

# Use of South African blast-furnace slag for ceramic purposes

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## SYNOPSIS

A method is described whereby finely ground glassy granulated blastfurnace slag mixed with small quantities of clay, whiting and quartz has been used for making ceramic tiles in the laboratory. The tiles were semi-dry pressed and devitrification as well as sintering occurred during firing. The properties of the resulting product compared favourably in many respects with ordinary ceramic flooring materials.

## INTRODUCTION

Blastfurnace slag, a waste product from steel plants, is at present being used for many purposes. Air-cooled, it is used as aggregate for concrete, for road making and as a fill under buildings and engineering structures. A large proportion of slag is quenched in water resulting in a glassy granulated slag with latent hydraulic properties. In a milled form it is used for the manufacture of portland blastfurnace cements and, overseas, for supersulphate slag cement. Slagwool prepared from molten slag is used as an insulating material.

Slag bricks of a simple shape are produced overseas by pouring the molten slag into cast iron moulds. During cooling partial crystallization of the slag takes place, resulting in crystals embedded in a glassy phase; the amount of glass in the bricks varies considerably, depending on the rate of cooling. The bricks produced in this way are porous, of medium hardness and are used for the construction of floors and pavements.

When glassy granulated slag is reheated to about 800°C devitrification takes place and a crystalline slag results.<sup>1</sup> This behaviour of the glassy slag is similar to that found in glass-ceramics and suggests the possible use of the material for the production of crystalline ceramic materials. A number of publications have been devoted to this subject.<sup>2,3,4,5</sup> In some instances the slag was remelted after the addition of certain additives such as sand and nucleating agents to obtain better control of the crystallization. Forming operations similar to those used for glassware were carried out and during a subsequent heat treatment nucleation and crystallization took place. One material known as 'Slagceram' obtained in this way has excellent properties for a number of applications.<sup>6</sup> The remelting of a mixture of slag and various additives at temperatures as high as 1 300° to 1 500°C to obtain a homogeneous melt reduces the economic advantages resulting from the cheapness of the raw material. Because of the high production costs only ceramic articles with special properties are made in this way.

Hinz, Müller and Wihsman<sup>7</sup> obtained a 'Sinterslag' material from a copper slag. The slag powder was dry pressed and the material after firing at 1 080° to 1 130°C in a reducing atmosphere had a very high strength and low porosity.

## THE RAW MATERIAL

Five different blastfurnace slags of South African origin were used for the present investigation. The chemical compositions of the granulated slags are given in Table I.

TABLE I

CHEMICAL COMPOSITION OF THE SLAGS (PER CENT)

Constituents	Slag No.				
	I	II	III	IV	V
SiO <sub>2</sub>	33.72	35.41	30.77	30.63	32.08
CaO	44.14	33.18	31.48	38.31	38.50
MgO	7.67	15.60	17.11	14.45	11.69
Fe <sub>2</sub> O <sub>3</sub>	1.99	2.27	2.49	0.87	0.74
Al <sub>2</sub> O <sub>3</sub>	13.53	11.72	15.62	13.98	13.57
S=	0.88	0.94	1.67	1.04	1.62
Na <sub>2</sub> O	0.27	0.22	0.28	0.24	0.49
K <sub>2</sub> O	1.03	0.74	0.60	0.57	0.42
TOTAL	100.23	100.08	100.02	100.09	99.11

All the above slags are of the 'basic' type with a SiO<sub>2</sub> content not higher than 36 per cent. The difference in the amounts of iron oxide caused a variation in the colour of the slags, viz from light grey (V) to brown (III). The iron was present partly in the form of FeO and partly of Fe and it had a strong influence on the sintering behaviour of the slag body.

X-ray diffraction analysis of the granulated slags showed that most of the slag material was in a glassy state. Only one of the five slags (III) indicated the presence of a small percentage of crystalline material.

Heating of the slags to a temperature of between 800° and 900°C resulted in crystallization. Up to a temperature of 1 160°C the bond between the particles was low, giving very little strength to a body formed from slag powder. At temperatures above 1 200°C sintering and partial melting of the slag took place. As the sintering interval for slag compositions is very small, certain additions to the slags had to be made.

## SPECIMEN PREPARATION

The five slags were mixed with clay, whiting, felspar and quartz powder in various proportions after which

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the mixtures were dry-milled to a fineness such that practically all the material passed a 200-mesh Tyler screen.

The mineralogical composition of the clay, in the following order of relative abundance was: kaolinite, illite, quartz, pyrophyllite and felspar. The amount of quartz in the clay was approximately 22 per cent while the felspar represented less than five per cent.

Different quantities of water were used to mix these materials and tiles were pressed in a flypress at a maximum pressure of 20 N/mm<sup>2</sup>. It was found that 10 per cent water sufficed for mixing and pressing and the tiles were sufficiently strong for handling. However, the addition of 0.5 per cent of ethyl cellulose ether to the water improved the dry strength to some extent.

After drying at 110°C for approximately 16 hours the tiles were fired in a global electric furnace to temperatures ranging between 1 200° and 1 250°C depending on the slag used as well as on the composition. The heating rate was approximately 1°C/min and the soaking time 4–5 hours, followed by slow cooling.

Initially the tiles warped but this problem was solved by variation of the clay content. Good results were obtained by incorporation of certain amounts of wollastonite into the mixes but because of economic considerations it was decided against the further use of this material as an additive. Replacing of wollastonite by quartz powder and whiting produced surface defects in the form of blisters but when the amount of quartz was reduced the blisters disappeared and good results were obtained. It was found that whiting and quartz allow good control over the sintering behaviour of the slag body, which is necessary to compensate for the normal fluctuations in the slag compositions. An increase in whiting increased the sintering temperature while an increase in quartz or felspar decreased the sintering temperature. Table II gives the chemical compositions of the materials used as additives.

