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Crystalline phases and physical properties of modified stoneware body with glaze sludge

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Abstract

Ceramic stoneware body has been modified with ceramic and glass industrial wastes by replacing 25-100% as flux in the formula. The effects of solid wastes added to the bodies were studied after firing in the temperature range 950-1280 °C. The physical properties of linear shrinkage, bulk density, apparent porosity, water absorption and 3-point bending strength were determined. A composition which related to the general stoneware properties was found when using soda-lime cullet and glaze sludge. It had a firing range lowered to 1050-1100 °C. SEM results demonstrated the sintered microstructure increased in density with increase in solid waste in the modified body. XRD results after firing showed the crystalline phases comprised of mullite, albite calcian and quartz. Thermal expansion was measured in the range $6.53-6.67 \times 10^{-6} \, \text{K}^{-1}$ at 30-500 °C. The modified bodies were capable of forming prototype products by slip casting and jiggering.

Keywords: Stoneware body; Glaze sludge; Glass cullet; Low firing temperature; Crystalline phase

1. Introduction

Ceramic manufacturing requires the reduction of production costs, especially the energy costs by developing the firing process and equipment. Many publications have reported that firing temperature can be lowered by addition of fluxes into the formula. Tulyaganov et al. [1] studied the influence of lithium oxide as an auxiliary flux on the properties of triaxial porcelain bodies. The desirable properties for tableware porcelains could be obtained if the Li₂O-content did not exceed 1.5 wt%. Salem et al. [2] reported a dilatometric study of shrinkage during the sintering process for porcelain stoneware bodies in the presence of nepheline syenite, with the maximum densification rate found with 10.0 wt% of nepheline syenite addition. Whereas the main approach of reducing firing temperature is to improve the formulation of the body and glaze, it became difficult to maintain the raw materials costs when the chemical additions were made. Additionally, raw materials preparation is an important variable, having an effect on the firing temperature, Kivitz et al. [3]. They studied the effect of preparation of the raw materials on the lowering of the porcelain firing temperature, and found that the sintering temperature had been decreased by approximately

production and has the advantage of lowering costs further. Since many wastes contain an abundance of alkali and alkaline earth

oxides, the production cost decreased according to the lower the

firing temperature used in ceramic manufacturing. Solid wastes

such as glass cullet, stone residue and fly ash have been used in

Recycling of industrial wastes aids environmentally friendly

180 °C after 720 min grinding of the raw materials.

stoneware and porcelain stoneware tile bodies. Tucci and et al. [4] reported that 10% sodium feldspar replacement with soda-lime scrap-glass could lower the firing temperature and gave better mechanical characteristics, attributed to enhanced microstructural homogeneity. Montero et al. [5] used calcium carbonate residue from the marble industry in manufacturing ceramic tile bodies. They showed that the residue reacted easily with phyllosilicates and quartz, providing better sintering of the original powder. This

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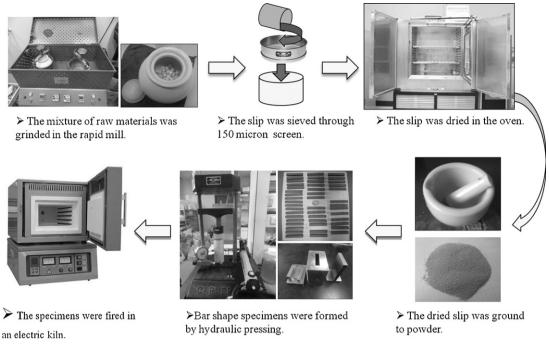


Fig. 1. Preparation of the trial specimens.

Table 1 Chemical compositions of raw materials and selected industrial wastes.

| Oxides | Raw materials (wt%) | | | | | | | | | |
|-------------------|---------------------|--------|-------------|--------------------|--------------|-----------------------|--|--|--|--|
| | Ball clay | Kaolin | Silica sand | Potassium feldspar | Glaze sludge | Soda lime waste glass | | | | |
| SiO ₂ | 55.50 | 46.59 | 99.36 | 68.33 | 58.09 | 71.16 | | | | |
| Al_2O_3 | 26.78 | 36.06 | 0.20 | 16.75 | 10.23 | 1.12 | | | | |
| Na ₂ O | 0.20 | _ | _ | 2.39 | 5.49 | 13.46 | | | | |
| K ₂ O | 2.39 | 1.60 | 0.04 | 11.08 | 1.36 | 0.23 | | | | |
| MgO | 0.29 | 0.75 | 0.04 | 0.28 | 0.71 | 4.18 | | | | |
| CaO | 0.45 | 1.05 | 0.01 | 0.32 | 6.05 | 8.94 | | | | |
| BaO | 0.02 | _ | _ | _ | 0.89 | 0.19 | | | | |
| TiO ₂ | 0.32 | _ | 0.06 | _ | 0.12 | 0.20 | | | | |
| Fe_2O_3 | 1.73 | 1.59 | 0.09 | _ | 0.14 | 0.48 | | | | |
| ZrO_2 | _ | _ | 0.02 | _ | 9.82 | 0.02 | | | | |
| ZnO | 0.01 | _ | _ | _ | 3.23 | _ | | | | |
| Others | 0.12 | _ | 0.04 | _ | 1.98 | 0.02 | | | | |
| LOI | 12.19 | 12.36 | 0.13 | 0.85 | 1.91 | 0.00 | | | | |

