4 Stability of Commercial Grazes on Ceramic Bodies

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ABSTRACT

Undesirable defects of network of cracks (crazing) are investigated in commercial glazes applied on two ceramic exterior wall tiles, one of which comparatively, had high thermal coefficient of expansion and the other had low thermal coefficient of expansion. The study shows that R_2O_3 and RO_2 components of the glazes and the expansible characteristics of the tiles affect Δ warpage of the glazed tiles, which phenomenon subsequently results in failures of crazing after autoclave test.

Keywords: glazes, coefficient of expansion.

INTRODUCTION

Delayed network of cracks in glazes applied on individual whitewares is a menace both to the manufacturer and user of ceramics. A ceramic glaze is not only meant to cover blemishes in order to render the ware on which it is applied more pleasing to the eye and touch but also to render the ware mechanically strong and readily cleanable.

The first requirement for a ceramic coating is derived from the fact that it must be applied to and bond with the substrate on which it is applied[1]. On cooling from the glazing temperature the coated substrate contracts. The coefficient of expansion of the coating and the body on which the glaze is applied must be sufficiently close together in order to eliminate stresses and strains which result in crazing. Although the expansion and the substrate should be close, they should not be identical [2].

Crazing in most glazes are not visually observable immediately after firing, but rather results after sometime of usage of the ceramic. This delayed crazing appears mostly in washing basins, toilet bowls, wall tiles and other ceramic wares resulting in weaknesses and unsightly look of the ceramic.

It is the aim of the author to study the durability against time of use of experimental glazes designed for commercial applications. In this exercise Δ warpage measurements and autoclave tests were conducted alongside the examination of the effect of the variable components (R_2O_3 and RO_2) of the glazes in order to ascertain the usefulness and durability of these glazes.

EXPERIMENTAL PROCEDURE

The formula,

$$\begin{matrix} 0.15KNaO & \\ 0.425CaO & xAl_2O_3 \\ 0.525ZnO & ySiO_2 \end{matrix}$$

was employed for the composition of glazes in which x, y, represented mole equivalent variables. Details of these variables are presented in **Figure 1**. These variables offered twenty glazes composed from raw materials whose characteristics are shown in Table 1.

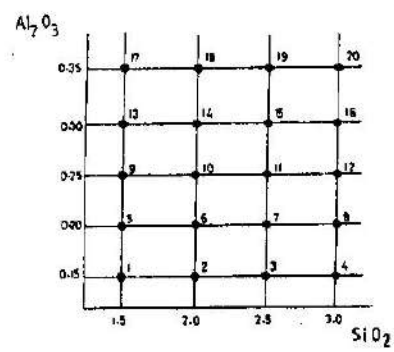

Fig.1. SiO_2 and Al_2O_3 mole equivalents of glaze

Each glaze was applied on the surfaces of two different exterior wall tiles labelled A and B received from a manufacturer. Tile A was reported by the manufacturer as having a high thermal

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Table 2: Physical characteristics of fired clays.

Raw Materials	Formula	Mol. Weight
Feldspar	$0.45K_2O$	476.0
Lime stone	$CaCO_3$	100
Zinc Oxide	ZnO	81.4
Clay	Al_2O_3 $2,3SiO_2$ $2.62H_2O$	289
Silica Sand	SiO_2	60.1
Alumina	Al_2O_3	102

coefficient of expansion, while tile body B was reported to have low thermal coefficient of expansion. Twenty tiles of each kind were used for each glaze which was applied by waterfall method permitting $8.0 + 0.2/100cm^3$ of glaze on each tile. The glazed tiles were fired to 1150°C for a duration of 30 minutes in a laboratory roller hearth kiln. Their glost fired characteristics are shown in Figure 2. After firing the warpages of the glost fired samples were measured. Before undertaking the glost fire, however, the warpage of the bisque fired

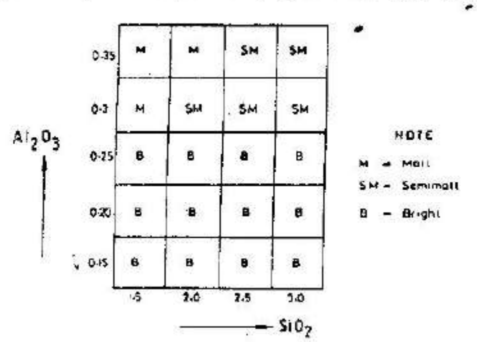


Fig. 2 Glaze appearance on tile at 1150 °C

tiles, as received, were measured. The difference in the warpage measurements of the bisque and glost fired tile, gives the ∆ warpage of a tile. The warpage was measured by a special electronic and computerised equipment designed for this purpose. The average reading of the four corners of each tile gives the value of the warpage of tile.

