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Study of the chemical durability of colored archeological Glasses in the aqueous aggressive media

دراسة المقاومة الكيميائية للزجاج الأثري الملون
في الأوساط المائية المختلفة التراكيز

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Abstract:

The alteration of glassy materials is the result of an extremely complex process and involves the chemical composition of glass and the environment to which it was submitted.

The objective of this work is to shed some light on the early stages of alteration exposed to the atmosphere of archaeological glasses in various sizes and colors (clear, blue, red, green, yellow and purple) glass palace of Ahmed Bey Constantine in Algeria.

To evaluate and quantify the alteration of glasses, tests were performed on samples of local archaeological glass. An experimental accelerated deterioration began in function of pH (acidic, basic and neutral medium) time (time for the accelerated changes , go three hours to 240 hours, and three months to a year for changes in free atmosphere) and temperature (the ambient temperature of 25°C and 80°C) in order to understand the various atmospheric factors involved in these processes of alération glasses.

Keywords: Archaeological glass, deterioration, durability, environment.

ملخص

يتمثل هذا العمل في دراسة تأثير الرطوبة باختلاف أنواعها على أهم الخصائص الكيميائية والضوئية للزجاج الأثري الملون لقصر احمد باي بقسنطينة، مع تعيين مدى مقاومته الكيميائية خاصة بالنسبة للأوساط المائية المختلفة التراكيز (معتدل،حامضي وقاعدي) مع جملة من المتغيرات الجوية و الزمنية (درجة الحرارة والمدة الزمنية). الغاية من هذه الدراسة هو تحديد أهم آليات تلف الزجاج الأثري .

الكلمات المفتاحية :الزجاج الأثري، المقاومة الكيميائية، التلف، العوامل الطبيعية .

Introduction:

Like all materials the glass is subjected to the action of its environment and this from the beginning of its production and the subsequent interactions more or less continuous changing its appearance and its characteristics: it is deteriorating.

At first, these interactions between the glass and the atmosphere create changes, first of its outer surface [1], then these changes are moving in thickness, and finally it is the heart of the wall that can be achieved [2].

Air pollution is primarily responsible for the deterioration of ancient glasses; conservation currently poses many problems due to the even partial knowledge of corrosion mechanisms [3]. The glasses are usually iridescent and / or who have lost their opaque or transparent colors of origin: they have experienced a phenomenon of alteration due to hydrometeors [4], producing a dark crust due to bacterial activity on the external surface [5].

1-Römich H , Böhm T , Deterioration of glass by atmospheric attack , Climatic and Atmospheric Effects on Materials and Equipment, 1999, p187-202.

2-Greiner E ,Wronowa-LeszekStoch, Influence of environment on the surface of ancient glasses, Journal of Non-Crystalline Solids ,1996 , p 118-127.

3-Davison S , Conservation and restoration of glass, Butterworth-Heinemann, Oxford ,2003,p 349-365.

4-Carmona N, Garcia H, Gilca C , Chemical degradation of glasses under simulated marine medium, Materials chemistry and physics, 2005,p 92-102.

5-Carmona N , Laiz L , Gonzalez J M , Garcia-Heras M., Villegas M A , Saiz-Jimenez C, biodeterioration of historic stained glasses fron the Cartuja de Miraflores ,international Biodeterioration and Biodegradation , Spain, 2006 ,p155 –161.

The first two mechanisms are now well known in the glasses easily altered medieval type, and to a lesser extent in non-glass (or harder) altered modern type [6].

The main forms of damage produced the glass windows can be classified into two types:

- Purely accidental breakage due to natural factors, mechanical manipulation such as human, wind, earthquakes,
- By human intervention the glass itself by producing internal tensions process and / or opacification, loss of transparency and color alterations.

The second form of alteration is due to the interaction of the glass surface with several atmospheric conditions such as humidity and varieties of different rain (especially acid rain) promoting the phenomenon of leaching of the glass (micro-pores and changing the appearance of the surface) and is also due to the composition of air pollutants (particles, gas) in turn promote the presence of a thin film on the surface of colored glass (opacification and loss of transparency) as well as-biological agents attacking bacterial the glass surface (gray and color change of the glass surface) [7].

