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Ceramics International 28 (2002) 393–400

CERAMICS INTERNATIONAL

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Development of ceramic tiles from common clay and blast furnace slag

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Received 28 May 2001; received in revised form 11 June 2001; accepted 2 August 2001

Abstract

With an objective of making ceramic tile, granulated blast furnace slag (GBFS) and common clay were mixed whereby calcia: silica ratio (w/w) varied from 0.04 to 0.86. Calcia and silica combined to form wollastonite as the major phase in the sintered microstructure. Excess silica combined with magnesia, iron oxide and alumina to form enstatite, fyalite and alumino silicates respectively during sintering. Optimum compositions were found to be where calcia-silica ratio were in the range of 0.1–0.3 where mechanical strength and water absorption of the fired specimen were in the range of 28–38 MPa and 2.5–0.1%, respectively. Physical properties of the sintered specimen are explained on the basis of XRD and SEM analysis. Formation of wollastonite in the sintered compacts with finer grain size was found to be an important parameter for increase in strength. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Ceramic tile; Granulated blast furnace slag; Wollastonite

1. Introduction

Blast furnace slag (BFS) contains all the essential ingredients which may be properly utilised for making various consumer items. Quenched blast furnace slag is mainly used for the production of cement where slag is primarily utilised as one of the raw materials replacing clay. Other established use of the blast furnace slag is in the manufacture of different building materials like floor tiles, outside and inside facing of walls [1,2], providing roof covering or making separating walls [3,4]. Potential uses also include providing abrasion resistant lining in mineral dressing plants, in pipes including sewer pipes, channels, wear plates, non-skid load surfaces, counter tops for kitchens [4] and chemical laboratory and as high temperature insulators.

The main disadvantage of blast furnace slag is the presence of a large amount of lime in its composition. On the contrary, common clay usually contains a low amount of lime but it contains a large amount of silica and iron oxide making it a low melting composite. A proper mixing of common clay with blast furnace slag may produce a balanced composition whereby desired improved properties of the products may be attained by the formation of wollastonite in the microstructure of the sintered compacts. Formed wollastonite will impart many favourable properties such as higher mechanical strength, improved thermal shock resistance, low thermal expansion and superior electrical properties to the sintered compacts. In the present investigation, lime: silica ratio was varied from 0.04 to 0.86 by mixing common clay with blast furnace slag in varied proportions and the property of the sintered products made therefrom were analysed to arrive at an optimum composition.

2. Experimental procedure [4]

2.1. Raw materials

Beneficiated common clay (West Bengal, India) and granulated blast furnace slag (GBFS) from Durgapur Steel Plant (West Bengal, India) were used for this study. Chemical analysis of the raw materials are shown in Table 1. The GBFS was milled in a pot mill for 48 h and sieved through 100 mesh (BS).

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PII: S0272-8842(01)00107-9

Table 1
Chemical analysis report of common clay and blast furnace slag

Constituent	Common clay	Blast furnace slag
SiO_2	71.19	34.39
Al_2O_3	12.84	27.89
Fe_2O_3	4.69	1.84
TiO_2	Tr	1.04
CaO	2.75	29.42
MgO	Tr	7.97
K_2O	1.73	1.51
Na_2O	0.54	0.44
L.O.I	6.06	0.28

2.2. Sample preparation and firing

The clay and slag were mixed in the proportion as shown in Table 2.

The batches were mixed and wet milled in a pot mill for 12 h to make a slurry. The slurry was sieved to pass through 200 mesh BS (75 μm) and dried at a temperature 110±5 °C. The dried lumps were ground and mixed with 0.2–1% PVA as binder and then granulated and moistened with the addition of 5–8% water. The moistened granules were pressed into rectangular shapes of dimension 5×5×3 cm, 10×10×3 cm and 15×10×3 cm tiles using a hydraulic press under 30 MPa pressure.

The green tiles were dried at 110 °C±5 °C and the drying shrinkage was measured. The dried samples were fired at 1150, 1175 and 1200 °C with 2 h. soaking in an electric furnace. The firing shrinkage of the fired tiles was also measured.