TABLE II

CHEMICAL COMPOSITION OF ADDITIVES (PER CENT)

Constituents	Clay	Whiting	Felspar	Quartz
Fe <sub>2</sub> O <sub>3</sub>	1.03	0.01	0.03	0.01
SiO <sub>2</sub>	59.85	1.95	66.66	99.31
Al <sub>2</sub> O <sub>3</sub>	28.61	0.30	18.81	0.42
CaO	0.93	51.71	0.36	0.21
MgO	1.24	3.38	—	—
K <sub>2</sub> O	0.58	—	9.99	—
Na <sub>2</sub> O	0.34	—	3.75	—
TiO <sub>2</sub>	0.82	—	—	—
L.I.	6.44	42.70	0.17	—
TOTAL	99.84	100.05	99.77	99.95

Various properties of the fired specimens such as modulus of rupture, water absorption, bulk density, specific gravity, true porosity and resistance to abrasion were determined.

The modulus of rupture was determined on specimens 70 mm × 35 mm × 10 mm with 50 mm between the knife edges. For determining the water absorption the specimens were boiled in water for five hours and then allowed to soak in the water for 24 hours. The specific gravities were determined on powdered (—100 mesh Tyler) portions of the tiles.

Full-size tiles of 70 mm × 70 mm × 10 mm were abraded with carborundum (SiC) with a particle size of approximately 0.42 mm — 0.59 mm and a hardened mild steel disc revolving at 400 rev/min under a load of 120 N. The grinding area was 1 766 mm<sup>2</sup> and the grinding time 2.5 minutes.

## PROPERTIES

The compositions given in Table III were the most promising for making floor tiles and all the tests were carried out on them.

TABLE III

COMPOSITIONS

Materials used	Compositions (per cent)					
	1	2	3	4	5	6
Slag I					37.5	37.5
Slag II		75.0				37.5
Slag III	75.0				37.5	
Slag IV			76.0			
Slag V				77.0		
Clay	7.2	6.0	8.0	8.0	7.2	6.2
Whiting	10.0	11.2	9.0	10.0	10.0	11.0
Felspar	7.8	7.8			7.8	7.8
Quartz			7.0	5.0		
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0

Before firing, the tiles were light-grey in colour but changed after firing to rather pleasing shades of brown, light-brown, yellow-brown and off-white. By intermixing the slags in various proportions a further range of colours was obtained. Almost any shade of colour can be obtained by adding ceramic body stains to the slag mixes.

The properties of the experimental tiles were compared with those of commercial split and quarry tiles and as can be seen from the data in Table IV the slag tiles compare favourably in some respects with these commercial tiles. They are denser and have lower water absorption and higher resistance to abrasion (lower values of cm<sup>3</sup>/cm<sup>2</sup>). As could be expected, these tiles do not have a high resistance to acid attack. When the A.S.T.M. method (boiling in sulphuric acid for 48 hours) was used to determine acid resistance, the material disintegrated into a fine powder.

Of the compositions made, Nos. 4 and 3 gave the best results and also had the lightest colour (off-white).

X-ray analysis on powdered (—200 mesh Tyler) portions of the tiles showed that they were well crystallized. Melilite, a solid solution between akermanite

(2 CaO.MgO.2 SiO<sub>2</sub>) and gehlenite (2 CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>)<sup>8,9</sup> was the major phase present in all the tiles; some spinel (MgO.Al<sub>2</sub>O<sub>3</sub>) also occurred.

TABLE IV  
PROPERTIES

Com-positions	Linear firing shrinkage (%)	Modulus of rupture N/mm <sup>2</sup>	Water absorption (%)	Bulk density g/cm <sup>3</sup>	Specific gravity	True porosity (%)	Abrasion cm <sup>3</sup> /cm <sup>2</sup>
1	9.5	43.80	0.20	2.47	3.01	17.96	0.139
2	10.6	35.70	0.14	2.46	2.98	17.44	0.125
3	10.6	53.99	0.17	2.56	2.98	14.08	0.104
4	11.0	48.16	0.18	2.64	3.01	12.30	0.087
5	9.6	44.92	0.14	2.46	2.96	16.90	0.128
6	9.4	44.72	0.24	2.48	2.97	16.49	0.135
Split tile	—	—	1.56	2.37	2.64	10.22	0.170
Quarry tile	—	—	12.31	2.04	2.75	25.83	0.72

The apparent discrepancies in the values of the modulus of rupture in relation to porosity for the different compositions could possibly be related to the amount of glass phase present and the crystal size of crystalline phases. Microscopic examination of the tiles made from compositions 3 and 2, which had the highest and lowest modulus of rupture respectively, showed that composition 3 had less glass phase, less iron and smaller crystals than composition 2.

It should be noted that the sintering range was small and that the furnace atmosphere and heating rate had a strong influence on the sintering behaviour. Best results were obtained in a furnace with a neutral to slightly reducing atmosphere.

## CONCLUSIONS

Utilization of blastfurnace slag for the production of ceramic articles offers the possibility of obtaining a high quality product for a wide range of applications. It was found that the above compositions for ceramic tiles could be shaped by extrusion after organic plasticizers were added but this method of shaping resulted in a higher shrinkage of the final product. Casting of slag body compositions to form articles of a more complicated design was also successfully carried out as well as the application of a ceramic glaze to the articles in a second firing cycle.

Generally the production of slag ceramics would be of interest if it could be done in co-operation with a blastfurnace steel plant or if the slag offered economic advantages over conventional raw materials. From the technical point of view the use of slag in the manufacture of floor tiles holds promise and warrants further work in this field.

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