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A COMPARISON OF FLUXING EFFECTS OF GRANITE AND FELDSPAR ON RED CLAY BODY COMPOSITION

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ABSTRACT

In this study, raw materials, red clay, granite and feldspar were characterized in terms of particle size distribution, chemical and mineralogical composition. Technological properties such as bulk density, liner shrinkage, water absorption and mechanical strength of ceramic specimens fired at 1000, 1050 and 1100 °C were evaluated. Microstructural analyses of fired ceramic samples were carried out by X-ray diffraction and scanning electron microscopy. The results showed that granite powder rich in alkaline and alkaline earth oxide accounted for better technological properties of the ceramic product than pure feldspar. The ceramic product with flexural strength of 72.48 MPa, water absorption of 0.11 % and bulk density of 2.59 g/cm^3 could be produced using granite as a fluxing raw material. However, when feldspar was used as fluxing raw material, the maximum technological properties of the ceramic product obtained after firing at 1100 °C were flexural strength of 48.63 MPa, water absorption of 0.12 % and bulk density of 2.45 g/cm^3.

Keywords: *Firing, Microstructure, Traditional ceramic, Clays, Red clay product*

INTRODUCTION

Red clay based products such as floor tile, roof tile and cooking wares have received much attention in the recent past in Sri Lanka as well as in other countries. Major reasons are abundance of red clay, and the possibility of its low temperature vitrification (Garcia et al., 1990; Kingery et al., 1995; Conville and Lee, 2005) compared to china clay and ball clay. Another key advantage is the possibility to incorporate different types of industrial waste material such as petroleum waste (Pinheiro and Holanda, 2009), oily waste (Monteiro et al., 2007), fine steel sludge (Vieira et al., 2006), ornamental rock powder waste (Moreira et al., 2008), granite powder waste (Vieira et al., 2004) and sludge of wastewater treatment plants (Monteiro et al., 2008) into red clay body composition. Therefore, further development of red clay based products would reduce the rapid consumption of less available ball clay and china clay, and in addition, provide a satisfactory solution for environmental problems generated by industrial waste materials. Clay minerals illite and montmorillonite in red clay and impurity minerals such as goethite and mica facilitate vitrification of red clay at low temperatures (Garcia et al., 1990; Kingery et al., 1995). However, usage of a high content of clay in the body composition of red clay products results in severe defects of the final product such as dimensional variation, warpage and blotting (Riley, 1951; Vander beck and Everhart, 1951). To overcome these defects, the well-known solution is to increase the quartz content of the body composition. However, this would increase the maturing temperature and decrease the strength and other mechanical properties of the final product (Mattyasovszky-Zsolnay, 1957; Warshaw and Seider, 1967). As a result, the firing cost would increase and the quality of the final product would decrease. Therefore, replacement of a certain amount of clay with a good fluxing raw material is necessary to reduce the firing energy cost and to obtain a high quality product.

Feldspars are well known fluxing raw materials used in the traditional ceramic industry. Feldspar of high purity is needed to obtain whiteness of white ceramic products such as porcelain. However, the purity level of feldspar is not so important for red clay products. Therefore, the use of pure feldspar for the red clay product is a waste of valuable raw material that can be used for more advanced applications such as porcelain, ceramic glaze coatings and enamels.

Since granite is made up of fluxing minerals such as feldspar and mica (Strens, 1976), there is a high potential to use granite as a fluxing raw material in red clay products. A number of studies have been performed to incorporate granite waste powder from granite cutting and polishing industries into red clay body composition of roof tile (Monteiro et al., 2004; Torres et al., 2009), bricks (Vieira et al. 2004), and floor tile (Torres et al., 2007). They have mainly focused on how to incorporate waste materials into the body composition of red clay products, and did not study on the fluxing action of granite on red clay products. In the literature, fluxing capabilities of granite and feldspar have not been compared and granite could be a useful replacement for costly feldspar. Therefore, the main objective of the present investigation is to compare the fluxing capabilities of granite and feldspar in red clay products.

MATERIAL AND EXPERIMENTAL PROCEDURE

CHARACTERIZATIONS OF RAW MATERIALS

Local red clay used for roofing tiles in large scale in Sri Lanka was used in the present study. Pure quartz powder (particle size < 53 μm) of known chemical composition was used. Feldspar was obtained from a local deposit which is currently used by ceramic industries in Sri Lanka. Granite sample was collected from Arangala, 52 km away from the capital Colombo of Sri Lanka. Both feldspar and granite samples were separately crushed and ground in a ball mill to pass through the 53 μm sieve. Chemical composition of raw materials was measured by Atomic Absorption Spectroscopy (AAS, GBC, Avanta). Mineralogical analyses were performed using optical methods and X-ray Diffraction (XRD, Siemens, D 5000). Particle size distribution of clay-silt fraction, feldspar and granite powder was assessed using a laser particle seize analyzer (Fritsch, Analysette 22).

