PRODUCTION OF ION EXCHANGE GLASS FOR USE IN CERAMICS WITH BACTERICIDE PROPERTIES

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ABSTRACT:

The idea of putting together the bacteriostatic and/or bactericide property with those traditionally found in ceramic coverings appeared some years ago and many efforts have been made to lead to an industrial scale production of these materials. Heavy metals are used to give bactericide and/or bacteriostatic properties and the use of silver is widespread, which performs best in this sense. This effect is known as the oligodynamic effect. These materials are known to considerably improve their bactericidal performance when they are in the ionic form in the ceramic. Ceramic firing as traditionally carried out has an upper temperature bound around 1150 °C and brings with it the difficulty of leaving the silver in the ionic form. In this work, with a view to solving this problem, a sodium-rich glass was formulated. Sodium maximises the ion exchange, however it decreases the chemical resistance of the glass; due to this problem, the glass was optimised with regard to the sodium content. The number of Ag^+ ions exchanged with Na^+ and the silver concentration profile in the glass layer were determined. The results were analysed performing tests with the micro-organisms: Staphylococcus aureus, Escherichia coli, Bacillus cereus, and Pseudomonas aeruginosa.

KEY WORDS: Antimicrobial glass, Ion exchange glass, Silver

1. INTRODUCTION

The bactericide effect of small amounts of metallic ions has been known for a long time[1,2,3] because ancient civilisations already stored water in silver pots to keep it potable for a long time. This effect is known as the oligodynamic effect. Silver and its salts have been widely utilised in water treatment and many other products, such as creams for preventive treatment of infections in patients with burns and for post operation treatment[4, 5, 6, 7]. Studies reported by Lukens[8] in 1971 describe the fungus toxicity of elements in relation to their position in the periodic table. The toxicity in a specific group increases with atomic weight. Silver and osmium are the most toxic elements. Martin[9], in 1969 showed another way of classifying elements regarding fungus toxicity, putting them in a decreasing order: Ag > Hg > Cu > Cd > Cr > Ni > Pb > Co > Zn > Fe > Ca. He also reported a study correlating concentration, exposure time, pH and temperature effects in using silver for water treatment. He furthermore studied the effect caused by impurities such as phosphates, calcium, chlorine and sulphides.

Although Pelkzar[10], in 1968, asserts that metallic silver has a bactericide/bacteriostatic effect, Berger[11] in 1976 states that such an effect is higher when compared to the effect caused by silver in ionic form Ag^+. Goetz[2], 1943 asserts that silver is germicide only if it is in contact with the cell surface and when the silver atom is in its excited state or ionised state.

On the other hand, the ceramic industry has incessantly looked for new properties. The bactericide property has been studied for application in ceramics and patents have been granted[12, 13, 14 15], with industries producing these materials in some countries. The difficulty in leaving silver in ionic form and thus optimising its bactericide effect is considerable, knowing that coating ceramic glazes requires a thermal treatment of approximately 1200 °C. Ahmed[16], 1997, points out that at temperatures higher than 470 °C, silver ions whose source is $AgNO_3$, go on to coexist with silver atoms Ag^0. Silver solubility in glasses is low, Navarro[17], 1991, about 1%, reducing the possibility of directly adding a higher amount of this in the glass network.

In this work an Ag^+ ion exchange was performed in glasses having a high sodium content.

2. EXPERIMENTAL PROCEDURE

A glass was developed with a high percentage of sodium and lithium, which maximises ion exchange with silver, and whose chemical composition can be seen in table 1. The composition has some fractions similar to those utilised in other studies on ion exchange in glass[16, 18, 19, 20].

Oxides	SiO_2	Al_2O_3	Na_2O	Li_2O
% by weight	72	3	20	5

Table 1. Composition of the glass utilised in the ion exchange.

The absence of other elements normally found in commercial glasses is due to an optimisation effected in order to perform the ion exchange. Pieces were put in a crucible containing 98% $NaNO_3$+ 2% $AgNO_3$, in weight, milled and mixed. After that, thermal treatment was carried out for two hours at 400 °C in a laboratory oven in air. When the pieces were taken out, they were carefully cleaned using ultrasounds for 15 minutes immersed in acetone. Then they were treated with acetic acid and further washed with distilled water. Before using them in the microbiological tests all the pieces were put though an autoclave at 120 °C and one atmosphere of pressure for 30 minutes. Bacteria Staphylococcus aureus ATCC 25923 and Escherichia coli ATCC 25922, Bacillus cereus and Pseudomonas aeruginosa were utilised for the microbiological tests. Plate Count Agar was utilised as culture medium. The applied methodology was that by diffusion in adapted gel and by the minimum inhibitory and minimum bactericide concentration adapted test (CIM, CBM)[21, 22, 23]. The incubation temperature was 36 °C for 24 hours.