[6-]Lombardo T , mechanisms of alteration of calcium sodium glass in polluted urban atmosphere,university of Paris XII - Val de Marne, 2002, p143-145.

[7-]Saiz-Jimenez , C-Application of molecular nucleic acid-based techniques for the study of microbial communities in monuments, International Microbiology, 2005,p 153–230, Voir aussi : Saiz-Jimenez, C, Laiz L , Occurrence of halo tolerant/halophilic bacterial communities in deteriorated monuments, International Biodeterioration and Biodegradation, 2000, p 319–326. Voir aussi : Jupille J, The surface of the glass structure and physical chemistry, Acad Sci, Paris, 2001, p 303-320.

This work aims to determine the relative importance of an exhibition of archaeological glass to each of these mechanisms of environmental pollution in order to get some clarification processes in aqueous alteration.

1. Experiment :

The samples in this study are fragments of glass archaeological glass (dating from about 1832) of different colors: blue, green, yellow, purple, red and transparent, taken at the Palace of Ahmed Bey (Constantine / Algeria).

To understand the different behavior of window glass against the alteration, it is necessary to know their chemical composition. The chemical composition was determined by X-Ray Fluorescence spectrometer Philips PW 2420 kind Studies Centre of Technology and Building Materials of Boumerdes.

Different times and regions, the chemical composition of the glasses is significantly variable, mainly in terms of flux used.

Thus, the old glasses consist of a majority of silica and one or more melting oxides allowed to lower the melting point of the silica. These fluxes, are found primarily soda and potash, calcium oxide and magnesium coming in second position.

In addition, the color of the glasses was obtained by the addition of rich pigments of transition elements (cobalt is responsible for the blue color while copper gives a red or green depending on its valence).

We therefore consider the damage as the result of an interaction between the atmosphere and on the development of a contact surface between them.

This work is to present the alteration of glasses that have undergone different types of alteration. Besides that, several parameters influencing alteration were tested : These are pH, leaching time and temperature.

Accelerated aging tests have been undertaken to assess and measure the glass alteration. The samples were immersed for 3 hours at a temperature of about 80 °C in three aggressive alkaline solutions (neutral pH of 7.3, made of a mixture of half a mole of Na_2CO_3 and NaOH mole different pH = 8, 9, 10, 11, 12, 13 and 14 and in extreme acidic solutions made from a hydrochloric acid normality of HCl with various pH = 1, 2, 3, 4, 5 and 6.

Experiences in time (duration 3 hours) short for which the system is still far from saturation must be able to quantify the mechanisms of glass dissolution and incremental releases of the elements and to study the behavior of glass under different pH values.

The experiments conducted over longer time can track the evolution of the rate of weathering quantified as a function of mass loss.

Glass samples were immersed in three highly corrosive conditions (basic conditions (Na_2CO_3 and NaOH), pH = 8.85 , acid medium (HCl) to pH = 3.25 and the distilled water of pH = 7.3) for a series of time: 3, 6 , 12, 24 , 48, 96 , 144, 196.240 hours in a temperature near 80 °C.

To identify the influence of temperature on the rate of weathering of the glass , we repeat the same protocol alteration in ambient temperature (25 °C) for 3 , 6. 9 and 12 months.

These leaching experiments will eventually be faced with the results of natural weathering conditions.

2. Results and discussion

2.1 Characterization of material

The results of the chemical analysis (Table1) indicated that these archaeological glass (from the palace of Constantine) are studied glasses of sodium family, contain main component was the network-forming oxide SiO_2 (65.56 to 67.47%), while as alkali oxides Na_2O network-modification (15.34 to 17.55%) and K_2O (0.16 to 1.63%).

The network-stabilizing glass, alkaline earth oxide CaO 10.35 13.45%.

These high concentrations of calcium and the presence of barium strontium suggest that the presence of calcium is not accidental and related to the addition of other fluxes, but correspond to the deliberate use of limestone as flux.