SAMPLE PREPARATION

Different formulations were prepared for testing by mixing various proportions of clay-silt, granite, feldspar and quartz as shown in Table 1. Mixtures (500 g) were prepared by ball milling the constituents with water (1:1) for 30 minutes. The resultant slurry was oven dried overnight at 110 °C and powdered gently to pass through a 250 μm sieve. The powder was kept in a desiccator for 24 hours. Rectangular specimens, 70 mm × 2.5 mm ×3 mm, obtained from uniaxial pressing at 20 MPa were dried at 110 °C for 24 hours and fired in a laboratory furnace at 1000, 1050 and 1100 °C. The rate of heating was 20 °C/ minute with 20 minutes soaking at the maximum temperature and cooling was allowed by natural convection inside the furnace after it was turned off. These specimens were tested for linear shrinkage, bulk density, flexural strength and water absorption. Linear shrinkage was measured using Mitutoyo caliper. Bulk density of the fired samples was determined through the Archimedes' method with water immersion. Water absorption was determined according to the test method of ISO-standard 10545-3. Three point flexural rupture strength was determined by universal testing machine (model LT 10 KS, Tinius Olsen) using a crosshead speed of 0.5 mm/min. The microstructure of the fracture surface of selected fired samples was studied under a Scanning Electron Microscope (SEM, Model 1420, LEO).

Table 1 The mixing proportion of raw materials in tested formulations

Formulations	Clay-silt (wt.%)	Quartz (wt.%)	Feldspar (wt.%)	Granite (wt.%)
F1	80	10	10	--
F2	70	10	20	--
F3	60	10	30	--
F4	50	10	40	--
G1	80	10	--	10
G2	70	10	--	20
G3	60	10	--	30
G4	50	10	--	40

RESULTS AND DISCUSSION

CHARACTERIZATION OF RAW MATERIALS

Figure 1 shows the particle size distribution of clay-silt fraction of red clay, feldspar and granite samples used in the ceramic body formulations. The particle-size of both feldspar and granite samples are less than 40 µm, and 60 % of each sample has particles less than 20 µm. The distribution pattern of particle-size of both feldspar and granite are almost equal (Figure 1). Therefore, it can be assumed that the particle size of samples may not have an effect on property variations of the final product. In addition, 72 % of particles obtained from clay-silt fraction of red clay contain particles that are less than 10 µm.

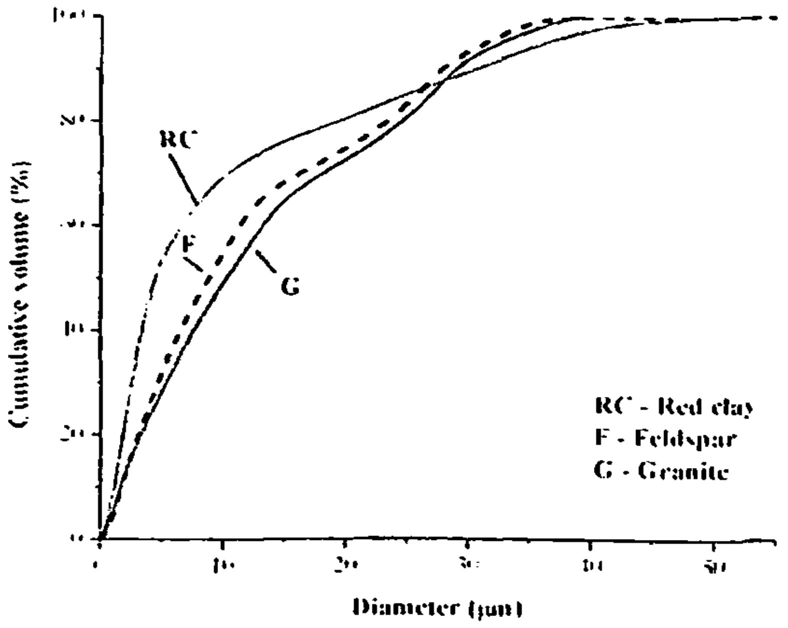

Fig. 1 Particle size distribution of raw materials.

