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Journal of the European Ceramic Society 24 (2004) 3169–3175

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Effect of substitution of fly ash for quartz in triaxial kaolin–quartz–feldspar system

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Received 10 June 2003; received in revised form 25 September 2003; accepted 11 October 2003

Abstract

Quartz was progressively replaced by 5, 10 and 15 wt.% fly ash (a byproduct of Indian thermal power plant) in a traditional triaxial porcelain composition consisting of kaolinitic clay, quartz and feldspar. The effects of this substitution upon firing at different temperatures (1150–1300 °C) were investigated by measuring the linear shrinkage, bulk density, porosity and flexural strength. Quantitative estimation of mullite and residual quartz content was done by XRD and microstructures of some selected samples were studied using SEM. The results show that fly ash containing samples achieved higher densities (max. 2.46 g cm^{-3}) in the entire temperature range (1150–1300 °C) of firing and matured early than a traditional porcelain composition. The maximum flexural strength (70.5 MPa) was obtained at 1300 °C in the 15 wt.% fly ash containing sample compared with (61.1 MPa) obtained in the traditional porcelain sample. XRD studies reveal higher mullitization in fly ash containing samples. SEM photomicrographs of the polished and etched specimens of 1300 °C heated samples show the presence of quartz grains and secondary mullite needles embedded in feldspathic glassy matrix. Quartz grains (25–50 µm) are associated with circumferential cracks around them.

Keywords: Fly ash; Microsctructure-final; Mullite; Porcelain; Waste materials

1. Introduction

Triaxial porcelain is one of the most widely studied ceramic systems. Composed primarily of clay–quartz–feldspar, it has got diverse applications like whiteware, stoneware, insulators, etc. Extensive research on porcelain for a long time [1–3] confirmed its complexities, so there remain significant challenges in understanding porcelain in relation to raw materials, processing science, phase and microstructural evolution. In a porcelain composition, clay provides plasticity and green strength during forming stage, and contributes to mullite formation after firing. Quartz acts as filler material whose coarse grains provide resistance to cracking during drying and form skeletal network during firing to reduce pyroplastic deformation. Fluxing action of feldspar above 1000 °C leads to densification in the presence of a reactive liquid phase that partly dissolves quartz and clay which leads to formation of interlocked acicular mullite crystals embedded in feldspathic glass.[4,5] Alternative fluxes (like nepheline syenite), filler materials (like alumina) and other mineralising agents[6,7] have been incorporated in traditional porcelain composition to study their effect on microstructural development, mechanical and other related properties.

Increased generation of electricity through thermal route involving combustion of pulverized coal leads to huge production of fly ash and is in fact a matter for great concern. Research activities around the world are aiming at gainful utilization and disposal of fly ash. Use of fly ash in the production of building bricks and pozzolanic cements are already in practice. High value added products like wear resistant ceramic liner, glass ceramics, synthetic mullite, cenosphere, fly ash–Al matrix composite, wool can be made from fly ash.[8–11] Uses of fly ash in ceramic tile composition have also been tried by many authors.[12–14] But, these studies considered mainly partial substitution of clay by fly ash in the porcelain bodies. Kumar et al.[14] incorporated fly ash up to 25–30 wt.% in place of clay in porcelainized stoneware composition to get a product that conforms to EN specification for tile. They noticed increase in

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doi:10.1016/j.jeurceramsoc.2003.10.008

strength up to 25–30 wt.% fly ash addition, beyond which the strength decreased. In another work,[15] clay and feldspar were partly replaced by fly ash to produce wall tile. However, effect of substitution of fly ash for quartz is not widely reported in the published literature. Since fly ash is a combustion product containing quartz and mullite phases, it has very low shrinkage, which is an essential criterion for a filler material in porcelain composition. Research findings of the present authors[16] have shown some beneficial effect of fly ash incorporation in porcelain composition in place of quartz. In this investigation, fly ash was incorporated progressively into a parent porcelain composition and its effects on the physico-chemical properties were studied. Quantitative estimation of quartz and mullite was done to indicate the influence of fly ash on porcelain composition by replacing quartz. Microstructural features of some selected samples were also examined through SEM of the polished and etched surface of the vitrified specimens.