The aluminum contents vary slightly and are around 0.59 to Al2O3 1.90% while the concentration of magnesium does not exceed 0.80% MgO.

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Oxides	Percentage (%)					
	Clear	Green	Red	Yellow	Blue	Purple
SiO_2	67.47	66.73	68.63	65.98	65.92	65.56
Al_2O_3	0.84	1.90	0.59	0.71	0.59	0.61
Fe_2O_3	0.20	0.25	0.09	0.36	0.27	0.29
CaO	13.45	10.35	11.34	12.54	12.67	2.14
MgO	0.72	0.06	0.11	0.11	0.16	0.10
SO_3	0.46	0.23	0.24	0.53	0.63	0.76
K_2O	0.26	1.63	0.20	0.28	0.34	0.16
Na_2O	15.34	16.32	17.22	16.06	17.86	17.55
P_2O_5	0.01	0.03	0.02	0.02	0.02	0.10
TiO_2	0.05	0.04	0.04	0.04	0.04	0.04
MnO	-	-	-	1.68	0.59	1.23
Co_3O_4	-	-	-	0.19	-	-
CuO	-	1.31	-	-	-	-
Weight Loss	0.31	0.28	0.60	0.80	0.40	0.74

Table 1. *Chemical composition of archaeological glass (Palace of Ahmed Bey)*

The transition metals were found in this case, MnO (1.23%) for purple glass, CO_3O_4 (0.19%) for the blue glass, CuO (1.31%) for glass green coloring to yellow coloring is the glass composition of the iron oxide (0.09%) and alumina (0.59%) (Ferric oxide and alumina) and MnO (0.59 %) For red glasses then adopt two different structures of the technique:

- The plate's lenses: a colorless thick support is coated with a thin layer red glass,
- Laminated glass: their cut has irregular alternation red and colorless layers.

Laminated glass is obtained by successive tempering of glass cane in glasses of different colors.

The use of unrefined natural products for the manufacture of glasses windows is responsible for the presence of a large number of elements: Fe_2O_3, TiO_2, P_2O_5 other ≈ 0.80% at low ppm levels as (ZnO, BaO, PbO, Cl) and the product of aggressive environmental (CO_2, NO_x and SO_2et materials organic).

These different compositions can be actually considered signature manufacture of glasses. Indeed, they provide information not only on the nature of the products used for the manufacture of glass, but also the know-how of master glass makers at the scene of supply, as well as the time of their manufacture.

Oxide-forming SiO_2 network has expanded to 60 %, which according with an average stability or type five classification according to Muller so are glasses types typical of the transition period Medieval-Renaissance [8].

2.2 Experimental Alteration :

The alteration of archaeological glasses in physiological solutions artificial whose major compositions are expressed from the measured

[8]-Foy D , Glazing Antiquity and the Middle Ages, Archeologia, 2005,p 48-58.

weight losses, or alternatively, release curves and silica (earth alkali, alkaline, boron) movable members [9].

The weight loss measured are probably the most accurate data. From the released amounts of silica, one can calculate the total mass of dissolved glass (congruent dissolution macroscopically).

2.2.1 Effect of pH :

The overall behavior of different glasses against the pH can be understood following the change in their mass loss as a function of pH .Figure 1 above represents the mass loss of the glasses studied for different alterative solutions.

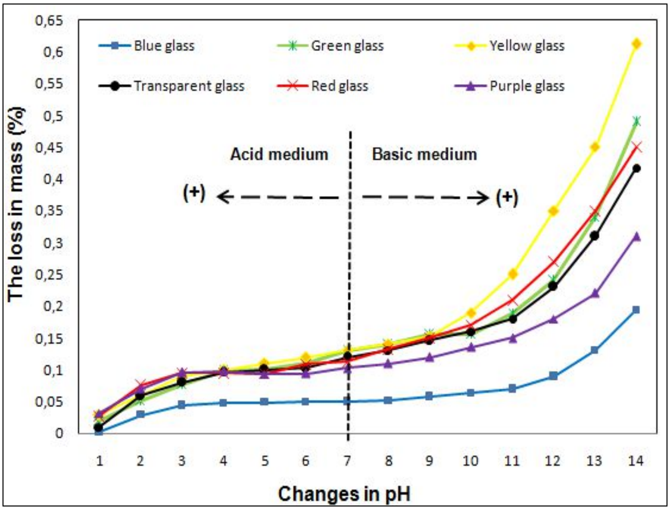

Figure 1. *The evolution of mass loss as a function of pH.*

In general, all studied glasses show neighbors versus pH behavior, the dissolution of these glasses decreases effect of pH 1 to pH 4 then

