

Process design for the production of a ceramic-like body from recycled waste glass

Part 2 *The effect of fabrication variables on the physical properties of the fired body*

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The influence of fabrication variables on the sintering behaviour of a ceramic-like body containing 90% recycled waste glass was inferred from measurements of some of the fired properties (moduli of rupture and elasticity, firing shrinkage, bulk density and porosity). Interpretation of these results in terms of viscous sintering theory indicates the relative influence on the sintering behaviour of factors such as particle size and distribution, clay binder content and plasticity, pressing pressure, heating/cooling rate, firing temperature and time, thus enabling the fabrication variables to be optimized. Comparison of the physical properties of the resulting glass-based bodies with those of commercial ceramic tile bodies indicates that the glass-based bodies are very comparable with the best ceramic tiles tested, and considerably better than several commercially-produced clay-based bodies.

1. Introduction

Part 1 of this paper [1] describes a ceramic-like body consisting principally of ground waste glass with a small amount of clay binder to impart a degree of green strength to the pressed shape. By contrast with most of the previously-described glass-clay composites, the intention was that the fired strength of the present body should result primarily from inter-particle sintering of the glass powder, with a possible secondary contribution from the intergrowth of crystalline devitrification products. Participation of the clay binder in fired strength development was not sought, since to meet the objective of maximum energy economy in the production of the body, low firing temperatures were necessary, under which conditions strength development in clay is minimal.

Previous studies of the sintering of glass powders have been interpreted in terms of viscous diffusion, for which the fractional linear shrinkage $\Delta L/L_0$ after sintering for time, t , can be expressed by an equation developed by Frenkel [2]:

$$\Delta L/L_0 = \gamma t/2a\eta, \quad (1)$$

where γ is the surface tension, a is the average particle radius and η is the viscosity of the glass at the sintering temperature. The temperature dependence of sintering is introduced through the viscosity term, which has an Arrhenius type temperature dependence;

$$\eta = A \exp(Q/RT). \quad (2)$$

The validity of Equations 1 and 2 in describing the sintering of glass spheres of narrow size range has been confirmed by several workers [3–5], while a few experiments with mixtures of spheres of two different particle sizes can be described by the same equation [5]. On the other hand, angular grains of crushed glass did not show the linear relationship with time predicted by Equation 1, their sintering rate also being more rapid than for spheres of equivalent diameter [6]; this was attributed to the sharper radii at the points of contact which cause the system to behave as one composed of considerably smaller particles [6].

Although the clay binder concentration is purposely kept low in the present body, the significantly smaller particle size of the clay with respect to the glass powder may result in a fine coating of clay on the glass particles which could markedly interfere with their sintering, by altering the surface tension or viscosity of the glass. The viscosity of the glass can also be influenced by the presence of water vapour, being reported to be inversely proportional to the square root of the water vapour partial pressure, at higher pressures [7]. Any absorbed or hydroxyl water not removed in the drying process should therefore enhance the sintering of the body.

In addition to the good mechanical strength expected from a sintered glass body, it should be possible to achieve other desirable physical properties (low porosity, high dimensional stability) by the appropriate choice of fabrication and firing conditions. This paper reports the effect of these fabrication variables on the sintering behaviour of the body, as reflected by some of the more important practical physical properties (modulus of rupture, modulus of elasticity, firing shrinkage, bulk density and porosity). The fabrication variables investigated here include those already taken into account in connection with the green strength studies (particle size distribution of the glass powder, type and proportion of the clay binder, proportion of mixing water, pressing pressure) and in addition the variables associated with the firing process (the heating/cooling rate and the soaking temperature and time). Since the present glass-based body is envisaged as a substitute for some types of conventional clay-based ceramics, comparative physical measurements made under the same conditions on a range of commercial ceramic tile bodies are also reported here.

2. Experimental procedure

As with the green strength experiments reported in Part 1, a series of standard fabrication conditions were adhered to. In each series of experiments the only parameter to be altered was that parameter under investigation, the other conditions being kept constant. The standard conditions were:

- glass particle size: — 44 mesh (353 μm),
- binder type: "Ultrafine" halloysite,
- binder concentration: 10% by weight,
- water content: 6.7%,
- pressing pressure: 40 MPa,
- firing rate: 180° C h⁻¹,

- soaking temperature: 915° C,
- soaking time: 30 min.

The bodies for the firing tests were individually batched, the total dry weight of each sample being 150 g. After weighing, the dry components were thoroughly mixed by passing through a 44 mesh sieve to break up agglomerated binder, mixed with the necessary amount of water and pressed in a 128 mm square steel mould with demountable sides. Light oiling of the mould surfaces was occasionally necessary to assist demoulding, after which the pressed body was turned out onto a flat alumina ceramic bat which had been dusted with alumina powder to prevent the body sticking during firing. Firings were carried out in a 0.1 m³ electric potter's kiln with a programmable temperature controller. The temperature in the region of the sample was monitored by an independent Pt—Pt 13% Rh thermocouple and recorder. The samples were stacked on their bats in racks, a maximum of 6 samples being fired at one time to minimize the effect of possible temperature gradients in the kiln.

After firing, the shrinkage of each specimen was measured by laying it on a sheet of chart paper, cutting out around the specimen and weighing the paper, this weight being compared with that of the same piece of paper cut to the size of the original die. By repeating this procedure six times per specimen and comparing only those weighings made of exactly the same piece of chart paper (to eliminate the effect of differences in thickness throughout a roll), reproducibility within 0.05% could typically be achieved for the linear shrinkage values.

