CERAMIC PIGMENT OBTAINED FROM IRON ORE RESIDUE

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ABSTRACT

The objective of this work was to develop a pigment for ceramic glazes from residue of the beneficiation of iron ore. The residue was incorporated at 6% (mass) in suspensions (1.80 g/cm^3 density and 30 s viscosity) of white, transparent and matte glazes, which were applied as thin layers (0.5 mm) on engobed and not fired ceramic substrates, which were fired in laboratory roller kiln in a cycle of 35 minutes and maximum temperatures between 1050 and 1180 °C. The residue and glazes were characterized by chemical (XRF) and thermal (DTA and optical dilatometry) analyses, and the glazed tiles by colorimetry and visual analyses. The results showed that the pigment embedded in the transparent glaze results in a reddish glaze suitable for the red ceramic industry.

1. INTRODUCTION

The objective of this work was the development of a pigment for ceramic glazes derived from industrial waste from the beneficiation of iron ore, and the study of the pigment colour variation as a function of temperature and type of glaze.

2. EXPERIMENTAL

The iron ore waste– 12 000 tons of waste produced on daily basis – was provided by a Brazilian mining company. White, transparent and matte frits were used as glaze matrices. The chemical composition of the residue and frits was determined by X-ray fluorescence (XRF). The thermal behaviour of the frits was determined by optical dilatometry (heat stage microscopy) and for the residue by differential thermal analysis (DTA).The glaze compositions were made using 91.8% frit, 7% kaolin, 0.2% TPP and 1% NaCl (mass %). The samples were ground (10 min, 30% water) and 6 mass % of pigment (iron ore residue) was added in the suspensions of white, transparent and matt glazes. The pigmented glazes were applied (0.5 mm layer) as ceramic suspensions onto unfired and not engobed ceramic substrates (semi stoneware). In sequence the samples were fired in a gas laboratory roller kiln at the maximum temperatures of 1050ºC, 1100ºC, 1130ºC and 1180ºC with a cycle of 35 min. Finally, the fired samples were subjected to colour, texture and brightness tests of the glazed surfaces. The colour and brightness were determined by the spectrophotometric technique, using a spectrophotometer with spherical d-8 geometry (BYK-Gardner) with readings ranging from 400 nm to 700 nm, observation angle of 10º and D65 illuminant. The brightness was determined using the same equipment, but with reflection angle of 60º. The texture was determined visually.

3. RESULTS AND DISCUSSION

The results of the chemical composition of the frits and residue are shown in Table 1.

Element (mass %)	Transparent	White	Matte	Residue
Al_2O_3	7.2	7.5	3.4	2.3
B_2O_3	8.1	2.8	0.6	-
BaO	1.9	0.5	13.9	-
CaO	1.1	6.4	19.3	0.1
Fe_2O_3	-	-	-	71.7
K_2O	2.9	3.4	1.2	-
MgO	0.4	3.6	2.5	-
Na_2O	5.6	0.8	2.8	-
PbO	-	-	0.9	-
SiO_2	72.0	52.7	53.1	20.1
ZnO	0.1	10.3	1.1	-
ZrO_2	0.3	11.9	1.1	-
LOI	-	-	-	5.5

Table 1. Chemical analysis (XRF and AA) of the frits (%) and iron ore residue

The residue of iron ore used in this study as a pigment was characterized by differential thermal analysis, not shown. The thermogram indicates that between 80 and 550ºC the iron ore residue undergoes a mass loss of 5.7%, corresponding to an endothermic peak with a maximum at 328ºC, associated with the decomposition of some component of the residue, probably the transformation (dehydration) of goethite to hematite (Spinelli, 2002; Milanez *et al*., 2005, Bernardin *et al*., 2006). The addition of the pigment based on waste from processed iron ore alters the characteristic temperatures of all frits, Table 2. For transparent and matte frits the addition of the residue containing iron ore decreases the characteristic temperatures, but the addition of this residue increases the characteristic temperatures for the white frit. Probably the zinc and zirconium oxides present in the white frit are reacting with the iron oxides present in the iron ore residue, forming compounds with higher characteristic temperatures. This assumption must be confirmed by X-ray diffraction, not performed in this work.

