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Effects of fly ash additions on the mechanical and other properties of porcelainised stoneware tiles

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The effect of fly ash additions on the mechanical properties of porcelainised stoneware tile composition has been investigated. Fly ash additions in the range of 0–40 wt% have been added in to the tile body composition, wet milled, spray dried, shaped and fired at 1250°C. The MOR strength improved with increasing fly ash content and reached maximum when 25–30 wt% fly ash used, and with greater additions it decreased. A linear correlation between strength development and mullite formation was found. The tiles with 25 wt% fly ash had improved bending strength, abrasion resistance and hardness compared to the conventional tiles and conform to all other properties at an EN standard specification.

1. Introduction

The Porcelainised stoneware tiles are low porosity, dense products with high technical performance [1–3], particularly with respect to abrasion and frost resistance, modulus of rupture and resistance to chemical attack. It is also possible to produce these tiles as imitations of stones such as granite, marble, sandstone, travertine, etc. Due to the improved mechanical properties and aesthetic appearance, the last decade has shown a marked growth in porcelainised stoneware tiles. In Italy [4], the total production of porcelainised stoneware tiles in 1980s was 8 $m \cdot m^2$ (around 2% of domestic tile production) and has reached 127 $m \cdot m^2$ (22% of domestic tile production) in 1997 and the total production world-wide has risen about 250 mm^2.

The selection of raw material for stoneware tiles is of utmost importance as it plays a vital role in ultimate product quality. A typical stoneware body consists of SiO_2 and Al_2O_3 as major oxides and CaO, MgO, Na_2O, K_2O and ZrO_2 as minor compounds. Fe_2O_3 and TiO_2 is kept to a minimum as they lead to a coloured tile body. For supplementing these compounds, the raw material is selected from a group of plastic and non-plastic minerals. Clayey minerals such as kaolinite, illite, montmorillonite, etc. belong to the first group and contribute to strength development of green tiles. The second group consists of feldspar, felspathoid, quartz, pigmatite and quartzites, and are used as flux. Dondi *et al.* [5] studied the influence of chemical composition on microstructural and mechanical properties of stoneware tiles. They found that increasing the alumina content of the composition improved the mechanical strength of the tiles. Similarly, Harada *et al.* [6] also reported that additions of alumina to the feldspathic porcelain body could raise the flexural strength from 80 to 150 MPa.

Fly ash is a by-product of thermal power plants resulting from the combustion of pulverised coal in the coal furnaces. The annual generation of fly ash in India is around 90 million tonnes out of which only 10% is used and rest being disposed causing serious environmental problems [7]. This alarming magnitude of fly ash generation has attracted the attention of scientists, technologists and policy makers. Various efforts are being made at R&D institutes and universities to develop technologies for the gainful utilisation of fly ash and the technical work done has gained prominence for further action towards commercialisation.

The major constituents of fly ash are SiO_2, Al_2O_3 and Fe_2O_3 with some minor constituents such as CaO, MgO and TiO_2, and thus may be considered as low cost resource materials for alumino-silicates. The potential of fly ash as a raw material for the ceramic industry has been reviewed by Sen *et al.* [8]. Uses of fly ash in ceramic tiles are reported in the literature [9–12]. Kumar *et al.* [13, 14] studied the effects of fly ash incorporation on the mechanical properties of ceramic tiles and found that a small amount of fly ash addition improves the scratch hardness and strength of the ceramic tiles. Xing *et al.* [15] studied the sintering mechanism of tiles containing 60–75% fly ash in temperature range of 1000–1080°C. They reported a high traverse strength of 72 MPa for tiles and excellent thermal shock resistance.

On the basis of literature it was found that a controlled amount of fly ash addition improves the mechanical properties of ceramic tiles. Based on this observation, the present study was carried out to use fly ash as a source of alumino-silicate compounds to develop porcelainised stoneware tiles. Various compositions have been developed using increasing proportion of fly

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ash. The mechanical properties of tiles were studied with respect to fly ash content. Attempt has been made to correlate the properties with XRD phases.

