity approaches a minimum during the final stages of sintering.

The expression for true porosity P_t, shows that the true porosity passes through a minimum when the bulk density passes through a maximum. Properties such as mechanical strnegth, dielectric strength and firing shrinkage also show strong correlation with porosity.

2.8.5 Bulk density

Bulk density is defined as the ratio of the mass of a material to its bulk volume. The close relationship between porosity and bulk density has been shown by Norris et al. (1979) to justify the use of bulk density measurements to establish vitrification characteristics of fired bodies. Williams et al. (1963) had used bulk density measurements as quality control of properties to monitor conditions in large kilns, and to study variations in firing conditions. Beech and Norris (1961) also suggested the use of bulk density to establish the optimum physical properties of fired bodies.

The percent theoretical density of a fired body is calculated from the bulk density and true specific gravity values;

$$\text{Percent theoretical density} = \frac{\text{Bulk density}}{\text{True specific gravity}} \times 100 \quad \ldots (7)$$

2.8.6 Water absorption

The water absorption expressed as a percentage, is the ratio of the water absorbed after a specimen has been sufficiently immersed in water to the mass of the dry specimen. Water absorption values are useful in assessing the degree of vitrification of a fired body. According to Budnikov (1964), the water absorption values for best types of technical porcelain are about 0.5 percent. Porcelains with water absorption values as high as 1.5 percent may be used for low voltage insulation while bodies suitable for high voltage insulation have water absorption (unglazed) values of less than 0.1 percent.

Bodies which are absolutely non-porous are highly desirable for high voltage insulation and outdoor applications since the risks of dielectric breakdown and corona discharge are minima for such bodies.

2.8.7 Specific gravity

The apparent specific gravity is defined as the ratio of the dry mass to the mass of an equal volume of water. The volume of water represents the volume of the impervious portion of the body. In contrast, the true specific gravity is the ratio of the dry mass to the mass of water whose volume is equivalent to the true volume of the body (volume of impervious portion-volume of closed pores).

The true specific gravity of a ceramic product is of importance in comparing bodies of different compositions and for calculating the true porosity and percent theoretical density which are key indicators of the degree of vitrification and densification of fired bodies. Specific gravity data are also related to electrical, thermal and mechanical properties of ceramics.

2.8.8 Mechanical strength of fired bodies

Mechanical strength of a material is a measure of its ability to retain its shape when subjected to various forces. Mechanical strength test is a standard quality control measure and is useful for purposes of design, research, and comparison of different body compositions.

Experiments on the strength of polycrystalline ceramics have revealed the complex nature of this property and is known to be strongly influenced by temperature, environment, size, shape and loading geometry of the part being tested. Its composition, microstructure, surface conditions as well as its prior thermal and mechanical history also affect the results of such tests.

Modulus of rupture correlates with other mechanical strength properties such as tensile and compressive strengths and it is generally the easiest and most economical test procedure available. The test is made on a long bar of either rectangular or circular cross section, supported near its ends by two knife edges of suitable span. The load is applied at a controlled rate by means of a third steel knife edge (three point loading).

Various attempts have been made to correlate microstructural parameters with the strength of polycrystalline ceramics. The best known of such efforts was the work of Knudsen (1959) which predicted highest strengths for ceramics of low porosity and fine grain size:

$$\sigma_{max} = Kd^{-a}e^{-bP} \quad \ldots\ldots \quad (8)$$

where σ_{max} = fracture strength

d = average grain size

P = fractional porosity

K, a, b = constants

Duckworth (1953), in a discussion following a paper by Ryskewitsch (1953) correlated the strength-porosity characteristics of porcelains subjected to bending and torsion tests and concluded that experimental data from both sources satisfied the following relation;

$$\sigma = \sigma_0 e^{-bP} \qquad \ldots\ldots \quad (9)$$

where σ = strength of porous body

σ_0 = strength of non-porous body of the same material

P = porosity expressed as a fraction

b = constant having a value between 4 and 7 for all experimental data.

The similarity of Knudsen and Ryskewitsch - Duckworth relations is apparent and the relations give a theoretical basis for the observed increases in mechanical strength with decreasing grain size and fractional porosity.

In polycrystalline ceramics, microcracks both within the body and on the surface act as fracture initiating flaws. These microcracks often result from thermal expansion mismatch between the glass phase and the residual quartz grains. The boundary stresses which develop are often sufficient to initiate cracks which subsequently act as stress concentrators. Messer (1983) studied the effect of flaw size on the mechanical strength of pottery bodies and observed that flaws which combine with closed pores are the most dangerous in reducing the load bearing area and hence the mechanical strength.

Mechanical strength is also influenced by the constituents of the body as well as their proportions. Triaxial porcelain consisting of clay, feldspar and quartz has improved mechanical strength nearer the high clay corner of the triaxial diagram. Waye et al. (1963) attributed

the improved mechanical strength to a decrease in internal strain due to smaller difference in thermal expansion between the crystalline phases and the glass phase.

A high proportion of undissolved quartz grains is detrimental to strength. Inspite of the disadvantages of the use of free quartz in whiteware bodies which have been pointed out by Dinsdale (1963), Waye et al. (1963), and Warshaw and Seider (1967) quartz is still being used in whiteware manufacture because of its abundance and economic considerations. Rather than use alternative body fillers such as alumina or zirconia which are rather expensive to process, improvement in processing methods have resulted in siliceous whitewares with satisfactory mechanical properties. Mattyasovsky-Zsolnay (1957) provided an example in the literature which showed that quartz grains in the range of 15 to 30μ are beneficial to mechanical strength which he attributed to favorable prestresses induced in the matrix. He also reported a reduction in strength when the body constituents were ground for exceptionally long period.

The prestress hypothesis is by no means universally accepted. Waye et al. (1963), in opposing the prestress hypothesis, attributed the increase in strength with decreasing quartz grain size to a decrease in the localization of stresses. Warshaw and Seider (1967) reviewed the literature on the mullite and the prestress hypotheses and admitted that abundant experimental evidence existed in support of the two views but they considered them inconclusive. Instead, they proposed that increases in strength as the quartz grain sizes reduce (down to a certain limit) are due to the transition in the type of fracture from inter-connected matrix fracture for large quartz grains to internal and peripheral fracture with small amount of non-interconnected matrix fracture. The

authors strongly believe that quartz grains (25μ and below) act as barrier to crack propagation when stress is applied while larger quartz grains (150 down to 50μ) contain complete or nearly complete fracture paths before the body is stressed.

Mechanical strength is also significantly improved by glazing. Bettany and Webb (1940) pointed out that over 30 percent improvement in mechanical strength is possible if body is glazed with a suitable glaze mixture which puts the body under compression when fired. These compressive stresses are able to heal the surface cracks resulting in an improvement in mechanical strength.

Because of the close correlation between mechanical, thermal and electrical properties the course of development in processing and body composition is to meet the need of improved mechanical strength.

2.8.9 Dielectric strength

Dielectric strength is a measure of the resistance of an insulating body to electrical breakdown and it is the property which determines the ability of the body to withstand high voltages. The dielectric strength of any material varies with the thickness of the sample, the temperature at which the test is carried out, the rate of voltage increases, the waveform of the applied voltage and shape of the electrodes. It is an important test specified for electrical porcelains. The measured values depend on a number of factors but is usually considered to be in the range of 9.84 - 15.9 kV/mm for high-voltage insulators (Thurnauer, 1954).

The routine testing of insulators in production is important in controlling quality and comparing porcelains of different body compositions. While mechanical requirements often dictate thickness of

insulators far greater than needed to withstand electrical stress, dielectric strength serves as a guide in estimating the electrical safety factor:

$$ESF = \frac{U_b}{U_o} \qquad \ldots\ldots (10)$$

where ESF = Electrical safety factor,

U_b = Dielectric breakdown voltage,

U_o = Operating voltage.

The theory of electric breakdown is extremely complicated and the values of dielectric strength calculated on the basis of structure and various material parameters frequently disagree with experimental data. This divergence is attributed to the presence of microcracks and other defects in the material whose effects are difficult to consider in calculations. Although electrical porcelain has virtually no apparent porosity it commonly has a true porosity of about 5 percent. These pores combine with the microcracks making it possible for charge carriers to carry current over comparatively point to point route through it.

The three postulated mechanisms of dielectric breakdown in insulating material are, (i) discharge or corona mechanism, (ii) thermal mechanism and (iii) the instrinsic mechanism.

In many dielectric strength tests on insulating bodies, breakdown is caused by electrical discharges which produce high local fields. The discharge usually occurs in surrounding medium, thus increasing the test area and producing failure at or beyond the electrode edge. Discharges may occur in closed pores or bubbles that are present. These processes may continue until a complete failure path is formed between the electrodes.

The process of dielectric breakdown caused by local overheating arising from electrical conduction is known as thermal breakdown. The local overheating increases to a point at which thermal instability occurs and permits a rush of current which results in melting and eventual failure.

At low field strength there is a certain direct current conductivity corresponding to the mobility of a limited number of charge carriers, notably the alkali ions and others related to electronic and ionic imperfections. As the field strength is increased the conduction increases and a field emission from the electrodes makes sufficient number of electrons available for a burst of current which produces breakdown channels bridging the porcelain and rendering it unusuable as an insulator. This critical field is called the intrinsic dielectric strength. It cannot be determined from dielectric strength tests, although the mechanism itself may be involved.

In recent years there has been considerable interest on the effect of porosity and the form of the test pieces on the measured value of dielectric strength. Gerson and Marshall (1959) used a statistical approach to determine the effect of porosity on the dielectric strength of porous ceramics and found that the breakdown field decreases logarithmically with increasing porosity. Shearouse et al. (1956) observed that edge effects which are particularly high for conventional discs are reduced by special design of the test pieces. They also pointed out that particle alignment and distortion during processing affect the dielectric strength significantly. Oliver and Waye (1970) suggested that samples be designed to have concave depressions at the centre as a way of reducing uneven electric stresses near the point at which breakdown occurs.

In determining the dielectric strength of an insulating material, the rate of increase of the voltage is such that failure occurs in about one minute. The dielectric breakdown voltage, V_b, is recorded and the thickness, t, of the specimen at the point of failure is determined with a micrometer screw gauge. The dielectric strength is calculated from the relation:

$$U_b = \frac{V_b}{t} \qquad \ldots\ldots \quad (11)$$

where U_b = dielectric breakdown strength

V_b = dielectric breakdown voltage

t = thickness at the point of puncture

The standard thickness of the test specimen is about 6.35mm and the specimen must have sufficient size to prevent flashover. The size of the electrodes, the type of medium surrounding the test specimen and the temperature at which the test is carried out are always stated in a report since these factors affect the measured value of the dielectric strength significantly.

CHAPTER THREE

EXPERIMENTAL PROCEDURE

In this chapter, the experimental procedures used in the course of this study are described. The processing methods for the beneficiation of clays, feldspar and quartz are described. This is followed by a description of the method for mineralogical characterization by X-ray diffraction. The procedure for the determination of rheological properties of clays and porcelain slip is described in detail. The various procedures for measuring the selected green and fired properties are also fully described. A description of the method of preparation of thin sections of fired samples and the procedure for microstructure study by optical microscopy technique is presented. Finally, the method of measuring the dielectric strength is described.

3.1 Processing of Clays

About 20 kilograms of Kankara clay was mildly pulverised on a flat steel plate using a cylindrical steel rod. The powder was sieved through a 120 mesh screen and dried at 110°C in a Gallenkamp oven Type OV-420, for a period of 12 hours. It was then stored in a closed container ready for use.

About 20 kilograms of Bukuru clay was soaked in water for a period of 24 hours to allow for complete slaking and dissolution of some of the impurities present. Excess water was then removed and fresh water added. This process was repeated ten times and it served as a washing method for the purification of the clay. The clay was then blunged vigorously with hand and left undisturbed for 48 hours during which the coarse particles settled at the bottom of the container. The slurry of the finer clay

particles was dewatered with porous biscuit-fired clay pots. The water content of the slurry was adjusted to give a slip density of about 1.5 kilograms per liter. It was stored in a closed container ready for use.

3.2 Processing of Feldspar and Quartz

About 25 kilograms of Okene feldspar was soaked in water for a period of 24 hours after which the rocks were thoroughly washed in running water. The feldspar rocks were calcined at 900°C in a Wenger electric kiln for a period of five hours. The calcined rocks were then crushed in a Jurgens jaw crusher, Type BB-24, to obtain size reduction of the order of 2 millimeters. The crushed feldspar grains were charged into a large Boulton ball mill to which sufficient water and pebbles had been added. The ball mill was run for 20 hours after which the mixture was discharged into a container and allowed to settle into a cake. The excess water was removed and the cake spread on a drying pan to dry in ambient air. After 48 hours, the powder was further dried at 110°C in a Gallenkamp electric oven for a period of 12 hours. The powder was then sieved through a 120 mesh and stored in a closed container.

Quartz was similarly processed according to the processing scheme for feldspar. The quartz rocks were soaked and washed, calcined, crushed and ball milled and the dry powder was screened and stored in a closed container.

3.3 X-Ray Examination of Beneficiated Raw Materials

The mineralogical compositions of Kankara clay, Bukuru clay, Okene feldspar and Amper quartz were qualitatively determined with a Philips X-ray diffractometer, using a nickel filtered Cu-Kα radiation, and

operated on a voltage of 40 kV and a current of 30 mA. The scanning speed was 2θ per minute while the paper speed was 2 centimeters per minute. The time constant was set at 2 while the counting rate was 2×10^3 counts per second for clays and 10^4 counts per second for feldspar and quartz.

A teaspoonful of the powder of each of the beneficiated raw materials was used to fill a standard specimen cell and excess powder removed by means of a sharp razor blade. The surface of the powder was gently pressed with a glass slide to provide a flat undisturbed surface for x-ray examination.

3.4 Rheological Properties

3.4.1 Rheological properties of Kankara clay

Four batches of Kankara clay slip designated K1, K2, K3 and K4 were prepared. Each batch was prepared by dispersing 200 grams of Kankara clay in 145 grams of distilled water and blunging for 30 minutes with a Gallenkamp mixer, Type SS-420.

The effect of sodium silicate on the rheological properties of Kankara clay slip was investigated with batch K1. Sodium silicate (140°Tw) diluted with equal volume of water was used for the test. Measurements of apparent viscosity were made with a Brookfield constant shear viscometer Model RVT, using spindle 3 and a selected speed of 20 revolutions per minute. The slip was blunged for 15 minutes after 0.0075 percent of sodium silicate was added. The apparent viscosity was determined within 15 seconds of cessation of stirring. The spindle was allowed to rotate for 60 seconds in the slip so that the shear rate would be constant before the apparent viscosity was measured. This procedure was repeated for subsequent increases in the concentration

of sodium silicate.

The apparent viscosity values corresponding to concentrations of sodium silicate in the range of 0.0075 to 0.0525 percent were recorded and a plot of the apparent viscosity against sodium silicate concentration was obtained from the data.

The effect of sodium carbonate (analar grade) on the rheological properties of Kankara clay slip was investigated with batch K2 following the procedure outlined above. The range of sodium carbonate concentrations was 0.001 to 0.005 percent.

The third batch (K3) had 0.01 percent of sodium carbonate added before the changes in apparent viscosity with sodium silicate concentrations were investigated. The amount of sodium carbonate was increased to 0.02 percent for batch K4 before the effect of sodium silicate on the rheological properties was investigated.

3.4.2 Rheological properties of Bukuru clay

Two batches of Bukuru clay slip designated U1 and U2 were prepared from Bukuru clay slurry whose specific gravity had been adjusted to 1.44 to correspond to water content of 45 percent. Each batch was prepared from 600.0 grams of slurry.