The specimens were then fixed onto flat glass plates with thermosetting cement and ground accurately flat and parallel using a Jones—Shipman 540 surface grinding machine with diamond-bronze wheels. After removal of cutting oil in an acetone ultrasonic bath, each specimen was cut into 25 mm × 4.5 mm strips with a fine diamond saw. In order to avoid plucking of the cut edges, the test pieces were again mounted on flat glass plates with double-sided adhesive paper, both test piece and plate being cut. All specimens for mechanical testing were then baked out at ~ 500° C to remove the last traces of oil or solvent. Breaking tests were carried out on these strips in an Instron Universal Testing Machine, using a three-point loading method [8]. The cross-head speed used in all tests was 2 mm sec⁻¹, and in most cases four test pieces from each specimen were

available for testing, the quoted value being the mean of all determinations. The stress–strain curves resulting from these breaking tests were linear, indicating classical brittle failure. The elastic modulus, E , of the specimen was determined from the slope of the curve (W/D) by the relationship [8]:

$$E = \frac{WL^3}{4bd^3D}, \quad (3)$$

where W is the value of force measured from the load–deflection curve, D is the deflection corresponding to the force W , L is the distance between the supports, and b and d are the specimen width and thickness respectively.

The modulus of rupture, σ , of the specimen was determined from the load, P , at which the specimen failed, by the relationship [8]:

$$\sigma = \frac{3PL}{2bd^2}. \quad (4)$$

The reproducibilities of these moduli were typically within 5%.

The bulk density of each ground strip was determined by accurate weighing and measurement of all the dimensions. The results quoted are the mean for all strips from the same sample.

The apparent porosity of each sample was measured by a water penetration method [9], in which weighed samples were boiled in distilled water for 5 h, allowed to stand in the water for a further 24 h, blotted dry and re-weighed. The quoted values are again the mean of all determinations. Reproducibilities within 0.1% porosity were obtained for most specimens.

3. Results and discussion

3.1. The effect of the glass particle size distribution on the fired properties

The effect of the glass particle size distribution on the physical properties of the fired body are shown in Fig. 1, for which the samples of various particle sizes were as previously defined [1]. Also included in Fig. 1 for comparison are corresponding green strength data taken from Part 1 of this paper. Fig. 1 shows that a progressive increase in the proportion of fines in the sample results in a progressive increase in the degree of sintering, as reflected in increased strength, elasticity, density and shrinkage, and decreased apparent porosity. This result is as expected from viscous sintering theory [2], which predicts that the rate of sinter-

ing is inversely proportional to the mean grain size (Equation 1). Furthermore, the relationship between shrinkage and maximum particle size is almost linear, appearing to confirm the finding of Henrichsen and Cutler [5] that glass compacts composed of more than one particle size behave similarly to compacts of identically-sized grains. The deviation from linearity noted in the shrinkage curve at smaller particle sizes indicates the region where the percentage of coarse particles has decreased to the point where the fine particles fill the interstices, under which conditions the rate of shrinkage decreases to an approximately constant value [5]. From a practical viewpoint, the improvement in physical properties resulting from an increased proportion of fines must however be offset by the additional grinding needed to produce glass powder of finer particle size, and it should be noted that the standard maximum particle size (353 μm) gives good mechanical properties, density and apparent porosity, and an acceptable shrinkage value. Maximum particle sizes greater than 353 μm lead to a marked deterioration in mechanical properties, and, particularly, an undesirable 11% increase in apparent porosity.

3.2. The effect of binder type on the fired properties

Table I shows the physical properties of bodies prepared under standard conditions using three different clay binders (kaolinite, halloysite, and Na-bentonite as previously described [1]). Table I indicates that the fired properties of the glass-based body are not very sensitive to the type of clay used as a binder. The reason for the high apparent porosity of the body containing kaolinite is not clear, but the fact that its density is comparable with that of the other bodies suggests the retention of an open-channel pore structure in the former, similar perhaps to the cellular structure reported to develop in ground-glass compacts containing 7.5 to 15% mica [10]. The present differences between the three clays cannot however be explained as in the mica case in terms of the high-temperature release of hydration or hydroxyl water [10], since all three clays used here evolve water at 650 to 700° C [11].

The bentonite used here was known to contain significant concentrations of alkalis and iron, the fluxing action of which is reflected in the low apparent porosity of that body. This suggests that in practice the chemical constitution of the binder