2. Experimental

The raw materials used in the present study were fly ash collected from one of the captive power plants of Eastern India, a highly plastic clay, feldspar and calcined quartz. The chemical composition of the raw materials was carried out by conventional wet analysis methods. The standard batch composition used as reference consisted of 50 wt% kaolinitic clay minerals, 30 wt% feldspar, 15 wt% quartz, 5 wt% of other additives and designated "T1". The other batches were prepared using 5, 10, 15, 20, 25, 30, 35 and 40 wt% fly ash by substituting kaolinitic clay and named T2, T3, T4, T5, T6, T7, T8 and T9 respectively. Every batch was wet milled with a dispersing agent for 6 hours. Colouring pigments were added during wet milling in separate batches to produce colouring effects. The slurry obtained after milling was spray dried and compacted into the desired shapes using uniaxial pressure of 300 kg/cm^2. To get the "salt and pepper" effect, granules of different colours were mixed before compaction. The shaped samples were air dried then fired at 1250°C for 60 minutes in air. The rate of heating was kept at 10°C/minute.

The polishing of the tiles were done in three stages. First, the surface was levelled with coarse silicon carbide abrasive. Then the tiles were polished by progressively reducing the superficial roughness by using a series of decreasing sized silicon carbide abrasives. Finally, the tile surface was polished with an alumina paste to get mirror finish.

The phases present were identified by XRD techniques using Ni filter and Cu K_α radiation. The microstructure of the fractured surface of sintered specimen containing 25 wt% fly ash was examined by SEM (JEOL JSM 840) with an EDX attachment. A Leitz Optical Microscope was used to study the polished surface of tiles.

The bulk density and water absorption of the tiles were measured by a water displacement method. The thermal expansion of the specimen was measured using a Dilatometer (STA 409, NETZSCH, Germany). The bending strength of specimens was measured on $150 \times 25 \times 25$ mm bars by applying the three-point load on a Richle Testing Machine. Young's modulus was measured by an acoustic resonance method. A Universal testing machine was used to determine the compressive strength. The scratch hardness of the tiles was measured on a Moh's scale. Vickers microhardness (Hv) was measured by the indentation technique at 500 gm load with a Leitz Hardness tester. Five indentations were made on the samples polished with alumina paste. Morgan Marshall abrasion Index was used to investigate the rate of abrasion.

3. Results and discussion

The chemical analyses of the raw materials are given in Table I. The Fe_2O_3 and other impurities present in fly ash are low. The low carbon content (<2.07%) in the composition is considered suitable for ceramic application. The result of quantitative XRD analysis of the fly ash is summarised in Table II. Around 40% phase is crystalline, 57% is glassy and 3% unidentifiable. Among the crystalline phases, mullite and quarts are the major phase.

The chemical composition of the porcelainised stoneware tiles is given in Table III. The chemical composition of fly ash based tiles can be compared with that of commercial vitrified stoneware tiles. It can be observed from the table that SiO_2, Al_2O_3 and Fe_2O_3 increase with fly ash content.

Figs 1 to 9 includes the physico-mechanical properties of both green and vitrified tiles in relation to fly ash content. A gradual loss in flexural strength of green tiles was observed with the increasing fly ash content (Fig. 1). This is due to non-plastic behaviour of fly ash, which is substituting for the plastic clay. However, T1 to T6 compositions had sufficient strength for handling while, T7 to T9 compositions had very low strength and thus the rate of rejection was very high during handling. This problem can be overcome by using a plastic binder. The linear shrinkage of the vitrified tiles (Fig. 2) decreased with the fly ash content. This may be due to the reason as the fly ash replaces

TABLE I Chemical analysis of raw materials

Constituents (wt%)	Fly ash	Clay	Feldspar	Quartz
SiO_2	61.8	52.5	65.2	98.2
Al_2O_3	27.9	26.3	19.4	0.3
Fe_2O_3	2.6	1.9	0.2	0.1
TiO_2	1.0	0.6	0.2	Trace
CaO	1.7	3.6	0.2	0.1
MgO	0.3	–	0.0	–
Na_2O	–	0.2	4.3	–
K_2O	–	0.4	9.8	–
L.O.I.	2.0	14.0	0.5	–

TABLE II Quantitative phase analyses of fly ash

Phases	Volume %
α-Quartz	15.4
Mullite	21.3
Magnetite spinel	2.4
Hematite	1.3
Glass	57.0