2. Experimental

For chemical analysis of the raw materials, gravimetric method was utilized to determine SiO_2 and Al_2O_3 whereas Fe_2O_3, CaO and MgO were estimated volumetrically.[17] Alkalies were determined by flame photometry.

Five kilograms of each batch (P, PF5, PF10 and PF15) were prepared according to batch composition presented in Table 1. All the batches were mixed separately and wet ground in a pot mill for a duration of 14 h to get the desired fineness (residue less than 1.5% on 200 mesh BS sieve). The slurry obtained was screened, dried at 110 °C, powdered to break the agglomerate and granulated to small particles for better compaction using 6–7% moisture. Samples of 60×14×5 mm were hydraulically compacted using uniaxial pressing at 300–350 kg cm^{-2}. The shaped samples were dried at 110–120 °C for 24 h till the moisture content reduced to less than 0.5%. The apparent porosity of the green samples was measured by liquid displacement method using xylene as immersion medium. The dried samples were fired at different temperatures (1150–1300 °C) for a soaking period of 120 min in an electrically operated laboratory furnace using on/off control system. A constant heating rate of 8 °C/min was maintained in each firing. Finally, the fired samples were subjected to physical tests such as linear shrinkage, apparent porosity and bulk density. Bulk density (B.D.) and percent apparent porosity (A.P.) of the fired samples were measured using the conventional liquid displacement method according to Archimedes principle. Flexural strength (three point bending) of the fired samples was determined by universal testing machine (INSTRON 5500R). For X-ray diffraction experiment, Philips 'X-Pert Pro' diffraction unit, attached with secondary monochromator, automatic divergence slit and nickel filter, was used to get monochromatic Cu-$K\alpha$ radiation. The instrument was run at step scan mode with step size (0.02) and 8 s time per step, within 2θ angle 5–75°. The collected data was refined using Profit software. X-Pert plus and Quasor software based on Rietveld were used to calculate the percentage of mullite and quartz, where standard quartz and mullite were used as reference material. For reliability of data, each sample was scanned several times. The fitted curve matched well with the raw data and 'goodness of fit' varied from 2.5–4 among different samples. Microstructural features of polished and etched (5% HF, 3 min) surface were examined through SEM (LEO 430i).

Table 1
Batch compositions (wt.%)

Batches	Kaolinitic clay	Feldspar	Quartz	Fly ash
P	45	30	25	0
PF5	45	30	20	5
PF10	45	30	15	10
PF15	45	30	10	15

3. Results and discussion

The results of the chemical analysis of the raw materials are given in Table 2.

The chemical analysis results indicate that quartz used in this study is relatively pure. In addition to SiO_2 and Al_2O_3, fly ash contains some other oxides such as TiO_2, Fe_2O_3, CaO, etc. Kaolinitic clay and potash feldspar are of normal type generally used in porcelain body. As fly ash is a burnt material, the phases present in fly ash were detected by XRD; this latter confirms the presence of 18% mullite and 23.8% quartz (Fig. 1).

Table 2
Chemical analysis of the raw materials

Major chemical constituents (wt.%)	Kaolinitic clay	Feldspar	Quartz	Fly Ash
SiO_2	45.41	66.48	98.66	59.26
Al_2O_3	34.39	17.29	0.39	27.97
Fe_2O_3	1.13	0.14	0.07	4.00
TiO_2	0.89	0.02	0.01	2.92
CaO	1.07	0.31	0.10	2.63
MgO	0.76	0.03	0.02	0.56
Na_2O	0.87	2.94	0.09	0.54
K_2O	0.42	11.95	0.12	0.60
L.O.I.	14.67	0.71	0.37	1.12

