BACTERICIDAL CERAMIC GLAZES. INFLUENCE OF THE FIRING CYCLE.

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ABSTRACT

Biocidal properties are one of the most widely demanded functionalities in today's ceramic sector to create hygienic and safe environments. Silver, typically incorporated into the glaze in a variety of ways, is the most widely used element to achieve such properties on ceramic surfaces. However, incorporating silver into an unfired tile poses problems due to the chemical and physical transformations that both the glaze and the biocide itself undergo during the firing stage. Furthermore, the high temperatures (over 1000ºC) used in ceramic manufacturing generate significant variability in terms of biocidal efficiency depending on different variables, such as glaze composition, the method used to incorporate the biocide, the thermal cycle, and even the microbiological test method.

The aim of this work is to study the influence of thermal cycle variables on the production of ceramic surfaces with bactericidal properties. To do so, ceramic glazes with silver were prepared by incorporating it in different earthenware and porcelain stoneware tile compositions, both in the glaze mass and sprayed as a suspension on the unfired layer. The workpieces obtained were fired at different temperatures using the appropriate thermal cycle for each composition. Electron microscope analysis made it possible to assess the evolution of biocide content in the glaze during firing. The results obtained show a decrease in silver content on the glassy surface as maximum temperature and duration of the heat treatment are increased. Furthermore, validation of the biocidal properties in both the earthenware and porcelain stoneware surfaces obtained showed that they have high and very similar bactericidal attributes in both cases.

1.INTRODUCTION

Biocidal properties are one of the most widely demanded functionalities in the ceramic industry today to create hygienic and safe environments [1]. Silver, usually incorporated into the glaze in different ways, is the most widely used element to achieve such properties on ceramic surfaces [2][3].

The biocidal action of silver on ceramic surfaces is attributed to its oligodynamic effect, which is the ability of certain metals to exert a toxic effect on microorganisms. In oligodynamic materials, the diffusion of Ag^+ ions in the ceramic matrix in which they are embedded exerts a toxic effect on bacteria, thus altering their biological processes, inactivating them and preventing their proliferation [4][5]. One of the most commonly used species of bacteria to assess biocidal action is *Escherichia coli*, a Gram-negative bacterium that is present in our intestine and can indicate faecal contamination [6][7]. Furthermore, because it can easily acquire resistance to antibiotics, it can rightly be considered as a micro-organism that is difficult to control [8].

Incorporating silver into unfired bodies poses problems because of the chemical and physical transformations both the glaze and the biocide itself undergo when the body is fired [9][10]. Furthermore, the outcome of incorporating silver varies in its biocidal effect depending on different variables, such as composition of the glaze, method used to incorporate the biocide, thermal cycle, and even the microbiological test method employed.

The aim of this work is to study the influence of thermal cycle variables on the development of ceramic tile surfaces with bactericidal properties.

2. EXPERIMENTAL PART

The study reported herein analyses the influence of the firing cycle on the development of ceramic tile surfaces prepared with silver to obtain a bactericidal effect. To that end, two glaze compositions - one for earthenware and the other for porcelain stoneware tile - were prepared with silver (Ag) incorporated via a commercial suspension of nanoparticles.

In the first part of the study, the behaviour of Ag in the earthenware and porcelain stoneware tile glazes was compared with that of a porcelain sanitaryware glaze and a porcelain tableware glaze. To do that, workpieces were made from each of the materials by spraying the nanoparticle suspension with an Ag laydown of 4 g/m^2 onto the unfired glaze layer. In addition, in order to measure the effect of incorporating the biocide into the earthenware and porcelain stoneware tile compositions, a second method was tested in which the Ag was added to the glaze mass. In that case, the glazes were prepared with a 1% Ag content by weight by adding the appropriate amount of Ag nanoparticle suspension. Table 1 shows the workpieces prepared and the reference codes allocated to each.

Glaze	Ag incorporation	Ag content	Reference
Earthenware tile	Spray	4 (g/m^2)	AZ-P
Porcelain stoneware tile			POR-P
Porcelain sanitaryware			SAN-P
Porcelain tableware			VAJ-P
Earthenware tile	In glaze mass	1 % by weight	AZ-M
Porcelain stoneware tile			POR-M

Table 1. *Surfaces prepared by spraying and incorporating Ag into the glaze mass.*

The coated workpieces were fired using the relevant heat treatment for each of the ceramic products tested. In the case of the earthenware and porcelain stoneware tile samples, maximum temperatures of 1100ºC and 1200ºC, respectively, were used, with a total thermal cycle duration of 60 minutes. For the sanitaryware and tableware porcelain, maximum firing temperatures were 1260ºC and 1360ºC and the entire thermal cycle lasted 600 and 420 minutes, respectively. The microstructure and composition of the resulting surfaces were analysed by scanning electron microscopy (SEM), both before and after firing in order to monitor Ag distribution in the glaze and its integration into the glass phase on firing. To achieve that, both the surface and cross-section of the samples were observed and photographed using the backscattered electron signal from a field emission scanning electron microscope equipped with an energy dispersive X-ray microanalysis (EDX) system.