TABLE III Chemical composition of porcelainised stoneware tiles

Constituents (wt%)	T1	T2	T3	T4	T5	T6	T7	T8	T9
SiO_2	68.2	68.5	68.9	71.0	71.2	71.6	71.9	72.2	72.5
Al_2O_3	20.9	20.9	21.0	21.1	21.1	21.2	21.2	21.2	21.5
Fe_2O_3	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.9	1.0
TiO_2	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6
CaO	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.4	1.4
MgO	1.1	1.1	1.1	1.0	1.0	1.1	1.1	1.0	1.0
Na_2O	2.8	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.6
K_2O	2.1	2.1	2.0	2.0	2.0	2.1	2.1	2.1	2.0
ZrO_2	1.6	1.6	1.6	1.7	1.7	1.6	1.7	1.7	1.6

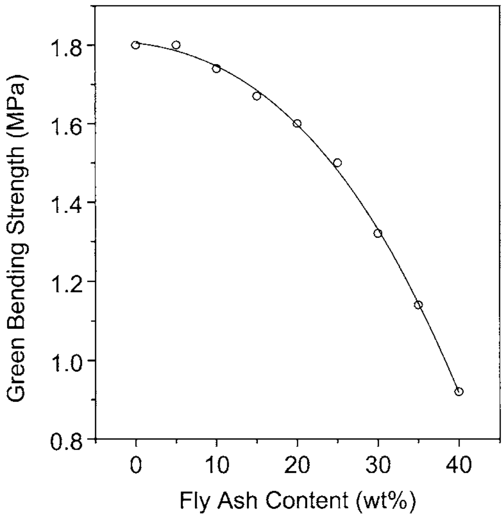


Figure 1 Variation in green bending strength of tiles in relation to fly ash content.

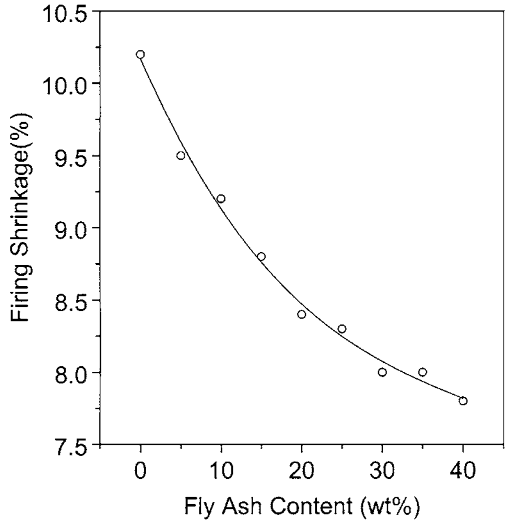


Figure 2 Variation in firing shrinkage of tiles in relation to fly ash content.

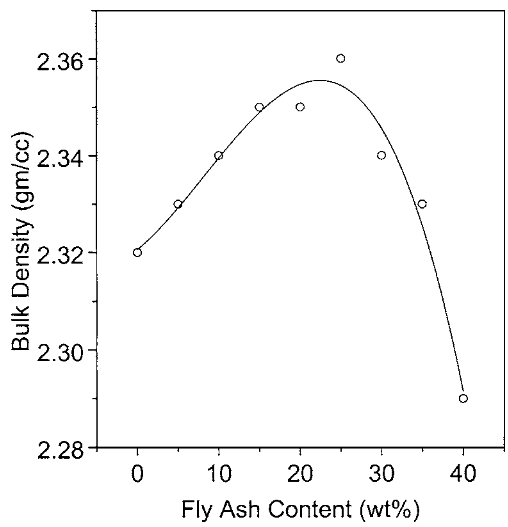


Figure 3 Variation in bulk density of tiles in relation to fly ash content.

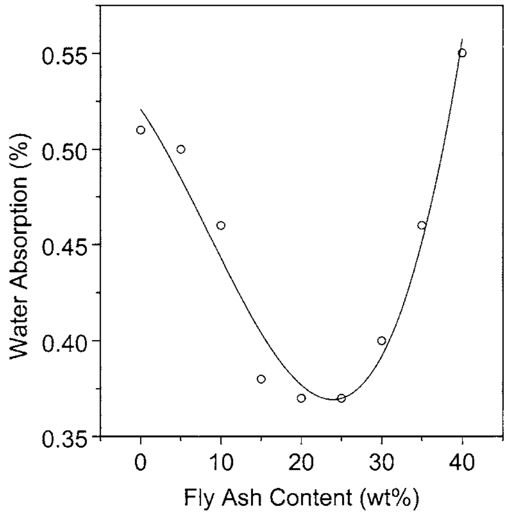


Figure 4 Variation in water absorption of tiles in relation to fly ash content.