[9]-Paul A , Chemical durability of glasses, J. Mater. Sci, 1977, p 2246-2268.

stabilizes up to the value of pH = 8 to 9 beyond this pH value increased mass loss is remarkable.

In strongly acidic (pH = 1 to 4), the dissolution of single ternary glass ($SiO_2.CaO.Na_2O$) can be described by two successive mechanisms, each with its own kinetics.

An initially fast release of selective ion exchange Na^{+} and Ca^{++}, leaving a residual layer of hydrated silica which is then completely dissolved. The first mechanism (fresh glass attack by H^{+} ions) is slowed by the diffusion transport across the surface while the second layer has an almost constant speed. This scenario, possibly complicated by the precipitation of secondary phases involving a residual layer of silica or alumina complex nature, can be applied to most silicate glasses.

Dissolution in strongly acidic solutions is characterized by a quick release of all the elements. Its duration is variable and depends on the temperature of alteration and the composition of the glass. In this region, all the mono and divalent elements selectively dissolves over silicon for different glasses studied.

It is disclosed that the loss in mass is inversely proportional to the relative content of hydronium ions[10], that despite the intense dissolution exchange with the captions of the glass matrix (network formers and modifiers such as Al, Fe and alkalis) phenomenon due to the imbibitions of the gel that forms on the surface is believes its volume (hence the total weight of the glass).

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[10]-Melcher M, Wiesinger R, Shrriner M , Degradation of glass artifacts: application of modern surface analytical techniques. Accounts of chemical research, 2010, p 916-926.

The chemical composition of these glasses plays a very important role in the regime leaching especially the proportion of alkalis that with their increase, the glass becomes soluble either by exchange or by training with these other components detergents. Even the different types of glass have one to comprise strong acids due to their similar chemical compositions in what major's elements (have soda-lime glasses, SiO_2, CaO and Na_2O).

A pH near neutrality (pH= 4 to 9) the idea of leaching of alkali-controlled diffusion through a low permeability and low residual soluble layer, and macroscopic scale, it is as if the dissolution was congruent to which the surface layer is probably stabilized (Corrosion rate almost constant for all glass samples).

The maximum dissolution and alteration stabilizes it says: In this area some time after that the rate of extraction of alkali through the H^+ ion exchange is reduced and it will be equal to the rate of decomposition so complete decomposition of the glass O-M network.

By cons in the basic domain Glass suffered a beginning of another fashion alteration (destruction of network Si-O-Si) by the hydroxyl group of the basic solution which increases with increasing pH. This stage is characterized by the end of the alteration in an acid medium and the beginning of an another type of glass corrosion in basic environments the third stage (pH>9), growth leaching to increase hydroxyl in solutions that promote the degradation of skeletal SiO_2 (the structural glass network) and the formation of hydrated silicates such as product tampering, degraded thereafter and react with the alkali metal ions and the transport solution.

Glass dissolution in basic media after the destruction of the network described by the following steps: Water adsorption, ion exchange Formation salt and leaching so based on the nature of the alteration glasses have a high loss mass relative to the acid environment due to its classification as glasses silicates (silica as major component).

The variation of the mass loss for the different colors of glass due to the presence of other metal oxides and the same content variation Na_2O and silica in the chemical composition. Thus accelerating the dissolution (corrosion of the glass) by raising the pH related to the solubility solubilization of alkali and alkaline earth (which consumes protons).

