Reformulation of Fine Translucent Porcelain

Kai Ming Kian

CONTENTS

Acknowledgments

I would like to dedicate this thesis to my parents and my wife for their patience, help and support.

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Summary

A low-clay version of fine translucent china was designed to have desired properties and acceptable behaviour during manufacture.

Low-clay contents of 10 to $15^{w}/_{0}$ were employed to reduce the deterious effects of preferential clay particle alignment and its adverse effect on colour. For example, alignment of clay particles in cast wares causes anisotropic drying and firing shrinkages and these cause distortion. Replacing clay with a prefired body with low Fe and Ti contents, as in the present case, allowed a very white material to be produced. The prefired body was made with calcium carbonate, aluminium trihydroxide, quartz and a small fluxing addition of an hydrated magnesium carbonate.

Desification of a whiteware is enhanced by increasing volume fraction of the viscous liquid and reducing by its viscosity. Both of these also enhance sagging. Consequently, compositional change cannot on its own lead to the favourable combination of high density, required to give translucency, with little sagging, that will allow wares to be fired without significant distortion. It was found by trail and error that use of finer particles reduced the sagging occurring in the densification heat treatment and enhanced densification. This finding allowed the body to be designed so that it densified without sagging excessively.

After establishing this important result, an iterative approach was employed to produce a ware that was very white , translucent , had the required thermal expansion coefficient for glaze fitting, shrank acceptably during the first firing and did not sag during the second firing that stimulated glost firing.

The finding on sagging was applied to an anorthite/mullite porcelain body that was under development. This body was also made with a low-clay content and the same prefired body. This whitware has potential to replace bone china and hard porcelain for use in the servere service conditions of hotels and restaurants. It has a higher fracture toughness than hard porcelain but has the same scratch resistant glaze and is more resistant to thermal shock. The sagging of the anorthite/mullite porcelain was substantially reduced while the body was densified. This was achieved by using a combination of finer particles and a reduction in the liquid-phase content that developed during firing.

Abbreviations

CPF	Coarse prefired
FPF	Fine prefired
FTC	Fine translucent china
NS	Nepheline syenite
PDS	Product design specification
PEGs	Polyethelene glycols
PMMA	Polymethylmethacrylate
PSD	Particle size distribution
PVA	Polyvinyl alcohol
TEC	Thermal expansion coefficient

Chapter 1 Introduction and Aims of The Present Study

1.1 Previous Studies on Low-clay Whitewares at Sheffield

This project was part of a programme of work at Sheffield to investigate whether whitewares made with a low-clay content offer worthwhile advantages over their conventional equivalents. Whitewares are ceramics that are white in colour, are conventionally made with 30 to 60 $^{w}/_{o}$ clay and are used for a range of products, e.g. tableware ceramics, sanitary wares and for high-voltage insulators. Most of the studies in the Sheffield programme have been directed towards tableware ceramics.

In addition to clay, conventional whitewares are made with a flux and a filler. The flux is either Cornish stone, feldspar, nepheline syenite or bone ash. The filler is most usually quartz but can be alumina or bone ash.

There are several reasons for reducing the clay content to the 10 to 15 $^{w}/_{o}$ level used in the Sheffield studies. Most are because clay causes the shrinkage that occurs on both drying and firing to be anisotropic. Significantly, reducing the clay content precludes the use of traditional wet plastic forming techniques. However, for production of tableware ceramics in countries with high labour costs, wet plastic forming is being replaced by powder pressing for flatwares and pressure casting for items that cannot be pressed. In future, injection moulding may be introduced to produce cups with attached handles. These techniques should be suitable for low-clay bodies with the addition of suitable binders and plasticisers.

The first worker at Sheffield to use a highly reduced clay content was Okojie (1992). His thesis dealt with a body whose conventional equivalent was electrical porcelain. That is, a whiteware based on clay, feldspar and quartz. He replaced part of the raw clay with prefired clay (EEC Molochite). He found that he could obtain similar strengths to those of conventional electrical porcelains but with lower fracture toughness values. That is, his low-clay whitewares tended to contain fracture-initiating flaws of smaller size than in conventionally produced material.

The second worker was Mohd.Noor (1995). He examined the use of four different prefired whiteware bodies as the replacement for part of the raw clay, in quartz-containing vitrified bodies. Two of the prefired bodies were fluxed with feldspar and two with mica. Two of the bodies, one made with each flux, were prepared with a combination of aluminium trihydroxide and quartz to reduce the iron oxide content to improve whiteness. One whiteware was made with a commercially-produced calcined clay as the prefired component. All the whitewares produced were opaque and, like the low-clay whitewares made by Okojie, the fracture toughness values were lower than for conventional wares but the strengths in some cases were comparable. The increase in cost without significant improvement in properties means that it is unlikely that such the low-clay whitewares would be viable commercially.

The third worker was Capoglu. He developed white translucent bodies with a low-clay content, which are described in a patent (Messer et al 1998). One body was labelled W3 in the patent. He used a prefired body consisting of anorthite, mullite and glass to replace both part of the clay and the flux and filler. This was labelled M17 in the patent. The final bodies were composed of 10 to 15 $^{w}/_{o}$ clay and two prefired materials. These had the same composition but each was milled to have a different median particle size. The coarser component had a median particle of ~20μm and the finer had a median size of ~2μm. These were used to achieve efficient particle packing with the micron to submicron clay. Bodies made with 10 to 15$^{w}/_{o}$ clay had thermal expansion coefficients from 4.5 to $5*10^{-6}$/°C, which means that a chemically durable and scratch-resistant glaze having a high-silica content can be applied to the wares.

The fourth worker, Jafari, (1995) applied the low-clay approach to bone china. He produced white, translucent bodies with both reduced clay and bone ash contents. These bodies have to be called bone porcelains as they do not fit the British Standard specification of containing at least $35^{w}/_{o}$ β-tricalcium phosphate to be called bone chinas. They had significantly lower thermal expansion coefficients than bone chinas ($6.5*10^{-6}/°C$ compared to 8.5 to $9*10^{-6}/°C$) as a result of the reduction in the β-tricalcium phosphate content as this phase has a thermal expansion coefficient of $\sim 12*10^{-6}/°C$ (Iqbal et al 2000). These bone porcelains were made with the prefired body developed by Capoglu.

In parallel with the study carried out by the author, two other workers were engaged studying low-clay whitewares of the of the type developed by A.Capoglu. These workers were Batista (2001) and Wong (2001).

Batista and the present author were concerned with anorthite/ mullite porcelain bodies, adapted from the W3 composition, which were prepared in the large quantities in the pilot plant of WBB Technology Ltd in Newton Abbott Devon. S.Batista initially carried out laboratory studies on mixing and calcination of the prefired body made in the pilot plant by Dr. West. Dr. West was a research assistant employed on an EPSRC research grant. The importance of producing the whiteware on a substantial scale in the pilot plant was that a spray dried press body could be prepared. The use of a spray dryer producing sufficiently coarse granules for pressing typically requires batch sizes of at least 50 kg. One aim of Batista's project was to design a granulate that could be fully compacted at the low pressures (~30MPa) employed in automated commercial flatware presses, without the granulate adhering to the press tooling, to form ware that would have sufficient strength to be fettled and handled robotically. This work was carried out as simultaneously the particle size of the prefired bodies were altered to improve the densification behaviour of test pieces, which were used to investigate fracture toughness and strength. Bend strengths in excess of the target value of 100MPa were achieved. A major reason for studying material formed from a spray dried granulate was to see whether using a low clay content would prevent enlarged pore formation occurring during firing. Such pores develop in wares made with a substantial ball clay content as a consequence of clay particle alignment in the granules. Typically, this causes an additional residual porosity of around 3% that reduces fracture toughness and strength. No enlarged pores within the compacted granules were found after firing for the low-clay bodies

The aims of the study carried out by Wong (2001) were to design an injection moulding feedstock, to use it to mould a cup with an attached handle and to investigate whether the low-clay moulded material would shrink in an essentially isotropic manner. The binder system adopted was developed in the Department to be partially leachable using water as the solvent (Anwar et al 1995,1996). It was initially composed of $80^{w}/_{0}$ water-soluble polyethelene glycols (PEGs) with molecular weights of 600, 1000 and 1500, and $20^{w}/_{0}$ polymethylmethacrylate (PMMA). The PMMA was introduced in the form of an aqueous emulsion comprising $40^{w}/_{0}$ of the polymer having particles of 0.1 to 0.2 μm diameter. Its function was to hold the mouldings together during leaching. The feedstock was designed using iteration of its solids content, the low-clay whiteware body composition, the particle sizes of the prefired bodies and the composition of the binder. Wong successfully moulded the cup and showed that shrinkage of the injection moulded material was essentially isotropic. This means that cups can be glazed after leaching and drying and then fired without developing an oval cross-section. The binder developed in this study consisted of $75^{w}/_{0}$ PEG_{3400} + $15^{w}/_{0}$ PMMA+$10^{w}/_{0}$ Stearic acid. The stearic acid was introduced as a lubricant, which allowed higher solids content feedstocks to be moulded. These were typically~$63^{v}/_{0}$. The higher molecular weight PEG (molecular wt. 3400) was used to shorten the time required for the moulding to set.

1.2 The Present Study and Its Aims

In the present study, a prefired body composed of anorthite, mullite and glass was used in a study mainly directed at producing a fine translucent china. A leading manufacturer has a problem in manufacturing conventional fine translucent china as larger diameter plates tend to sag during the second firing in which the glaze is fired-on to the plates. An objective of this study was to see whether a viable fine translucent china could be designed and produced which would not have this problem In addition, an important finding on sagging learnt whilst developing the fine translucent china was applied to improve the design of the body (W3) developed by Capoglu. The W3-type of body is thought to have significant commercial potential, if it can be produced at an acceptable cost. With this in mind, attempts were made to produce a body with lower content of prefired material, in a manner similar to that employed in the first phase of the study on fine translucent china.

A design approach was adopted in these studies. This involves establishing the product design specification and endeavouring to achieve the specified objectives and constraints using an iterative approach to process and product development. The methodology of this approach is discussed in section 2.3.1.

Although the previous studies on low-clay whitewares have demonstrated that the materials have some advantages over their conventional equivalents there are disadvantages. A common disadvantage is the additional cost of replacing a naturally occurring mineral with a prefired component. However, there is little prospect that a novel whiteware with significantly improved set of characteristics and behavioural properties can be made by simply using the conventional raw materials as, in the long history of whitewares, all potentially viable combinations are likely to have been tried.

Chapter 2 Background

2.1 Introduction

In this chapter, topics relevant to the present study are introduced. In order to understand more fully the reasons for the consequences of the compositional design of the whitewares studied in this project, e.g. why a low clay content is used or how translucency is attained, a background on whitewares is given. Unless otherwise stated the information on whitewares is taken from the text books by Dinsdale(1986), Rado(1988) and Ryan and Radford(1987). This chapter starts with a brief description of the raw materials used both conventionally and also used in the present work and their roles in the forming and firing. The types of whiteware currently made are reviewed. Emphasis is placed on the characteristics and behavioural properties of the translucent wares with which the low-clay versions have to complete. This is followed by a description of the methods used to prepare bodies and form them into the required tableware shapes. Emphasis is placed on powder pressing and casting as these are used in the present study. Consideration is then given to viscous composite sintering, the process by which densification occurs in both conventional wares and those investigated in this study.

A design methodology was adopted in the present study. That is, the objective was to design a total process, from the starting materials through to the fired product, to produce a product with specified properties after firing and manageable behaviour during processing. Before giving the thinking and methodology employed, it is necessary to introduce some general ideas on ceramic properties and processing. These are followed by an outline of the design approach adopted and discussion of the uniformity concept that is used to interpret some of the observations.

2.2 Background on Whitewares

2.2.1 Raw Materials

The raw materials for whitewares can be grouped by their function as: clays, fluxes and fillers

Clays used in the whitewares industry have as their major constituent the mineral kaolinite with ideal formula

$$Al_2O_3.2SiO_2.2H_2O.$$

This has a layered crystalline structure which leads to the particles having a platy shape.
Clay is formed from the weathering of feldspar in granite. Clay found at the site of conversion is called primary or residual clay, whereas clay transported from the site of conversion, usually by water, is called sedimentary clay.

China clays are residual clays composed largely of kaolinite and mica. These are white-burning materials because they are relatively low in Fe_2O_3 and TiO_2. Typical compositions are shown in Table 2.1. Particles have platelet diameters from submicron to a few microns and thicknesses 1/30 to 1/5 of the diameter. The clay is washed out of the rock using high pressure water jets. Quartz and coarse mica are removed by sedimentation.

Kaolins are sedimentary clays mainly composed of kaolinite with small amounts of montmorillonite , silica and mica and other minerals. The particle sizes are similar to those of china clay. These clays fire white to cream in colour. Typical compositions are shown in Table 2.1.

Ball clays are sedimentary clays having only a moderate kaolinite content. They contain some organic materials such as lignite and minerals such as quartz, illite, montmorillonite and mica. These clays tend to be very fine with most of the platelets having diameters that are submicron in size. They have higher contents of both $Fe_2O_3$and TiO_2 than found in china clays and burn to a cream to brown or grey colour .Typical compositions are shown in Table 2.2.

Fluxes include such materials as feldspar, nepheline syenite and Cornish stone. The feldspar minerals are albite, with an ideal formula of $Na_2O.Al_2O_3.6SiO_2$, and orthoclase, with an ideal formula of $K_2O.Al_2O_3.6SiO_2$. Feldspars contain both sodium and potassium. Those that mainly contain sodium are called soda feldspars and those that mainly contain potassium are called potash feldspars. With a more even mixture of sodium and potassium, the feldspars are called mixed soda-potash feldspars. Nepheline syenite contains the mineral nepheline ($Na_2O.Al_2O_3.2SiO_2$) as well as feldspars. Cornish stone is used in England and is a partially weathered granite consisting of feldspar, mica, quartz and kaolinite. It is less powerful than nepheline syenite. Typical compositions of the fluxes are given in Table 2.3. The feldspars contain substantial fractions of quartz, whereas nepheline synite is essentially quartz free. They are all low in Fe_2O_3. Fluxes are ground to have median particle sizes of about 10 μm.

Fillers include quartz, alumina and bone ash. Quartz can be beneficiated sand, quartzite rock or calcined and ground flint pebbles (in England this is called flint-in the USA flint can be fine quartz). Quartz that is low in Fe_2O_3 is used. It is ground to have median particle size~10μm.

Alumina is sometimes used to replace part or the whole of the added quartz in whitewares to increase the strength.

Bone ash is calcined and ground cattle bone. Chemically it is hydroxyapatite ($Ca_5.(PO_4)_3.OH$). It is used in bone china partly as a flux but mainly as a filler.

Location/content,%						
Material	**Georgia (USA)**	**North Carolina (USA)**	**South Carolina (USA)**	**Florida (USA)**	**Cornwall (UK)**	**Cornwall (UK)**
Compound						
SiO_2	44.4	47.3	44.6	46.1	48.0	50.2
Al_2O_3	39.6	36.4	39.5	38.8	36.9	34.1
Fe_2O_3	0.4	1.0	0.5	0.7	0.7	0.8
TiO_3	1.7	0.1	1.4	0.4	-	0.1
CaO	-	-	0.1	0.2	0.1	-
MgO	-	-	0.1	-	0.3	0.3
K_2O	0.1	1.3	0.5	0.3	1.6	4.1
Na_2O	0.1	0.3	-	-	0.1	0.2
Ignition loss%	13.7	13.6	13.3	13.5	12.3	10.2
Mineral						
Kaolinite	-	-	-	-	84.0	66.0
Mica	-	-	-	-	13.0	23.0
Quartz	-	-	-	-	-	-
Feldspar	-	-	-	-	1.0	9.0
Other	-	-	-	-	2.0	2.0

Table 2.1 Typical china clay and kaolin compositions (ASM Handbook 1991)

Location/content, %						
Material	**Kentucky (USA)**	**Kentucky (USA)**	**Tennessee (USA)**	**North Devon (UK)**	**South Devon (UK)**	**Dorset (UK)**
Compound						
SiO_2	55.6	51.6	61.0	63.0	52.0	54.0
Al_2O_3	28.6	28.6	24.5	24.0	30.0	30.0
Fe_2O_3	1.0	0.9	1.0	0.9	1.2	1.4
TiO_2	1.8	1.7	1.3	1.5	1.0	1.2
CaO	0.1	0.1	0.1	0.2	0.2	0.3
MgO	0.4	0.5	0.1	0.4	0.4	0.4
K_2O	1.1	0.5	1.7	2.4	2.1	3.1
Na_2O	0.1	0.2	0.4	0.5	0.3	0.5
Ignition loss, %	11.4	15.9	9.7	6.8	12.2	8.8
Mineral						
Kaolinite	-	-	-	45.0	64.0	57.0
Mica	-	-	-	28.0	22.0	32.0
Quartz	-	-	-	26.0	11.0	11.0
Feldspar	-	-	-	-	-	-
Other	-	-	-	1.0	3.0	-

Table 2.2 Typical ball clay composition (ASM Handbook 1991)

Oxide(%)	**Potash feldspar**	**Soda feldspar**	**Cornish stone**	**Nepheline syenite**
K_2O	11.9	2.2	4.6	9.8
Na_2O	2.8	8.0	3.7	7.4
Al_2O_3	19.0	19.9	12.0	24.0
SiO_2	65.8	67.2	76.0	57.0
K_2O+Na_2O	14.7	10.2	8.3	17.2

Table 2.3 Chemical composition of fluxes (A.Dinsdale 1986)

2.2.2 Roles of the components

Green state

Clays, particularly ball clays, with added water produce a plastic or workable mass. Ball clays also provide binding power, i.e. green strength to the body.

The flux and filler particles are relatively coarser than the clay particles, particularly the ball clay, which allows efficient particle packing to be achieved. These coarse particles increase the stiffness of wet bodies and reduce the tendency of such bodies to slump. That is they raise yield stress. They reduce shrinkage during drying and hence reduce drying distortion. Similar results occur when coarse-ground fired clay or whiteware body, known as grog, is added to the body.

During firing

Clay provides fine pores to drive the densification process. Clay reacts with feldspar to produce a viscous liquid, which, in endeavouring to minimise the liquid surface area, closes the pores.

Feldspars provide alkali oxides to reduce the viscosity of the alkali aluminosilicate liquid.

Quartz at temperatures of ~ 1100°C is hardly reactive and hence is a filler. It progressively dissolves as the temperature is raised by alkali oxides diffusing into the quartz grains. This produces a solution rim around the dissolving quartz grains. The absorption of the alkali oxide increases the viscosity of the alkali aluminosilicate liquid and increases the firing range of the body.

Alumina hardly dissolves in the surrounding viscous liquid during firing and is more accurately described as a filler than quartz.

Bone ash releases calcium oxide, which reacts with the clay to form anorthite, to become beta tricalcium phosphate. If further calcium oxide is removed by reaction with the clay, low melting point phosphates form transient liquids which aid densification but exacerbate sagging (Jaffari, 1995)

On cooling

Quartz undergoes a phase transformation from β to α quartz. This involves a small contraction, which can put the glaze into compression.

2.2.3 Whiteware Body Compositions

Several whiteware bodies have compositions based on about 50% clay, e.g. of 25 $^{w}/o$ china clay and 25 $^{w}/o$ ball clay, and 25 $^{w}/o$ feldspar and 25 $^{w}/o$ quartz. A mixture of clays is used that provides an acceptable combination of whiteness and plasticity or workability. Typical body compositions are given in Table 2.4.

Bodies can be classified on the basis of either containing open porosity or not. Bodies with open porosity are earthernwares. Bodies with no open porosity are said to be vitrified. These are electrical porcelains, sanitarywares, stonewares, porcelains, fine translucent chinas and bone chinas. The vitrified bodies can be divided into two groups depending on whether they are opaque or translucent. Electrical porcelains, sanitarywares and stonewares are opaque, whilst porcelains, fine chinas and bone chinas are translucent.

	Earthenware	**Bone china**	**Hard porcelain**	**Sanitary whiteware**	**Sanitary fireclay**	**Wall tile**	**Electrical Porecelain**
Clay							
Ball clay	25	-	10	23	-	22	25
China clay	25	25	40	24-	-	22	25
Fireclay	-	-	-	-	60	-	-
Flux							
Stone	15	30	-	-	-	15	-
Feldspar	-	-	20	20	-	-	25
Filler							
Quartz/ Flint	35	-	30	33	-	41	25
Bone	-	45	-	-	-	-	-
Grog	-	-	-	-	40	-	-

Table 2.4 Typical body compositions (Dinsdale,1986)

In whitewares that are translucent, a small proportion of light which is incident on the surface of the ware passes through to emerge from the opposing surface. The emergent light has undergone substantial scattering at internal boundaries, where there is a change of refractive index. Consequently, the light emerges in a diffuse manner. The intensity of the transmitted light decreases exponentially with the thickness of the ware as illustrated in Figure(2.1).

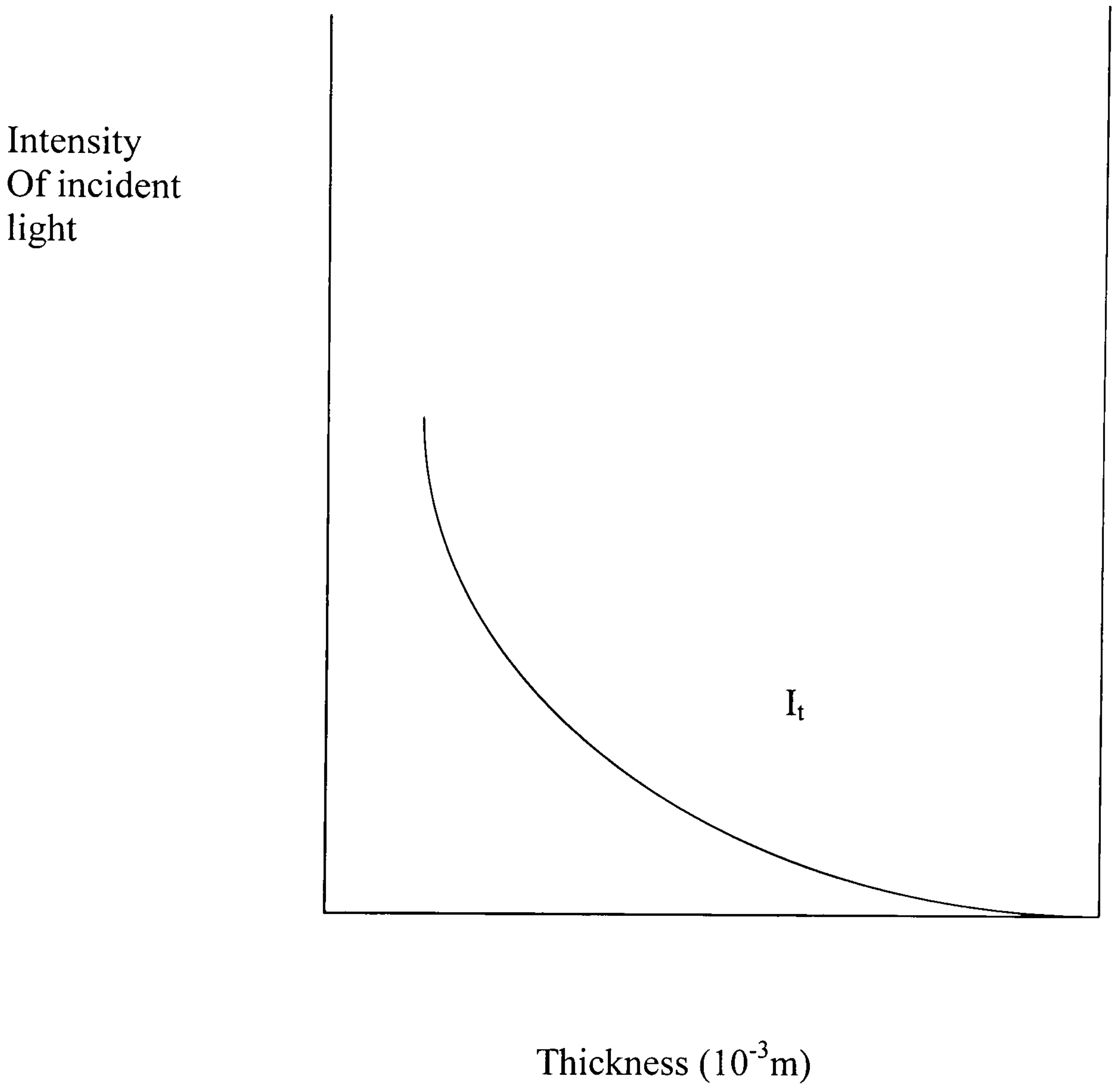

Figure2.1 Transmission for a sample of bone china at various thickness.

To enhance translucency, the scattering of the light passing through the whiteware has to be minimised. This is achieved by having only a small difference in the refractive indices of the solid phases at each of the phase boundaries. Translucent wares consist of crystalline grains and pores dispersed in a glassy matrix. The grains should have refractive indices that are similar to that of the glass. It is also necessary to keep the number of boundaries encountered by light travelling through the ware to a minimum. To achieve this, the grains should preferably be a few microns in size and the concentration of the pores has to be minimised.

Fine Translucent China (FTC)

Materials in this category can be called soft porcelains. They are biscuit fired at temperatures around 1230°C under oxidising conditions and glost fired at around 1100°C. There is little property data available on this class of whiteware. They are made in the U.K from white firing clay (~33 $^{w}/_{0}$) with quartz as a filler (~33 $^{w}/_{0}$) and Cornish stone (~33$^{w}/_{0}$) as the flux. The flux and filler are the coarse components of the body with median sizes of ~10 μm. FTCs are composed after firing of residual quartz, mullite and glass. They are expected to have lower glass content than hard porcelain and so should exhibit a higher strength, that is, greater than 50 MPa. They will probably be more glassy than electrical porcelain, which has the strength ~90 MPa, and so should have typical strength which is lower than this value. Their translucency arises from the close match of the refractive indices of the glass, which should be around 1.5, and quartz which is 1.53. The primary mullite crystals, which will have coarsened somewhat during firing, have a refractive index of ~1.64. The raw material costs will be fairly low, with the whitest-firing china clay costing ~£225/tonne, and the flux and quartz each costing less than £150/tonne.

Hard Porcelain

Hard porcelain is made mainly in continental Europe. Only one company, the Worcester Royal Porcelain Company, produces it in the U.K. Its formulation is variable but a typical recipe would be close to: 50$^{w}/_{o}$ clay, 25$^{w}/_{o}$ feldspar and 25$^{w}/_{o}$ quartz.

The flux and filler constitute the coarse fraction of the body with median sizes of ~ 10 μm. A biscuit firing up to 950°C is employed merely to harden the product so that it can be decorated and glazed. In the second firing, the body and glaze mature together. This firing has a maximum temperature of ~1400°C. For part of the firing, a reducing atmosphere is employed. This is to reduce the iron ions in the material so that they are present as Fe^{2+} rather than Fe^{3+} ions. This gives the ware a slightly greenish colour rather than a straw coloured appearance. The reduction also prevents bloating that would be caused by the evolution of oxygen that accompanies the reduction of iron that would otherwise occur during heating to the maximum temperature.

Hard porcelain is an extremely glassy product with only around $30^{v}/_{o}$ of the fired body being crystalline. Mullite is the main crystalline phase but some quartz may remain after most has been dissolved. This depends on the heat treatment employed. Because of the high glass content, it is expected that the fracture toughness of the body will be low, although no values have been found in the literature. Typical values of K_{IC} for glass are 0.7 to 0.8 $MPam^{-1/2}$. However, it is known that introduction of crystals into glass increases the K_{IC} value. For example electrical porcelains contain about $40^{v}/_{o}$ crystalline material and have K_{IC} values typically twice those of glass of 1.3(Agbarakwe, 1984), to 2.1 $MPam^{-1/2}$ (Banda et al 1988).

The low values of toughness and strength make hard porcelain prone to edge chipping. This problem has been exacerbated by the use of powder pressing. Flatware produced from spray dried granulates is more porous than that produced by plastic forming. This is a result of the formation of enlarged pores at the centres of the compacted granules as a result of the anisotropic shrinkage caused by aligned clay platelets. Clay particles become aligned at the surfaces of spray dried granules during granule formation so that their large plane faces are tangential to the granule surfaces. On compaction, the granules deform plastically by flowing to meet their neighbours. Facets form at the contacts, whose surfaces retain the clay alignment. It is considered that, on firing, the shrinkage anisotropy causes an enlarged pore to develop in each compacted granule. This introduces a few percent of additional porosity over that would present in plastically formed or slip cast wares of the same composition. This will reduce the fracture toughness to make the powder pressed wares have a lower toughness than those that are plastically formed or cast.

The reduction of the clay content was expected to reduce or eliminate the formation of the enlarged pores at the compacted granule centres.

The glaze, which is fired on at ~1400°C, is silica rich. It has a low thermal expansion coefficient $\sim 4 * 10^{-6}/^{\circ}C$. It is hard, chemically durable and resistant to being scratched. It is capable of withstanding severe service use, but the inability of the hard porcelain body to resist edge chipping limits in-service lifetime.