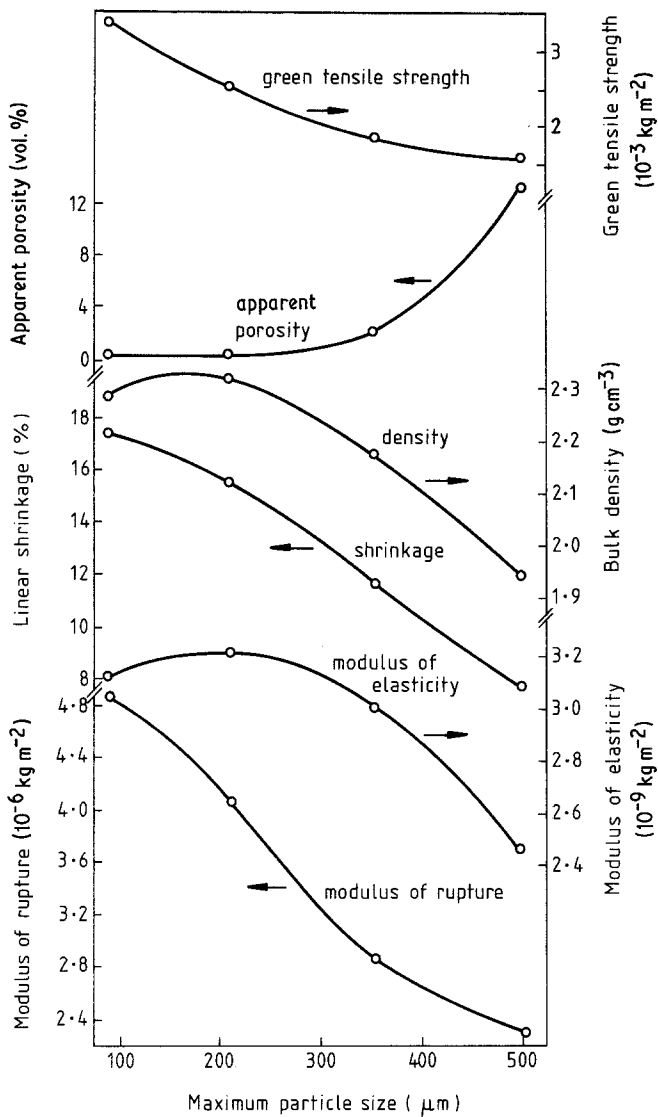


Figure 1 Effect of particle size on green strength and fired properties of the "standard" body.

might be exploited to lower the firing temperature; careful control would need to be exercised however to ensure that unacceptable deformation, warping or colouration was not thus introduced.

3.3. The effect of binder content on the fired properties

The effect of varying the content of halloysite binder in the "standard" body is shown in Fig. 2, which also includes green strength data for comparison.

A progressive deterioration is noted in all the fired properties with increasing binder concentration, consistent with increasing interference with inter-glass particle sintering and more clay-like behaviour at higher binder concentrations. This trend is in opposition to the green strength characteristics,

which markedly improve at higher binder concentrations, again reflecting increasing clay-like behaviour. In a practical body based on the present halloysite binder, the most realistic compromise seems to be 10% binder, as adopted in the standard conditions, since this gives reasonable green strength without undue deterioration of the fired properties.

3.4. The effect of mixing water content on the fired properties

The effect on the fired properties of varying the amount of mixing water in the "standard" body is shown in Fig. 3, which also includes green strength data, for comparison. Fig. 3 shows that a maximum occurs in both the fired properties and the green strength in a body containing 4%

TABLE I Influence of binder type on the fired properties of the "standard" body

Measured property	Binder		
	"Ultrafine" halloysite	BDH kaolinite	Na-bentonite
Modulus of rupture (Kg m^{-2})	3.31×10^6	2.90×10^6	3.59×10^6
Modulus of elasticity (Kg m^{-2})	2.73×10^9	2.40×10^9	3.16×10^9
Linear shrinkage (%)	12.23	8.29	10.51
Bulk density (g cm^{-3})	2.18	1.95	2.19
Apparent porosity (vol%)	1.10	17.81	0.53

mixing water, but all the properties deteriorate progressively with increasing water content above 4%. Thus, it appears that the factors controlling green strength development (maximum inter-particle contact and compaction behaviour) are also important in the development of good fired

properties. The decrease in sintering rates at increasing water contents above 4% requires comment, since it might not have been predicted from previous work in which the sintering of glass was shown to be enhanced by the presence of water vapour, which is thought to change the

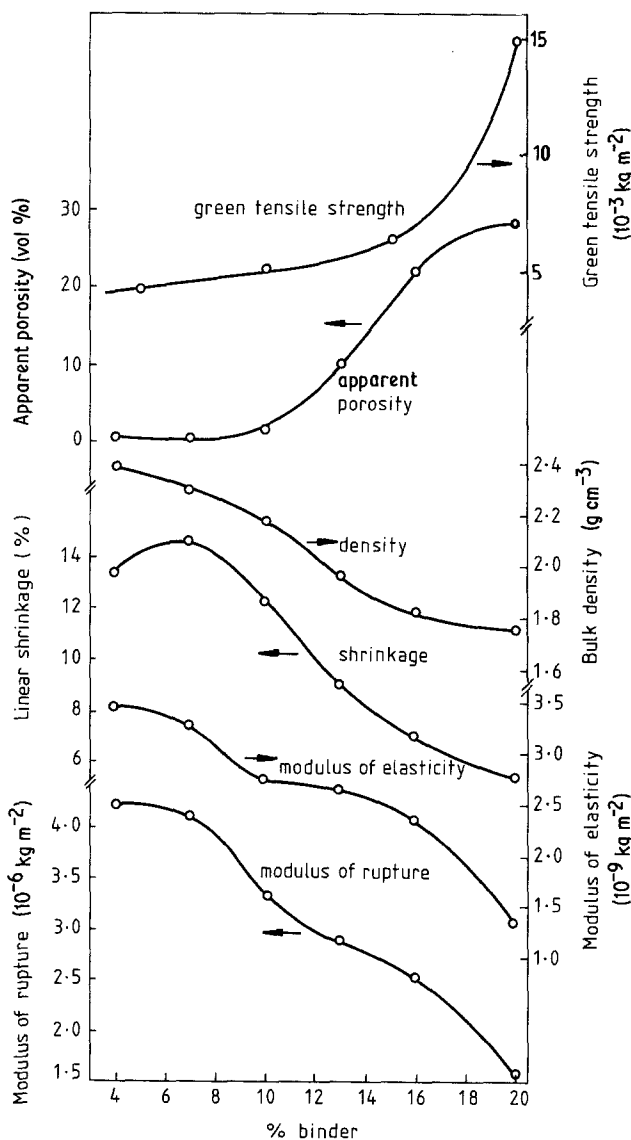


Figure 2 Effect of halloysite binder concentration on green strength and fired properties of the "standard" body.