The effect of sodium carbonate on the rheological properties of Bukuru clay was investigated with batch U1. Sodium carbonate solution was prepared by dissolving 2.0 grams of auhydrous sodium carbonate in 0.10 liters of distilled water. Part of this solution was used to treat batch U1 and the changes in apparent porosity corresponding to the increases in sodium carbonate concentrations were determined following the procedure outlined in section 3.4.1. Apparent

viscosity values corresponding to sodium carbonate concentrations in the range of 0.005 to 0.075 percent were recorded and a plot of apparent viscosity against sodium carbonate concentration obtained. The sodium carbonate concentration corresponding to the minimum apparent viscosity was determined from the graph.

The second batch U2, was used to investigate if viscosity of Bukuru clay slip could further be reduced by treating it with sodium silicate after it had been treated with an amount of sodium carbonate which gave the minimum apparent viscosity in the previous test. This amount was found to be 0.04 percent of sodium carbonate and the slip was treated with it and then blunged for 15 minutes. Thereafter the effect of sodium silicate was investigated following the procedure already outlined.

3.4.3 Rheological properties of porcelain slip

Based on the suggestions by Norton (1956), Rhodes (1973), and Johnson and Robinson (1975) the ranges of body compositions selected for this study were limited to 40 to 50 percent clays, 25 to 35 percent feldspar and 20 to 30 percent quartz. The plastic clay content was also limited to 10 percent of the clay fraction for each body so as to minimize the effect of the high impurity content of the clay.

A porcelain body whose body composition was well within these ranges was selected and the effect of sodium silicate on the rheological properties of the porcelain slip was investigated. The body consisted of 45 percent clays (40.5 percent Kankara clay and 4.5 percent Bukuru clay), 30 percent feldspar and 25 percent quartz. A 600.0 gram slip consisting of 33 percent distilled water was prepared from 162.81g of Kankara clay, 18.09 grams of Bukuru clay, 120.6 grams of feldspar and 100.5 grams of quartz.

The order of constituent addition was as follows: 0.016 grams of anhydrous sodium carbonate (0.004 percent of dry mass) was added to 198.0 grams of distilled water contained in a one gallon ball mill. 18.09 grams of Bukuru clay was then added and dispersed by stirring the suspension. 0.20 milliliters of sodium silicate (140° Tw) solution which has been diluted with equal volume of distilled water, was added and this was followed by the addition of Kankara clay, feldspar and quartz.

The amount of sodium carbonate was limited to the minimum required to deflocculate the given amount of Bukuru clay. However, its concentration did not adversely affect Kankara clay because of the sequence of batch preparation which allowed most of the salt to react with Bukuru clay before Kankara clay was added to the batch.

The ball mill was tightly sealed with a cover after 120 dense porcelain balls were added and then run for 22 hours.

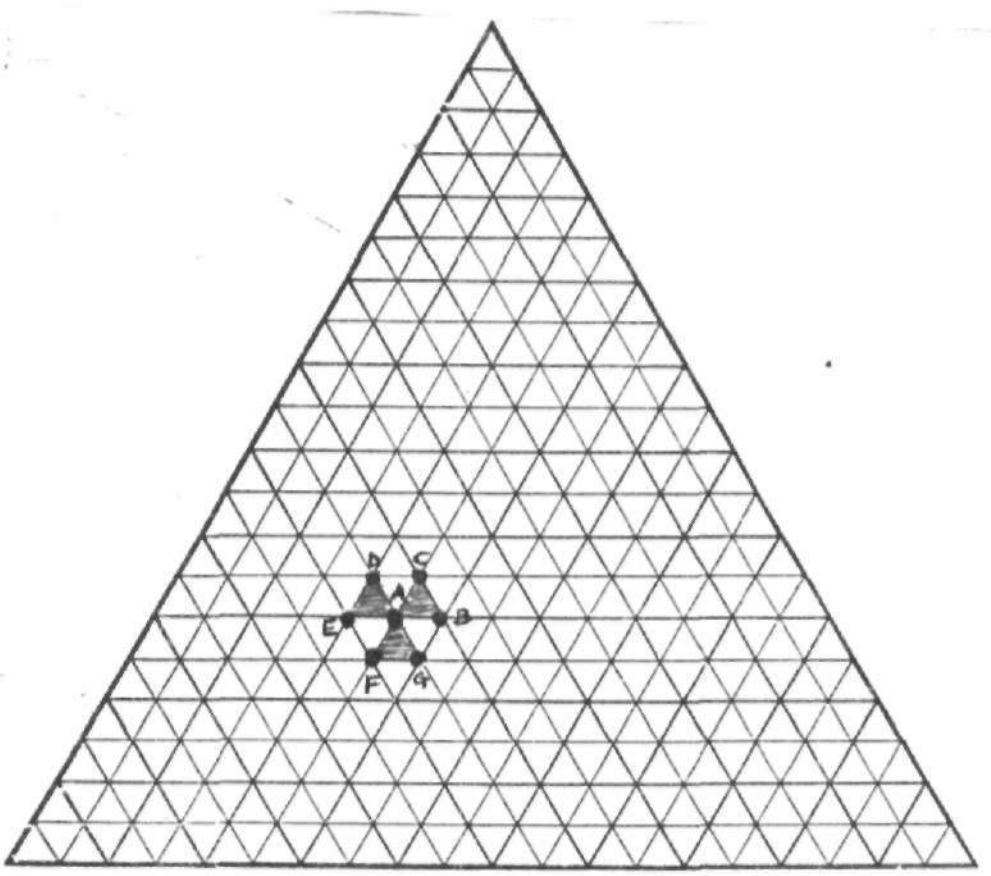
The finished slip was further treated with sodium silicate solution and changes in apparent viscosity as the concentration of sodium silicate was increased were determined by the procedure already outlined. Thixotropy was taken as the increase in apparent viscosity over a three minute period during which the slip remained undisturbed. The range of sodium silicate concentration used was 0.017 to 0.10 percent of dry mass.

3.5 Slip Preparation

Seven body compositions were selected close to the high clay corner of the triaxial diagram shown in fig. 6. They were chosen primarily because of the findings in the literature which were discussed in the

last section. The proportions of body constituents for the selected bodies are given in Table 3.1.

100% FELDSPAR



100% CLAY 100% QUARTZ

Fig. 6. Seven selected body compositions for triaxial porcelain (designated as Bodies A, B, C, D, E, F and G in the triaxial diagram).

Table 3.1: Seven selected body compositions of triaxial porcelain.

Raw Materials	Body Designation						
	A	B	C	D	E	F	G
Okene feldspar	30	30	35	35	30	25	25
Amper quartz	25	30	25	20	20	25	30
Kankara clay	40.5	36	36	40.5	45	45	40.5
Bukuru clay	4.5	4	4	4.5	5	5	4.5
TOTAL CLAY	45	40	40	45	50	50	45

A 1800.0 gram slip was prepared for each of the seven body compositions. The water content was limited to 33 percent in all cases. The quantities of sodium carbonate and sodium silicate required to maintain fluidity were determined from the deflocculation curve of porcelain slip obtained in the last section. 0.004 percent of sodium carbonate and 0.05 percent of sodium silicate were sufficient to maintain fluidity during batching.

The weighed body constituents were dispersed in 594.0 grams of distilled water in the order which was outlined in the last section. The mixture for each body was wet ball-milled for 22 hours. The batch compositions of the seven body compositions are given in Table 3.2.

Table 3.2:- Batch compositions of seven bodies

Raw Materials	Body Designation						
	A	B	C	D	E	F	G
Okene feldspar (g)	361.80	361.80	422.10	422.10	361.80	301.50	301.50
Amper quartz (g)	301.50	361.80	301.50	241.20	241.20	301.50	361.80
Kankara clay (g)	488.43	434.16	434.16	488.43	542.70	542.70	488.43
Bukuru clay (g)	54.27	48.24	48.24	54.27	60.00	60.00	54.27
Water (g)	594.0	594.0	594.0	594.0	594.0	594.0	594.0
Sodium carbonate(g)	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Sodium silicate (g)	0.60	0.60	0.60	0.60	0.60	0.60	0.60

3.6 Slip Casting

Specimens for the determination of dry and fired properties were prepared by casting 14 cylindrical rods for each of the seven slips that had been prepared. All the specimens were cast in molds of the type shown in Fig. 7. The prepared slip was gently poured into the assembled molds up to the rim and more slip was subsequently added as the process of dewatering continued. The process of refilling the molds (solid casting) was continued until no further shrinkage was noticed. Excess cast layer which formed over the rim of the molds were trimmed to prevent the development of stresses as the cast layer shrinks from the mold surface. The cast specimens were released from the molds after 4 hours.

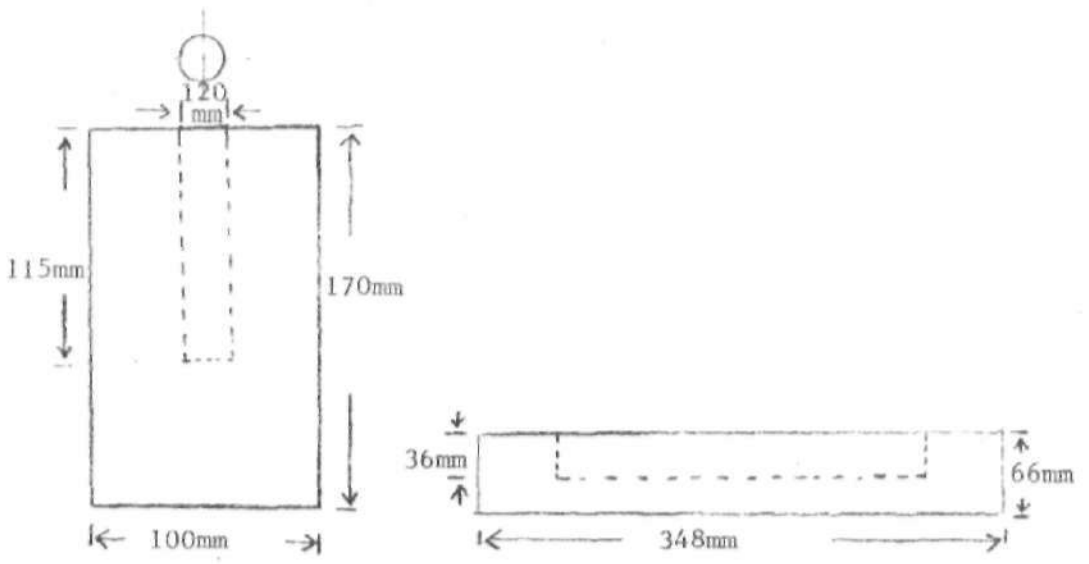


Fig. 7. Designs of plaster of Paris molds for casting cylindrical rods and discs. Umar (1985).

Disc-shaped specimens were prepared from the seven slips by casting in a rectangular mold with a flat casting surface. Cast layer was produced for each slip by pouring the slip into the plaster mold and allowing it to cast for 25 minutes. The remaining slip was gently poured out of the mold (drain casting) and the mold hinged at about 70 degrees to the horizontal to allow excess slip drain cleanly from the cast layer. After 30 minutes the cast layer was cut into disc-shaped specimens by means of a hollow cylindrical metal piece in the form of a cookie cutter. The thickness of the specimens was measured with vernier callipers and the casting rate for each slip was expressed as the cast thickness in 25 minutes.

3.7 Drying and Firing of Specimens

The cast specimens were air-dried for a period of 24 hours after which they were dried for 24 hours at 110°C in a Gallenkamp electric oven, Type OV-420. They were cooled to room temperature in a dessicator in which they were subsequently stored before being fired.

Eight specimens of each of the seven batches were fired on a controlled schedule in a Griffin electric furnace. The firing and cooling schedules are shown in Fig. 8.

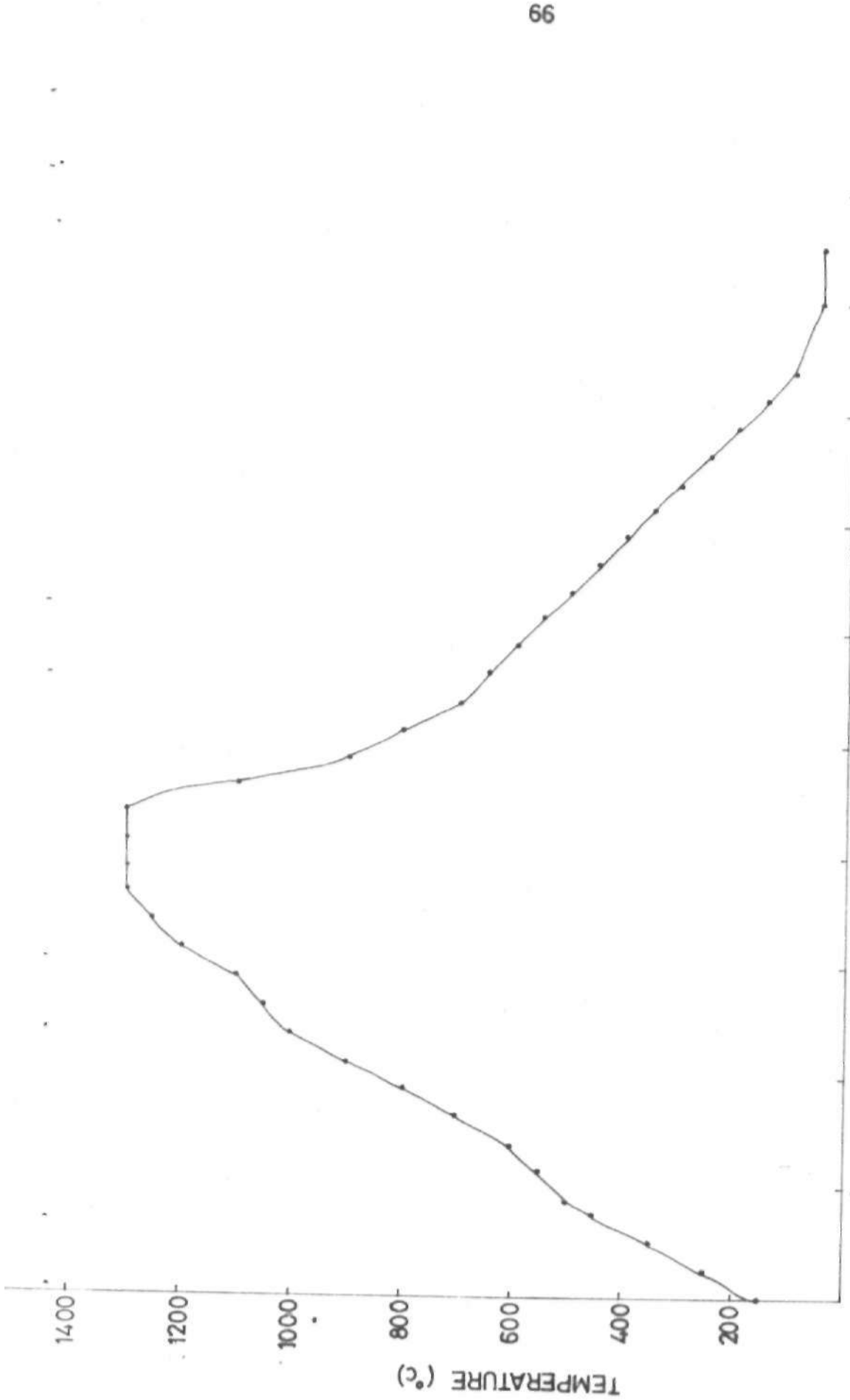


Fig 8 - Firing and cooling schedules for the porcelain samples

3.8 Determination of Porcelain Properties

3.8.1 Green modulus of rupture

A three point loading, with a span of 6.35 cm was used on a hand operated loading device. Standard strength testing machine was not used due to poor sensitivity for the accurate determination of green strength.

The experimental set-up for the determination of green strength is shown in Fig. 9. The arrangement is similar to that recommended by Singer and Singer (1963).

