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Effect of fly ash on the physico-chemical and mechanical properties of a porcelain composition

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Abstract

The ceramic industry is one of the largest consumers of natural raw materials but has also the capacity and potential to make significant contributions in solving environmental problems by consuming solid rejects of various industries.

In a traditional triaxial porcelain composition quartz was fully substituted by fly ash. The effect of this substitution and subsequently firing the specimens at different temperatures (1100–1300 °C) were investigated by measuring related properties. Optimum properties were obtained with the specimen having 30% fly ash. Requirement of feldspar was found to be reduced to 20%. The flexural strength of the porcelain body reached a maximum value of 72.3 MPa at 1300 °C while the apparent porosity value reached almost zero. There was around 20% increase in flexural strength in comparison to that of the conventional triaxial body. Higher proportion of feldspar above 20% resulted in narrowing the vitrification range. Mullite content was found to increase with increasing proportion of fly ash. SEM studies revealed the presence of α-quartz and secondary mullite needles embedded in a glassy matrix. Extensive cracking around the quartz grains was also observed. Intense interlocking of fine mullite needles was found to be responsible for development of higher flexural strength in fly ash incorporated porcelain body.

A composition has been proposed where fly ash as high as 30% can be accommodated. Thus, an alternative use of an otherwise waste material is proposed, which can be converted into economic benefit and at the same time offering a possible solution to problems so far as environmental and waste disposal are concerned.

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Keywords: D. Porcelain; Quartz; Fly ash; Mullite needles

1. Introduction

A wide range of conventional ceramic compositions, the basis for whiteware industries, is essentially a mixture of kaolinite clay, quartz and feldspar. Extensive research on porcelain for a long time [1–3] confirmed its complexities and there remain significant challenges in understanding porcelain in relation to raw materials, processing parameters, phases and microstructure evolution. In a porcelain composition, clay makes the forming process easier and provides green strength as well as rigidity to the fired product. Feldspar as a flux helps the densification process. Quartz acts as an inexpensive filler material which remains non-reactive during firing at low temperature and forms a liquid of high viscosity at higher temperature.

During firing of the porcelain compositions, only a small portion of quartz gets dissolved in the melt while the rest remains unreacted. The free quartz undergoes phase transformations which leads to development of stresses and adversely affects the mechanical strength. In view of increasing demand for porcelain with improved mechanical properties, various attempts were made to substitute quartz with non-conventional materials such as alumina [4,5], zircon [6], alumino-silicates [7–10] or cordierite [11].

Growth of industry is placing an enormous pressure on the environment through the volume of natural raw materials consumed, the amount of waste produced and the amount of energy used. Recycling can help solving important issues related to storage of wastes and simultaneously the preservation of natural raw materials which is fast depleting. To take advantage of this opportunity, wastes must be regarded as possible raw materials and should be carefully characterized in order to predict their behaviour during processing and their effects on the final products. The ceramic industry is one of the

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largest consumers of natural raw materials but has also the capacity and potential to make significant contributions in solving problems associated with wastes [12,13]. The use of industrial wastes as alternative raw materials can be considered viable only if the manufacturing process remains essentially unchanged and the quality and characteristics of the product are not unduly affected.

The meaningful utilization of industrial waste materials has been acclaimed world over not only as an economic opportunity [14], but also as a step towards solving problems of environmental pollution. Research activities around the world are aiming at gainful utilization of fly ash and India is not an exception. Fly ash has been considered as low cost resource material for alumino-silicate and many authors [15–18] have tried to use fly ash as a partial substitution of clay in the development of ceramic tiles. In another work by Dana et al. [19], early maturity and higher densities in the temperature range 1150–1300 °C was reported when quartz was progressively replaced by fly ash. Utilization of up to 30% fly ash as a replacement of sand stone and feldspar in the development of wall tiles was also claimed by other authors [20].

In the present investigation, quartz was fully substituted by fly ash in a porcelain composition and feldspar was incorporated stepwise so as to obtain a composition with optimum feldspar content and maximum utilization of fly ash. The reason for this selection is twofold. First, fly ash being a combustion product has very negligible shrinkage, which is an essential criterion for a filler material in porcelain composition. Secondly, as fly ash contains fluxing components, an attempt has been made to utilize this as a partial replacement of feldspar in the composition. The aim of this work is to develop vitrified porcelain ware with effective utilization of fly ash, and to study its mechanical properties with temperature and compositional variations. Thus, an alternative use of an otherwise industrial waste material is proposed, which can be translated into economic benefits and an important and welcome relief on environment.

2. Experimental

2.1. Sample preparation

China clay, plastic clay, feldspar and fly ash were used for the present study. Fly ash, as received, was thoroughly washed with water and sieved through 75 μm BS sieve, passed through magnetic channel and dried for use in batch trials. The operation rendered a material with more or less consistent quality.