Bone China

Bone china is traditionally made from $50^{w}/_{o}$ calcined bone, $20^{w}/_{o}$ Cornish stone and $30^{w}/_{o}$ clay.

Bone ash is obtained by calcining cattle bones at ~1000°C. It is approximately hydroxyapatite ($Ca_5(PO_4)_3(OH)$) in composition. It is milled to produce a powder with a median particle size of ~5μm.

Cornish stone is commonly used as the fluxing component of the body and is usually milled to have a median particle size of ~10μm.

The clay component is mainly china clay with a low Fe_2O_3 content. To improve plasticity, a little ball clay(~$3^{w}/_{o}$ of the body) can be introduced and possibly ~$0.5^{w}/_{o}$ of bentonite. Bone china is typically biscuit fired at ~1230°C for 3 hrs in an oxidising atmosphere. During the firing, artefacts have to be supported to prevent unacceptable changes in shape. These come about when artefacts either sag under their own weight or when anisotropic shrinkage is resisted and the stresses that consequently develop cause the ware to distort. Glost firing is typically carried out at 1090-1100°C. Traditionally, a fritted, lead oxide-containing glaze has been applied. This has been matched to the rather high TEC of bone china, which is $\sim 8.5*10^{-6}/°C$. This type of glaze has a high reflectivity as a consequence of the high refractive index resulting from the presence of lead oxide. Because of legislation in the U.S.A, particularly California, new lead-free glazes have had to be developed. Currently a fritted glaze made of an alkali-borosilicate composition has been adopted. Because the glaze has to have a high thermal expansion coefficient (TEC) to match that of the body, the glaze has to contain a substantial amount of alkali oxide. This not only increases the TEC but reduces both the viscosity at a given temperature and the hardness of the glaze . Consequently, the glaze on bone china is prone to being scratched and this limits the lifetime of the ware in severe service conditions.

The strength of bone china is high, with modulus of rupture values reported in the range of 97 to 111MPa (ASM Handbook 1991). Hence bone china is not prone to edge chipping. The high strength is considered to come from the fact that bone china is highly crystalline i.e. its glass content is only $30^{w}/_{o}$. The crystalline phases that develop on firing are β-tricalcium phosphate ($Ca_3(PO_4)_2$) and anorthite ($CaO.Al_2O_3.2SiO_2$). The former comprises about $45^{w}/_{o}$ and the latter $25^{w}/_{o}$ of the body (Dinsdale 1986).

2.2.4 Body Preparation

2.2.4.1 Introduction

The most commonly used preparation methods employ an intermediate body slip. These are illustrated in Figure 2.2. It shows the approaches followed in English potteries where the whole whiteware body is not generally milled. Increasingly, it is becoming the practice for potteries to buy ready prepared bodies from specialised manufacturers. These may be in the form of spray dried bodies which can be transformed into a plastic body, using route F in Figure 2.2, and to slip by blunging with water.

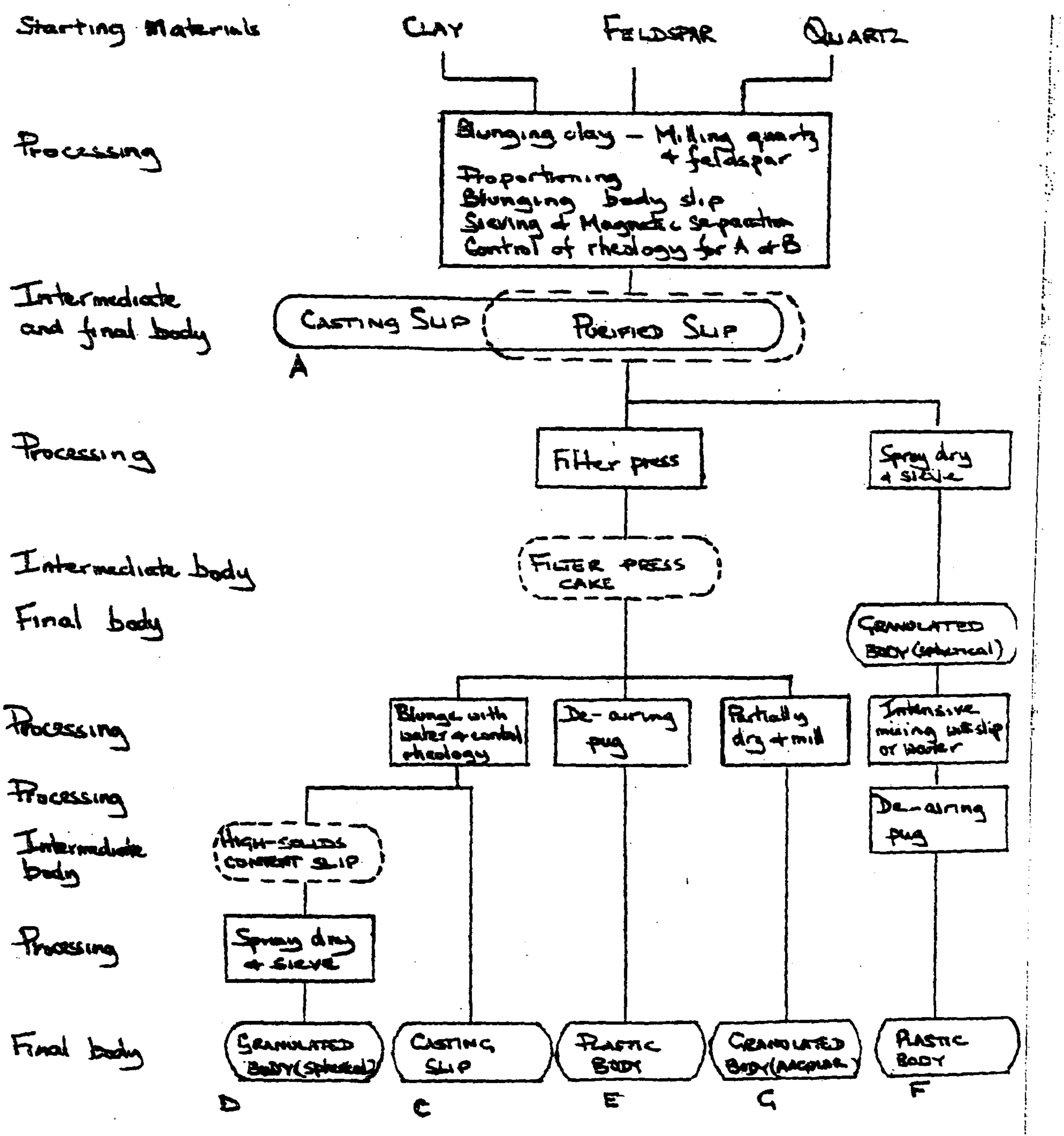

Figure 2.2 Methods for preparing whiteware bodies based on preparation and purification of an intermediate whiteware slip.

An intermediate body slip is used for several reasons:

- wet methods avoid dust, which is important as all silica containing components can cause fatal lung diseases;
- wet mixing allows agglomerates to be dispersed to allow compositional uniformity to be achieved on a small scale of size;
- batching wet avoids having to dry clays, which can absorb several weight percent of moisture from the atmosphere;
- body slips can be sieved to remove coarse impurities (quartz and lignite), and passed over magnets, to remove iron-bearing impurities;
- where filter pressing is employed, water soluble salts are removed.

2.2.4.2 Processing Operations

i) Blunging

This is a wet mixing process used to disperse clay lumps to produce a slip and to mix clay slip with the other body components, i.e. flux and filler. It is carried out commercially in a large tank, usually octagonal in shape to induce some turbulence, where the water and solids are mixed with a rotating blade.

ii) Milling the Flux and Filler

Size reduction of the flux and filler materials is carried out by wet ball milling. The cylindrical milling chamber is lined with either polyurethane or blocks of silica, porcelain or alumina. The milling media are either alumina, porcelain or flint pebbles, with the pebbles being the cheapest. Wear of the milling media and lining introduces materials that are acceptable. The bulk volume of the media is approximately 50% of the chamber volume. The slurry occupies the interstices between the milling media. A solids content of ~40 $^{v}/_{o}$ may be used. The mill is rotated at about 70% of the speed that would cause the media to be held against the chamber wall by the centripetal force . The milling of quartz and feldspar is continued until a median particle size of~10μm is attained.

iii) Proportioning

Slurries of the clay, flux and filler are stored in stirred vessels until they are required. Some of each slurry is pumped in turn into a chamber where its volume and mass are measured. This allows the slurry density to be calculated. The mass of each slurry required to make a selected quantity of whiteware body having a particular composition is pumped into a blunger.

iv) Sieving and Magnetic Separation

Blunged body slip is passed through a vibrating sieve with an aperture of typically 100 to 150µm. The slip is then passed over magnets to remove accidentally incorporated iron fragments.

v) Dewatering

This can be carried out by either filter pressing or by using a spray dryer. The former method uses less energy by requires more labour than the latter.

In filter pressing, slip is pumped under pressure into a series of chambers formed between plates. The chambers are lined with filter cloths. Water passes through these cloths and out along the channels in the supporting plates forming the chambers.

Filter cake builds up progressively with water removal until each of the chambers is essentially filled with plastic body. The pumping is stopped and the chambers opened so that the cakes can be removed. The cakes vary in water content. Around the inlet to each chamber the cakes are much wetter than elsewhere. Because the water content is variable within each cake and between cakes, the plasticity is variable. To obtain uniform plasticity, the cakes are passed through a vacuum pugmill. This mixes the plastic body by shearing and shredding it prior to reconsolidating it under a vacuum, to avoid entrapping air, by extrusion. Problems arising from the use of a pugmill include the development of clay particle alignment and the pick-up of iron or iron oxide that causes dark specks to appear in the ware after firing.

Spray drying produces a granulate consisting of quasi-spherical agglomerates that need to have a minimum median size 80-100μm to be free-flowing . For use in powder pressing the size needs to be larger to avoid the granulate being blown out of the tooling on die closure. The process involves breaking the body slip into small droplets in a chamber fed with air heated to 500-600°C. The atomised slip has a high surface area for efficient heat transfer. Droplets lose water by evaporation and shrink in size. The outer surface of a droplet becomes a plastic body which resists shrinking. However, with further loss of water the most deformable, i.e. moist, region of the surface is forced to collapse inwards to produce an internal cavity. The size of the cavity relative to granule depends on the solids content of the slip; i.e. with a higher solids content, the volume fraction of the cavity decreases. A high solids content is also required for an efficient process i.e. less water is evaporated per unit mass of granulate formed. In order that a slip having a high solids content may be pumped, it is deflocculated. It may be a consequence of the use of a highly deflocculated slip, that allows fine clay particles, particularly those of ball clay, to move with the water through the plastic body forming at the granule surface during drying, to be deposited at the granule surface. These clay particles orientate themselves with their large plane faces tangential to the granule surface. This leads to compacts formed by pressing a spray dried granulate to develop on firing, as already mentioned, enlarged pores at the centres of the compacted granules. It is usual to leave a residual moisture content of up to $2.5^{w}/o$ in the granules so that they exhibit sufficient plasticity for the pressing operation.

The type of spray dryer used in the whiteware industry employs nozzle atomisation . This is illustrated in Figure 2.3. The slip is pumped through a swirl chamber and then a nozzle to induce rotation in the fountain that emerges from the nozzle. The rotation of the granulate and air speeds up in the conical section at the base of the drying chamber and the larger granules separate out from the gas stream. The separated granules collect in the base of the dryer in the rotary valve. Periodically this rotates so that granulate leaves the chamber without admitting a significant amount of air into the system. The air and the finest granules leave the chamber to pass through a small cyclone, which removes most of the solid material before passing up the stack and through the exhaust fan. With the fan drawing air through the system, the drying chamber is at a pressure slightly below atmospheric so that material should not leak outwards.

Figure 2.3 Spray dryer with nozzle atomizer

2.2.5 Forming Operations

2.2.5.1 Introduction

As already stated, low-clay whitewares cannot be formed by the conventional wet plastic forming techniques but should be formable with suitable additives by powder pressing, casting and by injection moulding. Test-pieces throughout this study were formed by pressing bodies that had been hand granulated. Towards the end of the work, trials were carried out to see whether drain casting is a method by which hollow ware could be produced. For the low-clay approach to be successfully applied to tableware ceramics, all the required shapes must be formable.

To illustrate the problems that arise from clay particle alignment in conventional plastic forming, that are overcome using powder pressing for conventional whitewares, a brief review of wet plastic forming is presented. Although problems caused by macro-scale variation in clay particle alignment are overcome by using pressing, a problem resulting from alignment of clay on the micro-scale occurs. This is the formation of enlarged pores at compacted granule centres that has been described. It was anticipated that the use of low-clay whiteware would minimise this problem and it has very recently been shown by Batista (Messer et al 1999) that the problem is eliminated. The use of injection moulding of low-clay whitewares into cups with attached handles is one possible approach to replacing the wet plastic forming method in current use. It has been shown (Turnbull, BEng 1996) that bone china test-pieces that are formed by injection moulding shrink anisotropically in a similar fashion, but to a lesser extent, to the way wet plastically formed material shrinks. It was anticipated that low-clay whiteware formed by injection moulding would shrink more isotropically and, in very recent work by Wong (Messer et al 1999), this assumption has been shown to be correct as the shrinkage was found to be essentially isotropic.

Powder pressing, which is the forming technique of first preference, will be reviewed to explain how reducing the clay content proves to be beneficial. Casting without applied pressure and pressure casting, both of which are required for tableware production of the low-clay whiteware will then be reviewed. The pressure casting of cups with attached handles is an alternative technique to injection moulding that might be used replace conventional plastic forming. When conventional wares are cast a number of problems arise from the variation of particle alignment from place to place. These problems should be significantly reduced by using a low-clay whiteware.

2.2.5.2 Wet Plastic Forming

The conventional method of making flatware and shallow bowls is by using the jiggering version of the roller-head process. This is illustrated for a plate in Figure 2.4.

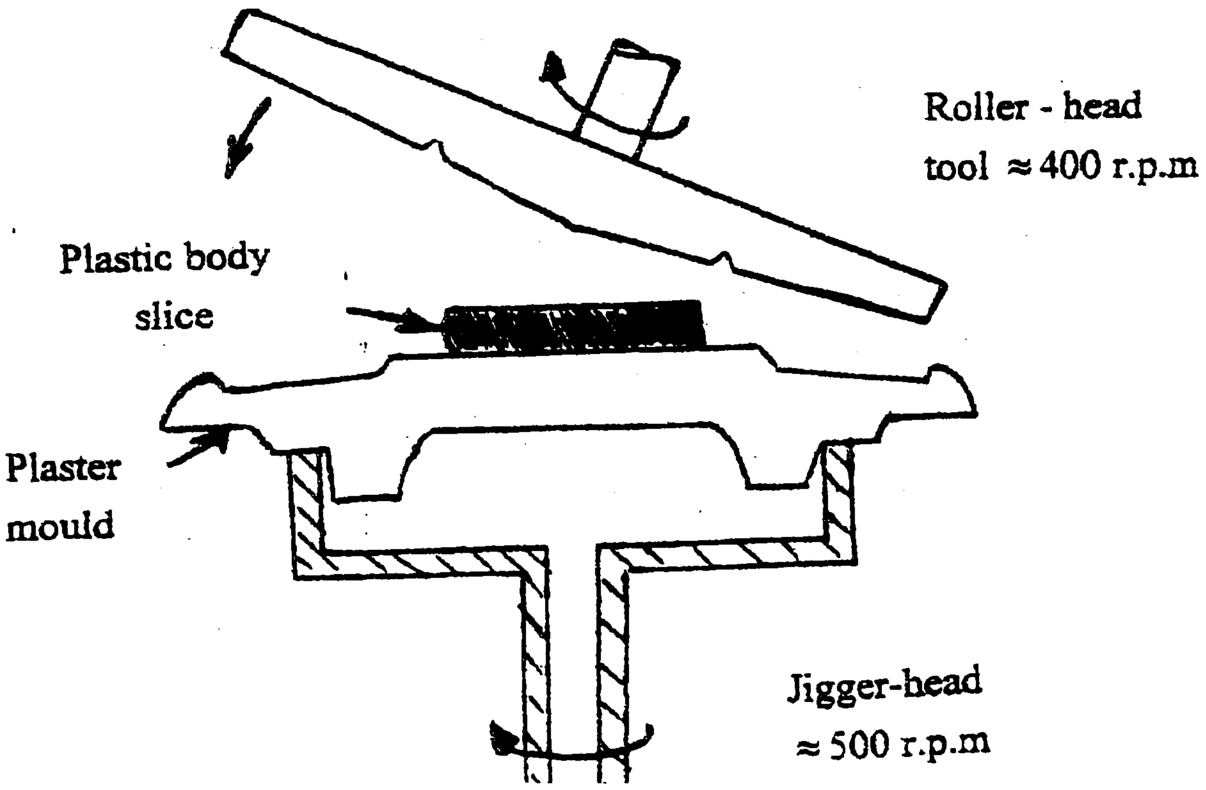

Figure 2.4 The roller-head technique for flatware

A slice of plastic body, cut from a column extruded from a vacuum pugmill, is placed centrally on a plaster of Paris mould. The air from behind and within the mould is removed by connecting the supporting jigger head to a vacuum system. In this way the body slice is held firmly onto the plaster mould. The roller-head tool and jigger head rotate about their axes in the same direction but at different speeds. The roller head tool, which is usually made of steel and is heated to prevent body sticking to it, is lowered and the body slice spread and sheared to cover the mould surface. An excess of ~25% of body is used to ensure full coverage of the mould in case the slice is placed off centre. The excess is trimmed away by a knife situated at the edge of the mould. The body has to be highly plastic to be spread across the mould without rupturing. This is achieved by having a moisture content that is too high for the formed plate to be removed immediately from the mould. Consequently, the plate plus the mould is removed from the jigger head and passes through a dryer. This means that a substantial number of moulds have to be in service. As the moulds have only a limited life of up to 150 cycles, because the wear causes a change in their shape, much labour is used in their continual replacement.

For bodies like bone china, which are not highly plastic, the front surface of the plate is prone to splitting. This is the stretched-face fault.

The clay particles become aligned during plastic deformation, such that over most of the plate their large plane faces are parallel to the surface of the plate. This leads to the diametral shrinkage being significantly less than the shrinkage through the plate thickness as illustrated in Table 2.5 (Cubbon et al. 1982)

Body Type	**Firing Shrinkage of Plate**	
	Across Diameter	**Thickness**
Porous Earthenware	8.8%	13.8%
Vitrified Hotelware	8.8%	12.6%
Bone china	10.8%	20.0%
Hard Porcelain	11.3%	20.5%

Table2.5 Firing shrinkage of various whiteware plate (Cubbon et al. 1982)

Differences in clay particle alignment in the foot ring of the plate and in the plate within the foot ring can cause distortion on firing in which the section of the plate within the foot ring is either deflected up or down. Plates in which the former occurs are called humpers and those in which the latter occurs are called whirlers. Another problem caused by clay particle alignment is called the centre-pip fault. The clay at the centre of the plate is less well sheared during forming than elsewhere. Consequently, clay particles at the plate centre tend to retain whatever alignment was imposed during the pug milling operation. The clay particles at the centre of the pugged slice may be randomly orientated or have some alignment imposed by the shearing that occurs in the extrusion die on leaving the pug mill. The material at the plate centre consequently shrinks through the thickness on firing less than elsewhere to leave a raised region at the centre.

Plastic forming using the roller-head technique is a fast process that is suitable for short to high production runs. This is because plaster moulds are cheap to produce initially. However, the requirement to continually renew them, the high scrap rate of body and ware before firing, typically 35% from using both excess material and the faults in making, and loss of fired ware through specking as a result of pug milling the plastic body is leading to progressive replacement of the roller- head technique by either powder pressing or pressure casting. However, neither of these techniques is suitable for non-repeated short production runs because of the high costs of the moulds in both cases. Powder pressed plates do not suffer the distortion caused by the macro-alignment of the clay particles and, from the viewpoint of shape fidelity, are of higher quality.

Flatware or shallow bowls that are not circularly symmetric can be produced by a plastic pressing method called the Ram process. In this method, a pugged slice of body is pressed between two halves of a high-strength plaster mould. The body flows to fill the mould with excess body exuding through a gap left between the two halves of the mould when pressing is complete. In flowing, the body is sheared and clay particles become aligned with their large plane faces parallel to the surfaces of the mould. This occurs in the region outside the area occupied by the body slice. The two surfaces of the body slice in contact with the plaster tend not to deformed and so retain the orientation of the clay in the body slice. On firing, the outline of the body slice becomes visible as the material within this area shrinks less through the thickness than elsewhere. This problem prevents ware of the highest quality from being made by this technique. Alternatively, casting can be employed.

Cups are made by a jolleying version of the roller-head method. A slice of body cut from a small diameter pugged column is dropped into a plaster of Paris mould. The cavity can have the shape of either the external surface of the whole cup, except for the handle, or the bowl of the cup without a pedestal. Alternatively , the cavity may be shaped to give a thick-walled vessel from which the external profile of the bowl and pedestal can be formed in a subsequent turning operation on a lathe. In this roller-head technique, a rapidly rotating tool is lowered into the rotating mould to cause the body to be forced upwards to cover the wall of the mould. Surplus body at the top of the mould is cut away. Where subsequent shaping by turning is required, the body is dried to the leather-hard state and turned on an automatically operated lathe using a profile turning method. In this way, the final shape of the bowl and the pedestal can be attained. In some cases the bowl is attached manually to a separately formed pedestal by slip joining. Handles are attached using the same method.

Attempts are being made to reduce the labour intensive nature of this method of forming. Three alternative approaches are the use of (a) roller-head, lathe turning and slip joining of handles but with the process carried out by robots, (b) injection moulding and (c) pressure casting.

2.2.5.2 Powder Pressing of Flatware

About twenty years ago, machine makers introduced automated equipment to press, fettle and sponge flatware. One form of the technique has been called combination pressing (Reed 1989) because it involves an initial uniaxial compaction, achieved by a moving punch that forms the top surface of the ware, followed by further compaction, achieved by applying oil pressure to a polyurethane rubber diaphragm. A sketch of the tool set for a plate for a system in which the plate is positioned horizontally is given in Figure 2.5.

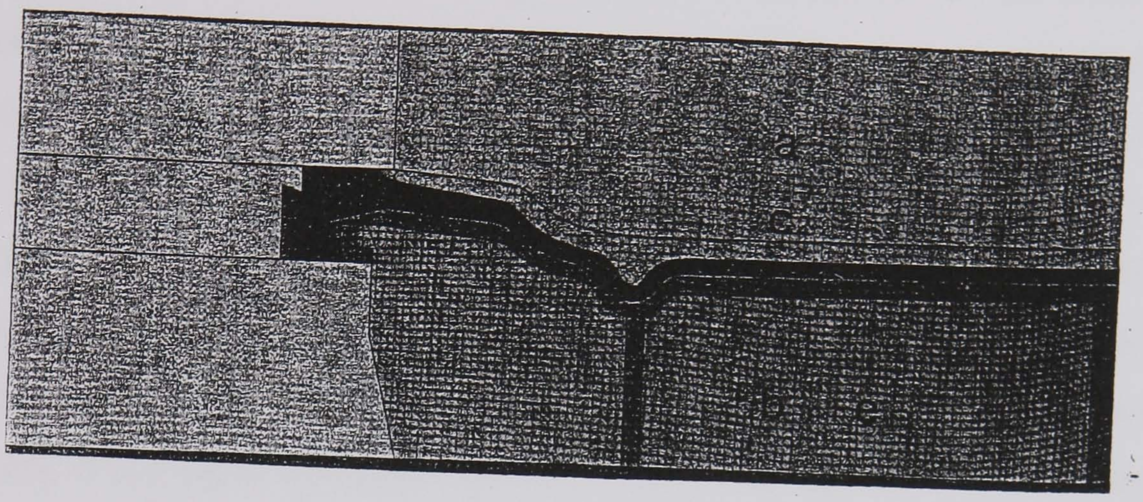

Figure 2.5 In combination pressing of a flatware piece, mechanical pressure is produced by (a) hard punch surface and a complex lower punch consisting of (b) hard material and (e) pressurised hydraulic liquid pressing up against a flexible surface membrane in contact with (C_2) the flatware piece

The mould is moved on a carosel from station to station. First, a measured quantity of granulate is deposited onto the rubber membrane. At this stage, the membrane is sucked back against its supporting back plate. In the next station, the granulate is sculpted with a rotating template to have a surface profile that matches as closely as possible the profile of the top punch. As the granulate flows readily, steep surfaces cannot be produced. At the next station, the top punch is introduced and lowered to partially compact the granulate by moving at the centre of the mould up to about 60% of the distance that would be required for full compaction at the maximum oil pressure that will be applied. Pressurised oil is then introduced through oil ways in the backing plate positioned around the foot ring of the plate and at the plate centre to complete the pressing operation. The top punch is then raised and the plate is then lifted by a suction pad and placed on the automated sponging and feltling equipment. The ware must have sufficient strength to withstand the automated handling treatment. In bodies that contain little ball clay, such as bone china and the low-clay whitewares, this strength has to be provided by adding a small percentage (~1%) of binder such as polyvinyl alcohol (PVA). To ensure that the granules are compacted to eliminate the intergranular voids and cavities within the granules at the maximum pressure of 30MPa that these presses deliver, the granules containing little ball clay have to contain plasticisers such as glycerol, polyethylene glycol and water. Usually the organic plasticisers are up to the 1% level and water up to 2.5%. The granulate has to be designed so that it does not stick to the top punch or rubber membrane. Powder pressing can produce about 80% of tableware i.e. plates, shallow bowls, and saucers. It is a rapid technique and the tooling, although initially expensive at ~£10,000 per tool set, has a very long life. The total process for pressing, i.e. body preparation and forming, involves significantly less labour than the roller-head method.

2.2.5.4 Casting

This can be carried out for tableware manufacture without and with externally applied pressure. The former is called slip casting, which uses porous plaster moulds, and the latter is called pressure casting, which uses porous plastic moulds. There are drain casting and solid casting versions of the process, however, only the solid casting version of the pressure casting technique is used in tableware manufacture.

i) The Slip Casting Process

In drain casting without externally applied pressure, a suspension of particles in water, the slip, is poured into plaster of Paris mould. The plaster of Paris mould is composed of needle-shaped crystals of gypsum ($CaSO_4.2H_2O$), which have a significant amount of pore space between them. Typically the porosity is ~50%. The needles are wetted by the water of the slip, which is drawn into the plaster by capillary action to occupy the pore space. As this happens, the particles in the slip are deposited on the mould surface and a layer, the cast, progressively builds up with time. The resistance to the flow of water into the mould mainly results from the cast, which has a lower permeability than that of the mould. The resistance increases with the increasing thickness of the cast. This results in the thickness of the cast at any instant being proportional to the square root of casting time. When the cast layer reaches the required thickness, the surplus slip is decanted from the mould and the cast left to dry. As more water is drawn into the mould and the water evaporates from the surface of the cast, the cast shrinks. This is because the films of water between the particles in the cast are reduced in thickness as the cast dries. The cast also becomes stiffer. To avoid distortion, the drying must be as uniform as possible, so that the whole of the cast is released from the mould surface roughly at the same time. For some shapes, the casts shrink onto the plaster. To avoid damage in such a case, the cast must be capable of undergoing sufficient plastic deformation without rupture.

For drain casting, both surfaces of the cast have essentially the same shape. The advantage of this version of the process is that hollow-ware can be formed having internal dimensions that are larger than those of the entrance to the interior of the item. A teapot is an example of a tableware item of this type.

In solid casting without an externally applied pressure, cast layers form on two opposing plaster surfaces. The two opposing surfaces can have different shapes. An example of a tableware item that can be made by solid casting is an oval plate. During casting the mould is continually topped up with slip to replace the water being absorbed by the mould. The casting process is completed when the two layers meet. Drying results in shrinkage, which may require the cast to plastically deform in some directions to avoid rupturing. This is necessary for plates, which have a shape that prevents free shrinkage diametrally. A similar problem occurs for the handles of cups and jugs when these are cast attached to the bodies of these vessels. Although the bodies are drain cast, the handles should be solid cast. The inner surfaces of the handles shrink onto the plaster during drying, which requires them to deform plastically to avoid tearing.

ii) Pressure Casting

In pressure casting of tableware, pressure is applied to the slip in the cavity between two halves of a mould that are clamped together until the cast is formed. The mould is usually composed of, or faced with, a porous plastic. Pressures up to 4MPa are applied to the slip, which means that a substantial force has to be applied to clamp the mould halves together when casting items with large surface areas.

Pressure casting is used to reduce the casting time significantly from that required for slip casting. It also eliminates the labour-intensive manufacture of plaster moulds. Plaster moulds have a short life of ~100 cycles, whereas plastic moulds operate for several thousand cycles.

The time required for casting depends on the thickness of the cast and its permeability, which depends on how densely the particles pack and the sizes of the particles. The particle packing depends on the size distribution of the particles in the slip and the pressure applied during casting. Wares made with a substantial proportion of ball clay take longer to cast than those, like bone china, that have little ball clay in their formulations.

