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Synergistic effect of fly ash and blast furnace slag on the mechanical strength of traditional porcelain tiles

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Abstract

Fly ash and blast furnace slag, the by-products of Indian thermal power plant and steel plant, were gradually added to a traditional kaolin—quartz—feldspar based porcelain tile compositions singly and in combination by replacing a part of quartz and feldspar, respectively. The effects of such additions were studied by measuring the linear shrinkage, bulk density, water absorption and flexural strength of the samples heated in the temperature range of 1150–1200 °C. The results reveal that additions of both the by-products have beneficial effects towards mechanical strength. The strength improvement was mainly due to the presence of microcrystalline components such as mullite and quartz in fly ash and alkaline earth oxides in blast furnace slag. Slag containing compositions with or without fly ash vitrified at an early temperature (1175 °C) and achieved highest strength at this temperature compared to 1200 °C for normal and fly ash bearing compositions. Specific combinations of fly ash and slag in the ratio of 1:1 and 1:2 have shown the development of highest flexural strength (>70 MPa) at 1175 °C due to their lowest R_2O:$R'O$ (R = K, Na and R′ = CaO, MgO) and moderately higher SiO_2:Al_2O_3 ratio. Beyond this temperature, the strength drastically reduced due to the formation of glassy phases at higher temperatures. XRD studies were also carried out to find out the differences in phase evolution due to addition of fly ash and blast furnace slag to traditional porcelain composition.

Keywords: D. Porcelain; Fly ash; Blast furnace slag; Ceramic tile

1. Introduction

A traditional porcelain batch consists of kaolin, quartz and feldspar. The role of each of these raw materials on the physico-mechanical behaviour of such triaxial porcelain bodies has been studied in detail by many authors [1–9]. Due to the gradual depletion of naturally occurring minerals, there is a recent trend to substitute these minerals by alternative source of raw materials, which are abundantly available as overburden wastes. In such attempts, few authors have utilized fly ash, a by-product of thermal power plant as alternative source of alumino-silicate raw material by replacing a part of naturally occurring kaolinitic clays in porcelain tile compositions [10–13]. They found that replacement of 25–30 wt.% of kaolinitic clay by fly ash is beneficial as it has close resemblance with clay in their chemistry and inherently contain some micro crystalline components such as quartz and mullite. Dana et al. [14] in their recent studies substitute a part of quartz by fly ash in triaxial porcelain tile compositions. They observed higher mullitization in fly ash containing samples that resulted in maximum strength at 1300 °C. Some authors also reported use of iron and steel slag in porcelain tile compositions [15–20]. They observed that alkaline earth oxides present in slag favours early maturing of porcelain bodies due to their strong fluxing action. Dana et al. [21,22] also found some beneficial effect of blast furnace slag in triaxial porcelain composition by replacing a part of feldspar. The research work of the above authors mainly dealt with an individual effect of fly ash and slag on the physico-mechanical behavior in porcelain compositions. Combined effect of fly ash and slag in traditional triaxial porcelain composition by replacing a part of quartz and feldspars is rarely reported.

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Table 1
Batch compositions (wt.%)

Batches	Kaolinitic clay	Feldspar	Quartz	Fly ash	B.F. Slag
NP	45	30	25	0	0
FP	45	30	10	15	0
SP	45	15	25	0	15
FSP-1	45	27	19	6	3
FSP-2	45	24	22	3	6
FSP-3	45	22	18	7	7

In the present investigation, the combined effect of fly ash and blast furnace slag is studied by replacing a part of quartz and feldspars respectively in a triaxial traditional porcelain tile composition. The physico-mechanical properties such as shrinkage, bulk density, water absorption and flexural strength are compared individually with the traditional, fly ash and slag-based compositions. The differences in their strength behaviour and phase evolution are also studied and discussed in the paper.