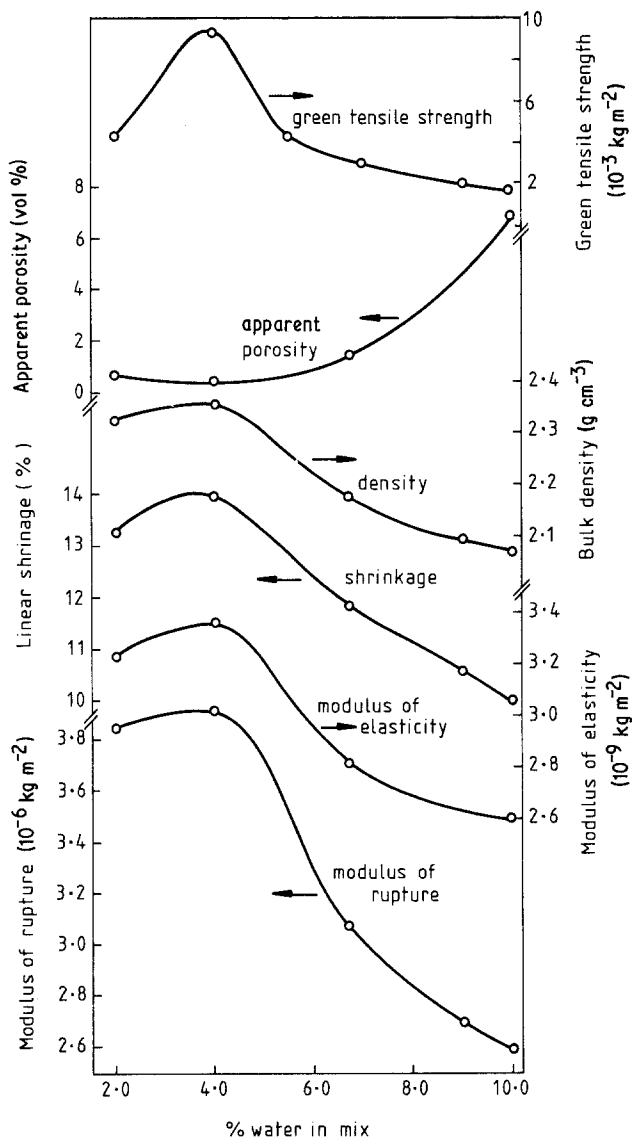


Figure 3 Effect of mixing water content on green strength and fired properties of the "standard" body.

viscosity of the glass [7]. It should be noted that the only water which will survive the drying process and thus influence the subsequent higher-temperature processes is that water which is strongly adsorbed on the glass surfaces or present as hydroxyl water in the clay binder. A thermogravimetric (TG) experiment carried out in air on a small cylindrical "standard" body containing 6.7% mixing water indicated that overnight drying at 110°C removed 6.36% of the mixing water. The surface area of the "standard" glass powder, measured by BET nitrogen adsorption is $0.27 \text{ m}^2 \text{ g}^{-1}$; taking the area of an adsorbed water molecule as $4.5 \times 10^{-3} \text{ nm}^2$, the weight of one monolayer of tightly bound water adsorbed on the surface of one gram of glass powder is $1.8 \times 10^{-3} \text{ g}$,

or 0.18% by weight. According to the TG experiment, this water is removed gradually over the temperature range 110 to 340°C ; a 1.7% weight loss due to the removal of hydroxyl water from the halloysite binder is also observed at 455 to 570°C . This suggests that only a monolayer or so of water survives the drying process, and although this water is likely to play an important role in green strength development by contributing to the bond between the glass surfaces and their fine coating of binder, the maximum in Fig. 3 cannot be explained in terms of this small amount of retained water. A more likely explanation is that the maximum in Fig. 3 occurs where sufficient water has been added to satisfy the rheological requirements of the clay for optimum pressing

behaviour. Deterioration of the fired properties at higher water content is due to detrimental changes in the pressing behaviour of the body. From a practical standpoint, the water content should be kept low, but since its optimum value depends both on the nature and concentration of the binder, it would best be experimentally determined for any particular body. For the present body, Fig. 3 suggests that a water content of 4% is more appropriate than the 6.7% water arbitrarily chosen as the standard test condition.

3.5. The effect of pressing pressure on the fired properties

The effect of varying the pressing pressure is shown in Fig. 4. As would be expected an increase

in pressing pressure produces an improvement in the fired properties of the body, but over the limited pressure range of this work, these changes are not large. The decrease in shrinkage with pressing pressure is similar to behaviour noted in self-vitrifying clay-based materials at or below the maximum densification temperature [12], for which a linear relationship was reported between the sample shrinkage and the logarithm of the pressing pressure, independent of firing time or grain size. Although the present results show no such logarithmic relationship, similar shrinkage mechanisms, possibly involving participation of a locally-formed liquid phase [12] could also apply in the present case. In practice, further improvements in the physical properties of the glass-based