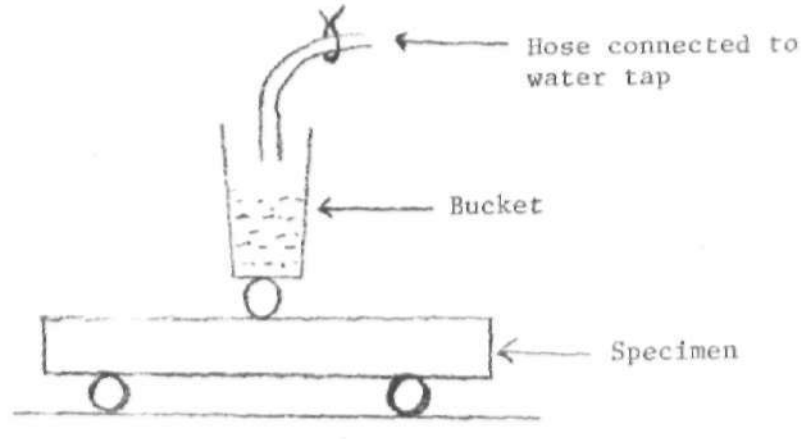


Fig. 9:- Experimental design for the determination of green strength.

Each of the cylindrical specimens was supported on two knife edges and a third knife edge attached to the buttom of a 20 liter capacity bucket was applied at the midpoint of the specimen and supported carefully with hand. Water from a tap was directed into the bucket and it provided a loading rate of 100 Newtons per minute until fracture occurred. The applied load was determined by weighing the bucket and water in a top loading balance. The diameter of the specimen at the point of fracture was determined with vernier callipers and the value of green modulus of

rupture was calculated by using Equation (5).

Four tests were conducted for each batch and the mean value of the green modulus of rupture as well as the standard deviation were calculated and recorded.

3.8.2 Fired modulus of rupture

Modulus of rupture tests were performed on four fired specimens of each of the seven batches using Denison mechanical strength testing machine, Type No. T. 42.C.2. A three point loading with a span of 6.35 centimeters was used on the testing machine and the loading speed was adjusted to 2.54 centimeters per minute. All tests were carried out at room temperature.

The load at fracture was recorded and the diameter of each specimen at fracture point was measured with vernier callipers and the value for the fired modulus of rupture was calculated using Equation (5). The average value for each batch as well as the standard deviation were calculated and recorded.

3.8.3 Dry-to-fired shrinkage

The length and diameter of five dry specimens of each batch were determined with vernier callipers. The fired length and diameter of the same specimens were determined after successful firing. The shrinkage in length and diameter were calculated as a percentage of the dry length and diameter respectively. The ratio of the diameter shrinkage to length shrinkage was also calculated for each batch. The average value as well as the standard deviation were determined for each batch and recorded.

3.8.4 Fired weight loss

The fired weight loss was determined for the five specimens used for the shrinkage test. The dry specimens were weighed on a top loading balance (reading accurately to 0.01 grams) and the fired weights were similarly determined. The fired weight loss was calculated as a percentage of the dry weight. The average value for the five measurements for each batch and the corresponding standard deviation were calculated and recorded.

3.8.5 Water absorption, bulk density and apparent porosity

Four specimens of each of the seven batches were selected for the tests. The test specimens were freshly fractured and dried to constant mass by heating in a 150°C oven for 24 hours. The specimens were cooled to room temperature in a dessicator and the dry mass of each specimen was determined with a top loading balance (reading accurately to 0.01 grams).

The test specimens were heated in boiling water for a period of five hours and were allowed to soak for additional 24 hours. The saturated mass of each of the test specimens was determined after they were carefully wiped dry with a moistened cloth.

The suspended mass of each specimen immersed in water was determined and values for the dry mass, saturated mass and suspended mass for each specimen were used to calculate the water absorption, bulk density and apparent porosity in accordance with ASTM C373-72.

The average value for four representative specimens of each batch was calculated and recorded.

3.8.6 True specific gravity, true porosity and percent theoretical density

Only the specimens of batches which have developed good mechanical strength and good vitrification characteristics were selected for these tests as the experimental data will be used to select the best body compositions amongst the seven body compositions investigated.

Each specimen was ground separately in a vibratory mill until the particle sizes were finer than 50μ. The powder was then heated to constant mass in a 150°C oven. About 10 grams of dry powder was introduced into a specific gravity bottle whose mass had been determined with an analytical balance (reading accurately to 0.0001 grams). The mass of the specific gravity bottle and powder was again determined with the balance. Distilled water was added to the powder until the bottle was completely full and no air bubbles were present. The mass of the specific gravity bottle containing powder and water was measured. The mass of the specific gravity bottle filled completely with distilled water was measured.

The true specific gravity was calculated as the ratio of the mass of the dry powder to the mass of equal volume of distilled water in accordance with ASTM C329-56.

The true porosity was calculated from the bulk density and true specific gravity data for each of the selected batches by using Equation (6). The percent theoretical density was similarly calculated by using Equation (7).

3.8.7 Optical microscopy

Thin sections were prepared from specimens representing the seven batches. A thin slice was cut from each of the seven specimens and polished on one side with grades of abrasive powders ranging from 800 to 120 microns. The polished surface of each section was cemented to a glass slide by means of araldite adhesive and dried on a hot plate. The thickness of the thin section was further reduced by grinding followed by polishing until microstructure was revealed by polarized light.

The thin sections were studied with Leitz petrographic microscope, Type Auto-Lux II with a fitted camera. Photomicrographs of thin sections were taken at different magnifications.

3.8.8 Dielectric strength

Only the body composition with the highest mechanical strength and good vitrification characteristics (zero water absorption and apparent porosity values) was selected for this test. Eight discs prepared by drain casting were 50 millimeters in diameter and approximately 6.35 millimeters thick. The discs were air-dried for 24 hours after which they were dried at 110°C in an electric oven. The dried specimens were cooled in a dessicator before they were conditioned for the test.

Electrodes were applied on six discs by coating them with silver paint and drying at 110°C for about 6 hours. To avoid the possibility of flashover, the silver electrode was not extended closer to the edge of the disc than 10 millimeters.

Each of the conditioned specimens was arranged between two equal-sized lead-in electrodes made from brass. The diameter of the contact area of the cylindrical brass electrodes was 25 mm. They were applied on the coated portion of the test specimen. The puncture tests were carried out under transformer oil. A.C. voltage source (Metropolitan-Vickers) was connected to a transformer with a 230/75000 rating. The circuit was completed by connecting the lead-in electrodes to the terminals of the transformer. (Fig. 10).

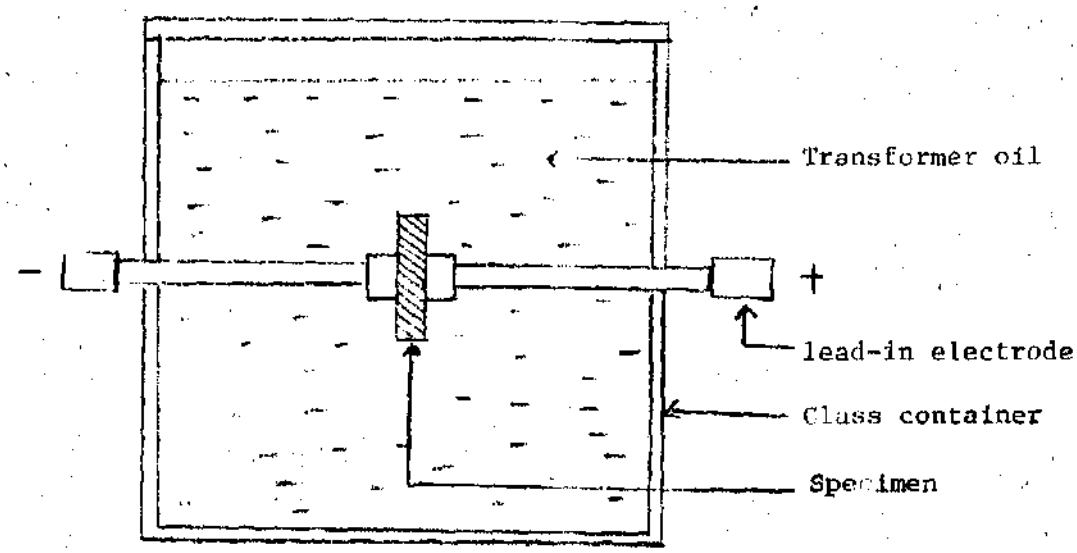


Fig. 10. Experimental set-up for the determination of the dielectric strength of a porcelain disc.

A short time test at the rate of 1 kilovolt per second was carried out on each specimen and the dielectric breakdown voltage recorded. The thickness at the point of puncture for each specimen was determined with a micrometer screw gauge and recorded.

The dielectric strength was calculated by using Equation (11) and the average of the measured values as well as the standard deviation were calculated and recorded.

CHAPTER FOUR

RESULTS AND DISCUSSION

The results of this investigation are presented in this chapter. The results of the mineralogical analysis of the beneficiated raw materials are first presented, followed by a discussion of the results of the investigation of the rheological properties of Kankara clay, Bukuru clay and porcelain slip. The results of the green and fired properties tests are presented and are compared for the seven body compositions selected for the study. Data for the specifications for low-voltage and high-voltage porcelain insulators are provided and are used to assess the quality of the developed bodies. Some of the results of the investigation are also compared with published work on related studies. Attempt is made to outline the processing conditions and suitable body compositions for high-voltage porcelain manufacture.

4.1 X-Ray Examination of Beneficiated Raw Materials

Fig. 11 shows the x-ray diffraction pattern of a sample of Kankara clay. The principal crystalline phases in the sample were identified by using the search manual of Joint Committee on Powder Diffraction Standards (JCPDS). The most intense peaks in the diffractogram corresponding to the d-spacings d_{oo1}(7.10 Å) and d_{oo2}(3.56 Å) were associated with crystalline kaolinite (JCPDS 29-1488). Potash feldspar was identified in the sample by its principal peaks at d_{oo2}(3.18 Å), d_{111}(4.02 Å) and d_{220}(3.80 Å) (JCPDS 22-462). The peak at 3.34 Å suggested that crystalline quartz may be present although this peak could also be associated with potash feldspar.

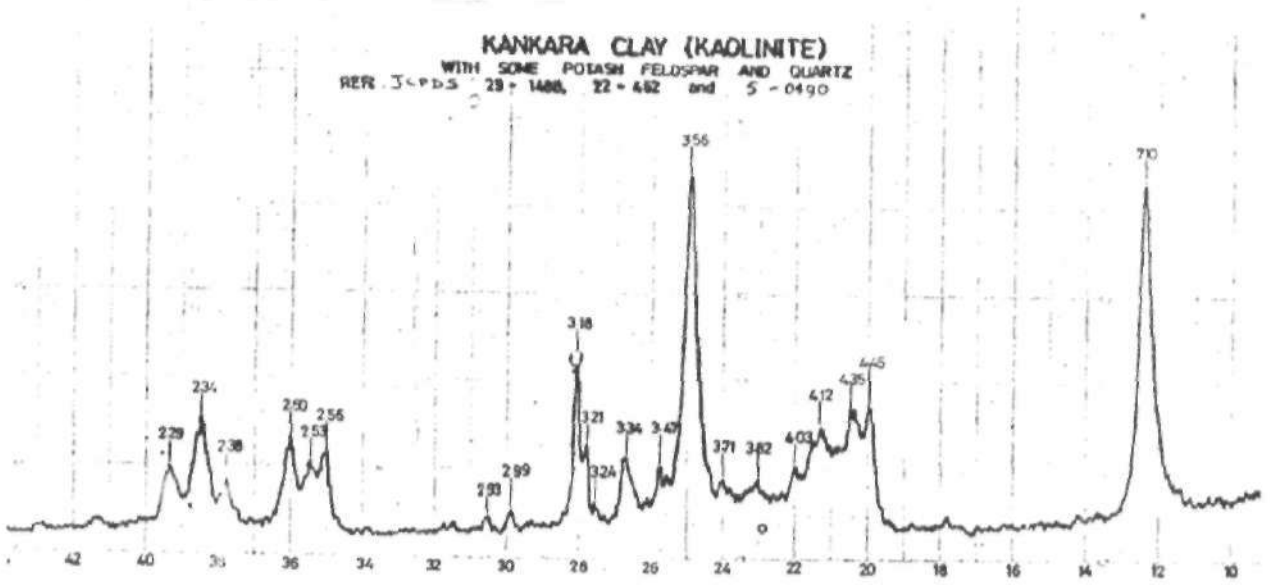


Fig. 11:- X-ray pattern of Kankara clay

The presence of potash feldspar as impurity in the clay sample gives strong indication that Kankara clay may have its origin from the kaolinisation of feldspathic rocks (Keller, 1985).

The x-ray pattern reveals that kaolinite is the principal crystalline specie in Kankara clay sample and this fact has recently been inferred from differential thermal analysis (Ahmed, 1986).

Fig. 12 shows the X-ray diffraction pattern of Bukuru clay. The peaks at 7.10 Å and 3.56 Å correspond to kaolinite minerals. Crystalline quartz was also identified in the sample by the peaks at d_{101} (3.343 Å) and d_{100} (4.26 Å) (JCPDS 5-0490).

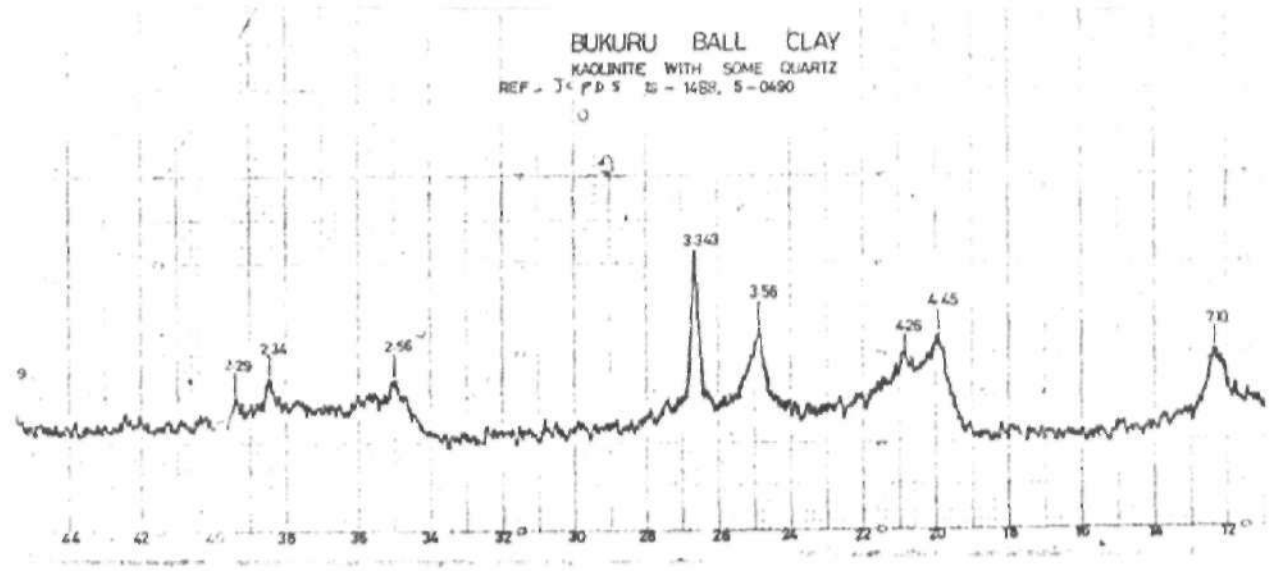


Fig. 12:- X-ray diffractogram of Bukuru clay

X-ray pattern of Okene feldspar is shown in Fig. 13. Microcline was identified by the peaks at d_{002}(3.24 Å), $d_{\bar{2}01}$(4.21 Å) and $d_{\bar{2}02}$ (3.27 Å) (JCPDS 22-687). Orthoclase was also identified by the peaks at d_{002}(3.18 Å), d_{220}(3.34 Å) and d_{130}(3.83 Å). However, some peaks associated with microcline and orthoclase were missing in the diffractogram indicating that the two minerals may be existing as a binary solid solution in the deposit.