In the second part of the study, as a means of verifying the influence of temperature on Ag behaviour in the various glazes, its evolution during the firing process was studied. To do so, samples were taken during the thermal cycle corresponding to each product at intermediate temperatures, namely 500ºC, 950ºC and 1000ºC. In the case of the porcelain stoneware tile and sanitaryware porcelain, additional samples were tested at 1100ºC, and at 1100ºC and 1200ºC for the tableware porcelain. The surface of the samples was analysed by SEM-EDX to determine how Ag content evolved during firing in each of the test materials.

The third part of the study consisted of determining the bactericidal properties of the earthenware and porcelain stoneware tiles made using the two different methods of incorporating Ag. For that purpose, the method applied was the one laid down in ASTM E3031-15 (*Standard Test Method for Determination of Antibacterial Activity on Ceramic Surfaces*), developed specifically for ceramic surfaces, using *Escherichia coli* as the test bacterium [1][11]. In the test, the bactericidal property of the surface was determined by comparing colony forming units (CFU) of the micro-organism on that surface (CFU/cm^2) with a control surface (blank) 24h after a known inoculum of the micro-organism was applied to each of the samples at a temperature of 35ºC. In order to evaluate whether the starting glaze with no Ag displayed any bactericidal properties, a soda-lime glass was used as a second blank.

3.RESULTS AND DISCUSSION

3.1 MICROSTRUCTURE CHARACTERISATION

Firstly, Ag distribution was studied on both the fired and unfired surfaces to determine the influence of the type of glaze in the firing process.

Figure 1 shows the surface micrographs taken by scanning electron microscopy (SEM) of the unfired earthenware pieces prepared with Ag incorporated by spraying (AZ-P, Figure 1a) and into the glaze mass (AZ-M, Figure 1d). Irregular surfaces composed of particles of the unmelted glaze raw materials are observed, showing in the enlarged micrographs (Figure 1b & e) that Ag is distributed on the unfired frit particles in the form of nanoparticle aggregates. The overall surface analysis obtained by EDX indicates Ag_2O contents of 2.1 wt% and 1.1 wt%. The surface micrographs of the porcelain stoneware tile, tableware and sanitaryware glazes tested show a very similar appearance to that of the earthenware tile glazes, all of them displaying Ag nanoparticles as aggregates deposited on the unfired glaze particles.

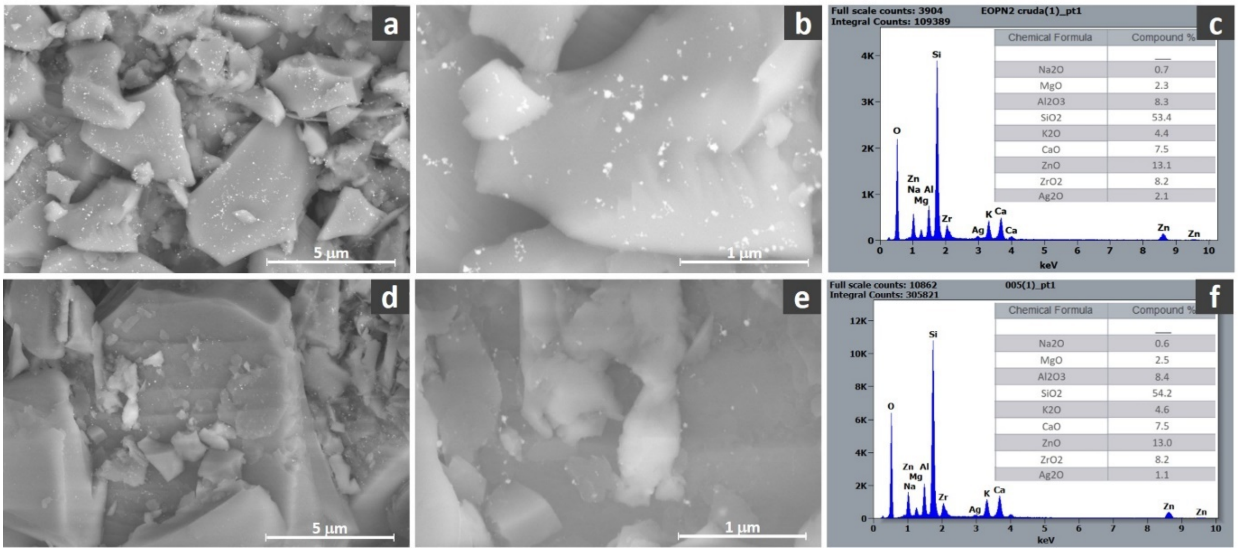


Figure 1. SEM micrographs and EDX analysis of the surface of the unfired AZ-P (a,b,c) and AZ-M (d,e,f) samples.

Table 2 shows Ag_2O content in the SEM-EDX analyses of the unfired surfaces in the study.