2. Experimental

Two kilograms of each batch (NP, FP, SP, FSP-1, FSP-2 and FSP-3) 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 mm × 14 mm × 5 mm were hydraulically compacted using uniaxial pressing at 30–35 MPa. The shaped samples were dried at 110–120 °C for 24 h till the moisture content reduced to less than 0.5%. The dried samples were fired at three different temperatures (1150, 1175 and 1200 °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 (L.S.), water absorption (W.A.) and bulk density (B.D.). Bulk density and % water absorption 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-Kα radiation. Vitrified tile sample was also tested for polishing with diamond paste after initial grinding with SiC powder. Since, incorporation of fly ash and B.F. Slag to normal porcelain composition in place of quartz and feldspar adds some extra amount of colouring oxides such as Fe_2O_3 and TiO_2, colour measurement was also carried on vitrified tile surfaces. The resulting vitrified samples were investigated by colour measurement following ASTM-C609-71, a colorimeter instrument type Hunter Lab with attached standard colours was used.

3. Results and discussion

All the raw materials were chemically analyzed by the known method [23] and the results are given in Table 2.

The analysis shows that kaolinitic clay, quartz and feldspar used in the present study are of normal type. Fly ash contains SiO_2 and Al_2O_3 as major oxide constituents with TiO_2, CaO and Fe_2O_3 slightly in higher side. Blast furnace slag has SiO_2, CaO and Al_2O_3 as major oxide constituents. An earlier XRD study of the authors [16] confirms the presence of mullite and quartz in fly ash, whereas slag shown only a diffused hallow around 30° (2θ) indicating its glassy nature. The experimental compositions are exhibited in the form of a triangle (Fig. 1)

Table 3 provides the chemical composition of the experimental bodies. The major oxide constituents present are shown in Fig. 2. Traditional porcelain (NP) is characterized by high SiO_2:Al_2O_3 ratio and alkaline oxide ($K_2O + Na_2O$), whereas fly ash porcelain (FP) is characterized by moderate SiO_2:Al_2O_3 ratio and higher alkaline oxide. Slag porcelain bodies without/with fly ash (SP and FSP series) are char-

Table 2
Chemical analysis of the raw materials

Major chemical constituents (wt.%)	Kaolinitic clay	Feldspar	Quartz	Fly ash	B.F. Slag
SiO_2	45.41	66.48	98.66	59.26	35.35
Al_2O_3	34.39	17.29	0.39	27.97	19.15
Fe_2O_3	1.13	0.14	0.07	4.00	0.60
TiO_2	0.89	0.02	0.01	2.92	0.77
CaO	1.07	0.31	0.10	2.63	36.56
MgO	0.76	0.03	0.02	0.56	2.99
Na_2O	0.87	2.94	0.09	0.54	0.81
K_2O	0.42	11.95	0.12	0.60	1.29
MnO	–	–	–	–	2.09
L.O.I.	14.67	0.71	0.37	1.12	0.21

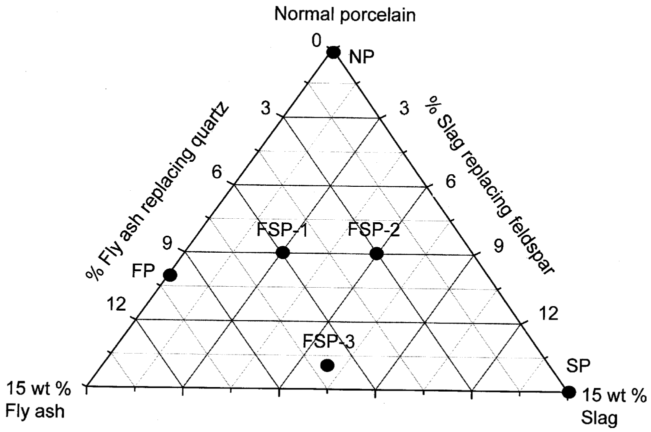

Fig. 1. Classical triangular representation of the experimental porcelain tile compositions.