<8%, linear shrinkage at <14% and a bending strength up to 88 MPa. The use of solid wastes such as, glass cullet and glaze sludge to modify the firing temperature of stoneware body is in the interests of ceramics industry. The sintering behavior and crystalline phases developed can be investigated to describe the affect of solid waste addition to the properties of product.

2. Materials and methods

Raw materials used in this research composed of clays (ball clay:kaolin = 4:1 by weight), potassium feldspar and silica sand which were varied in the composition. The trial compositions were ground and mixed in a rapid mill for 10 min as shown in Fig. 1. The slip was sieved through 150 μ m and dried in the oven. The dried slip was ground to powder before hydraulic pressing at 2000 psi to 10 mm \times 10 mm \times 50 mm bars. The sample bars were fired at 1280 °C for 60 min and each body formula was

tested for the stoneware properties including linear shrinkage (ASTM C326-03), water absorption (ASTM C373-88), apparent porosity (ASTM C373-88), bulk density (ASTM C373-88) and 3-point bending strength (ASTM C674-88). The most suitable formula was used as the reference stoneware body.

Several industrial wastes were selected as additions for the fusion test and were analyzed for chemical composition before calculating the formula of the starting powders. The chemical composition of raw materials and selected industrial wastes are shown in Table 1. The trial bodies were prepared by replacement of potassium feldspar in the reference stoneware body with 25, 50, 75 and 100% of glaze sludge. Raw material composition of the trial formulas 25GS–100GS is shown in Table 2. After the properties were investigated, the suitable formula was selected and modified again by adding 5, 10, 15 and 20% of soda-lime cullet in order to improve properties and achieve lower firing body.

Table 2
Raw material composition of the reference stoneware body and 25GS-100GS formulas

| Mixtures | Raw materials (wt%) | | | | | | | |
|----------------|---------------------|--------|----------------|-----------------------|-----------------|--|--|--|
| | Ball clay | Kaolin | Silica sand | Potassium feldspar | Glaze sludge | | | |
| Ref. stoneware | 48 | 12 | 20 | 20 | _ | | | |
| 25GS | 48 | 12 | 20 | 15 | 5 | | | |
| 50GS | 48 | 12 | 20 | 10 | 10 | | | |
| 75GS | 48 | 12 | 20 | 5 | 15 | | | |
| 100GS | 48 | 12 | 20 | _ | 20 | | | |

The specimens were prepared using the same procedure and fired in the temperature range $950-1280\,^{\circ}\text{C}$ with a heating rate of $5\,^{\circ}\text{C/min}$ and soaking for 60 min. The trial bodies were tested for the stoneware properties as listed above. The trial bodies with the best properties after firing at lowest temperature were selected to investigate the sintering and crystallization behavior.

Crystalline phases and chemical composition were analyzed by XRD (JEOL, JDX-3530) and XRF (Philips, PW-2404) while SEM/EDS was used to observe the microstructure of the fired bodies. The thermal behavior was observed by dilatometer (Netzsch, DIL 402 PC). The selected modified body was used to form product prototypes via slip casting, using 45% water for a 3 kg batch and 0.6% Na₂SiO₃, mixed in pot mill for 9.5 h. Particles size and distribution was measured by means of a Malvern, Mastersizer S Ver. 2.19.

