INFLUENCE OF KILN ATMOSPHERE AND TRANSITION METAL CONCENTRATION ON SHADES IN CERAMIC TILES

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The iron contained in clays is usually found as hematite (Fe_2O_3) and sometimes as hydroxides or oxides with a lower valence. At about 500°C, ferric hydroxide ($Fe(OH)_3$) converts to ferric oxide (Fe_2O_3), which is stable in an oxidising atmosphere (when oxygen partial pressure is greater than its decomposition pressure). When oxygen is lacking, which happens in some cases, hematite decomposition to a lower valence oxide (FeO) causes colour differences (shades) to arise.

Iron sulphate was added in different proportions to a previously selected, typical twice-fire composition. Cylindrical test specimens, 10 mm thick with a 25 mm, were formed on a laboratory press for this study.

The test specimens were fired in a fast-fire kiln in a controlled atmosphere, injecting oxygen at variable flow rates for each set of iron-containing specimen compositions.

These heat treatments involving atmosphere and chemical composition were accompanied by X-ray diffraction (XRD), differential thermal analysis (DTA) and reflectance spectrophotometry.

The ceramic phases in the fired compositions were identified by XRD, analysing the effect of iron oxide and atmosphere on phase formation. In this case, the specimens were powdered after firing.

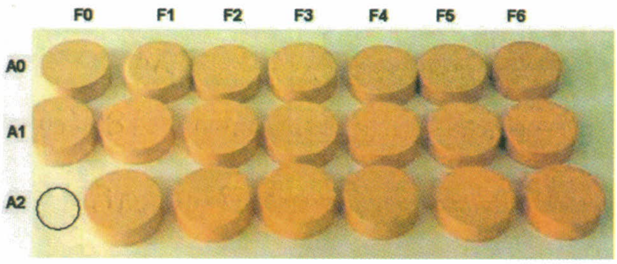

Figure 1. Photograph of the iron oxide-containing samples heat treated in different oxygen atmospheres. F0=starting composition; F1=0.8%Fe; F2=1.6%Fe; F3=2.4%Fe; F4=3.2%; F5=4.0%; F6=4.8%Fe; A0=with no oxygen in the kiln; A1=5l O_2/min; A2=10l O_2/min.

DTA served to monitor the reactions arising with the set atmosphere and iron additions. Powdered and unfired samples of the studied composition with iron additions (Fx) were used. The test started at room temperature and ran up to 1200°C at a heating rate of 10°C/min for all the specimens. The atmosphere involved (Ax) was held in the firing chamber throughout the test.

Reflectance spectrophotometry was used to determine the reflectance percentage of the samples at a given wavelength in the visible spectrum region.

The phases that appeared in the compositions with and without iron additions were basically the same. The difference was the diopside phase, which appeared as $Ca(Mg,Al)(Si,Al)_2O_6$ in the starting composition and as $Ca(Mg,Fe,Al)(Si,Al)_2O_6$ in the compositions to which iron was added.

As the difference lay in the diopside phase, this phase may be considered responsible for the variation in colour.

Diopside is a typical phase in the twice-fire process, and appears during heating of the material at temperatures exceeding 950°C from dolomite ($CaMg(CO_3)_2$), together with silica (SiO_2) and alumina (Al_2O_3) from the clayey minerals [5].

The photograph in Figure 1 shows the sets of specimens with their relative iron contents (F0 to F6) and oxygen flowrates used in the kiln (A0 to A3).

When oxygen was fed into the kiln (A1 and A2 compared to A0), the test specimens exhibited greater homogeneity. This appears indicative of the effect of oxygen atmosphere in eliminating or reducing shades. The opposite occurred when iron (FeSO4) was added in a neutral atmosphere (F4 and A0 compared to F6 and A0), which yielded a less homogeneous product.

The thermograms in Figure 2 show the reactions that arose in the material during firing in terms of kiln atmosphere and iron oxide concentration.

The reactions were found to become more endothermic as iron concentration rose and more exothermic as the oxygen flow increased. These findings matched the XRD data.

Figure 3 plots reflectance percentage versus wavelength.

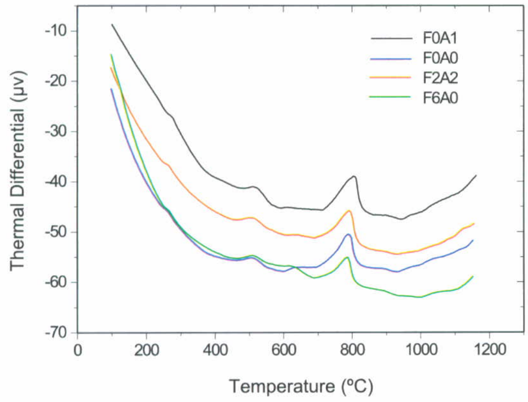

Figure 2. Differential thermal analysis (DTA) of the studied compositions, illustrating the effect of the iron oxide addition and oxygen atmosphere.

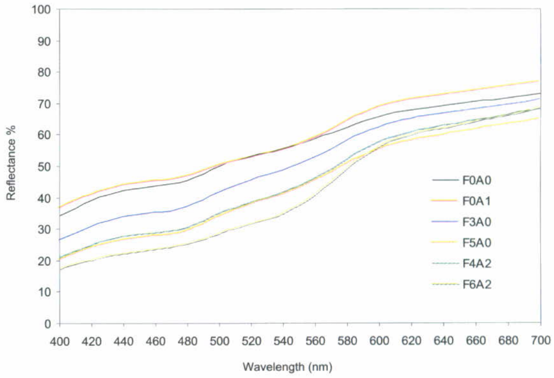

Figure 3. Reflectance percentage versus wavelength, showing the effect of the iron oxide addition and oxygen atmosphere.

It can be observed that reflectance increased when the atmosphere became more oxidising, which indicates that the difference in colour was smaller, while the opposite occurred when the iron concentration was raised in the specimens, which is agreement with the thermal analysis data.