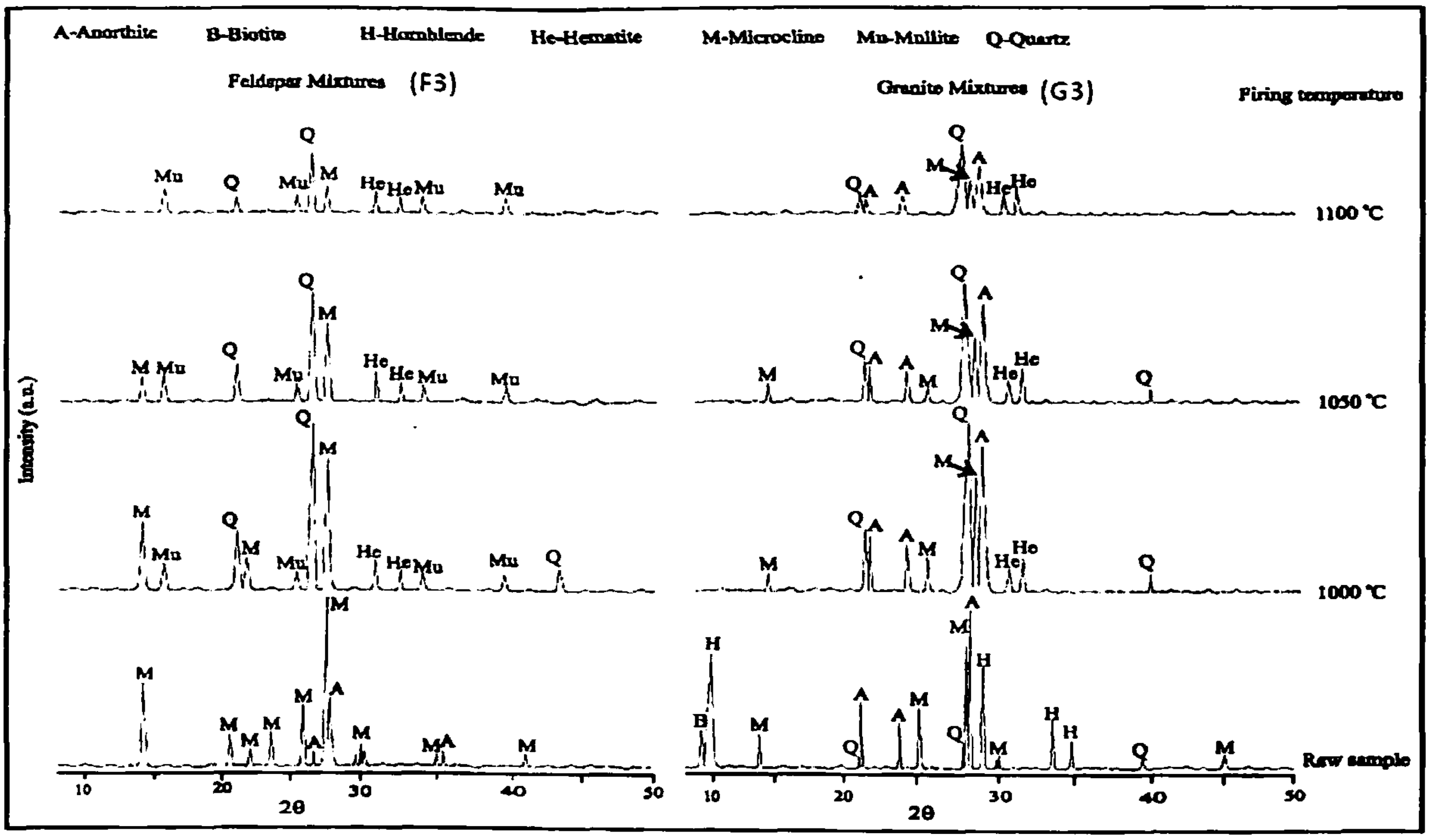

Fig. 2 X-ray diffraction patterns of raw feldspar and granite and fired samples of formulations F3 and G3 at different firing temperatures.

Optical microscopic studies and XRD data revealed that the major rock forming minerals of granite samples are microcline ($KAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$), hornblende ($Ca(Mg,Fe)_4Al(Si_7Al)O_{22}(OH,F)_2$), quartz ($SiO_2$), and biotite ($K(Mg, Fe)_3AlSi_3O_{10}(F, OH)_2$) (see Figure 2). The major crystalline phase in the selected feldspar is microcline. Anorthite is present as a minor constituent of feldspar grains. Kaolinite and illite are the mineral phases found in the red clay sample (see Figure 3). The feldspathic minerals such as microcline and anorthite as well as biotite mica are typical fluxing materials which favor the formation of glassy phase above 900 °C (Barth, 1969). In addition, hornblende can be considered as a potential fluxing material at high temperatures since it contains Mg and Ca ions which favor the formation of a glass phase.