2.3. Measurement of flexure strength

Specimens for flexural strength measurement were prepared by slicing the fired tiles followed by polishing upto 10 μm flatness. Sample dimensions were 100×100×10 mm. Strength was measured by Instron Testing machine using the three point loading device. The strength was calculated from the breaking load using the formula:

$$S = 2PL/3bd^2 \tag{1}$$

where, S = flexural strength (kgf/cm^2), P = load (kg), L = span (cm), b = breadth (cm) and d = thickness (cm).

Table 2
Batch composition (wt.%)

Sample No. composition (g)	1	2	3	4	5	6	7	8	9	10	11
Common clay	100	90	80	70	60	50	40	30	20	10	0
Slag	0	10	20	30	40	50	60	70	80	90	100

2.4. Measurement of water absorption

Water absorption of the fired samples was measured following IS specification [5]. The sample was immersed in boiling water in such a way that water can circulate freely on all sides of the specimen. Water was allowed to boil continuously for 5 h followed by natural cooling to room temperature. Water absorption of the specimen was calculated by Eq. (2).

$$\text{Water absorption}(\%) = \left\{(M_2 - M_1)/M_1\right\} \times 100 \tag{2}$$

where M_1 and M_2 are the weights of the dry and soaked samples, respectively.

2.5. XRD studies

XRD analysis was performed on raw materials (clay and GBFS) and sintered samples by using Philips X-ray PW 1730 Diffractometer using CuK_α radiation and Ni-filter.

2.6. SEM analysis

SEM analysis was carried out on selected sintered samples by LEO S430I.

2.7. Thermal analysis

DT and TG analysis of clay and GBFS were carried out by NETZSCH Thermal Analyser, Model 4045 upto 1000 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterisation of raw materials and sintered specimens

Raw materials were characterised by chemical, thermal and XRD analysis. Results of thermal and XRD analysis are shown in Table 3. From Tables 1 and 3 it appears that the clay used was of illitic type [6] containing substantial amounts of quartz in it. The analysis of GBFS indicated the presence of wollastonite in it along with appreciable amounts of spinel, mullite and also periclase.

After proportioning and mixing, each composition was chemically analysed, and shown to be in conformity with the calculated chemical composition of the specimen and are given in Table 4. A closer examination of Table 4 indicated that SiO_2, Fe_2O_3, Na_2O+K_2O decreases and Al_2O_3, MgO+CaO, TiO_2 increases when clay was gradually replaced by GBFS in the composition. Basicity of clay and GBFS[determined by the formula: basicity = $(MgO+Al_2O_3+CaO)/SiO_2$] was 0.22 and 1.89, respectively. Basicity of each composition was calculated and a smooth transition of basicity from 0.22

Table 3
Mineralogical identification through DTA and XRD of the raw materials

DTA and XRD analysis	Common clay		Blast furnace slag
1. Characteristic DTA peaks			
Endothermic	130 °C;	560 °C	xxx
Exothermic	–	–	
2. XRD analysis			
Major phase	Quartz, illite/muscovite and haematite		Wollastonite, spinel, mullite and periclase

to 1.89 is reflected in the series of samples selected for the present study. Another important factor which determines the property of the sintered product is lime–silica ratio in the specimen which varied from 0.04 in clay to 0.86 in GBFS. Stoichiometric ratio of lime–silica in wollastonite, an important desired phase, is around 0.90. XRD analysis of the sintered samples (figure not shown) indicated the formation of wollastonite in all the samples and the amount of it was found to increase with increasing GBFS in the specimen composition. XRD diagram for sample 6 containing Clay: GBFS in the proportion of 50:50 in its composition and fired at 1200 °C is shown as representative one (Fig. 1). Calculated composition on the basis of XRD of different sintered (1200 °C) specimens is shown in Table 5.