After working out the ∆ warpage of all glazed tiles they were put in an autoclave for the study of the effect of moisture on them. A vapour pressure of $10Kg/cm^3$ was exerted on the glazed tiles for a duration of 1 hour.

RESULTS AND DISCUSSIONS

All glazes were visually observed to be good glazes, fitting the tile bodies as received after glost firing at 1150°C. The characteristic features of these glazes were glossy or bright, semi-matt and matt (Fig.2). The bright tile, it was noted, had gradation of crystals development embedded in the glassy matrix, while the matt glazes had well developed crystals of anorthite, gahnite and quartz[3].

From the examination of the experimental Zeger formula it can be deduced that for any physical or chemical changes to result in heat processing it is only the variables of R_2O_3 and RO_2 which should effect any changes as the mole equivalents of RO and R_2O are constant in all glazes composed. This observation warrants the study of the effect of these oxides on the glazes.

In order to examine the effect of Al_2O_3 and SiO_2 on the physical characteristics of the glazes a careful study is made of ∆ warpage of tiles against Al_2O_3 content on one hand and against SiO_2 content on the other. Later the glazes were subjected to autoclave test for the study of the effect of moisture absorption by the glazed tiles. The study results are shown in Figures 3, 4 and 5.

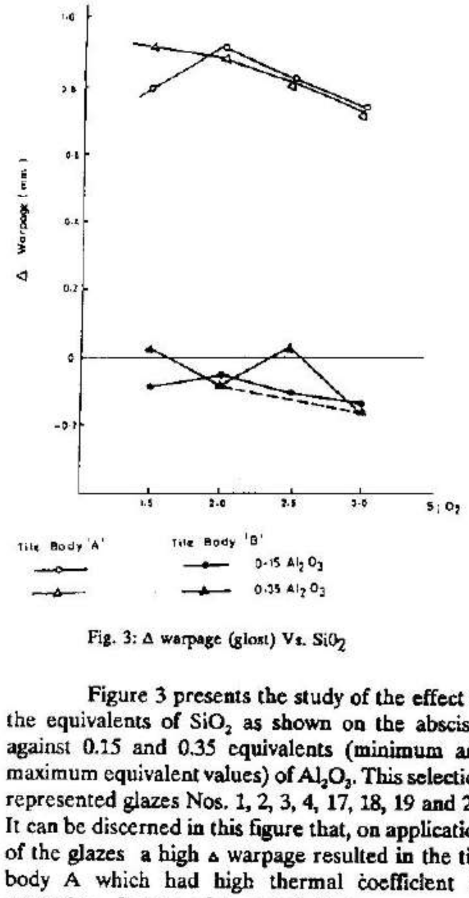


Fig. 3: ∆ warpage (glost) Vs. SiO_2

Figure 3 presents the study of the effect of the equivalents of SiO_2 as shown on the abscissa against 0.15 and 0.35 equivalents (minimum and maximum equivalent values) of Al_2O_3. This selection represented glazes Nos. 1, 2, 3, 4, 17, 18, 19 and 20. It can be discerned in this figure that, on application of the glazes a high ∆ warpage resulted in the tile body A which had high thermal coefficient of expansion. It was also noted that warpage ∆ decreases linearly as the SiO_2 content increases