Temperature (ºC)	Transparent	White	Matte
Sintering	761	931	815
Softening	928	1076	901
Sphere	1014	1134	1134
Half-Sphere	1190	1176	1171
Melting	1293	1323	1191

Table 2. Characteristic temperatures (optical dilatometry) of the frits with the addition of the iron ore pigment (ºC)

Figure 1 shows the surface appearance and colour of the transparent, matte and white glazes pigmented with the iron ore residue, applied on non-engobed single-fired ceramic tiles that were fired between 1050 and 1180ºC. At 1050ºC the three glazes (transparent, matte and white) show a reddish colour, which is widely used in red ceramic industry (bricks and roof tiles). At 1100ºC, the glazes show different appearances depending on the type of frit. The transparent glaze has maintained the reddish colour, while the white glaze presents a light brown colour and the matte glaze presents a brown colour with a slight yellowish tinge. At 1130ºC, the glazes also show different colours depending on the type of frit. The transparent glaze kept the reddish colour, but with a decrease in tonality, and a yellowing. The white glaze appeared as a lighter and yellowish brown. Finally, the matte glaze shows a yellowish glaze very similar to the titanium yellow glazes used in the brick industry.

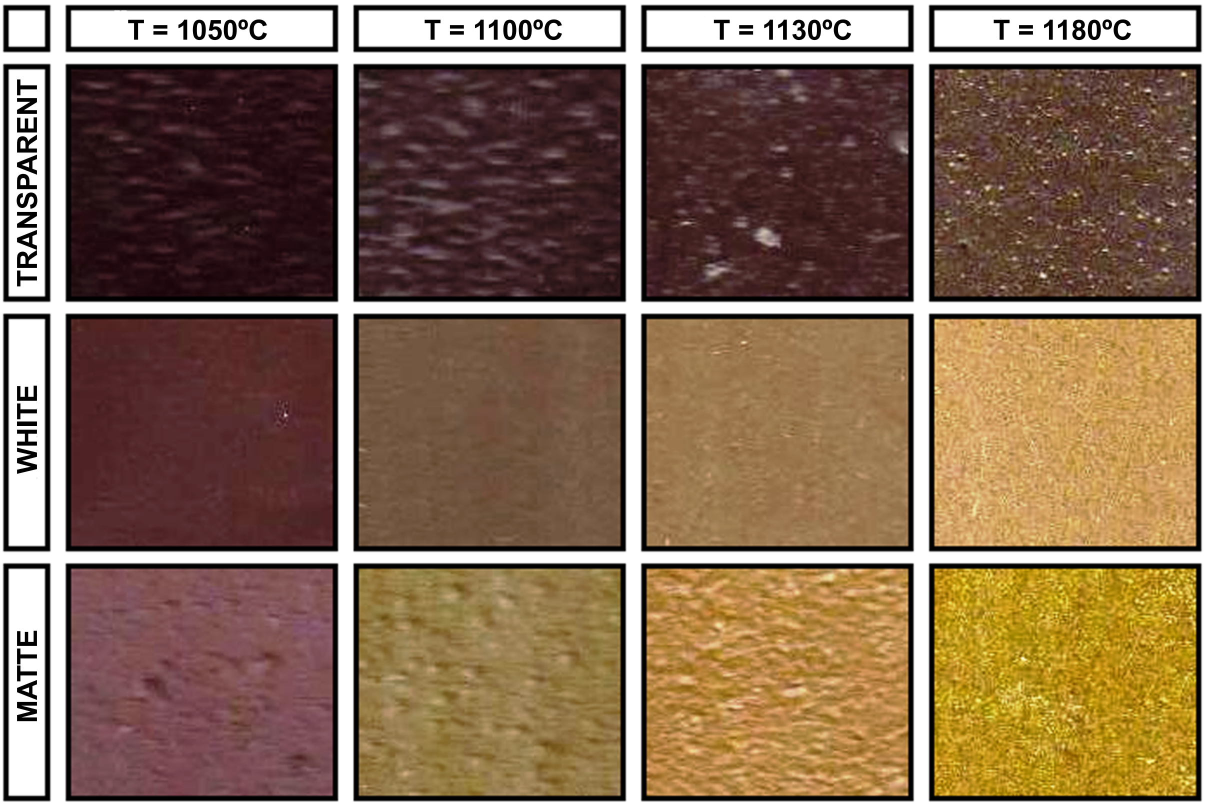

Figure 1. Surface appearance and colour of the transparent, matte and white glazes pigmented with the iron ore residue in function of the firing temperature

Figure 2 shows the reflectance spectrum for the transparent glaze with the iron ore pigment. One can see that between 450 and 620 nm the transparent glaze fired at 1180ºC shows a higher reflection than samples fired between 1050 and 1130ºC, being lighter. Therefore, the thermal stability of the pigment obtained from iron ore residue added to the transparent frit is obtained up to 1130ºC, Figure 2. Above this temperature the glaze fades.