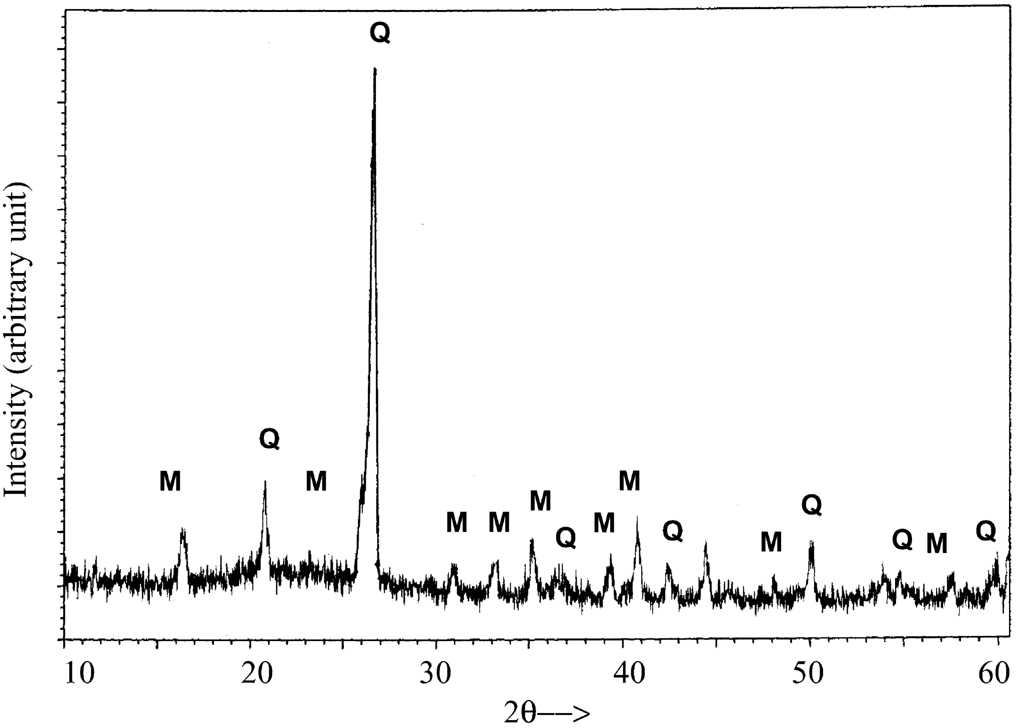


Fig. 1. XRD pattern of fly ash (Q = Quartz, M = Mullite).

The oxide compositions of all the batches were calculated on calcined basis and the results are given in Table 3. From Table 3 it may be noted that, with progressive addition of fly ash by replacing quartz, alumina content of the batches increases, followed by decrease in silica content. The percentage of other mineralizing oxides, such as TiO_2, Fe_2O_3, CaO and MgO, are also in higher side in fly ash containing batches, although there is no significant changes in alkali content.

The variation in percent linear change (%L.S.) with heating temperature is represented in Fig. 2. From the figure it may be observed that the normal porcelain composition (batch P) showed steady increase in linear shrinkage up to 1250 °C, beyond which the curve almost flattened. Similar trend was observed for the fly ash containing compositions (PF5, PF10 and PF15) too. Incorporation of fly ash in place of quartz increases the linear shrinkage values in the entire firing range (1150–1300 °C). This may be attributed to the presence of fluxing alkaline earth and other oxides in fly ash, which enter the glassy phase, decreasing its viscosity and resulting higher shrinkage in these samples. The authors[16] observed that replacement quartz for fly ash didn't bring about any significant change in the initial porosity. The average green porosity of all the batches was found to be 34.34% with a standard deviation of 0.68.

The variation in bulk density (B.D.) with heating temperature is given in Fig. 3. All the compositions showed increasing trend in their bulk density with temperature and this is due to increased consolidation with temperature. The bulk density increases with fly ash content and reached maximum (2.46 g cm^{-3}) in 'PF15' at 1300 °C. Fly ash bearing batches showed higher B.D. in the entire temperature of firing due to higher amount of Al_2O_3 present in these compositions and also the presence of low silica glass (less viscous) helps in better liquid phase sintering.