3.2. Results of sintering

The values of firing shrinkage, water absorption and flexural strength were co-related with the lime–silica ratio in the Figs. 2–4. Fig. 2 represents properties of the samples fired at 1150 °C. The values of firing shrinkage decreased with the increase in lime–silica ratio. The same trend was also noted for specimens fired at 1175 and 1200 °C (Figs. 3 and 4). Water absorption values for the samples fired at 1150 °C was found to increase with the increase in lime–silica ratio. Water absorption values of the samples fired at 1175 and 1200 °C (Figs. 3 and 4) initially decreased with increase in lime/silica ratio upto 0.3 followed by continuous increase. The values of flexural strength were higher for samples of lime–silica ratio in the range 0.1–0.4 when fired at 1150, 1175 and 1200 °C.

The chemical component of the slag used in the present investigation belongs mainly to the system SiO_2–Al_2O_3–CaO–MgO. Normal mineralogical composition of such type of slags, as reported [7–10] comprises gehlenite ($2CaO\cdot Al_2O_3\cdot SiO_2$), akermanite ($2CaO\cdot MgO\cdot 2SiO_2$) and wollastonite (CaO SiO_2). But the slag under present investigation contains less calcia (29.42%) and higher alumina (27.89%) compared to commonly available GBFS. The amount of silica (34.39%) and magnesia (7.97%) were however in the normal range. XRD pattern of GBFS (Fig. 5) indicated mostly glassy phase in it.

Phases characterised in the sintered mass were found to be Wollastonite (major) and Enstatite (formed due to reaction between magnesia and silica). Besides these, some low melting phases in the MgO–SiO_2 system (Enstatite) and FeO–SiO_2 system (Fyalite) are also likely to form in the sintered mass. In the specimens 8 and 9, containing a higher proportion of GBFS, mullite was formed. In all other systems except 8 and 9, $Al_2O_3\cdot SiO_2$ was also found as one of the major phases. Thus calcia–magnesia and alumina were consumed to form respective silicates and the rest of the silica remained in the microstructure as crystobalite and tridimite as indicated in the XRD analysis. Alkali metals help to form low melting silicates in such systems.

With increasing amount of GBFS in the specimens, calcia–silica ratio increases progressively leading to increase in wollastonite content of the sintered specimens with decreasing liquid formation. An optimum

Table 4
Calculated chemical composition of specimen as per the batch composition

Composition	1	2	3	4	5	6	7	8	9	10	11
SiO_2	71.19	67.51	63.83	60.15	56.47	52.79	49.11	45.43	41.75	38.07	34.39
Al_2O_3	12.89	14.39	15.89	17.39	18.89	20.39	21.89	23.39	24.89	26.39	27.89
Fe_2O_3	4.69	4.41	4.12	3.84	3.55	3.27	2.98	2.70	2.41	2.13	1.84
TiO_2	Tr	0.10	0.21	0.31	0.42	0.52	0.62	0.73	0.83	0.94	1.04
CaO	2.75	5.42	8.08	10.75	13.42	16.09	18.75	21.42	24.09	26.75	29.42
MgO	Tr	0.80	1.59	2.39	3.19	3.99	4.78	5.58	6.38	7.17	7.97
K_2O	1.73	1.71	1.69	1.66	1.64	1.62	1.58	1.58	1.55	1.53	1.51
Na_2O	0.54	0.53	0.52	0.51	0.50	0.49	0.48	0.47	0.46	0.45	0.44
Lime–silica ratio	0.04	0.08	0.12	0.17	0.24	0.31	0.38	0.47	0.58	0.70	0.86
Basicity	0.22	0.31	0.40	0.51	0.62	0.71	0.92	1.11	1.32	1.58	1.89