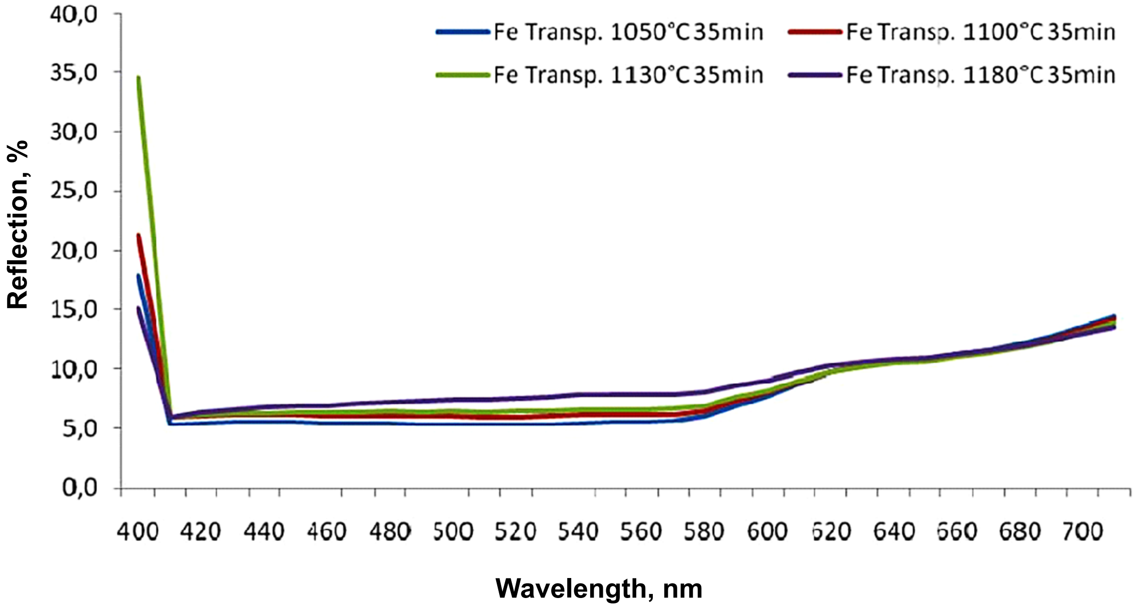

Figure 2. Spectral curves for the transparent glaze containing iron ore pigment and fired between 1050 and 1180ºC

In turn, the white glaze containing iron ore pigment shows a great variation in tonality at all firing temperatures. At 1050ºC the pigmented glaze is dark, with less reflection at all wavelengths, and the reflection of the white glaze increases with increasing firing temperature up to 1130ºC, but at 1180ºC the reflection declines again, making the glaze lighter than the samples fired at 1130ºC. Finally, the matte glaze shows the biggest changes in tonality with the variation of the firing temperature. There is a great variation in tonality from 1050ºC, when the glaze shows a constant tonality between 400 and 580 nm, and the tonality becomes lighter from 580 to 700 nm. At 1100ºC the behaviour of the glaze is inverted, and it shows a gradual increase in tonality from 400 to 700 nm, and the glaze is even darker than at 1050ºC for the shortest wavelengths. The matte glaze fired at 1130 and at 1180ºC exhibits similar behaviour to the sample fired at 1100ºC, but always becoming darker, with less reflection at all wavelengths. The pigmented matte glaze fired at 1180ºC is the darkest of all samples. To be noted is the great variation in tonality for the white and matte glazes in relation to the transparent glaze, the effect being evident of the pigment composed of the iron ore waste in these glazes. To better understand the tonality variation related to the glaze composition an X-ray diffraction study is required, which has not carried out in this preliminary study.

4. CONCLUSIONS

Regarding the use of iron ore residue as a ceramic pigment, the main conclusions are:

1. According to the chemical analysis, the iron ore residue is mainly composed of iron oxide and silica;

2. The thermal analysis shows that the iron ore residue is suitable for use as a ceramic pigment at intermediate temperatures. The residue is thermally stable between 500 and 1100ºC, i.e. it does not present any reaction that can interfere in the firing process;

3. Regarding the use of the iron ore residue as a pigment in transparent, white and matte frits: the addition of the residue in the transparent frit does not cause any significant change in colour with increasing temperature. However, the addition in white and matte frits causes major changes in glaze colour and tonality for those frits with increasing temperature;

4. The addition of the iron ore processing waste has changed the characteristic temperatures of the frits, lowering the softening and melting temperatures for the transparent and matte frits, and increasing these characteristic temperatures for the white frit;

5. Analysing the temperatures used in this study, the temperature that resulted in the desired colour for the roof tile industry, a reddish colour, is 1050ºC for all glazes. Also, at 1100ºC the transparent glaze shows satisfactory results.

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