3. Results and discussion

The body formula which composed of 12% kaolin, 48% ball clay, 20% silica sand and 20% potassium feldspar by weight was selected to be the reference stoneware body in this work. It has 12.24% linear shrinkage, 2.40 g/cm³ bulk density, 0.07% apparent porosity, 0.03% water absorption and 61.97 MPa bending strength after firing at 1280 °C; these were the comparative properties to be compared to the commercial

Table 3 Chemical compositions of the reference stoneware body and 25GS-100GS formulas.

| Oxides | Formulas/components (wt | 1%) | | | |
|--------------------------------|-------------------------|--------|--------|--------|--------|
| | Ref. stoneware | 25GS | 50GS | 75GS | 100GS |
| SiO ₂ | 69.300 | 68.670 | 68.840 | 67.990 | 68.160 |
| Al_2O_3 | 23.225 | 23.147 | 22.494 | 22.497 | 21.880 |
| Na ₂ O | 0.728 | 0.857 | 0.989 | 1.149 | 1.316 |
| K ₂ O | 4.010 | 3.477 | 2.874 | 2.264 | 1.626 |
| MgO | 0.341 | 0.392 | 0.410 | 0.436 | 0.466 |
| CaO | 0.604 | 0.809 | 1.133 | 1.357 | 1.637 |
| BaO | 0.056 | 0.110 | 0.143 | 0.202 | 0.221 |
| TiO_2 | 0.201 | 0.199 | 0.213 | 0.221 | 0.231 |
| Fe ₂ O ₃ | 0.986 | 1.034 | 1.020 | 1.029 | 1.043 |
| ZrO_2 | 0.145 | 0.653 | 1.221 | 1.797 | 2.207 |
| ZnO | 0.006 | 0.217 | 0.335 | 0.536 | 0.669 |
| Others | 0.069 | 0.110 | 0.223 | 0.307 | 0.436 |
| LOI | 0.387 | 0.396 | 0.215 | 0.370 | 0.279 |

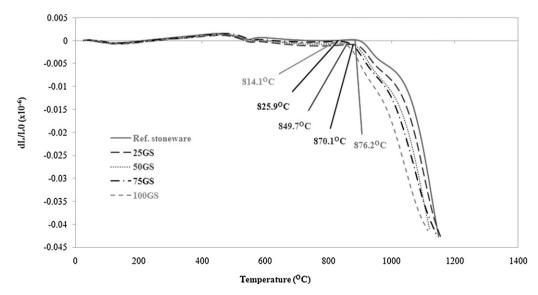


Fig. 2. Sintering point of the reference stoneware body and 25GS-100GS trial bodies.

stoneware body. The fusion test of the industrial wastes showed that glaze sludge from a ceramic tile industry can melt at temperature below 1100 $^{\circ}\text{C}$ and can replace feldspar in the reference stoneware body. The effect of glaze sludge additions to the reference stoneware body was studied by dilatometry. The sintering point of the reference stoneware body is 876.2 $^{\circ}\text{C}$ as shown in Fig. 2. The sintering point of trial bodies decreased continuously to 814.1 $^{\circ}\text{C}$ when increasing amounts of the glaze sludge replaced potassium feldspar in the reference formula.

Chemical composition of the trial bodies was analyzed by XRF and the results are shown in Table 3. The total amount of flux formed in the body increased with the addition of glaze sludge. It was clearly apparent that the various kinds and high quantity of alkali and alkaline earth oxides contained in the glaze sludge result in the lower sintering temperatures of the trial bodies.

Table 4 and Fig. 3 show property changes with firing temperature of (a) linear shrinkage, (b) bulk density, (c) apparent porosity, (d) water absorption and (e) bending strength when the glaze sludge was added (25–100%) replacing potassium feldspar. The fired properties improved with increasing amounts of glaze and rise in firing temperature. The linear shrinkage at 1100 °C was in the ranges 6.51–6.86%, bulk density was 2.08–2.15 g/cm³, apparent porosity was

