

**Means of conservation and restoration of archaeological glasses
(Case of palace Ahmed Bey glasses - Constantine)**

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Abstract:

The alteration of the glassy material resulting from extremely complex process involving both the chemical composition of glass and the environment to which it is submitted. In this context is our job to be focused on mechanisms for alteration of glass in water. The objective of this work is to provide some clarification on the first stages of alteration of glass exposed to the atmosphere and means of restoration of archaeological glass palace Ahmed Bey of Constantine. To assess and quantify the alteration of glasses, tests were conducted on samples of local archaeological glass such as chemical analysis RX glasses studied, the chemical durability, morphology by SEM and optical transmission, and an experimental accelerated deterioration in function of pH, time and temperature to understand glasses studied the faces various atmospheric factors. For means of restoration is the goal of this work, we opted for another method from sodium silicate (glass soluble), the results are translated by a spectral behavior of the transmission glasses studied, which confirms the effectiveness of the method applied.

Keywords : Restoration, Conservation, Archaeological glass, Durability, environment, changes.

الملخص :

ينتج عن تلف المادة الزجاجية عمليات معقدة للغاية، والتي تنطوي على كل من التركيب الكيميائي للزجاج وطبيعية البيئة المحيطة به. في هذا السياق، يركز عملنا على تحديد آليات تلف الزجاج الأثري لقصر أحمد باي كنموذج في الأوساط الكيميائية المختلفة التركيز، وذلك قصد تقديم بعض التوضيحات بشأن المراحل الأولى من تغير خواصه الأصلية خاصة الخواص البصرية.

ومن أجل تقييم وقياس تدهوره، أجرينا جملة من الاختبارات المخبرية على غرار تعيين التركيبة الكيميائية والبنوية علي عينات زجاجية من مشربية القصر، مع تحديد متانته الكيميائية في مخلف الأوساط المائية، هذا من جهة. ومن جهة أخرى، قمنا بتنظيف زجاج القصر بمحلول محضر من السيليكات الصود وتطبيقه عليه بطريقة محددة. ومن ثم قياس الشفافية والانتقال البصري للزجاج الأثري قبل وبعد التطبيق، والتي أثبتت نجاعتها من خلال النتائج المتحصل عليها.

الكلمات المفتاحية: الزجاج الأثري، المقاومة الكيميائية، الشفافية الضوئية، العوامل الطبيعية، الترميم.

1. Introduction

A glass, like all materials, is subjected to the action of its environment from its production, and successive interactions more or less continuous, it changes its appearance and characteristics: it deteriorates. At first, these glass-atmosphere interactions create changes that its sole interest surface (E. Greiner-Wronowa, 1996:121) then altering advances to the depth, and it is his very heart that can be achieved (H. Römich and T. Böhm ,1999 : 189) .

Air pollution is primarily responsible for the deterioration of old glasses and their conservation currently poses many problems still partial knowledge of the mechanisms of corrosion (N. Carmona et al, 2005:94-96)

Generally you can see iridescent glass, others opaque that lost their transparency or their original colors: these glasses have been a phenomenon of alteration hydrometeors (N. Carmona et al ,2006 :157), and glasses cover d a dark crust due to bacterial activity on the surface of another part (JM . González and C. Sáiz-Jiménez, 2005:155).

The first two mechanisms are now well known for glasses unsustainable medieval type glasses and to a lesser extent for durable glasses, type glass modern (C. Saiz-Jimenez and L. Laiz, 2000: 321-323).

This work aims to determine the relative importance of each of these mechanisms on a glass archaeological presentation polluted environment, to provide some clarification on the mechanism of alteration in aqueous medium and possible restoration.

2. Experiment

The samples are fragments of glass from a window at the palace of Ahmed Bey (Constantine) dating from about 1832 of different colors: blue, green, yellow, purple, red and transparent.