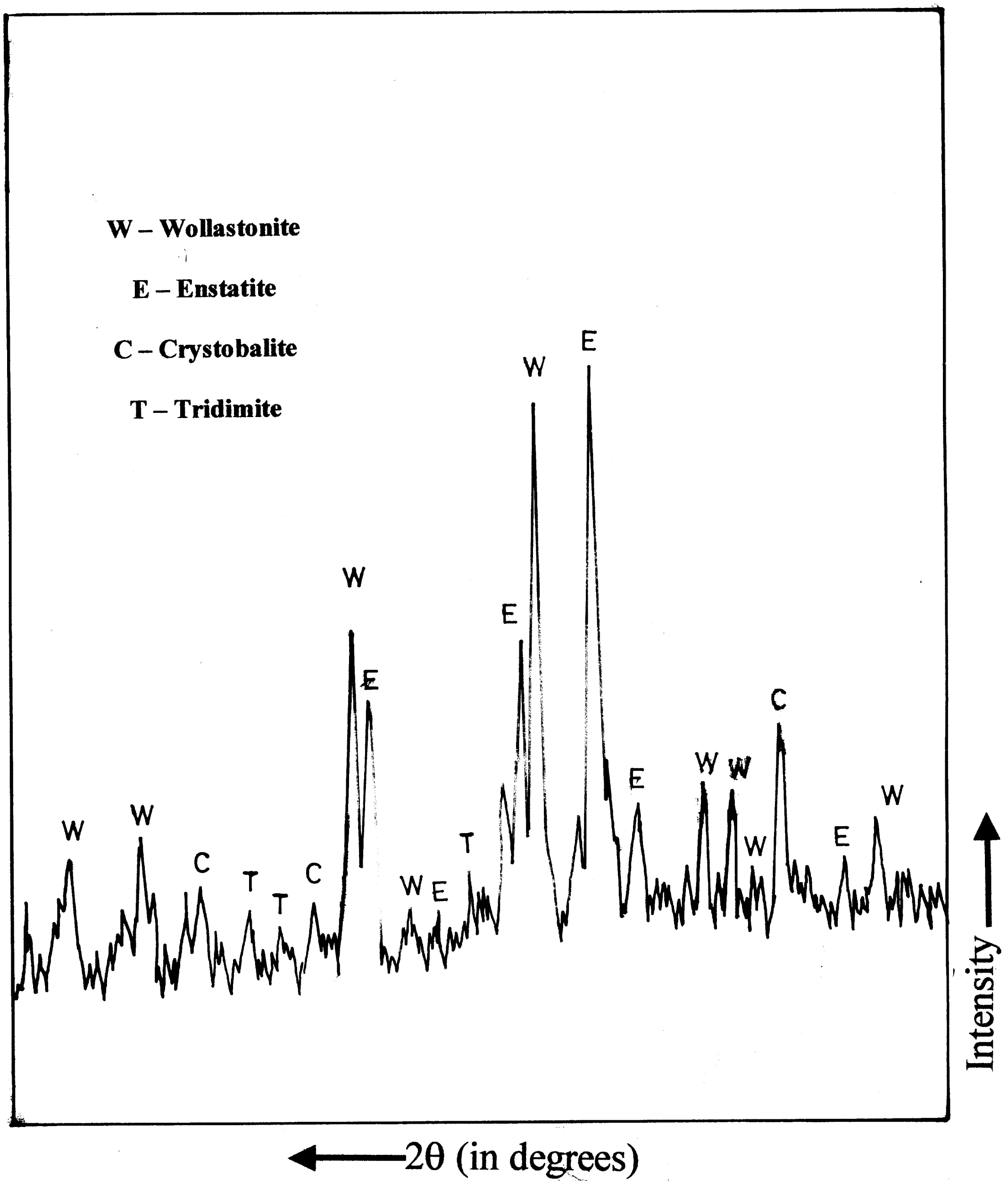

Fig. 1. XRD diagram of sample No. 6 fired at 1200 °C.

Table 5
Calculated composition of different phases in the specimen sintered at 1200°C

Phases present	Amounts of different phases (wt.%) in specimen										
Sample No.	1	2	3	4	5	6	7	8	9	10	11
$CaO \cdot SiO_2$	5.75	11.33	16.89	22.47	28.05	33.61	39.19	44.77	50.35		
$MgO \cdot SiO_2$		2.02	4.02	6.05	8.07	10.07	12.09	12.69	16.14		
$Fe_2O_3 \cdot SiO_2$	6.48	6.09	5.69	5.30	4.95	4.52	4.11	3.73	3.33		
$Na_2O \cdot SiO_2$	1.07	1.05	1.03	1.01	0.99	2.67	0.96	0.93	0.91		
$K_2O \cdot SiO_2$	2.85	2.82	2.79	2.74	2.71	0.97	2.61	2.61	2.56		
$Al_2O_3 \cdot SiO_2$	20.62	23.02	25.42	27.82	30.98	32.58	35.02	–	–		
$3Al_2O_3 \cdot 2SiO_2$	–	–	–	–	–	–	–	32.75	32.80		
SiO_2	57.02	48.44	39.88	31.30	21.91	13.22	5.59	3.09	–		
Al_2O_3	–	–	–	–	–	–	–	–	1.44		