Five different body mixes (compositions F1–F5) were used (Table 1). In the compositions fly ash:feldspar ratio progressively varied by gradual incorporation of feldspar as a partial replacement of fly ash, keeping the clay component content constant at 50%. All the batches were mixed separately and wet ground in a pot mill for 24 h to get the desired fineness (residue less than 1% on 200 mesh BS sieve). The slurry obtained was sieved and made into casting slip after adjusting the rheological properties of the slip to the desired level. Slip was adjusted with requisite doses of electrolyte (sodium carbonate and sodium silicate) and the rheological properties were controlled with pint weight (weight of 500 ml of slip in grams), fluidity and thixotropy. Fluidity and thixotropy were measured with Gallenkamp Universal Torsion Viscometer using a bob of 11/16 in. dia. and 32 SWG wire. Specimens were made by slip casting method in plaster of paris moulds. Rectangular bars of 150 mm × 15 mm × 8 mm were cast. The specimens after drying and finishing were fired between 1100 °C and 1300 °C at a temperature interval of 50 °C in an electric furnace. The average heating rate was 2.5 °C/min and the specimens were allowed a soaking for 1 h at the respective firing temperature before the furnace was switched off for cooling.

Table 1
Batch compositions (wt%).

Batches	China clay	Plastic clay	Feldspar	Fly ash
F1	25	25	10	40
F2	25	25	15	35
F3	25	25	20	30
F4	25	25	25	25
F5	25	25	30	20

2.2. Measurements

Chemical analysis of the raw materials was carried out following standard procedure.

The particle size distribution of different ground body mixes was determined using Malvern Particle Size Analyser, Model 2602 LC adopting laser diffraction technique. All the experiments were carried out using 63 mm lens and under identical conditions.

The fired specimens were subjected to physical tests viz. linear shrinkage, flexural strength, apparent porosity, bulk density and relative density. Bulk density and percent apparent porosity were measured using the conventional water displacement method according to Archimedes principle. True density of the specimens was determined from respective powdered material using specific gravity bottle. Relative density was determined using the standard equation (relative density = bulk density/true density). Flexural strength (3-point bending) was determined in a universal testing machine, Instron 5500R with a crosshead speed of 2 mm/min. For each specimen 8 bars were tested and average was taken and reported.

Microstructure was studied by SEM analysis on selected sintered samples (polished and etched with 5% hydrofluoric acid for 3 min) using a LEO-S 430 I apparatus.

Concentration of crystalline phases was estimated for some matured selected samples from X-ray diffraction (XRD) line profile analysis using Rietveld analysis by X'Pert High Score Plus software (PANalytical). The XRD patterns of the samples were recorded in X'Pert Pro MPD diffractometer (PANalytical) operating at 40 kV and 30 mA using Ni filtered CuK_α radiation. The XRD data were recorded in step-scan mode with step size 0.02° (2θ) from 6° to 70°. Standard (a known amount of a pure crystalline phase) calcium fluorite was added to the sample to calculate the weight percentage of vitreous and crystalline phases in the sample using Rietveld analysis by X’Pert High Score Plus software (PANalytical). The quality of fitting was assessed from difference plots as obtained from Rietveld analysis by comparing observed diffraction patterns with the simulated patterns and also “Goodness of Fit” which varied from 1.70 to 2.76 among different samples.

3. Results and discussion

The results of the chemical analysis of the raw materials have been presented in Table 2. The chemical analysis results indicated that the china clay sample was of normal type, SiO_2 and Al_2O_3 were the major constituents with low Fe_2O_3 and alkali ($K_2O + Na_2O$) content. Plastic clay was rather high in SiO_2 and low in Al_2O_3. The result of fly ash indicated that carbon content (in terms of L.O.I.) was within limit (below 1.5%) whereas appreciable amount of ferruginous ($Fe_2O_3 + TiO_2$) and calcareous ($CaO + MgO$) impurities were present, 5.63% and 4.62% respectively. Total alkali content was 2.05%. XRD studies of raw natural materials (Fig. 1a) show that feldspar contains microcline, albite, muscovite and quartz whereas plastic clay and china clay both contains koalinite, muscovite and quartz in varying proportions.

XRD analysis (Fig. 1b) indicated the presence of 18% mullite and 23.8% quartz in fly ash sample.