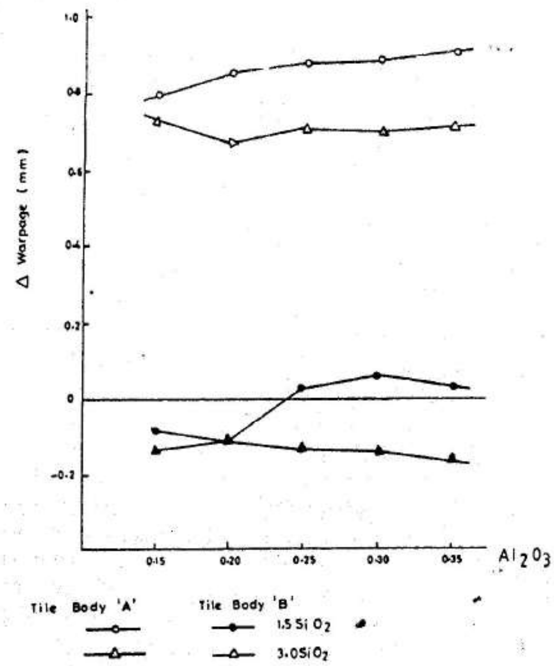


Fig. 4: Δ warpage (glost) Vs. Al_2O_3

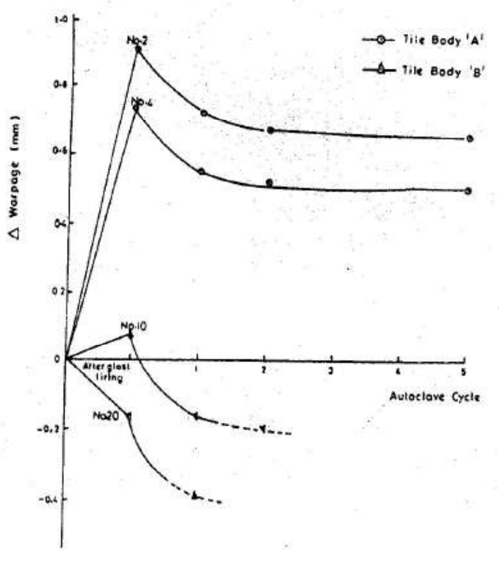


Fig. 5: Δ warpage Vs. Autoclave cycle

except at 1.5 mole equivalents of SiO_2. Between the equivalents of 0.15 SiO_2 and 2.0 SiO_2 warpage increases as silica has formed a glass[3]. This glass phase should decrease thermal expansion of the glazes[4] but rather Δ warpage of the tiles increases. After the equivalents of 2.0 SiO_2, silica formed quartz crystals[3] which should increase the thermal expansion of the glazes thereby lowering warpage. The linear decrease as stated above can be accounted for by the decrease in the anorthite, gahnite and quartz crystals content of the glazes[3] or precisely an increase in the glassy phase of the glazes.

Tile body B which had low thermal coefficient of expansion resulted in very low Δ warpage values with increase in SiO_2 content of the glazes. With SiO_2 content of 2.5 equivalents one finds that Δ warpage values slightly rises above zero. This phenomenon is thought to be an experimental error hence the experimental result is extrapolated from 2.0 to 3.0 equivalents of SiO_2 to bring about possible correction.

Figure 4 shows the study of the effect of equivalents of Al_2O_3 as stated on the abscissa in the presence of 1.5 and 3.0 equivalents (minimum and maximum values) of SiO_2. This choice represented glazes Nos. 1,4,5,8,9,12,13,16,17 and 20. Examination of tile body A shows that Δ warpage increases with increase in Al_2O_3 content of the glaze while the warpage reduced considerably in tile body B.

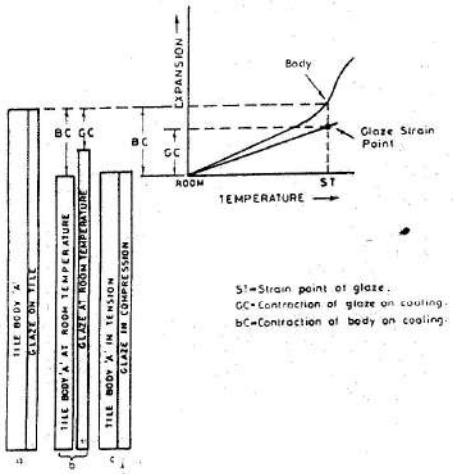
It was, however, noted that the Δ warpage results of all glazed tiles did not show any immediate results of crazing.

In order to investigate further the effect of possible stresses in the glazes against time of use the tiles were put in an autoclave and a vapour pressure of $10Kg/cm^2$ was exerted on them for 1 hour. It was noted that the tiles expanded with the absorption of moisture setting the glazes in tension. The results of this test are presented in Figure 5. In this figure, the autoclave cycles are plotted against large and small values of Δ warpage of the selected tiles. In this selection tiles of glaze Nos. 2 and 4 are representative samples of large Δ warpage values while tiles of glaze Nos. 20 and 10 are represntative samples of small Δ warpage values.

As can be discerned in the Figure 5, glazed tile body B has expanded by moisture absorption setting glaze Nos.20 and 10 in tension. Glaze No.20 with Δ warpage below zero could go through the autoclave test only once before failure of crazing sets in, while glaze No. 10 with Δ warpage 0.1 could go through only 2 cycles of test before crazing results.