Sample microstructure analyses were carried out by optical microscopy (Carl Zeiss – Neophot 30) and scanning electronic microscopy (Philips XL30), helped by energy dispersive X-ray spectroscopy facilities (EDAX). X-ray diffractions with a diffractometer Philips Xpert using a copper Kα radiation, with voltage of 40 kV and current 30mA; scanning in 2θ was 0.01 degrees per second. A Philips XRF instrument was utilised for chemical analysis.

3. ACTING MECHANISM OF THE Ag^+ ION ON BACTERIA

The main acting mechanisms of metallic ions on bacteria are based on the microbial cell characteristics. A normal live cell contains a great number of enzymes that are responsible for metabolic processes[10,24]. A live cell also presents a semi permeable membrane (cytoplasmic membrane) that keeps the integrity of the cellular content, controlling in a selective way substance transport. Any damage in any one of these levels can lead to cell death.

3.1. DAMAGE IN THE CELL WALL:

The accumulation of ions along the cell wall unbalances the permeability besides provoking damage to it, because displacements of ions will occur in the cytoplasm attempting to neutralise the charges.

3.2 INHIBITION OF A SPECIFIC ENZYME:

There are many different types of enzymes on the cells. The inactivation of an enzyme can occur for many reasons, among them the combination of one of its components, the sulphydryllic group –SH, with metallic ions, for example silver, copper and mercury. Silver coming from a salt (like nitrate) joins the sulphur of –SH group according to the scheme bellow:

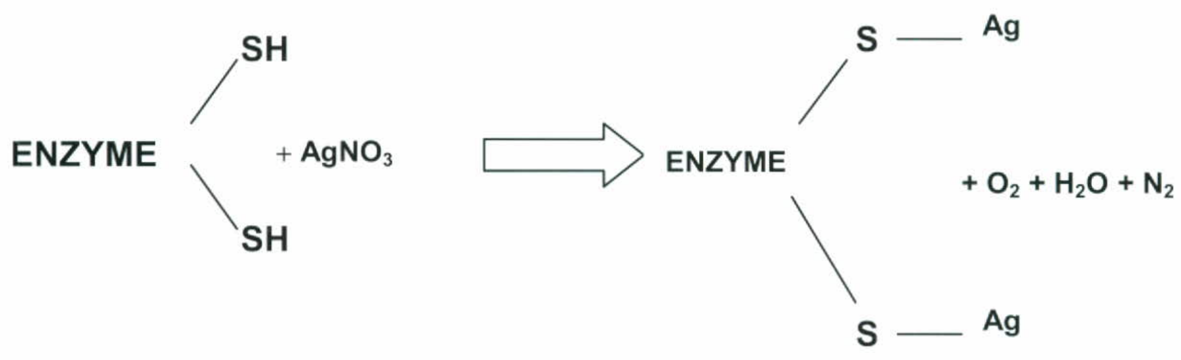


Figure 1. Reaction scheme of the metallic ion and the sulphydryllic chain, presented in enzymes.

3.3 – EFFECT ON NUCLEIC ACIDS:

Certain synthetic chemical agents and some natural substances are powerful inhibitors of ADN and ARN synthesis. The mutation that occurs due to the exposure of a cell to the Ag^+ ion is classified as a chemical mutation. They are also referred to as inducted mutations to distinguish them from spontaneous mutation. Chemical mutations can be subdivided in: - substitution of nitrogenized based; - addition of nitrogenized based; - deletion of nitrogenized based;

Although there are other mechanisms that act in destroying a microorganism by metallic ions, these three previously mentioned ones stand out and prevail over the others.

4. ION EXCHANGE MECHANISM

AG^+ and Na^+ ions are monovalent and have similar ionic radii. Several studies[16,11,19,20] point to the Na^+ ion as the best exchanger with the Ag^+ ion. Ag^+ ions are more polarised than Na^+ ions and have higher ionisation energy and an even higher electronegativity[20]. Sharaf affirms that the electronegativity difference and higher ionisation energy for the Ag – O bonds when compared to Na – O bonds, indicate a higher covalent character for the first bond. This increase of the covalent character for AG – O bonds can be the reason to form this second bond, where silver replaces sodium in the glass network, forming Ag – O – Si bonds in replacement of the Na – O – Si bond.

