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

Part 1 *The effect of fabrication variables on green strength*

I. W. M. BROWN, K. J. D. MACKENZIE
Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand

The development of an energy-economic process is described for converting recycled waste glass into a versatile material with fired properties at least comparable with those of conventional clay-based ceramics. The glass is ground to −353 μm powder, blended with up to 10% clay binder and pressed to the required shape before firing. An experimental investigation of the effect of compositional and fabrication variables on the green strength of such a body shows that the best methods for optimizing the green strength are by the appropriate choice of pressing pressure and drying conditions rather than by adjusting either the particle size distribution of the powder or the binder content, both of which options can adversely affect the fired properties of the body.

1. Introduction

Many thousands of tonnes of glass are discarded daily throughout the world, much in the form of non-returnable bottles and containers. In the developed countries, a growing interest in conservation of resources and ecological preservation has led to an increase in the recovery of solid wastes including glass, some of which is re-melted. Recycled glass cullet for this purpose must essentially be colour-separated, since mixtures of oxidized (clear and green) glass and reduced (brown) glass cause foaming problems in the glass tank when melted together. One constraint on the amount of recycled glass which can be used for re-melting is therefore the degree of colour-separation which can be achieved at the collection depot. In New Zealand, collection of efficiently colour-separated cullet has proved difficult; much of the waste glass collected is of mixed colour, necessitating the present investigation of alternative uses.

Since glass is an important constituent of conventional ceramic bodies such as vitrified earthenware in which it is formed *in situ* by reaction of clay and quartz with feldspars, consideration was given to the use of colour-mixed cullet as a ceramic raw material. This idea is not new; in 1965 Tauber and Crook [1] described a body prepared from lightweight shale and 5 to 20% crushed glass which when fired at 950° C for 4 h produced a composite material, bonded together by a partially devitrified glass matrix. Developments in waste disposal technology in the USA have led to the recovery from incinerator wastes of glassy shards which are too contaminated for re-melting; these have been crushed and combined with clay to form a body containing 40% glass which fires satisfactorily at 900 to 1000° C [2, 3]. Demonstration tiles fabricated in this way have been installed in the foyer of a building in Florida, but commercial production does not otherwise appear to have begun. A different type of body incorporating inorganic debris (mine tailings, crushed demolition rubble, etc.) containing 13 to 94% crushed glass and 6% ball clay as a binder has also been described [4]. This material has been vibrocast into panels up to 61 cm square and 5 cm thick and fired at 890 to 900° C. Marketed under the trade name Thixite, its best documented use to date has been in the construction of a demonstration "ecology pavilion" in Denver, Colorado. Another recently-described glass-containing material consists of 12.5 to 22.5% −200 mesh glass powder, the

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balance being a red mud occurring as a waste product from bauxite processing operations [5]. Tiles fabricated from this body are claimed to have useful sound absorption properties [5]. Another composite material formed from re-cycled glass powder and phlogopite mica [6] is claimed to have superior mechanical strength and thermal insulation properties because of its cellular structure, while yet another variation consists of 60% glass chips, 30% quartz sand and 10% low melting point glass which fluxes the body when fired at 860° C [7]. The latter body is pressed with a paraffin binder which burns off below 480° C.

The major role of the glass component of these materials is as a fluxing or bonding agent for the clay or rubble particles which constitute a considerable proportion of the bulk (the exception is the higher-glass Thixite composition which is almost totally glassy). Most of the previously-described bodies contain binders (typically ball clay, lignin, sodium silicate or sodium fluorosilicate) and all were pressed or vibrocast.

The aim of the present work was to develop a process for producing a body containing essentially 100% mixed-colour waste glass, but having ceramic-like properties and which could be fabricated by standard ceramic techniques. The absence of a conventional ceramic tile industry in New Zealand suggested that the fabrication of tiles would be a commercially sensible initial objective; consequently all the development and testing reported in these papers was based on simple tile shapes. However, another of the objectives was that the material should be versatile, and there is no reason why the body described here should not be fabricated in any shape which can conveniently be pressed. In developing the present body, other objectives were that any necessary fillers or binders should be indigenous, that the fired properties should be at least comparable with those of conventional clay-based bodies, and that the firing process should be energy-economic. The body described in these papers meets all these objectives.