Sample	Ag_2O (wt%)
AZ-P	2.1
POR-P	1.9
SAN-P	1.9
VAJ-P	1.6
AZ-M	1.1
POR-M	1.1

Table 2. *Ag_2O content detected on the surface of the unfired samples.*

The sprayed workpieces reveal a higher Ag concentration than the earthenware and porcelain stoneware pieces with Ag added to the glaze mass (AZ-M and POR-M). Moreover, in the latter, the Ag_2O content detected (1.1 wt%) is very close to the 1% of the metallic Ag added to the glaze mass.

The variation in Ag_2O content detected in the samples where Ag was applied to the surface is due to the different way the biocide suspension penetrates during spraying, highlighting the influence of unfired glaze layer characteristics on the deposited coating. The role of the glaze in the coating–glaze interaction has been previously reported in several studies in which the interaction of inks applied by inkjetting with the unfired glaze layer was examined [12][13], and a relationship between particle size distribution of the glaze and pore structure of the unfired layer with ink penetration was found. Those studies showed that as average glaze particle size and distribution width decreased, so did ink penetration. The different product types tested in our work indicate the same effect on Ag content detected on the surface after application.

Figure 2 presents a cross-section of the unfired earthenware specimen with the Ag incorporated by spraying (AZ-P). The micrographs obtained at different magnifications show the presence of Ag nanoparticles inside the unfired glaze layer, confirming penetration of the biocide suspension during spraying. Similarly, in the micrographs of the unfired porcelain stoneware tile, sanitaryware porcelain and tableware pieces also obtained by spraying, Ag nanoparticles are observed at different depths as a result of the suspension penetrating into the glaze layer.

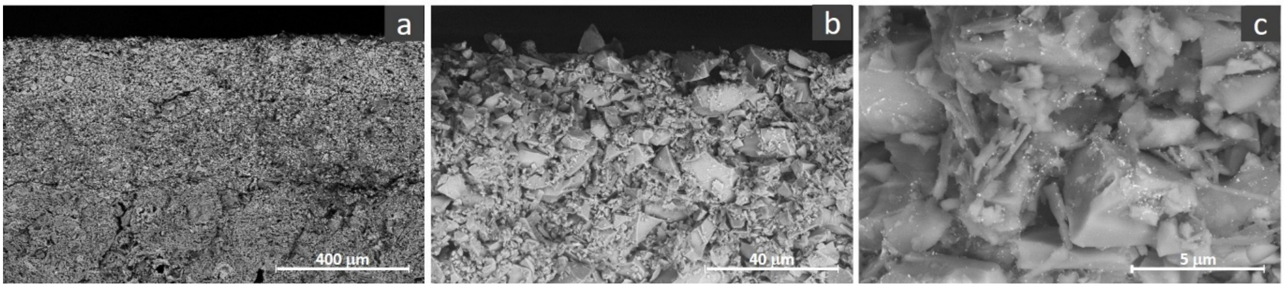
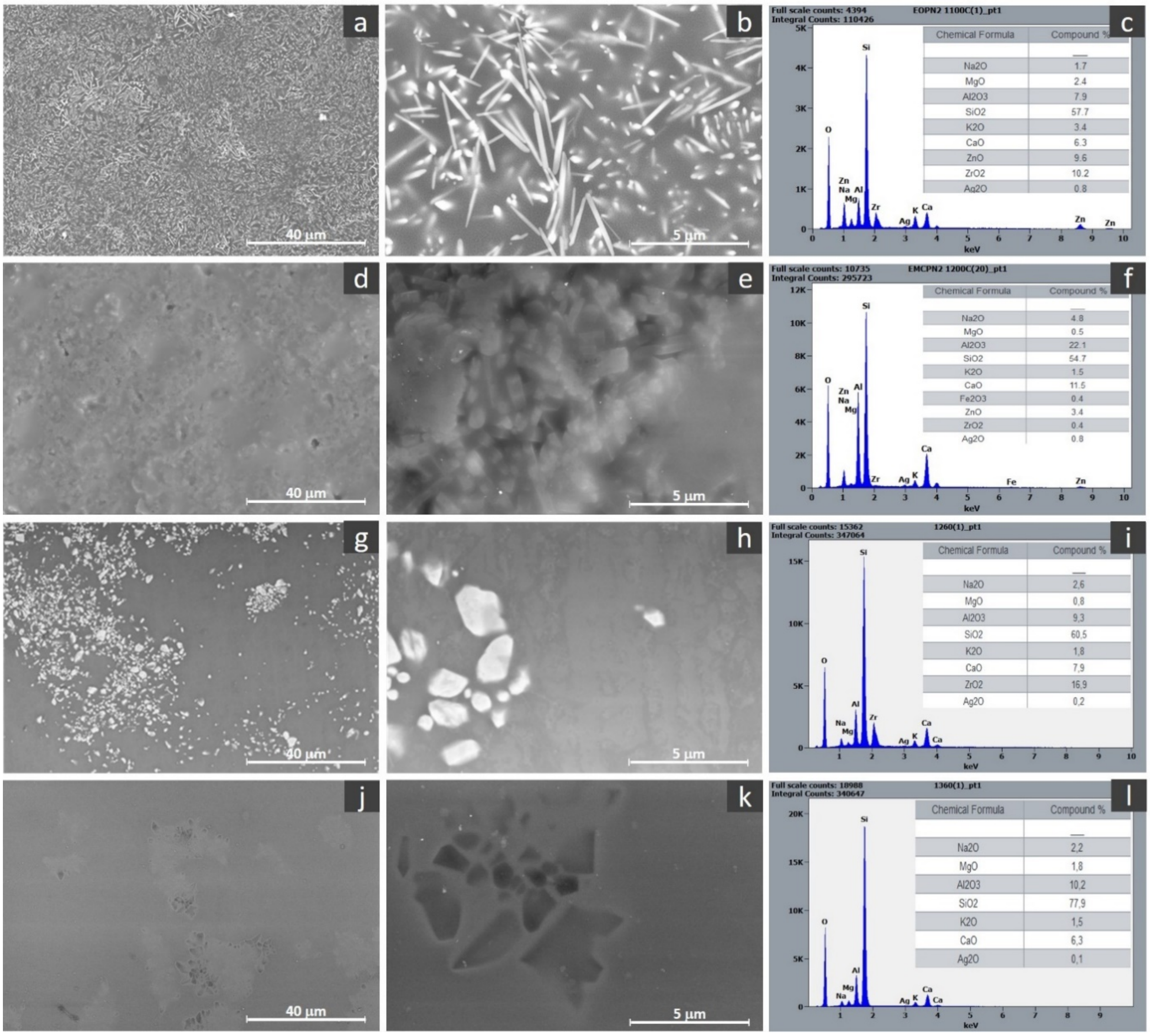