Table 3
Oxide compositions of the experimental bodies

Oxide constituents (wt.%)	Batches			
	P	PF5	PF10	PF15
SiO_2	73.63	71.44	69.25	67.05
Al_2O_3	18.41	19.98	21.55	23.13
Fe_2O_3	0.64	0.87	1.09	1.31
TiO_2	0.46	0.63	0.79	0.96
CaO	0.68	0.82	0.97	1.11
MgO	0.40	0.43	0.46	0.50
Na_2O	1.47	1.49	1.52	1.55
K_2O	4.31	4.34	4.37	4.40

The variation in apparent porosity (A.P.) with heating temperature is shown in Fig. 4. The figure reveals that all the samples achieved around 1% apparent porosity at 1300 °C and this indicates almost complete densification at this temperature. Fly ash containing bodies (PF5, PF10 and PF15) mature early than normal

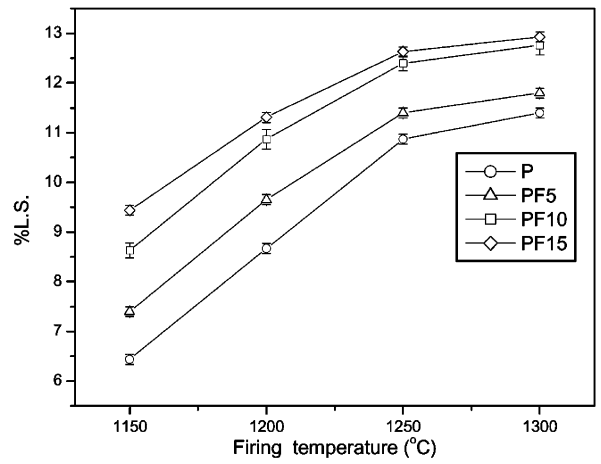


Fig. 2. Variation in percent linear change with heating temperature.

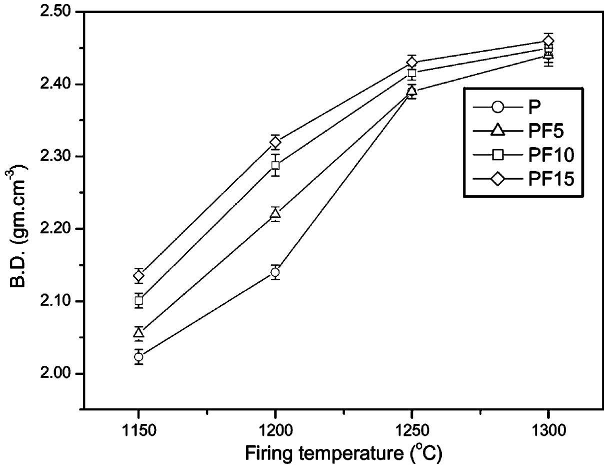


Fig. 3. Variation in bulk density with heating temperature.

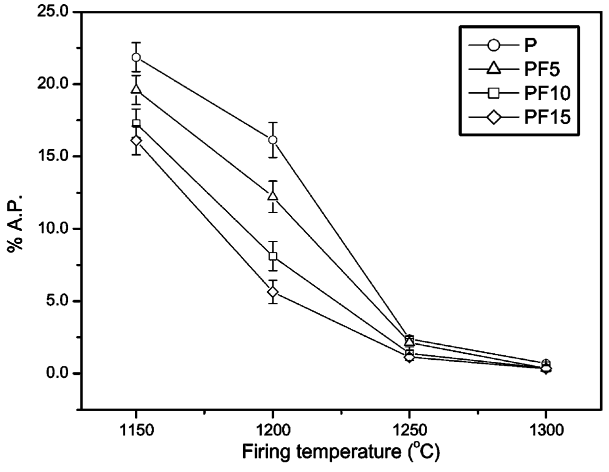


Fig. 4. Variation in apparent porosity with heating temperature.