The oxide compositions of all the batches were calculated on calcined basis and the results are presented in Table 3. Fig. 2a represents the variation of SiO_2/Al_2O_3 ratio with respect to fly ash/feldspar ratio. The SiO_2/Al_2O_3 ratio decreased marginally (from 2.16 to 2.32) with progressive increase in fly ash/feldspar ratio. However, significant decrease in alkali content (5.57–2.87) was observed with increasing fly ash/feldspar ratio (Fig. 2b) which is quite obvious as there was progressive decrease in feldspar content. Reverse trend was observed in case of alkaline earth oxide content and ferruginous oxide content (Fig. 2c and d). The presence of alkaline earth oxides in association with ferruginous oxides in mixes with higher proportion of fly ash is expected to influence the vitrification behaviour of the body mixes.

The particle size distribution of different body mixes is presented in Fig. 3. There was very little difference in the distribution of fine particles among the mixes studied.

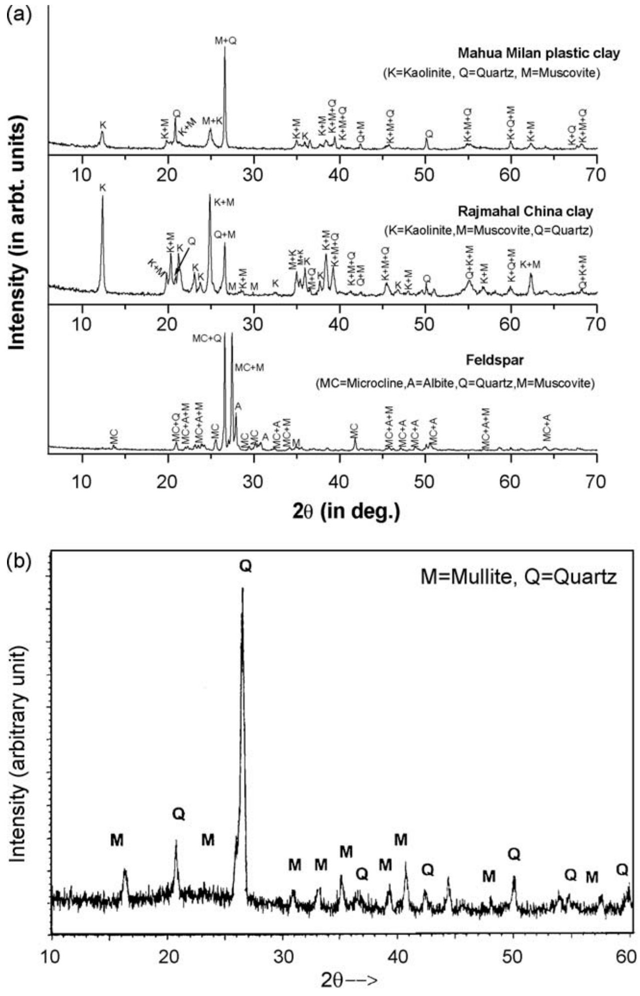

Fig. 1. (a) XRD patterns of raw natural materials used (plastic clay, china clay and feldspar). (b) XRD pattern of fly ash.

The variation in percent fired linear shrinkage with increasing fly ash content is presented in Fig. 4a. From the figure it may be observed that there was a steady decrease in linear shrinkage up to 1200 °C with gradual increase in fly ash and beyond this temperature the curve first increased and then more or less flattened indicating very insignificant effect on linear shrinkage with increasing fly ash content in the mix. At 1300 °C, specimens F4 and F5 (containing 25% and 20% fly ash respectively) showed distinct over firing tendency.

Table 2
Chemical analysis of the raw materials.

Oxide constituents (wt%)	China clay	Plastic clay	Feldspar	Fly ash
SiO_2	46.68	63.50	64.98	60.63
TiO_2	0.89	1.91	0.08	1.18
Al_2O_3	35.29	22.44	17.98	25.68
Fe_2O_3	1.90	1.64	0.18	4.45
CaO	0.28	0.93	0.48	3.22
MgO	0.50	0.33	Tr.	1.40
Na_2O	0.60	0.20	2.58	0.29
K_2O	0.28	0.90	12.87	1.76
L.O.I.	13.12	7.94	0.84	1.41

Table 3
Oxide compositions of the experimental bodies (fired basis).

Oxide constituents (wt%)	F1	F2	F3	F4	F5
SiO_2	61.80	62.00	62.20	62.40	62.61
TiO_2	1.30	1.24	1.19	1.13	1.07
Al_2O_3	28.57	28.17	27.78	27.38	26.99
Fe_2O_3	2.75	2.54	2.32	2.10	1.88
CaO	1.85	1.71	1.58	1.43	1.29
MgO	0.86	0.79	0.72	0.64	0.57
Na_2O	0.55	0.66	0.78	0.89	1.01
K_2O	2.32	2.88	3.44	4.00	4.56