Figure 2. *SEM micrographs at different magnifications of the cross-section of the unfired AZ-P sample.*

Figure 3 shows the surface micrographs at different magnifications and SEM-EDX analysis of glazes sprayed with Ag and fired according to the appropriate thermal cycles and maximum temperatures for each of the materials tested. The micrographs of the glazes for earthenware tile (AZ-P, Figure 3 a,b) and porcelain stoneware tile (POR-P, Figure 3d,e) show the presence of devitrified crystals, which in the case of the AZ-P sample are white and acicular in shape and correspond to zirconium silicate, while in the case of the POR-P sample, they are larger and lamellar in shape and correspond to calcium crystalline phases.

The porcelain glazes (SAN-P, Figure 3 g,h) and (VAJ-P, Figure 3 j,k) show a different microstructure to that of the tile glazes, where the presence of crystalline particles immersed in the vitreous phase can also be seen, but in this case they are not devitrifications but come from unmelted particles of the crystalline raw materials that make up the glaze. EDX spot analyses of these particles indicate that they are mainly zirconium silicate in the sanitaryware porcelain and quartz in the tableware porcelain. Observation of the glazes at higher magnifications does not reveal any presence of Ag particles, so it is possible that they dissolved during the thermal treatment and are integrated in the glassy phase, where they remain in the proportions detected by the EDX analyses. A comparison of Ag_2O contents in the different glazes shows that in the earthenware and porcelain stoneware tile glazes (Figure 3 c,f), the Ag content had decreased compared to that on the unfired surfaces (Table 2) although both samples still exhibit 0.8% Ag_2O by weight on the end surface. However, in the porcelain glazes (Figure 3 i,l), Ag reduction is more pronounced, with 0.2 wt% and 0.1 wt% Ag_2O after firing. The different final Ag contents in the fired samples compared to the unfired samples indicates the influence of the thermal cycle on how Ag content evolves in the glazes.



Chemical Formula	Compound %
	—
Na2O	1.7
MgO	2.4
Al2O3	7.9
SiO2	57.7
K2O	3.4
CaO	6.3
ZnO	9.6
ZrO2	10.2
Ag2O	0.8

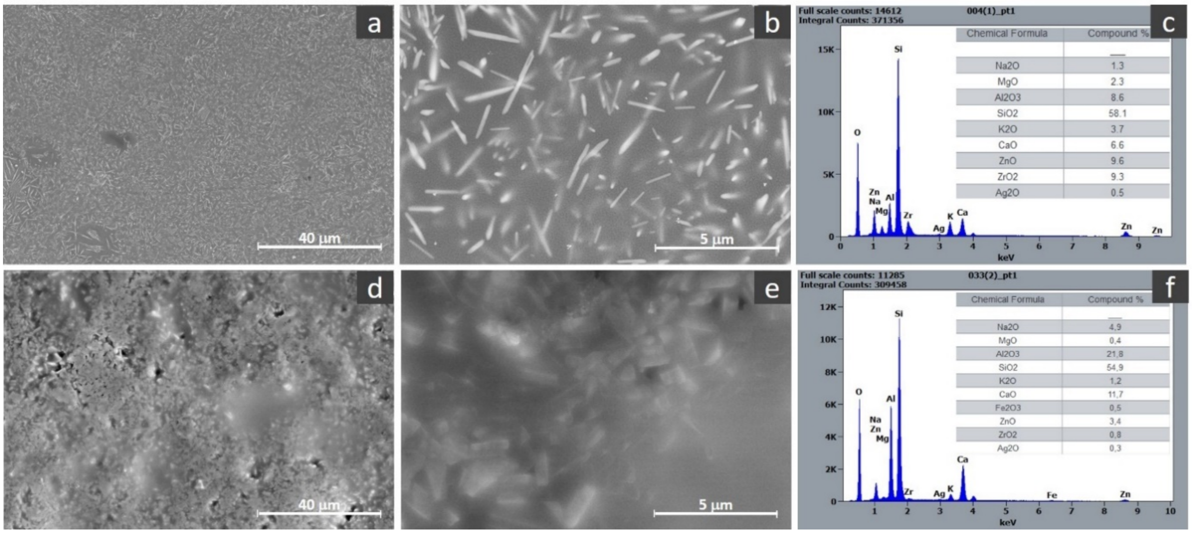
Chemical Formula	Compound %
	—
Na2O	4.8
MgO	0.5
Al2O3	22.1
SiO2	54.7
K2O	1.5
CaO	11.5
Fe2O3	0.4
ZnO	3.4
ZrO2	0.4
Ag2O	0.8