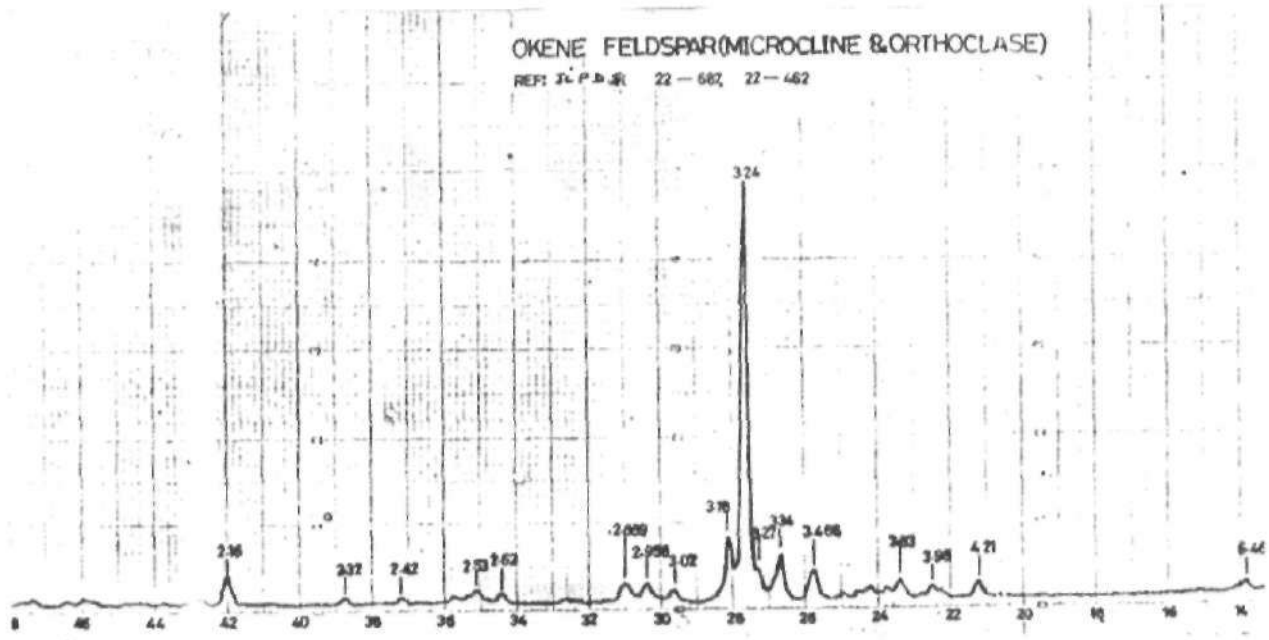


Fig. 13:- X-ray diffraction pattern of Okene feldspar

Fig. 14 shows the x-ray diffractogram of Amper quartz. All the peaks in the pattern correspond to the principal peaks of alpha quartz (JCPDS 5-0400). The only crystalline phase detected in this sample is essentially crystalline quartz although amorphous silica phase may be present.

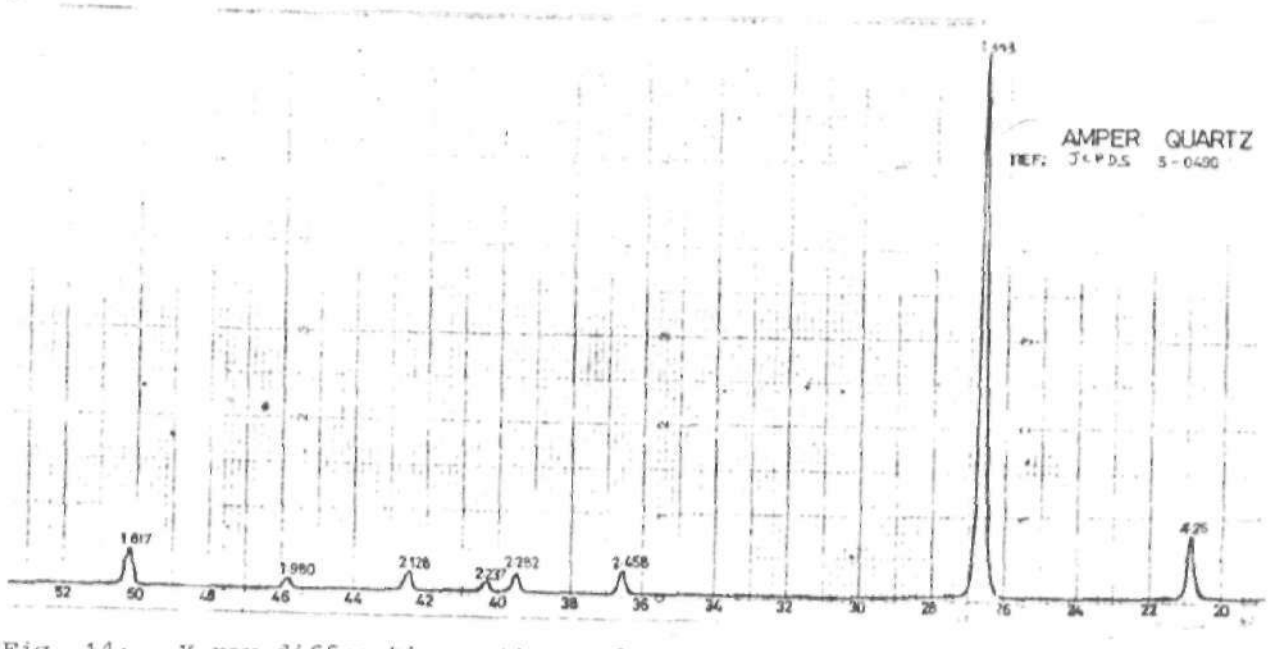


Fig. 14:- X-ray diffraction pattern of Amper quartz

4.2 Rheological Properties of Kankara clay, Bukuru Clay and Porcelain Body Slip

Fig. 15 shows the deflocculation curves for three batches of Kankara clay slip. Curve 1 shows the variation of the apparent viscosity with sodium silicate concentrations. Curve 2 shows the variation of the apparent viscosity with sodium silicate concentration after 0.01 percent sodium carbonate was added to batch (K3). Curve 3 represents the deflocculation curve of batch (K4) to which 0.02 percent sodium carbonate was added. Although there were broad siliarities in the ways in which the apparent viscosity varied with sodium silicate concentration, they did not behave in exactly the same manner. For example, the minimum apparent viscosity for the slips increased with the addition of 0.01 percent and 0.02 percerrt sodium carbonate to batches K3 and K4 respectively. A minimum apparent viscosity value of 3.85 poises was obtained for 0.03 percent sodium silicate for batch K1. The addition of 0.01 percent sodium carbonate increased the initial apparent viscosity of batch K3 from about 16 poises to 29.30 poises. A minimum apparent viscosity value of 13.40 poises was achieved at 0.05 percent sodium silicate. The addition of 0.02 percent sodium carbonate to batch K4 increased the initial apparent viscosity from about 16 poises to 35.0 poises. A minimum apparent viscosity value of 23.50 poises was achieved at 0.07 percent sodium silicate.

Above the sodium silicate concentration corresponding to the minimum the apparent viscosity gradually increased as the sodium silicate concentration was increased for the three batches.

The observed increases in apparent viscosity when 0.01 percent and 0.02 percent sodium was added to batch K3 and K4 respectively were

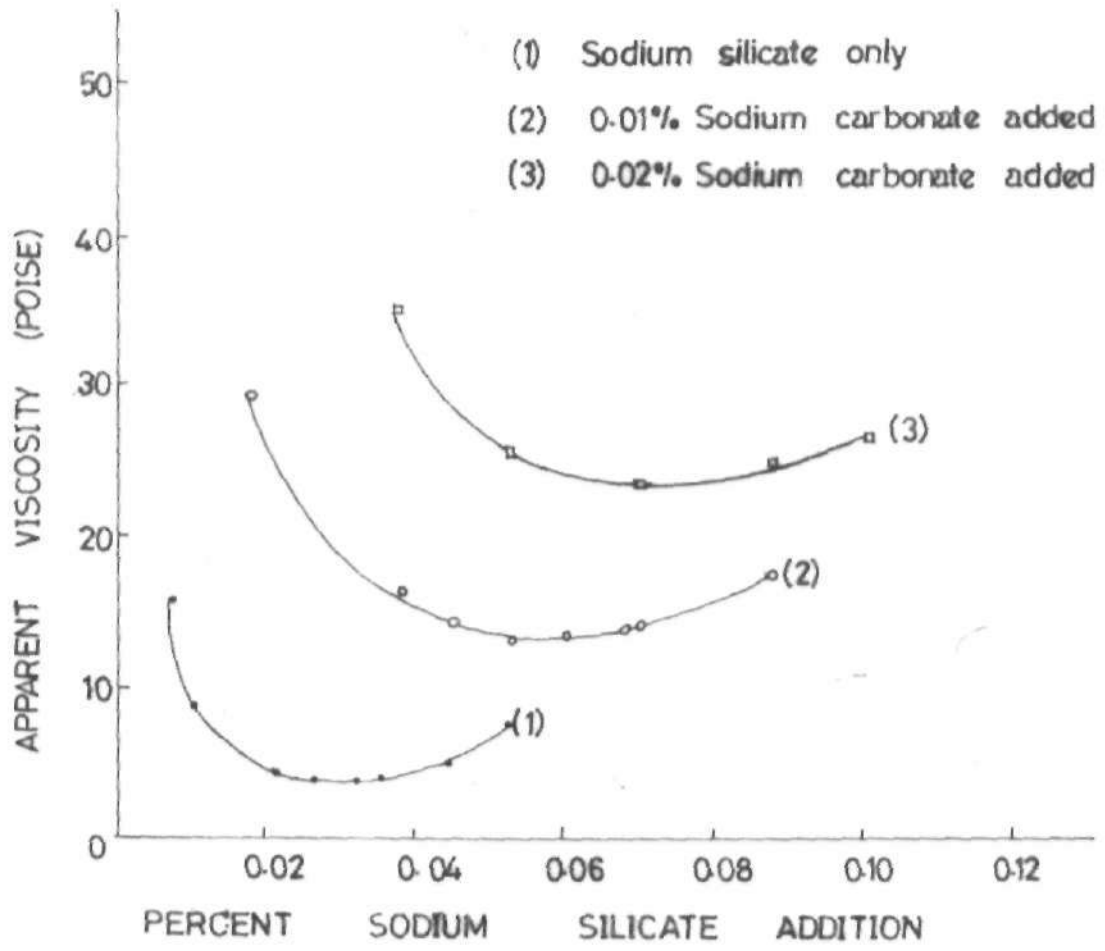


Fig. 15 - Deflocculation curves for Kankara clay slips

further confirmed in Fig. 16 in which the deflocculation curve showed increases in apparent viscosity as sodium carbonate concentration was increased from 0.001 to 0.005 percent.

Fig. 17 shows the deflocculation curve of Bukuru clay slip. The curve shows the variation of apparent viscosity with sodium carbonate concentration. The apparent viscosity decreased as the sodium carbonate concentration was increased from 0.005 to 0.05 percent. However, the apparent viscosity increased at higher concentrations. The minimum apparent viscosity value of 17.5 poises was achieved for 0.05 percent sodium carbonate.

Fig. 18 shows the variation of apparent viscosity with sodium silicate concentration after the addition of 0.04 percent sodium carbonate to Bukuru clay slip. Sodium silicate apparently had a pronounced effect on the slip as the fluidity was greatly improved. A minimum apparent viscosity value of 1.25 poises was obtained for 0.04 percent sodium silicate concentration.

Fig. 19 shows the variation of apparent viscosity with sodium silicate concentration for the porcelain body slip treated with 0.004 percent sodium carbonate. The apparent viscosity decreased rapidly as the sodium silicate concentration was increased from 0.02 to 0.04 percent. A minimum apparent viscosity value of 8.50 poises was achieved for 0.061 percent sodium silicate concentration. Thixotropy was more pronounced at low concentrations of sodium silicate and was completely destroyed when the concentration of sodium silicate exceeded 0.06 percent.