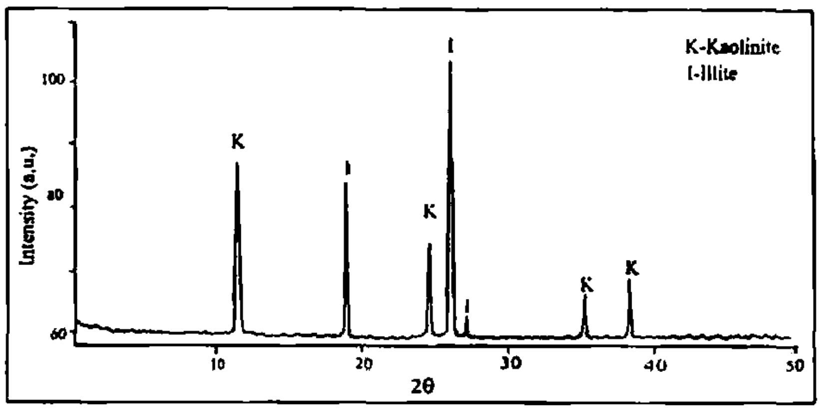

Fig. 3 X-ray diffraction patterns of red.

The chemical compositions of the used raw materials are given in Table 2. The results indicate that in each raw material, SiO_2 is the predominant oxide, followed by Al_2O_3. The total content of main fluxing oxides (Na_2O and K_2O) of clay-silt fraction, feldspar and granite are 4.37, 16.44, and 9.98 wt. % respectively. The total content of auxiliary fluxing oxides ($CaO+MgO+Fe_2O_3$) of above raw materials is 8.62, 0.45 and 3.18 wt. % respectively. Even though granite contains lower amounts of main fluxing oxides than feldspar, it has a higher amount of auxiliary fluxing oxides than feldspar. Therefore, it can be suggested that the fluxing ability between feldspar and granite may not be much different.

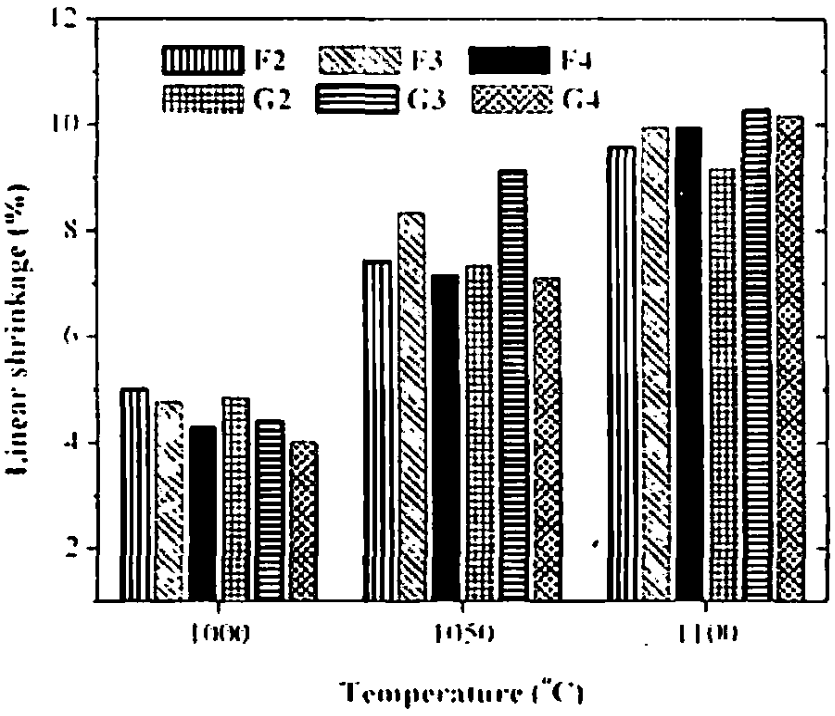

Fig. 4 Linear shrinkage of samples fired at different temperatures.