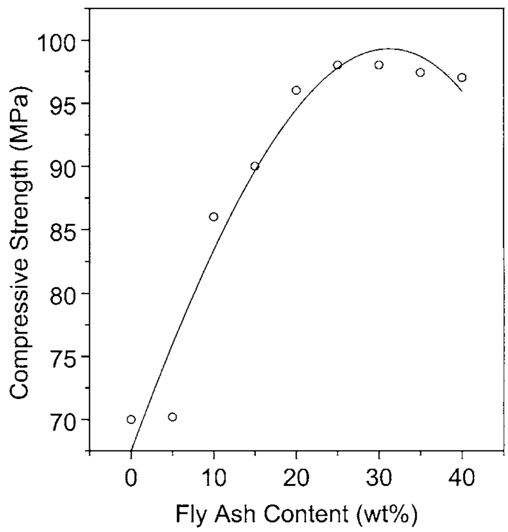


Figure 5 Variation in compressive strength of tiles in relation to fly ash content.

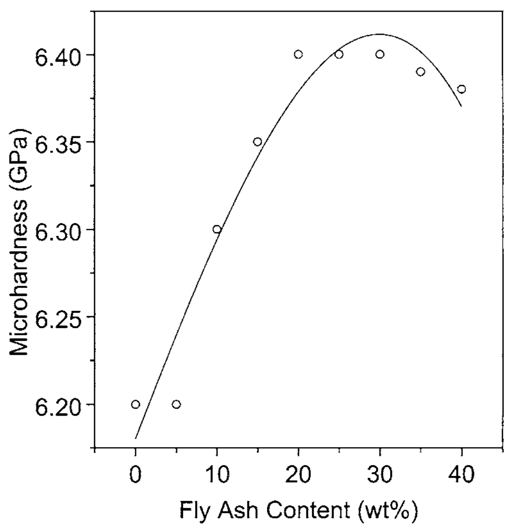


Figure 6 Variation in microhardness (Hv) of tiles in relation to fly ash content.

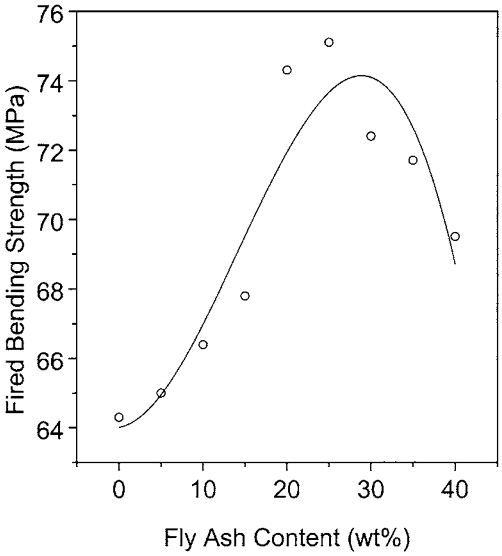


Figure 7 Variation in fired bending strength of tiles in relation to fly ash content.

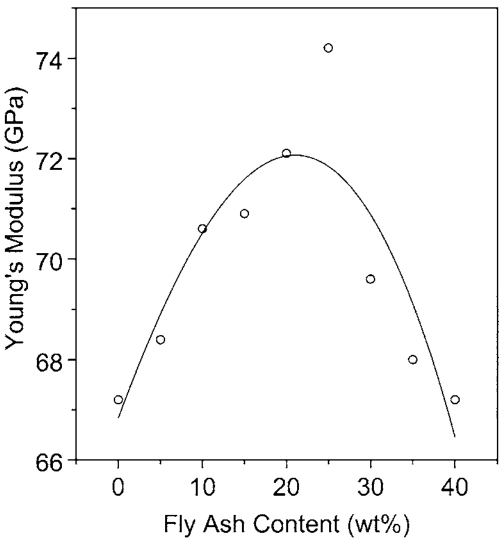


Figure 8 Variation in Young's modulus of tiles in relation to fly ash content.