In common with the previously-described glass-containing bodies [1–6], the raw cullet was crushed and ground to a powder and pressed to the required shape. To give the body sufficient green strength to handle, a small amount of binder and water had to be added; by contrast with most of the previous glass composite bodies, the binder was solely to promote green strength, and played a negligible part in the development of fired strength, which was primarily due to sintering of the glass particles. Several binders were investigated but the most useful class of binder for the present purpose was found to be clay. After pressing, the green body is dried and fired to a soaking temperature at which it is held for a time below slowly cooling. The body can then be decorated and glazed in the conventional way.

In developing this process, the effects of the various fabrication variables on the final properties of the body were investigated, to identify those factors which most strongly influence the body characteristics and therefore required careful control. The various fabrication variables are:

(a) the particle size distribution of the glass powder,

(b) the type of clay binder,

(c) the proportion of clay binder,

(d) the proportion of mixing water,

(e) the pressing pressure,

(f) the heating/cooling rate,

(g) the maximum firing temperature (soaking temperature),

(h) the dwell time at the soaking temperature.

Part 1 of this paper reports the effects of variables (a) to (e) on the green strength of the body, while Part 2 covers the effect of all these variables on the fired properties, which are also compared with the properties of clay-based ceramic materials. Fundamental aspects of the sintering and recrystallization processes are treated in Part 3.

2. Considerations of green strength and their application to the design of a glass-based body

The ability of an unfired body to hold together (the green strength) arises in clay-based bodies from the electrostatic interactions between the clay particles. In bodies such as the present one consisting principally of non-clay particles, the cohesive forces within the grains arise from the surface reactivity of the broken bonds at the grain surfaces, and their interaction with any polar molecules which may be present (e.g. clay particles or mixing water). Consequently, the green strength of a purely glass compact is extremely low, but can be increased significantly by the addition of even small amounts of clay and water. Since the fired strength of the present body depends on the achievement of the maximum amount of inter-glass

particle sintering, the content of clay binder must be kept as low as possible, consistent with the attainment of sufficient green strength to allow the transfer of the body from the mould to the kiln. The most effective use of small amounts of binder depends on a very uniform distribution of the clay component throughout the body; efficient dry mixing is therefore essential.

A second consideration in the development of green strength in a glass-based body is the role of the mixing water, which, in a glass body not containing binder confers a degree of cohesion to the bulk, by interaction with the reactive surfaces of the grains. By contrast, the interactions between clay particles increase as the water film separating them is removed. Thus, the green strength of a clay body increases as the water content decreases, and use is made of this fact by drying at room temperature or above. In a composite body of predominantly glass particles with a small clay content, the effect of the mixing water concentration and drying procedures is determined by a balance of all these factors and is best optimized experimentally.

The third factor influencing green strength is the particle size distribution of the powder components of the body, which influences both the packing characteristics of the powder and the capillarity of the liquid between the particles, the capillary force being inversely proportional to the powder size.

In the experimental investigation of all these parameters, described below, it must be remembered that in some cases, conditions which lead to a superior green strength may result in poor fired characteristics (high shrinkage, severe warping, etc.). Since the overall aim is to achieve the best possible fired product, some sacrifice of green strength may have to be accepted because of the nature of the body.

3. Experimental procedure

Preliminary experiments were made on waste soda-lime glasses, and indicated that identical results are obtained with window glass or bottle glass, either as mixed or colour separated cullet. The tests reported here were made on waste window glass. The as-received glass was roughly washed, drained and passed twice through a jaw crusher, before being passed twice through a steel disc mill and sieved to -44 mesh (353 μm). The coarse fraction ($+44$ mesh) was then ground in a laboratory mechanical mortar and pestle until it passed 44 mesh. The particle size distribution of the resulting powder is shown in Fig. 1, and was used as the standard material in all subsequent experiments, except those in which the particle size distribution was deliberately altered.

The binder used in most of these experiments was a New Zealand halloysite, ("Ultrafine" grade, NZ China Clays, Ltd), chosen because of its local availability. For comparison two other clays were tried; these were an English kaolinite (BDH "Supreme") and a NZ bentonite (Nelson Lime and Marble Co., Na-bentonite).