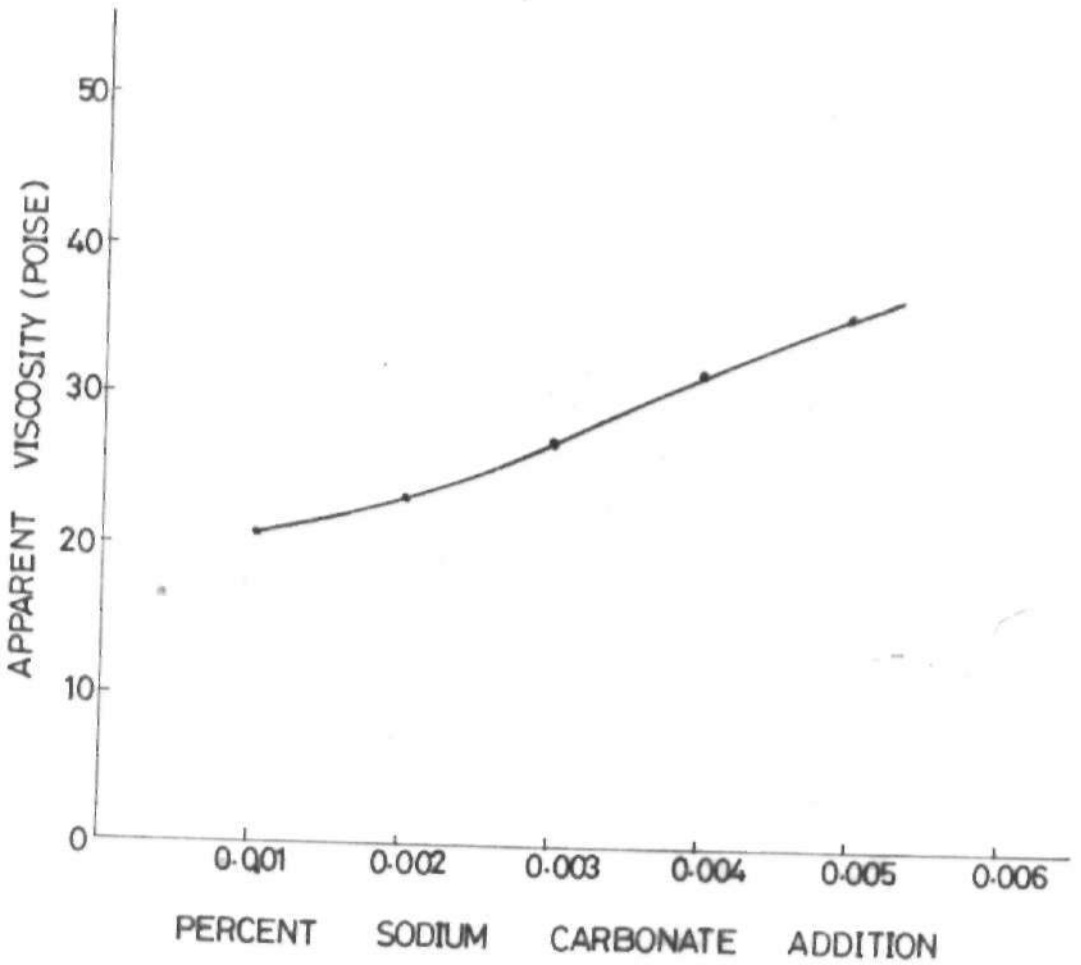


Fig 16 - Deflocculation curve for Kankara clay slip

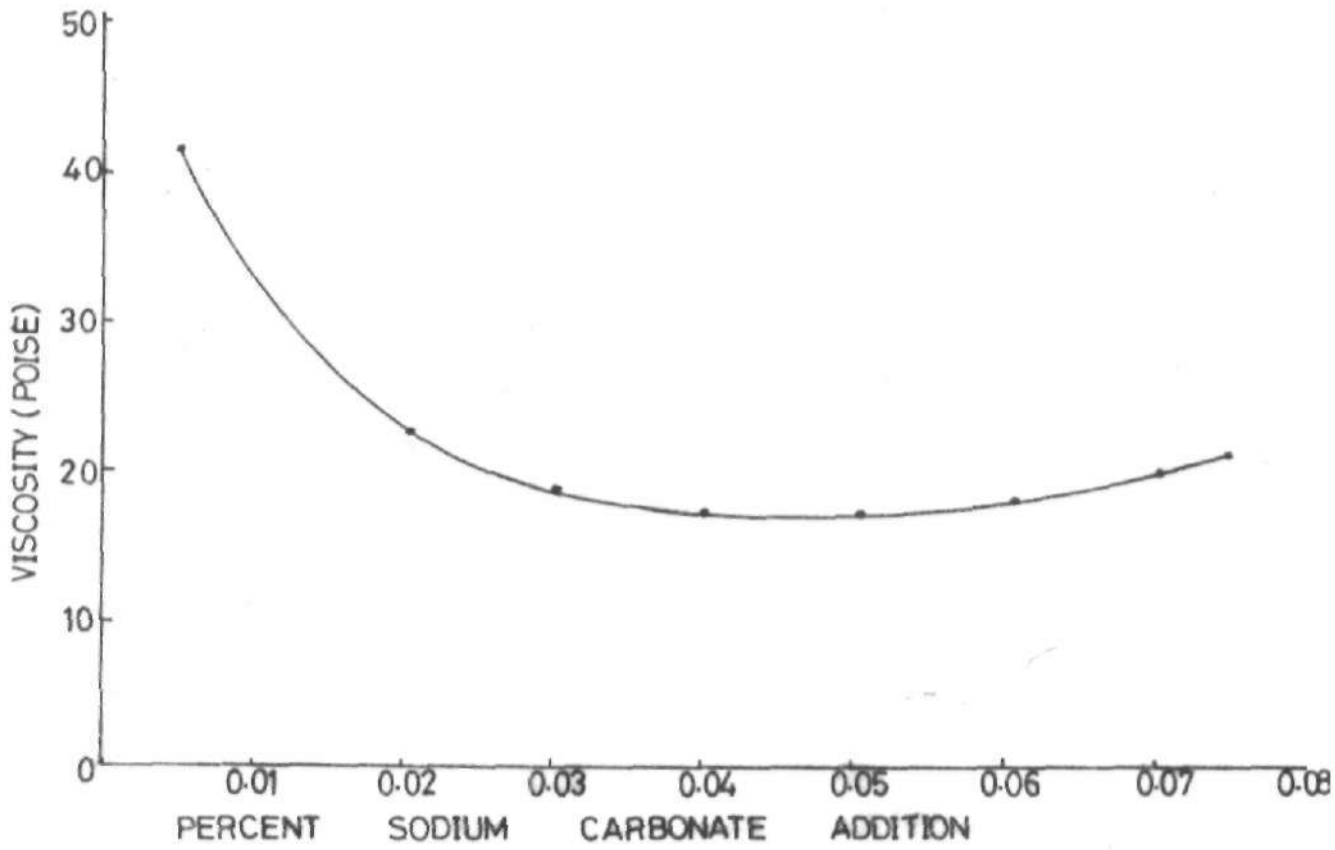


Fig. 17 Deflocculation curve for Bukuru clay Slip

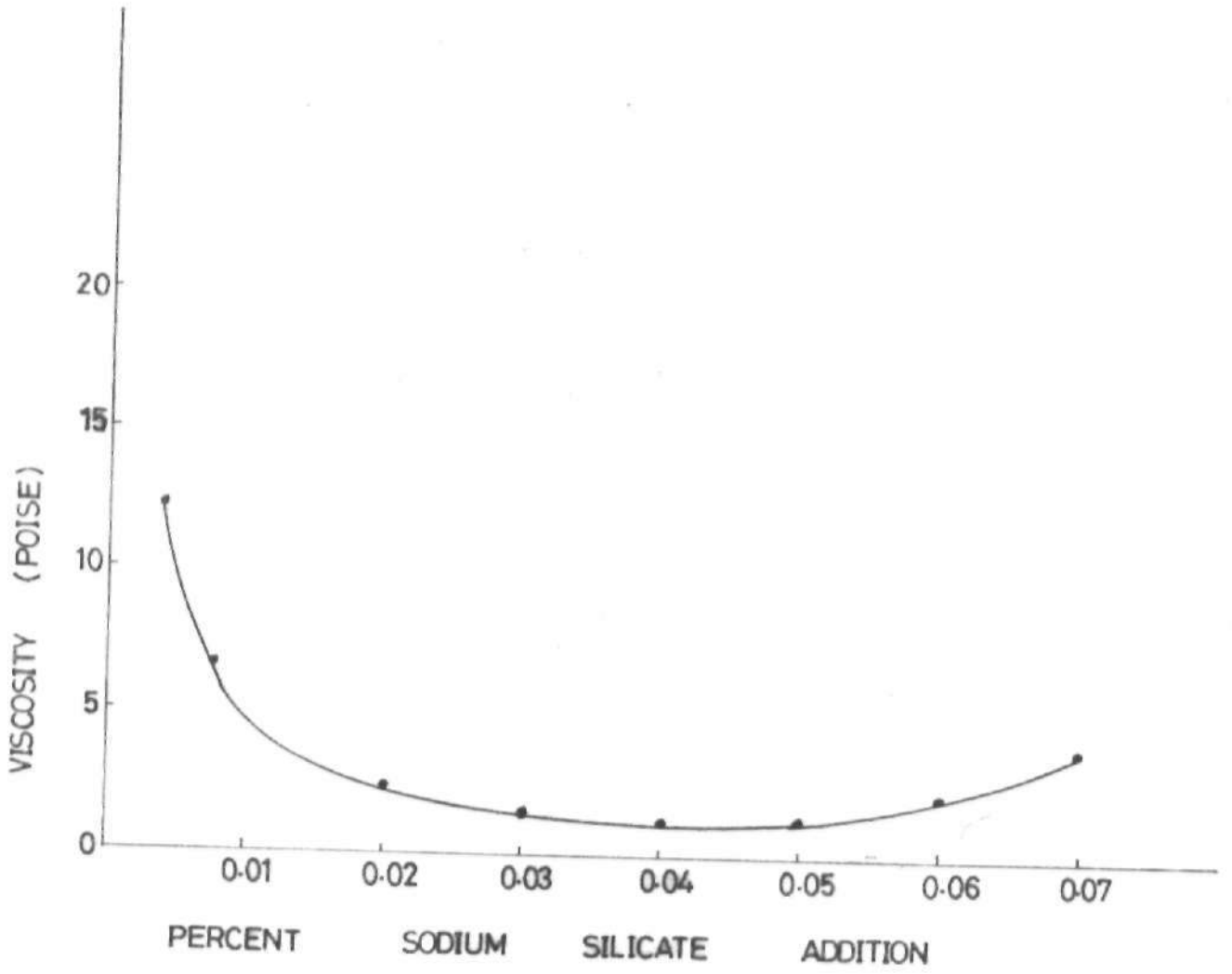


Fig. 18 – Deflocculation curve for Bukuru Clay slip (0·04 percent sodium carbonate added during batching)

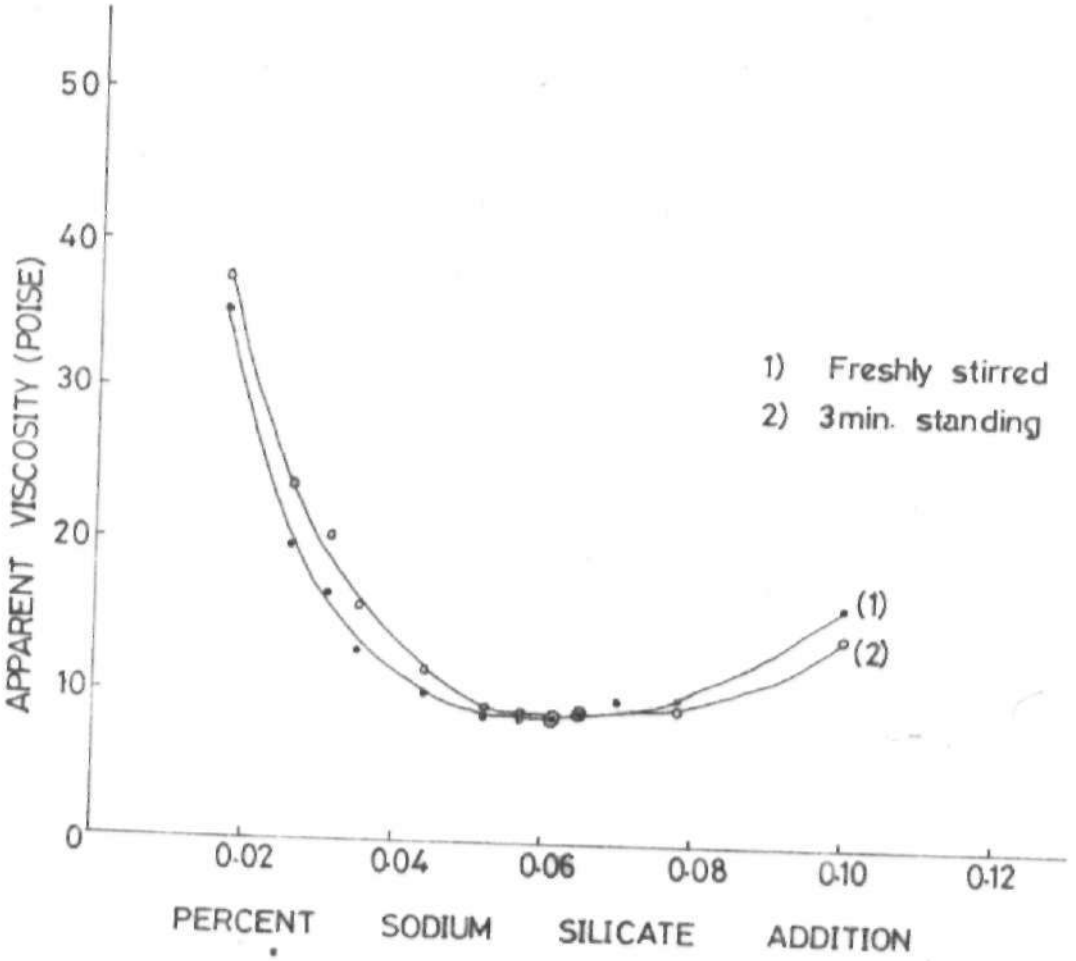


Fig 19- Deflocculation curve for Kankara clay - based porcelain casting slip (0·004 percent Na_2Co_3 added)

A surprising feature of the results for Kankara clay slips blunged with small concentrations of sodium carbonate was the observed increases in apparent viscosity. Fig. 16 further confirmed this observed effect for sodium carbonate concentration in the range of 0.001 to 0.005 percent. A plausible explanation for this effect is that the sodium ions produced as a result of the ionisation of sodium carbonate in the clay suspension did not replace the counterions present at the clay surfaces. The Hofmeister series, according to Grimshaw (1958), indicates that the bond energy for sodium ions is smaller in comparison to the principal ions associated with natural clays. The replacement of such strongly adsorbed cations by sodium ions is only possible if such cations form insoluble carbonates or silicates which are then sequestered out of solution. The result showed that cation exchange reactions did not occur significantly to cause improvement in the flow properties. Instead, the sodium ions migrated close to the basal surface due to the electrostatic interaction of the negatively charged basal surfaces and the positively charged sodium ions. As a result, the electrical double layer which developed at the basal surfaces was compressed and their effective potential reduced to the extent that coagulation by van der Waals forces was enhanced. The increase in apparent viscosity was attributed to the flocculation of the clay particles in the face-face pattern and the formation of links between these flocs (Rand and Melton, 1977).

The significant reduction in apparent viscosity of Kankara clay slip with sodium silicate suggested that the silicate ions were responsible for the observed decrease in apparent viscosity since sodium ions had been observed to cause the apparent viscosity to increase even at small concentrations. van Olphen (1977) suggested that the adsorption of silicate anions at the clay edges would lead to a positive edge

charge reversal. The clay edge surfaces would develop negative electrical double layers and this would result in the breakdown of the edge-face structure with a significant reduction in the inter-particle forces. The decrease in apparent viscosity as the concentration of the silicate anions was increased was apparently due to the adsorption of these ions and the subsequent disruption of the inter - particle links.

The increases in apparent viscosity for higher concentrations of sodium silicate were attributed to the build up of the excess sodium ions close the clay basal surfaces. The effect of this build-up was discussed earlier for the case of Kankara clay slip treated with only sodium carbonate. The increases in apparent viscosity were gradual because the number of inter-aggregate links which developed between the flocs were fewer than that of the inter-particle links in the edge-face mode of particle aggregation for the under-deflocculated slip.

The lower values of apparent viscosity achieved for Bukuru clay slip suggested that favorable cation exchange reactions involving sodium ions and counterion at clay basal surfaces apparently occurred in addition to the positive edge charge reversal by silicate anion adsorption.

The rheological properties of porcelain body slip was greatly influenced by the flow characteristics of the clays present in the body slip. The minimum apparent viscosity (8.50 poises) recorded for the slip was higher than 5.0 poises which Dale (1964) recommended as apparent viscosity of a casting slip. The 33 percent water content of the slip was considered high as most industrial slips have water content limited to about 28 percent. The high proportion

of water required to prepare Kankara clay - based porcelain slip was necessary to produce manageable slip properties as preliminary investigations revealed that slips prepared with lower water content would not deflocculate sufficiently to produce satisfactory casting slip.

The increased demand for water by Kankara clay - based porcelain to improve fluidity and casting characteristics might be due to the presence of strongly adsorbed counterions which promoted long range order in the immobilized water structure developed at the clay-water interface. The presence of such ions as H_3O^+, Al^{3+}, Ca^{2+} , Mg^{2+}, etc. in clays makes the development of fluidity difficult as these ions are water structure promoters (Lawrence, 1958a) and are not readily replaced by sodium ions. If sodium were substituted for these strongly adsorbed ions, the amount of water required to form a slip of high solid concentration would reduce and the slip would also have reasonable fluidity and casting properties since the sodium ions disrupt the rigid water structure making it possible for clay particles to be readily dispersed in suspension.

The porcelain slip showed considerable thixotropy when under-deflocculated. The thixotropy was moderate at 0.05 percent sodium silicate concentration. The instability shown by the slip when the thixotropy was destroyed was due to the inability of the clay particles to form a network of links required to prevent the segregation of coarse (nonclay) particles. To overcome this problem of instability and inhomogeneity, the slip is made moderately thixotropic by under-deflocculating it with just enough concentration of sodium silicate which would allow residual inter-particle and inter-aggregate links sufficiently strong to prevent the segregation of coarse

particles.

4.3 Green and Fired Modulus of Rupture

Results obtained for the green modulus of rupture tests for seven body compositions are shown in Table 4.1. The values for the various body compositions are plotted on a triaxial diagram (Fig. 20). High clay bodies, as anticipated, developed higher green strength than bodies containing a high proportion of quartz. Fig. 20 shows that bodies A, D, E and F have green modulus of rupture values higher than 3.40 MN/m^2. These bodies had clays in the proportions of 45 to 50 percent and quartz (20 to 25 percent). Bodies B and G which contained 30 percent quartz had the lowest values.