On completion of casting, the slip reservoir is isolated from the mould and water is fed back through one half of the mould to separate the cast from the mould surface. The mould is opened with the cast attached to the other half of the mould. Water is fed back through this part of the mould to separate the cast, which is removed either manually or robotically. The cast is then fettled and sponged. The separation process causes problems for bodies with high permeability, such as bone china, as the water used to effect separation enters the surface of the cast. This makes the surface soft and difficult to handle without distortion. This is expected to be a problem for low-clay whitewares, which will have a high permeability. A possible solution, which has been shown to work in the pressure casting of alumina, is to add a wax emulsion to decrease the permeability (Betz et al. 1997).

iii) The Requirements of Casting Slips

For drain casting without externally applied pressure, the following requirements should be met (Messer 1991a):

a) the slip should be pourable to fill all recesses of the mould;
b) coarse particles must not settle out;
c) the slip should have a high casting rate;
d) the casting rate should not be so high that control of cast thickness is lost;
e) there should be sharp demarcation between the cast and the slip;
f) good drainage of the slip is required;
g) the slip should produce a cast with a small drying shrinkage;
h) the slip should produce a cast that is firm with a high green strength;
i) the slip should not contain bubbles as these cause surface pinholes and internal voids in the cast;
j) the slip should be made with as little water as possible, consistant with point a, to reduce the energy and time required to dry the moulds.

For solid casting without applied pressure the requirements are: a, b, c, g, h, i and j. For solid casting with applied pressure the requirements are: b, c, g, h and i.

All the requirements except b and c can be achieved with a highly deflocculated slip in which the particles at long range repel one another. To achieve b and c requires that the slip is, to some degree, flocculated, that is some particles have become attached to each other. Hence, the best compromise enabling all ten requirements to be met is to use a partially deflocculated slip.

iv) Surface Chemistry and Rheology

The state of flocculation is controlled by the surface chemistry of the particles which determines the interparticle forces. These in turn have a strong effect on slip rheology, casting rate and microstructure of the cast. The method for achieving the low viscosity suspension required for pouring and decanting when the slip has a high solids content entails the use of repulsive interparticle forces that arise from either surface adsorbed ions or polymers. In the former technique (electrostatic stabilisation), a diffuse double layer of ions is formed from ions in solution (counter ions) around a particle and oppositely charged sites on the particle surface. With the latter technique, either neutral (steric stabilisation) or charged (electrosteric stabilisation) polymers are added to the suspension. A repulsive force is required to prevent any coulombic attraction or van der Waals attraction, which is always present, causing particles to agglomerate. In a fully deflocculated slip all the particles repel one another at long range. At short range, there is an energy barrier that must be exceeded for particles to come together. If the particles should be brought into close proximity, they attract one another and agglomerate. With particles repelling each other, there is no extensive particle-particle structure in the slip. During flow, the particles can easily move past each other and hence there is no yield stress. The slip behaves, except at very high solids content, as a Newtonian liquid. A viscosity η can be defined, which is constant with shear strain rate, $\dot{\gamma}$. This is shown in Figure 2.6.

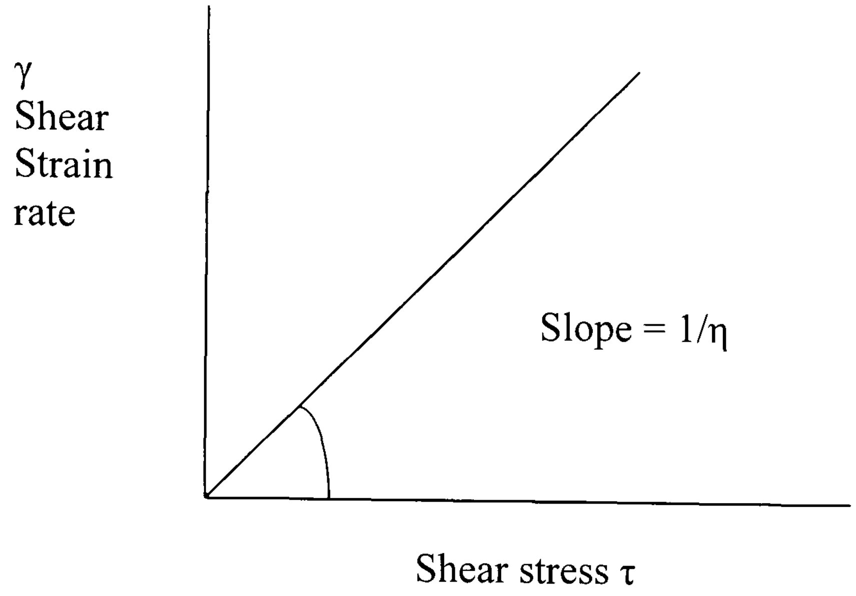

Figure 2.6 Newtonian liquid.

With a conventional whiteware slip, the clay particles dominate the rheological behaviour because they are present in the highest concentration on a number basis. With a low-clay whiteware, the other particles will be present in higher concentrations on a weight basis but the clay particles may still have the highest concentration on a number basis as the ball clay is very fine. However the flocculation behaviour of the other finely milled particles may play an important role.

In a flocculated slip, particles become attached to each other. The clay platelets may link up so that their edges are attracted to the large plane faces of other clay platelets to form a "house-of-cards" structure. This occurs when clay is in pure water because the large plane faces carry a negative charge and their edges are positively charged. The clay particles form a very open, poorly, packed structure through the slip that may be able to keep the non-plastic particles in suspension. For the slip to flow, this structure has to be broken. This requires a shear stress larger than a critical value τ_c, to be applied. The flow behaviour, which involves the clay particle structure being continuously broken and reforming, is approximated by a rheological model liquid, the Bingham liquid. Bingham behaviour is illustrated in Figure 2.7.

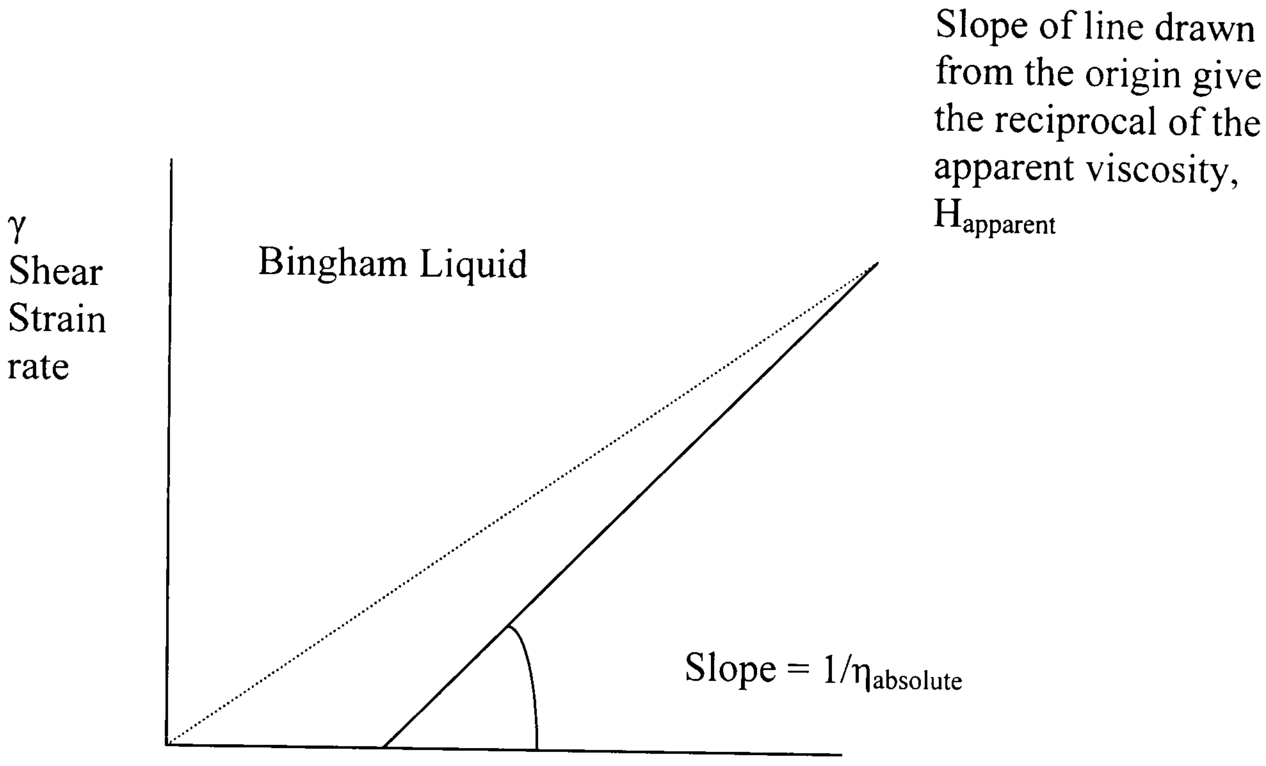

Figure 2.7 Bingham liquid.

It can be seen from the figure that the apparent viscosity decreases with the shear strain rate (essentially the flow rate) increasing.

Deflocculants commonly in use for whiteware slips are mixture of sodium silicate and sodium carbonate and proprietary polymers such as Dispex N40 made by Allied Colloids.

V) Cast Behaviour

The use of a fully deflocculated slip produces a dense cast with the clay platelets packed face to face. At the mould surface, the clay platelets tend to align with their large plane surfaces (faces) parallel to the mould surface. The cast has a low permeability and so casting is slow. However, the cast is firm and the slip has a low viscosity (no yield stress). Therefore on decanting the surplus slip, the slip drains freely without disrupting the cast. Throughout casting, the relatively coarse flux and filler particles will sediment as the slip has no particle-particle structure to prevent their descent. Consequently, the base of the cast will contain a higher proportion of flux and filler than the walls. On drying, the cast may not shrink sufficiently to detach itself from the mould because it is well packed. Shrinkage depends on the water content of the cast and on the size distribution of the particles, which affects the density to which the particles can pack.

The use of a highly flocculated slip produces a cast with an open structure. This comes from the 'house-of-cards' structure of the clay particles in the slip. The cast has a high permeability and the thickness increases rapidly with time. Throughout casting, the non-plastic particles are prevented from sedimenting by the flocculated clay structure in the slip, provided the weights of these particles are not sufficient to break this structure. Similarly, small bubbles cannot rise to the surface as the upthrust cannot break the structure. On decanting the surplus slip, as the consistency of the slip and cast are similar, the cast is disrupted.

The best result is a compromise and is obtained by partially deflocculating the slip so that all the requirements listed in section 2.2.5.4(iii) are met.

It should be noted that the green strength of the cast will depend on the size and size distribution of the particles as these affect the number of particle-particle contacts. Ball clay or any other very fine clay is required to provide binding power to give the green body sufficient strength for handling. However, the use of very fine particles reduces the casting rate, as they make the size of the pore channels in the cast smaller. Also, the use of ball clay increases the drying shrinkage because of the increased number of water films between the particles in unit thickness of the cast.

Vi) Advantages, Disadvantages and Faults with Casting

Casting is a labour-intensive process, as the ware requires fettling, and it is only used to make wares that cannot be made by plastic forming or powder pressing. Drain casting is used to form thin-walled objects and is the only technique available to produce hollowware. Casting also allows the manufacture of large thin-walled objects such as sanitaryware items, without application of large forces.

The cost of an individual plaster mould is low but many are needed. Casting is a slow process, so that many moulds must be in operation, and the lifetime of the moulds is short. Preparation of the pattern and master moulds is expensive.

Making a consistent product requires control of every operation employed and the characteristics of the starting materials, slip rheology is prone to change as whitewares are made from minerals rather than refined chemicals.

Although, deaired slips are used, air bubbles may still be present in the slip. These can become pinholes on the surface of the cast. They can arise from accidental introduction of dried slip into the slip in the mould. Water in the slip enters the dry material displacing the air between the particles.

Drying causes problems as evaporation of water from the surface of ware can never be uniform. Non-uniform drying can cause distortion and cracking.

Alignment of the clay platelets parallel to the mould surface causes the drying and firing shrinkage to be anisotropic. This causes stress to arise which can result in distortion of the ware with circular cross-sections becoming oval.

Some other faults are caused by clay alignment, which should be alleviated for low-clay whitewares. It is expected that low-clay whitewares will exhibit significantly less anisotropy of both drying and firing shrinkage. So that wares with circular cross-sections will retain their shape on drying and firing. With multi-part moulds, flashing occurs at the joints. Although the flash is removed during fettling, a seam can reappear after firing. This occurs because the localised alignment of the clay platelets is different from elsewhere and so the local firing shrinkage is different. Similar behaviour can occur on mould filling. Two faults that occur are casting spot and slip meets. Casting spot occurs where the slip hits the mould as it poured in. As slip flows around the mould during filling, coating the surface as it flows, two liquid fronts can meet. Along the line at which they meet, the clay platelets in the cast may not be parallel to the mould surface.

Another fault that may be caused by platelet alignment is wreathing. This is the formation of an undulating surface on drain cast ware at the cast/slip interface for slips that are too deflocculated. It is postulated that variations in the alignment direction of the clay platelets in the cast result in localised variation in the permeability of the cast layer, so that the casting rate varies from place to place (Cubbon et al 1986).

2.2.6 Viscous Composite Sintering

All whitewares densify during firing through the presence of a large volume fraction of liquid phase. The liquids have to have high viscosity otherwise the whitewares would slump. The liquids are viscous because they are silica-rich.

In whitewares made from clay, quartz and a feldspathic mineral, the liquid arises from the interaction of alkali oxide from the flux with the clay and quartz. The composition of the liquid phase will vary with position throughout the whiteware. Near to a feldspar grain, the liquid will contain a higher alkali oxide content than elsewhere. In the solution rim around quartz particles, the silica content would be high.

With the formation of the viscous liquid, the crystalline grains are drawn together to reduce the interfacial energy of the liquid. If γ_{LV} represents the specific surface energy of the viscous liquid and A is the surface area, the driving pressure to reduce the porosity in the system comes from the reduction of the product;

$$A\gamma_{LV}$$

by the reduction of the surface area A. The initial stage of sintering can be modelled by considering neck growth between two spheres of viscous liquid. This leads to the rate of shrinkage being given by (Kingery 1976)

$$\frac{d}{dt}\left[\frac{\Delta l}{l}\right] \propto \frac{\gamma_{LV}}{\eta_r}$$

where η is the viscosity of the viscous liquid and r the radius of the spheres. The viscosity is highly temperature dependent, decreasing rapidly as temperature increases. It may be described by an equation of the form:

$$\eta=\eta_0 \exp {}^{E}/_{RT}$$

for a viscous liquid of fixed composition where η_0 is a constant, E an activation energy, R the gas constant and T the absolute temperature.

The final stage of sintering can be modelled by treating the system as a block of viscous liquid containing equal size pores that do not contain a gas. This is the Mackenzie-Shuttleworth model (Mackenzie et al 1949) which gives the sintering rate as

$$\frac{d\rho'}{dt} = \frac{3\gamma_{LV}}{2r_0\eta}\left(1-\rho'\right)$$

where ρ' is the relative density, r_0 is the initial radius of the particles, η is the viscosity of the viscous liquid, γ_{LV} is the surface tension and $(1-\rho')$ is the pore volume.

This model is an oversimplification in that the pores will be of various sizes, they will contain a gas that exerts of pressure resisting pore closure and that the whiteware is composed of a mixture of crystals in a viscous liquid matrix and not just a viscous liquid.

In addition, gas in the pores can dissolve into the viscous liquid and diffuse from small pores, where it is under a relatively high pressure, to larger pores where the pressure is relatively low. This allows the smaller pores to continue shrinking and can cause larger pores to grow in size. The net effect is that the bulk density of the whiteware reaches a maximum value and then starts to fall. The ware is then said to be overfired and to be bloating. In the extreme, near surface, large pores can form surface blisters.

It is interesting to note that the translucency of wares, such as bone china, is improved if they are overfired. Pores have a refractive index of 1, which is significantly different from the values for the glass and crystalline phases that constitute the whiteware. Consequently, pores scatter light. The presence of a high concentration of very small pores can render the whiteware nearly opaque. Their elimination at the expense of creating a higher porosity in the form of a much lower concentration of significantly larger pores results in less light scattering and significantly by improves translucency.

In the case of hard porcelain, the severe heat treatment given during densification causes the mullite needles to coarsen. The refractive index of the mullite is significantly higher than that of the glass that surrounds them (1.64 compared to 1.48) (Dindale 1986) so that a significant amount of light will be scattered by the mullite. With the mullite coarsening, the number of boundaries encountered by light passing through the ware is reduced and translucency improved.

The viscous liquid that develops in bone china to effect densification is partly derived from the breakdown of the bone ash. It has been found (Jaffari,1995) that reducing the bone ash causes more bone to break down causing more liquid phase to form. This can be explained as follows. Hydroxyapatite loses 1/3 CaO on transforming to β- tricalcium phosphate . This CaO can combine with the clay to form anorthite. However, if the CaO demand by the clay cannot satisfied on the release of the CaO in forming β-tricalcium phosphate, this compound is broken down to form calcium phosphates with low melting points. The bone ash content of bone china therefore plays a very key part in determining how the ware densifies and sags under its own weight.

2.3 Product and Process Design

2.3.1 Introduction

The design of a ceramic product and the processing scheme to make it meet specified requirements can be treated in a similar way to that used for the design of products and their manufacture in other branches of engineering. A simple model for the design process, derived from a model used in mechanical engineering, is presented.

2.3.2 The Design Process

A model used in mechanical engineering for product design is given in Figure 2.8 (Pugh, 1991 and Wright, 1998). The modified scheme adopted in this study is given in Figure 2.9. The starting point can be considered as the Product Brief. This is a statement of the market requirements or user needs of the product.

The detailed requirements of the product are then established, as fully as possible at the early stage in the design process, in the Product Design Specification (PDS). This comprises a set of objectives and constraints that must be met for the product to be fit for its purpose at an acceptable cost. An objective can be defined as a requirement for which specific values of properties or behaviour cannot be given, either because what can be achieved is unknown at the early stage of the design process or because a particular requirement is subjective, such as the requirement to be aesthetically pleasing. A constraint is a requirement that is fully specified and must be met for the engineering product to be acceptable.

The design process is iterative in nature and must include both feedback and feed-forward links as shown in Figures 2.8 and 2.9. As the design process proceeds, some of the objectives may be rewritten as constraints and some of the constraints may be up-rated or down-rated in the light of new understanding.

A design tool, known as a Requirement Tree, is sometimes employed to help establish the PDS (Wright,1998). In this, the Top Level Requirement (see Figure 4.1a, b and c is in Chapter 4) can be a simplified statement of the Product Brief.

The requirements that are implicit in this statement are progressively drawn out in each successive level of the Requirement Tree. This is done, by asking what the statement at a given level means and producing answers that constitute the next lower level. The collection of statements given at the lowest levels of the completed.

The requirement tree can be extended by adding the means by which the requirements are met. This leads to the next stage of the design process, the Concept Solution.

In this, one or more imagined products are conceived. These, it is thought, might have characteristics that fulfill the PDS and are products that can be made.

An analysis of these potential products and the processing to make them is undertaken to see which might be the best solution to adopt. This is the Concept Selection stage. For ceramic products, the analysis may require some preliminary experimental work to be carried out to test critical aspects of the processing scheme. As a result of this analysis, a modified Concept Solution may be produced or even changes made to the PDS.

The next stage of the design process is the Product and Process Development phase. In this, the starting materials, the processing methods and processing equipment have to be chosen followed by extensive iterative trials to establish the values of the processing variables. During this phase of the design process many modifications and changes will be explored in order to achieve the constraints and objectives of the PDS, which itself may have to be altered.

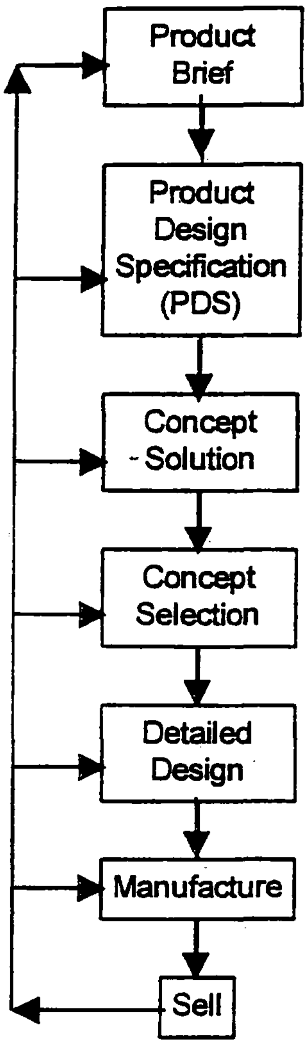

Figure 2.8 Model for product design used in mechanical engineering.

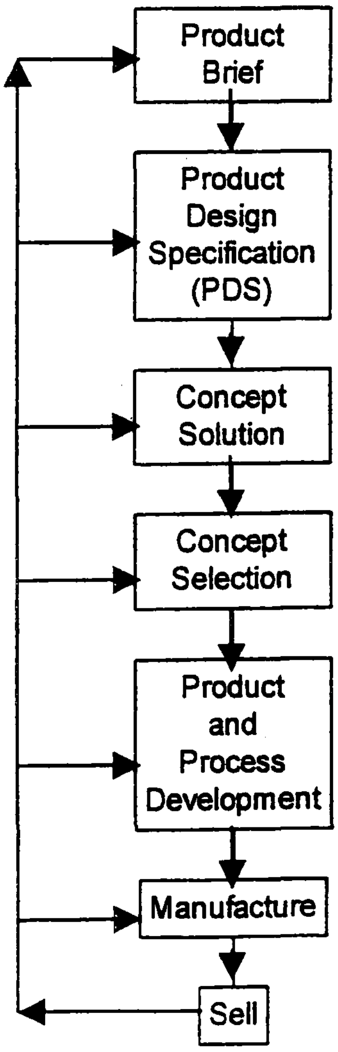

Figure 2.9 Modified model for product design used in present study

2.3.3 Process and Product Development

2.3.3.1 Introduction

Before discussing the methodology employed to develop the processing to give the product the required behaviour during processing and the desired final properties, some general ideas on ceramic processing will be presented. The ways these are presented, and the terminology employed have been developed by Messer in several papers and lectures (Messer et al., 1983a, 1983b, 1989). He makes a distinction between two classes of property, that is characteristic and behavioural properties.

2.3.3.2 Characteristics and Behavioural Properties

In the first class are those properties needed for the description of a material in a given state. These are called characteristic properties, and it is these that are obtained when a material in a particular state is characterised. There are two kinds of characteristic property, constitutional and structural.

Properties such as the quantity of each of the phases present, either solids, liquids or gases and their compositions or concentrations, and the porosity are called constitutional characteristics.

The shapes, sizes, positional and orientational information on each of the phase regions present, as well as information on their ionic or atomic configurations is encompassed by the term structural characteristics.

The second class of property is derived from the way a material behaves when its state is changed by subjecting the material to a stimulus or a treatment. For example, when materials are heated most expand. The expansion is the response of the material to being heated. From this behaviour, which is not a property, a behavioural property called the thermal expansion coefficient can be defined. Other behavioural properties are drying and firing shrinkages, elastic moduli, tensile strength, fracture toughness, dielectric strength, magnetic permeability and relative permittivity.

Messer asserts that the way a material behaves when subjected to a stimulus or treatment of some kind depends both on the treatment and the characteristic properties of the material. Hence, the behavioural properties are seen to depend on the characteristic properties.

2.3.3.3 The Nature of Ceramic Processing

Ceramic processing comprises a linked set of activities in which the characteristic properties of the starting materials are progressively modified, changed and developed to become those of the final product. Generally, at no stage in the processing scheme are the characteristics of an intermediate product obliterated. Rather, the characteristics at all preceding stages influence the outcome of the final stage of processing. Hence, an holistic approach to processing is essential. This way of thinking can be shown to be required by considering a simple processing scheme in which each processing operation is applied in sequence. Let the characteristic properties of the starting materials be represented by the symbol S. The first processing operation, P_1, transforms these characteristic properties into those of the first intermediate product by P_1 operating on S to give,

$$P_1(S)$$

where $P_1(S)$ represents the characteristics of the first intermediate product. These are transformed into the characteristics of the second intermediate product by process operation P_2 operating on $P_1(S)$ to give,

$$P_2[P_1(S)]$$

After n operations, the characteristics of the final product are represented by,

$$P_n\{P_{n-1}(\text{--------}P_2[P_1(S)]\text{---})\}$$

If any characteristic property of the starting materials or any of the values of the processing variables are changed then the characteristics of the final product are changed.

An alternative way of considering a processing scheme is illustrated in Figure 2.10 (Messer,1991b). In this figure, the scheme comprises a set of processing operations carried out sequentially and each operation has associated processing variables that can be changed. The sensible, usable range of each variable is represented by a vertical line. The value used for a variable is denoted by an x. Changes can be represented by raising or lowering their positions. In practice, some process variables may only be changed in discontinuous ways, for example, the size of milling media used. A pathway can be plotted through the processing scheme linking the values of the process variables used. There are clearly an infinite number of possible pathways.

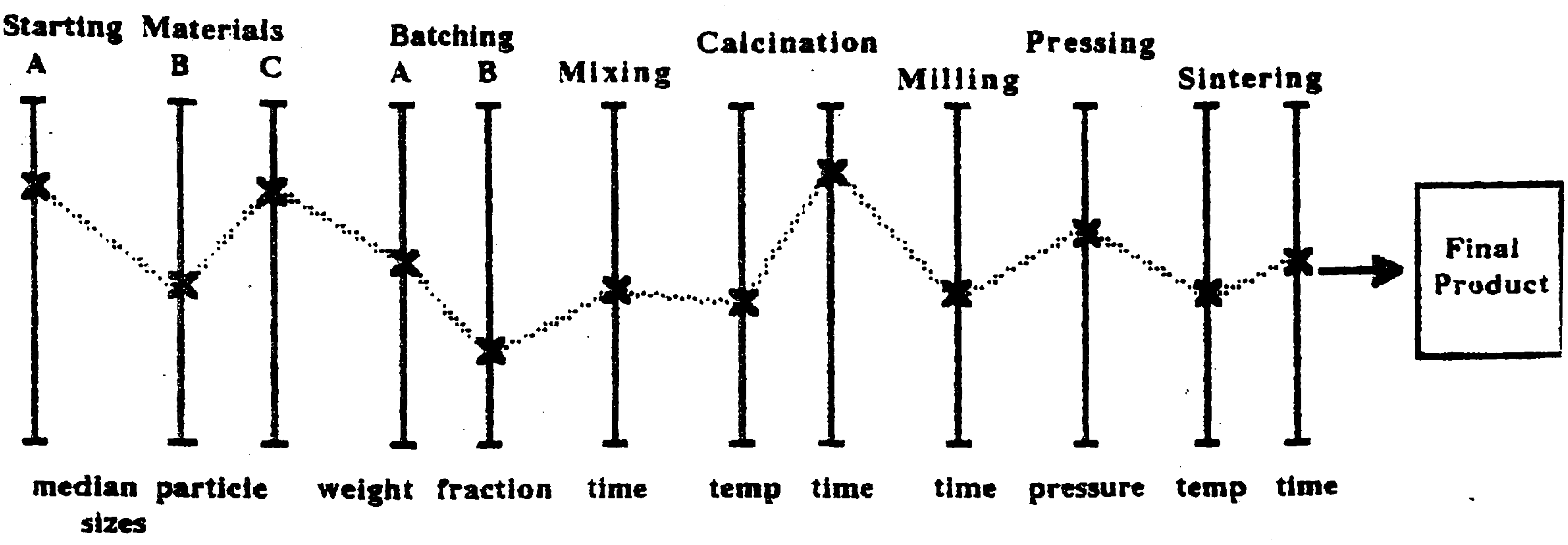

Figure 2.10 Alternative way of considering a processing scheme

2.3.3.4 Iterative Process Development

The pathway is sought in process design, which is deemed to give the best combination of behaviour during processing, properties for the final product and cost. Such design also involves the selection of the starting materials, the process methods and equipment to be used in the processing scheme. The design inevitably involves compromises.

The methodology employed in this study to design the processes and final product uses iteration from an initially chosen pathway. This method relies on the designer having a significant body of general knowledge concerning how materials tend to behave when subjected to particular processing operations and also knowing how the desired behaviour and behavioural properties of intermediate products and the final product are influenced by their characteristic properties. When such general understanding is not available, the methodology becomes one of trial and error. However, analysis of the outcomes of a number of such trials provides insights so that, with new understanding, the methodology eventually returns to the iterative mode. Although with iteration, changing the value of a processing variable or a starting material characteristic in a given direction should effect an expected change in behaviour or of a particular property in the required direction, the extent of the change will not be known. If the change is too little or too much, established by analysing intermediate and final products, the next iteration can be made to bring the behaviour or property more into line with requirements.

Iterative changes may involve altering the value of only one processing variable or one characteristic of the starting materials at a time or may involve altering the values of several processing variables or characteristics together. It should be borne in mind that changing the value of one processing variable or one characteristic will usually involve several characteristics in the final product changing. Also, situations arise where it is known that an acceptable final product would not be made if a change to one variable were not in some way compensated by simultaneously changing the values of other variables. Provided that the intermediate and final products are analysed so that their deficiencies are appreciated and understood and the effects of altering processing variables and starting material characteristics is sufficiently well understood, the iterative approach to process and product design can be highly effective.