TECHNOLOGICAL PROPERTIES

Figure 4 and Figure 5 show the variation of linear shrinkage and bulk density against temperature for ceramic products having varying proportions of feldspar and granite. It was revealed that linear shrinkage and bulk density of all ceramic bodies increased with increasing firing temperature. In addition, the results also showed that increasing of fluxing materials (feldspar or granite) decreased both linear shrinkage and bulk density at 1000 °C. Formulation of granite containing samples shows the highest linear shrinkage and bulk density both at 1050 and 1100 °C. Even though formulations F4 and G4 show lowest linear shrinkage and bulk density at 1050 °C, F2 and G2 show the lowest values at 1100 °C. The results measured in formulations F1 and G1 were subjected to the blotting at all temperatures and were neglected in analyzing data reported hereafter.

Table 2 Chemical composition and loss on ignition of raw materials (n- number of samples analyzed)

Constituents (wt.%)	Clay-silt (n=4)	Feldspar (n=3)	Granite (n=3)	Quartz (n=2)
SiO_2	52.98	64.15	71.8	99.20
Al_2O_3	22.01	18.74	13.68	0.32
FeO (total)	6.84	0.06	1.94	0.01
Na_2O	2.36	2.80	3.17	0.05
K_2O	2.01	13.64	6.73	0.02
CaO	1.22	0.35	0.89	0.04
MgO	0.56	0.04	0.35	0.17
TiO_2	0.91	--	0.21	0.02
LOI	11.11	0.02	0.82	0.08

The observed results could be explained by considering vitrification of a ceramic product. Vitrification is a phenomenon associated with the formation of a liquid phase, which tends to promote the densification of the product by rearranging the particles, through the action of surface tension and capillary forces (Reed, 1976). The amount and viscosity of the liquid phase control the extent of vitrification of the final product. The high amount of a glass phase with lower viscosity has a pronounced effect on the vitrification of the product. Even though feldspar commences to form liquid glass phase above 900 °C, further increase in temperature is needed for the formation of higher amount of glass phase with lower viscosity (Schairer and Bowen, 1947). Therefore, feldspar forms a small amount of liquid phase with high viscosity at 1000 °C. However, clay mineral, illite, can form the glass phase around 950 °C (Kingery et al., 1995; Riley, 1951). Therefore, samples with higher fraction of clay-silt form high amount of glass phase at 1000 °C. As a result, the samples containing a higher fraction of feldspar or granite show a low vitrification at 1000 °C. It also suggests that the fluxing effect of both feldspar and granite is not significant at 1000 °C. However, fluxing raw materials are playing a major role on the formation of glass phase with increasing temperature. Consequently, the bulk density of the samples increases when the body composition contains more fluxing material. The formation of high amount of the liquid glass phase with lower viscosity at high temperature resulted in an increase of bulk density and linear shrinkage of each formulation with increasing firing temperature (see Figure 4 and Figure 5).

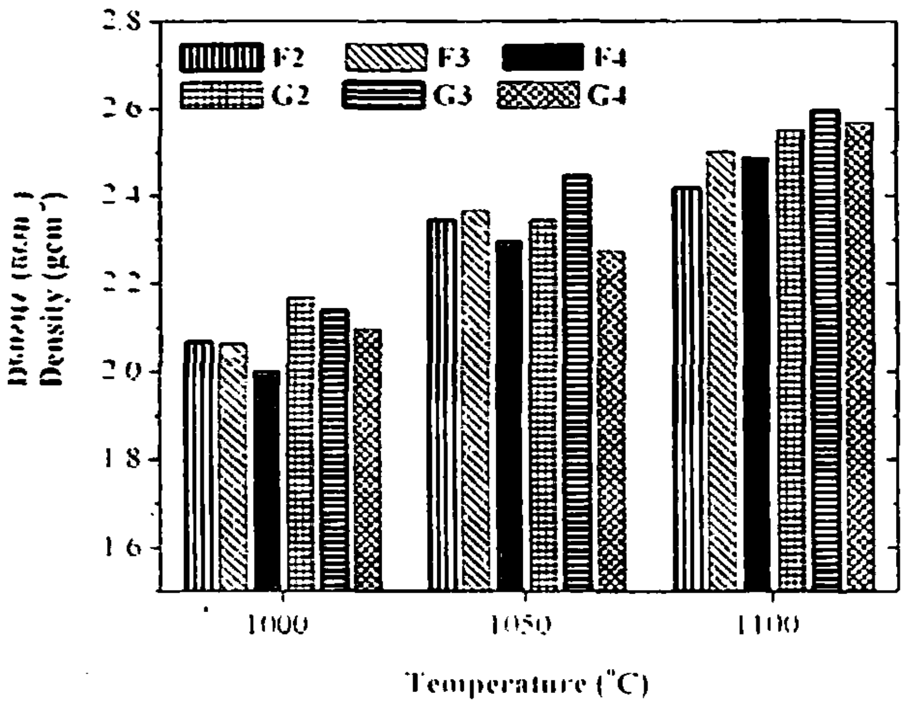

Fig. 5 Bulk density of samples fired at different temperatures.