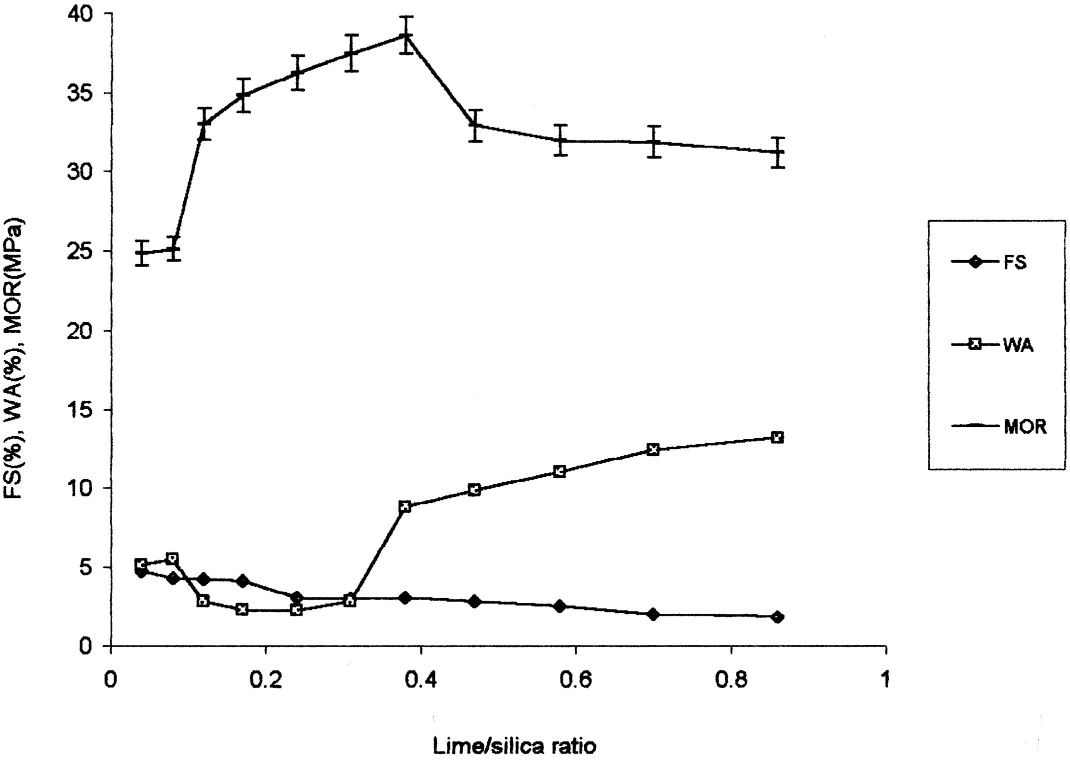

Fig. 2. Effect of lime–silica ratio on firing shrinkage (FS), water absorption (WA) and flexural strength (MOR) when fired at 1150 °C.

