STUDY OF SILVER ACTIVATION AS A BIOCIDE ON GLAZED CERAMIC SURFACES

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1. INTRODUCTION

The COVID-19 pandemic has evidenced the importance of disinfection for protecting public health [1-3]. Nowadays, public authorities and citizens are more aware of the need to protect their homes, buildings, and cities in order to safeguard themselves from future pandemics and develop healthier environments, which is why the demand for products with biocidal properties has increased notably.

Compounds are currently available that contain silver, copper, zinc, or titanium dioxide, which exhibit biocidal characteristics [4-5]. The introduction of these compounds into consumer goods by means of low-temperature (<500°C) processes does not alter the characteristics of such biocides, which facilitates their use in products such as paints, textiles, and polymers.

The use of materials with biocidal properties, aimed at providing ceramic surfaces with bactericidal properties has been researched both in floor and wall tiles [6-8].

However, the existence of a high-temperature (>1000°C) thermal stage in ceramic tile manufacture modifies the characteristics of biocide compounds and conditions their behaviour. Thus, though they are able to integrate into the vitreous phase that forms at high temperature, they may remain unaltered, react with other compounds to form new crystalline species, and even sublimate during firing. This is the great difficulty of having biocidal ceramic materials since, depending on the chemical environment of the biocide, its ability to have this effect changes to a greater or lesser degree, or may even be cancelled out.

This study examines the activation of silver as a biocide in ceramic tiles glazes, with a view to verifying the influence of the chemical environment generated in the glaze during the firing process on its bactericidal activity. To this end, a wall tile glaze was used that gives rise to glossy vitreous coatings, and different contents in silver were introduced. The surface of the resulting fired glaze coatings was observed by scanning electron microscopy (SEM), verifying the integration of the biocide nanoparticles into the glassy phase. The determination of the colour of the fired glaze coatings obtained at different temperatures evidenced the interaction with silver in the aesthetic properties of the final surfaces. Microbiological tests were carried out to determine the bactericidal activity of the surfaces, while chemical tests were performed to assess their ion leaching capability.

2. EXPERIMENTAL

This study was conducted using a wall tile glaze composition made up of 92 wt% crystalline frit and 8 wt% kaolin, from which 3 glazes with an Ag content of 0.1, 0.2, and 0.4 wt% were prepared by adding different amounts of a suspension of Ag nanoparticles.

After applying and firing the formulated glazes at a peak temperature of 1100ºC, the resulting vitreous coatings were characterised, determining their colour and gloss, and observing and analysing their microstructure by scanning electron microscopy (SEM). In addition, the bactericidal activity of the surfaces was assessed using *Escherichia coli* bacteria in accordance with standard ISO 22196:2011. In this test, the bactericidal activity of a surface is determined by comparing the colony forming units (CFUs) of the microorganism at this surface (CFU/cm^2) and at a control surface (blank), after 24 h from a known inoculum of the microorganism on each sample at a temperature of 35ºC. To establish whether the starting glaze without Ag exhibited any bactericidal activity, a sodium calcium glass was used as second blank.

The leachability of the Ag$^+$ ions in the glazes was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). For this, cylindrical test pieces were prepared beforehand by slip casting from suspensions of the test glazes. After drying, the test pieces were fired according to the thermal cycle used for wall tiles at a peak temperature of 1100ºC. The fired test pieces were immersed in an aqueous solution at 4% acetic acid, and the leached ion concentrations were measured 3 days after test start. The tests were carried out in a climate chamber kept at a constant temperature of 35ºC.