5. RESULTS AND DISCUSSION

5.1 ION EXCHANGE

The difference in the coloration serves as the first indication that an ion exchange has occurred. The ion exchange was already used to supply the yellow colour in cathedral stained glass windows[17]. Normally after the ion exchange process, thermal treatments are carried out to accentuate the colour and provoke a silver diffusion in the interior of the glass and, even have crystallites grow of metallic silver. This growth begins to occur around 470 °C. The transition of ionic silver to metallic silver produces a loss in the bactericide properties. The loss in the bactericide properties can be observed comparing samples where the ion exchange was carried out; some of these samples were further treated for two hours at 400 °C, 500 °C and 600 °C. This diminishing of the bactericide property can be evidenced by the area reduction in the inhibition halo, as described in figure 2. The diffusion increases with rising temperature, but the effect of crystallite formation appears when this temperature reaches 470 °C. For this reason a decrease in antimicrobial properties occurs

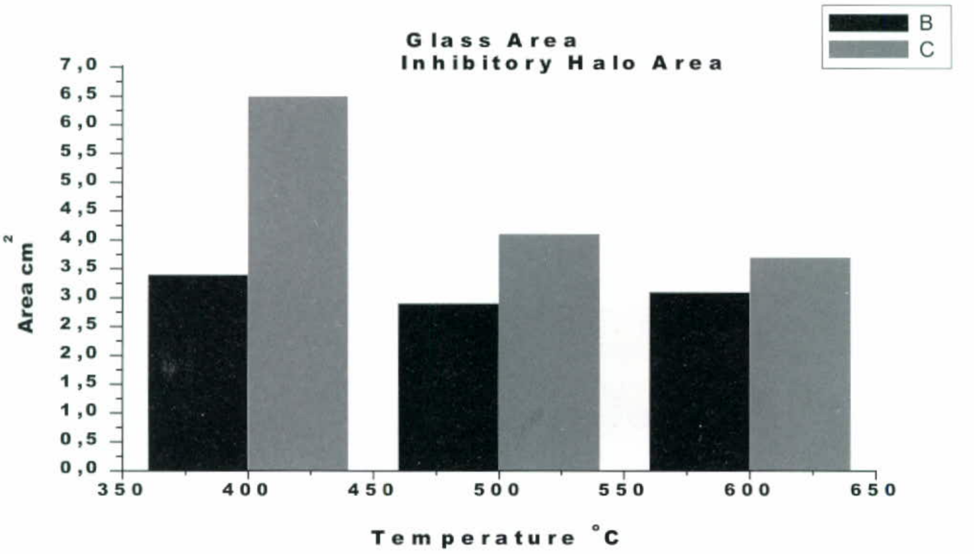
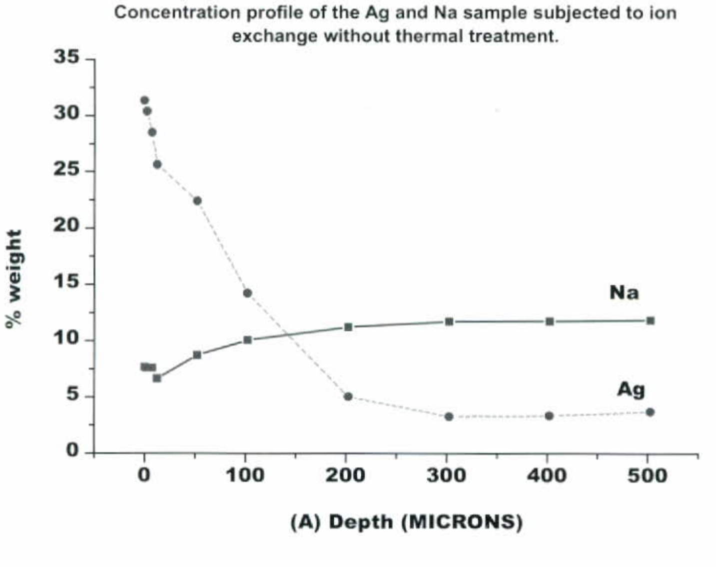


Figure 2. Effect of glass thermal treatments on microbial growth.



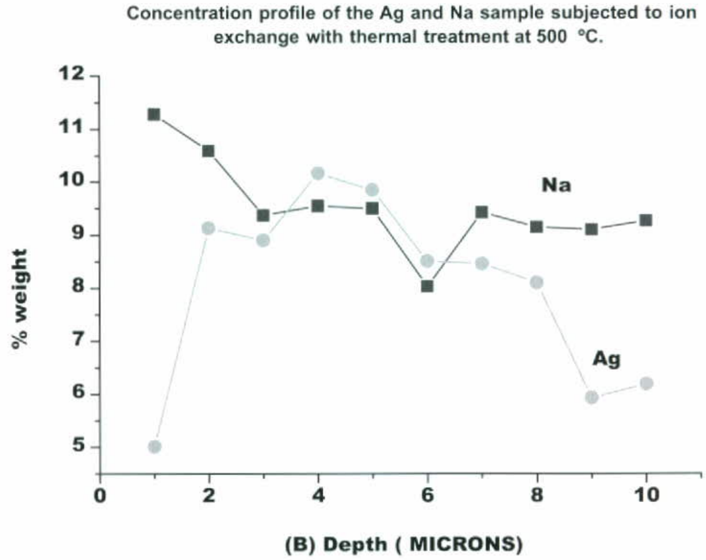


Figure 3. Sodium and silver concentration profile in a glass sample, with and without thermal treatment (B and A, respectively).