The main forms of alteration encountered in stained glass can be classified into two types: breakage may be purely accidental by several natural factors such as wind, earthquake, human actions or due to internal tensions glass itself and the opacification , loss of transparency and change color, this type of deterioration is due to the interaction of the glass surface with several atmospheric agents such as moisture and different types of rain (especially acid rain) encouraging leaching phenomenon of the glass (micro pores and changing the appearance of the surface), air pollutants with its composition (particles, gas) which in turn promote the presence of a thin film on the surface of stained glass (opacification and loss of transparency) (S. Davison,2003:350-353) and biological agents and attack the bacterial surface of the glass (gray and change the color of the glass surface) (J. Jupille,2001:305-309) .

So the damage is regarded as a consequence of an interaction between the atmosphere and the material as it develops the material-atmosphere interface.

To highlight these aspects, it is interesting to provide analysis of SEM and measuring the optical transmission charges on these fragments of stained glass at the palace for the relationship developed: structural durability and study the mechanism of alteration in function loss of transparency.

To evaluate and quantify the alteration of glass, accelerated aging tests were undertaken by immersing samples in three aggressive (neutral pH of 7.3, basic solutions that are made mixture of half a mole of Na_2CO_3 and a mole NaOH of different pH = 8, 9, 10, 11, 12, 13 and 14 and in the end acids made from hydrochloric acid of 1 N HCl with different pH = 1, 2, 3, 4, 5 and 6), for 3 hours time at a temperature near 100°C . The experiences short time for which the system is still far from saturation, would quantify the mechanisms of dissolution of glass and differential releases of the elements and to study the behavior of glass for different values of pH.

These experiments will eventually face Leach to the results obtained in natural weathering.

The alteration of archaeological glasses in artificial physiological solutions can be expressed from the mass loss of measured or, alternatively, curves for the Liberation of silica and movable (alkaline, alkaline earth, boron) (M. Melcher, 2010: 921). Mass losses measured are probably less precise data, because of weight gain (low but unknown) related to hydration. From the released amounts of silica, one can calculate the total mass of glass dissolved (dissolution macroscopically congruent) (R.G. Newton, 1979: 311-313). To achieve the goal of this work, namely to characterize, understand and quantify the mechanisms of alteration affecting the archaeological glasses submitted to the environment, fragments of window glass were taken to the palace Bey of Constantine.

The objective was to assess the possibility of performing for the first time in the palace, restoration techniques on the types of glass used in windows to describe their state of degradation.

Under the proposals, the choice of technology depends on the ability of enforcement on both scales glass (pieces, the vital site), as proven by a comparative study of transparency (a measure of transmission for the different colors and transparent glass from the palace) glass before and after restoration. The technique is used to quench the removal is to immerse the glass after washing these samples WATER lukewarm hot 50°C temperature in a bath of a liquid solution of soluble glass (silicates soda) with a pH of 13.2, a temperature of 50°C spawning a period of 10 hours, then, removes glasses, or they will be washed with warm water at high pressure. The solution is prepared using sodium silicate AFRKAVER-of-ALGERIA JIJEL .

3. Results and Discussion

The SEM observations on the external sides of life are most often a layer much broader and continuous, consisting mainly of products precipitate responsible for part of the clouding of the surface of the glass blue, red and yellow figure N°1 and the same faces there micro-cracks in the surface of the window causing its peeling and flaking of gray in the surface of the glass green and purple glass). There is also the presence of micro-organisms, fungi, bacteria and algae on the surface of the glass.

The observation of the alteration of windows MED shows the formation of a thin film on the surface due to several factors atmospheric and products tampering, alteration or biological (micro-organisms, fungi, bacteria and algae) that this translates by the loss of transparency of these windows .