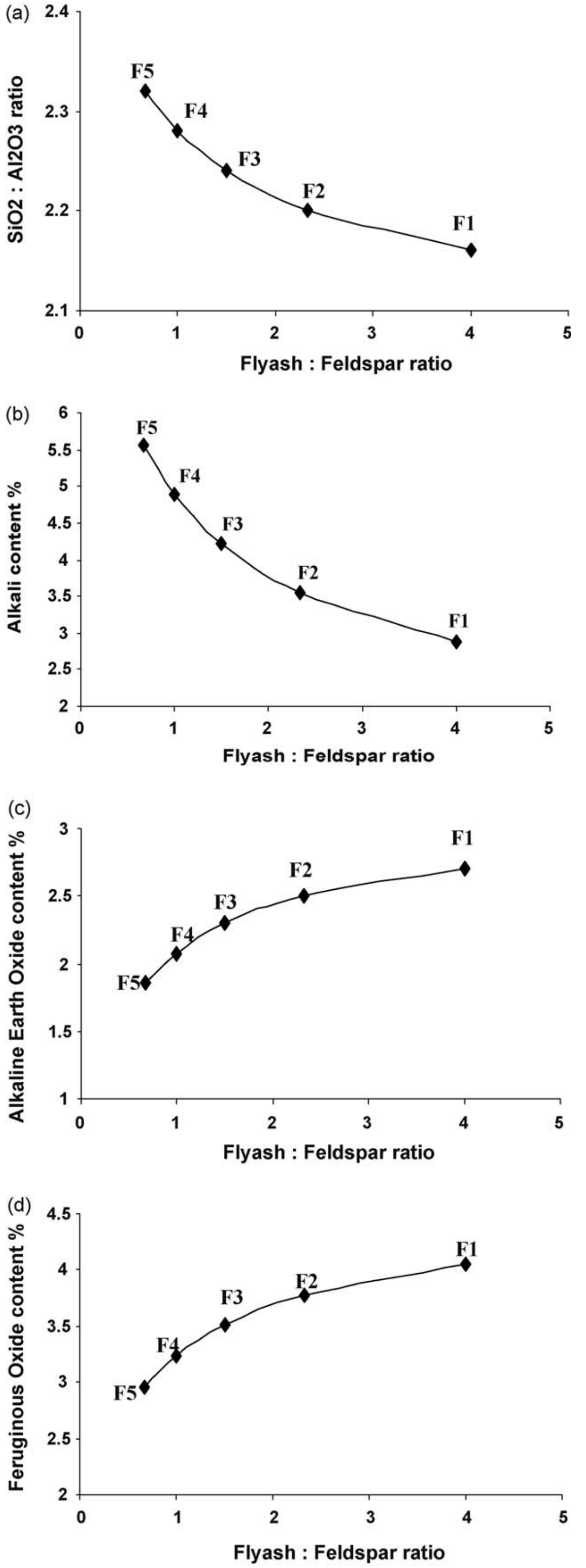

Fig. 2. (a) Variation of SiO_2:Al_2O_3 with fly ash/feldspar ratio. (b) Variation of alkali content with fly ash/feldspar ratio. (c) Variation of alkaline earth content with fly ash/feldspar ratio. (d) Variation of ferruginous oxide content with fly ash/feldspar ratio.

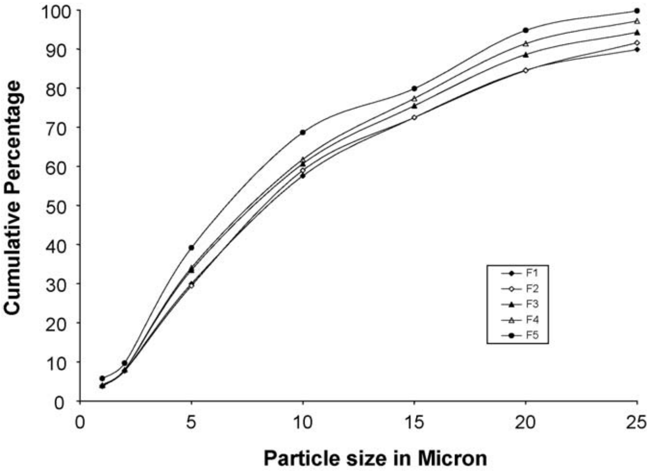

Fig. 3. Particle size analysis of different body mixes.

The variation in bulk density (B.D.) with increasing fly ash content is given in Fig. 4b. The nature of the curves was very similar to those of Fig. 4a. Bulk density value reached a maximum (2.39 g/cm^3) with mix F3 (fly ash content 30%) at 1300 °C. When fly ash was further decreased at the expense of feldspar marked decrease in bulk density values was observed at this temperature (1300 °C) indicating over firing tendency. Presence of higher proportion of feldspar in association with ferruginous and calcareous minerals led to the formation of low viscous glass, the volume of which increased with increasing temperature and thus leading to over firing at temperature above 1250 °C.