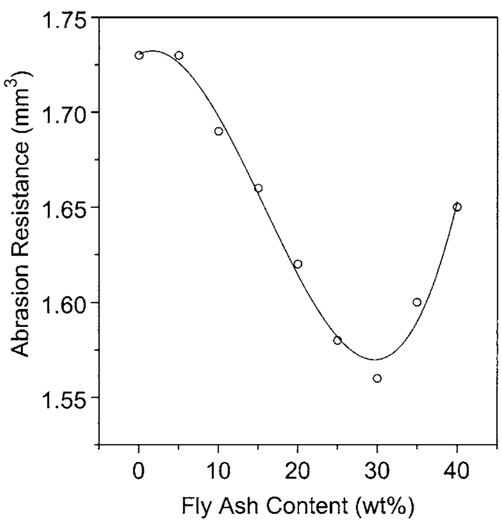


Figure 9 Variation in abrasion resistance of tiles in relation to fly ash content.

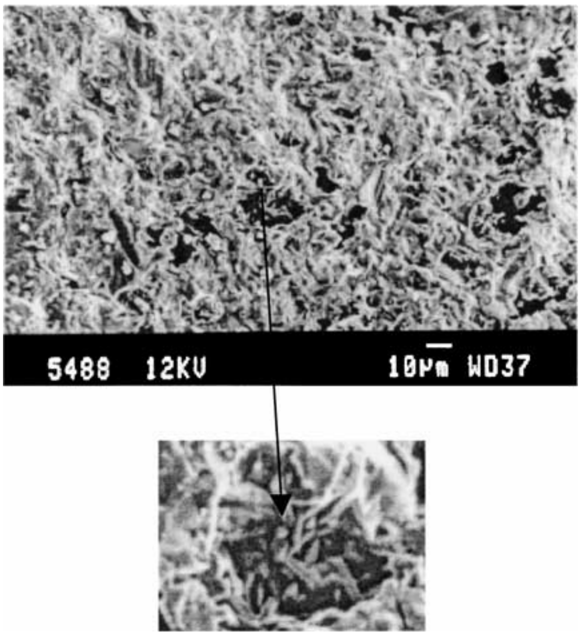
TABLE IV Quantitative phase analysis (vol. %) of 1250°C fired porcelainised stoneware tiles in relation to fly ash content

Constituents	T1	T2	T3	T4	T5	T6	T7	T8	T9
Mullite	10	10	12	13	16	17	17	14	13
Quartz	23	22	23	24	23	21	18	16	16
Amorphous	63	65	62	63	59	61	65	67	69
Others	4	3	3	–	2	1	–	3	4

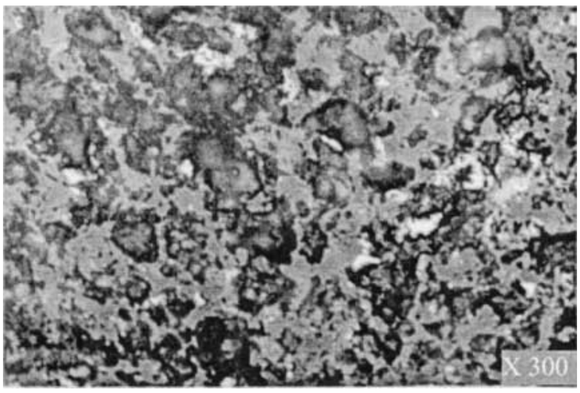
the kaolinitic clays, the compositions contain progressively less of the fluxing oxides, therefore the viscosity rises and the rate of consolidation is reduced. The bulk density (Fig. 3) increased with the fly ash content and reached maximum (2.36 gm/cc) in T6. The decreased in density in T7 to T9 is due to the reduced rate of sintering with the same reason as explained for reduced shrinkage. The water absorption decreased with the increasing fly ash content attaining minimum value in T6 composition and then increased (Fig. 4). This is again due to the same reason, where the reduced rate of sintering in T7 to T9 composition caused the presence of more pores in tile body. The compressive strength (Fig. 5) and microhardness (Fig. 6) were increased with fly ash and found maximum in case of T7 composition while the bending strength (Fig. 7), Young's modulus (Fig. 8) and abrasion resistance (Fig. 9) were maximum in T6 composition. A linear relationship between bulk density, bending strength, Young's modulus and abrasion resistance was found.