2.3.3.5 Uniformity in Processing

The uniformity concept (Messer et al. 1983a) is a powerful tool in the design of ceramic processes. It can be stated generally in the following way. For a material to behave uniformly on a given scale of size when subjected to a treatment of some kind, the treatment must be applied uniformly throughout the whole of the material, which itself must have uniform characteristic properties on the given scale.

A key area of concern in the processing of all ceramics that shrink during sintering is the uniformity of this shrinkage. For a ceramic to shrink uniformly on a given scale of size requires the ceramic to be uniformly heated and for its characteristics to be uniform on the given scale. Non-uniform heating of the ceramic will result in non-uniform shrinkage, which mirrors the heat treatment given to each region of the ceramic as well as how the characteristic properties of the green ceramic vary from place to place.

Consider that a green ceramic is cut into a number of equal-sized parts and that each part is analysed to establish its composition, particle size distribution (PSD), porosity and particle orientation. These are the characteristics that strongly affect the densification and shrinkage behaviour. If the parts, within the precision of experimental measurement, have the same composition, PSD, porosity and particle, that are randomly aligned then the green ceramic can be said to be essentially uniform on the scale on which the ceramic has been subdivided. Such a ceramic would shrink uniformly on the examined scale of size provided it is uniformly heated.

Consider that a ceramic has been subdivided into 20 parts and one or more of the characteristic properties of the parts found to vary. An equivalent ceramic would shrink non-uniformly on the scale of the subdivision. As this is a moderate fraction of the whole ceramic, the ceramic would distort during firing as stresses develop between contiguous regions endeavouring to make each of the regions shrink similarly. Hence, macroscale non-uniformity of either the temperature or the characteristic properties will cause the ceramic to distort.

Consider that a ceramic has been subdivided into very small parts each containing 1000 particles, and one or more of the characteristic properties found to vary from part to part. An equivalent ceramic, which is uniformly heated, would shrink non-uniformly on this small scale of size. The resulting differential shrinkage would be accommodated by the enlargement of some of the existing pores. The overall shape of the ceramic will not change, although the surface will be rougher than for a ceramic that is essentially uniform on this small scale of size. Hence, microscale non-uniform characteristics cause pore enlargement.

The essential difference between macroscale and microscale non-uniformity of the characteristics is the rate at which their values change with distance. Macroscale non-uniformities arise through either non-uniform treatments given to the material or non-uniform responses of the material to uniform treatment because of its variable characteristics (e.g. variation in particle or granule sizes and shapes). Macroscale non-uniformities of a green ceramic often have a symmetry and the values of a characteristic property tend to change slowly and systematically with distance. A macroscale non-uniformity can conveniently be described with the aid of a map showing how the values of certain characteristics, such as porosity, vary from place to place across a section of the green ceramic. Microscale non-uniformities change rapidly with distance in random ways by varying amounts. An index for the system as a whole, such as the mixing indices (Messer, 1983b) used to describe the compositional uniformity, might be employed to describe the microscale non-uniformity of a particular characteristic.

In general, it can be said that the process operations should be designed to attain and maintain uniformity of the characteristic properties on all appropriate scales of size throughout the entire processing scheme if an undistorted ceramic with a low residual porosity is to be produced. Densification in many cases occurs more rapidly and the residual porosity after firing is lower when green ceramics approach the uniform state on a scale of size that is sufficiently small that the pores which enlarge, because of non-uniform firing shrinkage, remain small enough to be closed during the sintering process. One caveat must, however, be included. If there is evolution of a gas during sintering, open pore closure should be designed to occur after the gas has left the system. A green ceramic that is more uniform with respect to porosity on the small scale tends to reach zero open porosity at a lower sintering temperature or in a shorter sintering time. This has been demonstrated by comparing a plastically formed whiteware with powder pressed versions of the same body (Agbarakwe el at. 1989). The more uniformly porous, plastically-formed test-pieces achieved open pore closure at a lower sintering temperature than those that were powder pressed. However, because of a gaseous mechanism of pore growth, probably connected with the evolution of oxygen because of the change in the valence state of the iron impurity from Fe^{3+} to Fe^{2+}, the powder pressed test-pieces attained minimum residual porosities that were lower than the minimum porosity of the plastically formed test-pieces. The gas must be removed at either a lower temperature or earlier time in systems like this, as occurs when a reducing atmosphere is used to fire hard porcelain. Alternatively, the sintering rate must be slowed down by use of either coarser particles, reduced flux or increased filler content.

2.3.3.6 Concluding Remarks

Designing a total processing scheme to make a product with the desired properties at an acceptable cost involves activities which need intuitive, imaginative thinking and those that can be carried out in a systematic, logical fashion based on experimental observations. Both types of activity require a broad understanding of both processing and properties if they are to be navigated successfully. Each of the processing operations must be designed to give an acceptably uniform treatment and to be compatible with preceding and subsequent operations in the total processing scheme.

Chapter 3: Design of a Fine Translucent China

3.1 Introduction

The work described in this chapter is concerned with the design of a fine translucent china (FTC) using the low-clay approach. A design requirement was that the biscuit fired ware would not sag during the glost firing at 1100°C. Further requirements were that it should be white, translucent and have a thermal expansion coefficient (TEC) of 6 to $6.5*10^{-6}/°C$ to fit the glaze currently used for FTC bodies.

In order that ware can be made without distortion, sagging during biscuit firing has to be kept within certain limits. To establish these, commercial bone chinas were used as standards. Bone china is known to be prone to sagging and yet can be fired satisfactorily with supporting kiln furniture. It was considered that if FTC could be made which sagged in a similar way or less than bone china, it would be possible for it to be biscuit fired without distorting unacceptably.

The FTC composition was to be based on the prefired material developed by Capoglu and Messer and described in a patent (Messer el at. 1998), which comprised anorthite ($CaO.Al_2O_3.2SiO_2$) as the major phase (~76%) with mullite ($3Al_2O_3.2SiO_2$) (~8%) and glass (~16%) being the minor phases (Mulenga, MSc 1995). The prefired material chosen is labelled M17 in the patent . This was to provide the coarse component of the body, with the medium-size component to be composed initially of a mixture of finely milled M17, finely milled quartz and finely milled nepheline syenite as the flux. The fine component of the body was to be clay, composed of equal amounts of china and ball clay.

3.2 Experimental Procedures

3.2.1 Introduction

The M17 prefired material was prepared by the mixed oxide route from starting materials comprising calcium carbonate, aluminium trihydroxide, quartz with some magnesium carbonate (strictly $(MgCO_3)_4Mg(OH)_2.5H_2O)$) added as a flux. Following calcination of well-mixed batches of the starting materials, the prefired material was ground to two sizes, labelled coarse prefired (CPF) and fine prefired (FPF). These were combined in various proportions with quartz, a flux and clay plus, on occasions, other constituents to make whiteware bodies. These were heat treated to see how they would densify and sag during the biscuit firing and sag during the firing required for glazing.

To assess sagging, two commercially produced bone chinas were examined. Bars were produced from spray dried granulates and these were given a heat treatment sufficient to densify them. During this heat treatment the bars were only supported at their ends. The two materials behaved very differently, but the one that sagged the least set the target for the present study.

3.2.2 Characteristics of the Starting Materials

Aluminum Trihydroxide ($Al(OH)_3$)

The aluminum trihydroxide was obtained from Alcan Chemicals Europe. Its grade was DH101. For a chemically refined product it is reasonably cheap as it is made in vast quantities in the Bayer process to make aluminum from bauxite. It contained almost no impurities that would reduce the whiteness of the product. The iron oxide (Fe_2O_3) content is quoted as being 0.008% and the titanium dioxide content at zero. The main impurity at 0.25% is Na_2O from the Bayer process, but this is inconsequential in the present work.

Aluminum trihydroxide losses approximately 34.5% water on being heated.

Quartz (SiO_2)

The quartz used in this work was a low iron-containing mineral typically used in high-quality whiteware manufacture. The supplier was James Kent Ltd Stoke-on Trent and the grade was Loch Aline. This was 99.8% SiO_2 with only a trace amount of Fe_2O_3 (0.009%) and no detected TiO_2.The chemical analysis is shown in Table 3.1. Quartz grade having median sizes of ~11 μm, 5μm and 2.4 μm was used in this study.

Chemical Composition w/o	
SiO_2	99.8%
Al_2O_3	0.05%
Total Fe_2O_3	0.009%
Na_2O	<0.05%
K_2O	<0.01%
CaO	<0.02%
MgO	<0.05%
Loss on Ignition	0.07%

Table 3.1 Chemical analysis of Loch Aline crystal glass sand

Nepheline Syenite

The nepheline syenite was of the North Cape variety which has a typical composition shown in Table 3.2. It was purchased from James Kent Ltd., of Stoke-on-Trent. In the as-supplied state it had been milled to have a particle size of ~10µm. It was also milled finer in the Department to have a median size of 1.3µm.

Potash feldspar

Potash feldspar obtained from James Kent Ltd., Stoke-on-Trent had a median size of approximately 10µm. It was milled in the Department to a median size of ~1.5µm. The chemical analysis is in Table 3.2.

Type	**Potash Feldspar**	**Nepheline Syenite**
SiO_2	65.40	57.0
TiO_2	-	-
Al_2O_3	18.70	23.80
Fe_2O_3	0.06	0.12
CaO	0.51	1.70*
MgO	-	-
K_2O	11.10	9.10
Na_2O	3.36	7.80
Li_2O	-	-
LOI	0.29	1.10
Total	99.42	100.62

* This includes 0.30%BaO and 0.30%SrO

Table 3.2 Chemical Analysis of Feldspathic Minerals

Bone Ash ($Ca_5(PO_4)_3.OH$)

The bone ash used throughout this work was kindly provided by Josiah Wedgwood and Sons Ltd.

A chemical analysis was not available but the bone ash had been milled to have a median particle size of approximately 3µm. In this study the bone ash was further milled for 72 hours to obtain a median particle size of 1.76µm.

China Clay composed mainly of kaolinite ($Al_2O_3.2SiO_2.2H_2O$)

The china clay used in this study was Super Standard Porcelain Clay (SSPC) from ECC International Ltd. This clay has low iron oxide and titania contents at 0.39% and 0.03% respectively and so fires to a very white colour. The other main impurities are alkali and alkaline oxides which will act as fluxing additions. The chemical analysis is shown in Table 3.3 below.

Chemical Analysis (Mass%)	
SiO_2	47.0%
Al_2O_3	38.0%
Fe_2O_3	0.39%
TiO_2	0.03%
CaO	0.10%
MgO	0.22%
K_2O	0.80%
Na_2O	0.15%
Loss on Ignition	13.0%
Total	99.69%

Table 3.3 Chemical analysis of Super Standard Porcelain Clay

Ball Clay

The ball clay, which was used in this study was Hymod Prima grade. It was kindly supplied by EEC International Ltd. Typical of ball clays, this material contains a high content of iron oxide (1.4%) and titania (1.3%) shown in Table3.4, and so its use has to be limited to avoid significant deterioration in the colour of the whiteware.

Chemical Analysis (Mass %)	
SiO_2	54
Al_2O_3	30
Fe_2O_3	1.4
TiO_3	1.3
CaO	0.3
MgO	0.4
K_2O	3.1
Na_2O	0.5
Loss on ignition	8.8
C	0.3
Total	100.1

Table 3.4 Chemical analysis of Hymod Prima

Calcium Carbonate Precipitated ($CaCO_3$)

Calcium carbonate was supplied by Fison Scientific. It was fine powder of high purity with the particle size of 9μm. The chemical analysis of this powder is shown in Table 3.5.

The as-received powder was milled down to 1.3μm median particle size for 5 days. This was done by having 600 grams of $CaCO_3$ milled with 900ml of water in a two litre porcelain pot. The pot was half filled with alumina milling media of ~10mm diameter.

Assay>98%	
Total trace elements (%)	
Cl	<0.05%
Fe	<0.05%
Pb	<0.001%
Cu	<0.01%
Mg	<0.2%
K	<0.05%
Na	<0.2%
Zn	<0.01%
S	<0.05%
P	<0.05%
Si	<0.1%

Table 3.5 Chemical analysis of Calcium Carbonate Precipitated

Magnesium Carbonate (hydrated,basic,heavy)

The material sold under this name is really $(MgCO_3)_4Mg(OH)_2.5H_2O$. It was obtained from Fison Scientific and was of high purity. The chemical analysis is shown in Table 3.6.

Specification	
Total trace elements (%)	
Ca	<1%
Cu	<0.001%
Fe	<0.05%
Pb	<0.02%
K	<0.5%
Na	<0.01%
Total S	<0.5%
Total P	<0.01%
Total Cl	<0.05%
Total Si	<0.05%
Residual after ignition	42-45%

Table 3.6 Chemical analysis of Magnesium Carbonate (hydrated, basic,heavy)

3.2.3 Preparation of M17

The composition of M17 is given below

Starting Material	**Weight%**
$CaCO_3$	19.35
$Al(OH)_3$	40.60
SiO_2	37.70
$(MgCO_3)_4.Mg(OH)_2.5H_2O$	2.35
Total	100

Table 3.7 M17 composition

A batch of the starting materials weighing 1kg was placed in a 5 litre porcelain milling pot containing alumina milling balls (~10mm diameter), whose bulk volume occupied half the milling chamber. Approximately 600 cm^3 of tap water was then added to the pot. The pot was rotated for 1 hour at a speed at which the milling balls cascaded (approx 70% of the critical speed at which the balls stay against the wall of the rotating pot).

The slurry was poured out of the pot into plaster sinks to remove the bulk of the water. Additional water was used to wash the residual slurry out of the pot and to remove the slurry coating the milling balls. After one day in the plaster sinks the cakes could be removed for drying in an electrically heated oven. The drying at 110°C was completed in 24 hours.

The dried cakes were broken up in a porcelain mortar with a porcelain pestle. The fine powder produced was then spread out on a plastic sheet to be granulated. A fine mist of water droplets was sprayed onto the powder with about $10^{w}/o$ water being added as uniformly as possible. The powder was mixed and agitated by hand with the hand encased in a plastic glove.

In this way the powder was formed into a granulated body. This was passed through a 4mm sieve and the material retained on a 2mm sieve placed in an alumina crucible for calcination. The oversized and undersized granules were regranulated. The purpose of granulation was to produce a body that, after calcination, could easily be broken down to produce a feed material for milling.

The granulated material was calcined in alumina crucibles in an electrically heated kiln (Lenton furnace, serial no. 3604) with 12 silicon carbide heating elements. The chamber size was 520*400*210 mm. The temperature was programmed and controlled with a Eurotherm system. The temperature was increased at 3°C/min to 1350°C and held at this temperature for 3 hours. The cooling rate was initially 3°C/min until the kiln cooled at its natural, slower rate.

The material was well-reacted with only anorthite and mullite being detected by x-ray analysis. The material was also observed by optical microscopy to be composed of dense regions that were large enough to allow dense particles having the desired 20μm median size to be produced by milling.

The granulation process was not very successful in making the calcined material easy to break up. Considerable effort was required to fragment the calcined material as the granules had bonded so strongly to each other. Large lumps of the calcined product were wrapped in polyethene sheets, placed on an anvil and hit with a heavy hammer to reduce the pieces to a few millimetres in size.

The crushed material was placed in the 5 litre porcelain mill with the 10mm diameter alumina balls occupying half of the chamber and wet milled. Typically 600 grams of calcine was milled with 900 cm^3 of water. Because of the coarse feed, the milling was inefficient and typically required three days for the powder to be milled to approximately 20μm median size. The mill was stopped periodically and a representative sample was withdrawn for particle size measurement. This was carried out using a Coulter LS130 particle size analyzer. This system uses laser diffraction.

A coarsely milled material having median size of 19.6μm was produced.

A finely milled material with a median size of 2.3 μm was produced with 5 days milling. An even finer material with median size of about 1.5μm needed about 7 days milling.

3.2.4 Final Body Preparation

Batches of 100 grams of various compositions were prepared by wet mixing in plastic bottles with 60cc of water. The bottles were rotated on rollers and contained three alumina balls to aid mixing. First the fine components i.e. clays and materials milled to ≈2μm were placed in the bottles with water and milling balls. These were mixed for 45minutes. The coarse material was then added and the mixing continued for 15minutes.

The binder used was 0.5% polyvinyl alcohol (PVA, molecular weight 13,000 to 23,000, hydrolysed 87-89%) combined with 1.0% polyethylene glycol (PEG, molecular weight 4000) as a plasticiser. The 0.5 grams of binder and 1 gram of plasticiser were dissolved in 20 cm^3 of warm water and then added to the mixed slip and thoroughly stirred.

The complete mixture was poured into a porcelain bowl and dried in an oven at 80°C for 2 days. The dried cake was broken up in a porcelain mortar with a porcelain pestle and the fine powder spread out on a plastic sheet for granulation. This was carried out as previously described but the granules were smaller. Granules passing through a 450μm sieve and retained on 210μm sieve were stored, for later pressing, in a sealed bottle. Granules larger than 450μm and smaller than 210μm were regranulated.

3.2.5 Forming of Test Pieces

Bars 120*20*4mm used as test-pieces for studying sagging, were formed by pressing the granulated bodies at 40 MPa . The hardened steel die used to make the bars was formed from several pieces bolted together.

The die was assembled and then the die cavity was overfilled with granulate. The surplus granulate was swept away without compacting the granulate in the die. The die was then tapped so that the granules packed slightly, allowing the top punch to be positioned in the cavity before placing the die between the platens of the press. After pressing, the die was taken apart to remove the pressed bar. The bars weighed around 16 grams.

Discs 25mm diameter were pressed at 40MPa for density measurement after firing. The hardened steel die was filled in the same way as the bar die. After pressing, the discs were typically 4.5mm deep and weighed approximately 3.5grams

3.2.6 Firing

The firings were carried in the same kiln that had been used for the calcinations. Bars to be tested for sagging were positioned symmetrically across the 87mm gap in the refractory brick support (see Figure 3.1 on section 3.2.7). They were placed on alumina powder to prevent them sticking to the brick. Discs were placed on the alumina powder on the refactory brick along side the bars. Bars to be used for examining sagging in the second, lower temperature firing (1100°C soak), to simulate the glost firing, were fired fully supported on a flat surface formed by a piece of refractory brick coated with alumina powder.

Most of the firings to densify the test pieces were carried out with a soaking temperature of 1230°C for a soaking time of 3 hours. The temperature was increased at 3°C/min and initially cooled at the same rate. Occasionally the soaking temperatures and times were changed but the ramp up and down rates of 3°C/min was left unchanged.

3.2.7 Assessment of Sagging

Bone china is known to be prone to sagging but can be fired satisfactorily to produce all the required tableware shapes if supported by appropriately shaped kiln furniture. It was therefore considered that bone china could be used as a standard for sagging in the test used in this study. It was assumed that if any of the bodies being studied sagged to a similar extent whilst being densified, then, it should be possible to produce all the required tableware shapes from these bodies without noticeable distortion.

Bone china bodies in the form of spray dried granulated powders were obtained from two of the leading manufacturers in the U.K. These bodies were pressed at 40 MPa into bars having dimensions of 120*20*4mm. They were given heat treatments with a soaking temperature of 1230°C for 3 hours and up and down ramp rates of 3°C/min. During firing, the bars were placed on alumina powder on a refractory brick with only their ends supported as shown in Figure 3.1. This was achieved by removing a section of the brick so that an 87mm central span of a bar was left unsupported. The bars from one of the supplier sagged by ~10mm, whereas those from the other supplier deformed so much that they fell into the gap between the supporting surfaces of the brick. For bars that remained supported, the sagging was determined by placing them upside down on a flat surface and measuring the maximum height of their lower surfaces above the flat surface (Figure 3.2).

From these observations on how bone china sagged, it would appear that provided bars did not fall into the gap between the supports, the sagging would be acceptable. Nevertheless, attempts were made in the development work on the FTC to change the composition and particle size of the constituents so as to minimise the sagging and the porosity for the chosen, fixed heat treatment.

As the powder densities of the fired bodies, which were made with different compositions and with the components having different particle sizes, were not measured, the bulk densities of the test-pieces were used with the amount of sagging to establish a simple index for comparison purposes. This involved dividing the bulk density in gcm^{-3} by sagging in mm and multiplying by 1000. High values of this index would be obtained with the desired combination of a high density coupled with a low value of sagging.

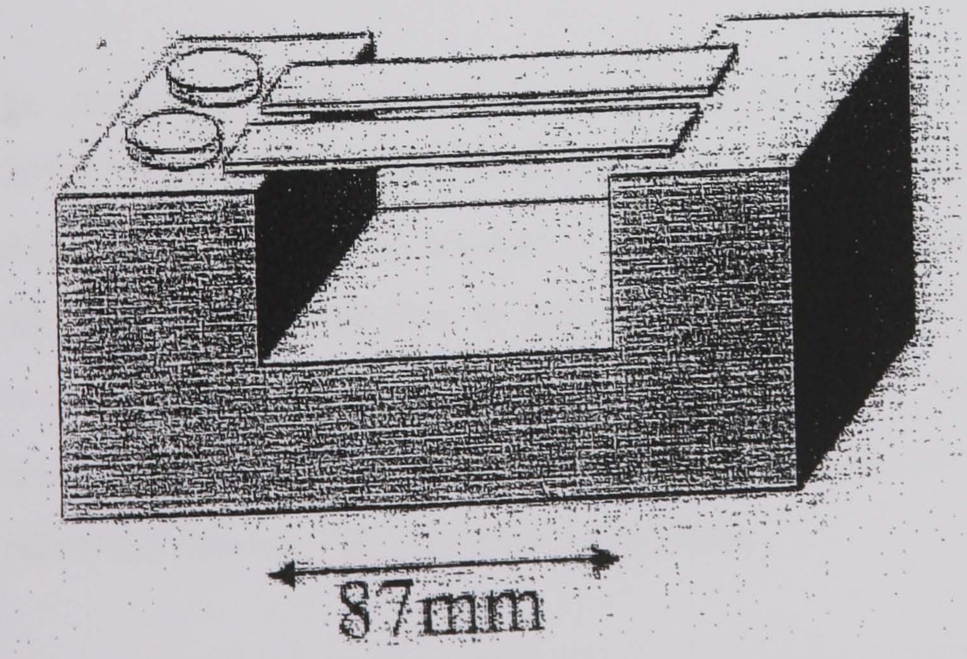

Figure 3.1 Firing brick with dimensions of span.

Sag = Height-Thickness

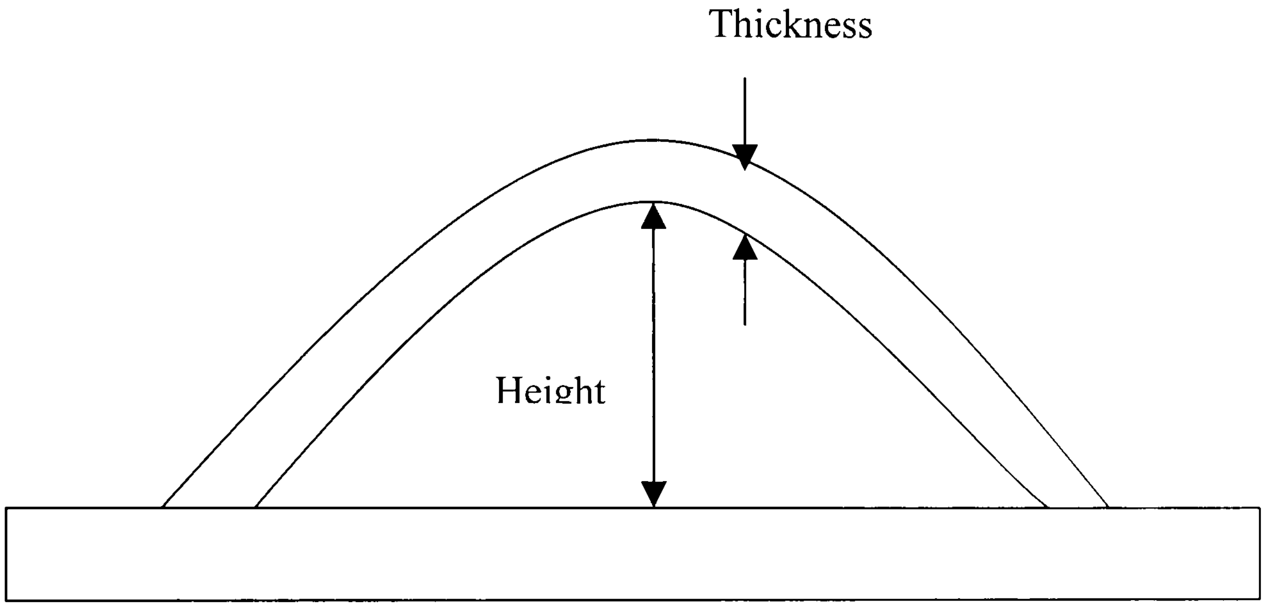

Figure 3.2 Measuring sag

3.2.8 Design and Development of Fine Translucent China

The design of FTC should be such that a standard bar with dimensions 120*20*4mm has acceptable behaviour in the sagging test (i.e. remain supported) whilst being densified to produce a very white, translucent material at 1230°C with a soaking time of 3hrs. In additon, the average TEC of the fired body over the range 20-600°C was to be 6 to 6.5 *10^{-6}/°C. A bar that had been fired fully supported at 1230°C, so that it was flat, was required not to sag when refired to 1100°C for 30mins. This simulated glost firing.

The body formulations initially had to be developed on a trial and error basis whilst attempting to gain some understanding of the factors that affected densification and sagging. When this understanding was achieved, it was possible to use an iterative approach to design the body so that all the requirements could be met.

The initial body design was based on:

the use of a low clay content of 15%, to minimise the deleterious effects of clay particle alignment;

the use of from 40 to 60% coarse material(~20μm) combined with 60 to 40% finely milled material (~2μm) to minimise firing shrinkage. Values of ~11 to 13% for the linear shrinkage would be acceptable;

the incorporation of quartz into the body to increase the thermal expansion coefficient of the body and reduce the use of the more costly prefired material. It was known that bodies, such as the anorthite/mullite porcelain body, W3 (Messer et al., 1998), based mainly on the prefired material had TECs of 4.5 to $5*10^{-6}$/°C. The change in volume of the quartz at the β to α phase transition at 573°C and the high TEC of α quartz below its transition temperature should increase the TEC of the fired body;

the incorporation of a flux, either nepheline syenite, bone ash or potash feldspar, to reduce the firing temperature from that used for a W3-type body of ≥1280°C to 1230°C, the temperature typically employed for an FTC body.

The body formulations tested are listed in Table 3.8 on page 73. It was not known whether the densification heat treatment would result in the test-pieces being underfired, optimally fired or overfired. Compositions were sought which would yield a high density with little sagging. Those compositions having the higher values of the density/sagging index were identified and the possible reasons for the more favourable combination of density and sagging sought.

In the earlier formulations(Q1 to Q22) nepheline syenite was used as the flux. These formulation are listed in Table 3.8 . Some trials followed in which bone ash was empolyed as the flux on its own or combined with nepheline syenite. This formulations are listed in Table 3.9. It was found, however, that the bodies containing bone ash appeared to be coloured light brown in transmission although white in reflection. Consequently, the use of bone ash was eliminated for this reason.

From the explanations given in the literature for densification through and in the presence of a liquid phase, it is known that if the proportion of liquid phase is increased or if the viscosity of a fixed proportion of liquid is reduced that the densification rate should increase. The sagging would also be expected to increase in both of these cases as either more liquid or a more fluid liquid should facilitate either flow of the body as a whole and the relative movement of the solid grains in the bar under the influence of the tensile and shear stresses resulting from the weight of the unsupported section of the bar.

It can be observed that the higher values for the density/sagging index for compositions up to Q42 tend to occur when the flux content is lower than 10%, particularly for 6 and 8%. It is possible that higher flux contents resulted in more liquid than was necessary to minimise porosity for the heat treatment given and consequently caused sagging to increase and possible overfiring to occur so that a low value of the index was obtained.

During the course of this study it became known to the author that the equilibrium constitutions of the bodies not containing bone ash could be calculated as a function of temperature using the F.A.C.T thermodynamic program. It was also realised that the viscosities of the liquids at equilibrium could be calculated using a program established by Jaffari (1995). Dr A.Watson, currently at Leeds

University, kindly calculated the equilibrium constitutions of many of the bodies studied from their oxide contents. The author used the data obtained on the constitutions of the liquids to compute the viscosities at 1230°C. Surprisingly all the viscosities were similar at ~$2*10^4 \pm 10\%$ Poise.

The percentages of liquid phase in the formulations computed using FACT are listed in Table 3.8 and in Figure 3.3 the density/sagging index is plotted against liquid content. From this it is clear that the liquid content is not a totally dominant variable affecting sagging. However, although highly scattered the index does exhibit some tendency to decrease with increasing liquid content.

