

STUDY OF THE EFFECT OF INSOLUBLE PARTICLE SIZE AND COMPOSITION ON THE INTERACTION WITH FRITS IN GLAZE DEVELOPMENT

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ABSTRACT

In this study, glazes with different quartz and alumina waste contents of 0, 5, 10, and 20% were prepared. It was observed that the quartz particles tended either not to be wetted by the glaze or to remain practically without adhering to the glaze at surface, leading to abrasive effects. On the other hand, the alumina particles were wetted well by the glaze and were able to dissolve in the glaze; if they were at the surface could provide a non-slip effect. The glaze structure changed with the dissolution of these particles, and it became more depolymerised as more particles dissolved in the glaze.

1. INTRODUCTION

The addition of certain particles that, during firing, do not react with the frit particles to form glazes, gives rise to phenomena that can either enhance these glazes or lead to glaze defects. One such enhancement is related to slipping, i.e. to the development of non-slip flooring [1]. On the other hand, depending on the particle and its size, defects such as pores or bubbles can develop [2]. In this study, the interaction of different types of particle additions was analysed, in order to be able to modify their reaction with the frit particles during firing. The work was conducted using optical microscopy, electron microscopy-semi-quantitative analysis by EDS, and micro-Raman spectroscopy.

2. EXPERIMENTAL

The study was conducted with a transparent frit that is widely used in the ceramic tile industry. Particles were added from a waste made up solely of quartz and alumina particles. A glaze composition was prepared with mixtures of 0, 5, 10 and 20% waste content. The glaze was fired in a conventional cycle at 1150 °C and the resulting earthenware tiles were analysed by the techniques mentioned above. A Leica DM-LM optical microscope was used, in addition to a FE-SEM Hitachi 4700 S scanning electron microscope coupled to an EDS-Noran instrument; the Raman microspectrometer was a Renishaw InVia microspectrometer using 514 nm laser and averaging 10 analyses. The Raman Confocal and StreamLine system was used to analyse 50x50 mm surfaces and depths of 20 µm.

3. RESULTS AND DISCUSSION

The microstructure of the resulting glazes, at the surface and in cross-sectional slices, is shown in Figure 1. It may be observed that at the glaze surface, the glass that formed tended to wet the waste particles, wholly or partly covering them. On the other hand, the cross-sectional slice shows that the glaze tended to move the waste particles towards the surface, which was due to the modification of the surface tension by the waste particle. This displacement led to surface irregularities that modified the surface roughness and hence its non-slip effect. However, in Figure 1-d it may be observed that the surface irregularity contained at least two particles, whose composition is detailed in Table 1.

Oxide	(1)	(2)	(3)
SiO_2	95.3	68.1	26.7
Al_2O_3	2.1	10.7	63.3
CaO	1.3	8.3	0.7

Table 1. Chemical composition at the points in Figure 1.

The Table shows that the quartz particle was displaced towards the surface of glaze, with an alumina particle lying underneath this, embedded in the glaze.

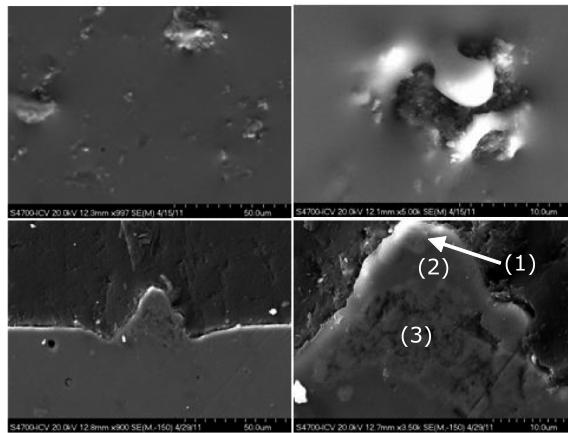


Figure 1.- Glaze microstructures. Surface (a and b). Cross-sectional slice (c and d).

This effect has been found on other occasions, either inside the glaze or at the surface, as shown in Figure 2. The figure displays different particles embedded in the glaze, which had not dissolved in it, whose composition is detailed in Table 2. The results in Figure 2 and Table 2 indicate that the quartz particles were not embedded in glaze or were rejected by it, either forming bubbles (pores) when they were inside the glaze or roughness when they were at the glaze surface. The roughness produced by the quartz particles was quite sharp, making their non-slip effect rather abrasive.

On the other hand, the alumina particles were embedded in the glaze and were wetted by it, giving rise to roughness of micrometric size when they were at the glaze surface. In this case the non-slip effect depends on the particle content or the quantity of particles at the glaze surface.