In the experiments reported here, a series of standard fabrication conditions were adhered to. In each series of experiments only one parameter was altered, the other conditions being kept constant. The standard conditions were:

maximum particle size: -44 mesh (353 μm);
binder type: "Ultrafine" halloysite;
binder concentration: 10% by weight;
water content: 6.7%; and
pressing pressure: 40 MPa.

In addition the effect on the green strength of drying the standard body for varying times both at room temperature and 110° C was studied.

The green-strength tests were carried out in a Hounsfield Tensometer apparatus on 10.0 g discs of 25 mm diameter. Loadings were carried out both on the flat surface of the discs and on the

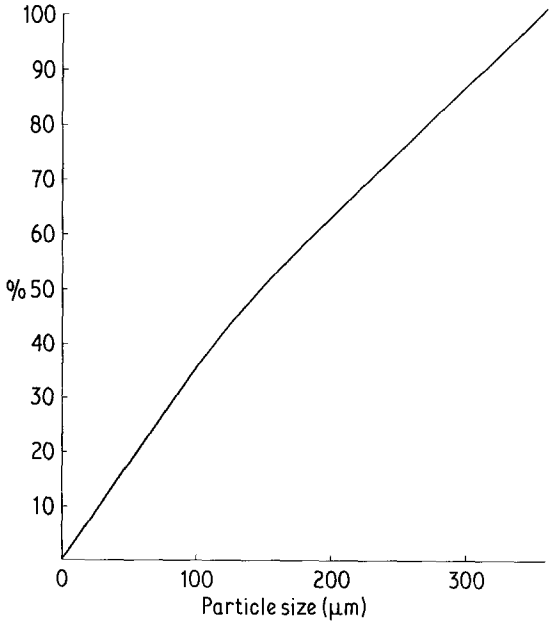

Figure 1 Cumulative particle size distribution of the "standard" glass powder starting material.

diameter; the measurements reported here are all of the latter type, since this has been shown [8] to be related to the tensile strength, T, of the body by

$$T = 2P/\pi dt, \quad (1)$$

where P is the breaking load, and d and t are the disc diameter and thickness respectively. This type of test, which is essentially a crushing strength test, was adopted because of the rather low green strength of the body and the difficulty of fabricating bar or rod-shaped specimens such as are used in more conventional three-point loading tests. All the crushing tests were carried out in duplicate, the results showing reproducibility better than 5%. Although the use of an unusual test method militates against meaningful comparisons with published values for other materials, its purpose here was to provide internally consistent comparisons of the effect of the various fabrication variables.

4. Results and discussion

4.1. The effect of glass particle size on green strength

The variation of green strength of the "standard" body with glass particle size is shown in Fig. 2.

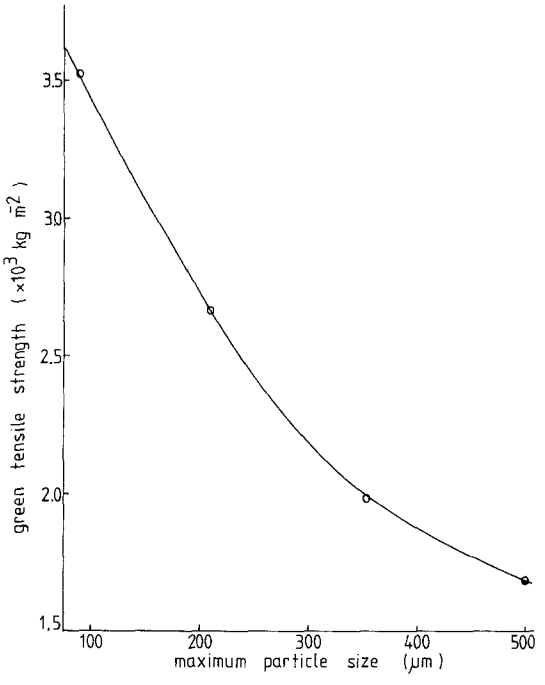

Figure 2 Variation of green strength of "standard" body with the maximum particle size of the glass powder. Green strength measured within 4 min of pressing.