On the other hand, it is reported that high amount of clay fraction rich in illite leads to formation of glass which does not entrap air in the body (Riley, 1951). The incorporation of the high amount of clay-silt fraction (80 wt.%) in formulations of F1 and G1 resulted in blotting the samples.

Figure 6 shows the variation of water absorption against firing temperature in the studied samples having varying proportions of feldspar and granite. The water absorption permits evaluation of the open porosity of the final product and gives an indication of the vitrification extent of the final product. It can be clearly seen that the results of water absorption are closely in agreement with the observed variations in bulk density and linear shrinkage. Water absorption of studied samples of different composition decreases with increasing firing temperature (see Figure 6). This is due to the formation of a high amount of glass phase with lower viscosity which decreases the porosity and increases density of the ceramic body. Further, the water absorption of the samples fired at 1000 °C increases with increasing content of fluxing materials (for both granite and feldspar), supporting the results observed in the bulk density. Samples containing granite show slightly higher water absorption than the samples containing feldspar after firing at 1000 °C. However, samples containing granite show lower water absorption than feldspar mixtures after firing at 1050 °C. This indicates that granite facilitated vitrification of the ceramic body more than feldspar at 1050 °C. It could be noticed that, except formulation F2 and G2, all ceramic bodies show very low water absorption (< 1 %) after firing at 1100 °C. These results reveal that, except the F2 and G2, all bodies have achieved a high vitrification at this temperature. This indicates that the content of the fluxing material

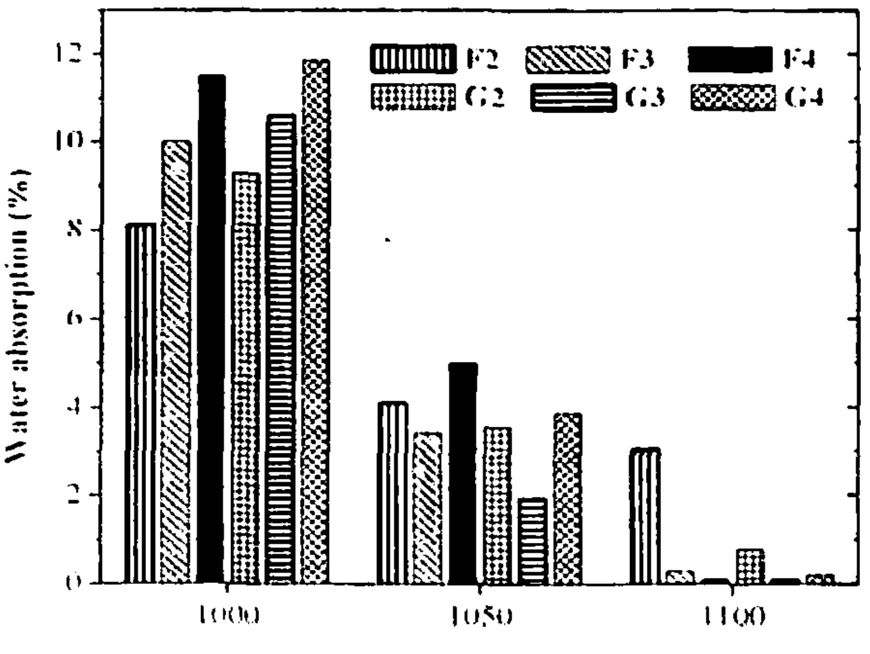

Fig. 6 Water absorption of samples fired at different temperatures.