Chemical Formula	Compound %
	—
Na2O	2,6
MgO	0,8
Al2O3	9,3
SiO2	60,5
K2O	1,8
CaO	7,9
ZrO2	16,9
Ag2O	0,2

Chemical Formula	Compound %
	—
Na2O	2,2
MgO	1,8
Al2O3	10,2
SiO2	77,9
K2O	1,5
CaO	6,3
Ag2O	0,1

Figure 3. *Surface micrographs at different magnifications and EDX analysis of samples AZ-P (a,b,c) and POR-P (d,e,f).*

The surface micrographs of the AZ-M and POR-M glazes (Figure 4) reveal that incorporating Ag in the glaze mass does not produce alterations in the glaze microstructure compared to that obtained when Ag is incorporated by spraying (Figure 3). EDX analyses also reveal a reduction in Ag content on the fired surfaces compared to the unfired surfaces (Table 2), where Ag_2O contents of 0.5% and 0.3% by weight, respectively, were detected.



Chemical Formula	Compound %
Na2O	1.3
MgO	2.3
Al2O3	8.6
SiO2	58.1
K2O	3.7
CaO	6.6
ZnO	9.6
ZrO2	9.3
Ag2O	0.5

Chemical Formula	Compound %
Na2O	4,9
MgO	0,4
Al2O3	21,8
SiO2	54,9
K2O	1,2
CaO	11,7
Fe2O3	0,5
ZnO	3,4
ZrO2	0,8
Ag2O	0,3

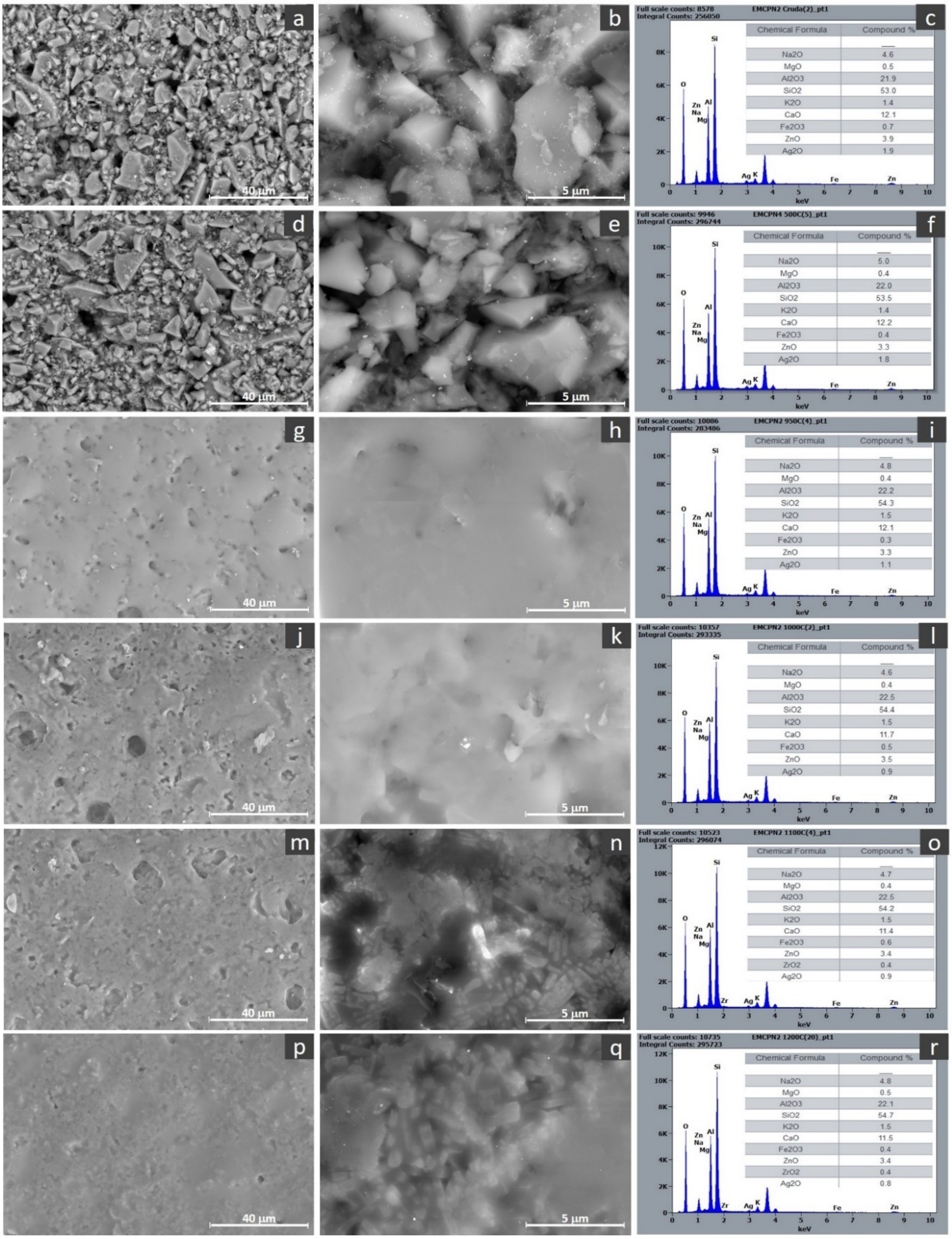
Figure 4. *Surface micrographs at different magnifications and EDX analysis of AZ-M (a, b, c) and POR-M (d, e, f) samples.*