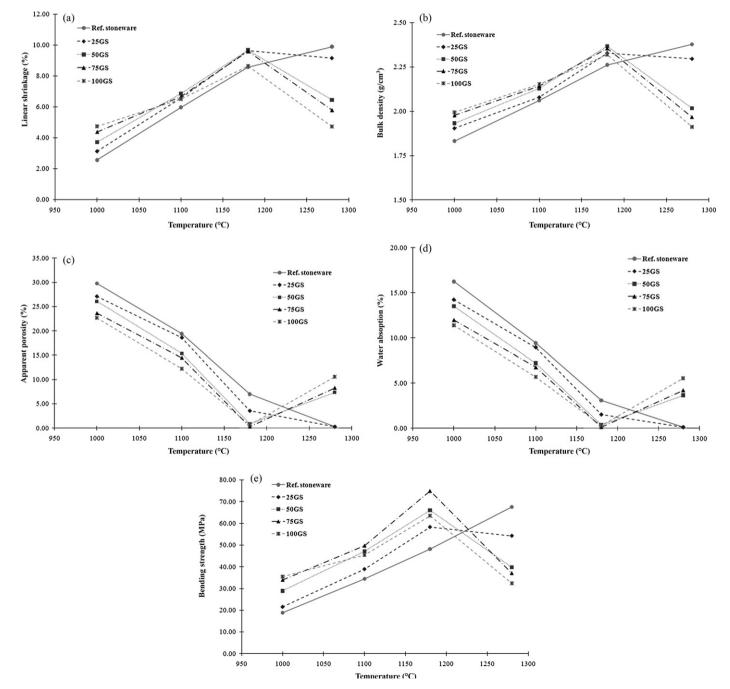


Fig. 3. Properties of the reference stoneware body and 25GS-100GS trial bodies, in relationship to the firing temperature. (a) Linear shrinkage, (b) bulk density, (c) apparent porosity, (d) water absorption and (e) bending strength.

Table 4
Properties of the reference stoneware body and 25GS-100GS trial bodies in relationship with firing temperature.

| Formula | 1000 °C | 1100 °C | 1180 °C | 1280 °C |
|---------------------------------------|------------------|------------------|------------------|------------------|
| (a) Linear shrinkage (%) | | | | |
| Ref. stoneware | 2.56 ± 0.08 | 5.97 ± 0.07 | 8.58 ± 0.24 | 9.90 ± 0.17 |
| 25GS | 3.14 ± 0.11 | 6.58 ± 0.11 | 9.65 ± 0.18 | 9.16 ± 0.25 |
| 50GS | 3.73 ± 0.09 | 6.86 ± 0.05 | 9.68 ± 0.47 | 6.46 ± 0.14 |
| 75GS | 4.39 ± 0.16 | 6.68 ± 0.11 | 9.59 ± 0.14 | 5.79 ± 0.53 |
| 100GS | 4.74 ± 0.12 | 6.51 ± 0.16 | 8.64 ± 0.23 | 4.73 ± 0.11 |
| (b) Bulk density (g/cm ³) | | | | |
| Ref. stoneware | 1.83 ± 0.02 | 2.06 ± 0.03 | 2.26 ± 0.03 | 2.38 ± 0.01 |
| 25GS | 1.90 ± 0.02 | 2.08 ± 0.03 | 2.33 ± 0.02 | 2.30 ± 0.01 |
| 50GS | 1.93 ± 0.02 | 2.13 ± 0.02 | 2.37 ± 0.01 | 2.02 ± 0.01 |
| 75GS | 1.98 ± 0.06 | 2.14 ± 0.03 | 2.36 ± 0.01 | 1.97 ± 0.01 |
| 100GS | 1.99 ± 0.04 | 2.15 ± 0.01 | 2.32 ± 0.01 | 1.91 ± 0.01 |
| (c) Apparent porosity (%) | | | | |
| Ref. stoneware | 29.77 ± 0.69 | 19.41 ± 1.33 | 7.00 ± 1.45 | 0.30 ± 0.41 |
| 25GS | 27.08 ± 1.00 | 18.59 ± 1.67 | 3.55 ± 0.71 | 0.27 ± 0.37 |
| 50GS | 26.08 ± 6.78 | 15.35 ± 1.01 | 0.87 ± 0.32 | 7.36 ± 0.87 |
| 75GS | 23.62 ± 3.00 | 14.48 ± 1.44 | 0.29 ± 0.40 | 8.28 ± 0.37 |
| 100GS | 22.68 ± 1.98 | 12.25 ± 1.50 | 0.71 ± 0.49 | 10.59 ± 0.95 |
| (d) Water absorption (%) | | | | |
| Ref. stoneware | 16.25 ± 0.51 | 9.43 ± 0.81 | 3.10 ± 0.68 | 0.12 ± 0.17 |
| 25GS | 14.22 ± 0.70 | 8.95 ± 0.95 | 1.53 ± 0.31 | 0.12 ± 0.16 |
| 50GS | 13.50 ± 0.55 | 7.21 ± 0.53 | 0.37 ± 0.14 | 3.65 ± 0.44 |
| 75GS | 11.99 ± 1.96 | 6.76 ± 0.76 | 0.12 ± 0.17 | 4.21 ± 0.18 |
| 100GS | 11.39 ± 1.23 | 5.69 ± 0.72 | 0.30 ± 0.21 | 5.54 ± 0.52 |
| (e) Bending strength (MPa) | | | | |
| Ref. stoneware | 18.91 ± 1.62 | 34.44 ± 2.08 | 48.21 ± 3.86 | 67.53 ± 4.83 |
| 25GS | 21.56 ± 2.19 | 38.92 ± 1.17 | 58.27 ± 4.11 | 54.24 ± 4.13 |
| 50GS | 28.91 ± 1.49 | 47.21 ± 0.71 | 66.03 ± 4.38 | 39.78 ± 1.43 |
| 75GS | 33.97 ± 2.11 | 49.76 ± 2.16 | 74.99 ± 3.65 | 35.57 ± 4.25 |
| 100GS | 35.48 ± 2.36 | 45.47 ± 2.25 | 64.54 ± 2.39 | 32.41 ± 2.81 |