On tile body A the glazes are found to be in compressive stress giving large Δ warpage values. It can be observed in figure 4 that glazes Nos. 2 and 4 successfully went through all five cycles of autoclave test. It is also observed from the test that Δ warpage reduced from 0.3mm to 0.2mm after the fifth cycle due to absorption of moisture by the tile body A in the autoclave test. The result demonstrates that a glaze in compression on a tile can also be placed in tension when the body on which it is placed absorbs moisture thereby reducing compressive values slightly. But this mechanism is not seen to affect crazing. The two glazes remain in compression, a characteristic feature all good glazes must have in order to avoid crazing.

The two characteristics of the effect of tensile and compressive streses in the glazed tiles in this study may be illustrated schematically in Figures 6 and 7 and 8. In Figures 6 and 7 ST is the temperature at which the glaze develops strain on cooling. In Figure 6 the body A shrinks by the amount BC while the glaze shrinks by the amount GC if they are separated. Since they are together, the glaze must be in compression while the body is in tension after cooling. This is a desirable and stable condition.

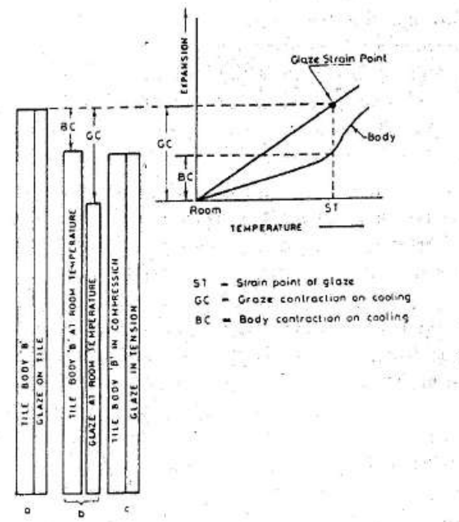


a. Relationship at strain point (ST).
b. Relationship between body and glaze (Seperated) at room temperature
c. Glaze in compression at room temperature.

Fig. 6: Expansion stress relationship in tile body 'A' (schematic)

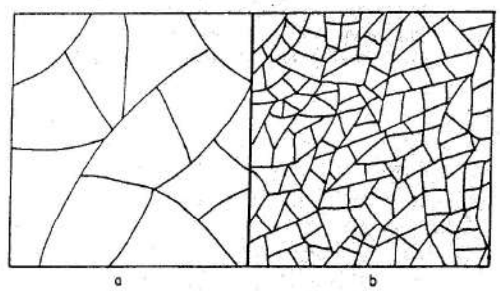
In Figure 7, the glaze contracts by the amount GC, while the body B contracts by the amount BC if separated. Since the two are bonded together the glaze is placed in tension by the body which is in compression. This is the condition for tensile crazing, the pattern of which is illustrated in Figure 8.

Figure 8 shows two chracteristic features on crazing phenomena normally observed on ceramic wares which are the result of tensile stresses developed in the glaze. Low tensile streses result in cracks with wide spaces in-between cracks in the glaze as shown in Figure 8a. High tensile stresses bring about fine network of cracks as shown in Figure 8b. The two features of crazing were observed in the experimental results.



a. Relationship at strain point (ST)
b. Relationship between body and glaze (Seperated) at room temperature
c. Glaze in tension at room temperature

Fig. 7: Expansion stress relationship in tile body 'B' (schematic)



a. Low stress in glaze.
b. High stress in glaze.

Fig. 8: Tensile crazing of glaze (schematic)

CONCLUSION

Variation in Al_2O_3 and SiO_2 content of glazes which have their bases (RO and R_2O) constant invariably affects the expansible characteristics of glazed tiles under study. The coefficient of thermal expansion of tiles is also observed to have an immense influence on the glazes applied on their surfaces as a high thermal coefficient of expansion of the tile conveniently put the glaze in compression only when its expansion is more than that of the glaze applied on its surface.

Any positive value of warpage that can go through the five cycles of autoclave can offer a durable glaze, as this value confirms compression in the glaze. But should the compression be too high it will result in shivering which was observed in some of the experimental results of tiles having very high warpage values.

Increased Al_2O_3 with decreased SiO_2 content ensures matt or cystalline glazes which can withstand tensile stresses without crazing because of the reinforcing nature of the crystal phase.

The test results give a clue to what may happen to the experimental glazes when used on the exterior tiles as received, particularly when exposed to moisture.

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