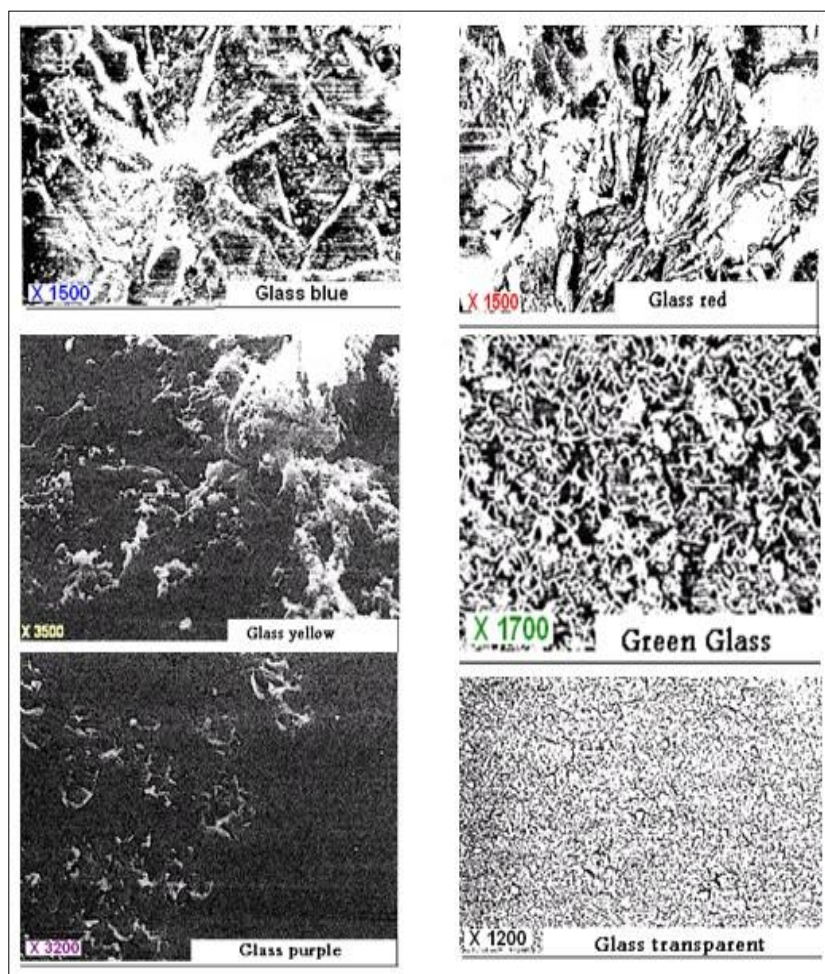


Fig .1.Observation a scanning electron microscope

of the surface of palace Ahmed Bey glasses

For the glass has a low transmission varies between 30 to 50% in the visible due to the disturbance of the surface, 58% transmission and in field infrared and sound transmission in ultraviolet.

For green glass, the transmission is made by two peaks: 400nm 25% transmission and 550nm 40% of transmission in the visible range that characterizes the visibility of certain colors through the glass, 70% or more in field of infrared by the glass against regarded as a filter in ultra violet.

Yellow for glass, the transmission is quite important in infrared and 70% decreases in the visible until filtering waves (500nm or less), however, a high transmission observed in ultra violet (Fig. 2). For the blue glass, the transmission is visible low in the month of 20% of the presence of cobalt by infrared 30% transmission and high transmission in ultraviolet (N. Papadopoulos and C. Drosou, 2012: 434).

The red glass is characterized by low transmission in the infrared 30% and strong in the ultraviolet, however, is characterized as a filter in the visible due an l'oxyde copper and manganese. In late for glass violet transmission is characterized by a low-intensity peak of 13% transmission in the visible and high transmission of 72% in infrared and considers as a filter for ultraviolet due to oxide MnO .

The transmission of these glasses studied is generally low due to the state of the surface affected by the different agents that promotes the formation of a thin film which reduces the transparency and the difference of opinion behavior via the areas of transmission is due to the differences in chemical composition element of transition.