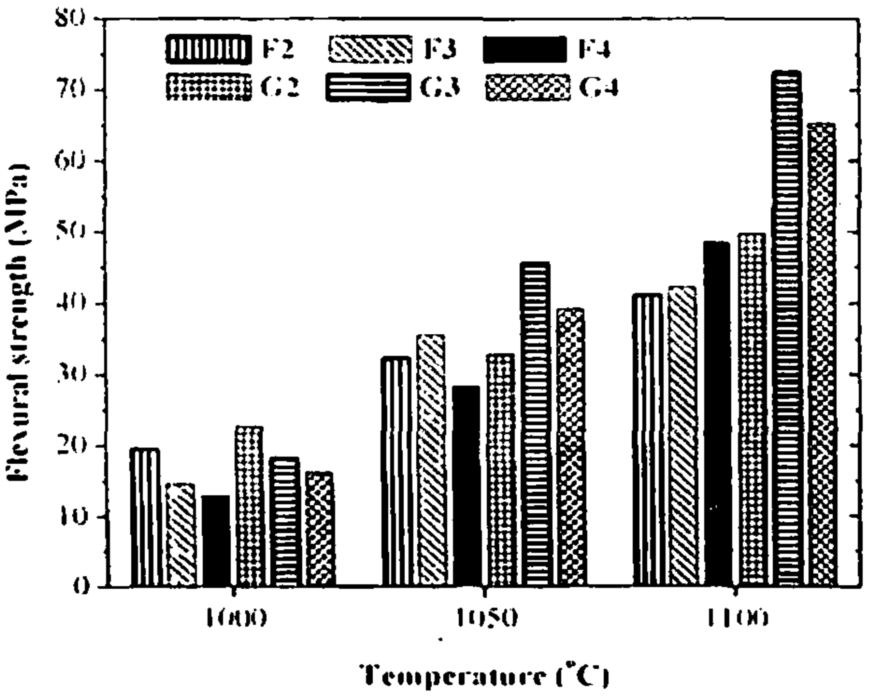

Fig. 7 Flexural strength of samples fired at different temperatures.

(feldspar and granite) has more effect on vitrification at this temperature than that caused by the clay-silt fraction (refer table 1 to see the difference of the body mixtures).

Figure 7 shows the variation of flexural strength against firing temperature in the fired bodies having varying proportions of feldspar and granite. The measured values show that flexural strength of each sample varies according to observed results on the linear shrinkage, bulk density and water absorption. It was observed that the flexural strength of all samples increases gradually with increasing temperature. In addition, the strength of the samples containing granite showed higher strength than the samples containing feldspar, at all temperatures. Furthermore, the samples of formulations G3 and G4 (see Table1) showed significantly higher strength after firing at 1100 °C when compared with the same formulation prepared using feldspar. The mechanical strength of this type of ceramic material depends on the effect of stress concentration on structural defects such as voids, pores and micro cracks. The larger defects result in lowering the strength of the material (Schneider, 2000). When the firing temperature increases, the liquid phase sintering becomes dominant due to the formation of a higher amount of glass phase in the body. As a result, large grains form, reducing pore spaces in the body. This results in increasing the flexural strength of the samples with increasing firing temperature. Further, granite contains a high percentage of alkaline earth oxides (CaO and MgO) (see Table 2) which can form high viscous liquid phases (Volf, 1990). However, feldspar contains high percentage of alkaline oxides (Na_2O and K_2O) which can form low viscous liquid phases (Wilson, 1995). The high viscous liquid phase has enabled to embed the new forming crystals and remaining residual crystals, enhancing the densification process. On the other hand, CaO and MgO can form glass phases with higher strength than the glass phases rich (Volf, 1990) in K_2O and Na_2O. Therefore, granite containing samples show a higher strength than feldspar containing samples.