The variation in apparent porosity (AP) with increasing fly ash content is given in Fig. 4c. Apparent porosity of the specimens gradually decreased up to 1200 °C as feldspar was progressively incorporated as a replacement of fly ash. At 1250 °C the apparent porosity values first decreased up to the fly ash content 25% and then abruptly increased indicating overfiring tendency. Similar trend was observed with the specimens fired at 1300 °C. The figure further reveals that specimens of mix F3 (fly ash content 30%) reached below 0.5% A.P. at 1300 °C indicating almost complete densification at this temperature. Specimens of mix F4 (having fly ash content 25%) attained the same value of AP at 1250 °C and beyond this temperature overfiring tendency was very conspicuous. This clearly indicates that presence of ferruginous and calcareous minerals (coming from fly ash) actually narrowed down the vitrification range. Specimens of mix F5 having 30% feldspar also showed over firing tendency even at 1250 °C without attaining vitrification (apparent porosity value <0.5%). This observation also confirms the results of Dana et al. [19] who observed that fly ash containing bodies mature earlier than normal porcelain.

The changes in flexural strength with fly ash content are shown in Fig. 4d. As expected, a decreasing trend in flexural strength was observed with increasing fly ash content up to 1200 °C. This is quite obvious as the proportion of feldspar was increased in the specimens more and more vitrification and consolidation would be observed. Beyond 1200 °C, the flexural