TABLE 4.1

Slip properties and green modulus of rupture cast specimens

Body Designation	Viscosity (poises)	Thixotropy (centi-poises)	Slip specific gravity	Casting rate (cm/25min)	Green modulus of rupture MN/m^2
A	11.25	25	1.72	0.72	3.62±0.02
B	11.00	25	1.71	0.87	3.27±0.1
C	11.00	50	1.71	0.80	3.36±0.08
D	11.25	50	1.72	0.74	3.44±0.07
E	11.50	25	1.71	0.76	3.60±0.06
F	11.25	25	1.71	0.75	3.74±0.08
G	11.75	25	1.72	0.72	2.62±0.1

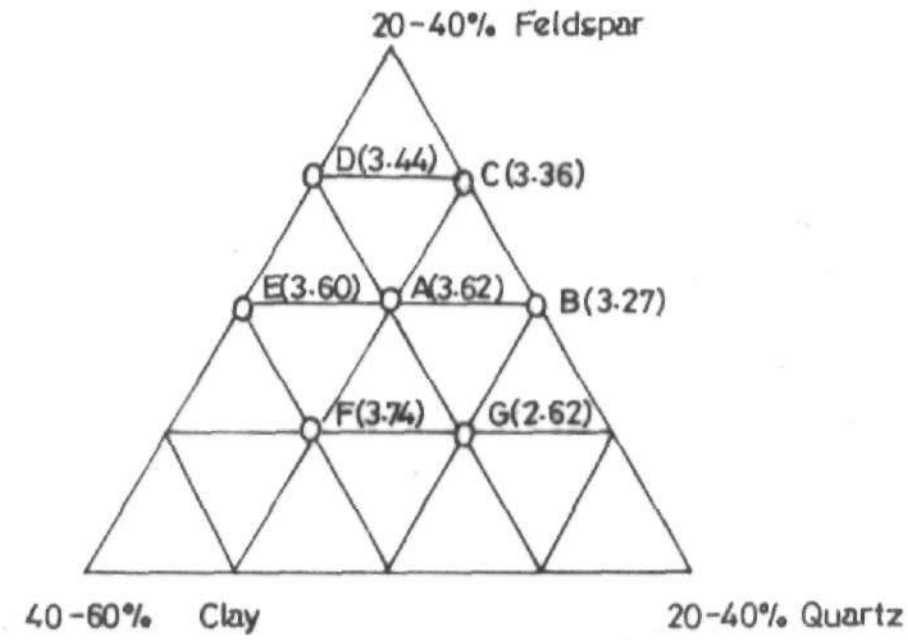


Fig 20 - Green modulus of rupture for triaxial porcelain bodies (expressed in MN/m^2)

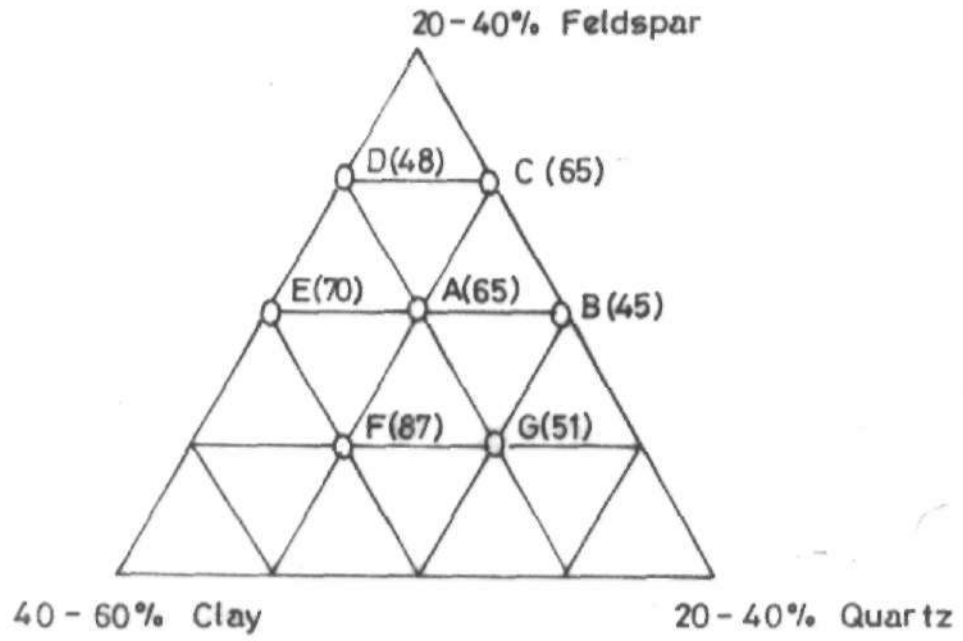


Fig 21 - Fired modulus of rupture for triaxial porcelain bodies (expressed in MN/m^2)

The results of the fired modulus of rupture test for seven bodies are shown in Table 4.2. Significant improvement in the fired strength was obtained by increasing the proportion of clays to 50 percent and limiting the proportion of quartz to a range of 20 to 25 percent (Fig. 21). Bodies showed reduced strength when the quartz content was increased to 30 percent. Bodies A, C, E and F had fired modulus of rupture values higher than 60MN/m^2. Bodies B and G containing 30 percent quartz had lower values. Body D which contained 20 percent quartz and 45 percent clay unexpectedly developed poor mechanical strength.

TABLE 4.2

Some properties of fired porcelain bodies

Body Designation	Dry to fired shrinkage (length)	Diameter shrinkage / length shrinkage	Fired Weight loss	Fired Modulus of rupture (MN/m^2)
A	12.43±0.07	1.27	5.08±0.04	65±5
B	12.36±0.06	1.20	4.51±0.07	45±3
C	12.93±0.05	1.23	4.64±0.02	65±2
D	12.98±0.2	1.25	5.11±0.07	48±7
E	13.10±0.1	1.23	5.52±0.06	70±3
F	12.61±0.07	1.31	5.51±0.09	87±10
G	11.64±0.3	1.30	5.02±0.04	51±3

The improved green strength for Bodies A, D, E and F was undoubtedly due to the high clay content and low quartz proportion. The size of the clay particles enhanced inter-particle contacts resulting in good packing characteristics during the process of casting and drying. As the quartz proportion was increased at the expense of clay, the grains characteristics altered and the number of clay - quartz boundaries increased. These boundaries served as sources of dangerous flaws which acted as stress concentrators and enhanced premature mechanical failure. The observed higher dry strength for Body F in comparison with Body E both of which contained 50 percent clay suggested that addition of quartz might have beneficial effect on dry strength. A mechanism by which green strength is enhanced by quartz was proposed by Williamson (1978). He believed that quartz grains could lie across fracture paths thereby inhibiting crack propagation during loading. However, as the proportion of quartz grains increased, the stresses developed at the grain boundaries were sufficient to give rise to dangerous flaws which resulted in a reduction in strength.

Investigations by Russel et al. (1949) into the casting characteristics of clays revealed that porcelain bodies produced under the best processing conditions have dry modulus of rupture value of about $3.89 MN/m^2$. The comparable values obtained for Bodies E and F in this study suggested that the processing scheme in the green state and, in particular the ball milling time, was adequate for the development of optimum properties of the unfired body.

Fig. 21 shows that a maximum value of 87 MN/m^2 was obtained for the fired modulus of rupture of Body F. This value is comparable to the values obtained for high voltage porcelain bodies investigated by Russel et al.(1949) (89.5MN/m^2), Waye et al. (1963) (93.8MN/m^2) and is even higher than the value quoted by Johnson and Robinson (1975) (83MN/m^2) for conventional high voltage porcelain insulators containing normally ground quartz.

The higher fired modulus of rupture values for Bodies E and F were apparently due to the fine particle structure of the clay particles which increased the speed of vitrification during firing. The low quartz content appeared to be less detrimental to mechanical strength of Bodies E and F.

Although Bodies E and F had the same amount of clay (50 percent clay), it was observed that Body F which had higher quartz content had higher green and fired strength than body E. It was therefore assumed that beneficial effects accrued when the quartz proportion was increased from 20 to 25 percent. The explanation put forward by Warshaw and Seider (1967) for the observed increases in strength with well ground quartz grains was that these grains acted as barrier to crack propagation when a stress was applied. However, the proportion of quartz which had this desirable effect on mechanical strength is limited by the fact that the stresses developed at the quartz-glass boundaries often give rise to cracks and other forms of flaws which would reduce the mechanical strenth. Examples of this effect were observed for Bodies B and G which contained 30 percent quartz. The fired modulus of rupture values for these two bodies were among the lowest (45 MN/m^2 and 51 MN/m^2 respectively).

4.4 Dry - to - Fired Shrinkage and Fired Weight Loss

The data on the dry - to - fired shrinkage in length is shown in Table 4.2. The differential shrinkage of the fired bodies is represented by the ratio of diameter to length shrinkage. This value is about 1.25 for all the seven bodies and it indicated that greater shrinkage occurred in the diameter of all the specimens. The shrinkage was higher for high clay bodies while low shrinkage was recorded for bodies containing 30 percent of quartz.

The fired weight loss, calculated as a percentage of the dry weight, was higher for high clay bodies although the values for all the bodies were close to 5 percent.

The shrinkage in clay bodies was caused by a decrease in volume due to the expulsion of water, carbon dioxide or sulfur dioxide and the sintering of the grains by capillary forces of the liquid phase (glass) and the subsequent expulsion of air from the pores during the process of densification and vitrification. Quartz in ceramic bodies remained essentially inert during heat treatment and acted as a skeletal framework to minimise shrinkage.

The large differential shrinkage between diameter and length observed for all the seven bodies was due to the preferred orientation of clay platelets parallel to the mold surface. The greater shrinkage in diameter was a result of the elimination of water films between the platelets.

The fired weight loss represented the loss in weight from the expulsion of hygroscopic and constitutional water contained

in the clays and from the expulsion of gases resulting from decomposition reactions during firing. The appreciable increase in the fired weight loss for high clay bodies was not unexpected since the clays were primarily involved in the changes which resulted in loss of weight.

4.5 Bulk Density, Apparent Porosity and Water Absorption

The results of the bulk density, apparent porosity and water absorption tests are shown in Table 4.3. The average bulk density of Bodies A, C, D, E and F which contained quartz proportions in the range of 20 to 25 percent was about 2.35 grams per cubic centimeters while Bodies B and G containing 30 percent quartz had lower values. It was also observed from the results that the proportion of quartz in the body affected the apparent porosity and water absorption as well. Only bodies containing 30 percent of quartz had apparent porosity and water absorption values higher than 1 percent. These results suggested that the proportion of quartz in porcelain bodies strongly influences their vitrification characteristics.

TABLE 4.3

Some Properties of Fired Porcelain Bodies

Properties	Body Designation						
	A	B	C	D	E	F	G
Bulk Density (g/cm^3)	2.36	2.27	2.35	2.36	2.34	2.35	2.20
Apparent Porosity (%)	0.35	5.36	0.02	0.88	0.00	0.00	9.14
Water Absorption (%)	0.15	2.36	0.01	0.37	0.00	0.00	4.01
True Specific Gravity			2.48		2.50	2.40	
True Porosity (%)			5.24		6.40	2.08	
Percent Theoretical density (%)			94.76		93.60	97.92	
Dielectric Strength (kV/mm)						11.3±0.3	

Fig. 22 shows that Bodies A, C, D, E and F had apparent porosity values in the range of industrial vitrification (apparent porosity value of less than 1 percent). The temperature at which apparent porosity is less than 1 percent is said to be the optimum temperature for the development of properties. Two of these bodies, E and F were absolutely non-porous. The higher values for bodies B (5.36 percent) and G (9.16 percent) indicated that these bodies apparently did not fully vitrify at $1300^{o}C$.

Fig. 23 shows that the water absorption values for Bodies A, C, D, E and F were less than 0.5 percent. In particular, bodies C, E and F yielded water absorption values in the range of technical vitrification (less than 0.05 percent). Only bodies B and G had water absorption values greater than 2 percent.

Low values for apparent porosity and water absorption for high clay bodies used in this study were due, in part, to the effective small particle sizes of the clay particles. The smaller the particle size, the higher the speed of vitrification at the maturing temperature the better the vitrification characteristics.

Normally ground quartz and feldspar are generally coarse (25 - 50μ) particles. The addition of a high proportion of quartz led to a reduction in sintering rate.

4.6 True Specific Gravity, True Porosity and Percent Theoretical Density

Table 4.3 shows the calculated values for the true specific gravity, true porosity and percent theoretical density. Bodies C, E and F were selected for these tests because their water absorption and modulus of rupture values indicated that they possessed good vitrification characteristics and were the most promising as electrical porcelain bodies. The true porosity values for the bodies: C (5.24 percent), E (6.40 percent) and F (2.08 percent) indicated that the bodies apparently developed maximum bulk density.

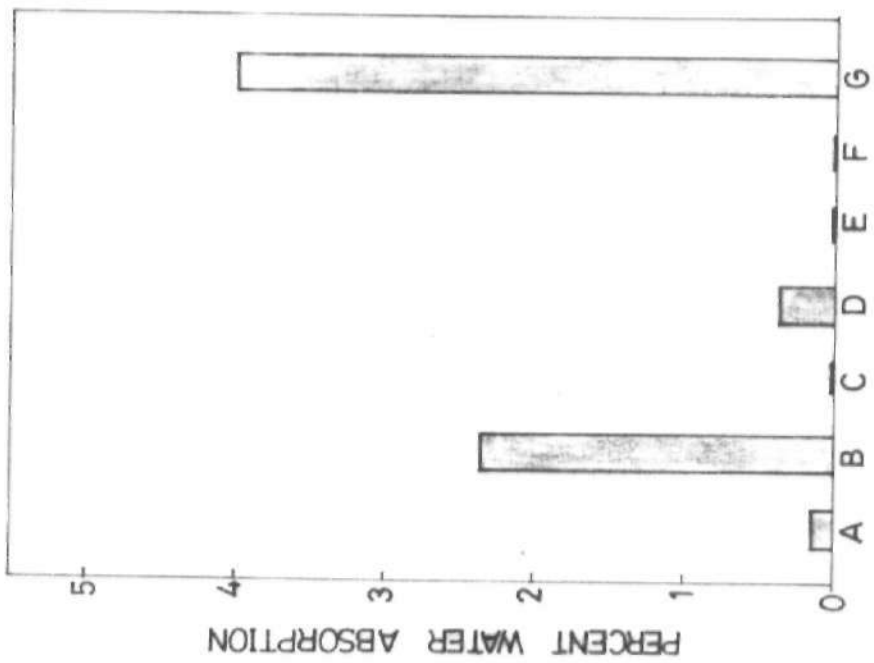


Fig. 23- Effect of variation in body composition on fired water absorption

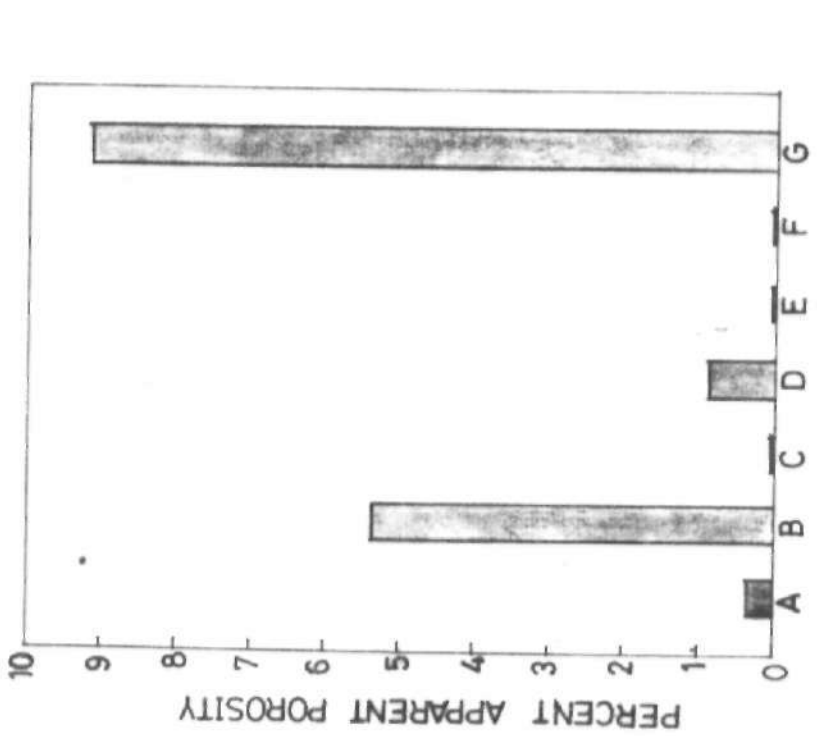


Fig. 22- Effect of variation in body composition on apparent poro

Beech and Norris (1961), and Williams et al. (1963) established close correlation between the bulk density and other physical properties. According to Beech and Norris (1961), bodies fired to about maximum bulk density are vitreous and they possess maximum mechanical and dielectric strength, maximum shrinkage and a minimum of closed pores.