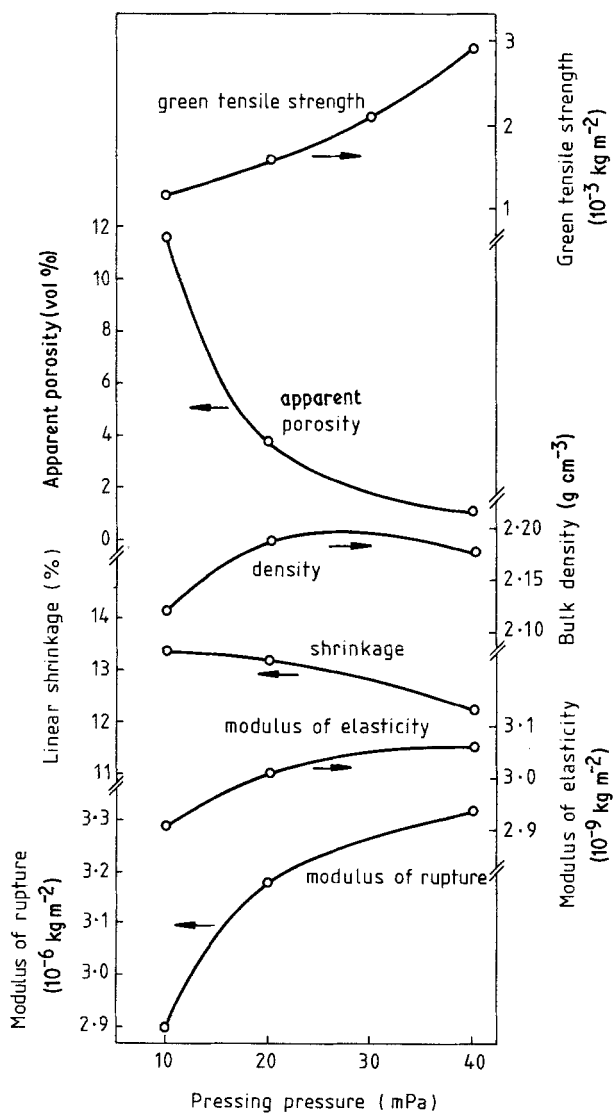


Figure 4 Effect of pressing pressure on green strength and fired properties of the "standard" body.

body appear certain to be achieved if fabrication was carried out at higher pressing pressures than those investigated here.

3.6. The effect of the heating/cooling rate on the fired properties

The effect of varying the heating and cooling rate is shown in Fig. 5. For the purposes of this work the heating and cooling rates were kept equal. For all tiles fired under the standard conditions of $180^{\circ}\text{C h}^{-1}$, cooling control was maintained to below 550°C (the glass annealing temperature), when the natural cooling rate of the furnace became the limiting factor. At faster rates, the temperature at which natural furnace cooling became the limiting factor progressively increased, but always remained below the glass softening temperature (720°C). Thus, although the samples in Fig. 5 were cooled to below the softening tem-

perature at the nominated rate, they were all annealed at a slower (though comparable) rate. Fig. 5 shows that apart from at the slowest heating rate, the degree of sintering, as reflected in the physical properties, is virtually independent of the heating rate. This interesting result suggests that the soaking treatment (30 min at 915°C) to which all the samples were subjected on reaching the soaking temperature was sufficient to nullify any differences in sintering behaviour introduced by different heating rates. The poor properties obtained at the lowest heating rate result from very severe devitrification of the glass powder during the prolonged heating-up period; the very high concentration of crystalline devitrification products (devitrite, $\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$, and cristobalite, SiO_2) found in this sample (see Part 3 of this paper) severely reduce the viscosity at the soaking temperature, thereby retarding sintering.

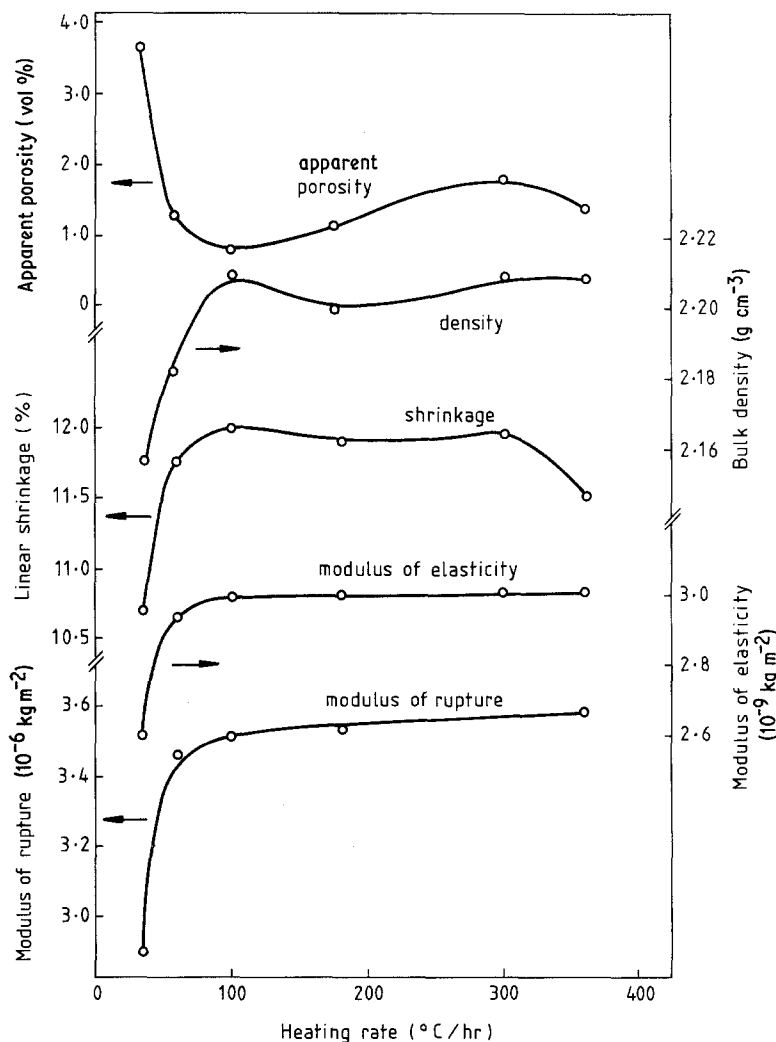


Figure 5 Effect of the heating/cooling rate on the fired properties of the "standard" body.

From a practical point of view, these results suggest that rapid firing rates are quite appropriate for this body provided a proper soaking time is provided at the maximum temperature; very slow firing rates can give less desirable results because of interfering devitrification reactions. However, the material must not be cooled below the annealing temperature (550°C) too quickly; this is particularly important in the firing of larger bodies.