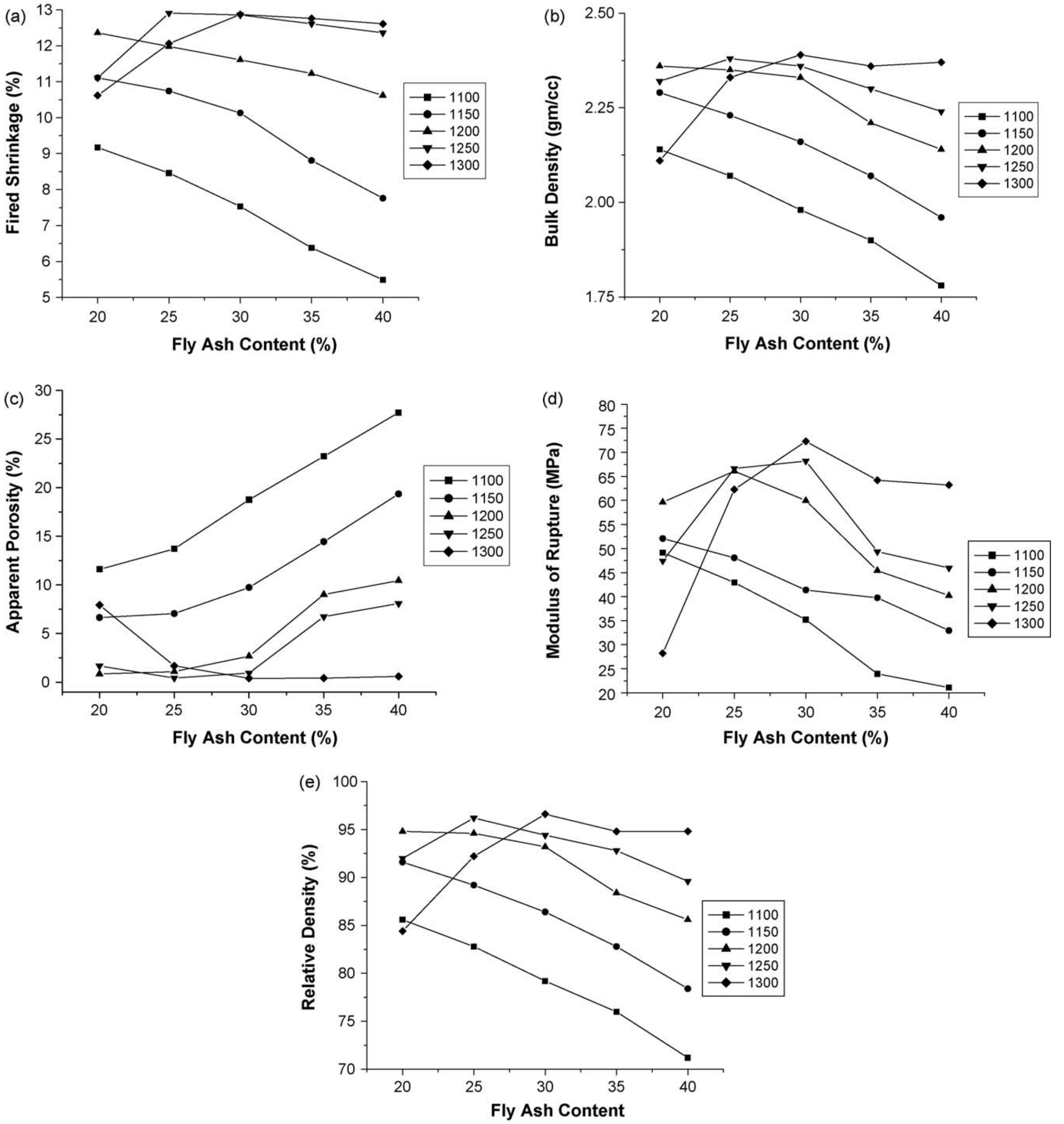

Fig. 4. (a) Variation of fired shrinkage with fly ash content. (b) Variation of bulk density with fly ash content. (c) Variation of apparent porosity with fly ash content. (d) Variation of modulus of rupture with fly ash content. (e) Variation of relative density with fly ash content.

strength values of the specimens increased with decreasing fly ash content and reached a maximum with 30% fly ash content and then decreased rapidly with further increase in feldspar as a replacement of fly ash due to overfiring. Specimens of mix F3 showed the highest flexural strength, 72.3 MPa, at 1300 °C. It is generally accepted that bending strength in ceramics decreases exponentially with increasing porosity, very much dependent on the amount of liquid phase present at the firing temperature as well as on the viscosity of the liquid phase [21,22]. With increasing feldspar content in the mix there will be rapid decrease in porosity of the specimen with increasing temperature due to the formation of higher volume of liquid phase. However, with increasing temperature residual quartz is likely to get dissolved in the melt and the viscosity will increase. In the present system the optimum condition was obtained with fly ash content between 25% and 30% while feldspar content was between 25% and 20% respectively.

To discuss the degree of densification, relative density rather than bulk density must be considered because the contents of the crystal constituents differ in the compositions. Fig. 4e

Table 4
Phase analysis (wt%) of selected specimens fired at different temperatures.

Temperature	Specimen F3			Specimen F4		
	Quartz	Mullite	Glass	Quartz	Mullite	Glass
1200	11.0	24.0	65.0	10.1	18.2	71.7
1250	7.5	25.0	67.5	7.0	21.0	72.0
1300	4.0	27.1	68.9	4.4	18.0	77.6

shows the relative densities of the compositions fired. Almost all the matured specimens attained around 95% relative density. Generally after the apparent porosity tends to reach zero, the closed porosity shows an increasing trend because of the 'bloating' on extended heating and the relative density abruptly decreases. The relative density of vitrified specimens reached the maxima at the highest firing temperature and a value of 96.6% was obtained with specimens of F3 (fly ash 30% and feldspar 20%) at 1300 °C. Specimens of F4 (fly ash and feldspar 25% each) reached a relative density value of 96.2% at 1250 °C and beyond this temperature the value decreased abruptly to 92.2%. At higher firing temperatures beyond vitrification the closed porosity increases resulting in bloating. The source of bloating has been reported by Norris et al. [20] and Kobayashi et al. [21] and the reason to be the expansion of O_2 gas released from the transformation of Fe_2O_3 to Fe_3O_4 or the expansion of the gas enclosed in the pores with temperature elevation. Both these two factors contributed significantly and the mixes with feldspar content above 20% could not achieve higher relative densities. Presence of ferruginous impurities in appreciable quantity (coming from fly ash) thus contributed significantly in shortening the vitrification range and causing over firing tendency.

In a separate experiment mechanical properties of specimens were studied with one composition similar to F4 but instead of fly ash, calcined quartz powder was incorporated (clay 50%, feldspar 25% and quartz 25%). The study revealed that with quartz containing body mix complete vitrification (apparent porosity value $<0.5\%$) could not be achieved even at 1300 °C. The new mix showed apparent porosity value 4.75% at 1250 °C while the same reached 1.36% at 1300 °C. MOR value of the specimen was 60.8 MPa at 1300 °C. The bulk density values attained 2.34 g/cm^3 (densification 93.6%) and 2.38 g/cm^3 (densification 95.2%) at 1250 °C and 1300 °C respectively. This may be inferred from these results that presence of fly ash in the compositions resulted in lowering the vitrification temperature. XRD analysis indicated appreciable mullite formation even at 1200 °C. It is evident from Table 4 that composition having more fly ash showed higher mullite content at all temperatures. Maximum mullite content was reported in specimens of mix F3 at 1300 °C and with increasing feldspar content, mullite formation decreased significantly probably due to more glass formation at lower temperature. Table 3 indicated that as feldspar was progressively incorporated replacing fly ash in the body mixes, there was gradual decrease in Al_2O_3 content and increase in SiO_2 content. Less mullitization in silica rich compositions was also observed by Schuller [23]. Further, mullite present in fly ash (Fig. 1b) also contributed towards ultimate mullite content in the specimens. Such body mixes rich in fly ash with no additional quartz became richer in both alumina and alkalies resulting in abundant mullite formation although optimum result was obtained with mix F3. Presence of Fe^{3+} and Ti^{4+} also helped in the formation of mullite from the glassy phase by replacing Al^{3+} in its structure. The same observation was also made by Chaudhuri [24,25] when those ions were added externally in a porcelain composition. However, with increasing alkali ions (mix F4) there was considerable decrease in the mullite content indicating that alkali ions (Na^+, K^+) possibly retarded mullite formation. The effect of temperature on mullite formation was not very significant, but an increasing trend was observed with progressive rise in temperature. In case of specimen of mix F4 which showed overfiring at 1300 °C indicated less mullite formation at this temperature. At 1300 °C liquid phase formation is more likely to occur with this particular composition in preference over mullite crystallization and consequently less mullite at this temperature was observed.