Table 3
Chemical compositions of the experimental bodies

Oxide constituents (wt.%)	Batches					
	NP	FP	SP	FSP-1	FSP-2	FSP-3
SiO_2	70.06	63.80	64.99	66.11	66.37	62.11
Al_2O_3	22.36	26.86	22.65	24.45	23.51	24.95
Fe_2O_3	0.61	1.25	0.69	0.89	0.75	0.87
TiO_2	0.44	0.91	0.56	0.70	0.65	0.73
CaO	0.65	1.06	6.50	2.01	3.14	3.32
MgO	0.38	0.47	0.86	0.77	1.12	1.15
Na_2O	1.40	1.47	1.05	1.29	1.18	1.11
K_2O	4.10	4.18	2.37	3.62	3.23	2.98
MnO	–	–	0.34	0.07	0.14	0.15

acterized by moderately higher SiO_2:Al_2O_3 ratio and higher alkaline earth oxides (CaO + MgO).

The variation in % L.S. with temperature is shown in Fig. 3. As normally observed, the shrinkage increases with heating temperature for all the compositions. The only slag containing body (SP) with higher amount of alkaline earth oxides (lowest $R_2O/R'O$) show highest shrinkage at 1175 °C compared to NP, FP and FSP series. At 1150 °C, although there is no distinct relationship observed between shrinkage and alkaline earth oxide content, a correlation may be seen from the Fig. 3 that shrinkage value increases with increase in alkaline earth oxide content beyond 1150 °C.

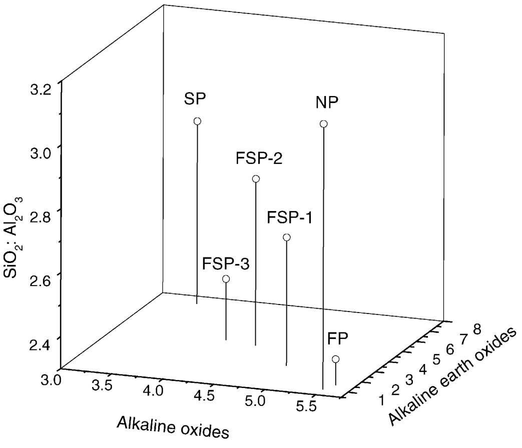

Fig. 2. Chemical composition of the experimental bodies, SiO_2:Al_2O_3—alkaline oxides (K_2O + Na_2O)—alkaline earth oxides (CaO + MgO).

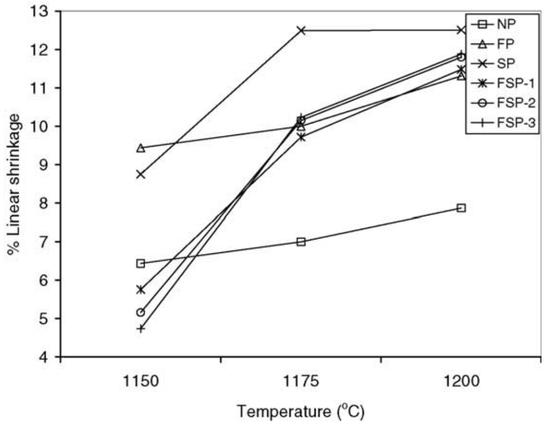

Fig. 3. Variation in % linear shrinkage with heating temperature.

In contrast to the present observation, Marghussion and Yekta [15] reported that alkaline earth oxide cause less shrinkage in comparison to alkali oxides, but at below 1100 °C, particularly for wall tile compositions. The nature of Fig. 3 in the present study agrees with this observation at below 1150 °C showing a tendency to cause less shrinkage in slag containing composition.

Variation in bulk density (Fig. 4) and percent water absorption (Fig. 5) also follow the similar trend. Slag containing bodies (SP and FSP series) shown higher B.D. in the temperature range of 1175–1200 °C followed by less than 0.5% W.A. It may also be observed that FSP-3, containing fly ash and slag in the ratio of 1:1, achieved highest densification (2.71 gm cm^{-3}) and minimum W.A. (0.14%) at 1200 °C compared to others.