3.7. The effect of soaking temperature on the fired properties

The effect of varying the soaking temperature is shown in Fig. 6, which indicates an expected improvement in the degree of sintering with increasing temperature up to about 920°C,

at which temperature the apparent porosity approaches zero. According to viscous sintering theory [2], the temperature dependence of the sintering process arises from the temperature dependence of the viscosity (Equation 2). The activation energy term, Q , can therefore be derived from an Arrhenius plot of the fractional shrinkage due to sintering. Treatment of the shrinkage results of Fig. 6 in this way leads to an activation energy of $\sim 73 \text{ kJ mol}^{-1}$ ($17.4 \text{ kcal mol}^{-1}$). The apparent viscosity of the present body can be calculated from Equation 1 by substituting a mean value for the particle radius of $8.8 \times 10^{-3} \text{ cm}$ and, following Henrichsen and Cutler [5], a value of $3 \times 10^{-5} \text{ J cm}^{-2}$ for γ . The viscosity thus calculated over the temperature range 820 to 940°C is 2.48

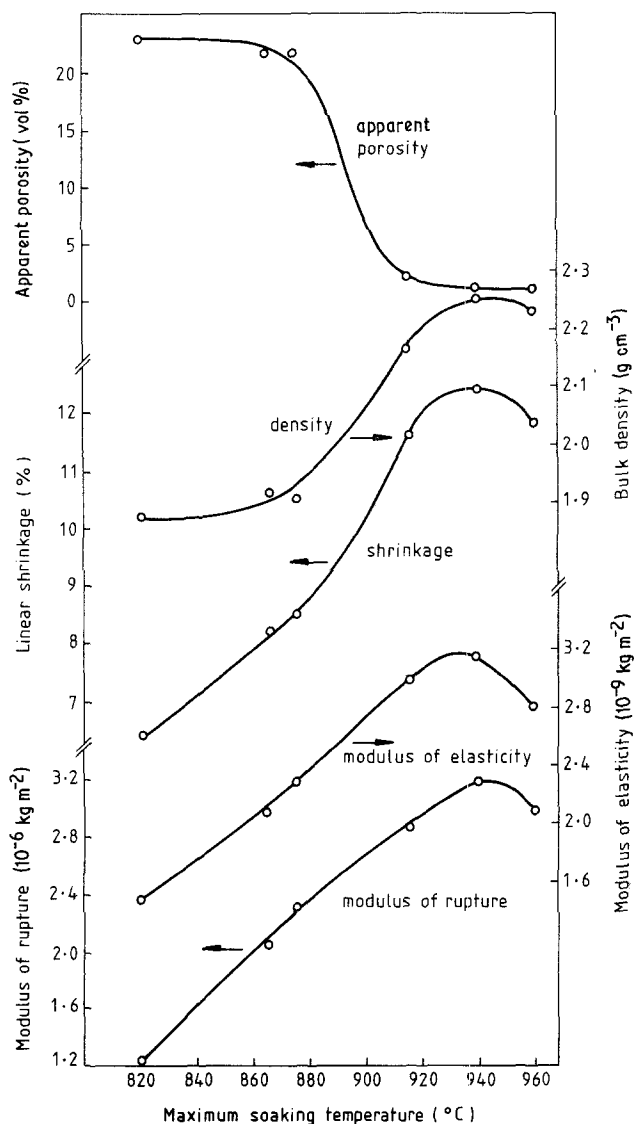


Figure 6 Effect of soaking temperature on the fired properties of the "standard" body.

to 4.79×10^8 poises. By comparison, the measured viscosity for a similar glass composition is typically:

$$\eta = 5.9 \times 10^{-8} \exp(66800/RT), \quad (5)$$

indicating viscosities of 6.3×10^4 to 1.3×10^6 poises for the same temperature range. Viscosities calculated from Frenkel's formula (Equation 1) have previously been found to be about four times larger in some cases than the true values [6], and the present use of Equation 1 may involve even greater errors due to its application in this case to angular rather than spherical grains, and the assumption of a mean particle size. Nevertheless, the gross discrepancies between the calculated viscosities of the present body and that of the component glass, and particularly the difference in sintering temperature dependence of the present body and that of the pure glass viscosity (17.4 and 66.8 kcal mol⁻¹ respectively) strongly suggest that the glass component of the present body behaves considerably differently from the pure glass, probably because of the presence of the clay binder. Further, in order to modify the glass properties to this extent, the binder probably exists as a fine coating on the surface of the larger glass particles; in view of the size disparity between the clay and glass particles, this suggestion is sensible.

From a practical viewpoint, the optimum soaking temperature of the present body is about 920°C for a soaking time of 30 min. This temperature represents a significant energy saving over the typical firing temperatures required by conventional clay-based ceramics.

3.8. The effect of soaking time on the fired properties

The effect of varying the time spent by the sample at the maximum soaking temperature is shown in Fig. 7, which indicates significantly poorer properties in samples fired to temperature and immediately cooled (zero soaking time). Fig. 7 shows that a 30 to 60 min soaking period produces a marked improvement in the fired properties, but still longer soaking times have a much less significant effect. The marked changes in the physical properties at shorter soaking times reflect the sintering kinetics, but could also include the effect of a temperature lag between the sample and furnace during the heat-up period. To investigate this latter possibility, an independent thermocouple was imbedded in 25 mm × 25 mm × 8.6 mm slab-