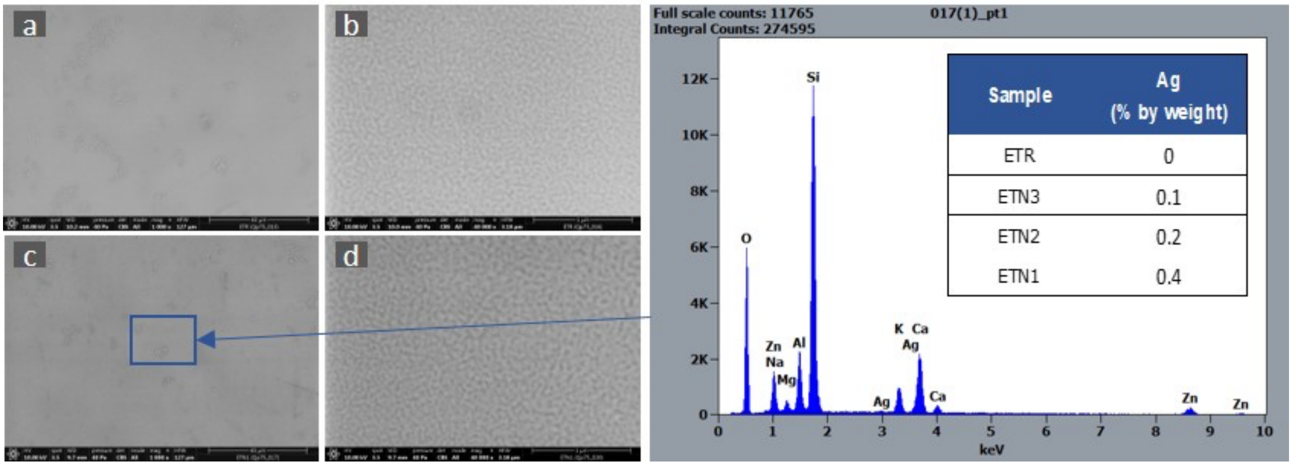
3. RESULTS

Table 1 shows the results of the determination of the aesthetic properties of the vitreous coatings obtained from the starting glaze and of the compositions formulated with different additions of Ag. Introducing Ag into the glaze composition led to a change in the chromatic coordinates and in the whiteness and yellowness indices. This change was of greater magnitude in the case of coordinate b*, whose increase, together with that of the yellowness index, indicated that the progressive addition of Ag nanoparticles to the composition raised the yellow shade of the fired glaze. On the other hand, the incorporation of biocide did not lead to changes in the gloss values, indicating that no crystallisation or increases in viscosity occurred to alter the surface roughness.

Sample	Ag (% by weight)	L*	a*	b*	Ia	Ib	Gloss
ETR	0	91.5	-0.14		10.1	54.9	96
ETN3	0.1	91.8	0.04	5.57	10.8	54.3	96
ETN2	0.2	91.6	-0.11	5.87	11.3	52.2	96
ETN1	0.4	91.3	-0.05	6.18	11.9	50.0	95

Table 1. *Chromatic coordinates, yellowness and whiteness indices and gloss of the starting glaze (ETR) and of the glazes with different Ag contents: ETN1, ETN2, and ETN3 fired at 1100ºC.*

Figure 1 shows surface micrographs at different magnifications of the starting glaze (a and b) and of the glaze containing a 0.4% Ag addition (c and d). The introduction of Ag did not modify the microstructure of the resulting vitreous coating and, in both samples, phase separation in the glassy phase together with the presence of devitrified crystals from the frit were observed. The energy-dispersive X-ray (EDX) analyses performed showed that the devitrifications corresponded to the diopside crystalline phase. On the other hand, the micrographs of the fired glazes exhibited no presence of Ag particles, indicating that the Ag nanoparticles dissolved during thermal treatment and thus integrated into the glassy phase, held in the vitreous coating in the amounts detailed in the table of Figure 1, as shown by the EDX analyses.



Sample	Ag (% by weight)
ETR	0
ETN3	0.1
ETN2	0.2
ETN1	0.4

***Figure 1**. Surface micrographs at different magnifications of samples ETR (a and b) and ETN1 (c and d)(left). EDX analysis of the surfaces (right).*

With a view to verifying the distribution of Ag and the elements present in the crystalline phases, the glaze surface with the largest Ag content (ETN1) was mapped.

Figure **2** (left) shows the surface of fired glaze ETN1 using the backscattered electron signal. The mapping results are shown on the right in Figure 2, revealing a practically uniform distribution of Ag and concentrations of Ca and Mg in the areas with crystals, confirming that diopside devitrifications were involved.