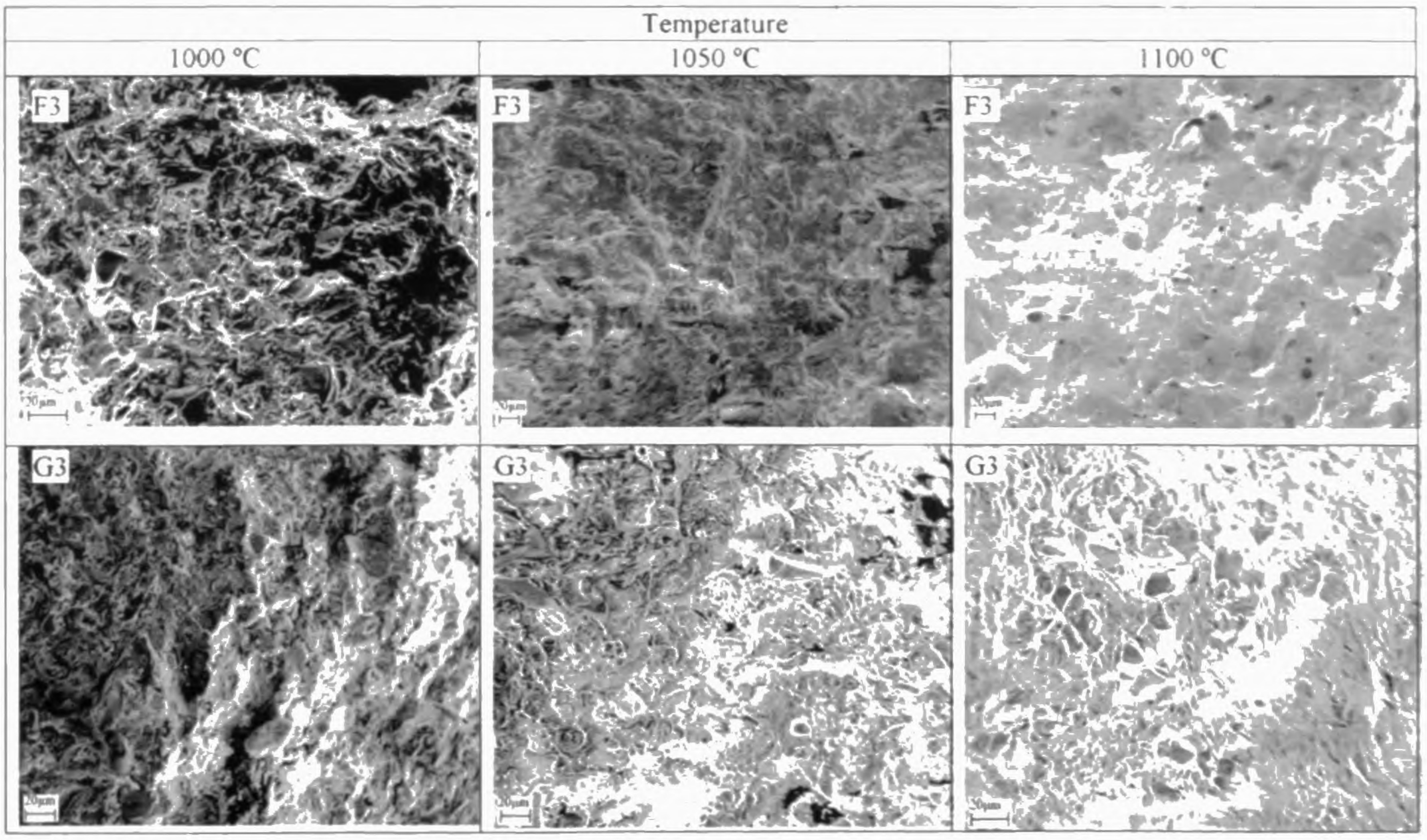

Fig. 8 SEM micrographs of fracture surface of selected samples (F3 and G3) fired at 1000, 1050 and 1100 °C.

Figure 2 shows the mineral phases identified in formulations F3 and G3 after firing at 1000, 1050 and 1100 °C. It was observed that crystalline phases of red clays such as illite and kaolinite disappeared, and mullite and hematite appeared as new crystalline phases in feldspar containing samples after the firing. Other than clay minerals, peaks of hornblende and biotite disappeared in samples of granites. However, mullite crystal phase was not identified in these samples. In addition, the peak intensities of microcline, anorthite and quartz were diminished in fired samples of both feldspar and granite with increasing the firing temperature. This may be due to the phase transformation of feldspar and quartz into glass phase with increasing temperature.

Fig. 8 shows SEM images of fracture surfaces of samples of formulations F3 and G3 after firing at 1000, 1050 and 1100 °C. The images clearly show that the porosity of the products of these formulas decreased with increasing firing temperature. Both samples fired at 1000 °C show number of interconnected pores. These interconnected pores have resulted in higher water absorption; lower bulk density and flexural strength (see Figures 4, 5 and 6). In addition, even though there is not much difference in microstructure between F3 and G3 fired at 1050 °C, there are a number of closed spherical pores in F3 sample fired at 1100 °C. The spherical pores are usually formed in matrices rich in a vitreous phase with lower viscosity (Maity and Sarakar, 1996). In contrast, the fracture surface of G3 fired at 1100 °C shows highly compacted body without closed pore spaces and it might also have resulted due to the high flexural strength and bulk density of granite containing samples fired at 1100 °C.

CONCLUSIONS

Microcline, biotite, anorthite and hornblende of granite can be used satisfactorily as fluxing mineral-materials for the body composition of red clay products. A product having higher flexural strength (72.48 MPa) and bulk density (2.59 g/cm^3) and less water absorption (<0.11 %) can be fabricated using granite powder. The body composition of the best product is 60 wt. % of clay-silt, 10 wt. % of quartz and 30 wt. % of granite. However, the best product from feldspar has lower flexural strength (48.63 MPa) and bulk density (2.45 g/cm^3). Therefore, feldspar can easily be replaced by cheaper granites for manufacturing red clay products.

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