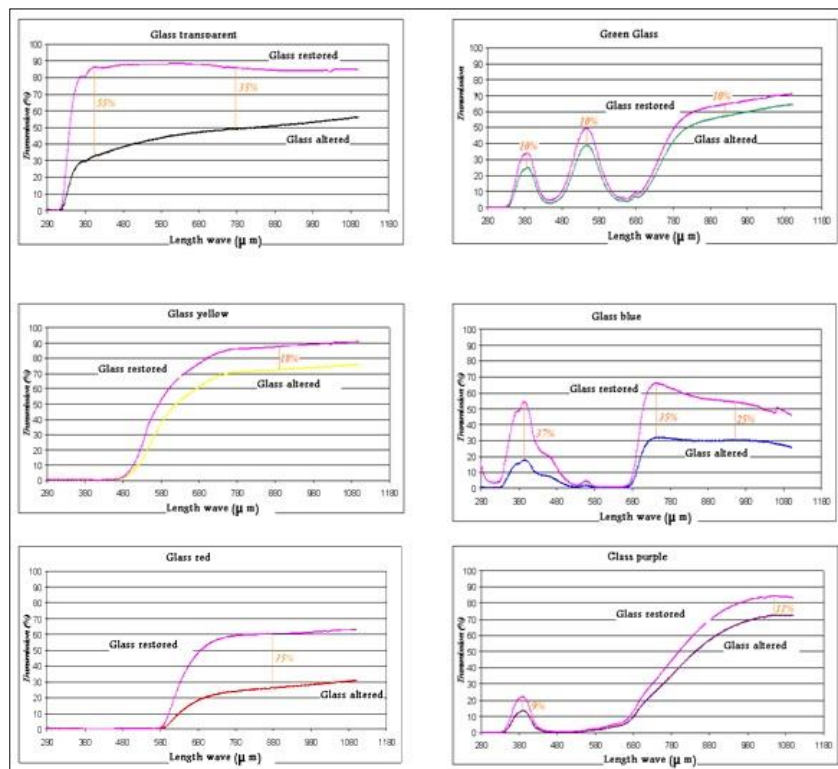
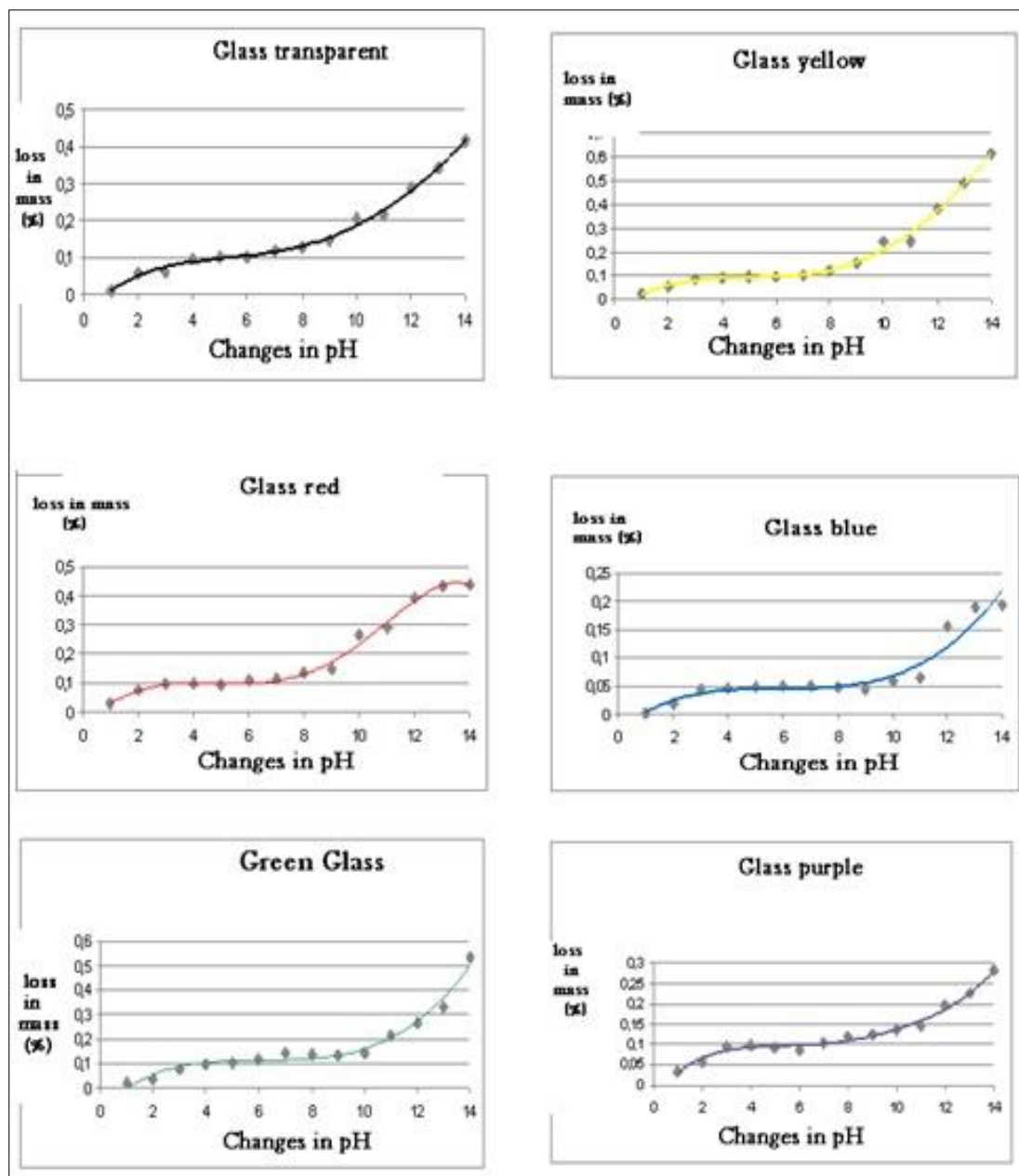


