Abstract

Thermal behaviour of reverberatory furnace copper slag was investigated using simultaneous thermal analysis (STA), dilatometry and X-ray diffraction techniques. The results were used to study the effect of progressive addition of copper slag to a standard floor tile body formulation. It was observed that SO₂ emission at high temperatures resulted in bloating of the bodies, limiting the possibility of slag addition to a maximum of 40 wt%. The most promising body, containing 40 wt% copper slag, after firing at 1025 °C for 1 h had a bend strength of 57 MN m⁻², water absorption of 2 wt%, hardness of 750 HV and a very good acid resistance.

1. Introduction

Slags, industrial by-products from metallurgical plants, have found many diverse applications, from production of hydraulic cements to ceramic building products and glass-ceramic materials. In the field of building ceramics, many investigations have been carried out on the use of slags, especially iron slags, as a raw material in the formulation of wall and floor tiles. Mizdut [1] reported on the production of wall tiles with no firing shrinkage containing up to 65 wt% iron slags. Myers et al. [2] have formulated wall tiles containing 25 wt% iron slag, exhibiting a firing shrinkage of < 1%. In Italy [3], 25–40 wt% iron slags have been added to a mixture of clays to produce wall tiles of good mechanical strength, and less than 1% firing shrinkage on 30 min firing cycles. Del Bufalo [4], Mascolo et al. [5], Ser-sale et al. [6] and Colella et al. [7] have also formulated various iron slag containing bodies in the field of building ceramics. In Iran [8] wall tile bodies containing 30 wt% blast furnace slag were formulated which after 5 min firing at 1060 °C gave a bend strength of 24 MN m⁻², water absorption of 16 wt% and a firing shrinkage of 0.1%. Nel and Tauber [9] used up to 75 wt% South African iron slags in the formulation of floor tiles and bodies of 0.2 wt% water absorption and bend strength of 43.8 MN m⁻² were obtained. Hinz et al. [10] processed a “sinter slag” material from a copper slag, which after dry pressing and firing at 1080–1130 °C in a reducing atmosphere, exhibited a very high strength and low porosity.

In the present investigation an Iranian copper slag was used for the first time in formulating unglazed floor tiles and the reaction sequences, phase compositions developed at each stage of firing and the physical properties of fired products were investigated.

2. Experimental procedure

2.1. Raw materials

Local raw materials, namely a reverberatory furnace copper slag from the Iranian National Copper Industries Co., a pyrophilitic clay (clay A) from Abadeh, a very plastic clay (clay B) from Latian, a feldspatic sand (sand C) and a quartzous sand (sand D) were used. The chemical and mineralogical compositions of these materials are given in Tables 1 and 2, respectively. A base body composition was first formulated by using the clay and sand constituents and then the slag was added to it to make the experimental body compositions.

Tables 3 and 4 give the base body composition and the composition of experimental bodies on raw material
2.2. Powder preparation and processing

A batch of base composition was first prepared by wet grinding raw materials in a ball mill for different times to obtain a residue of 5–7 wt% on a 63 μm (230 ASTM) mesh sieve. After drying the slurries, the experimental body mixtures were prepared by combining the base body batch with ground slag in different proportions according to Table 4. The mixtures were wet ground in a fast mill for 5 min and dried. The dried bath mixtures were then brought to a moisture content of 5 wt%, left to equilibrate for 24 h in a closed container and then were forced through a 0.84 mm (20 ASTM) mesh sieve for granulation purposes. The granulated powder were pressed in two steps using a laboratory hydraulic press, into 50×50×5 mm tiles, at initial and final pressures of 12 and 35 NM m⁻², respectively.

2.3. Firing

The specimens after drying at 110°C in a laboratory dryer, were fired at 1000, 1025, 1050 and 1075°C in an electric furnace at a rate of 5 K min⁻¹.

To identify the phases developed at different stages of firing, the specimens were taken out of the furnace after a 1 h soak at each predetermined temperature. For the determination of linear shrinkage, water absorption and bend strength the specimens were furnace cooled after soaking at the peak temperature for 1 h.

2.4. Properties characterisation

The linear shrinkage, water absorption, bend strength and microhardness were determined for each specimen. For the linear shrinkage the length of each specimen was measured to 0.05 mm before and after firing. For the linear shrinkage the length of each specimen was measured to 0.05 mm before and after firing.

Water absorption was determined according to the procedure described in ASTM C373 [11]. The bend strength was measured in four point bending with spans of 40 and 20 mm on an Instron universal testing machine using rectangular bars of 45×14×5 mm dimensions. On average six specimens were used for each strength measurement. The microhardness was measured by the Vickers diamond pyramid test, on polished specimens. Five indentations were made for each specimen with a time of 30 s at a load of 200 g.

The materials were also characterised by X-ray diffractometry (XRD), simultaneous thermal analysis.
(STA) and dilatometric techniques. The heating rates were 25 and 5 K min⁻¹ in STA and dilatometric tests, respectively.

3. Results and discussion

3.1. Fired properties

Fig. 1 shows that all specimens exhibited a permanent shrinkage after 1 h heating at 1000°C. Increasing the soaking temperature from 1000 to 1025°C resulted in more intense shrinkage, but a further temperature increase up to 1075°C first reduced the shrinkage and then caused a marked expansion in all slag containing specimens. The results of water absorption vs firing temperature shown in Fig. 2 indicates that by increasing the soaking temperature from 1000 to 1025°C the water absorption was decreased, due to the densification of specimens as a result of sintering. A further temperature increase from 1025 to 1075°C resulted in considerable water absorption increase. The bend strength vs firing temperature results shown in Fig. 3 indicates that by increasing the soaking temperature from 1000 to 1075°C the bend strength was first increased (1000–1025°C range) and then decreased, supporting the linear shrinkage and water absorption results. These results all suggest the possible occurrence of a bloating process in the slag containing specimens in the 1025–1075°C range.