An interesting feature may be noted from Fig. 5 that water absorption of SP and FSP series of compositions has been drastically reduced to less than 0.5% at 1175 °C while

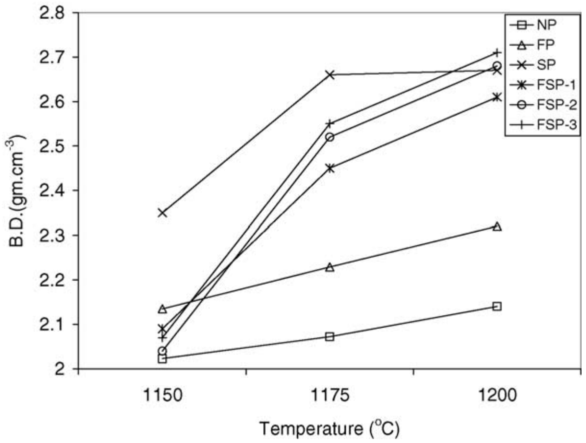

Fig. 4. Variation in bulk density with heating temperature.

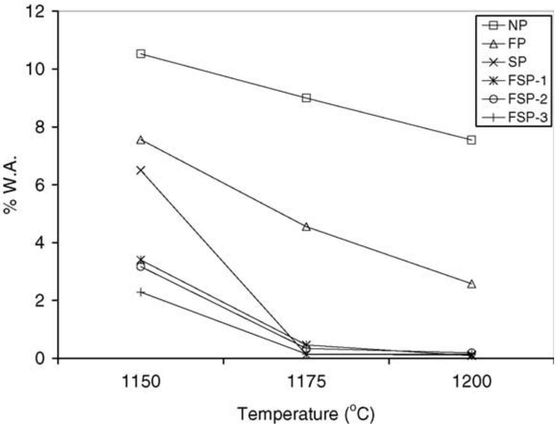

Fig. 5. Variation in % water absorption with heating temperature.

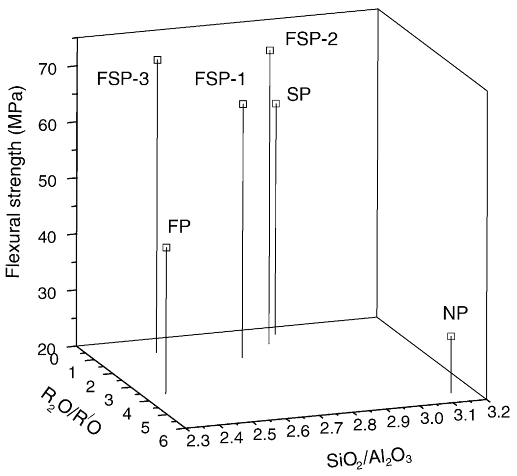

Fig. 7. Variation in flexural strength of the experimental bodies at 1175 °C with respect to $R_2O:R'O$ ($R = K$ and Na, $R' = Ca$ and Mg) and $SiO_2:Al_2O_3$.

normal porcelain (NP) and fly ash porcelain (FP) bodies did not achieve full vitrification (W.A. < 0.5%) even at 1200 °C. Presence of alkaline earth oxides in SP and FSP series of compositions might have assisted speedier formation of glassy phases and promoted the reaction with clay minerals present at this temperature. Harms [24] also observed similar effect of alkaline earth oxide in a porcelain body.

Fig. 6 illustrates the flexural strength behaviour of all the compositions at various temperatures. It may be seen that slag containing compositions with or without fly ash developed higher strength at 1175 °C compared to others, beyond which the strength decreases due to formation of more glassy phases. Combination of fly ash and slag in the ratio of 1:2 (FSP-2) and 1:1 (FSP-3) have shown highest strength development (>70 MPa) at 1175 °C. Addition of fly ash and slag singly in traditional porcelain composition although improved the mechanical strength, the combined effect was found to be more effective. Such synergistic composition of porcelain bodies containing both fly ash and slag shall be useful to produce high-strength ceramic tiles for industrial as well as domestic applications.