Fig .2. Specter transmission of palace Ahmed Bey glasses before and after restoration

The overall behavior of different lenses facing the pH may be apprehended following the evolution of their mass loss of function of pH.

In general, all glasses studied show behavior neighbors depending on the pH, The dissolution of these glasses decreases effect of pH = 1 to pH = 4, then stabilizes until the value of pH = 8 9 beyond that pH value increased mass loss is remarkable.

Leaching of glass leads to aqueous is based on the interaction of components of the solution with the glass surface is characterized by different steps:



*Fig .3. Curves evolution of the mass loss depending on the pH.
 Of palace Ahmed Bey glasses*

In acidic environments, the dissolution of ternary simple glass (SiO_2 CaO Na_2O) can be described by two successive mechanisms, each with its own kinetic. A selective ion exchange initially rapid release ions Na^+ and Ca^{++} by leaving a residual layer of hydrated silica which is completely dissolved.

The first mechanism (attack glass costs by H^+) being slowed by transportation DIFFUSIONNEL through the surface layer while the second has a speed roughly

constant. This scenario, possibly complicated by the precipitation of secondary phases involving residual layer aluminous silica or more complex, is transferable to most silicate glasses. The dissolution in acid solutions is strongly characterized by a rapid release of all elements. Its duration is variable and depends on the temperature and altering the composition of glass. In this region, all factors mono and divalent dissolves selectively compared to silicon for different glasses studied (T.M. EL-SHAMY,1972: 162) .It describes the mass loss is inverse proportion compared to the content of hydronium ion; that despite the dissolution by the intense exchange of cations with the glass matrix (modifiers and trainers network such as Al, Fe and alkalis) due to the phenomenon of imbibitions of the freeze forms on the surface which believes its volume (hence the total weight of the glass).

A pH near neutral idea of a leaching of alkali, controlled by diffusion through a little residual layer permeable and low solubility, and the macroscopic scale, it is as if the dissolution was congruent why the surface is probably stabilized speed corrosion practically constant in all samples of glass) .In this area that after some time the speed of extraction of alkalis by ion exchange of H + is decreasing and will be equal to speed decomposition so the total decomposition of the glass-OM.