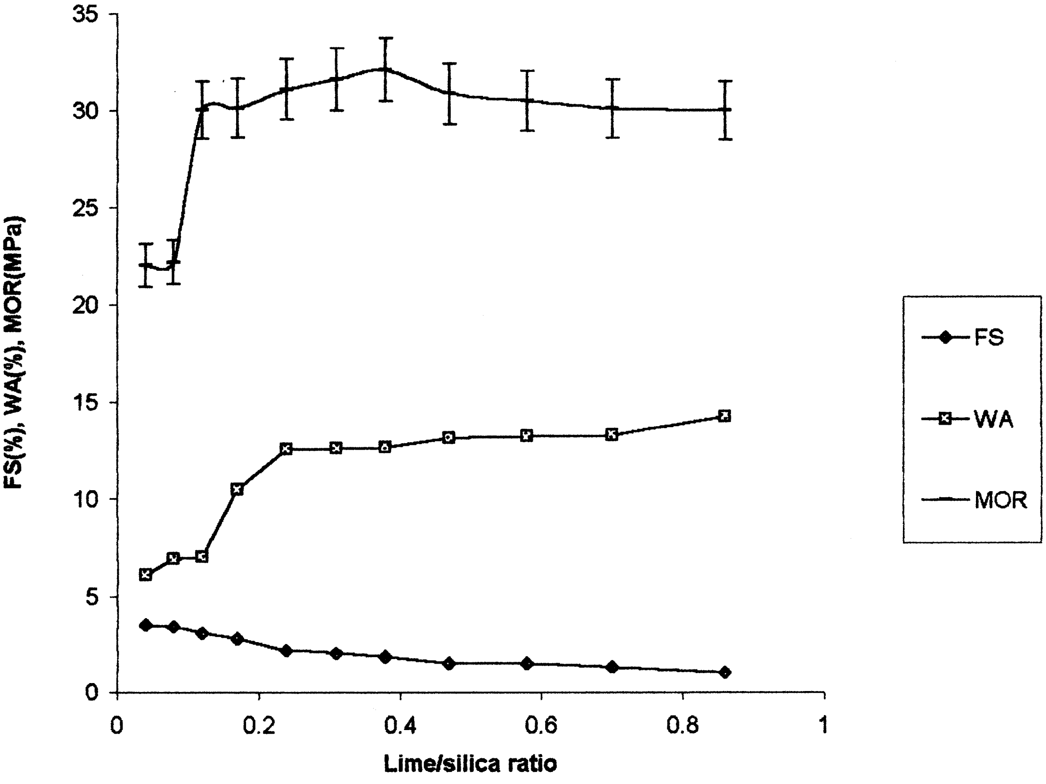

Fig. 3. Effect of lime–silica ratio on firing shrinkage (FS), water absorption (WA) and flexural strength (MOR) when fired at 1175 °C.