12.25–18.59%, water absorption was 5.69–8.95% and bending strength was 38.92–49.76 MPa. However, the properties started to decline due to over firing which occurred in some compositions when firing temperature was above 1180 $^{\circ}\text{C}$. The over firing causes a porous structure in the trial bodies lowering density, with reduced strength and high water absorption.

Although the bending strength of 100GS (100% glaze sludge replacement) as shown in Fig. 3(e) was lower than 75GS but the water absorption values especially at low temperatures (1000 and 1100 $^{\circ}$ C) were better than 75GS and both properties were still in the ranges of general stoneware body. This research intended to use industrial wastes in the ceramic body as much as possible. Therefore, 100GS was the most satisfactory formula

Table 5
Properties of 100GS trial body and 100GS-SG5 to 100GS-SG20 modified bodies in relationship to their firing temperature.

| Formula | 950 °C | 1000 °C | 1050 °C | 1100 °C |
|---------------------------------------|------------------|------------------|------------------|-----------------|
| (a) Linear shrinkage (%) | | | | |
| 100GS | 2.93 ± 0.12 | 4.73 ± 0.31 | 6.23 ± 0.19 | 7.34 ± 0.15 |
| 100GS-SG5 | 3.48 ± 0.16 | 5.20 ± 0.08 | 5.98 ± 0.09 | 7.13 ± 0.07 |
| 100GS-SG10 | 4.96 ± 0.30 | 6.29 ± 0.15 | 7.01 ± 0.08 | 8.29 ± 0.08 |
| 100GS-SG15 | 5.00 ± 0.04 | 6.09 ± 0.02 | 6.78 ± 0.06 | 8.25 ± 0.12 |
| 100GS-SG20 | 5.20 ± 0.09 | 6.08 ± 0.08 | 7.05 ± 0.04 | 8.80 ± 0.14 |
| (b) Bulk density (g/cm ³) | | | | |
| 100GS | 1.86 ± 0.04 | 2.00 ± 0.01 | 2.07 ± 0.07 | 2.19 ± 0.02 |
| 100GS-SG5 | 1.99 ± 0.02 | 2.07 ± 0.03 | 2.15 ± 0.01 | 2.23 ± 0.01 |
| 100GS-SG10 | 2.01 ± 0.03 | 2.12 ± 0.02 | 2.17 ± 0.02 | 2.28 ± 0.01 |
| 100GS-SG15 | 2.00 ± 0.03 | 2.09 ± 0.01 | 2.18 ± 0.01 | 2.30 ± 0.00 |
| 100GS-SG20 | 2.03 ± 0.01 | 2.09 ± 0.01 | 2.18 ± 0.01 | 2.32 ± 0.00 |
| (c) Apparent porosity (%) | | | | |
| 100GS | 28.45 ± 1.73 | 22.31 ± 0.63 | 18.86 ± 3.66 | 8.77 ± 0.88 |
| 100GS-SG5 | 23.14 ± 0.64 | 19.25 ± 1.40 | 13.61 ± 0.51 | 6.09 ± 0.25 |
| 100GS-SG10 | 21.38 ± 1.68 | 16.51 ± 1.23 | 12.40 ± 1.02 | 2.80 ± 1.05 |
| 100GS-SG15 | 21.99 ± 1.19 | 17.89 ± 0.33 | 11.20 ± 0.43 | 0.95 ± 0.22 |
| 100GS-SG20 | 20.88 ± 0.67 | 17.32 ± 0.38 | 10.59 ± 0.65 | 0.51 ± 0.08 |