3.2 INFLUENCE OF THE THERMAL CYCLE ON THE AG CONTENT IN THE GLAZE

In order to ascertain why Ag content decreases on the surfaces on firing and the effect that the duration and temperature of the thermal cycle have, a study was made of how Ag content evolves in the glazes during firing. To do so, test pieces were prepared with the different glazes and fired according to the standard thermal cycle for each material, with samples taken at different temperatures, as mentioned in Section 2 above. The pieces fired at the different temperatures were analysed with MEB-EDX to determine how Ag content on the surface evolves during firing.

Figure 5 shows micrographs at different magnifications and EDX analysis of the porcelain stoneware tile obtained by Ag surface spraying (POR-P) on the unfired and fired tiles at 500ºC, 950ºC, 1000ºC, 1100ºC and 1200ºC. The appearance of the surfaces at the different temperatures shows how the glaze microstructure evolves as the thermal cycle progresses. At 500ºC (Figure 5d,e), the surface has a very similar appearance to that of the unfired specimen (Figure 5a,b), where particles of the raw materials with the Ag nanoparticles deposited on them can be seen. As temperature increases up to 950ºC (Figure 5g,h), the onset of glaze melting and the generation of glassy phase, with the presence of some pores, can be observed. Given that the melting temperature of Ag metal is 960ºC and the literature states that when particle size is reduced to a nanometric scale, melting temperature decreases [14][15], it is possible that the nanoparticles will have melted at 950ºC and that the Ag is dissolved in the glassy phase.

The micrographs of the specimens fired at 1000ºC (Figure 5j,k) and 1100ºC (Figure 5m,n) reveal a microstructural development typical of a glaze with calcic crystalline phases [16][17], with the onset of crystal devitrification and the presence of large and irregularly shaped pores. Finally, at the maximum firing temperature (Figure 5p,q), crystals are seen to have grown and densification of the glaze layer to have increased, with a reduction in the number and size of the pores resulting from the generation of glassy phase. On the other hand, the micrographs do not show any white particles of silver, only some with a high zirconium content. The microstructure of the porcelain stoneware tile glaze prepared with Ag in the glaze body (POR-N) develops very similarly to the microstructure seen with sprayed Ag. Likewise, the AZ-P and AZ-M earthenware tile glazes display very similar evolution with temperature, except for the devitrified glaze type, and confirm the behaviour observed at maximum firing temperatures.



Full scale counts: 8578
Integral Counts: 256050
EMCPN2 Cruda(2)_pt1

Chemical Formula	Compound %
	—
Na2O	4.6
MgO	0.5
Al2O3	21.9
SiO2	53.0
K2O	1.4
CaO	12.1
Fe2O3	0.7
ZnO	3.9
Ag2O	1.9

Full scale counts: 9946
Integral Counts: 296744
EMCPN4 500C(5)_pt1

Chemical Formula	Compound %
	—
Na2O	5.0
MgO	0.4
Al2O3	22.0
SiO2	53.5
K2O	1.4
CaO	12.2
Fe2O3	0.4
ZnO	3.3
Ag2O	1.8

Full scale counts: 10086
Integral Counts: 283486
EMCPN2 950C(4)_pt1

Chemical Formula	Compound %
	—
Na2O	4.8
MgO	0.4
Al2O3	22.2
SiO2	54.3
K2O	1.5
CaO	12.1
Fe2O3	0.3
ZnO	3.3
Ag2O	1.1

Full scale counts: 10357
Integral Counts: 293335
EMCPN2 1000C(2)_pt1

Chemical Formula	Compound %
	—
Na2O	4.6
MgO	0.4
Al2O3	22.5
SiO2	54.4
K2O	1.5
CaO	11.7
Fe2O3	0.5
ZnO	3.5
Ag2O	0.9