2.2.2 Effect of time :

The leaching phenomenon is proportional as a function of time for different alteration aggressive environments:

In the neutral and acidic environments (Figure 2 and Figure 3) (alteration by dissolution of alkalis), the alteration is characterized by an aggressive speed stabilizes with time (48 hours) due to the complete removal of alkalis.

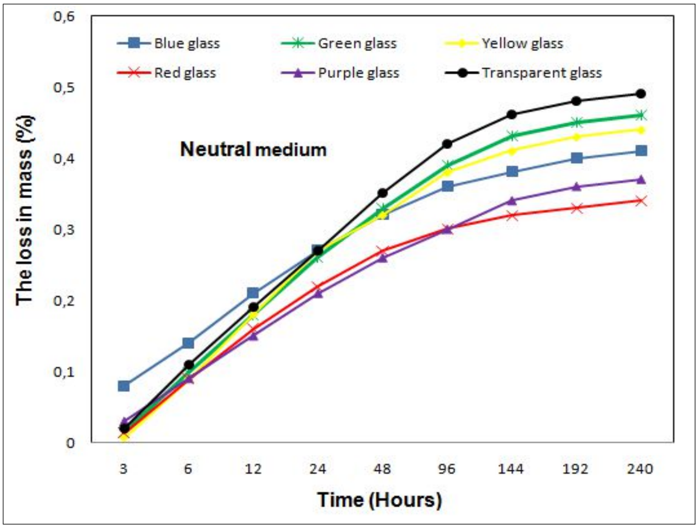

Figure 2. *The loss of mass as a function of time in the neutral medium*

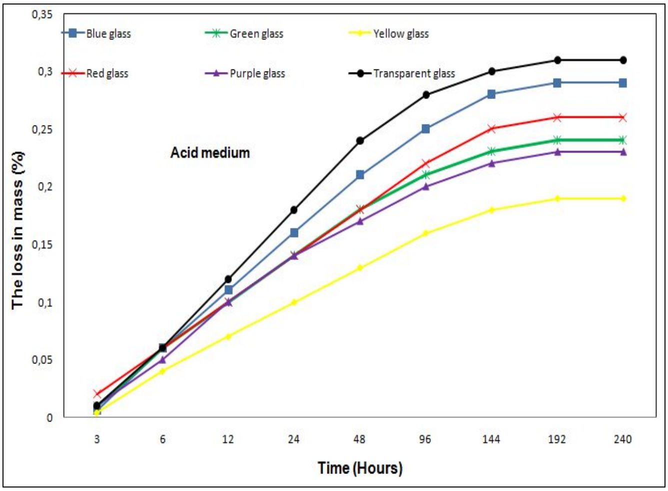

Figure 3. *The loss of mass as a function of time in the acid medium*

In the basic settings

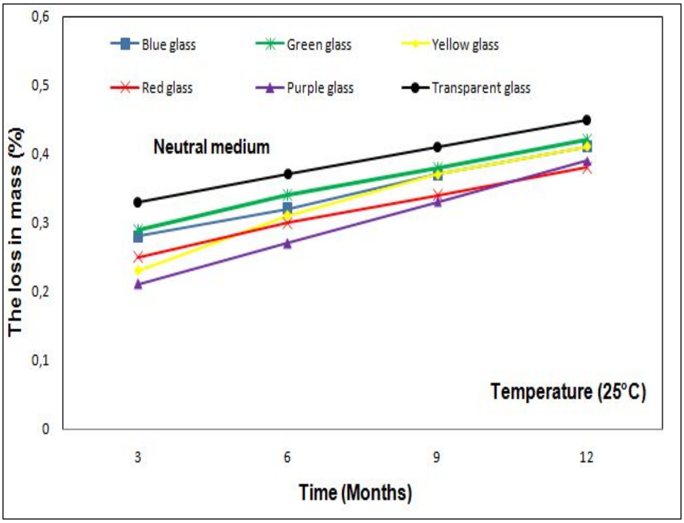

Figure 4. *The loss of mass as a function of time in the basic medium*

(Figure 4) the alteration rate is proportional to the time (destruction of the windows network).