Table 5 (Continued)

| Formula | 950 °C | 1000 °C | 1050 °C | 1100 °C | |
|--------------------------|------------------|------------------|------------------|-------------------|--|
| (d) Water absorption (%) | | | | | |
| 100GS | 15.30 ± 1.30 | 11.14 ± 0.37 | 9.19 ± 2.20 | 4.00 ± 0.43 | |
| 100GS-SG5 | 11.63 ± 0.43 | 9.32 ± 0.79 | 6.34 ± 0.27 | 2.73 ± 0.12 | |
| 100GS-SG10 | 10.66 ± 1.01 | 7.81 ± 0.67 | 5.73 ± 0.51 | 1.23 ± 0.47 | |
| 100GS-SG15 | 10.98 ± 0.74 | 8.57 ± 0.18 | 5.15 ± 0.22 | 0.42 ± 0.10 | |
| 100GS-SG20 | 10.29 ± 0.40 | 8.27 ± 0.21 | 4.87 ± 0.32 | 0.22 ± 0.03 | |
| (e) Bending strength | | | | | |
| 100GS | 23.55 ± 3.68 | 36.95 ± 2.00 | 40.81 ± 3.65 | 49.58 ± 0.74 | |
| 100GS-SG5 | 28.41 ± 4.10 | 38.44 ± 1.57 | 43.44 ± 3.03 | 51.07 ± 3.02 | |
| 100GS-SG10 | 30.86 ± 4.18 | 38.40 ± 4.15 | 45.79 ± 4.16 | 58.40 ± 4.33 | |
| 100GS-SG15 | 32.62 ± 3.05 | 43.96 ± 2.51 | 54.00 ± 4.78 | 75.92 ± 3.75 | |
| 100GS-SG20 | 35.31 ± 2.68 | 43.17 ± 2.62 | 53.79 ± 3.16 | 105.14 ± 4.37 | |

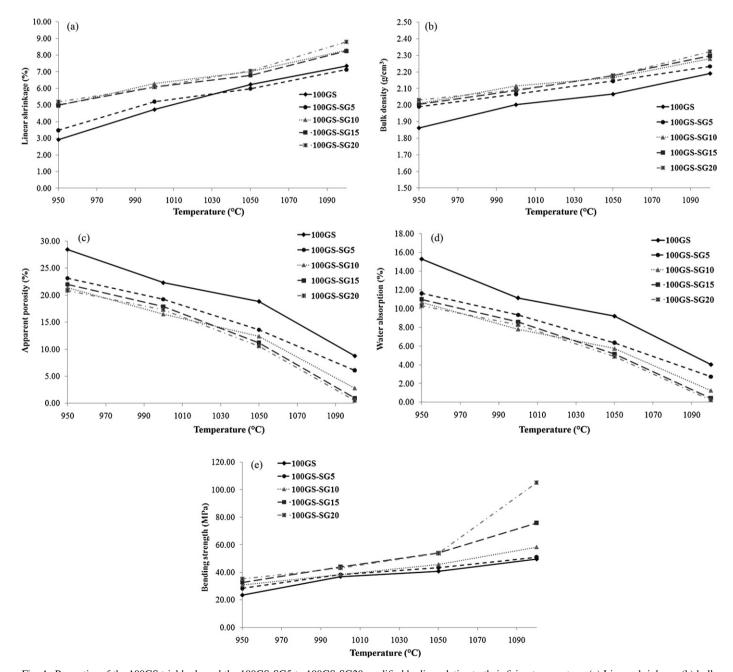


Fig. 4. Properties of the 100GS trial body and the 100GS-SG5 to 100GS-SG20 modified bodies relative to their firing temperature. (a) Linear shrinkage, (b) bulk density, (c) apparent porosity, (d) water absorption and (e) bending strength.

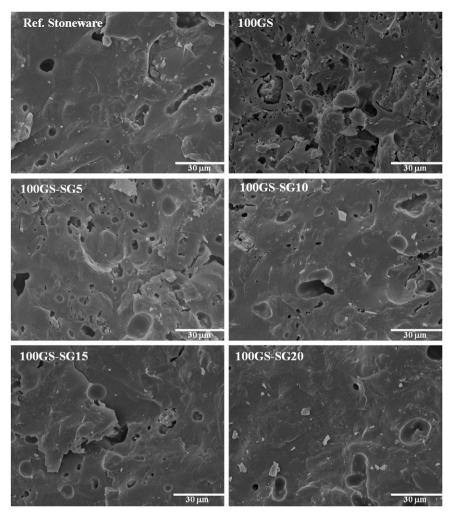


Fig. 5. SEM micrographs at $1000 \times$ magnification, of the fracture surfaces of the reference stoneware body after firing at 1280 °C, 100GS trial body and the 100GS-SG5 to 100GS-SG20 modified bodies after firing at 1100 °C.