The percent theoretical density of Body F (97.92 percent) suggested that the body attained a value close to its theoretical density as the total porosity was limited to only 2.08 percent. The failure to obtain fully densified body was apparently due to the presence of trapped gases in the closed pores which put a limit to the extent of densification possible during the final stage of sintering.

Attempts had been made to relate microstructural parameters to the mechanical properties observed for fired ceramic bodies. The studies by Ryshkewtch (1953) and Knudsen (1959) revealed that the mechanical strength increases logarithmically with decreasing fractional porosity as shown in Equations (8) and (9). The effect of porosity on the dielectric strength had also been investigated by Gerson and Marshall (1959). They established that the breakdown voltage increases logarithmically with decreasing fractional porosity.

The results of the investigations by Ryshkewtch (1953), Knudsen (1959), and Gerson and Marshall (1959) pointed out the

overriding importance of the porosity test in assessing the mechanical and dieletric strength of fired porcelains.

The observed highest value of modulus of rupture for Body F is in agreement with the statement of Ryshkewtch (1953) and Knudsen (1959) that higher strength is obtained for bodies containing a minimum of closed pores.

4.7 Optical Microscopy

Optical microscopy studies of specimens showed that a significant proportion of quartz remained undissolved in the glass phase. Three types of microcracks were associated with the residual quartz grains. These are termed grain boundary cracks, intragranular cracks and transgranular cracks (Warshaw and Seider, 1967). Grain boundary cracks (Plates III and IV) occurred between quartz grains and adjacent glass phase. Intragranular cracks are confined to within the quartz grains (Plates II and III) while microcracks which cross grain boundaries are termed transgranular cracks (Plate II).

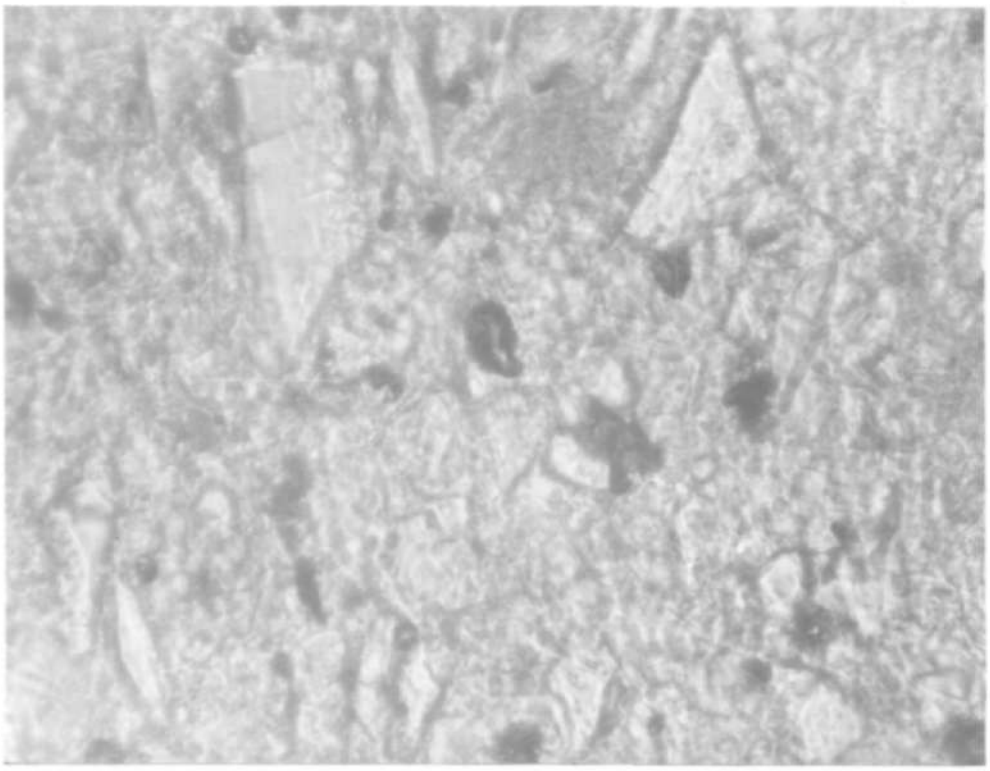


Plate I. Micrograph of a thin section of Body A (1600x).

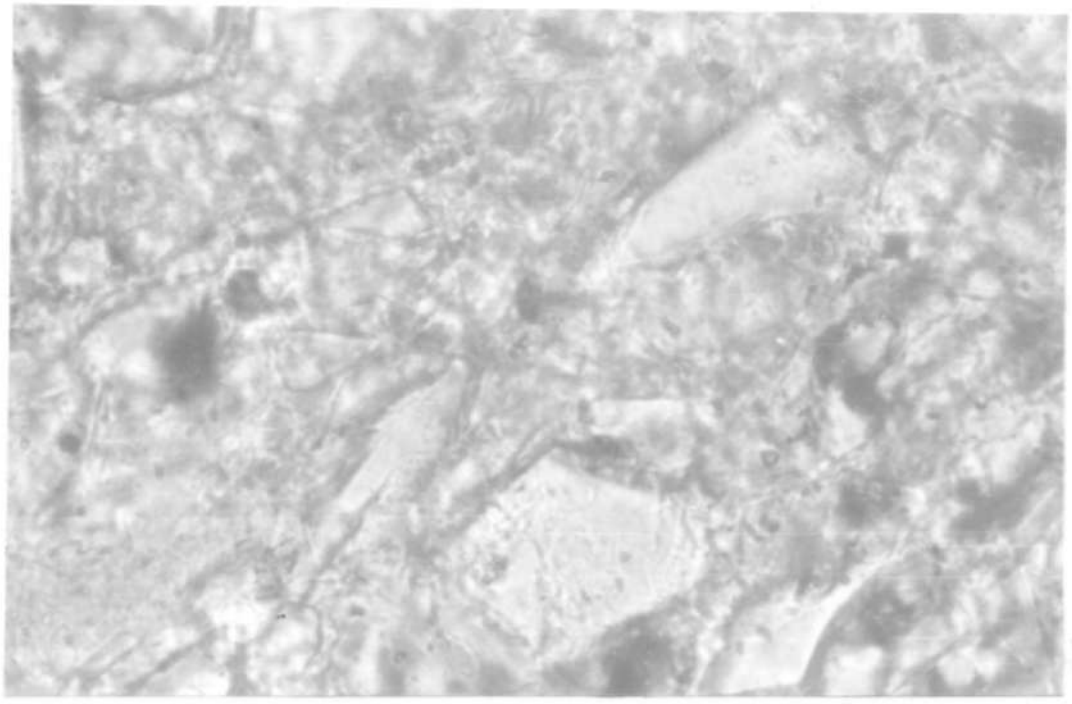


Plate II. Micrograph of a thin section of Body B (2520x).

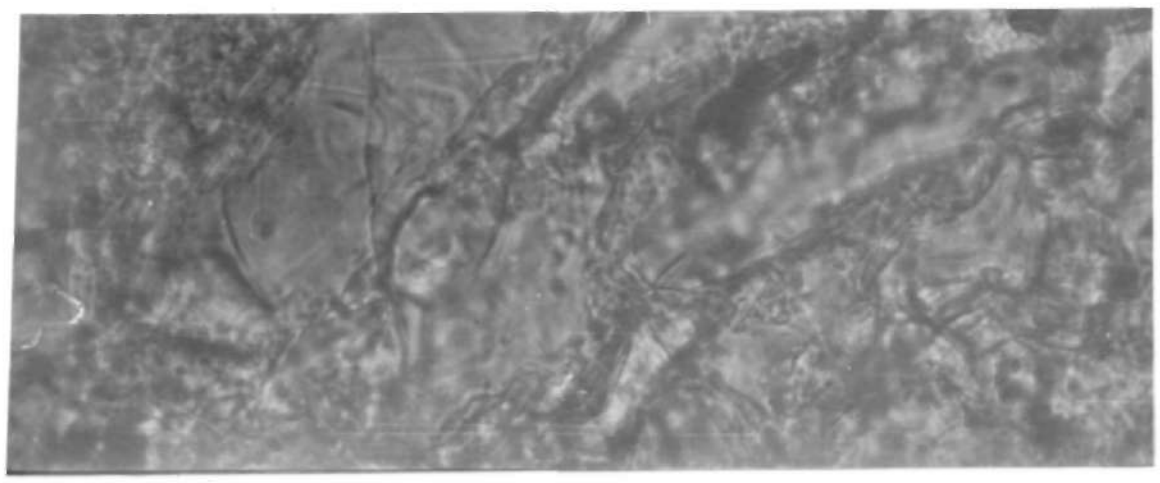


Plate III. Micrograph of a thin section of Body C (2520x).

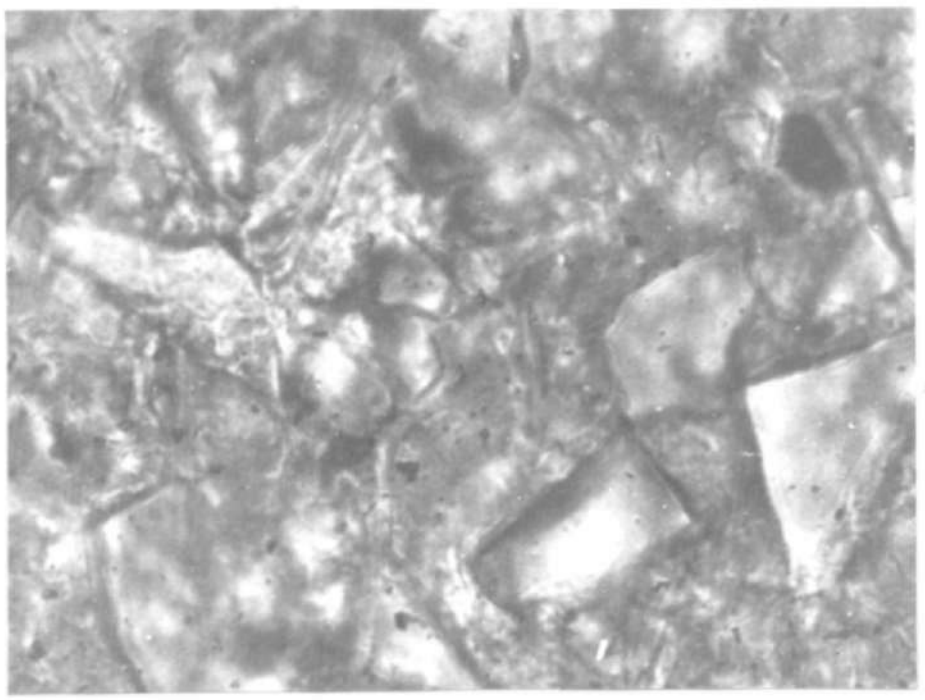


Plate IV. Micrograph of a thin section of Body D (2520x).

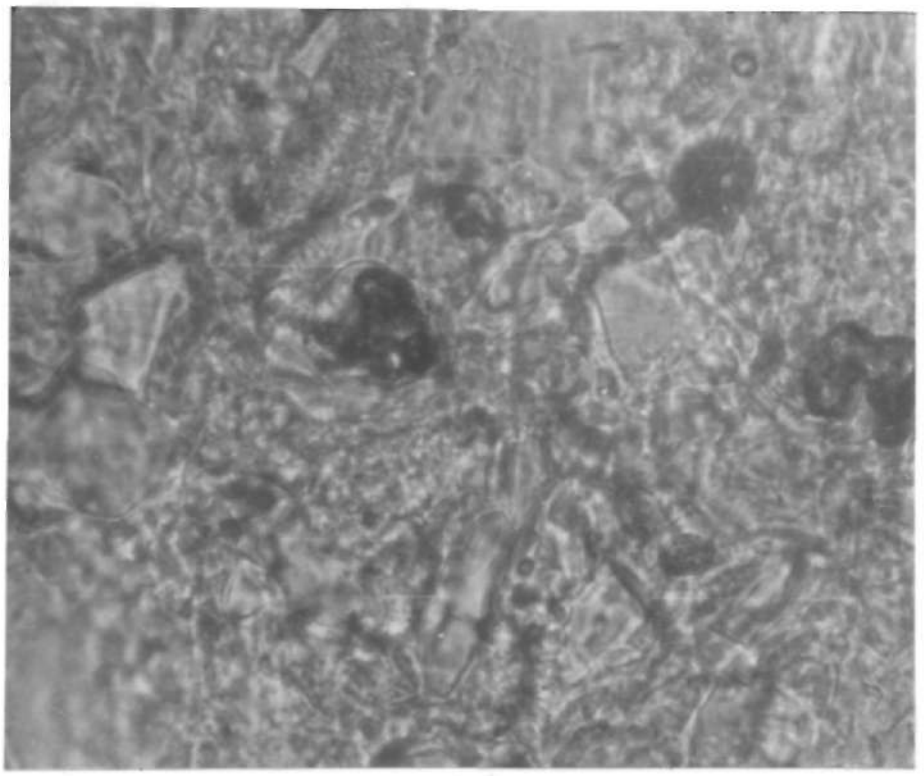


Plate V. Micrograph of a thin section of Body E (2520x).

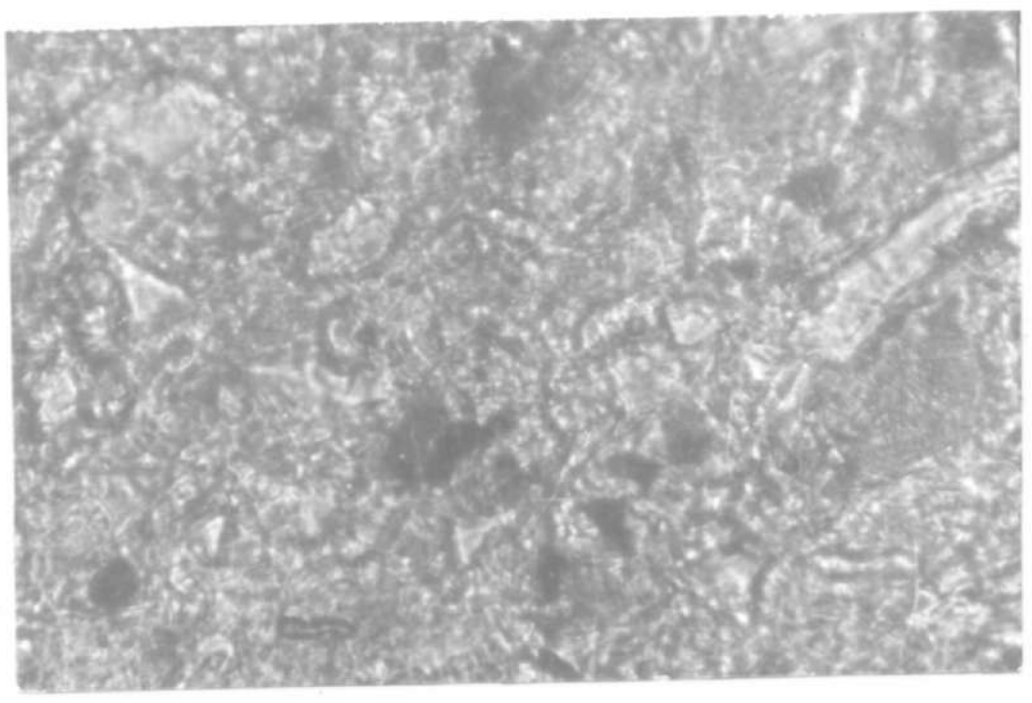


Plate VI. Micrograph of a thin section of Body F (1600x)

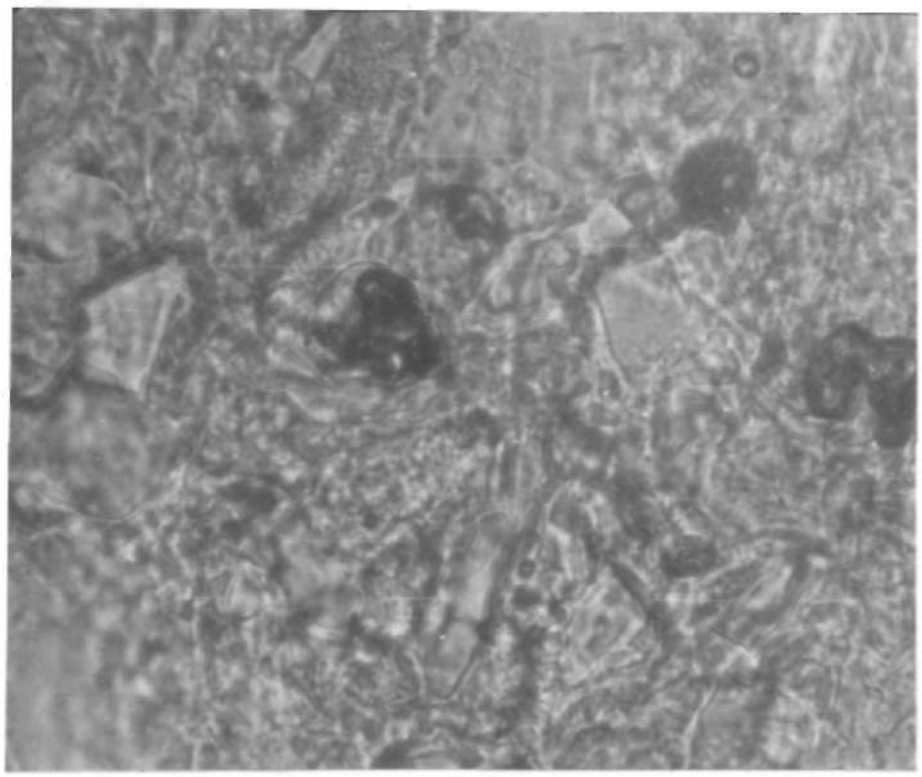


Plate V. Micrograph of a thin section of Body E (2520x).