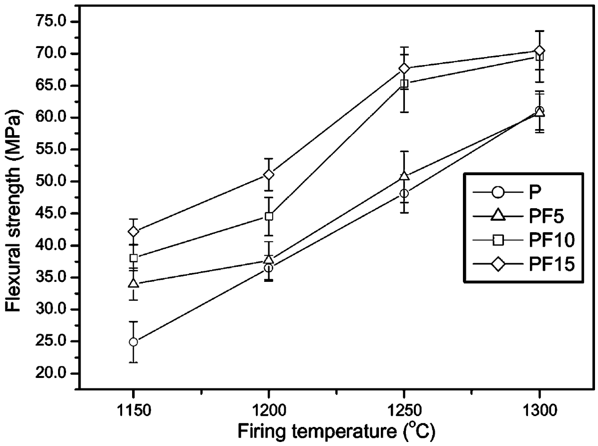


Fig. 5. Variation in flexural strength with heating temperature.

porcelain body (P) and the apparent porosity of the body containing 15% fly ash (PF15) was found to be lowest at all the temperatures. This may be due to formation of low silica glass, with other oxides present in fly ash, which has lower viscosity and flows easily to fill up open pores.

The changes in flexural strength with heating temperature are shown in Fig. 5. In general, an increasing trend in the strength is observed. The limited increase of strength in the 1250–1300 °C range corresponds well to the limited changes in porosity and density. The normal porcelain body, without fly ash (P), shows linear increase in strength with firing temperature and reaches the maximum value (61.1 MPa) at 1300 °C as expected. Body PF5 (containing only 5% fly ash in place of quartz) follows a similar trend and gives almost the same value at 1300 °C of the reference batch. The strength of body PF10 and PF15 shows a steady increase in strength with firing temperature and, although reaches maximum value at 1300 °C, its increase after 1250 °C is insignificant. This may be attributed to the formation of larger amount of low silica glass, in presence of fluxing components (Fe_2O_3, CaO, K_2O and Na_2O), more abundant in bodies PF10 and PF15 compared with PF5 and P ones. Again, the more heterogeneous matrix of larger liquid phase containing PF10 and PF15 batches arrested the faster increasing trend of bending strength. This phenomenon was also observed by O. Isik Ece.[18] Overall, the strength of fly ash containing samples is found to be higher at all the temperatures of heating due to a more abundant mullite formation, which is discussed in the later section with X-ray diffraction results.

It is evident from Fig. 6 that a gradual addition of fly ash by replacing quartz increases the mullite content at all temperatures but 1300 °C (sample PF10). The maximum mullite content is formed in the 15% fly ash containing body (PF15) and less mullitization occurred in the silica rich normal porcelain body (P). This observation of less mullitization in silica rich porcelain body was also made by Schuller.[4] Mullite present in the fly ash (Fig. 1) contributed towards this increase in mullite content. Further, such fly ash containing bodies with less quartz content became richer in both alumina and alkalies resulting in a more abundant mullite formation. Mullitization occurred in presence of foreign ions (e.g. Fe^{+3}, Ti^{+4}) which help to form mullite from the glass by replacing Al^{+3} in its structure. This observation was also made by Chaudhuri[6,7] by adding foreign ions externally in a porcelain composition. The effect of temperature on the mullite formation is not very significant in the lower range of heating temperature, but an increasing trend is observed at higher temperatures for all the compositions and it is more pronounced in the normal porcelain composition (P).

Fig. 7 illustrates the variation in residual quartz content with temperature of heating. It may be observed that residual quartz content decreases with fly ash addition. This observation is obvious as fly ash replaces quartz in PF5, PF10 and PF15 batches. Further it may be seen that residual quartz content decreases with heating temperature due to quartz dissolution.

The scanning electron photomicrographs of polished and etched specimens of all the compositions heated at 1300 °C are shown in Fig. 8 (a)–(h). The microstructure of all the experimental porcelain bodies in general consists of α-quartz and mullite in a glassy matrix. Formation and growth of clusters of needle shaped crystals are observed in pockets of each sample (Fig. 8(e)–(h)) and these crystals are attributed to secondary mullite, which is formed with the assistance of the melt by dissolution and reprecipitation of primary mullite at higher temperature. The PF5 and PF10 samples [Fig. 8(f) and (g)] show few elongated mullite[5] crystals too. Although two types of mullite (primary and secondary) are generally seen in the porcelain microstructure, scaly type 'primary mullite', which is formed directly from clay, is not distinctly observed in any of these photomicrographs. This is due to the transformation of primary mullite to secondary mullite at 1300 °C. The better interlocking and uniform distributions of comparatively smaller sized mullite needles in the glassy matrix are seen in all the cases and this probably explain the higher strength at 1300 °C. The stress generation and associated cracking around quartz grain [Fig. 8(a)–(d)] is observed in all the specimens due to rapid displacive phase transformation of quartz during cooling. The cracks are circumferential in nature as observed by other workers[19] in the feldspathic glassy matrix of the quartz based porcelain body. Since the quartz grains, as observed in these photomicrographs, lie between 25 and 50μm, the experimental bodies are less severe towards peripheral fracture and may exhibit rare matrix failure.