In constructing Fig. 2, the "standard" glass powder as defined in Fig. 1 was used to determine the 353 μm point. The "standard" powder was then cut at 210 and 89 μm, these values being seen from Fig. 1 to represent approximately two thirds and one third respectively of the "standard" material. To synthesize the coarser mix, Fig. 1 was extrapolated to 500 μm to estimate the required proportion (again approximately one third) of powder of size −500 to +353 μm which had to be added to the "standard" powder. The smooth trend to increasing strength with decreasing particle size (Fig. 2) reflects the increase in contact area with the clay binder as the surface area of the glass powder is increased and the disparity between the particle sizes of glass and binder is reduced. Over the glass particle size range examined here, an improvement in green strength of 100% is recorded; these green strengths are however all rather low, suggesting that reducing the particle size distribution much below the present range is not a very useful method for improving the green strength, especially in view of the energy expended in extra grinding and the increased firing shrinkage which may be introduced (see Part 2).

4.2. The effect of binder type on green strength

The green strengths of specimens pressed under standard conditions with three different clay binders are shown in Table I.

It is seen that the results obtained with the three different clays are all rather similar. Two factors which should influence the green strength-promoting functions of a clay are its particle size distribution and its electrostatic interaction (as reflected by its cation exchange capacity). Table I shows that the maximum particle sizes of all three clays used here are very similar, as are their particle

TABLE I Green strength of the standard body containing different clay binders (10% concentration) compared with properties of the clays

Binder	Green strength (10^3 Kg m^{-2})	Maximum clay particle size (μm)	Typical cation exchange capacity [9] (meq per 100 g)
BDH kaolinite	4.9	5	3–15
Na-bentonite	4.6	0.3	80–150
NZCC halloysite	3.1	2	5–10

size distributions, determined by a SediGraph apparatus; little variation in their binding properties due to particle size differences would therefore be expected. The typical cation exchange capacities of these clays vary widely however (Table I), that of bentonite being an order of magnitude greater than that of kaolinite or halloysite [9]. The green strength of the bentonite-containing body is nevertheless intermediate between those of kaolinite and halloysite, suggesting that this factor is of relatively minor importance in determining the green strength of these bodies.

Although the green properties of the glass body are relatively insensitive to the nature of the clay binder, the chemical constituents of the clay (particularly its iron or alkali content) can have a marked influence on the fired properties of the body (see Part 2). Similar considerations apply to non-clay binders such as sodium silicate, which was tested but found to cause unacceptable warping and bloating on firing.

4.3. The effect of binder concentration on green strength

The variation of green strength with binder concentration is shown in Fig. 3 for both halloysite and kaolinite binders.

Although a primary objective in designing the present body was to keep the glass concentration as high as possible, it was of interest to investigate the green strength up to 100% clay. Fig. 3 shows two unusual features: the halloysite-containing bodies have superior green strength to kaolinite at all but the lowest concentrations, and there is an extremely sharp increase in the green strengths of the halloysite-containing bodies at 15 to 20% clay content, a feature which is much less apparent in the kaolinite-containing bodies. These differences indicate a somewhat complex rheological situation in the glass–clay composites, with the possible formation of a coherent "structure" between the halloysite particles in the body at about 15% clay concentration. This situation is approach in the kaolinite-bonded body at a clay content of about 30%, which also corresponds to the theoretical content of fines required for the optimum packing of a mixture of coarse and fine powders [10]; the particle size of the clay binders ($< 2\,\mu m$) is sufficiently smaller than that of the major part of the glass powder (of which 65% is $> 100\,\mu m$) that the system might be approximated to a mixture of two widely differing particle sizes, for which such a relationship is predicted [10].