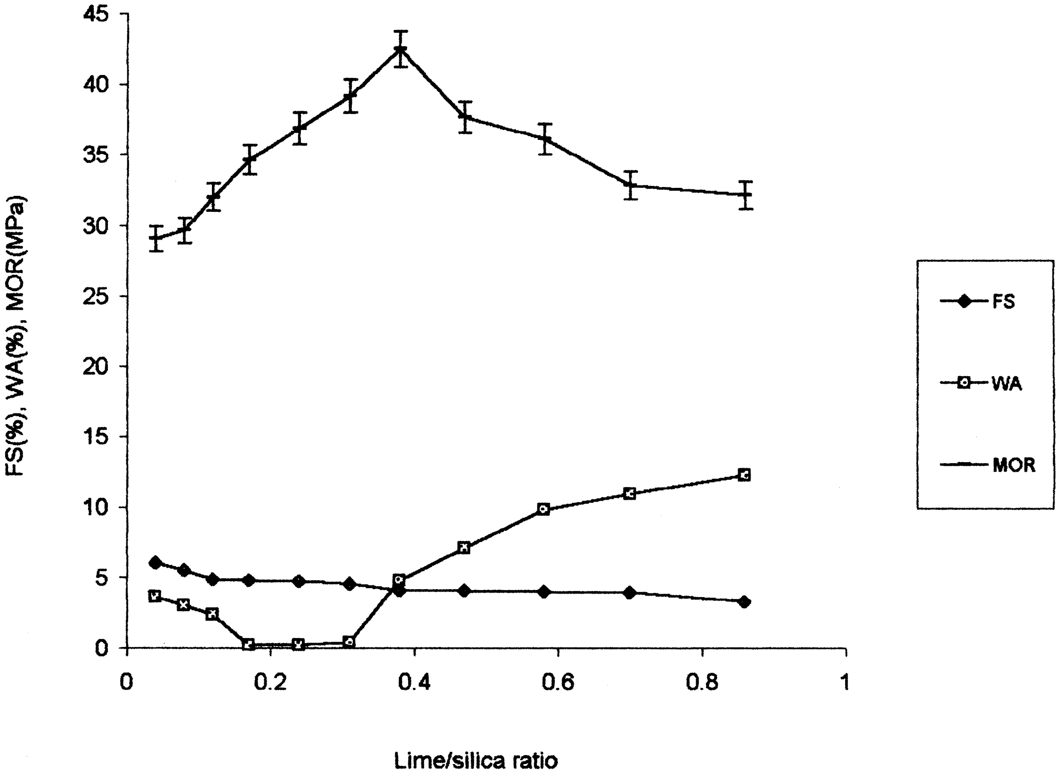

Fig. 4. Effect of lime–silica ratio on firing shrinkage (FS), water absorption (WA) and flexural strength (MOR) when fired at 1200 °C.

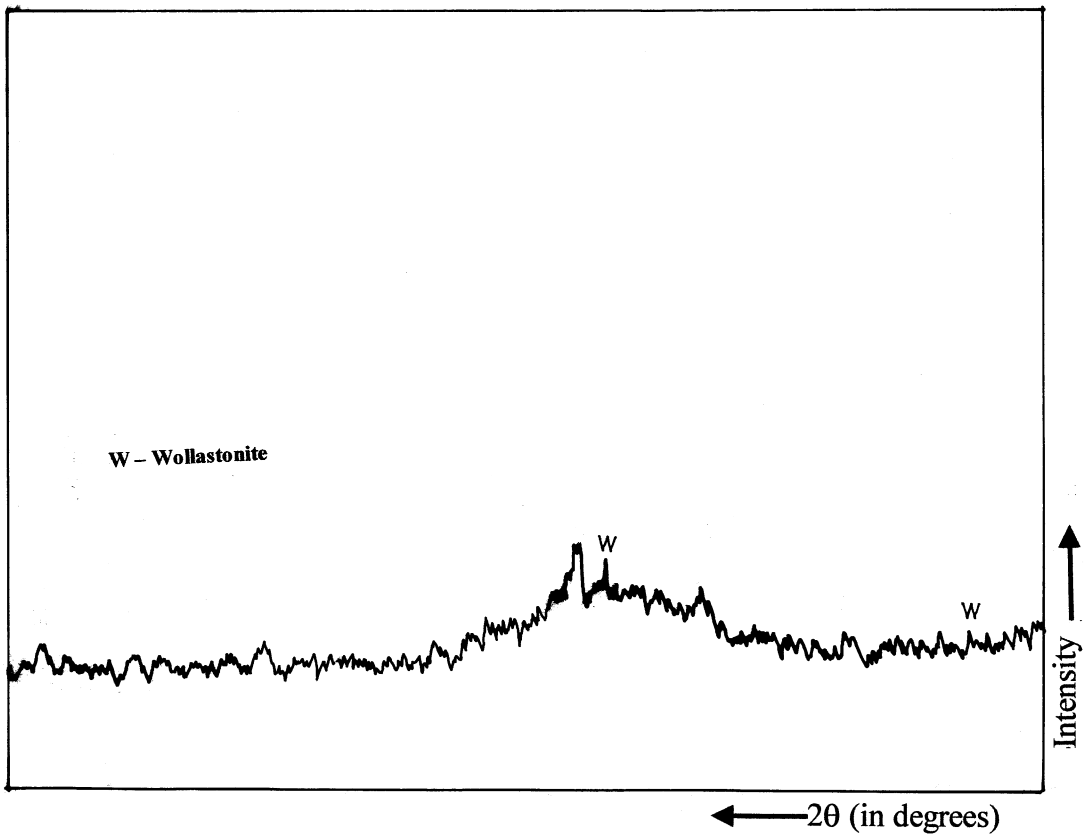

Fig. 5. XRD diagram of granulated blast furnace slag.