The growth of the leaching of the increase of hydroxyl in solutions that promote the degradation of the skeleton of SiO₂ (the structural glass) and the formation of hydrated silicates as product tampering, deteriorated thereafter and react with alkali ions and transport to the solution. So based on the nature of deterioration glasses have a high weight loss compared with acidic environments due to its classification as silicate glasses (silica as its major).

The change in weight loss for the different colors of glass due to the presence of other metal oxides (colors) and even change the content of Na₂O and silica in the chemical composition. Thus accelerating the dissolution (corrosion of glass) by raising the pH related to the solubility of alkali solubility and alkaline earth (which consumes protons).

The glasses show improvement restored optical properties vary in all areas of transmission:

For the glass restored, the values of transmission wait 90% in the visible with a gap of 55% and in the infrared with a gap of 35% from its origin. Red glass restored away from transmission is 35% to average the visible and infrared and keeps the same behavior (filter) in the field of ultraviolet observation and remarkable for glass yellow in what the value increases from 70% to 90% approximately (the gap is 18%).

For the purple and green glass, the difference varies from 9 to 11% in the visible (the transmission increases the valeur13% to 23% (purple glass), and 23% to 33% for 1 peak

and 40% to 50% from the 2nd peak (green glass)], and IR [transmission can expect the maximum 84% instead of 74%, and 71% instead of 61 %).

In the end the blue glass restored, the transmission spectrum has the same behavior as that of origin with a significant increase observed in all the areas studied, as well as changes in the value reached 35% average in the visible (for the 380nm peak of the maximum value is 55% instead of 18%, to 680 nm and is 78% instead of 33%) and the IR 25% with a maximum value of 55% instead of 30%.

So with this technique proposed restoration, glasses improve their transparency have always keeping the same spectral its origin, this observation can be said: This technique has no side effects during the treatment of these archaeological glasses, because the cleaning methods used to eliminate the filing of the layer of glass altered by the aqueous and biological agents.

The use of the restoration solution with their characteristics (nature, concentration) and the method of its application (time, temperature) are to improve the state of the surface: cleaning secondary (eliminates the rest of the deposit freeze weathering on the glass surface by dissolving). Filing of the solution (soluble glass) surface which reinforces the glass and forms a protective layer against the agents of deterioration. Without secondary interaction (alteration) of the solution with the glass surface due to the pH and components, so instead of weathering yields a deposit of glass in the same general properties with an increase in splinters of glass restored.

4. Conclusion

This study is focused on the alteration of glass in various archaeological aggressive media and means of restoration. The experimental weathering has been fixed to understand glasses studied the different sides' atmospheric factors. At the end of the work done on the alteration of archaeological glass palace Ahmed Bey of Constantine it shows the following: The study was conducted primarily on the degree of weathering (weight loss), morphology and surface condition (transparency).

- Observation of weathering by MEB stained glass is characterized by the formation of a thin film on the surface due to several factors atmospheric or by dust, rain, humidity (especially in the external sides) or by 'Macro-Bienne activity, which are translated by the loss of transparency.

The transmission of these glasses studies is generally low due to the state of the area affected by the various agencies that promote the formation of a thin film that reduces transparency and respect of the conduct opinion via the areas of transmission is due the difference chemical composition element of transition.

In general, the transmission varies between 13 to 50% in the visible range.

- For means of restoration is the goal of this work, we opted for a new method from sodium silicate (glass soluble), the results are significant and show a remarkable improvement in the transmission of glasses studied, the that the transmission in the visible from [13 to 50%] of glass altered to [23 to 90%] for glass restored, confirming the effectiveness of the method.

In addition, this technique has no side effects during the treatment of these archaeological glasses. So with this technique proposed restoration, glasses improve their transparency have always keeping the same spectral its origin.

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