Another hypothesis for the decreasing antimicrobial properties is that, with the thermal treatment, the amount of silver presented in the surface decreases, because it will tend to go by diffusion to the region of the piece with lower concentration, which means, to the interior of the piec[25]. The results shown in figure 3 confirm this hypothesis. EDAX was used to observe the evolution of the silver and sodium concentration in the glass. It can be ascertained that the sodium ion exchanges with silver, because as the silver concentration increases the sodium concentration decreases. The observations are according to what was affirmed by Goetz[2] in 1943, that silver is germicide only if it is in contact with the cell.

5.2 – ANTIMICROBIAL EFFECTS

The result of the tests by gel diffusion, where the inhibition halo can be observed, can be viewed in figure 4. Here a glass is presented that was subjected to an ion exchange with silver and another that was not subjected to this. In sample (A) it can be noticed that around the glass, an inhibitory halo has formed with the Staphylococcus aureus ATCC

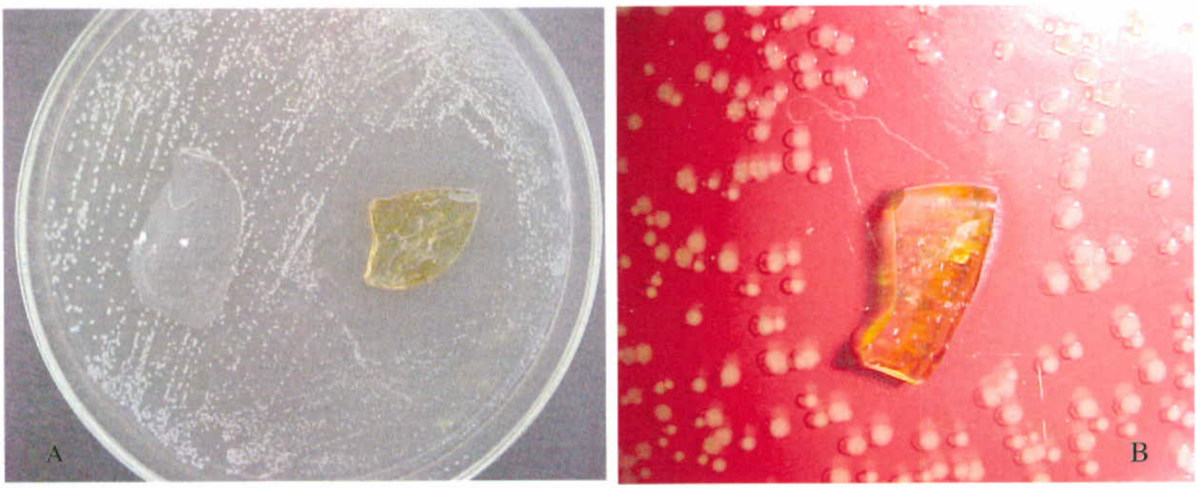


Figure 4 - Samples of ionic exchanged glasses. A) Inhibition halo with Staphylococcus aureus. B) Inhibition halo with Escherichia coli.

25923 culture. It can be observed that it inhibited the total growth, thus characterising the material as antimicrobial.

In sample (B), the halo was smaller. This occurred owing to the characteristic of the Escherichia coli microorganism, which is a gram-negative bacterium and presents a higher resistance to certain antimicrobial agents.

The adapted tests of minimum inhibitory and minimum bactericide concentration (CIM, CBM)[21], confirm the results above because with a concentration of the order of 0.0025g of powder glass, it was possible to avoid the growth of 200 μL of bacteria of an inoculum with turbidity corresponding to scale 0.5 Mc-Farland.

6. CONCLUSIONS

- The glass containing Na^+ carries out an exchange with the Ag^+ ion.
- The glass containing Ag^+ ions has bactericide/bacteriostatic properties.
- With thermal treatment, a transition of ionic silver to metallic silver occurs, which decreases the bactericide effect.
- The silver concentration at the surface decreases with the thermal treatment as a function of the diffusion to the interior of the piece.
- The ion exchange process is an efficient method to contribute bactericide/ bacteriostatic properties to ceramic materials.

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