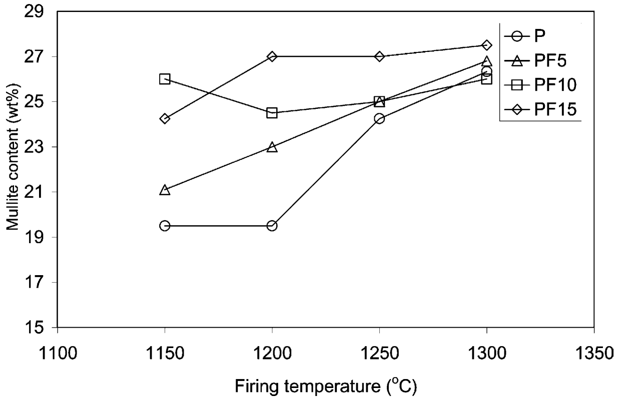


Fig. 6. Variation in mullite content with heating temperature.

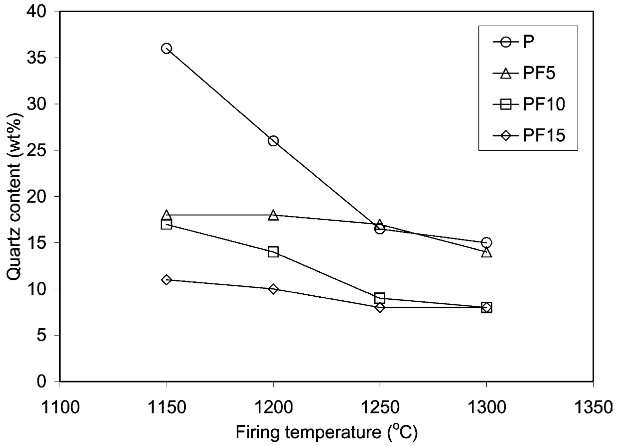
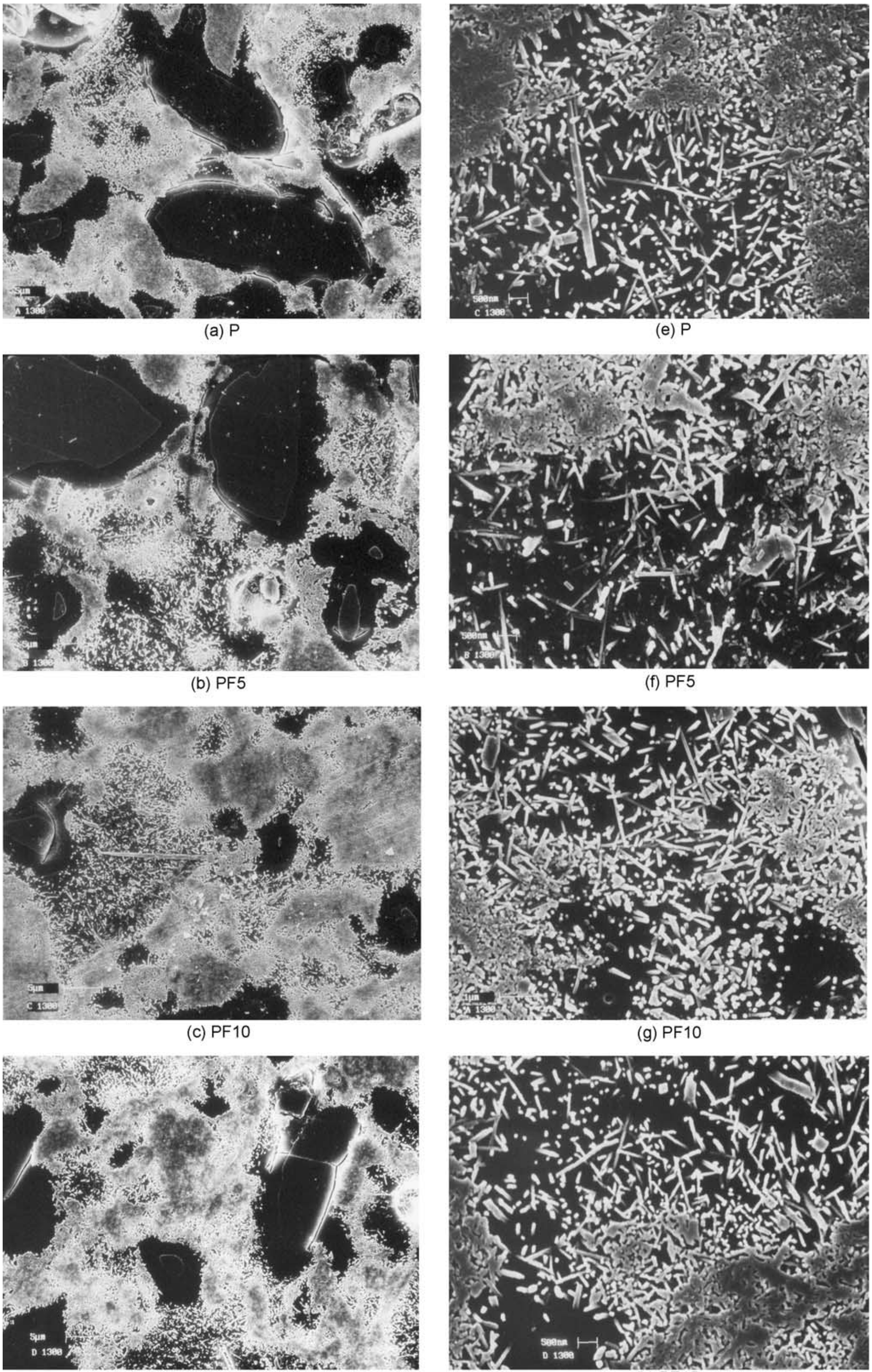