3.2. STA (DTA/TG) results

Fig. 4 depicts the STA results performed on a copper slag specimen. The TG curve reveals the occurrence of a marked weight gain in the 374–989°C range, following by a weight loss from 989 to 1040°C and a nearly constant weight region of 1040–1200°C. The exothermic peaks at 516 and 767°C in DTA trace can be related to the magnetite→maghemite and maghemite→hematite transformations, respectively [12]. The endothermic dip at 1040°C probably can be associated with the slag melting.

3.3. X-ray diffractometry

Fig. 5 illustrates the slag XRD patterns at various stages of firing. The major crystalline phases present after firing at 400°C were fayalite (2FeO·SiO₂), magnetite...
(Fe₃O₄), hedenbergite Ca(Fe,Mg)(SiO₃)₂ and hematite (α-Fe₂O₃). By increasing the temperature to 600°C the magnetite peaks disappeared from the XRD pattern, whereas the maghemite (γ-Fe₂O₃) peaks appeared and the fayalite peak heights decreased. As the temperature rise continued maghemite and fayalite peaks disappeared in the 700–800 and 600–1000°C ranges, respectively.
3.4. The cause of bloating

From the STA and XRD results it can be concluded that the weight gain observed in the 374–989°C range (Fig. 4) is mainly due to the oxidation of fayalite according to the following reaction:

\[
2\text{FeO} \cdot \text{SiO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \alpha - \text{Fe}_2\text{O}_3 (\text{hematite}) + \text{SiO}_2 \quad (1)
\]

The absence of any silica peaks in the X-ray diffraction patterns indicated the possible amorphous structure of the silica phase formed according to reaction (1) above. The weight loss observed >989°C (Fig. 4) can probably be associated with the oxidation of copper and iron sulphides present in minor amounts in the copper slag. To verify this deduction the furnace exhaust gases were analysed at different temperatures and the presence of SO\(_2\) was confirmed in the temperature range of 800–1200°C. Therefore it can be concluded that the weight loss due to the oxidation of sulphides was counter-balanced by the weight gain of fayalite oxidation up to 989°C, above which the weight loss process predominated. Above 1040°C the partial melting of slag probably prevented the gas escape and stopped the weight loss process.

To verify the cause of the endothermic dip observed at 1040°C in the DTA trace, a dilatometric test was performed on the slag. As shown in Fig. 6 the considerable shrinkage of the specimen in 975–1000°C range, confirms our previous assumption concerning the commencement of the melting process in this temperature range. The difference observed in the peak temperatures of the DTA and dilatometric traces probably resulted from the different heating rates employed in these tests. Considering the experimental evidence, the bloating of specimens can therefore be attributed to the SO\(_2\) emission accompanied by partial melting of slag, preventing free gas escape. Obviously the slag viscosity which depends on the composition and temperature is the most significant factor in this connection. This fact explains the observed differences regarding the behaviour of various specimens in the dimensional change vs temperature experiments. For example, specimen D, containing 60 wt% slag, exhibited the largest thermal expansion (bloating) >1075°C (Fig. 1), whereas specimen F (pure slag) showed almost no dimensional change at this temperature. This can be attributed to the composition differences. Specimen D containing more silica and less iron oxide was more refractory and developed a melt of higher viscosity, which in comparison with the liquid phase of composition F, prevented the gas escape more severely and caused more extensive bloating.

3.5. The most promising specimens

Fig. 7 shows the dimensional changes for different specimens in the 1000–1050°C range. It can be seen that specimens B and C showed the best tolerance towards temperature changes. These specimens also exhibited acceptable values for bend strength and water absorption. Specimen C containing more slag, which after firing at 1025°C gave a bend strength of 57 NM m\(^{-2}\), 2 wt% water absorption and a microhardness of 750 VH\(_{(200)}\), can be used as a standard unglazed floor tile.

3.6. Acid resistance

The presence of relatively little alkali oxides and large amounts of Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\) in the composition of specimen C, indicated the possibility of a high resistance to acids for these specimens. Performance of an acid
resistance test according to the procedure described in the ASTM C279 [13] revealed the excellent resistance of them against mineral acids (Type III for use where minimum absorption and maximum acid resistance are required), with higher water absorption values, but a very low weight loss (<2 wt%) as compared to the requirements of the ASTM standard.

4. Conclusions

1. Addition of 20–80 wt% copper slag to a standard floor tile composition increased the firing shrinkage and bend strength values and decreased the water absorption, up to a firing temperature of 1025°C, for all specimens.

2. The increase of firing temperature from 1025 to 1075°C reversed the firing behaviour of all slag containing specimens, resulting in lower bend strength and higher water absorption values owing to occurrence of a bloating process.

3. Performance of STA (TG/DTA) and XRD tests on copper slag revealed the transformations of fayalite to hematite and amorphous silica, magnetite to maghemite and hematite and emission of SO₂ due to the oxidation of sulphides.

4. Emission of SO₂ was mainly responsible for the occurrence of the bloating process.

5. An optimum slag content, which in the present investigation was 40 wt%, may be found which gives the best combination of properties.

6. The most promising specimens had a high resistance to mineral acids and may be used as acid resistant tiles.

References