Strength variations of all the experimental bodies at 1175 °C with respect to $R_2O:R'O$ and $SiO_2:Al_2O_3$ ratio is exhibited in Fig. 7. FSP-2 and FSP-3 are amongst the top in strength values (around 70 MPa) due to their lowest $R_2O:R'O$ and moderately higher $SiO_2:Al_2O_3$ ratio followed by FSP-1and SP, the second highest (around 60 MPa). NP and FP with higher $R_2O:R'O$ ratio possesses moderate strength (30 and 45 MPa, respectively).

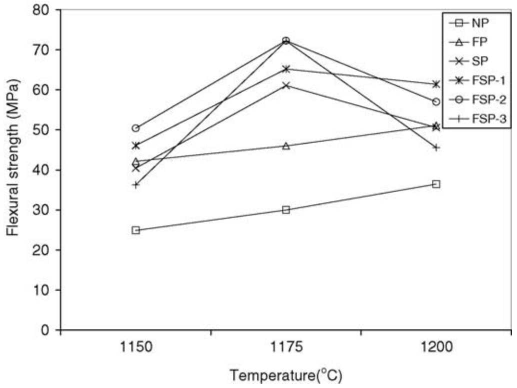

Fig. 6. Variation in flexural strength with heating temperature.

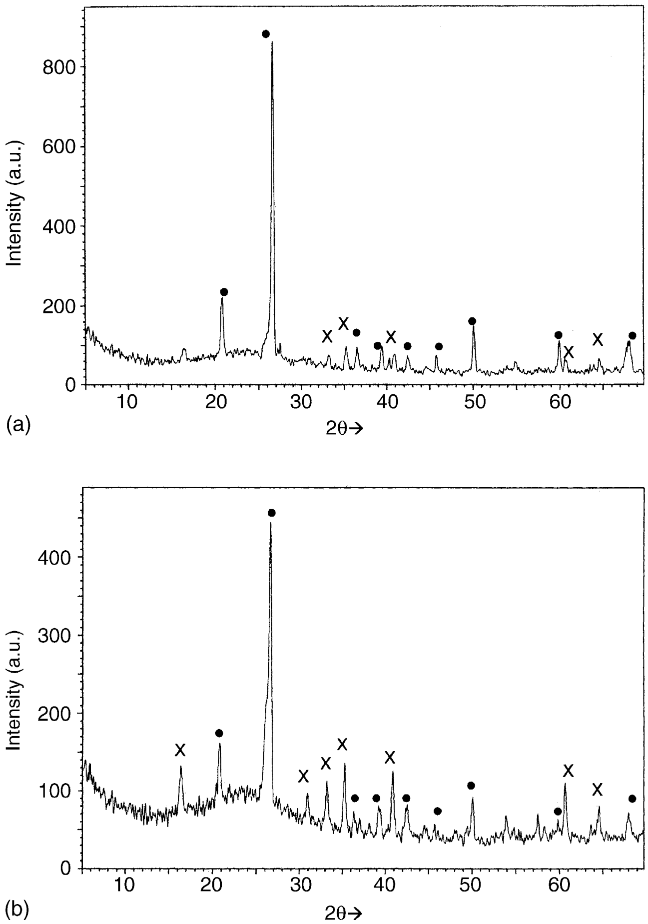

Fig. 8. XRD pattern of 1175 °C heated samples: (a) NP, (b) FP, (c) FSP-3, (d) SP [×, mullite; ●, quartz; ○, anorthite; △, gehlenite].