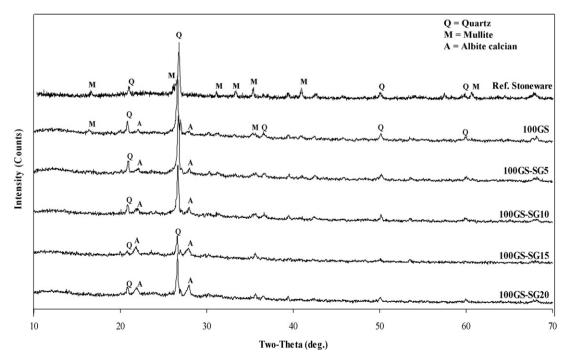


Fig. 6. XRD patterns of the reference stoneware body after firing at 1280 °C, 100GS trial body and 100GS-SG5 to 100GS-SG20 modified bodies after firing at 1100 °C.

which passed stoneware standard at lowest temperature 1100 °C. Its properties after firing were 6.51% linear shrinkage, 2.15 g/cm³ bulk density, 12.25% apparent porosity, 5.69% water absorption and 45.47 MPa bending strength. Regarding to plasticity property of the trial bodies, they were evaluated by jiggering process and found that 100GS had enough plasticity to form a good product.

The 100GS formula was modified by adding extra flux into the formula to lower the firing temperature and improve the firing range. The soda lime glass cullet was added 5–20% to make 100GS-SG5 to 100GS-GS20 formulas. The new modified body was fired at 950, 1000, 1050 and 1100 °C and the post fired properties were measured again, and compared to the 100GS trial body. Table 5 and Fig. 4 show how the properties changed, (a) linear shrinkage, (b) bulk density, (c) apparent porosity, (d) water absorption and (e) bending strength when 5–20% soda-lime glass cullet was added to the 100GS formula. The linear shrinkage of the 100GS-SG15 modified body was in the range 6.78–8.25%, bulk density was 2.18–2.30 g/cm³, apparent porosity was 11.20–0.95%, water absorption was 5.15–0.42% and bending strength was 54.00–75.92 MPa after firing at 1050–1100 °C. The linear shrinkage of the 100GS-

SG20 modified body was in the range 7.05–8.80%, bulk density was $2.18–2.32 \text{ g/cm}^3$, apparent porosity was 10.59–0.51%, water absorption was 4.87–0.22% and bending strength was 53.79–105.14 MPa. The results demonstrated that the 100GS-SG15 and 100GS-SG20 modified bodies provided the required stoneware properties after being fired at $1050–1100\,^{\circ}\text{C}$.

SEM micrographs in Fig. 5 showed the surface structure of 100GS and 100GS-SG5 to 100GS-SG20 compositions after firing at 1100 $^{\circ}$ C. The sintered surface and low porosity of 100GS-SG15 and 100GS-SG20 modified bodies has been observed for comparison with the reference stoneware body after firing at 1280 $^{\circ}$ C.

XRD was used to identify the crystalline phases present. Quartz (hexagonal) and mullite (orthorhombic) were found in the reference stoneware body, and in the trial and modified bodies as shown in Fig. 6. Albite calcian (triclinic) was not found in the reference stoneware body but was found in the trial and modified bodies. The volume fraction of mullite decreased while the albilte calcian increased in the modified bodies, as the amount of soda-lime glass cullet increased.

The SEM micrographs of the polished and etched surface (25 vol.% HF, 20 s) showed crystalline structures in the body.

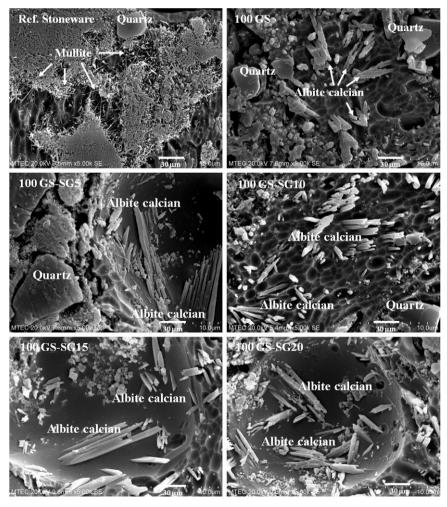


Fig. 7. SEM micrographs at 5000× magnification of the polished and etched surface of the fracture surfaces of the reference stoneware body after firing at 1280 °C, 100GS trial body and of the 100GS-SG5 to 100GS-SG20 modified bodies after firing at 1100 °C.