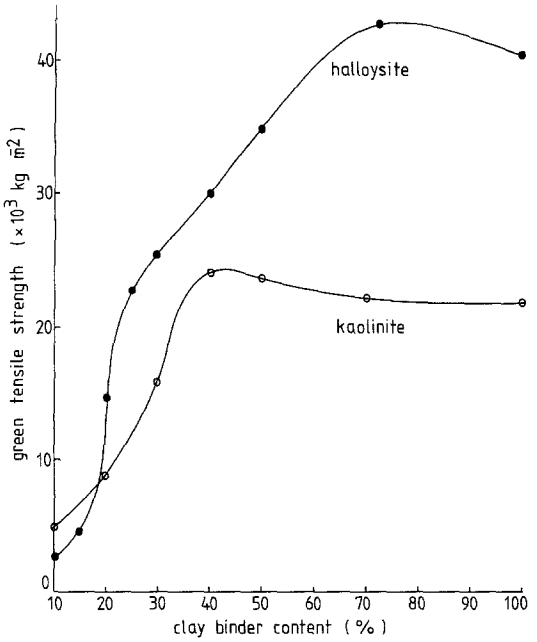

Figure 3 Variation of green strength of "standard" body with clay binder content for both halloysite and kaolinite. Green strength measured within 4 min of pressing.

Although the green strength at lower clay concentrations is comparatively poor, from a practical point of view, increasing the green strength by increasing the clay content causes a marked deterioration in the fired properties (see Part 2). A compromise must therefore be achieved between a sufficiently high green strength to allow the transfer of the body to the kiln and good fired characteristics. With the present glass powder and halloysite binder, an appropriate clay content appears to be 10%, the value chosen for the "standard" body composition.

4.4. The effect of proportion of mixing water on green strength

The variation of green strength with the proportion of mixing water is shown in Fig. 4 for two concentrations of halloysite binder.

It is seen that the rheological properties of this particular clay are such that the optimum workability of the body is achieved when the water content is approximately 40% of the binder content (but this factor may vary from clay to clay). For the present clay, a "standard" binder content of 10% requires 4% mixing water; at water levels lower than this the flow properties of the mix are inhibited whereas at much higher water

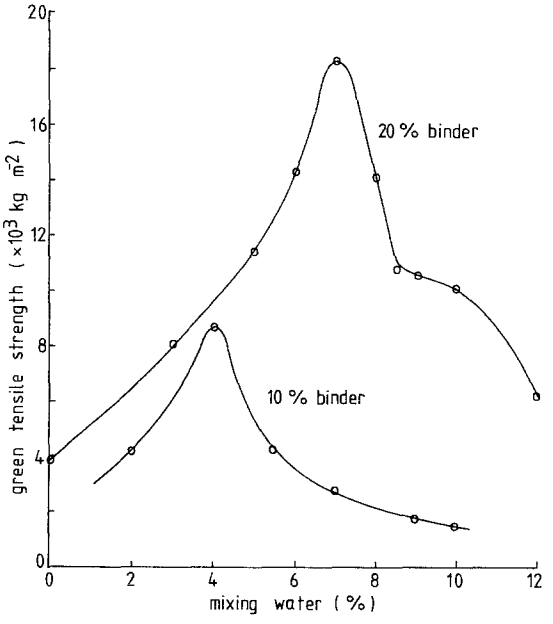

Figure 4 Variation of green strength of "standard" body with mixing water content for 10 and 20% halloysite binder. Green strength measured within 4 min of pressing.

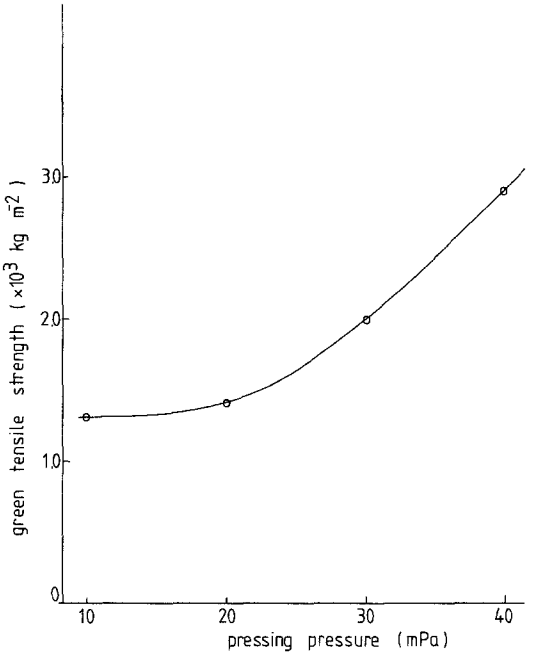

Figure 5 Variation of green strength of "standard" body with pressing pressure. Green strength measured within 4 min of pressing.

contents the excess water is physically squeezed from the body during pressing and the increased plasticity of the material makes demoulding increasingly difficult. The water requirement of other clays would need to be determined experimentally in each case.