A simple relationship between the equilibrium liquid content and sagging should not be expected for several reasons. For example, the bulk densities of test-pieces do not just continue to increase during firing when the liquid phase increases in content and/or fluidity. Such changes can take bodies given a fixed heat treatment from being underfired to overfired, which will cause the bulk densities to decrease. The bodies are not expected to reach equilibrium in the time taken to fire them and hence the computed liquid contents may not be appropriate. How closely a body approaches equilibrium for a fixed heat treatment will depend on the sizes of its particles, with bodies composed of finer particles achieving a closer approach.

It appears that there is some benefit in the use of finely milled quartz rather than quartz that is more coarsely milled. This can be seen by comparing Q9 and Q21. These bodies have the same compositions but the former had a higher density and sagged less. Finer quartz would improve compositional and particle size uniformity of the body on a small scale of size (say 50*50*50μm scale or smaller)

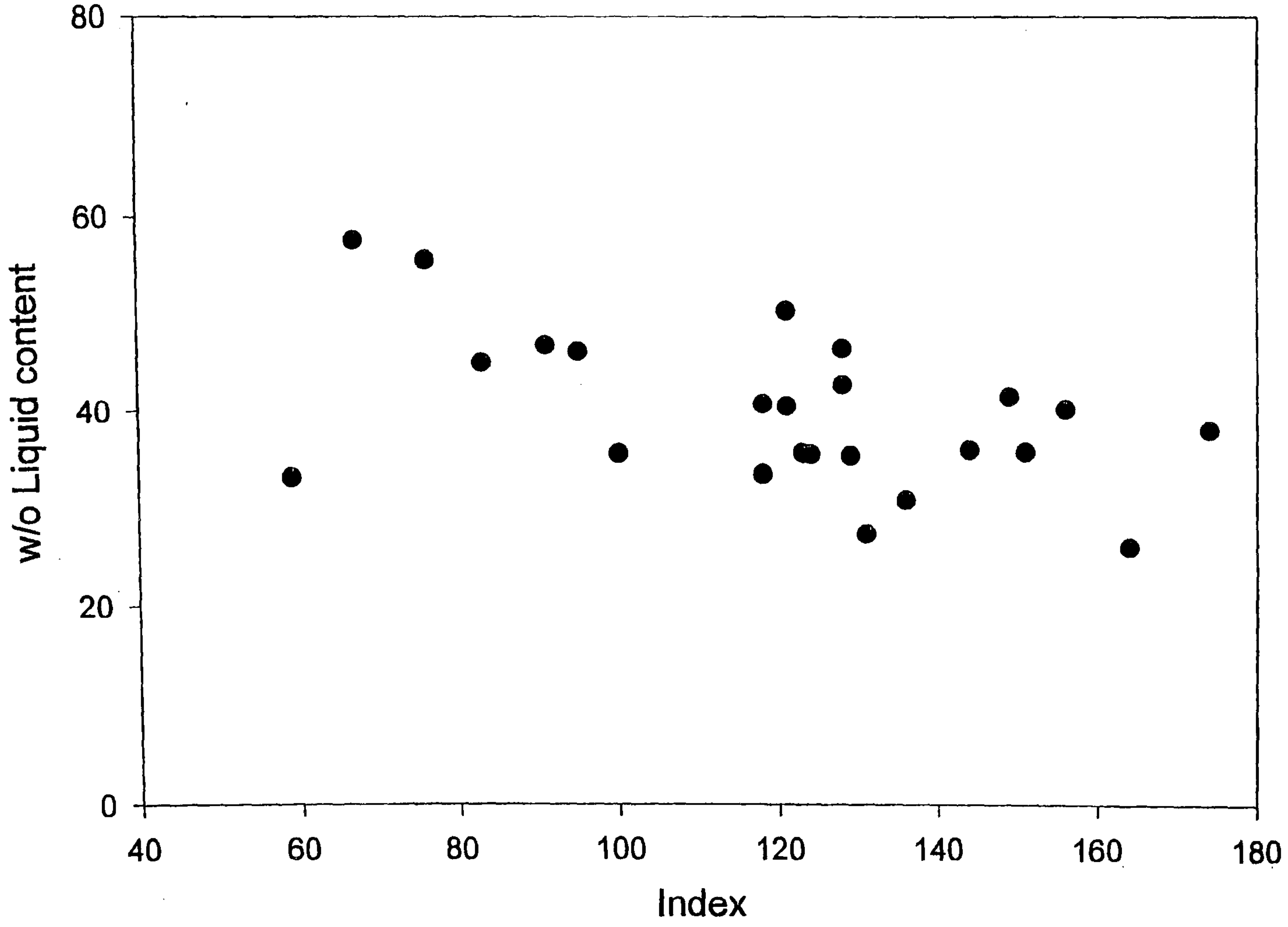

Figure 3.3 Density/sagging index vs liquid content calculated using the FACT program

and should enhance the densification rate. The finer quartz would more effectively absorb the alkali oxides from the nepheline syenite than the coarser quartz and so increase the viscosity of the liquid. This should reduce the tendency to sag and could reduce the densification rate. In whitewares composed of clay, quartz and a flux, reducing the size of the quartz has been shown to enhance densification (Monshi 1990). This suggests that the improved uniformity more strongly affects densification than absorption of the alkali oxide.

Formulations from Q43 upwards are given in Table 3.9. The important breakthrough in understanding came when bar Q43, having the same composition as Q9, was made with 60% finely milled prefired body instead of 60% more coarsely milled material The density was substantially increased from 2.42 gcm^{-3} for Q9 to 2.77gcm^{-3} for Q43 and the sagging reduced from 20mm to 14mm. The index increased from 121 for Q9 to 198 for Q43.

Increasing the amount of the liquid phase and/or its fluidity should increase the density and sagging during firing. However, reducing the particle size should increase density, and reduce bending by reducing the differential sintering shrinkage. Reducing particle size increases the surface area and hence driving pressure for densification and improves uniformity on a fixed small scale of size. Reducing particle size increases the surface tension stresses. The rate of the bend stresses arising from the unsupported section of the bar to the surface tension stresses is thus reduced. It should be possible, if finer particles are used, to achieve a high density with a reduced amount of liquid phase and/or reduced fluidity and so reduce the creep component of sagging i.e. the flow of the materials overall, and attain a higher value for the density/sagging index.

Sample Code	CPF $^{w}/o$	FPF $^{w}/o$	Quartz $^{w}/o$	Clay $^{w}/o$	Nephline Syenite $^{w}/o$	$CaCO_3$ /MgO $^{w}/o$	Al_2O_3 $^{w}/o$	Density ρ (g/cm^3)	Sagging s (mm)	liquid content ($^{w}/o$)	Index ρ/s
Q1	50	10	10*	15+	15			2.39	25	-	96
Q2	55	10	10*	15+	10			2.27	24	46.1	95
Q3	55	10	5*	15+	15			2.28	25	46.8	91
Q4	50	10	10**	15+	15			2.30	27	-	85
Q5	50	10	10***	15+	15			2.19	24	-	91
Q6	57	10	10*	15+	8			2.13	18	40.6	118
Q7	55		15*	15+	15			2.15	32	57.6	67
Q8	57		13*	15+	15			2.30	30	55.5	76
Q9	60		17*	15+	8			2.42	20	40.4	121
Q10	60		15*	15+	10			2.41	20	50.2	121
Q11	60		15***	15+	10			2.20	18	-	122
Q12	60		19*	15+	6			2.32	17	30.8	136
Q13	60		10*	15+	10		5	2.19	17	42.6	128
Q14	57.1		14.3*	14.3+	9.5	4.8C		2.08	25	45.0	83
Q15	57.1		14.3*	14.3+	9.5		4.8	2.05	16	46.4	128
Q16	57.1		11.4*	14.3+	7.6		9.5	2.17	12.5	37.8	174
Q17	60		18*	15+	7			2.27	15	35.6	151
Q18	65		13*	15+	7			2.31	16	35.8	144
Q19	65		18*	10+	7			2.21	18	35.5	123
Q20	60		23*	10+	7			2.12	17	35.4	124
Q21	60		17***	15+	8			2,22	25	-	88
Q22	50	10	15*	15+	6		4	2.23	15	41.3	149

Table 3.8a: Body formulations ($^{w}/o$), their densities and sagging behaviour when given a standard heat treatment of 1230°C for 3 hours.

* 2.4μm quartz ** 5μm quartz *** 11μm quartz

\+ 50:50 china clay : ball clay ++ china clay

Sample Code	CPF ^{w}/o	Quartz ^{w}/o	Clay ^{w}/o	Nephline Syenite ^{w}/o	Bone Ash ^{w}/o	$CaCO_3$ /MgO ^{w}/o	Al_2O_3 ^{w}/o	Molochite ^{w}/o	Density ρ (g/cm^3)	Sagging s (mm)	liquid content ^{w}/o	Index ρ/s
Q23	57	16*	15+	-	7		5		2.41	27	-	89
Q24	55	15*	15+	7			8		2.10	21	35.5	100
Q25	55	10*	15+	7			13		2.00	17	33.4	118
Q26	57	16*	16++	-	5		6		2.05	12	-	171
Q27	57	16*	16++	2.5	2.5		6		2.06	14		147
Q28	57	16*	22++	-	5		-		2.12	12		177
Q29	57	16***	22++		5		-		-	-		-
Q30	57	16***	16++		5		6		1.92	25		77
Q31	57	16*	16++		5	3M	3		2.25	24		94
Q32	40	19.5*	35++		5	0.5M			2.22	10		222
Q33	40	17*	15++	8				20	2.49	16	40	156
Q34	40	18*	15++	7		10C	10	-	2.00	34	33.2	59
Q35	40	13.3*	15++	6		0.5M	25.2	-	2.10	16	27.3	131
Q36	41	17***	15++	7				20	2.33	18	35.2	129
Q37	40	19.5***	15++	5		0.5M		20	2.30	14	25.9	164
Q38	40	19.5*	-		5	0.5M		35	2.40	16		150
Q39	40	17*	15++		8			20	2.43	25		97
Q40	40	20*	15++		5			20	2.16	11		196
Q41	40	19.5*	15++		5	0.5M		20	2.16	12		180
Q42	40	11***	15++		5		9	20	2.15	16		134

Table 3.8b: Body formulations (^{w}/o), their densities and sagging behaviour when given a standard heat treatment of 1230°C for 3 hours.

* 2.4μm quartz ** 5μm quartz *** 11μm quartz + 50:50 china clay : ball clay ++ china clay Molochite (prefired china clay) from ECC International milled to 2μm

Sample Code	CPF M17	FPF M17	Anorthite	Quartz	Ball Clay	China Clay	Potash Feldspar	N.S	Density g/cm^3	Sagging mm	% Shrinkage	Index	TEC
Q43	-	60 (2μm)	-	17*	7.5	7.5	-	8 (1.3μm)	2.77	14	18.5	198	-
Q44	-	60 (2μm)	-	17***	7.5	7.5	-	8 (1.3μm)	2.75	10	16.9	275	-
Q45	-	60 (2μm)	-	17*	7.5	7.5	-	8 (~10μm)	2.77	14	17.1	198	-
Q46	-	60 (2μm)	-	17***	7.5	7.5	-	8 (~10μm)	2.72	11	16.1	247	-
Q47	42 (10μm)	30 (1.4μm)	-	10*	5	5	8 (1.5μm)	-	2.72	14	13.7	194	-
Q48	42 (10μm)	30 (1.4μm)	-	10***	5	5	8 (1.5μm)	-	2.62	15	12.0	175	-
Q49	42 (10μm)	32 (1.4μm)	-	10*	5	5	6 (1.5μm)	-	2.74	13	13.8	210	
Q50	20 (10μm)	32 (1.4μm)	-	30***	-	10	8 (1.5μm)	-	2.75	20	13.1	138	6.4
Q51	42 (10μm)	-	32 (1.5μm)	10*	-	10	6 (1.5μm)	-	2.76	10	14.5	276	4.77
Q52	20 (10μm)	-	32 (1.5μm)	30***	-	10	8 (1.5μm)	-	2.75	17	11.8	162	6.2

Table 3.9: Body formulation($^{w}/_{o}$), their densities and sagging behaviour when given a standard heat treatment of 1230°C for 3 hours

* 2.4μm quartz *** 11μm quartz N.S= nepheline syenite

** 5μm quartz TEC=*10^{-6}°C^{-1} NB. Figures in brackets are the median particle sizes in μm

The use of finely milled components to make Q43 resulted in a high shrinkage of 18.5%. Q44 was made with coarser quartz of ~11μm median size rather than the material with nominaly 2.4μm median size and this reduced the shrinkage to 16.9%, partly because the density of Q44 was slightly lower and probably partly because the green body would have been more densely packed. Q44 has an even higher value of the index at 275 than that for Q43 at 198 as it sagged much less. At the first sight, this appears to be anomalous because the finer quartz in Q43 should have had a greater ability to absorb the alkali oxides during firing and this should have increased the viscosity of the liquid phase and reduced the sagging. The increased sagging for Q43 may have occurred because more of the quartz was transformed into a liquid even though the liquid phase would, consequently, have a higher viscosity. Neither Q43 nor Q44 was given a heat treatment which would have maximised its density. From some additional results for Q44 it can be appreciated that both Q43 and Q44 had been overfired (i.e. the density of the samples start to decrease after a maximum density is achieved at a lower temperature) when given heat treatments of 1230°C for 3hrs. For example, Q44 attained a bulk density of 2.81gcm^{-3} and a shrinkage of 17.1% when fired at 1200°C for 3hrs. The sagging was the same. This gave an index of 281. Q43 fired at 1160°C, a density of 2.71gcm^{-3} was obtained with a sag of 7.5mm. The index was 361. As Q43 was made with finer quartz it would be expected to be more overfired than Q44 at 1230°C for 3hrs.

Q45 differs from Q43 in being made with coarser nepheline syenite, The as-received flux which was used had a median size of ~10μm. This replaced flux that had been milled to have a median size of ~1.3μm. This modification reduced the shrinkage, probably through improved packing, to 17.1% for Q45 from 18.5% for Q43. The density and the sagging remained the same. A similar modification was carried out to change Q44 to Q46. The shrinkage was reduced from 16.9% for Q44 to 16.1% for Q46, the density decreased from 2.75 to 2.72 gcm^{-3} and the sagging increased from 10 to 11mm.

Finer flux particles in a body create finer pores because the shrinkage will be more uniform and these should enhance the sintering process and reduce sagging. However, the flux constitutes only a small weight fraction of the body and so the effects caused by changing particle size may be small. For finer flux particles, alkali oxides derived from the flux will be more uniformly distributed throughout the body and this should enhance sintering. The effect on bulk density will depend on whether the fired bodies before and after the change in flux particle size are underfired or overfired. Increasing the size of the flux particles should have a similar effect on density to that of reducing the severity of the heat treatment.

With Q45 and Q43 having the same bulk density values, it is possible that Q45 is underfired and Q43 overfired. This would be consistent with the change in flux particle size. The bulk densities for Q46 and Q44 suggest that Q46 is underfired whereas it is known that Q44 is overfired.

A firing shrinkage of 13% or lower was considered to be a design requirement. To achieve this, the particle packing had to be improved by having a mixture of relatively coarse and fine sizes. As increasing particle size would be detrimental to both sagging and density, the approach adopted was to reduce the median sizes of both the coarse and fine fractions from those previously used. Body Q47 was prepared with 42% of relatively coarsely milled prefired material with a median size reduced from 20μm to ~10μm and 30% finely milled prefired material with the median size reduced from ~2μm to ~1.4μm. Finely milled potash feldspar (~1.5μm median size) was introduced as a less potent flux than the nepheline syenite used in Q46 and the clay was reduced to 10%. This body densified well at 2.72gcm^{-3} and had a shrinkage value of 13.7%, which is close to the required value. It sagged 14mm and so had a high value of the index of 194.

Increasing the median size of the quartz from ~2.4μm in Q47 to ~10μm in Q48 caused the density to fall to 2.62gcm^{-3}, the sagging to increase to 15mm and the shrinkage to decrease to 12%. The decrease in density and shrinkage would be expected. The increase in sagging could have resulted from an increase in pore size associated with the coarser quartz and a reduced ability to absorb the alkali oxide.

Q49 was similar to Q47 but had a lower flux content of 6% rather than 8%. This was compensated for by increasing the fine prefired material to 32% from 30%. The density was increased to 2.74 from 2.72gcm^{-3}, which suggested that Q47 had been overfired, and the sagging deceased to 13mm. The shrinkage increased marginally to 13.8%.

Some further reduction in shrinkage was required but it was now considered time to adjust the composition so that the body would have a TEC in the range 6 to 6.5*10^{-6}/°C. To achieve this, Q50 was prepared with 30% of quartz having a median size of ~10μm with 20% coarse prefired material having a median size of ~10μm. The rest of the body was composed of 40% material at ~1.5μm plus 10% clay. The shrinkage at 13.1% was practically at an acceptable value. A high density of 2.75gcm^{-3} was achieved and the sagging was 20mm. The average TEC over the range 20 to 600°C was 6.4*10^{-6}/°C. This body essentially meets the design specification although a little high for both shrinkage and sagging. The microstructure of Q50 is shown in Figure 3.4a and b. The polished surface was etched in HF(40$^{v}/_{o}$)vapour for 30 seconds to remove the glass phase. In Figure 3.4a the quartz grains can be seen. In Figure 3.4b, crystals of anorthite and mullite can be seen but are difficult to distinguish.

A modification was then made to the fine prefired material, to reduce its liquid content in an attempt to reduce the sagging of the final bodies in which it is used. A composition to give pure anorthite was calcined at 1350°C for 3hrs. It was

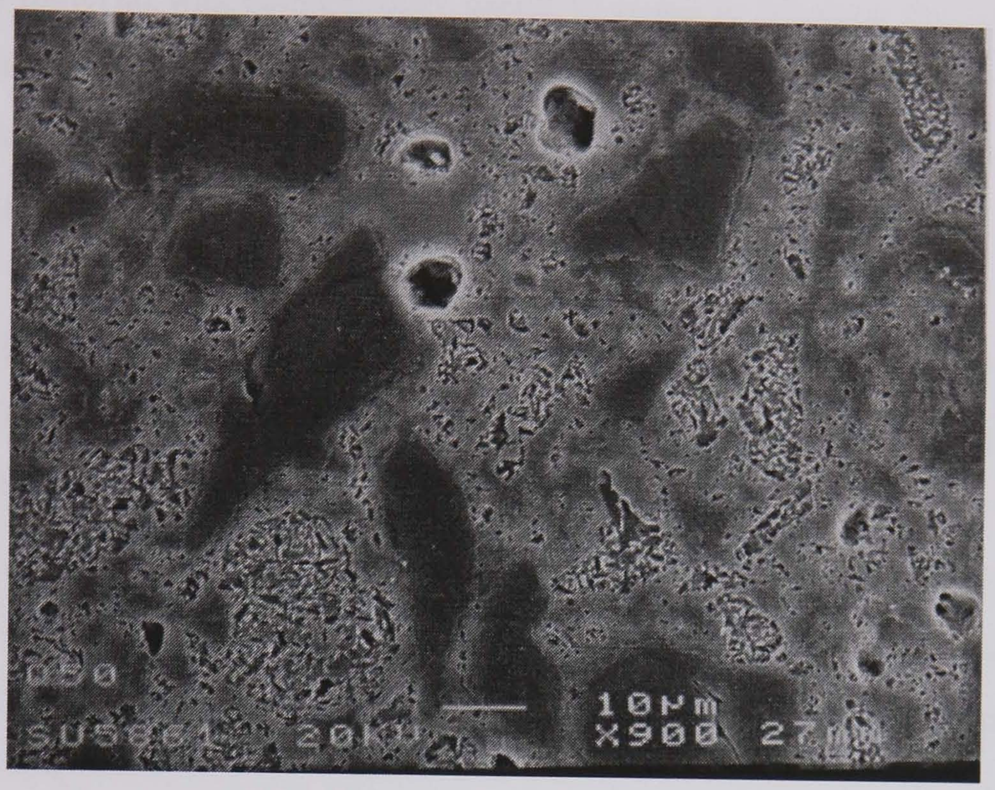

Figure 3.4a Polished and etched sections revealing quartz grains

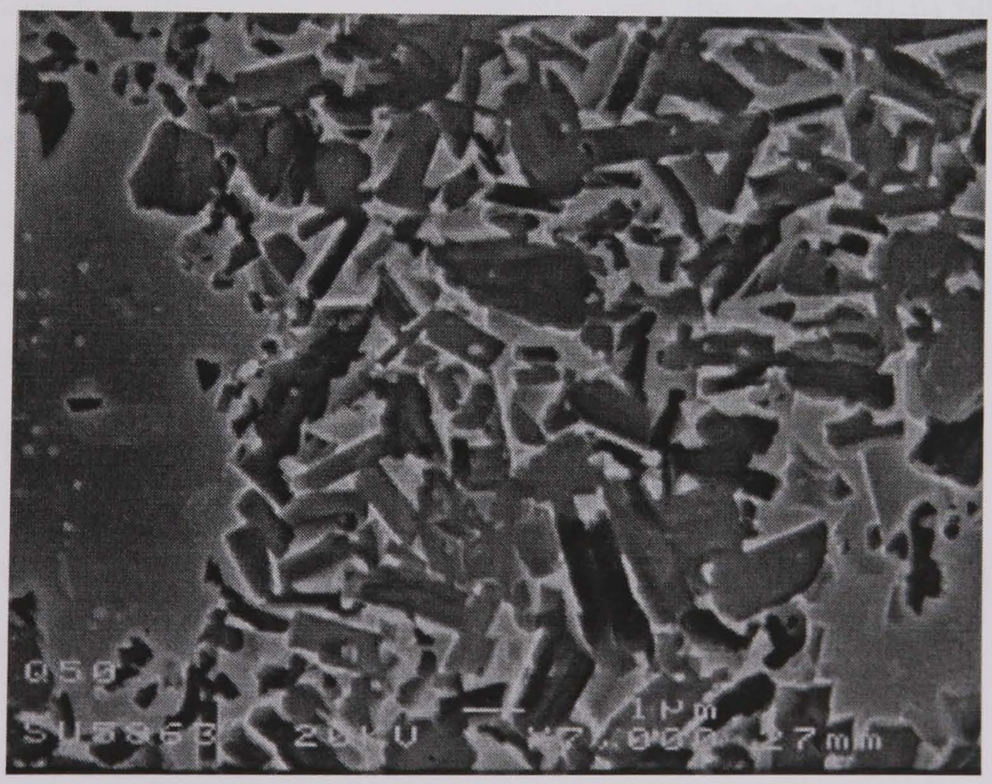

Figure 3.4b Polished and etched sections showing anorthite and mullite crystals

found that this material was considerably easier to crush to produce the feedstock for milling than the calcined M17 body. It was also somewhat easier to mill requiring ~3 days to achieve a median size of ~1.5μm rather than the 7 days used to achieve 1.4μm for M17.

The finely milled anorthite was tried out in Q51. This was similar to Q49 except for the replacement of fine prefired M17 with the anorthite and ball clay with china clay. The reduction of the liquid phase content in Q51 during firing compared to that in Q49 resulted in a higher density and less sagging. This suggests that Q49 might be overfired. The density/sagging index increased from 210 to 276. With little quartz in the body, the thermal expansion coefficient was low at $4.77*10^{-6}$/°C.

Q52 was prepared with the same composition as Q50 except for the change to the fine prefired component. This body shrank by 11.8%, which is less than Q50 at 13.1%, it sagged less at 17mm compared to 20mm and achieved the same high density of $2.75gcm^{-3}$. The TEC was $6.2*10^{-6}$/°C over the range 20 to 600°C. A lower shrinkage was achieved whilst attaining the same bulk density with a slightly coarser, fine component. This appears to be anomalous. However, it is likely that Q52 had a higher powder density than Q50, so that Q52 was probably somewhat more porous than Q50. A higher powder density could result from the use of pure anorthite as the fine prefired component rather than the M17 body that contained glass.

All the bodies made in this study were found not to sag when refired at 1100°C for 30mins, supported only at their ends, to simulate glost firing.

Concluding Remarks

Composition Q52 meets all the design requirements for a fine translucent whiteware. Fired at 1230°C for 3 hours it produces a very white, translucent material that has the required TEC for glazing. It does not sag excessively during the biscuit firing and not at all when fired at 1100°C to simulate glost firing. However, it is unlikely that such a body would be viable. The prefired component would be costly to make and it is doubtful if any advantages this low-clay body has over its conventional equivalent would be sufficient to justify the increased costs.

Nevertheless, through the development of this body an important result on sagging and densification has been established. To minimise the sagging that occurs because of the unsupported weight and to maximise densification, it is necessary to make the particles in the body fine. The reduction in the clay content to reduce or eliminate the deleterious effects of clay particle alignment has the undesirable consequence of reducing the proportion of the finest component in a pottery body. This adversely affects sagging, densification and particle packing. The beneficial effect of clay on the density/sagging index can be seen for body Q32. In the series up to Q42, it had the highest value of the index at 222. It can now be appreciated that this high value was attained because of the high content of very fine particles in Q32, i.e. the 35% of china clay.

At this juncture, it was considered that a whiteware, like the anorthite/mullite porcelain W3, composed mainly of prefired body, could be viable as it could have a combination of desirable features not available in any conventional whiteware. It was therefore decided to apply the findings of the work to date to further develop the W3 body.

Chapter 4 Further Development of an Anorthite/Mullite Porcelain

4.1 Design of the Porcelain

In order to appreciate the requirements of the body labelled W3 in the patent (Messer et. al. 1998), which is in effect an anorthite/mullite porcelain, a Product Design Specification was drawn up in the present study. To help to do this a Requirements/Means Tree was constructed. This is illustrated in Figure 4.1a, b and c. This starts with the Top Level Requirement in Figure 4.1a and leads at lower levels in Figure 4.1b and c to a collection of requirements, marked with asterisks, that can be combined to give the PDS as follows:

The product should be:
1) translucent;
2) white;
3) attractively shaped;
4) producible in full range of shapes, i.e. flatware and hollowware, without significant distortion;
5) producible using automated or mechanized processes;
6) capable to being glazed at temperatures of 1350°C to 1400°C and have a low TEC of ~4.5 to $5*10^{-6}/°C$ so that it can be coated with a chemically durable glaze of high hardness on all contacting surfaces;
7) producible with a low rate of specking and glaze defects;
8) underglaze or inglaze decorated using automated or mechanized processes;
9) strong ~ 100MPa;
10) thermally shock resistant;
11) made from materials of acceptable cost;

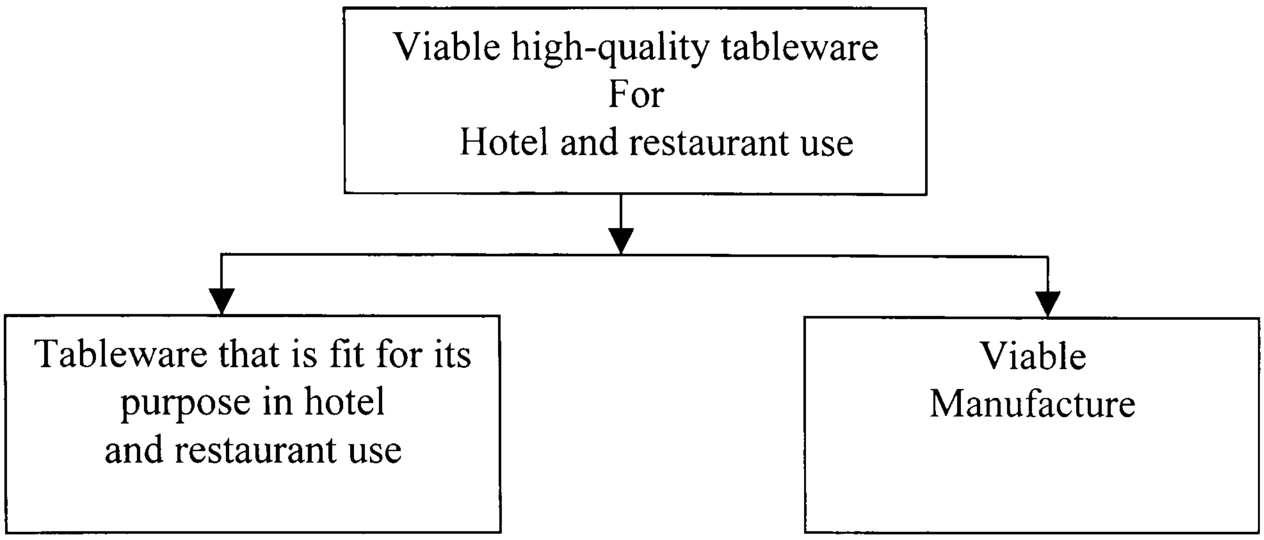

Figure 4.1a The requirement tree

The tree has been extended by adding the means of achieving some of the requirements and so goes some way to establishing the Concept Solution. The design that was proposed and developed by Capoglu and Messer (Messer et. al., 1998)) was a final body that was highly crystalline, composed mainly of anorthite and mullite and glass as the minor phases. This was to be prepared using the low-clay approach from materials with low contents of colouring oxides by the mixed oxide route.