Table 6
Slip conditions for casting the prototypes.

| Formula | Density (g/cm ³) | Flow rate (s) | Residue #325 (%) | Size distribution, D50 (µm) | Casting rate (min/5 mm) |
|------------|------------------------------|---------------|------------------|-----------------------------|-------------------------|
| 100GS-SG15 | 1.68 | 31.03 | 1.10 | 7.50 | 60 |
| 100GS-SG20 | 1.68 | 31.22 | 2.63 | 9.46 | 60 |

Table 7 Properties after firing of the prototypes.

| | Linear shrinkage (%) | | Bulk density (g/cm ³) | | Apparent porosity (%) | | Apparent porosity (%) | | Bending strength (MPa) | |
|--------------------------|----------------------|--------------|-----------------------------------|--------------|-----------------------|--------------|-----------------------|--------------|------------------------|----------------|
| | 1050 °C | 1100 °C | 1050 °C | 1100 °C | 1050 °C | 1100 °C | 1050 °C | 1100 °C | 1050 °C | 1100 °C |
| 100GS-SG15 100GS-SG20 | 6.41 6.67 | 7.72 7.87 | 2.17 2.18 | 2.28 2.30 | 12.40 12.07 | 2.48 0.87 | 5.71 5.54 | 1.09 0.38 | 45.91 42.13 | 68.69 72.73 |

The crystalline phases shown in Fig. 7 were determined from XRD patterns and EDS results. The XRD results showed needle shaped mullite was present with quartz in the reference stoneware body. The trial and modified bodies also had mullite in the XRD traces but it was not found in the SEM micrographs. Most of the crystalline structures found were quartz and albite calcian. Albite calcian has a rectangular to rod shaped form. Its volume fraction increased when the amount of soda-lime glass cullet was increased.

The modified bodies started to sinter at relatively low temperatures, then at 1050–1100 °C, the temperature was high enough to melt the fluxes and promote the formation of glass phase in the bodies. As a consequence the linear shrinkage, bulk density, apparent porosity and water absorption improved to levels that were comparable with the reference stoneware body. Normally, the presence of a glass phase may reduce the bending strength of the bodies. The result of bending strength from this work was different in that it was improved, as reported by Tucci et al. [4] who measured high mechanical strength when the fluxes such as soda-lime scrap glass was added into the body.

For the general ceramic body, the needle shape of the secondary mullite phase is the key crystalline structure responsible for the high strength but is usually to be found after firing at temperatures higher than 1250 °C [1]. Only the primary mullite phase is found after firing in the range 1050–1250 °C. Zhang et al. [8] studied crystal growth in glass ceramic and suggested that Na⁺, Mg⁺ and Ca⁺ cations diffused

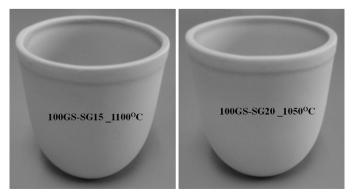


Fig. 8. The prototypes after firing at 1050 and 1100 °C.

to react with primary mullite, promoting crystallization in the glass matrix, resulting in diopside and albite forming in the glass ceramic. The mechanical strength was also improved with the increasing additions of crystallization promoters.

In this work, it is suggested that when the modified bodies with high flux content are partially melted at 1050–1100 °C, Na⁺ and Ca⁺ ions from the glass matrix could react with primary mullite to form albite calcian. Some secondary mullite may form but was only detected at a very low level. The main improvement in bending strength is attributed to albite calcian which was formed in the modified bodies. This is clearly dependent on how much glass phase and crystallization of the albite occurred at the lower temperatures in the modified bodies.

The 100GS-SG15 and 100GS-SG20 formulas were used to make up prototype products. The coefficient of thermal expansion (CTE) at 30–500 °C was investigated and found to be 6.53 and $6.67 \times 10^{-6} \, \mathrm{K^{-1}}$ for the 100GS-SG15 and 100GS-SG20 modified bodies, respectively. The body slips were prepared in 3 kg batches and the processing conditions are shown in Table 6. The biscuit firing was done at 800 °C. After glazing, the prototypes were fired at 1050–1100 °C. The properties were investigated and the results are shown in Table 7. On completion of product testing, the prototypes passed the national standards for stoneware product. The same formulas were used to form products by a jiggering technique in the factory. Some preparation conditions were modified and hollow ware was successfully produced with diameters up to 22 cm as shown in Fig. 8.

4. Conclusions

It can be concluded that ceramic glaze sludge can be used to replace feldspar in a stoneware body up to 100%. Incorporation with additional 15–20% soda-lime glass cullet, the firing temperature was reduced to 1050–1100 °C which is 180–230 °C lower than used for the reference stoneware body. The high concentration of alkali and alkaline earth oxides played the important role in lowering the firing temperature. Quartz, mullite and albite calcian phases were found in the modified bodies. 100GS-SG15 and 100GS-SG20 modified bodies have

been shown to have the required properties and capability to be made into commercial stoneware products.

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