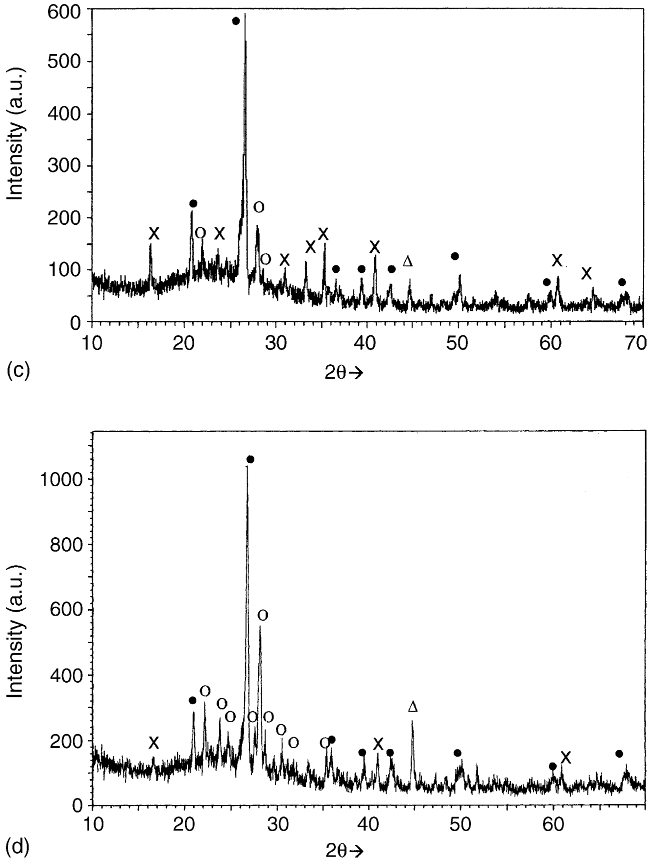

Fig. 8. (*Continued*).

Some of the selected samples (NP, FP, SP, FSP-3) heated at 1175 °C were subjected to XRD study. The XRD pattern confirms the presence of quartz and mullite in NP and FP samples (Fig. 8a and b) as major phases, while FSP-3 and SP (Fig. 8c and d) contain quartz, anorthite and mullite as major phases with minor amount of gehlenite. Mullite content in SP was significantly less than FSP-3 and that resulted lower strength in SP compared to FSP-3. The vitrified tile samples were also tested for polishing. A surface finishing of 1 μm was achieved and no surface defects were noted.

In modern day technology for the production of vitrified porcelain ware, particularly for tiles, greater attention is paid to the industrial development of white base body. The resulting vitrified porcelain tile samples obtained in the present investigation were subjected to colour measurement using the opponent-colour coordinate system developed by Hunter [25]. In this system, the third coordinate describes the lightness of colour and is usually denoted by *L*. The results are given in Table 4.

Table 4
L-value of 1200 °C fired porcelain tile compositions

Composition	*L*-value
NP	93
FP	80
SP	82
FSP-1	77
FSP-2	78
FSP-3	76

It may be noted that the normal porcelain tile composition (NP) showed higher *L*-value (whiter) due to the presence of lower amounts of Fe_2O_3 and TiO_2 compared to the fly ash and B.F. Slag based porcelain tiles. However a tile body with *L*-value of 75–80 range can also be used for the production of glazed ceramic floor tile.

4. Conclusion

Addition of fly ash and blast furnace slag in a traditional triaxial porcelain composition in the proportion of 1:1 and 1:2 was found to be beneficial towards improvement in mechanical strength and early vitrification at 1175 °C. Presence of microcrystalline components of quartz and mullite in fly ash and alkaline earth oxides in B.F. slag were responsible to develop anorthite and mullite phases which ultimately improved the mechanical strength. Such type of synergistic porcelain composition may find potential applications to manufacture high strength ceramic floor tiles for industrial as well as domestic buildings. Further, part substitution of natural minerals (quartz and feldspar) by overburden industrial by-products (fly ash and blast furnace slag) reduce the cost of raw materials, thermal energy without altering the requisite physico-mechanical properties.

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