Full scale counts: 10523
Integral Counts: 296074
EMCPN2 1100C(4)_pt1

Chemical Formula	Compound %
	—
Na2O	4.7
MgO	0.4
Al2O3	22.5
SiO2	54.2
K2O	1.5
CaO	11.4
Fe2O3	0.6
ZnO	3.4
ZrO2	0.4
Ag2O	0.9

Full scale counts: 10735
Integral Counts: 295723
EMCPN2 1200C(20)_pt1

Chemical Formula	Compound %
	—
Na2O	4.8
MgO	0.5
Al2O3	22.1
SiO2	54.7
K2O	1.5
CaO	11.5
Fe2O3	0.4
ZnO	3.4
ZrO2	0.4
Ag2O	0.8

Figure 5. *Surface micrographs at different magnifications and EDX analysis of the POR-P samples, unfired (a,b,c) and fired at 500ºC (d,e,f), 950ºC (g,h,i), 1000ºC (j,k,l), 1100ºC (m,n,o) and 1200ºC (p,q,r).*

Figure 6 shows the Ag_2O contents detected in the EDX analyses carried out on each glaze at the different firing temperatures tested. The resulting curves indicate the evolution of Ag content on the surface during firing for each glaze. In all the materials tested up to 950ºC, Ag content is very similar to that detected on the unfired surfaces. However, from 950ºC onwards, when Ag melts, a decrease in Ag_2O content on the glaze surface is detected, which is more noticeable in the workpieces prepared by spraying. This tendency is accentuated as temperature and firing cycle duration increase, such that in the porcelains (Figure 6 c,d), which are the materials with the longest heat treatments (420 and 600 min) and highest maximum firing temperatures (1260ºC and 1360ºC), Ag is seen to have been almost completely reduced in the final glazes (0.1% and 0.2% by weight of Ag_2O). In the earthenware and porcelain stoneware tile glazes (Figure 6 a,b), Ag content in the final surfaces is also seen to decrease, although given that they were fired at lower temperatures (1100ºC and 1200ºC) and with shorter thermal cycles (60 min), the decrease is not so pronounced and no major differences are detected between the two types of glaze, despite the different maximum firing temperatures used.

In regard to these two glazes, when comparing how the specimens made using one or other of the biocide incorporation methods evolve, a higher proportion of Ag can be detected in the samples prepared by spraying (AZ-P and POR-P), since it is concentrated on the surface, whereas in those containing the Ag included in the glaze mass (AZ-M and POR-M), it is distributed more homogeneously throughout the glaze layer. In both types of samples, the decrease in Ag in the final glaze is approximately 50% compared to the content detected in the unfired pieces. These results show that, with the biocide suspension and conditions used in this work, spraying is the more efficient preparation method, since with less Ag initially incorporated, higher Ag_2O concentrations are obtained on the surface of the final glaze.

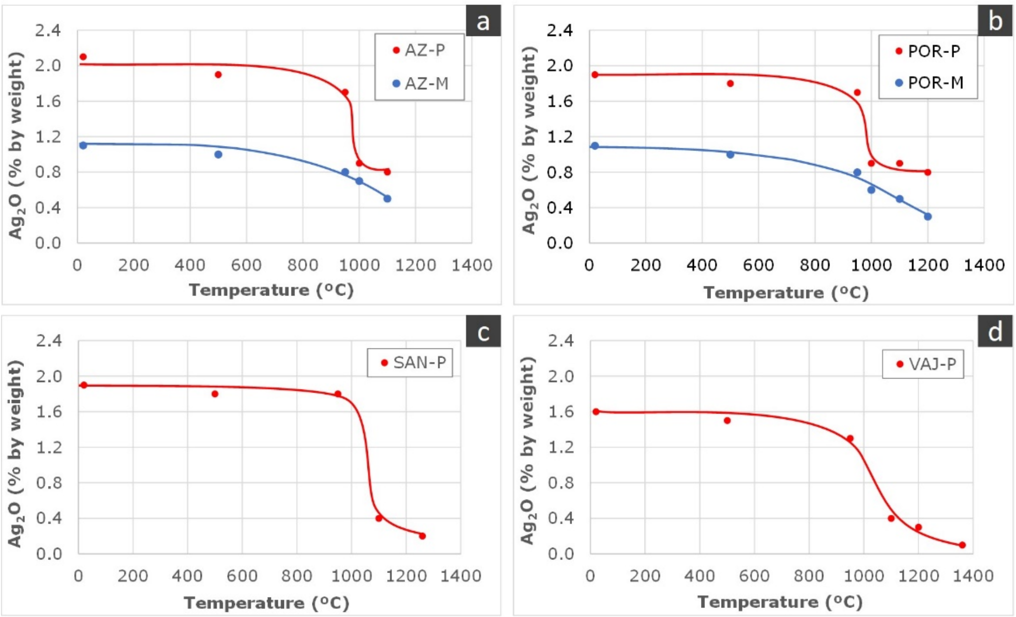


Figure 6. *Evolution of Ag_2O content with temperature on the surface of the glazes during firing: a) AZ-P and AZ-M, b) POR-P and POR-M, c) SAN-P and d) VAJ-P.*