shaped "standard" body samples and the temperature at the centre of the body compared with that of the furnace temperature. The experiment was carried out both by introducing the sample into a pre-heated furnace at 920°C, and by heating the sample at the "standard" rate of 180°C h⁻¹. Both experiments indicated a virtually negligible temperature lag in the sample; at the "standard" heating rate the sample and furnace temperatures were identical over the whole temperature range, while even under the instantaneous heating rate conditions simulated by placing the sample in a preheated furnace, the sample and furnace temperatures coincided within 8 min, indicating that the effect of thermal lag in this sample would become apparent only at furnace heating rates in excess of 112° min⁻¹. For all practical purposes, therefore, the effect of thermal lag can be ignored. The sintering equation (Equation 1) suggests that the degree of sintering shrinkage is linear with time, although shrinkage-time plots for angular grains show a marked curvature [6]. According to the data of Henrichsen and Cutler [5] for glass spheres of approximately comparable mean diameter (150 μm), shrinkages comparable with those observed in the present body (~10%) were recorded at comparable sintering times (~40 min) but at temperatures approximately 200°C lower than for the present body. The considerably lower sintering rate of the present body by comparison with pure glass spheres is almost certainly due to the presence of the clay component.

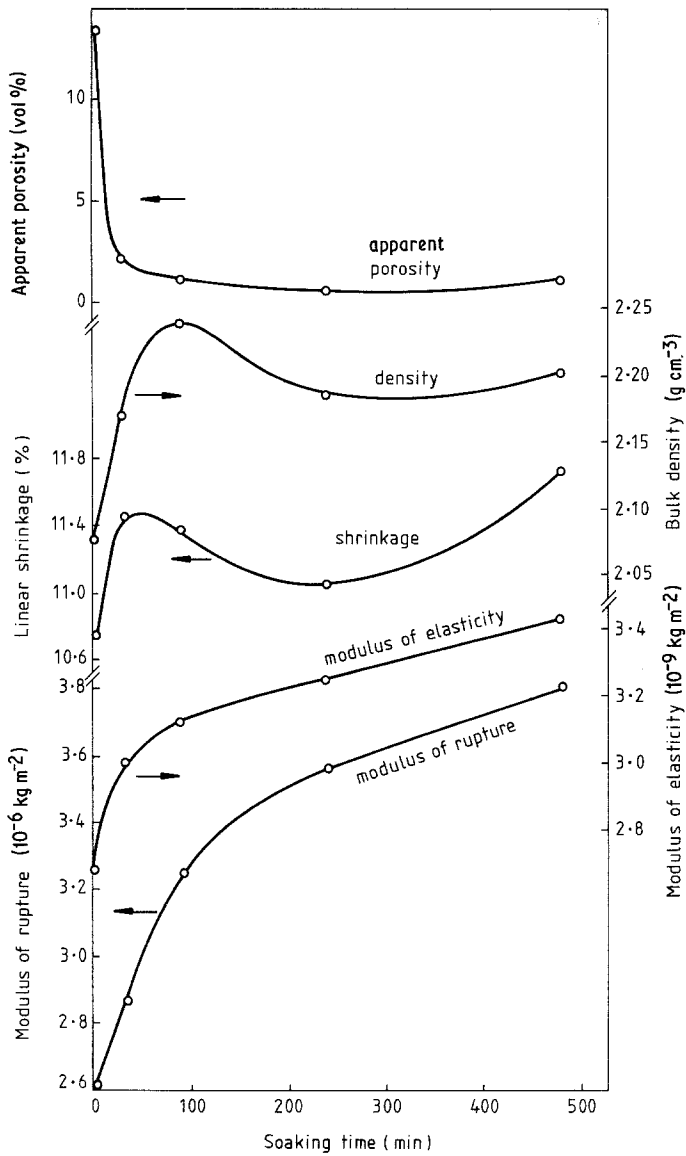
Additional information on the thermal properties of the present body can be derived from the temperature-time data of the slab sample in a pre-heated furnace. By plotting log(temperature) against time, a linear region can be identified, the slope of which is given by [13]

$$[\kappa\pi^2/4][1/a^2 + 1/b^2 + 1/c^2], \quad (6)$$

where κ is the thermal diffusivity of the body and a , b and c are the co-ordinates of the point within the body at which the temperature is measured. In the present case three linear regions were identified, giving values for κ of 2.15×10^{-4} to 1.06×10^{-5} cm² sec⁻¹ between 530 and 900°C. An alternative graphical approach, valid for an infinite slab [14], gave values of 1.32×10^{-3} to 1.24×10^{-5} cm² sec⁻¹ over the same temperature range. Since κ is related to the thermal conductivity, K , by

$$\kappa = K/\rho c, \quad (7)$$

Figure 7 Effect of soaking time on the fired properties of the "standard" body.



where ρ and c are the density and heat capacity of the body, values of K were calculated by substituting $c = 0.235$ to 0.285 for this temperature range [15], and $\rho = 2.2$. The thermal conductivities thus estimated fall in the range 1.25×10^{-4} to 6.3×10^{-6} cal sec⁻¹ cm⁻¹ °C⁻¹ at 500 to 900 °C. A scarcity of high-temperature thermal conductivity data for similar materials makes comparison difficult, but the lower-temperature value is comparable with those of diatomaceous earth brick, rock wool and firebrick at 400 to 500 °C (2 to 6×10^{-4} cal sec⁻¹ cm⁻¹ °C⁻¹) [16] and with that of a cellular mica-glass composite body (4.5 to 6.8×10^{-4} cal sec⁻¹ cm⁻¹ °C⁻¹ at 80 to 90 °C) [10].