The high crystalline content is required along with a low porosity to achieve a high fracture toughness for a whiteware of $K_{IC} \approx 2MPam^{1/2}$ All the phases in the whiteware have low average TECs, with anorthite at $\sim 4.3*10^{-6}/°C$ and mullite at $\sim 5.1*10^{-6}/°C$. These low values together with high strength (≈ 100MPa) will confer thermal shock resistance on the whiteware. The low TEC of the whiteware will allow a high-silica glaze to be fired on, provided the ware can withstand the high glazing temperature of ≥1300°C.

The anorthite has a refractive index of 1.58, which is expected to be close in value to the glass phase in the whiteware at≈ 1.5. This should help, in the absence of a high concentration of very fine pores, to confer translucency. The use of low clay

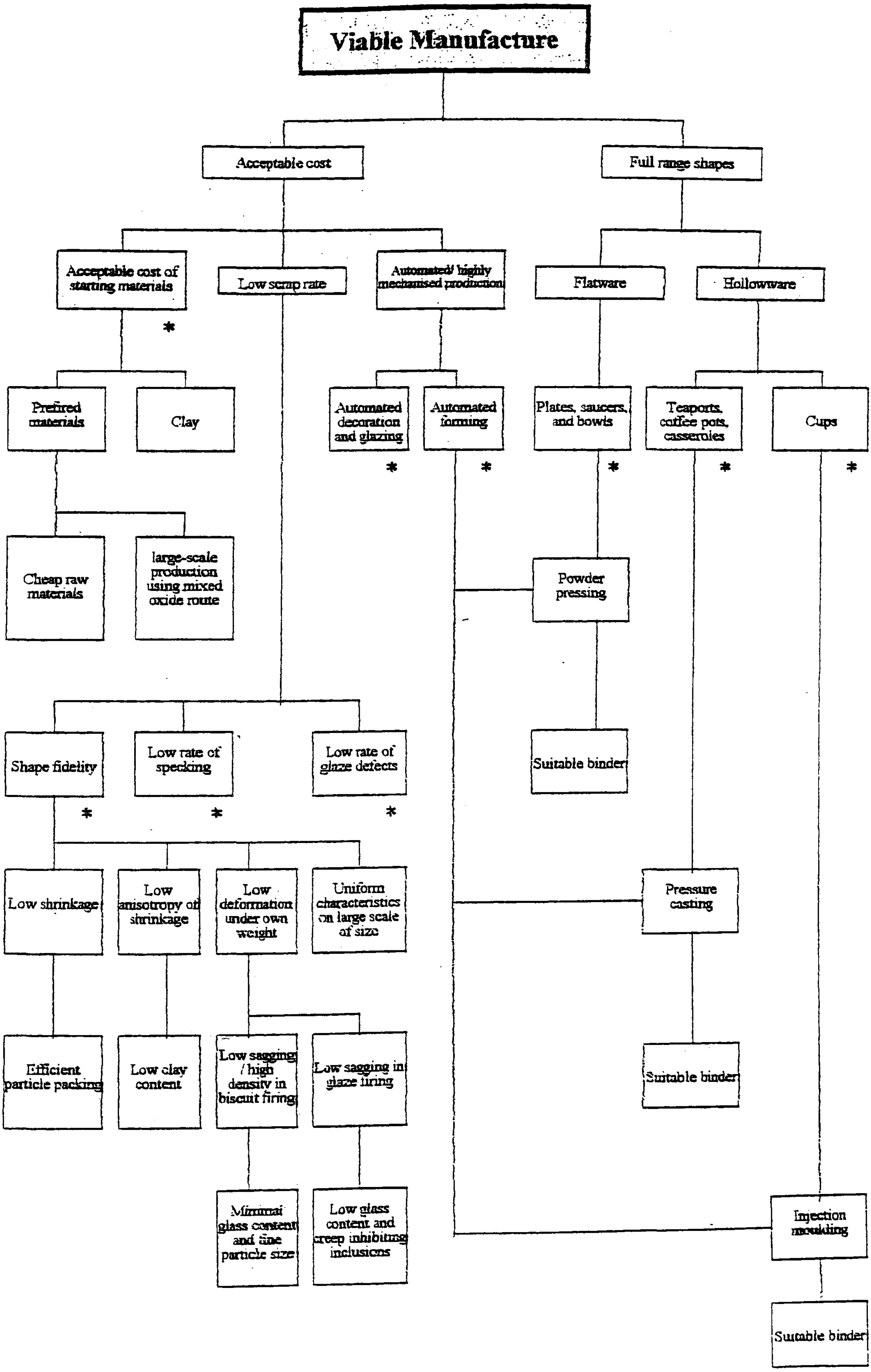

Figure 4.1b : Continuation of Requirement/Means Tree

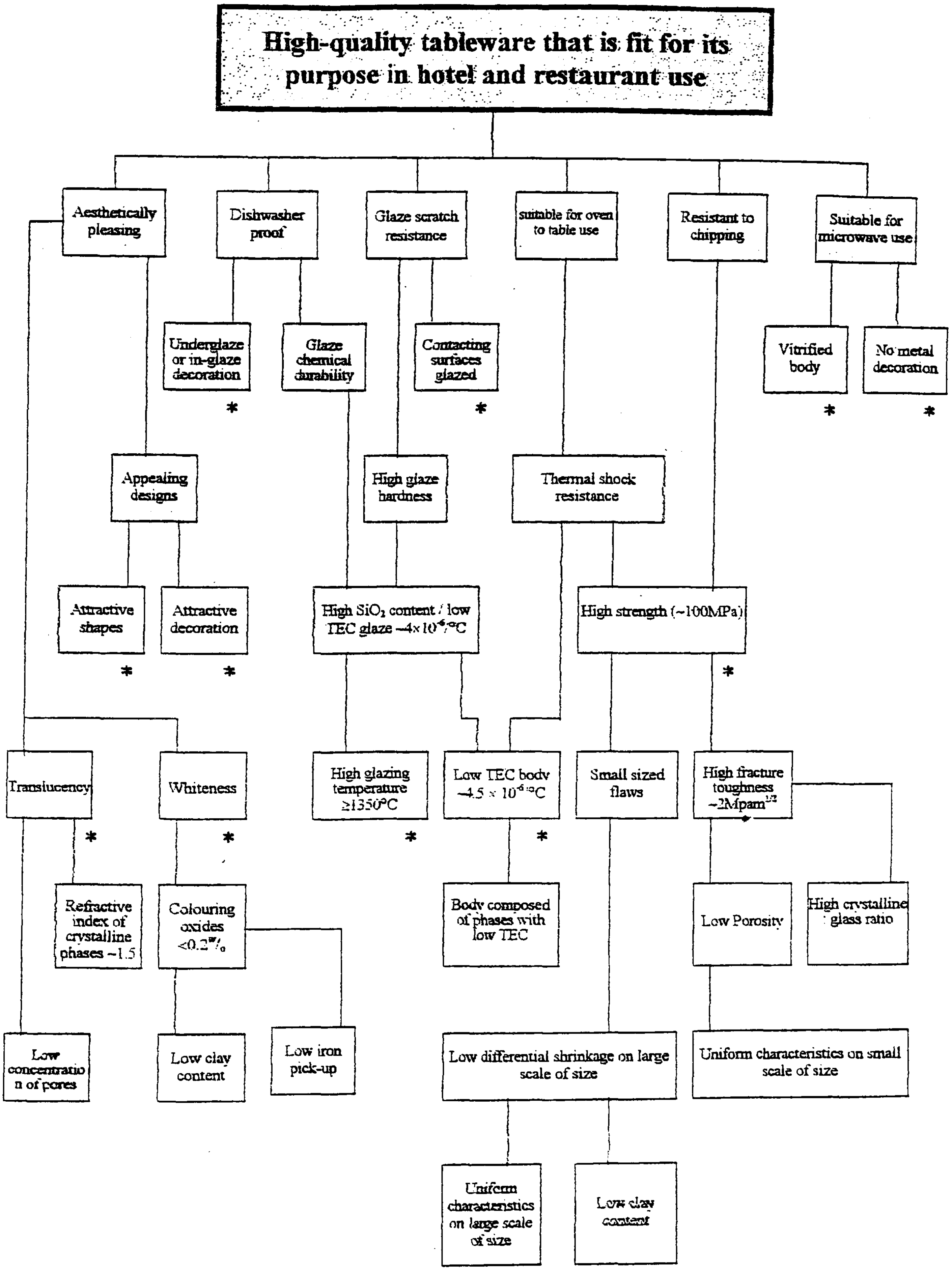

Figure 4.1c Continuation of Requirement/Means tree

content of 10 to 15% would help to reduce the iron and titanium contents of the final whiteware and with the other components having low contents of colouring oxides should help to yield a white body.

A major reason for using a low clay content was to reduce or eliminate the deleterious effects that arise from macro and micro alignment of the clay platelets. Macro alignment causes distortion and the formation of fissures to relieve tensile stresses arising from anisotropic shrinkage. The elimination or reduction in size of fissures that act as fracture-initiating flaws should increase the strength. This appears to have been demonstrated by both Okojie(1992) and Mohd Noor(1995) in studies using prefired clay to replace raw clay. These workers obtained strengths, measured using the ring test, of≈100MPa but with toughness values that were modest of ~1.3 to 1.4MPam$^{1/2}$. This indicates that the use of the low-clay approach reduces the fracture-initiating flaw size.

Alignment of the clay platelets on the microscale occurs in compacted spray dried granules and causes pore enlargement on firing. The elimination of enlarged pores in wares formed by compacting a spray dried press body by reducing the clay content should increase fracture toughness and hence the strength.

It is, however, disadvantageous to reduce the clay content with regard to sagging during the firing in which the ware is densified.

Another disadvantage of reducing the clay content, is that it precludes the use of the conventional plastic forming of flatware and some hollow ware items, such as cups.

Instead flatware, i.e. plates, shallow bowls and saucers, will have to be produced by powder pressing. This is an automated technique and is the technique that has to be used for conventional bodies in countries with high-cost labour if the whiteware industry is to survive. Cups present a particular problem because although they could be produced by casting, the process is significantly slower than the roller-head, plastic technique used for high-clay wares. Consequently, injection moulding is the proposed route for cup production with a low-clay whiteware and will have the advantage that cups will be moulded with the handles already attached. The study of the injection moulding of the anorthite/mullite porcelain has been successfully carried out by Wong in parallel with the present study.

Casting is used to form hollow ware, such as teapots, and so it is necessary to demonstrate that the anorthite/mullite porcelain can be formed in this way. This is the subject of Chapter 5.

It was shown by Capoglu and Messer (Messer et. al., 1998) that by designing the composition of the prefired material so that it developed mullite substantially reduced the sagging of the material in the second firing, i.e. effectively the glost firing. This behaviour is explained in Appendix I. Reducing sagging in both biscuit and glost firing and reducing the anisotropy of firing shrinkage by reducing the clay content should allow distortion to be minimized. To minimize differential shrinkage, the actual shrinkage should be kept low. A value of ~13% would be acceptable. This can be achieved by having a well-packed green body by using a range of particle sizes from the coarse prefired material down to those of the fine prefired material to the micron-to-submicron clays.

The whiteware should exhibit properties comparable with the best properties of bone china and hard porcelain (Dinsdale et al. 1966). The former is highly crystalline, strong (Modulus of rupture (MOR)~100MPa) and resistant to chipping. Unfortunately the glaze applied to bone china, which is fired on at~1090°C, is easily scratched. Hard porcelain, on the other hand, is highly glassy and so is easily chipped (MOR~50MPa). Its glaze, which is fired-on at a temperature of 1350°C is, however, hard and chemically durable.

4.2 Development of Anorthite/Mullite Porcelain

The composition of the W3 body, given in the patent (Messer et. al. 1998), which uses the M17 prefired material was;

Coarse Prefired	60%
Fine Prefired	25%
Ball Clay	7.5%
China Clay	7.5%

The coarse prefired component was specified in the patent (Messer et al 1998) as having the median particle size of approximately 20μm and the fine prefired component approximately 2μm. The sizes had been chosen to give good particle packing.

A batch of M17 was prepared and milled with the intention of producing these coarse and fine milled components. However the coarse material, when measured, was found to have a median particle of ~30μm instead of ~20μm whereas the finely milled material had the target median value of ~2μm. Two bodies were prepared but with less of the coarse component than the W3 body because its size was coarser than specified. The first body, coded K1, had a composition of:

Coarse Prefired M17 (~30μm median size)	50%
Fine Prefired M17 (~2μm median size)	35%
50:50 ball clay: china clay	15%

Heated to 1280°C for 3hrs, these discs initially 25mm in diameter body achieved a density of 2.63gcm^{-3}. The shrinkage was 9%, but bars initially 120*20*4mm sagged so much that they fell between the end sections of the supporting refractory brick when 87mm of bar was unsupported.

The second body made with these prefired components, coded K2, had a composition of:

Coarse Prefired (median size~30μm)	45%
Fine Prefired (median size~2μm)	40%
50:50 ball clay: china clay	15%

This body contained an increased amount of the finely milled component, which caused the density to increase to $2.76gcm^{-3}$ with a heat treatment of 1280°C for 3hrs. The shrinkage, at 12.6%, increased as would be expected. However, the increase in the content of fines did not prevent the bar sagging so much that it fell into the 87mm gap between the end sections of the refractory support.

New batches of M17 were prepared and milled longer to reduce the median particle sizes. The coarse component was milled to have a median size of approximately 11μm and the fine component to have a median size of approximately 1.5μm. To check that the effectiveness of fine material in reducing sagging and aiding densification, a body, coded K3 composed of 85% fine prefired material and 15% of a 50:50 mixture of ball and china clays was prepared. Fired at 1280°C for 3hrs, it attained a bulk density of $2.74gcm^{-3}$ and only sagged 9mm. This gives a very high density/sagging index of 304. With the use of only fine prefired material and clay, the body had, as expected, a high shrinkage of 17%.

A body, coded K4, having the proportions given for W3 was prepared i.e. 60%CPF, 25%FPF and 15% clay. In this case only china clay was used. This body densified poorly, only achieving $2.18gcm^{-3}$ on being fired at 1280°C for 3hrs. It would have been well packed, which with the low bulk density achieved, resulted in a very low shrinkage of only 4%. A bar sagged 14.5mm in the first firing. Another bar, which had been fired fully supported was found to sag 5mm when refired at 1280°C for 30mins.

Another body, coded K5, was produced with the coarse component reduced to 50% and the fine component increased to 35%. Again only china clay was used for the clay component. This body achieved a very high bulk density of 2.77gcm^{-3} when fired at 1280°C for 3hrs. It shrank 11.4%, showing it was well packed and sagged 21mm. Two modifications of this last body were prepared.

In the first body coded K6, 3% of a finely milled, pure mullite having a particle size ~3μm was introduced and the fine prefired component reduced to 32%. In addition, a 50:50 mixture of ball clay and china clay was used for the clay component. This body densified well achieving 2.72gcm^{-3} when fired at 1280°C for 3hrs. The shrinkage was 11.3% and the bar sagged less at 18mm. A bar of this composition did not sag at all when refired at 1280°C for 30mins.

In the second modification, coded K7, 3% of molochite, which is a prefired china clay composed of mullite (~55%) and glass, was used to replace 3% of the fine prefired component. The molochite had a median size of 15μm. A 50:50 ball clay: china clay mixture was used for the clay component. This body did not densify as well, achieving a bulk density of only 2.40gcm^{-3} when fired to 1280°C for 3hrs. The sagging was again 18mm. The shrinkage at 8.5% was reduced, as would be expected with a lower density and probably an improved particle packing.

A body, coded K8, with a reduced clay content of 10% was prepared. The clay component was solely china clay. The coarse prefired component was increased to 55% and the fine prefired component left at 35%. Fired at 1280°C for 3hrs, this body achieved only a moderate density of 2.45gcm$^{-3.}$ This gave a low shrinkage of 9% and the bar sagged 13mm. Fired at 1300°C for 3hrs, the density increased slightly to 2.52gcm^{-3}, the shrinkage increased to 10% and the sagging increased to 13.5mm. The density/sagging index for 1280°C was 188 and for 1300°C it was 187.

Three compositions were prepared with only ball clay (DBX grade from WBB) as the clay component as a way of increasing the fineness of the particles.

A body, coded K9, was made with 50% of CPF (~11μm median size), 40% FPF and 10% ball clay. Fired at 1280°C for 3hours, a high density of 2.77gcm^{-3}was achieved. The body shrank 11.2%, showing the green body was well packed. A bar sagged 18mm. When fired at 1260°C for 3hours, a density of 2.70gcm^{-3}was attained. The shrinkage was less at 10.6% but a bar sagged the same at 18mm. Fired at 1300°C for 3hrs, the lower density of 2.63gcm^{-3} was attained. This showed that the material had been overfired. This is confirmed by the shrinkage being reduced from 11.2% at 1280°C to 10.7%, whereas the sagging increased to 19mm.

In the next body, coded K10, the amount of both the coarse and fine prefired components were reduced to 48% and 38% respectively. The ball clay content was increased to 14% to compensate for the reductions. Bars were fired at 1280°C for times from 1hour to 3hours. The densities and sagging values are plotted as a function of soaking time at 1280° C in Figure 4.2. This body attained a very high density of 2.80gcm^{-3} when fired at 1280°C for 3hrs and an even higher value of 2.88gcm^{-3} when fired at 1300°C for 3hours. For both firing conditions bars sagged 19mm. The shrinkage values increased from 7.4% for a soaking time at 1280°C of 1hr, to 10.1% for 1.5hours, 10.8% for 2hours, 11.4% for 2.5hours and 11.6% for 3hours. At 1300°C for 3hours, the shrinkage was 11.9%.

The next body, coded K11, was made in 49% CPF, 39% FPF and 12% ball clay. Fired at 1280°C for 3hours, this body densified slightly less well than the previous two at 2.72gcm^{-3}. A bar sagged less at 17mm and shrank 10.2%. Fired at 1300°C for 3hours, the material overfired with the density decreasing to 2.64gcm^{-3}and the shrinkage to 8.8%. The sagging increased to 20mm. All these bodies achieved

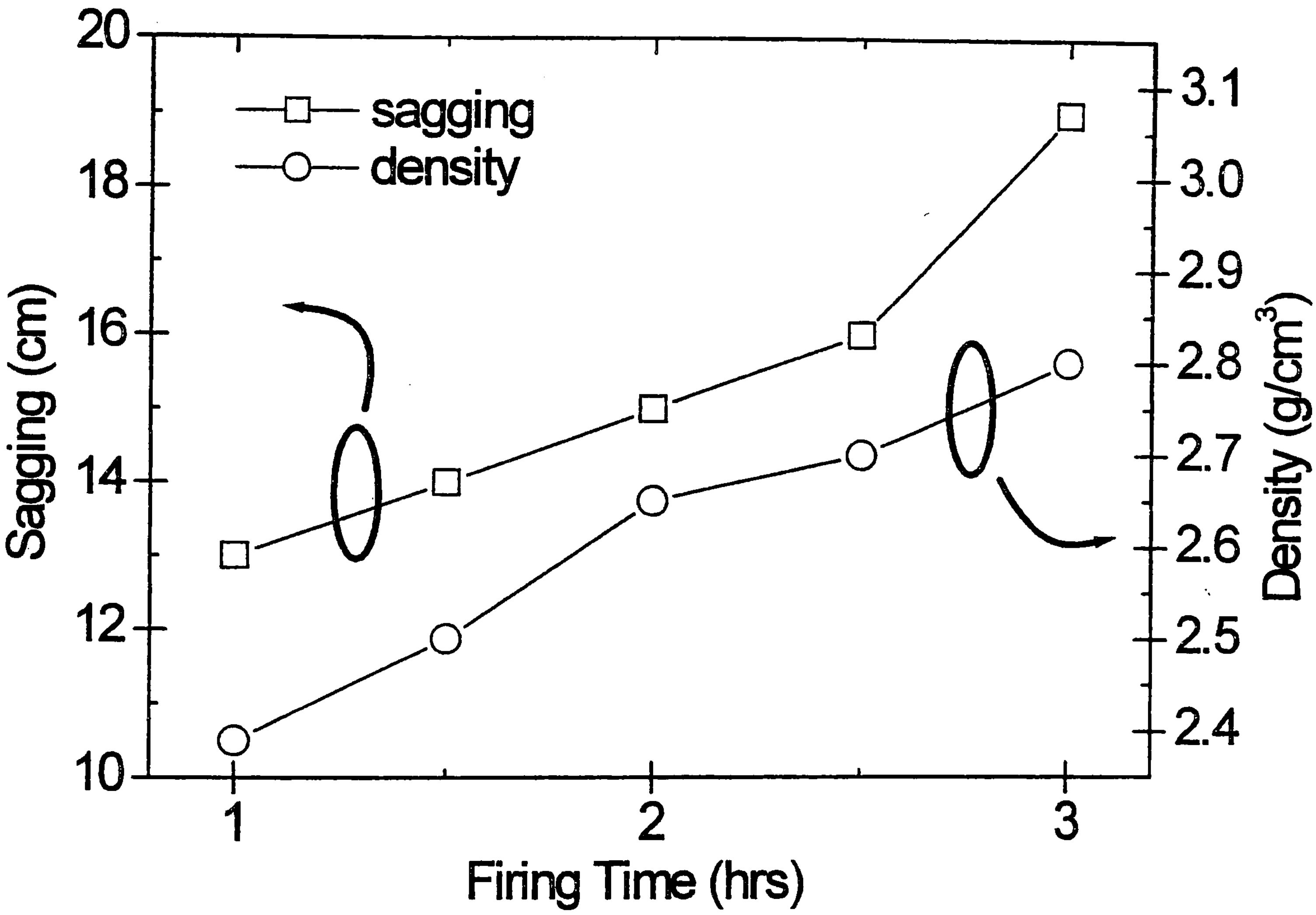

Figure 4.2 Densities and Sagging Vs Firing Time

acceptable, although rather high sagging. They all attained high densities and had acceptable shrinkage values. The use of only ball clay for the clay component introduces more iron and titanium and so degrades the colour.

When the batch of M17 had been used another was prepared and milled to produce the coarse prefired component. The median particle size of the new batch was ~9μm. In an attempt to reduce the sagging, a pure anorthite was prepared for the fine prefired component thereby reducing the liquid phase that should be present at temperature. The fine prefired material was milled to a median size of ~1.6μm. A body, K12, was produced with the following composition:

CPF (M17 with a median size of ~9μm)	50%
FPF (pure anorthite with a median size of ~1.6μm)	40%
China clay	10%

The firing temperature had to be increased to compensate for the use of pure anorthite. Fired at 1300°C for 3hours, a bulk density of only $2.64gcm^{-3}$ was achieved. The shrinkage was 13% and a bar sagged by only 11mm. A flat bar refired in a sag test at 1300°C for 30mins to simulate glazing sagged 3mm. Fired at 1320°C for 3hrs a bulk density of $2.75gcm^{-3}$ was achieved. The shrinkage increased to 14.2% but the sagging remained low at 11mm. This gave a high density/sagging index of 250. A flat bar refired at 1300°C for 30mins sagged only 1.5mm. This body essentially meets all the requirements apart from the shrinkage being higher than desired at just over 14% rather than 13% or lower. The shrinkage might come into line by increasing the median size of the coarse prefired component a little to, say, 11μm. This would lead to an increase in sagging. Alternatively, and preferably, the median size of the fine prefired material could be reduced. This should improve particle packing to reduce shrinkage and reduce sagging in the first firing.

The density of K12 was increased to 2.77gcm^{-3} by firing at 1340°C to 3hrs. For this heat treatment, the shrinkage increased to 15%. Increasing the firing temperature to 1360°C caused a further small increase in the bulk density to 2.78gcm^{-3}. However, the shrinkage decreased to 13.2%. This apparently anomalous situation is possibly resolved by assuming that the powder density would increase if more mullite were to form and lower shrinkage would result if the material were bloating, i.e. if pore growth was causing the body to expand.

To see whether sagging, particularly second firing sagging, could be reduced, the starting composition of K12 was modified to include some mullite. This body was labelled K13 . An addition of 3% of fused mullite, produced by Keith Refactories, replaced 3% of the coarsely milled M17. The median particle size of the mullite was ~10μm. The fine prefired content remained at 40% and again the clay component was china clay. This body achieved a similar density to K12 of 2.63gcm^{-3} when fired at 1300°C for 3hours. The shrinkage was marginally less at 12.2% but the sagging increased to 15mm. A bar refired at 1300°C for 30mins sagged 4mm, which was surprisingly more than that for K12 at 3mm. Results given in the patent (Messer el at, 1998),and discussed in Appendix I, appear to show that an increase in the mullite content reduces the sagging occurring during the second firing. Hence, this result is confusing.

When fired to 1320°C for 3 hours, the bulk density was the same as K12 at 2.75gcm^{-3}. Shrinkage for K13 was now marginally higher than for K12 at 14.5% compared to 14.2% and the sagging was significantly greater at 18mm compared to 11mm. Refiring at 1300°C for 30mins caused a bar of K13 to sag 3.5mm compared to 1.5mm for K12.

Quantitative XRD was employed to analyse K12 and K13 when fired at 1300°C. The 'Ratio of Slopes' method was employed (Monshi & Messer 1991) and the details are given in Appendix II. The analysis showed that the introduction of the fused mullite did result in K13 having a slightly higher mullite content. At room temperature the constitutions are:

K12	Anorthite	51.0%	**K13**	Anorthite	50.3%
	Mullite	15.4%		Mullite	17.7%
	Glass	33.6%		Glass	32.0%

The reason for K13 sagging more in both the first and second firings became apparent when the microstructures of K13 and K12were studied. K13 was found to be extensively fissured, as can be seen in Figure 4.3. Such fissures were not present in K12 (Figure 4.4). The presence of the fissures will increase the tensile stresses in the lower half of the sagging bars. Similar fissuring was observed by another worker in the Department (Abdul Rois, 1994) Figure 4.5. He found that with calcination of M17 at 1350°C for 10hrs, the mullite crystals grew in length and thickness and pushed the material apart, extensively fissuring the calcined material. The introduction of mullite having a median size of ~10μm appears to have caused a similar phenomenon, presumeably by causing the large mullite needles added to the body to grow in size more rapidly than the mullite in the prefired materials. Scanning electron microscopy, Figure 4.6, shows that the anorthite crystals are very fine at ~0.25μm. Part of a the mullite needle running across the fissure can be seen in Figure 4.6.

The average thermal expansion coefficients of the two bodies were measured over the range 20 to 600°C. The value for K12 was determined as $4.35*10^{-6}$/°C and that for K13 as $4.52*10^{-6}$/°C. The lower value for K12 results from its lower mullite content and higher anorthite content. On average, the TEC for mullite is ~$5.7*10^{-6}$/°C (Mulenga 1995), whereas that for anorthite is $4.3*10^{-6}$/°C(Batista 2001).

At this juncture a large-scale study funded by EPSRC and WBB Technology Ltd was undertaken involving Dr West producing substantial quantities of the prefired body in the pilot plant at WBB Technology Ltd in Devon. The compaction behaviour of spray dried material was studied as a function of binder, plasticiser and moisture by Batista. Plates and bowls were kindly pressed at J.Wedgwood & Son Ltd and Worcester Royal Porcelain Company. Batista showed that the use of low-clay eliminated the development of enlarged pores in the compacted granules. Injection moulding was studied by Wong, who demonstrated that cups with handles could be produced. The plastically formed material was shown to shrink isotropically. This allows cups to be single fired without distorting from having a round cross-section. The average strength of the body composition finally developed, when glazed, was exceptionally high lying between 150MPa for powder pressed test-pieces and up to 230MPa for injection moulded test-pieces.

In order to simplify the process used in the pilot plant only a single prefired component was produced rather than two . The first prefired body made had the following composition and was designated M17A(This was produced by firing at 1300° C for 6 hours):

$CaCO_3$	$19.3\,^{w}/_{o}$
$Al(OH)_3$	$40.6\,^{w}/_{o}$
SiO_2	$38.6\,^{w}/_{o}$
$(MgCO_3)_4Mg(OH)_2.5H_2O$	$1.5\,^{w}/_{o}$

This contained less magnesium than for M17, so that, according to the FACT program, less liquid phase would be produced.

It was found to be difficult to mill the coarse component down to have a median size of ~10μm, whilst at the same time eliminating coarse material with particle sizes up to 100μm. Consequently, the median size was reduced by milling to 6.0μm to reduce the size of the particles in the coarse tail of the particle size distribution. The fine prefired material was given a prolonged milling, but after 48hrs a median size of only 1.8µm had been achieved.

A body, coded K14, composed of 55% CPF, 35% FPF and 10% of 50:50 china clay: ball clay mixture was employed. This was spray dried with an addition of 1% PAF (a copolymer of PVA) and 1% of Zusoplast (a proprietory plasticiser). Both additives were obtained from Z&S. Heated at 1280°C for 3hrs the body attained a modest bulk density of 2.57gcm^{-3}. The shrinkage was 11.0%. However a test bar sagged so much that it fell between the end sections of the refractory support. Fired at 1300°C for 3hrs, the body overfired slightly with the bulk density of 2.56gcm^{-3} being achieved. Again the bar fell between the refractory supports and it shrank by 10.9%. At 1250°C, the bulk density was 2.20gcm^{-3}, the shrinkage was 6.7% and the sagging was 18mm.