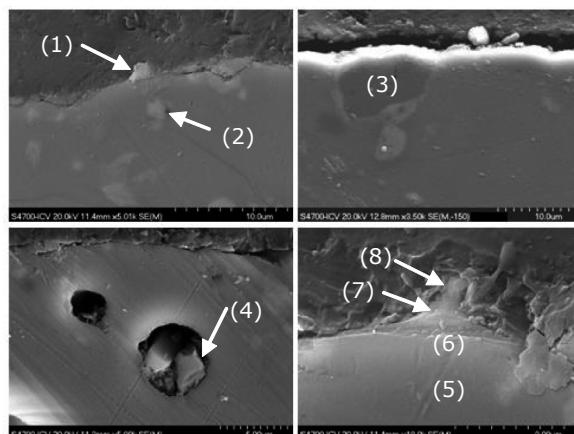


Figure 2.- Glaze surface microstructure.

Oxide	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO₂	94.6	42.5	32.6	95.3	50.1	59.1	65.11	71.8
Al₂O₃	2.2	50.3	60.1	2.1	34.3	30.7	23.6	16.4
CaO	1.5	2.6	0.7	1.4	11.1	8.2	8.5	8.3

Table 2. Chemical composition at the points in Figure 2.

The analyses performed by Raman spectroscopy in these samples are set out in Figure 3. It may be noted that as the waste content increased in the glaze, the spectra had less defined bands. This is because part of the added particles dissolved in the glaze, breaking its structure. The degree of glaze vitrification was calculated from the polymerisation index PI [3], which was 0.86, 0.62, 0.40, and 0.16 for additions of 0, 5, 10, and 20% waste particles, respectively. Taking into account that the glassy silica PI is close to 0.92, these values clearly show how the glassy network depolymerised as waste particles were added.

Confocal analysis with the StreamLine method enabled a depth of 30 μm in the glaze to be reached. The PI results varied from 0.40 to 0.14 in the glaze with 10% waste, and from 0.16 to 0.17 in the glaze containing 20% waste. This indicates that, depending on the analysed area, the glaze glass was able to depolymerise to a greater or lesser extent, as a function of waste particle dissolution in the glaze. Thus, when the dissolution maximised, the polymerisation (IP) of the glassy lattice was minimum.

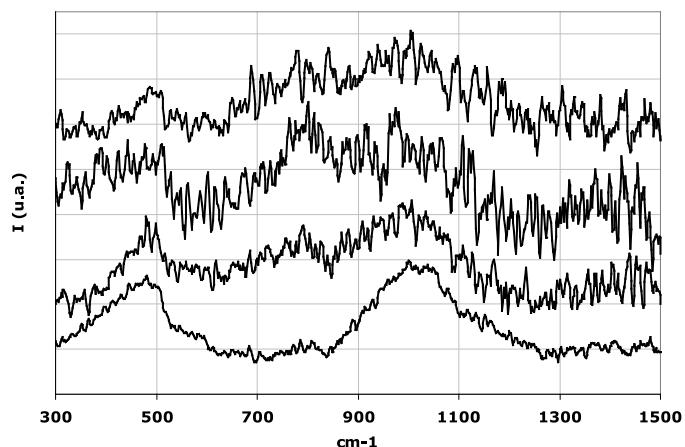


Figure 3.- Raman spectra of the studied glazes with particle additions.

CONCLUSIONS

This study shows how the addition of alumina and quartz waste particles gave rise to different phenomena in the microstructure and structures of the glaze. The quartz particles were not wetted by the glaze and when they were at the surface they were pushed up until they no longer adhered, which could give rise to abrasive effects. In contrast, the alumina particles were well embedded in the glaze, leading to roughness that could serve as a non-slip effect. The structure of the glaze changed with the dissolution of these particles, and became more depolymerised as more particles dissolved in the glaze.

REFERENCES

- [1] O. Ruiz, F. Sanmiguel, C. Gargori, G. Monrós, R. Lahoz, I. de Francisco. Estudio de la microestructura superficial de pavimentos cerámicos con propiedades antideslizantes. *Qualicer 2010*. Castellón.
- [2] E. Solera, T. Sierra, M. Villegas, A.C. Caballero, J.F. Fernández, J. de Frutos. Estudio de la porosidad de la superficie en esmaltes cristalinos. *Qualicer 2006*. Castellón.
- [3] S. Pérez-Villar, J. Rubio, J. L. Oteo. Study of colour and structural changes in silver painted medieval glasses. *J. Non-Crystalline Solids*. 354 (2008) 1833 - 1844.