To understand the mechanism of strength development with increasing fly ash content, quantitative phase analysis of the vitrified tiles was carried out and the results are summarised in Table IV. Although the quantity of SiO_2 and Al_2O_3 are more or less equal in all the compositions, the quantity of the phases is varying with fly ash content. The mullite quantity roughly corresponds to 30–60% of the quantity, which could have been potentially formed on the basis of available alumina in the composition. The mullite content increased with fly ash and reached maximum in T6 and T7 composition. The steady increase of mullite content up to T7 may be due to mullite, which was originally present in fly ash increasing with the increasing fly ash additions. Also, presence of secondary mullite in the composition might have helped in the formation of primary mullite by reaction of SiO_2 and Al_2O_3 during the sintering process. In T8 and T9 compositions, the decreased mullite content was balanced by an increase in glass phase formation. The quartz content is almost constant for compositions T1 to T5. Thereafter it appears to decline. The glass content is increasing slightly, suggesting a reaction between added quartz in the batch and the fly ash. The other phases present were corundum, anorthite and zircon but these could not analysed quantitatively due to very low proportions.

By comparing the data of Table IV with Figs 7, 8 and 9, it is found that the bending strength, Young's modulus and abrasion resistance were improved with increasing mullite content and deteriorated with increased amorphous phase content.



(a)



(b)

Figure 10 (a) SEM of fractured surface of T6 tiles fired at 1250°C. Enlarge section of pocket is also shown in Figure. (b) Optical micrograph of polished surface of T6 tiles.

Since the T6 composition had shown the best properties compared to all other compositions, scanning electron microscopy of the fractured surface and optical microscopy of the polished surface of T6 composition fired at 1250°C was carried out and the micrographs are shown in Fig. 10a and b. The dense microstructure is characterised by a very small number of pores. Interlocked mullite and quartz crystals are embedded in glassy matrix. The formations of needle shaped clusters of crystals are also observed in pockets (Fig. 10a, enlarged section). EDX analysis revealed that these crystals are of mullite and quartz compositions. The polished section (Fig. 10b) shows the uniform distribution of crystalline phased throughout the matrix. This dense microstructure is responsible for good mechanical properties of tiles. To study the suitability of these tiles for commercial application, a few $100 \times 100 \times 25$ mm tiles of T6 composition (25% fly ash) were produced by firing in a roller kiln using a short firing cycle of 60 minutes. The properties of these tiles are shown in Table V. The European Nation (EN) standard specification values were also included in Table V for comparison. These tiles had better abrasion resistance, bending strength and hardness and conform to all other properties to EN specification.

TABLE V Properties of T6 tiles (25 wt% fly ash) in comparison to EN standards

Properties	EN specification	Tiles of T6 composition
Water absorption (%)	<0.5	As per specification
Bending strength (N/mm^2)	>27	30–38
Abrasion resistance (mm^3)	<205	<150
Frost resistance	No defects	As per specification
Coefficient of thermal expansion ($\times 10^{-6}$)	<9	As per specification
Chemical attack resistance	No variations	As per specification
Thermal shock resistance	No alterations	As per specification
Moh's hardness	>5	7
Spot resistance	No variation	As per specification

4. Conclusions

The effect of fly ash additions on the properties of porcelainised stoneware tiles has been studied. The bending strength of the green tiles was adversely affected by the additions, however, compositions of up to 25 wt% fly ash had sufficient strength for handling. The bending strength, Young's modulus and abrasion resistance after firing was improved with fly ash additions and reached a maximum when 25 wt% fly ash was used. This is due to formation of a dense microstructure consisting of a network of mullite and quartz crystals embedded in a glassy matrix. The reduction in strength for the tiles containing more than 25 wt% fly ash is due to an increased glass phase content. A linear correlation between mullite formation and strength development was found. The tiles with 25 wt% fly ash conform all the EN standard specification. Improved scratch hardness, bending strength and abrasion resistance were some of the added advantages besides a valuable use of a waste material.

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