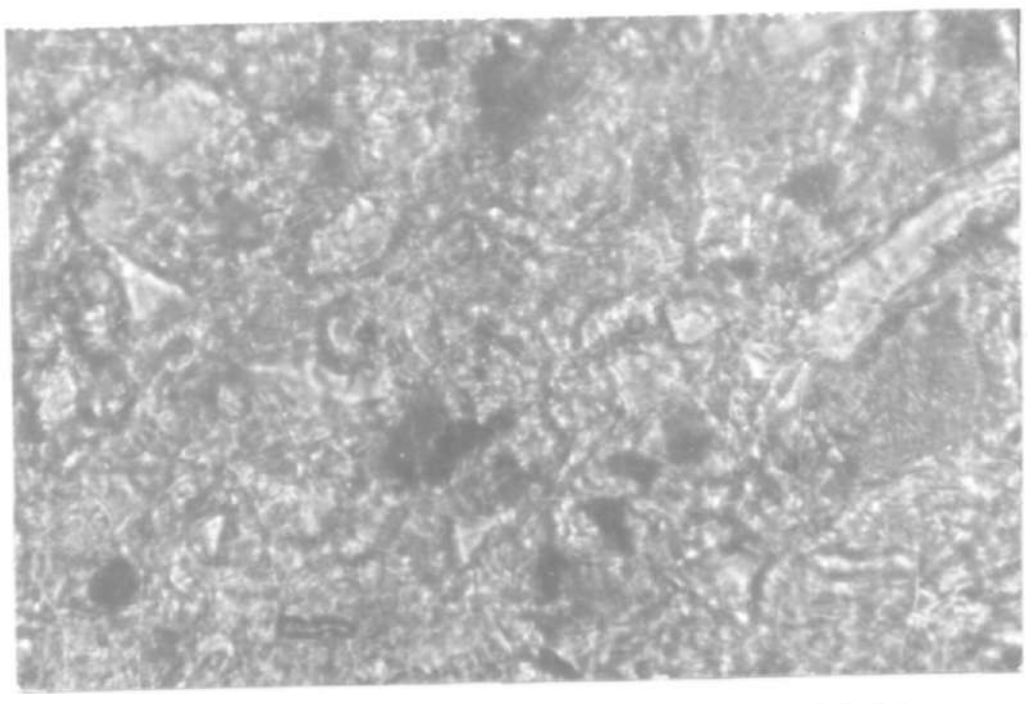


Plate VI. Micrograph of a thin section of Body F (1600x).

The micrograph of Body A (Plate I) showed few pores in addition to the undissolved quartz in the glass matrix. Extensive crackings were not observed in the quartz grains. However, the micrograph of Body B (Plate II) showed that the quartz grains exhibited both intragranular and transgranular cracks. Some of these cracks terminated in the isolated closed pores to form pore-crack system (Oral et al, 1983).

The micrograph of Body C (Plate III) showed that the undissolved quartz grains had grain boundary cracks and intragranular cracks. The solution rims were highly visible and the few isolated pores were situated close to the grain boundaries between the quartz grains and the glass phase. The micrograph of Body D (Plate IV) revealed a large proportion of undisssolved quartz. The angular shapes of the quartz grains showed that they were largely unreacted during firing. The micrograph provided an example of what appeared to be poor interactions between the body constituents during the process of firing.

Few pores, small-sized residual quartz grains and highly visible solution rims characterised the microstructure of Bodies E and F as revealed in Plates V and VI respectively. Mullite crystals could be indistinctly resolved in the micrograph of Body E (Plate V) while these crystals were easily distinguished in the micrograph of Body F (Plate VI).

Bodies with a high proportion of undissolved quartz were associated with intragranular and peripheral cracks which contributed to the observed low mechanical strength of such bodies. These microcracks generally developed as a result of the stresses developed from the differences in the thermal

expansion characteristics of quartz and the adjacent glass phase as well as the inversion and conversion reaction of quartz involving volume changes.

4.8 Dielectric Strength

The average value for the dielectric strength of 11.3 ± 0.3 kV/mm obtained for Body F compared reasonably well with the values reported by Thurnauer (1954) and Lee (1961) as specifications for low - and high-voltage porcelains. Thurnauer (1954) specified a minimum breakdown strength of 9.84 kV/mm for a 6.35mm thick disc-shaped specimen of a body used in high voltage insulation. The specimens used in this test were about the same size. Although dielectric strength depends on a number of factors the comparison on the basis of the size of the test specimen was reasonable.

A summary of the comparison of some of the measured properties in the study with experimental values obtained for electrical porcelains in similar studies is given in Table 4.4. Typical specifications for various types of porcelain are also given in Table 4.5.

TABLE 4.4

Comparison of Some Experimental Values of Electrical Porcelains

Properties	**Umar** (1985)	Russel *et al*. (1949)	Waye *et al*. (1983)	*Results of this study*
Specific Gravity	-	-	-	2.40
Bulk Density (g/cm^3)	2.26	-	2.45	2.35
Apparent Porosity (%)	0.19	-	0.06	0.00
Water Absorption (%)	0.08	0.013	-	0.00
Dry modulus of rupture (MN/m^2)	2.27	3.89	-	3.74
Fired modulus of rupture (MN/m^2)	84.65	89.5	93.8	87
Dry-to-fired shrinkage (%)	11.36	11.55	9.8	12.61

TABLE 4.5

Typical Specifications for Various types of Porcelain

Properties	Technical Porcelain Budnikov (1964)	Low Voltage Porcelain		High Voltage Porcelain	
		Lee (1961)	Thurnauer (1954)	Lee (1961)	Thurnauer (1954)
Specific Gravity	2.3-2.5	2.40	2.2-2.4	2.40	2.3-2.5
Bulk Density (g/cm^3)	2.25-2.35	-	-	-	-
Water Absorption (%)	up to 0.5	0.0-1.5	0.5-2.0	0.0-0.10	0.0
Bending Strength (MN/m^2)	68.6-88.2	41.46	24.13-41.36	72.39	62.05-103.4
Mean Coefficient of Linear expansion (c^{-1})	3.8×10^{-6}	-	$5.0\text{-}6.5 \times 10^{-6}$	-	$5.0\text{-}6.8 \times 10^{-6}$
Thermal Shock Resistance	-	-	moderate	-	moderately good
Dielectric Strength (kV/mm)	-	9.84	1.58-3.94	9.84	9.84-15.75
Dielectric Constant	-	6.0	6.0-7.0	6.0	6.0-7.0
Te - value (^{o}C)	-	-	300-400	535	200-500

This study had showed that changes in green and fired properties of a porcelain body may be brought about by varying the body composition. It is also well known that improvement in some of the properties are a consequence of the processing conditions which are applied in the production of the specimens. Such factors as ball milling time for individual constituents and body mixture, water content, types and concentration of electrolytes, as well as firing conductions (rate of heating, peak temperature, soaking period, cooling rate and duration of the firing schedule) are important process variables which must be adjusted if bodies must develop their optimum properties.

The results of this study indicated that Bodies C, E and F apparently developed optimum properties when assessed by the bulk density, porosity and water absorption tests. It is suggested that the processing conditions established for this study would be applicable for industrial production of electrical porcelain provided the same raw materials were used and the body compositions limited to the range of compositions for Bodies C, E and F.

It is pertinent to make a reference to the recent work by Umar (1985). The body composition investigated by the author consisted of 31 percent Kankara clay, 15 percent Bomo clay, 34 percent Okene feldspar and 20 percent Amper quartz. The results of the property tests are indicated in Table 4.4. The values for the bulk density, apparent porosity and water absorption suggested that the body did not develop optimum properties. It was probably under-fired, although it could also have been over-fired. However,

Body F which was one of the bodies investigated in the study consisted of 45 percent Kankara clay, 5 percent Bukuru clay, 25 percent Okene feldspar and 25 percent Amper quartz. It had zero water absorption and apparent porosity indicating that the body developed good vitrification characteristics.

CHAPTER FIVE

SUMMARY AND CONCLUSION

5.1 General

X-ray studies of the crystalline phases in the various raw materials established that kaolinite was the predominant crystalline specie in Kankara and Bukuru clays. Orthoclase was detected in Kankara clay as impurity while quartz was present in Bukuru clay. Okene feldspar consisted of a mixture of microcline and orthoclase and the absence of some peaks characteristic of microcline and orthoclase suggested that they probably existed as a binary solid solution in the deposit. The only crystalline phase detected in Amper quartz was alpha quartz.

The apparent viscosity of Kankara clay slip increased from 21.30 to 36.50 poises as the sodium carbonate concentration was increased from 0.001 to 0.005 percent. However, the apparent viscosity of Bukuru clay slip decreased from 42.0 to 17.5 poises as the sodium carbonate concentration increased from 0.005 to 0.05 percent. The unusual increase in the apparent viscosity of Kankara clay slip was attributed to a reduction of electrical potential at the clay surfaces and the formation of flocs as a result of the migration of excess sodium ions close to the clay surfaces. Only silicate ions of the two deflocculants, sodium carbonate and sodium silicate, appeared to have the greatest beneficial effect on the rheological properties of Kankara clay, Bukuru clay and porcelain body slips. Kankara clay-based porcelain slip could only be satisfactorily deflocculated when

the water content was increased to 33 percent. A minimum apparent viscosity value of 8.50 poises was obtained for the porcelain body slip at 0.06 percent sodium silicate concentration. The slip exhibited considerable thixotropy as the sodium silicate concentration was increased from 0.017 to 0.052 percent. However, it was destroyed completely when the concentration exceeded 0.061 percent.

For the bodies investigated, both green and fired modulus of rupture increased with clay content and for a given clay content they increased as the quartz content was increased from 20 to 25 percent and decreased as it was further increased to 30 percent.

The dry-to-fired shrinkage for the bodies investigated was approximately 12.5 percent while the average differential shrinkage between diameter and length was about 1.25. This was due to the preferred orientation of the clay platelets during the process of forming.

The porosity and water absorption values for the high feldspar body C, and high clay bodies E and F were less than 1 percent which is well within the range of industrial vitrification. However, the values of these properties for the high quartz bodies B and G were higher than 2 percent. These high values suggested that these bodies did not sufficiently vitrify at 1300^{o}C.

Microscopic studies of thin sections of the fired specimens showed that a significant proportion of quartz remained undissolved in the glass phase. Some of the residual quartz grains showed extensive fracturing.

Comparison of the properties of the porcelains developed with standard specifications for low and high voltage porcelain insulators clearly indicated that Bodies A, C, D and E are only suitable for low voltage applications while Body F is suitable for both low and high voltage insulation.

The results of this study have established suitable body compositions and the processing conditions for the production of electrical porcelains from local raw materials as opposed to imported ones.

5.2 Recommendations for Further Studies

The raw materials used in this study were characterised by their sources and by X-ray diffraction technique However, this is inadequate if these materials are to be compared to materials from other sources. It is recommended that characterization by chemical analysis, differential thermal analysis, thermogravimetry, infra-red spectroscopy, X-ray analysis, particle size and shape analysis, and electron microscopy must be carried out on the raw materials if their character must be well understood to permit the formulation of a body of predictable characteristics.

In this study direct comparison of bodies were made possible by limiting the variation in body composition to a small range. However, when comparing a large number of body compositions over a wide region of the triaxial diagram, the range-curve method, as described by Norris et al.(1979), is recommended for direct comparisons to be made under identical firing conditions.

Further studies aimed at formulating a suitable glaze composition should be initiated to facilitate the acquisition of relevant information for the commercial production of glazed and unglazed electrical porcelain insulators. It is recommended that research be aimed at the optimization of physical properties of porcelain by improvements in the processing conditions and through the use of mineralisers and quartz alternatives. This will facilitate the development of the capacity to produce specialised ceramic products such as spark plug insulators, mechanical components for industrial applications and various porcelain wares resistant to thermal shock and chemical attack.

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APPENDIX A

SEARCH MANUAL (JCPDS) FOR QUARTZ, KAOLINITE MICROCLINE AND ORTHOCLASE

5-0490 QUARTZ

dÅ	I/I_1	hkl
4.26	35	100
3.343	100	101
2.458	12	110
2.282	12	102
2.237	6	111
2.128	9	200
1.980	6	201
1.817	17	112
1.801	<1	003
1.672	7	202
1.659	3	103
1.608	<1	210
1.541	15	211

29-1488 KAOLINITE

dÅ	I/I_1	hkl
7.10	100	001
4.41	60	02-
3.56	100	002
2.55	25	201,130
2.491	30	135,200
2.430	5	-
2.375	20	003
2.327	40	202,131
2.20	5	132,201
1.980	10	203,132

APPENDIX A CONTD.

22-687 MICROCLINE

dÅ	I/I_i	hkl
6.736	5	110
6.486	5	001,020
5.923	4	$\bar{1}\bar{1}1$
5.800	3	$\bar{1}11$
4.603	3	021
4.213	51	$\bar{2}01$
3,984	12	111
3.924	6	$1\bar{1}1$
3.849	-	200
3.831	30	130
3.704	30	$\bar{1}30$
3.652	11	$\bar{1}\bar{3}1$
3.595	9	$\bar{2}\bar{2}1$
3.566	6	$\bar{1}31$
3.478	29	$\bar{1}\bar{1}2,\bar{2}21$
3.466	26	$\bar{1}12$
3.368	41	220
3.286	48	$\bar{2}02$
3.246	100	$\bar{2}00,002$

22-462 ORTHOCLASE

dÅ	I/I_i	hkl
6.44	60	020
5.86	20	$\bar{1}11$
4.25	30	$\bar{2}01$
4.02	90	111
3.80	80	130
3.49	20	$\bar{1}31,\bar{1}12$
3,33	70	220
3.18	100	040,002
3.00	70	131
2.93	70	$\bar{2}22$
2.83	60	022
2.65	60	$\bar{1}32$