Fig. 7. Variation in quartz content with heating temperature.

4. Conclusions

From the present investigations, the following conclusions are drawn:

1. Substitution of quartz by fly ash in a normal porcelain body increases the linear shrinkage, bulk density and decreases the apparent porosity in the entire temperature range of heating (1150–1300 °C). This may be due to the formation of low viscosity glass which flows easily and helps in better liquid phase sintering.
2. The mullite content increases with the addition of fly ash in place of quartz and thereby improves the flexural strength significantly. Expectedly, residual quartz content decreases with fly ash addition.
3. Scanning electron micrographs taken on the 1300 °C heated samples reveal the presence of α-quartz and secondary mullite embedded in the glassy matrix in general. Better interlocking and uniform distribution of comparatively smaller sized mullite needles in the glassy matrix explain the high strength achieved. The stress generation due to phase transformation of quartz and associated cracking around quartz grains are also seen in the SEM pictures.



(a) P (e) P

(b) PF5 (f) PF5

(c) PF10 (g) PF10

(d) PF15 (h) PF15

Fig. 8. SEM photomicrographs of polished and etched specimens of different composition fired at 1300 °C. (a–d) Show overall microstructure and (e–h) show growth of mullite in glassy matrix.

Acknowledgements

The authors would like to thank Dr. H.S. Maiti, Director, Central Glass and Ceramic Research Institute, Kolkata, India for his kind permission to publish this research work, Professor N.K. Mitra, Calcutta University, India for his valuable suggestions and encouragement during the course of this work. The authors express their thanks to Dr. (Mrs) D. Kundu, Dr. (Mrs) S. Sen and Mr. Asoke Mandal, CGCRI, Kolkata India for conducting chemical analysis and SEM studies. The authors also acknowledge the sponsorship of this research work by H&R Johnson (India) Ltd.

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