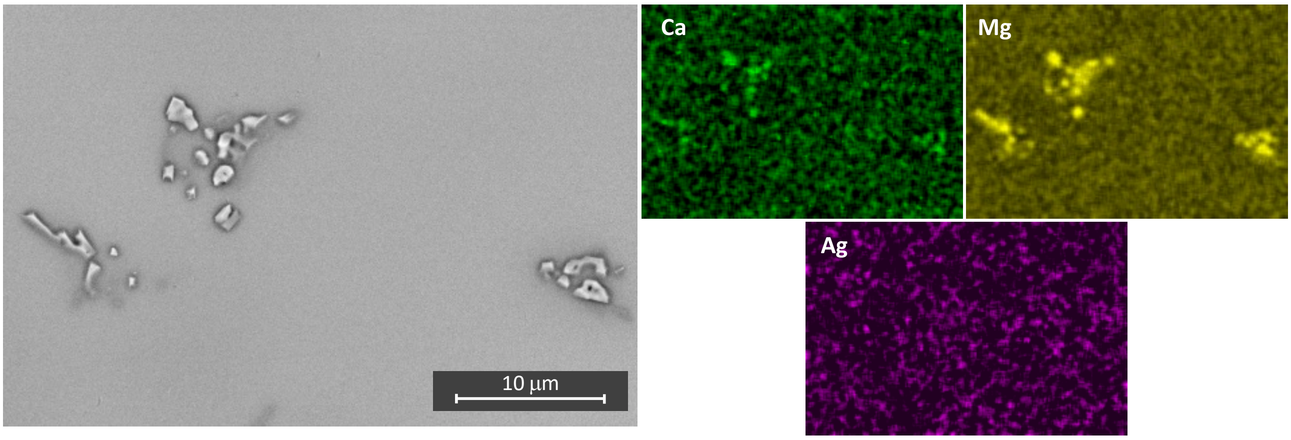


***Figure 2**. Micrograph of the surface of fired glaze ETN1 (left) and mapping (right).*

Figure 3 shows the results of the determination of bactericidal activity of the resulting vitreous coatings, expressed as CFU/cm^2, 24 h after a known inoculum of *E. coli* bacteria on each surface. The difference between the CFU number of fired glazes ETN1, ETN2, and ETN3, and fired starting glaze ETR, in addition to that of the glass used as blank, shows the bactericidal activity of the samples prepared with Ag. The fired glaze with the largest Ag addition (ETN1) was the most effective. Fired starting glaze (ETR) exhibited no bactericidal activity, as the greatest number of bacteria were recovered from it when the test ended. This was comparable to that of the sodium calcium glass, if the uncertainty associated with the test is taken into account.

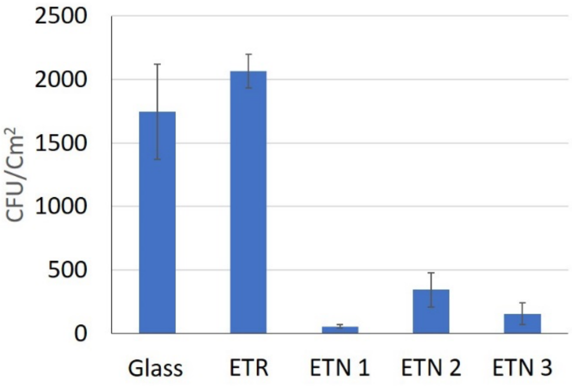


Figure 3. *Number of CFU of E coli/cm^2 at the end of the incubation time in the fired glazes with different Ag contents (ETN1, ETN2, and ETN3), the fired starting glaze (ETR), and the glass used for control.*

The following table lists the ion concentrations found after the dwell of the fired glaze test pieces in the leaching solution for 3 days at 35ºC. The results show that leaching of the Ag^+ ion occurred in the three test glazes and that the leached concentration was related to the amount of Ag introduced into glaze. This result indicates that one of the action mechanisms of silver could be related to leaching from the glassy phase.

Sample	$[Ag]_{content}$	$[Ag]_{leached}$
ETN3	0,1	0,12
ETN2	0,2	0,31
ETN1	0,4	0,41

Table 2. *Ag^+ ion concentrations leached from fired glazes ETN1, ETN2, and ETN3, 3 days after test start.*

4. CONCLUSIONS

The following conclusions may be drawn from this study:

- The progressive addition of Ag nanoparticles to the composition produced a change in fired glaze colour, increasing its yellowness, though not modifying its gloss.
- Microstructural analysis of the surfaces indicated that the Ag nanoparticles dissolved during thermal treatment and integrated into the glassy phase, Ag distribution being practically uniform in the surface of the vitreous coating.
- The tests of bactericidal activity revealed that the Ag-containing vitreous coating exhibited reduced growth of *E coli* bacteria, this reduction being greater as the biocide addition rose.
- Under test conditions, leaching occurred of the Ag^+ biocide ion in the glazes formulated with Ag, such leaching being one of the possible mechanisms of biocide activation. In addition, for the same chemical environment, biocide leaching depended on the amount of Ag added to the composition.
- Further tests are being conducted a view to studying in depth the silver activation mechanism and its relationship to the resulting bactericidal effect.

5. ACKNOWLEDGEMENTS

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