The poor densification of this body was connected with the presence of the coarse tail in the particle size distribution (PSD) of the coarse component. The best density attained was only about 94% of the theoretical maximum. However, even with low densities the strength of the final composition tested in the study was exceptional. The final prefired body, designated M17C, had a very high crystalline content of ~90% with ~70% anorthite and 20% mullite (private communication Batista). Bodies prepared with $50^{w}/_{o}$ coarse M17C (median size ~6µm), $38^{w}/_{o}$ fine M17C (median size ~1.8µm) and 12 $^{w}/_{o}$ china clay and injection moulded achie averaged strengths of ~160MPa.

Finally, a preliminary attempt at reducing the cost of the body was made. In this it was decided to see whether a dense translucent body could be produced by replacing the fine prefired component with a mixture of minerals which, on reaction, should produce the same composition. In a calcination heat treatment, components that degas, like $CaCO_3$ and aluminium trihydroxide, can be used as any large pores that form will be removed during milling. The minerals used in a final body must not degas substantially. Hence the calcium was introduced in wollastonite ($CaO.SiO_2$) rather than $CaCO_3$. The aluminium trihydroxide, which losses 34.5% of its weight when water is driven off, was replaced with a fine alumina. The material selected was a Reynolds alumina (grade 2000) having the median particle size of 2.2μm. The extra silica was introduced as quartz. To introduce the magnesium, the same $(MgCO_3)_4Mg(OH)_2.5H_2O$ was employed. The degassing of this component, as so little was added, was thought would not cause a problem. The mixture was milled to have a median particle size of 2μm. The body was composed of:

CPF M17A (~ 6μm) 55%

FPF M17A(raw mineral): 35%

  Wollastonite : 28.91%

  Silica : 34.89%

  Fine alumina: 34.27%

Magnesium carbonate : 1.94%

Ball Clay : 5.00%

China Clay : 5.00%

This body when fired at 1280°C for 3hours it attained only a low bulk density of 2.09gcm^{-3}. The shrinkage was 5% and the bar sagged 15mm. Fired at 1350°C, the bulk density increased to 2.28gcm^{-3}. The shrinkage was 8.2% but a bar fell into the gap between the refractory supports. At 1400°C, the bulk density increased to 2.48gcm^{-3} and the shrinkage increased to 8.6%. A bar fell into the gap on being tested for sagging. At 1430°C the bulk density achieved a value of 2.55gcm^{-3}. The shrinkage increased to 10.7% and, of course, the sag test bar fell into the gap. It can be seen that to achieve a similar bulk density with the fine component composed of raw materials to that achieved with a prefired fine component required the temperature to be increased from 1280°C to 1450°C. Two differences could contribute to this increase in temperature. The first is that the raw material-containing body was not as compositionally uniform as the body made with the prefired body on a small scale of size, say on the scale of size of a few cubic microns. The shrinkage on this scale was not as uniform and some enlarged pores developed. The second difference, is that the magnesium carbonate was distributed throughout the body. On heating some magnesium may diffuse into the coarse prefired body that constitutes 55^{W}/o of the body. Hence, there will be less magnesium in the fine material. As the magnesium determines the liquid content at a given temperature, there was less liquid in the fine material.

Its appears that it should be possible to reduce the amount of prefired material. To do this, the magnesium content of the prefired material should be reduced and the magnesium added to the final body should be increased.

Body K12 was the best formulation with the density of 2.75gcm^{-3} at 1320°C. The sagging is 11mm at that firing temperature. Hence a high temperature scratch resistance glaze can be used on this body.

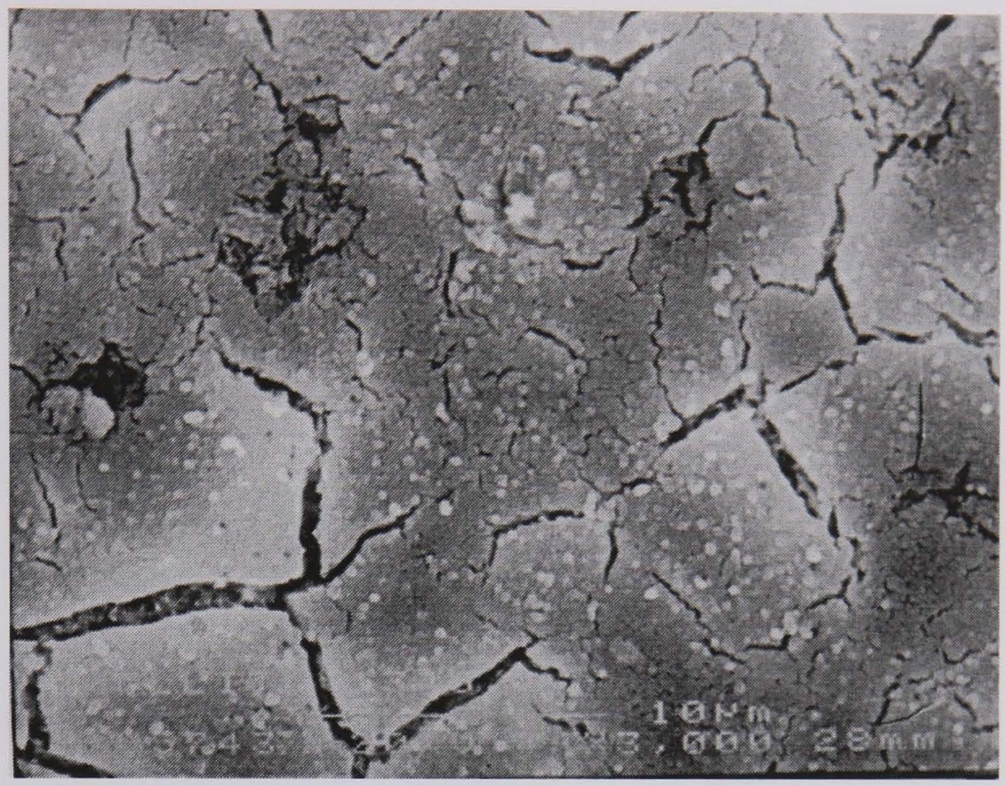

Figure 4.3 A polished and etched (HF vapour) section of Mul1
Showing extensive fissure

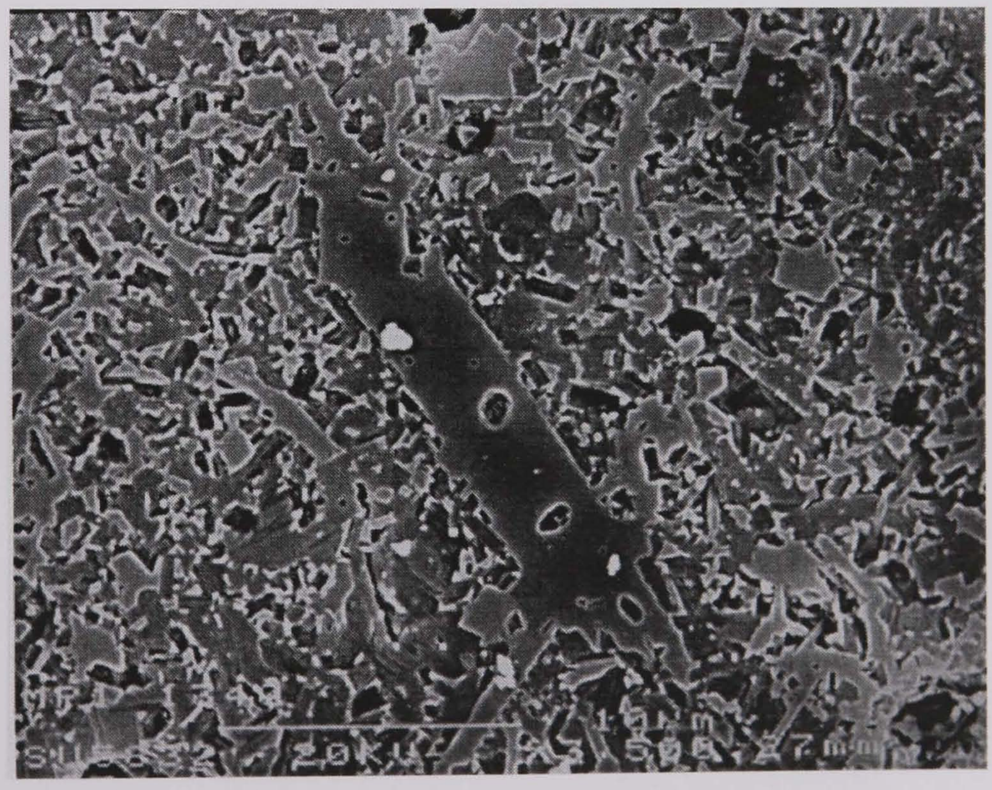

Figure 4.4 A polished and etched (HF vapour) section of MP1 showing a large mullite crystal by no fissuring

Figure 4.5 Fissures formed in M17 fired at 1350°C for 10 hrs (after Abduul Rois Abdul Mois 1994) by growth of mullite crystals

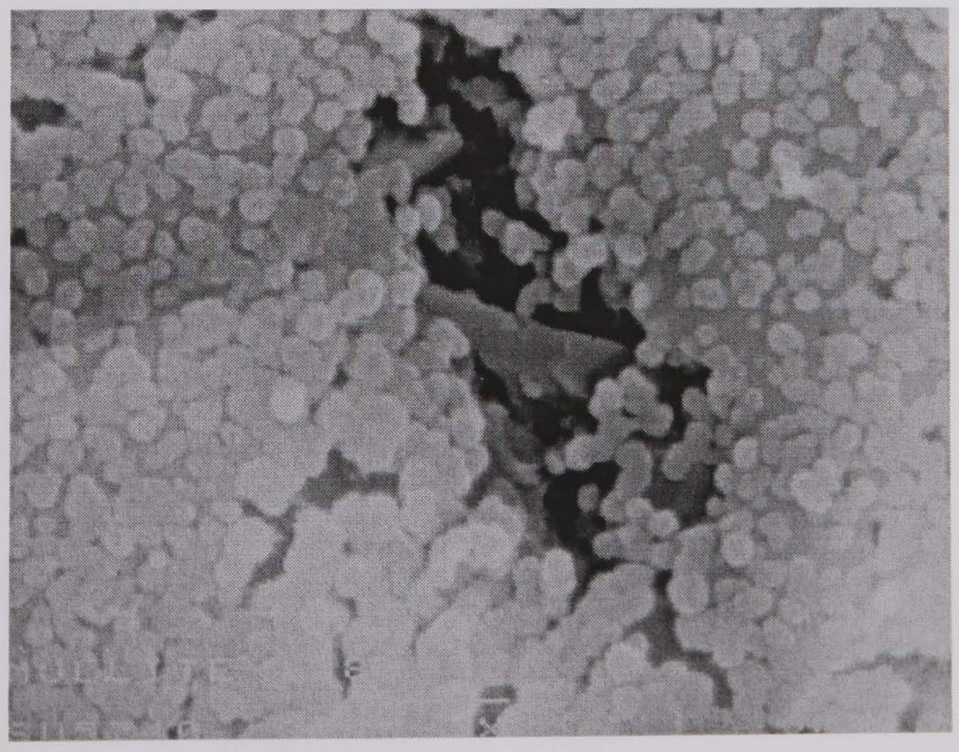

Figure 4.6 A polished and etched (HF vapour section of Mull showing fine anorthite crystals and a mullite crystal within a small fissure

Chapter 5 Slip Casting

5.1 Introduction

Prior to the slip casting study carried out in the present project a study was undertaken by Doll Said Ngah (1998) as part of his MSc programme . In the present study, and the one by Doll Said Ngah, material prepared in the pilot plant of WBB Technology Ltd was employed. The prefired material was M17A and the final body was composed of ;

CPF (M17A median size 6.0μm)	50%
FPF (M17A median size 1.8μm)	38%
China clay (SSPC grade from ECC)	6%
Ball clay (DBX grade from WBB)	6%

Doll Said Ngah found that sodium silicate or sodium carbonate could be used as deflocculants. He measured the rheological behaviour of slips composed of distilled water and either china clay (SSPC,ECC), ball clay (DBX,WBB), the fine prefired component or the complete body. The coarse prefired component was not studied on its own because it sediments too quickly. The shear strain rate $\left(\dot{\gamma}\right)$ was measured using a Haake viscometer, described later, as a function of shear stress for slips with various additions of deflocculants.

It was found by Doll Said Ngah that the rheological behaviour of freshly made body slips was not consistent and appeared to change rapidly with time.To investigate the effect of aging, which was thought to be caused by the leaching of calcium ions from the prefired material, Doll Said Ngah added some $Ca(OH)_2$ solution to various slips to see what would happen. The effects were complex and subtle although not great. With $Ca(OH)_2$ additions, introducing sodium silicate initially caused the yield stress to increase before, with further addition of sodium silicate, the yield stress decreased.

Doll Said Ngah found that partially deflocculated slips could be successfully cast but that the casts were fragile and it was practically impossible for them to be fettled without breakage. This was a consequence of the low clay content. Further, on handling a cast, powder was removed from its surface. To overcome these problems, PVA was introduced as a binder. Initially a 1% addition relative to the solids in a slip was made but powder was still removed from the surfaces of mouldings when they were handled. The polyvinyl alcohol PVA addition was increased to 2% and this prevented powder loss.

However, with this PVA addition all the casts cracked on drying. Although the body slips were partially deflocculated with the addition of sodium silicate so that they only exhibited a small yield stress, the casts behaved as if they had been obtained from flocculated slips. That is, they shrank a lot on drying and on removal from the mould the casts could be liquified by vibrating them. It was argued that the PVA molecules were preventing particle-particle contact.

The cracked casts in the leather-hard state exhibited more than enough strength to be handled and fettled. On firing they underwent a fairly high shrinkage of ~17.5%, indicating that the particles were poorly packed despite the body having a broad particle size range and the slip being partially deflocculated. This again suggests that in the cast the PVA had prevented the particles packing densely.

Clearly, a binder is necessary to provide sufficient strength for the cast to be fettled and to prevent powder loss from the surface on handling. However, PVA on its own appears unsuitable and so an alternative had to be sought. In the present study, gum arabic was used with PVA. The coarse and fine prefired bodies available at the time the work was carried out contained a 1% addition of PVA, hence trials were carried out on bodies with 1% of gum arabic and ~0.88% PVA (reduced from 1% because of the clay addition).

5.2 Slip Preparation

5.2.1 Starting Materials

The coarse and fine prefired components of M17A available at the time of the casting work had median sizes of 6.0μm and 1.8μm respectively as measured using the Coulter LS 130 particle size analyser. The clays used to for the body were Super Standard Porcelain Clay from ECC and DBX from WBB. The body slips prepared contained 50% CPF, 38% FPF, 6% china clay and 6% ball clay. One slip was made without gum arabic and another with 1^{W}/o addition relative to the solids content. The slips were each prepared with 1000grams of solid and 900ml of distilled water. Assuming an average powder density of 2.7gcm^{-3}, this gives a solids volume fraction of 29^{V}/o.

Body Preparation

First the fine prefired material and the two clays were added to the 900ml of water in a 5 litre porcelain milling pot. This contained alumina milling balls (10mm ϕ) occupying about 30% of the milling chamber volume (bulk volume of media = 0.5 chamber volume). The mill was rotated for 1hour and then the coarse prefired material was introduced and the mixing continued for a further 15min.

The deflocculant used in this study was an aqueous sodium silicate solution. This was prepared by dissolving 90 grams of solid sodium silicate into 2.5 litre of distilled water.

Slips, with and without various additions of sodium silicate solution, were stored in sealed plastic bottles and aged for various times prior to measurement of their rheological behaviour.

5.3 Rheological Study

Rheological measurements were made using a Haake RV20 viscometer available in the Department. This is a Searle-type of instrument in which the inner cylinder is rotated while the outer cylinder is stationary. The measuring sensor used was MV1 with an M5 measuring system. For every rheological measurement, 40ml of slip was employed.

The shear strain rate ($\dot{\gamma}$ s^{-1}) was increased linearly with time to $100s^{-1}$ in 1 minute and the shear stress determined at one second intervals. The shear strain rate and shear stress values were plotted so that the yield stresses and absolute viscosities of the slips could be determined.

It was stated by Schramm (Schramm, 1994) that for each sample and any fixed rotor speed n, i.e. a defined value of shear rate, $\dot{\gamma}$, the instrument will measure the corresponding true shear stress, τ. If the rotor speed and thus shear rate is subjected to programmed changes, the corresponding value of shear stress may only be indicated with some time lag. The higher the rate of rotor speed change and the higher the viscosity of the sample, the more the time lag increases. As a result of this time lag, the actual up-curve is observed to be above the true flow curve whilst the actual down-curve will be below the true flow curve. This is illustrated in Figure 5.1 from results obtained by Doll Said Ngah for slips made with ball clay, china clay, the fine prefired material and the full body slip. None of these slips had additions of deflocculant . Without the effect of time lag, the up and down curves could be coincident. It can be seen in Figure 5.1 that the gaps between the up and down curves are reduced as the yield stress decreases. The yield stress values determined in the present study and quoted in section 5.4, have been obtained from the up-curve of $\dot{\gamma}$ against τ. Consequently, they will all be lower than the true curve values as a result of the time lag error. For low yield stress values, the error is small.

5.4 Results of Rheological Studies

The rheological behaviour of the full body slip approximated to that of a Bingham fluid, although many curves exhibited a nose which resulted because the shear stress decreased presumably on breakdown of the structure in the slip. This is illustrated in Figure 5.2.

To obtain the yield stress values for the various slips, the approximately linearsections of the shear rate-shear stress curves have been extrapolated back to the shear stress-axis. In many cases the curves had a slight upward curvature which suggests that a more accurate model for the rheological behaviour would be a pseudoplastic fluid with a yield stress.

In Table 5.1 the yield stress values for a full body slip made without an addition of gum arabic are shown after 10 days aging for various additions of the sodium silicate deflocculant solution. These additions of 0.1ml to 0.4ml were made to the 40ml of slip used in the viscometer.

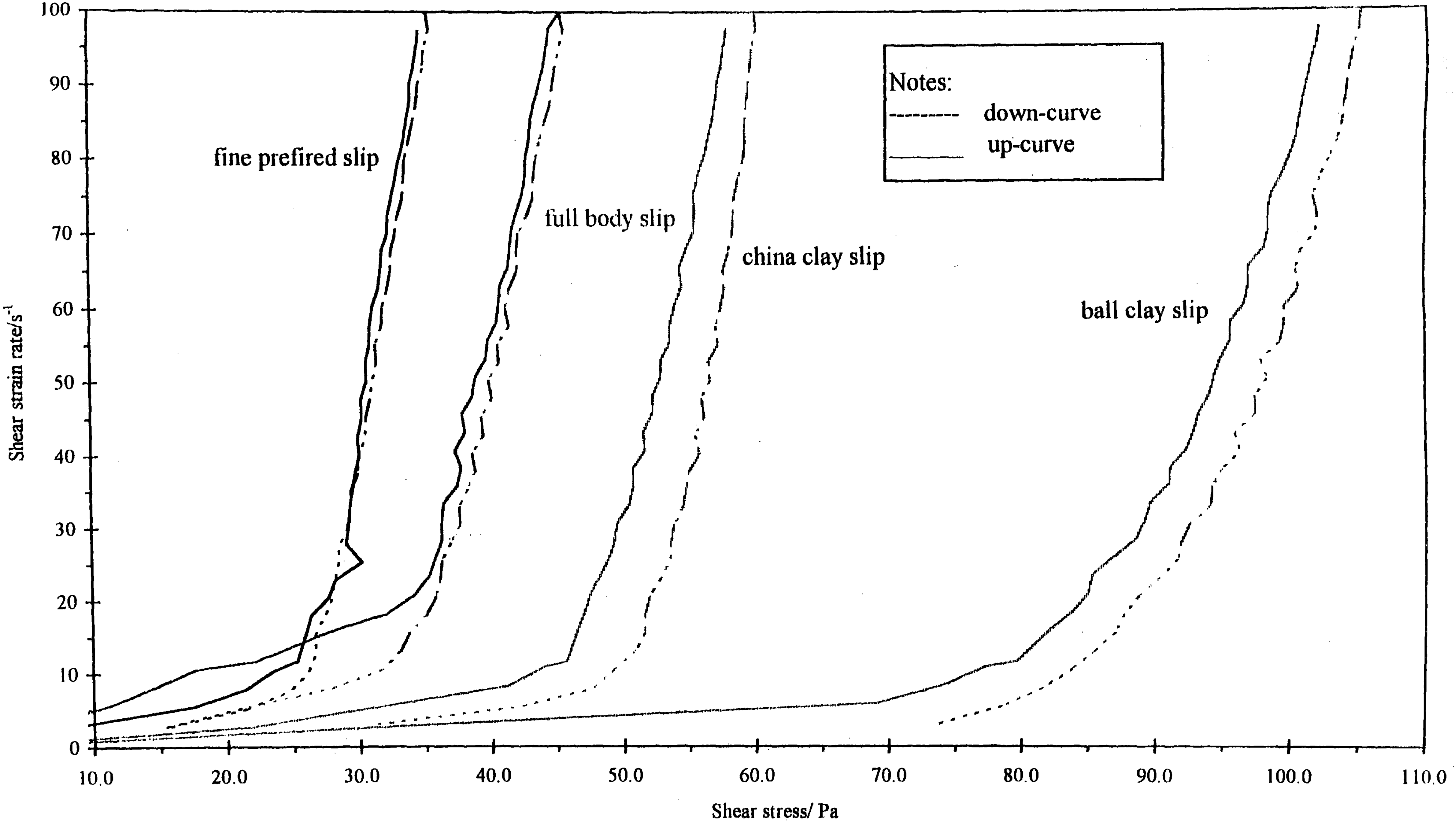

Figure 5.1 Time-lag error of viscometer on slip

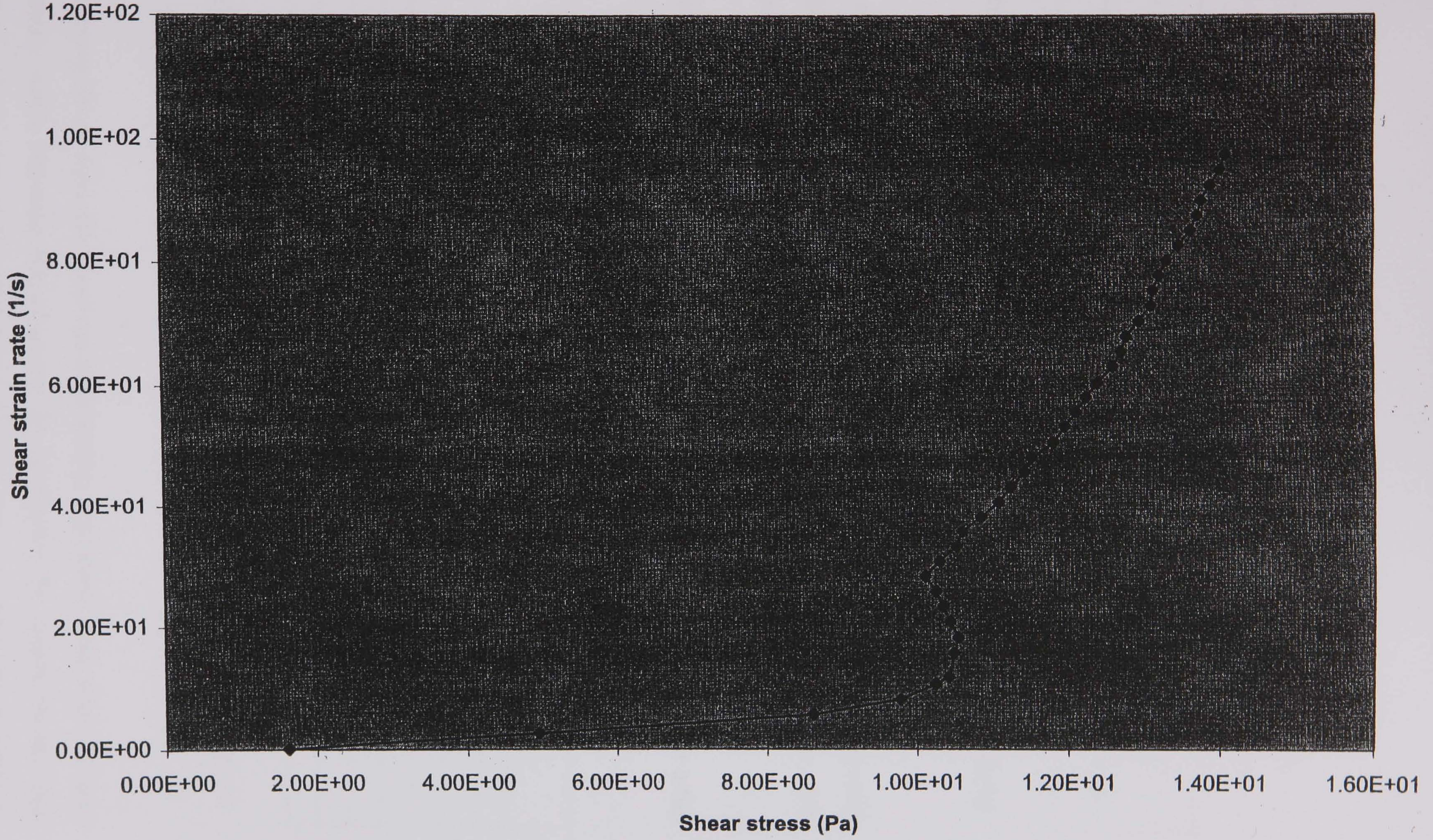

Figure 5.2 Shear strain rate Vs Shear rate for slip aged for 10days without an addition of deflocculant.

Sodium silicate solution/cm^3	**Yield Stress/Pa**
0	8.0
0.1	7.0
0.2	4.6
0.4	6.5

Table 5.1 Values of yield stress of full body slip without gum arabic after aging for 10 days for various deflocculant additions

The results show that sodium silicate deflocculates the body slip and that for some addition between 0.2 and 0.4ml of the solution, the slip becomes over deflocculated and an increase in yield stress occurs

Tables 5.2 shows how the yield stress varies with deflocculant additions for a full body slip containing a $1^{w}/_{0}$ addition of gum arabic after 4 and 10 days aging.

Sodium Silicate Solution/cm^3	**Yield Stress/Pa**	
	4 days	**10 days**
0	~1.5	3.5
0.1	~1.4	1.2
0.3	~3.2	0.8
0.4	~2.7	0.5
0.5	1.6	~0
0.6	1	~0

Table 5.2 Yield stress of full body slip with gum arabic after aging for 4 and 10 days for various deflocculant additions

After aging for 4 days the rheological behaviour was erratic but after 10 days essentially stable behviour was observed. By comparing the results for the slips with and without gum arabic aged for 10 days for the same deflocculant addition, it appears that gum arabic has a deflocculating effect.

5.5 Slip Casting

The process of slip casting involved pouring the slip into a plaster mould until it was full. The type of mould used had been prepared for casting conically shaped crucibles and had been shortened from its original size to reduce the amount of slip used each time. It was found that full body slips aged for 10 days and from 0.1 to 0.4ml of the sodium silicate deflocculant solution for 40ml of slip could be cast successfully. Using the 0.1ml per 40ml addition, the casting time of about one minute was found to give a cast of 2.5mm in thickness and so was adopted for most of the casting trials. After one minute, the surplus slip was poured off and the mould was held upside down for a few seconds to allow the cast to drain. The mould with the cast was left to dry until the cast shrank to release itself from the mould wall.

The behaviour of the casts in the moulds and after release was monitored throughout the period required for them to dry. They did not crack on drying and it was found that they were sufficiently strong in the leather-hard state to be fettled. The released casts were fully dried at room temperature before they were fired at a temperature 1320°C for three hours in an electric kiln. When fully dry, no powder loss from their surfaces occurred on handling. The shrinkage from the wet to the fired states was 15%.

Since the casting rate was very fast, some of the moulds were prewetted with water before casting took place to achieve a more controllable cast thickness.

5.6 Conclusion on Casting

It has been found that the low-clay, anorthite/mullite porcelain body can be drain cast using sodium silicate as a deflocculant with gum arabic and PVA as binders. To attain stable rheological behaviour, the slip had to be aged. A time of 10 days was sufficient but it is probable that a shorter time would be adequate. The binders provided sufficient strength for the casts to be fettled. They also prevented the loss of powder from the surfaces of the dry casts when these were handled. It is possible that the addition of PVA is not necessary and that gum arabic, possibly at higher level than $1^{w}/_{o}$, would be suitable on its own. However, this could not be tested as, at the time the study was carried out, the only prefired materials available contained PVA.

Chapter 6

Discussion of Sagging

In this study, the sagging of horizontal bars under their own weight has been of concern, both in firings to densify the bars and in second firings which simulate glost firing. The firing of bars simulates the behaviour of flatware items.