4.5. The effect of pressing pressure on green strength

The green strength variation of the "standard" body with pressing pressure is shown in Fig. 5.

As would be expected, increasing the pressing pressure produces a body with improved clay–clay and clay–glass contact and better packing of the particles, but over the pressure range which could be investigated in the laboratory, the improvement in green strength is not impressive. However, since commercial pressing pressures are typically of the order 20 to 200 MPa [10], the higher pressures being appropriate for oxide-based ceramics, a significant improvement in green strength may be expected when the pressing is carried out under industrial conditions.

4.6. The effect of drying on green strength

Fig. 6 shows the effect of drying both at ambient temperature and 110° C on the green strength of the "standard" body.

The maximum increase in green strength is recorded after standing for 4 h at ambient temperatures; an even greater increase in green strength is achieved by drying for the same time at 110° C. Although minor changes occur in the green strength during more prolonged drying (probably due to the re-distribution of any remaining water between the clay and glass components), these changes are insignificant by comparison with the 6- to 10-fold gain in green strength during the first 4 h. Drying the body is thus one of the most useful methods of improving the green strength since it exerts a very large effect without adversely affecting the fired properties; the fired characteristics of a tile aged at 110° C for 18 h before firing were found to be identical to those of a freshly pressed sample.

5. Conclusions

The following conclusions can be drawn:

(a) A ceramic-like pressed body of high glass content can be made from re-cycled waste glass. A small amount (~ 10%) of clay binder must be used to give the body sufficient green strength to survive demoulding and transfer to the kiln.

(b) The green strength of 25 mm square tiles of "standard" composition is such that the bodies can be handled without damage immediately following pressing. However the green strength can

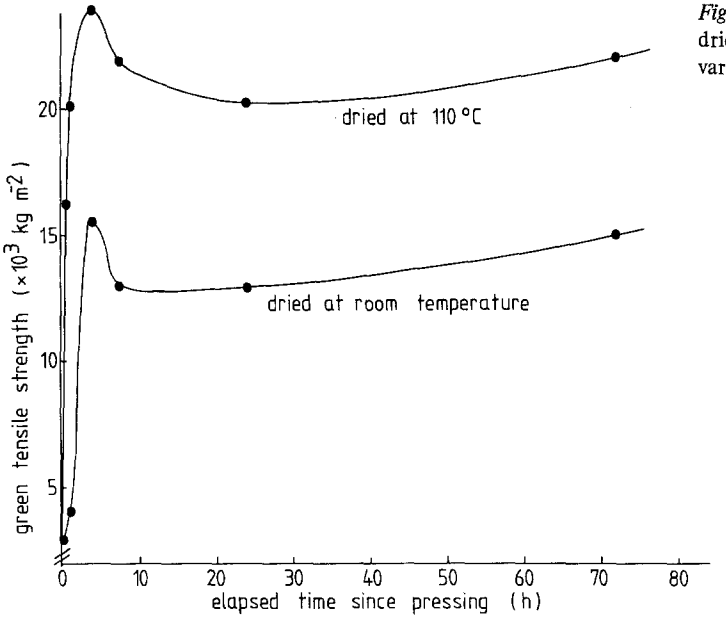

Figure 6 Green strength of "standard" body dried at room temperature and 110° C for varying periods.

be further improved, by (a) increasing the proportion of fines in the glass powder, (b) increasing the proportion of binder, (c) optimizing the mixing water content for the particular binder type and concentration being used, and (d) drying for up to 4 h at 110° C. Options (a) and (b) can adversely affect the fired properties, as will be shown in Part 2 of this paper, but options (c) and (d) do not interfere with the fired properties; the manipulation of these parameters therefore represents the best practical means of optimizing the green strength.

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