Table 6
General feature of microstructure of sintered specimens 2 and 6

Sample No.	Sphericity of grains	Aspect ratio of grains	Equivalent diameter(μm)	% of grains of less than (μm)				
				10	20	30	40	50
2	1.03–1.07	1.10–1.25	9.27–46.99	6.7	33.3	40.0	13.3	6.7
6	1.02–1.16	1.11–1.38	5.59–27.98	53.8	38.5	7.69	None	None

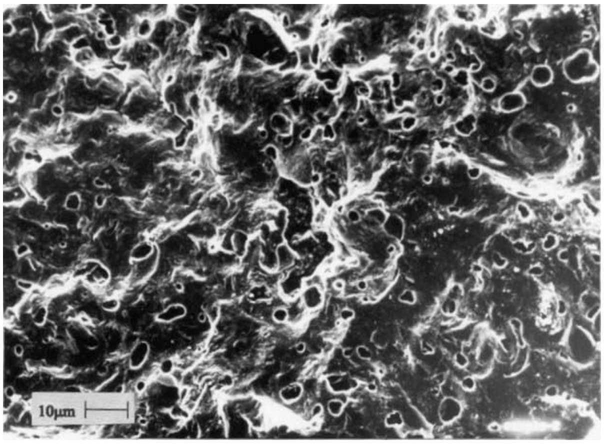

Fig. 6. Microphotograph of SEM of sample No. 2 fired at 1200 °C.

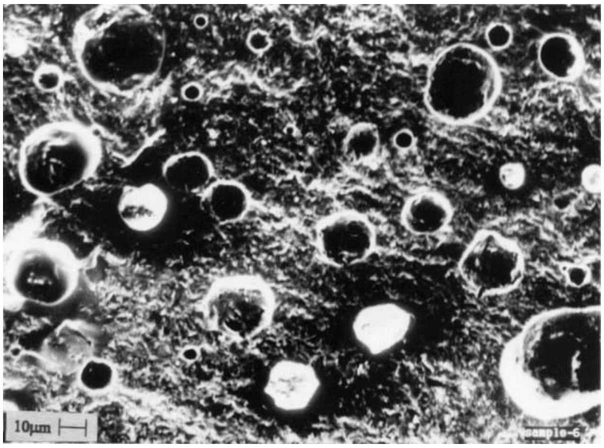

Fig. 7. Microphotograph of SEM of sample No. 6 fired at 1200 °C.

composition range was found with calcia–silica ratio in the range of 0.1–0.3 in which desirable properties of the sintered product could be achieved. This was due to sufficient wetting of different crystalline phases such as wollastonite by formed liquid.

SEM of the two samples is shown in Figs. 6 and 7 which represents sample No. 2 (containing 90% common clay and 10% GBFS) and sample No. 6 (containing 50% common clay and 50% GBFS). A study of the microstructure of the two samples revealed that the sample no. 2 contains larger crystals and more glassy phase whereas in sample No. 6 a large number of small crystals were embeded in less amount of glassy phase.

The microstructure was analysed and the general feature of two micro-structures is given in Table 6.

It appears from Table 6 that sample 6 contains much larger number of grains (compared to sample No. 2) of sizes less than 10 μm equivalent dia. Sample No. 6 contains no grains having sizes more than 30 μm equivalent dia. The mean (statistical) diameter of grains in sample 2 is 23.155 μm (S.D. = 9.78 with S.E. = 2.53) and sample 6 is 12.217 (S.D. = 5.95 and with S.E. = 1.65). This is one of the factors for the increase in the mechanical strength of the sintered compacts containing larger amount (not exceding 50%) of GBFS.

4. Conclusions

1. Ceramic tile could be made from a synergistic mixture of granulated blast furnace slag and common clay.
2. Composition that maintained calcia–silica ratio in the range of 0.1–0.3 were found to be optimum in which desirable properties of the sintered product could be achieved.
3. The increase in mechanical strength of the sintered specimen with increasing amount of GBFS upto 50% was due to the formation of large number of smaller grains embeded in the glassy matrix.
4. Use of higher amount of GBFS beyond the optimum composition range was found to be counter productive due to insufficient liquid formation at the sintering temperature.

Acknowledgements

The authors are thankful to the Director, CGCRI for his kind constant encouragement and permission to publish the work. Authors are also thankful to XRD, SEM and Analytical Chemistry Division for their constant cooperation for various testing in connection with the study.

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