It has been observed in this and other studies in the Department that the deformation occurring in a first firing is often significantly greater than that occurring in a second firing at the same temperature for the same soaking time. For example, in work undertaken by Capoglu for the patent (Messer et. al., 1998) two compositions containing bone ash were prepared and their first and second firing sagging compared with that for commercial bone china. The two bodies, labelled W1 and W2, where made into bars 120*20*3.5mm and fired at 1280°C for 3hours either fully supported or with an 87mm central span unsupported. The bars that had been fired fully supported were then given a second firing of 1280°C for 3 hours with the central span unsupported. The commercial bone china bars were similarly treated, except that a soaking temperature of 1230°C for 3 hours was used in each firing. The W1 whiteware sagged 2.5mm in the first firing and 2.2mm in the second firing. The W2 whiteware sagged 8.9mm in the first and 2.4 mm in the second firing. The values for bone china were 10.0mm and 6.6mm

It is proposed that there are two contributions to the deformation that occurs in the first firing. These are bending of a bar as a result of differential firing shrinkage caused by the bend stresses and bending caused by creep. In the second firing, only creep operates and the creep rate in this firing is expected to be lower than in the first firing because of reduced porosity. For the anorthite/mullite porcelain, the creep rate in the second firing is expected to be lower, because of the presence of large mullite needles which develop throughout the first firing and impede deformation. The effect of mullite on creep is discussed in Appendix I.

In this study, it has been shown that sagging in the first firing can be reduced by making the bar from finer particles. It is considered that reducing the particle size affects the differential shrinkage rather than the creep component of the deformation.

A rectangular bar, as shown in Figure 6.1, shrinks in the three mutually perpendicular directions x, y and z. In the section of the bar not in contact with the refractory support the shrinkage will be less in the x-direction at a given distance below the mid-plane than at the same distance above the mid-plane. This is because the stress in the x-direction is tensile below the mid-plane and compressive above the mid-plane, with the magnitude of these stresses being a maximum at the x y surfaces of the bar. The differential shrinkage is accommodated by the bar bending. Reducing the size of the starting particles increases the driving force for pore closure resulting from surface tension. As the particle size is progressively reduced, the effect on shrinkage in the x- direction of the compressive and tensile bend stresses should be reduced relative to the effect of surface tension of the pores which become smaller and smaller. In the limit, with vanishingly small particles and pores, the shrinkage in the top and bottom sections of the bar in the x-direction should be the same.

In the y-direction, the upper and lower sections of a bar should shrink at the same rate. This is to avoid stress development as these sections are joined.

Through the bar thickness, i.e. in the z-direction, the material in the upper and lower sections is free to shrink at different rates. It will shrink at different rates at different distances from the mid-plane. The shrinkage will be greater in the tensile region and maximum at the surface. The variable shrinkage in the z-direction allows the bar to densify whilst undergoing variable shrinkage in the x-direction.

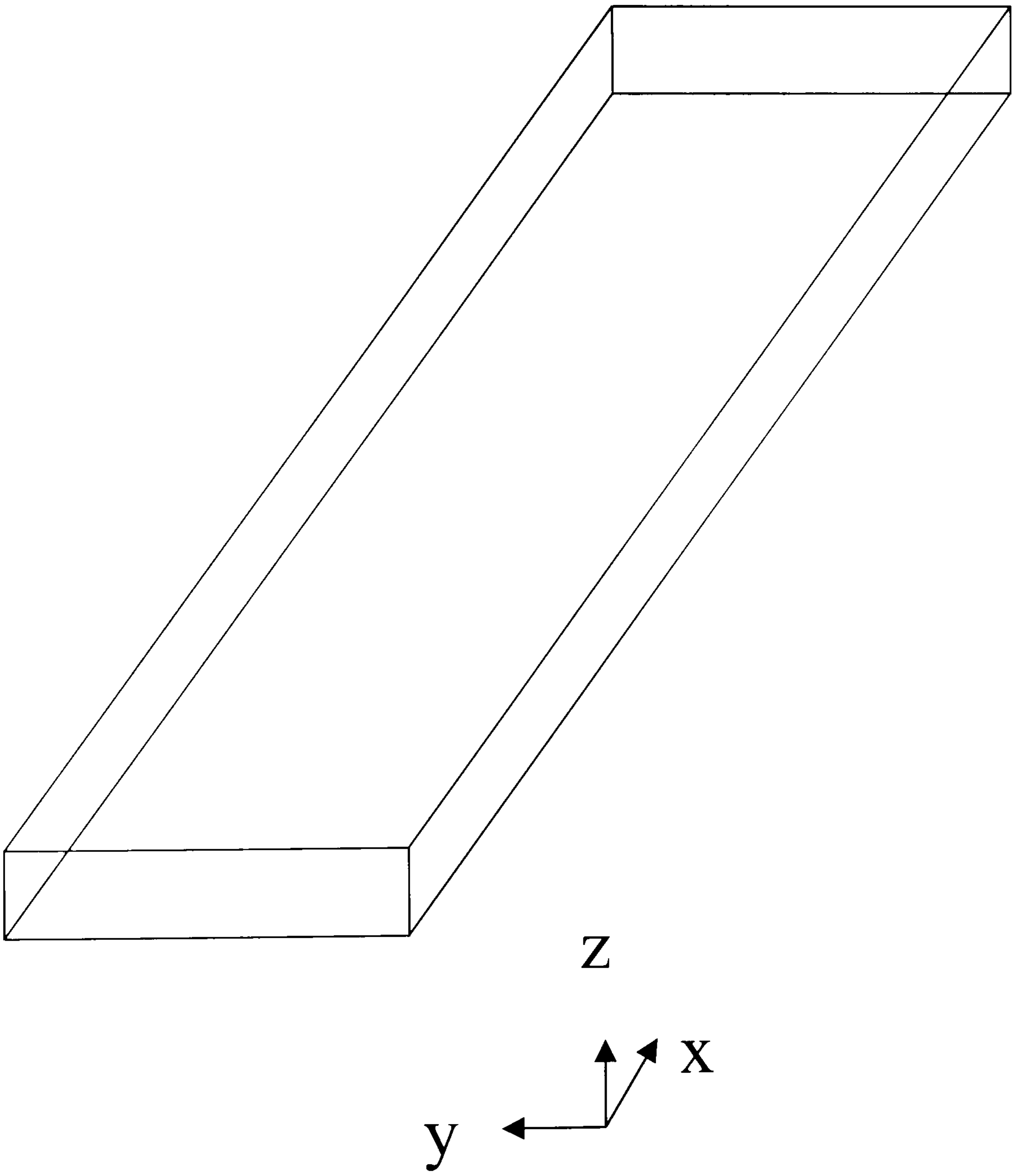

Figure 6.1 Directional firing shrinkage of a rectangular bar.

Creep should occur during the first firing as a consequence of stresses resulting from the weight of the central section of the bar not supported by the refractory brick and the presence of a viscous liquid phase between the crystalline grains. Creep will involve relative movement of the grains. The presence of pores will increase the stresses in their vicinity and relative movement of the grains and liquid may be facilitated by either of them being able to move into the empty pores.

The sagging in the second firing is expected to be less because much of the porosity has been eliminated. This means that the material cannot shrink differentially and so sagging is caused by creep. In this case, because many of the pores have been removed, the stress will be concentrated in fewer places and fewer grains and less liquid will be next to pores making easy relative movement less effective. In addition, the mullite crystals, which form needles and are randomly positioned and orientated throughout the material, reduce sagging. Their presence must make the relative movement of different regions of the bar as it creeps more difficult.

An interesting observation on the sagging occurring in the first firing was made in two examples where the sagging was measured as a function of firing time. In these examples, the sagging appears to increase with time and then to decrease.

In an FTC body having the following composition:

Coarse prefired material (M17)	25%
Quartz (11 μm median size)	25%
Fine prefired material (M17)	34%

Nepheline syenite	6%
Clay	10%

The sagging at 1230°C was observed for bars fired for different times. It increased from 11mm for a soaking time of 45 minutes to 14mm at 1.5h, 17mm at 2h, 18mm at 2.5h and decreased to 14mm at 3h. The shrinkage of this body as a function of soaking time can be used to see that with a 3h soaking time the body was overfired. The shrinkage values were 12.7% at 45 mins, 13.0% at 1.5h, 13.1% at 2h, 13.3 at 2.5h and 13.1% at 3h.

In a body having the following composition:

Fine prefired material (fluxed with bone ash)	60%
Quartz (11μm medium size)	17%
Clay	15%
Nepheline syenite	8%

The sagging at 1230°C was observed for bars fired for different times. It increased from 16mm at 45 mm, to 18mm at 1.5h and then decreased to 17mm at 3h. The shrinkage values were respectively 14.0%, 14.8% and 14.4%.

For both bodies the sagging decreased with overfiring. It is possible that a contribution to this behaviour comes from the fact that the top section of a sagging bar will be in compression and hence will densify faster than the bottom section which is in tension. The top section will then start to bloat and expand which could cause a bar to undergo some straightening.

In the first firing, a difference in the temperature of the top and bottom surfaces of the bar will cause bending because it will induce different densification rates. A higher temperature for the top surface would bend the bar to increase sagging and vice versa. In the first firing of plates supported on a setter, it would be expected that the top surface of the plate would heat up faster than the surface adjacent to the setter. To avoid the plate bending upwards, it is common practice for the plate to be placed on a setter whose top surface has a slightly different shape from that of the lower plate surface so that only the plate rim contacts the setter. On heating, the weight of the plate causes it to sag until its lower surface contacts the top surface of the setter and adopts its profile.

The elimination of porosity in viscous sintering is driven by the reduction in the surface area of the liquid covering the solid grains. This area is inversely related to the sizes (diameters) of the grains. The reduction in area reduces the total surface energy associated with the viscous liquid/vapour surface. The ease with which the solid grains are drawn together and the pore space reduced in volume depend inversely on the apparent viscosity of the solid/liquid assembly. Increasing the liquid volume and reducing the viscosity of the liquid, both of which can occur by increasing the temperature or by changing the composition of the whiteware, will reduce the apparent viscosity and facilitate densification of the porous system.

It should be possible to maintain the ability of a material to densify by offsetting some reduction in the volume fraction and fluidity of the liquid phase by reducing particle size to increase the driving force for densification. Reducing the volume fraction and fluidity of the liquid should reduce the creep rate of the material. Hence, reducing particle size and reducing both the volume fraction of the liquid and its fluidity should reduce the sagging that occurs during the densification heat treatment for wares subjected to bend stresses.

It is interesting to speculate on the significance of these ideas. Consider the three types of translucent whiteware in commercial production: these are FTC (fine translucent china), bone china and hard porcelain. Flatware items of FTC and bone china have to be fully supported in setters during the firing to densify them. The soaking temperature for these wares is typically ~1230°C. During the glost firing, the wares are supported from their foot rings or three point contacts on their undersides. The soaking temperature of the glost firing is typically ~1100°C. The lower temperature is used to minimise sagging by creep. Hard porcelain, by contrast, is densified and the glaze fired-on in the same heat treatment that has a soaking temperature of 1350°C to 1400°C. Flatwares are supported only from their foot rings. A small amount of sagging occurs, which is minimised by having thicker sections near the foot rings. It is possible to compensate for the small amount of sagging that occurs by making the profiles of the upper surfaces of plates within the foot rings convex.

Presumably the fact that hard porcelain is made with more clay, the finest component, than for either FTC or bone china, i.e. 50-60% compared to ~40% for FTC and ~30% for bone china, results in it undergoing less differential shrinkage. The apparent viscosity of hard porcelain for the shear stresses encountered must be high as hard porcelain flatware hardly sags. This could mean that hard porcelain has a yield stress that is not exceeded by the shear stresses arising from the weight, whereas stresses arising from the surface tension of pores are sufficient to cause pore closure. A high yield stress could arise initially from the presence of the network of primary mullite rod-shaped crystals derived from the clay. Coarsening of the mullite as firing proceeds could cause a reduction in the yield stress. However, the viscosity of the liquid phase should increase with firing time as alkali oxides diffuse into the quartz grains. This causes these grains to progressively dissolve with complete dissolution occurring in the most highly fired porcelains.

For FTC the apparent viscosity at its firing temperature of ~1230°C could be lower than for hard porcelain at 1350-1400°C as there is less primary mullite and less of the higher alkali oxide content will be absorbed into the quartz. FTC must have a relatively low apparent viscosity during the biscuit firing because, as described in Chapter 1, large diameter plates even sag unacceptably in the glost firing, i.e. at 130°C below the biscuit firing temperature.

The reaction of the components of bone china form different crystalline and liquid phases than those in hard porcelain and FTC. Primary mullite does not form and little is known about the liquid phase that is present during firing, as information on phase equilibria is not available. It is suspected that the presence of phosphorus from the break down of bone ash could make the liquid have a low viscosity. Small additions of around $1^{w}/o$, of calcium carbonate to a bone china mix have been shown by Majid Jaffari (PhD 1995) to reduce sagging and densification. The addition is thought to reduce the breakdown of β-tricalcium phosphate on removal of CaO, which is required to convert the clay to anorthite. Such breakdown is known to produce low melting point calcium phosphates. However Iqbal (Iqbal et al, 2000) have not been able to detect phosphorus in the glass phase of bone china at room temperature.

It is conceivable that FTC, bone china and the wares examined in this study could be redesigned so that they do not sag significantly during the heat treatments used to densify them. This would require size reduction of the non-plastic components in these bodies with some of them probably having to be milled to submicron sizes. The remainder would have to be milled to have a median size of a few microns so that the powder mixtures packed well to minimise firing shrinkage.

The compositions would be changed to reduce the proportions and, if possible, the fluidity of the liquid phases.

Several advantages would result from such a redesign, which would have to be set against the increased cost of milling material to finer particle sizes. The use of setters would be eliminated, which would reduce the cost of firing flatwares. If a firing to harden the wares has to be given to facilitate decoration and glazing, as when hard porcelain is fired at ~960°C, this firing could be carried out efficiently with the flatware items stacked one on another, as is the practice for hard porcelain. This results in very efficient use of the space in the kiln. It would be advantageous for FTC and bone china to be glazed at ~1230°C rather them 1100°C as it would be expected that more chemically durable and abrasion-resistant glazes could then be employed. However, the use of more finely milled non-plastic particles is likely to increase the firing shrinkage. With high-clay bodies, the shrinkage is highly anisotropic as the clay platelets are aligned on the large scale of size. High shrinkage coupled with high anisotropy would lead to high scrap rates because of unacceptable distortion.

Chapter 7

Conclusions and Future Work

In the first part of this study it was shown that a fine translucent china with required properties could be designed and made. In the process and product development phase, a trial and error approach was used at first to identify factors affecting sagging during the densification of the material. A formulation was sought that could be densified whilst undergoing only a limited amount of sagging. This study uncovered the important result that reducing particle size reduced sagging whilst enhancing densification. From this point onwards, the whiteware could be designed using an iterative approach to achieve the required combination of product properties and behaviour during manufacture. This allowed a translucent, white body with acceptable firing shrinkage and sagging to be made which had the required thermal expansion coefficient.

The finding that reducing the particle size reduced sagging was applied to the anorthite/mullite porcelain body originally formulated by Capoglaand Messer (Messer et. al., 1998). This had been designed to combine the best properties of bone china and hard porcelain. That is, to have a similar strength to that of bone china whilst being capable of being coated with a glaze that is both chemically durable and abrasion resistant. It was found that the body as formulated sagged severely during the first firing. The sagging could be reduced by decreasing the size of both the coarse and fine prefired components to give an acceptable level of sagging, whilst maintaining a sufficient difference between the coarse and fine median particle sizes to achieve good packing. Some alteration to the composition was made to material being made in the pilot plant. The magnesium content, which strongly affects the liquid content, was reduced. However, equipment to mill the fine prefired component down to a median particle size that was sub-micron was not available. It is considered that if this had been done and the liquid content reduced further, it might have been possible to fire the anorthite/mullite porcelain in a similar manner to hard porcelain. This would mean that only one high temperature firing would be required.

In a short study on slip casting, it was shown for the first time that it was possible to cast a low-clay body successfully. Previous attempts had resulted in the casts cracking on drying. Casting is required to produce hollow ware.

It is proposed that the use of finer particles reduced sagging during the densification heat treatment because it reduced the contribution arising from differential shrinkage caused by the bend stresses. Hard porcelain demonstrates that it is possible, with an appropriate design of the shape, to densify flatwares with glaze applied without the wares sagging significantly. It is suggested that the reason hard porcelain hardly sags during the densification heat treatment is because it is made with a high proportion of clay. This reduces the differential shrinkage. In addition, the high clay content provides the fine pores that have sufficient driving pressure for closure to effect densification with a material having a high apparent viscosity. Hard porcelain must have a high apparent viscosity at the stresses resulting from its weight, as sagging is small. It is proposed that future studies be carried out to see whether commercial FTC, bone china and anorthite/mullite porcelain might be redesigned so that they can be densified with their glazes applied. This will require making their non-plastic particles finer in size and reducing either the amounts of the liquid phases present during densification or their viscosities or both.

Appendix 1 The Effect of Mullite on Sagging During the Second Firing

Capoglu and Messer (Messer et. al., 1998) produced a number of bodies, labelled M1 to M19, for potential use as the prefired component for a low-clay whiteware. A combination of high density after being fired at 1350°C for 3 hours and low sagging when refired at 1280°C for 3 hours was sought. The first of the two heat treatments was envisaged at the time for the production of the prefired body and the second for the densification of the final whiteware. The compositions of the bodies M1 to M18(M19 contained ZnO and has been omitted), their bulk densities and the extent of sagging are given in Table A1, The compositions are given in terms of the oxide content. The sagging determined by Capoglu and Messer(Messer et. al. 1998) was that experienced by bars initially 120*20*3.5mm which were fired fully supported at 1350°C for 3 hours and then refired at 1280°C for 3 hours with the central 87mm section unsupported.

The equilibrium constitutions of the 18 compositions at 1280°C have been calculated by Dr A.Watson of Leeds University using F.A.C.T thermodynamic program. In addition, the viscosities of the liquid phases at 1280°C having the predicted compositions have been calculated. The program set up by Jaffari(1995) was used for this purpose. In addition, when tridymite is predicted to occur, the silica content of the liquid phase has been increased by the amount of tridymite and the viscosity recalculated. This was done because in the analysis of the prefired materials using XRD, tridymite was not detected.

Table A2 shows the composition of the liquid phase calculated using the FACT program plus the silica that is computes to be present as tridymite.

Table A3 shows the viscosities of the liquid phase, the amounts of liquid and solid phases computed for 1280°C. For compositions predicted not to contain mullite(M1 to M5) the only solid phase predicted to be present at equilibrium is anorthite. For these compositions, the viscosities were computed for the predicted equilibrium compositions of the liquid phases. For bodies M6 to M18, both mullite and tridymite were predicted. For these bodies, the amounts and the compositions of the liquid phases have been adjusted as described above. For these bodies, the predicted composition of each liquid phase was the same but the amounts differed a little. These amounts are shown bracketed in Table A3. The viscosity of the equilibrium liquid in bodies M6 to M18 at 1280°C was computed to be 2800 Poise.

It can be seen from Table A3 that bodies M6 to M18, which are predicted to contain mullite, sagged much less than those in which mullite should not form. Examination of the microstruture of M17 , the composition selected for whiteware preparation, revealed the presence of needle-shaped crystals of mullite commonly greater than 10μm in length. Sagging should be reduced if either the proportion of the liquid phase is reduced and/or the viscosity is increased. Using the predicted values for the amounts and viscosities, each member of the low sagging group (M6 to M18) contains a higher proportion of liquid with lower viscosity than in M2, M3, M4 when the tridymite in the low-sagging bodies is incorporated into the liquid phase. On the assumption that silica that should not form tridymite, the liquid content is increased its composition, is changed and it then appears that mullite crystals strongly inhibit sagging in the second firing.

At the other extreme, assuming the thermodynamic equilibrium constitutions are attained, it is more difficult to make such a clear assertion. However if M4 and M17 are compared, it would seem unlikely that an increase in viscosity from 26600 Poise to 28000 Poise the effect of which would be partly off set by an increase in liquid from 19.7% to 22.2%, would result in an eight-fold decrease in sagging. So it would seem that the presence of the mullite in M17 reduced the sagging.

Table A1: Composition of Prefired Bodies, their bulk densities after firing to 1350°C for 3h and sagging on refiring at 1280°C for 3h (Messer et. al. 1998)

Code	CaO w/o	Al_2O_3 w/o	SiO_2 w/o	MgO w/o	Density/ g/cm^3	Sagging/ mm
M1	18.79	30.53	49.43	1.25	2.40	6.30
M2	18.91	34.32	45.36	1.41	2.43	11.40
M3	18.64	33.91	44.79	2.66	2.46	12.80
M4	18.04	33.78	46.87	1.31	2.06	4.40
M5	17.82	33.37	46.26	2.55	2.47	6.20
M6	15.04	33.79	49.86	1.31	2.42	1.20
M7	14.85	34.03	49.84	1.28	2.37	1.00
M8	14.70	34.25	49.77	1.28	2.37	0.90
M9	14.73	35.41	48.57	1.29	2.24	1.10
M10	14.55	34.46	49.71	1.28	2.33	1.10
M11	14.58	35.72	48.44	1.26	2.13	0.70
M12	14.53	34.71	49.48	1.28	2.36	0.80
M13	14.55	36.38	47.78	1.29	2.09	1.00
M14	14.44	35.33	48.97	1.26	2.26	0.60
M15	14.41	35.98	48.32	1.29	2.05	0.70
M16	14.24	34.64	49.84	1.28	2.35	0.70
M17	14.26	34.89	49.57	1.28	2.36	0.50
M18	14.26	35.63	48.85	1.26	2.15	0.50

Table A2: Composition of the liquid phases in the Prefired Bodies calculated from the FACT Program. The silica content has been increased to account for tridymite

Code	CaO w/o	MgO w/o	Al_2O_3 w/o	SiO_2 w/o
M1	15.76	4.01	16.94	63.29
M2	11.81	9.38	21.12	57.70
M3	12.40	13.59	22.68	51.33
M4	9.45	6.61	22.16	61.78
M5	10.48	10.27	23.07	56.19
M6	7.17	4.62	17.79	70.43
M7	7.05	4.54	17.48	70.93
M8	7.03	4.53	17.45	70.99
M9	7.51	4.83	18.62	69.05
M10	7.02	4.52	17.41	71.05
M11	7.44	4.79	18.44	69.34
M12	7.09	4.57	17.59	70.75
M13	7.44	4.79	18.45	69.33
M14	7.18	4.62	17.81	70.39
M15	7.51	4.82	18.63	69.03
M16	6.89	4.43	17.09	71.59
M17	6.99	4.50	17.34	71.18
M18	7.18	4.62	17.80	70.41

Table A3: Fired Constitutions and Viscosities of Liquid Phases

Code	Viscosity/ Poise at 1280°C	w/o Liquid	Mullite w/o	Anorthite w/o
M1	9800	31.0	-	69.0
M2	19100	15.0	-	85.0
M3	22000	19.6	-	80.4
M4	26600	19.7	-	80.3
M5	26900	24.8	-	75.2
M6	17300	28.4(22.7)*	7.1	64.5
M7	16800	28.3(22.2)*	8.0	63.8
M8	16800	28.3(22.2)*	8.7	63.0
M9	18700	26.7(22.3)*	10.7	63.2
M10	16700	28.4(22.2)*	9.3	62.3
M12	18400	26.4(21.9)*	11.0	62.6
M13	17000	28.1(22.3)*	11.0	62.6
M14	18400	27.02(22.4)*	12.0	62.2
M15	17300	27.2(21.8)*	10.8	61.9
M16	18700	26.7(22.4)*	11.8	61.5
M17	16300	28.9(22.2)*	10.4	60.8
M18	16600	28.5(22.2)*	10.7	60.8
M19	17300	27.2(21.8)*	11.7	61.0

* w/o liquid with and without tridymite subsuming.

N.B the viscosity values of the liquid phases have been calculated at 1280°C for the compositions given in Table A2

Appendix II Quantitative XRD Phase Analysis

The "ratio of slopes" method (Monshi & Messer 1991) was used to determine the anorthite and mullite contents of two bodies K12 and K13. This method employs on internal standard which, in this case, was CaF_2.The required weight fraction of a phase in the body to be analysed is determined from the ratio of slopes of two linear plots passing through their respective origins, designated as the analysis and reference lines. The analysis line is obtained by plotting the intensity ratio of the required phase to the standard against the weight ratio of the body to the standard, for different proportions of the body and standard. The reference line for the required phase is obtained by plotting the intensity ratio against the weight ratio of the reference material to the standard, using a pure phase or a reference material of known composition.

Molochite was used as the reference material for mullite. This commercially prepared, calcined china clay (EEC International) is composed of mullite and glass. According to ECC International, the mullite content is 55%.

As the reference material for anorthite, a sample made to the formula $CaO.Al_2O_3.2SiO_2$ was prepared and fired at 1500°C. It was assumed that this would produce pure anorthite.

In this work, the slope for the reference line for mullite was determined by A. Mulenga (1995). The slope for this reference line using Molochite was 0.143. The anorthite reference line was 0.290 was established by Batista (PhD 2001). Their findings are shown in Tables AII.1a and b.

To carry out the analysis, samples of the two bodies, K12 and K13, were ground to fine powders. They were first crushed in a steel percussion mortar and then ground in an electrically driven agate mortar and pestle. Three mixtures of each of the powdered bodies were prepared with calcium fluoride with different weight ratios of the body to the standard. Each mixture was used to fill three sample holders for x-raying. To avoid the powders in a mixture separating as a consequence of having different particle sizes, they were mixed as pastes. Acetone was used as the liquid phase as this does react with the bodies or calcium fluoride. It is essential after mixing that the powders they are transferred as pastes into the sample holders. As acetone evaporates rapidly, the mixing procedure and transfer to the holders has to be carried out quickly.

The samples were x-rayed using a Philips system having a PW1730 generator with a tube voltage of 50kV and current of 30mA Monochromatic CuKα radiation, λ=0.154050nm was employed.

The calcium fluoride peak chosen for the work was 2θ=55.9° . The anorthite peak was 2θ=22° and the mullite peak at 2θ=33.2°. These peaks did not overlay with any other peaks obtained from the two bodies.

The peak areas were determined by scanning a limited range around each peak at 0.5°/min. The range covered were 20° to 24° 2θ to record the anorthite peak, 30° to 35° 2θ to record the mullite peak and 54° to 58°2θ to record the calcium fluoride peak.

Using a computerized x-ray system, "Traces", the background signal was substrated by the computer and the integrated intensities of the peaks were determined five time for each peak and the average taken. The intensity ratios were averaged. The resulting data for K12 for anorthite and mullite given in Tables AII.2a and b and for K13 in Tables AII.3a and b. The slopes of an analysis line is determined using a least squares fit of a straight line passing through the origin. This is done by fitting a line y=mx to the data where the weight ratio is x and the intensity ratio y. The slope m is given by

$$m = \frac{\sum_i y_i x_i}{\sum_i x^2}$$

For K12 the slope of the anorthite analysis line is 0.148. Using the reference line slope for anorthite of 0.290, the anorthite content is

0.148/0.290=51.0%

The slope of the mullite analysis line is 0.040, using the reference line slope of 0.143, the mullite content is

0.040/0.143×0.55=15.4%

The glass content of K12 is 100-(51.0+15.4)=33.6%

For K13, the slope of the anorthite analysis line is 0.146, which yields an anorthite content of 50.3%. The slope of the mullite anaysis line is 0.046 which yields a mullite content of 17.7 %. The glass content is 100-(50.3+17.7)=32.0%

Anorthite Refernce Line	
Weight Ratio x	**Intensity ratio Y**
4.941	1.415
1.841	0.516
0.913	0.245
$\sum xy$	8.165
$\sum x^2$	28.636
m	0.290

Table AII.1a) Slope of linear plot for anorthite reference line determined by Batista

Mullite Refernce Line	
Weight Ratio X	**Intensity ratio y**
1.83	0.230
1.06	0.204
0.400	0.065
$\sum xy$	0.663
$\sum x^2$	4.633
m	0.143

Table AII.1b) Slope of linear plot for mullite reference line determined by Mulenga

Anorthite (Peak)	
Weight Ratio **X**	**Intensity ratio** **y**
4.64	0.709
1.85	0.231
0.912	0.115
$\sum xy$	3.822
$\sum x^2$	25.78
m	0.148

Table AII.2a) Slope of linear plot for anorthite in K12

Mullite (Peak)	
Weight Ratio **x**	**Intensity ratio** **Y**
4.64	0.190
1.85	0.066
0.912	0.032
$\sum xy$	1.033
$\sum x^2$	25.78
m	0.040

Table AII.2b) Slope of linear plot for mullite in K12

Anorthite (Peak)	
Weight Ratio **X**	**Intensity ratio** **y**
4.71	0.699
1.85	0.254
0.911	0.112
$\sum xy$	3.864
$\sum x^2$	26.44
m	0.145

Table AII.3a) Slope of linear plot for anorthite in K13

Mullite (Peak)	
Weight Ratio **X**	**Intensity ratio** **Y**
4.71	0.215
1.85	0.088
0.911	0.043
$\sum xy$	1.215
$\sum x^2$	26.44
m	0.046

Table AII.3b) Slope of linear plot for mullite in K13

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