In order to understand the reasons for this decrease in Ag content on the glazed surface, a cross-sectional SEM-EDX analysis of the test pieces fired at maximum temperature was carried out to determine their composition profile in depth. Figure 7 shows Ag_2O content measured from the surface to a depth of 50 µm in the tableware porcelain glaze (VAJ-P), which is the sample where the greatest Ag reduction took place during firing. The concentration profile obtained shows an Ag_2O content close to 0.1% at all measured distances from the surface. The analyses carried out, bearing in mind the error margin associated with such determinations, reveal similar behaviour in the different glazes in the series, with Ag_2O contents at different depths similar to that at the surface in the sanitaryware porcelain and even lower in the case of earthenware and porcelain stoneware tile glazes. The results reveal that there was no migration of Ag from the surface to the interior of the glaze, so that the reduction in surface content may be due to volatilisation during firing.

This effect of the firing cycle on the Ag content in the final glaze has been documented by other authors in an earlier study carried out to obtain bactericidal sanitaryware porcelain. In that work, the reduction in Ag content during firing is associated with the high vapour pressure of Ag and its compounds at temperatures above 1200ºC [18].

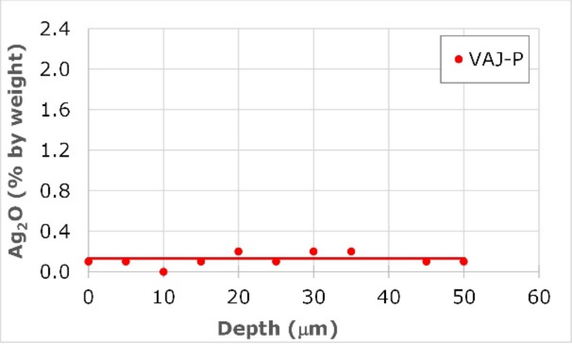


Figure 7. *Ag_2O content at different depths measured from the VAJ-P glaze fired at 1360ºC.*

3.3 BACTERICIDAL ACTIVITY

The biocidal properties of the earthenware and porcelain stoneware tile glaze surfaces tested with the two Ag incorporation methods were assessed by determining their bactericidal activity. To do so, the method defined in standard ASTM E3031-15 was used [1][11]. Table 3 shows the results of the test expressed as the percentage reduction in number of colony forming units (CFU) of *E. coli* in the glazes prepared with Ag compared to the same glazes with no Ag (ER) and to the float glass used as a blank after the incubation period. The table also shows the antimicrobial activity index (R) calculated as the difference between the logarithm of the CFU of *E. coli* on the surfaces with Ag compared to each glaze with no Ag (ER) at the end of the test. Japanese standard JIS Z 2801:2010 [19], adopted internationally as a reference for evaluating the antimicrobial efficacy of materials [9][20], states that a product is considered antimicrobial when its R value is greater than 2. The R values obtained indicate the high bactericidal activity in both the earthenware and porcelain stoneware tiles prepared using the two Ag incorporation methods tested, as the almost complete disappearance of the microbial population on these tiles shows.

Sample	Reduction in V (%)	Reduction in ER (%)	R
AZ-P	99.886	99.913	3.8
AZ-M	99.994	99.996	5.1
POR-P	99.993	99.996	4.9
POR-M	99.999	99.999	5.2

Table 3. *Percentage reduction of E coli CFU and antimicrobial activity index (R) on Ag-containing surfaces compared to Ag-free glazes (ER) and glass used as a blank (V).*

4.CONCLUSIONS

The main conclusions to be drawn from this work are as follows:

- It has been found that when Ag is sprayed in the form of a nanoparticle suspension, it penetrates into the interior of the unfired glaze layer, which in turn results in lower Ag content on the surface, the extent of which depends on particle size distribution in the glaze and on the porosity of the unfired layer.
- Whether Ag is sprayed on or incorporated into the glaze mass with earthenware and porcelain stoneware tile compositions in the proportions used in this study does not alter the microstructure of the resulting fired glazes.
- In the pieces obtained by means of the two preparation methods under study, Ag content on the glaze surface was impoverished during firing. This behaviour is more pronounced the longer the thermal cycle lasts and the higher the maximum temperature used.
- Surface and cross-section MEB-EDX analyses indicate that the decrease in Ag content on the tested surfaces starts at temperatures above the melting point of metal Ag (960ºC) and may be associated with its evaporation from the surface during thermal treatment.
- The incorporation of Ag in the form of nanoparticles, with the biocidal suspension and the conditions used in this work, is more effective when it is concentrated on the surface than when it is distributed throughout the glaze mass, since a smaller amount of Ag incorporated into the glaze results in higher concentrations of Ag_2O on the surface of the final glaze.
- The two Ag incorporation methods tested with the suspension used in this work enable glazed earthenware and porcelain stoneware tile surfaces to be produced with high and very similar bactericidal activity in both cases.

5.ACKNOWLEDGEMENTS

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