Table 5 indicates the probable oxide compositions of glassy phase of two selected compositions F3 and F4 respectively at varying temperatures. It is conspicuous from the result that with increasing temperature the glassy phase became richer in SiO_2 and poorer in Al_2O_3 indicating a lower viscous liquid phase at higher temperature. The reduction in viscosity facilitated the recrystallization of secondary mullite which has been reflected in Table 4. Although the mix F4 contained higher proportion of feldspar than that of mix F3, the analysis of glassy phases indicate that the viscosity would be rather on the higher side in case of F4 at all temperatures. However, as expected higher volume of glassy phase was observed in case of F4. This particular composition favoured the formation of glassy phase rather than crystallizing out secondary mullite.

Another observation from the XRD results was that the mixes contained appreciable quantity of quartz, although no quartz was added externally in the compositions. The entire quartz phase must have come from fly ash as well as from free

Table 5
Calculated composition of probable glassy phase present in different compositions (wt%) (considering mullite as $3Al_2O_3{\cdot}2SiO_2$).

Composition	Temperature	SiO_2	Al_2O_3	$Na_2O + K_2O$	CaO + MgO	$Fe_2O_3 + TiO_2$
F3	1200	68.36	16.21	6.49	3.54	5.40
F3	1250	70.60	14.55	6.25	3.41	5.20
F3	1300	73.38	12.06	6.12	3.34	5.09
F4	1200	65.82	19.97	6.82	2.89	4.51
F4	1250	68.53	17.21	6.84	2.90	4.52
F4	1300	68.23	18.63	6.31	2.67	4.16

silica present in the clay used. Residual quartz content decreased with increasing firing temperature irrespective of the mixes analyzed due to quartz dissolution in the glassy phase.

The scanning electron photomicrographs of polished and etched specimens of some selected compositions (F3 and F4) fired at 1250 °C and 1300 °C are shown in Figs. 5a and b and 6a and b. The microstructure revealed the presence of α-quartz and mullite as the major constituents in a glassy matrix. In all the cases dense microstructure was obtained and its influence on the ceramic properties is quite conspicuous. Formation and growth of cluster of needle shaped crystals were observed in pockets of each sample and these crystals are attributed to secondary mullite which was formed with the assistance of the melt by dissolution and re-precipitation of primary mullite at higher temperature. Dekeysen [26] observed that glassy phase is formed as a result of the diffusion of Al_2O_3 in to the SiO_2 zone while the mullite crystals grew as a result of the movement of SiO_2 into the Al_2O_3 zone. Further, when mullite is formed in the presence of a small amount of intergranular glassy phase, it always exhibits an acicular or elongated morphology as is evident from the microstructures (Figs. 5a and 6a). Analysis of microstructure presented in Figs. 5a and 6a further revealed that quartz grains were rather angular in nature while the grains tend to become round in specimens with higher feldspar content (mix F4). The grains are expected to react more intensely with the higher proportion of feldspathic melt resulting in rounding of the edges. The wide solution rim around quartz grains showed their extensive dissolution and as expected this increases with increasing temperature and thereby diminishing the size of the grains. Extensive cracking around the quartz grains was observed which was due to stress generation during cooling. The quartz grains, as observed in the photomicrographs, were between 25 μm and 40 μm. All the figures showed well formed needle shaped secondary mullite forming a network throughout the microstructure. The better interlocking and uniform distributions of comparatively smaller size mullite needles in the glassy matrix contributed significantly towards development of flexural strength. As temperature went beyond 1250 °C, the mullite needles tend to coarsen (Figs. 5b and 6b) leading to smaller number of larger needles. The observed variation in morphology and size of mullite crystals may be related to the gradient in viscosity of the relevant matrix and subsequent more rapid mass transport [27] when viscosity of the glassy phase decreased.