3.9. Comparison of the present body with clay-based tile bodies

Four commercial ceramic tiles (one floor tile and three wall tiles) were subjected to the same tests as the present glass body, both in the glazed and unglazed form. The unglazed commercial specimens were tiles from which the glaze had been removed by surface grinding, while for comparison with the glazed commercial specimens, some of the glass body test pieces were overglazed with an acid-resistant formulation of composition 50.0% SiO₂, 4.6% Al₂O₃, 12.0% B₂O₃, 11.8% Na₂O, 2.0% K₂O, 2.5% Na₃AlF₆, 6.0% BaO, 7.6% TiO₂ and 3.5% CaO. This glaze was found to be fully compatible with the glass body, and fires at 850

TABLE II Physical properties of commercial ceramic tile bodies compared with the "standard" glass body

Sample	Surface	Density (g cm ⁻³)	Apparent porosity (vol %)	Modulus of rupture (kg cm ⁻²)	Modulus of elasticity (kg m ⁻²)
C1, Floor tile, England	Unglazed	2.298	5.46	4.35 × 10 ⁶	3.21 × 10 ⁹
C1, Floor tile, England	Glazed	—	—	4.40 × 10 ⁶	3.12 × 10 ⁹
C2, Wall tile, England	Unglazed	1.702	34.35	1.89 × 10 ⁶	1.13 × 10 ⁹
C2, Wall tile, England	Glazed	—	—	2.40 × 10 ⁶	1.49 × 10 ⁹
C3, Wall tile, Philippines	Unglazed	2.350	0.56	7.08 × 10 ⁶	3.70 × 10 ⁹
C4, Wall tile, England	Glazed	1.698	35.16	1.65 × 10 ⁶	1.01 × 10 ⁹
"Standard" glass body	Unglazed	2.181	1.55	3.25 × 10 ⁶	2.98 × 10 ⁹
"Standard" glass body	Glazed	—	—	3.45 × 10 ⁶	2.81 × 10 ⁹

to 880° C. The results of the tests are shown in Table II.

The range of measured values of physical properties of the ceramic tiles is very large and reflects their quality and intended use. The properties of tile C3 are similar to those of a floor tile, whereas C2 and C4 appear to rely on the glaze for their strength and resistance to moisture penetration. The mean of data for 4 "standard" glass tiles (not necessarily representing the optimum tile) shows that density, apparent porosity and elastic modulus are comparable with the best ceramic tiles, and considerably better than C2 and C4. The modulus of rupture data indicate that the "standard" glass tiles are slightly weaker than typical flooring grade tiles, but are well within the broad range encountered for all floor and wall tiles.

4. Conclusions

The development of good mechanical and physical properties in the present body is related to the degree of sintering undergone by the body. Factors influencing the sintering rate in glass-containing compacts include:

(a) The particle size, morphology and distribution of the grains (the sintering rate is inversely proportional to the mean grain size and depends on the degree to which the fines fill the interstices),

(b) The viscosity of the glass, which is exponentially proportional to the temperature and inversely proportional to the square root of the water vapour partial pressure. It is also very sensitive to the presence of impurities such as the clay binder, and to the formation of crystalline devitrification products within the glass.

(c) The degree of interparticle contact, which depends on the concentration and plasticity of the

binder, the relative particle sizes of binder and glass powder, and the pressing pressure.

(d) The firing conditions (the sintering rate is exponentially proportional to the temperature and the degree of sintering varies linearly with time). Taking account of those factors, the fired properties of the present body can be optimized by: (i) Adjusting the particle size distribution of the glass grains to give good packing characteristics (in practice the advantages of this action must be balanced against grinding costs), (ii) using the minimum amount of clay binder consistent with acceptable green strength, and optimizing the amount of mixing water to satisfy the rheological requirements of the clay and produce good pressing behaviour, (iii) pressing the body at sufficiently high pressure to ensure maximum interparticle contact, (iv) firing at a sufficiently fast rate to avoid excessive devitrification, to a temperature just below the onset of glassy flow, and holding at this temperature for sufficient time to allow for essentially complete sintering. Cooling must not be too rapid below the annealing temperature.

For the body described here, the arbitrarily-adopted "standard" fabrication conditions meet these criteria, with the exception that the mixing water content would be better lowered to 4%.

The physical properties of "standard" glass bodies are very comparable with those of the best ceramic tiles tested, and considerably better than those of several commonly available ceramic wall tiles.

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References

1. I. W. M. BROWN and K. J. D. MACKENZIE, *J. Mater. Sci.* **17** (1982) 2164.
2. J. FRENKEL, *J. Phys. (USSR)* **9** (1945) 385.
3. G. C. KUCZYNSKI, *J. Appl. Phys.* **20** (1949) 1160.
4. W. D. KINGERY and M. BERG, *ibid.* **26** (1955) 1205.
5. R. E. HENRICHSEN and I. B. CUTLER, *Proc. Brit. Ceram. Soc.* **12** (1960) 155.
6. I. B. CUTLER and R. E. HENRICHSEN, *J. Amer. Ceram. Soc.* **51** (1968) 604.
7. I. B. CUTLER, *ibid.* **52** (1969) 11.
8. British Standard Test Method BS2782, method 302D (1970).
9. ASTM test method C373-72 (1972).
10. N. M. P. LOW, *J. Mater. Sci.* **15** (1980) 1509.
11. N. H. BRETT, K. J. D. MACKENZIE and J. H. SHARP, *Quart. Revs. Chem. Soc.* **24** (1970) 185.
12. F. SANDROLINI and G. MORICONI, *J. Mater. Sci.* **14** (1979) 2811.
13. H. S. CARSLAW and J. C. JAEGER, "Conduction of Heat in Solids", 2nd edition (Oxford University Press, London, 1959) p. 185.
14. E. D. WILLIAMSON and L. H. ADAMS, *Phys. Rev.* **14** (1919) 99.
15. D. E. SHARP and L. B. GINTHER, *J. Amer. Ceram. Soc.* **34** (1951) 260.
16. W. H. McADAMS, "Heat Transmission", 2nd edition (McGraw-Hill Book Co., New York, 1942) p. 387.

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