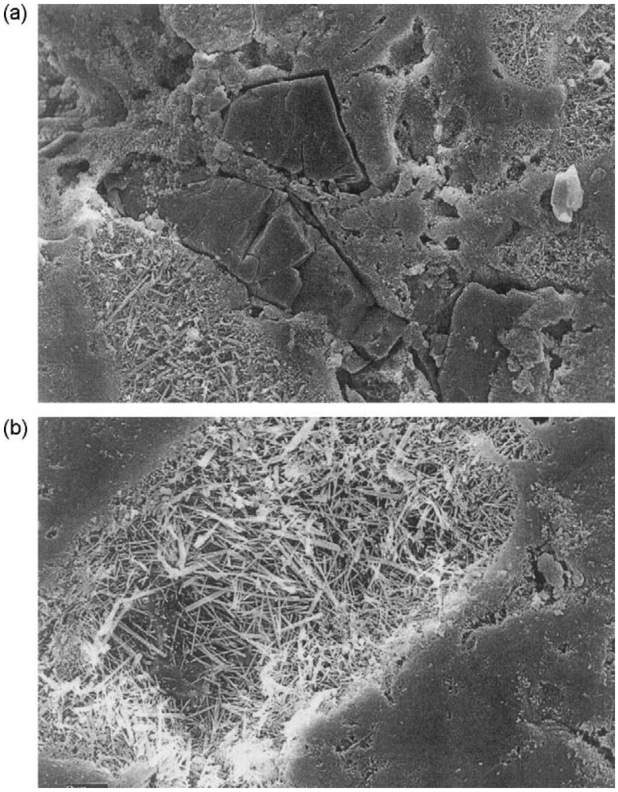

Fig. 5. (a) SEM micrograph of specimen F3 at 1250 °C. (b) SEM micrograph of specimen F3 at 1300 °C.

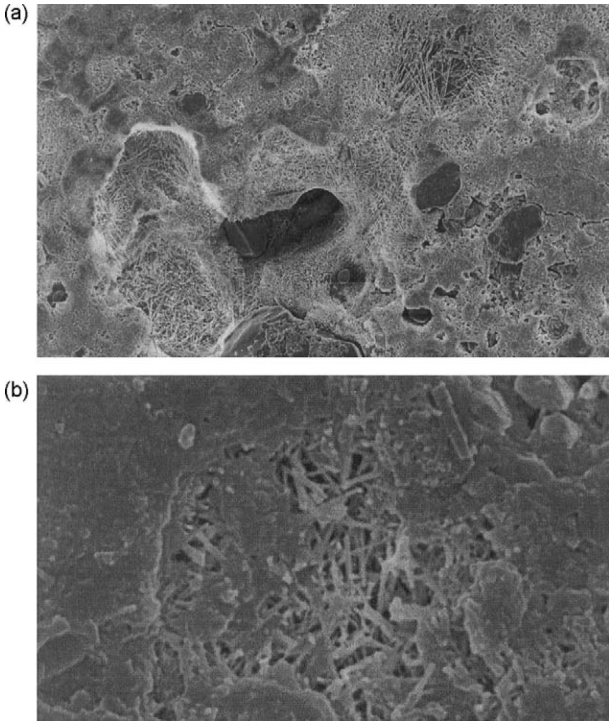

Fig. 6. (a) SEM micrograph of specimen F4 at 1250 °C. (b) SEM micrograph of specimen F4 at 1300 °C.

It is difficult to underscore the effect of any particular impurity on the mullitization process because the fly ash used in this study has noticeable amounts of number of impurities. It is generally acknowledged that iron (III) oxide and calcium oxide facilitate mullitization. Iron (III) oxide favours grain growth and probably leads to a microstructure with large elongated grains which were also observed by others [28]. There was appreciable decrease in mullite phase in specimens of F4. This composition contained significantly higher proportion of alkali oxide which possibly favoured the formation of glassy phase in preference to mullite.

4. Conclusions

From the present investigations, the following conclusions may be drawn.

(1) Optimum ceramic properties were obtained with composition having fly ash content between 30% and 25% while feldspar content between 20% and 25% respectively. Maximum flexural strength (72.3 MPa) was obtained with the composition having fly ash content 30% at 1300 °C when the apparent porosity reached almost zero.
(2) Presence of iron and calcium impurities in appreciable quantity in the fly ash narrowed down the vitrification range.
(3) Mullite content increased with increasing proportion of fly ash.
(4) Intense interlocking of fine mullite needles in the glassy matrix contributed significantly towards development of flexural strength. Coarsening of mullite needles was observed at higher temperature.

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