2.2.3 Effect of temperature:

Note that the rate of corrosion of the glass for 12 months (T = 25 °C) has lower than at high temperature values, this is due to: That the reaction mechanism (diffusion of hydrogen ions, the solubility of alkalis and even rupture phenomena of bridges in the network) is proportional to the temperature that promotes the speed difference, but the overall behavior of the corrosion remains the same [11].

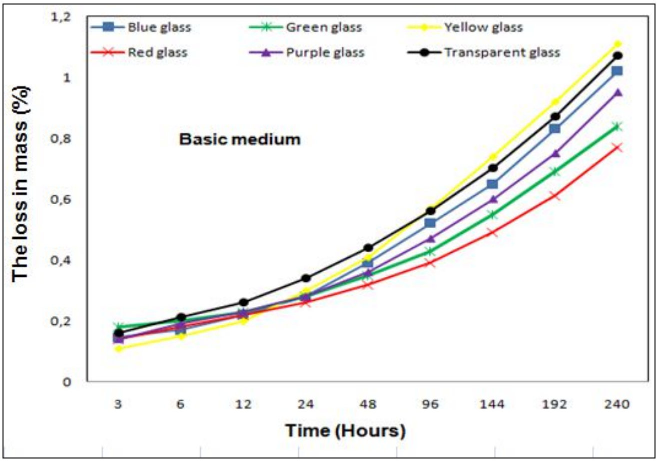

Figure 5. *The loss of mass as a function of time in the Neutral medium at room temperature [T = 25 ° C].*

From measurements of corrosion rate for different glasses studied this change is due not only related to the nature of aggressive environments but also the role of various components on the solubility of the glass (a Sustainability glass also increases when the oxides of the following elements are added, Al, P, Sn, Mn, Zr, Ti, Pb).

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[11]-Newton R.G , Sulfur dioxide and medieval stained glass, Society of Chemical Industry, Water and Environment Group, London, 1979,p 500-501.

These correlations are not generalized to all compositions silicate glasses, which raises the question of the relevance of "chemical durability preachers or preachers solubility" The theoretical reasons can lead to prefer chimico-structural index, the abundance of non-bridging oxygen, or a thermo-chemical index, assumed Representative of the solubility of the glass, the free energy of hydration.

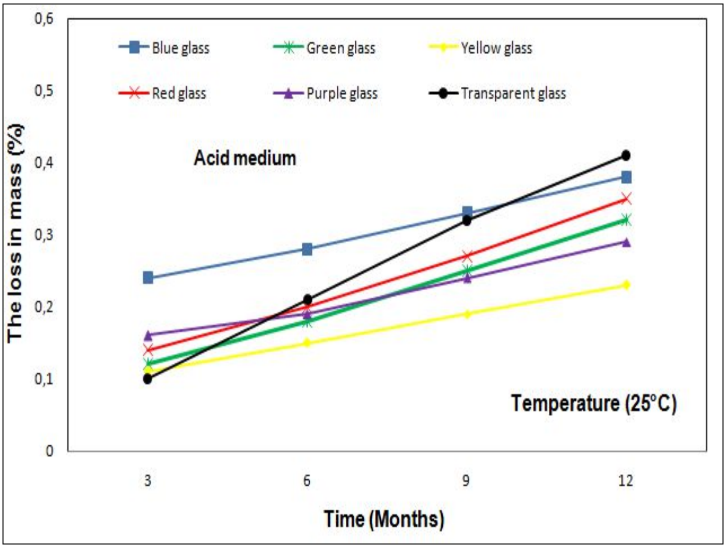

Figure 6. *The loss of mass as a function of time in the acid medium at room temperature [T = 25 ° C].*

Preacher thermo-chemical it has been shown by various authors the free hydration energy of a glass, calculated from the data on thermodynamic components, correlated very approximates its initial dissolution rate determined window.

Reached a state of saturation reversibly (Glass in equilibrium with the solution). Reversibility explicitly assumes a congruent process the that the dissolution of silicate glasses [12], because of the existence of extraction selective elements, is irreversible essential.

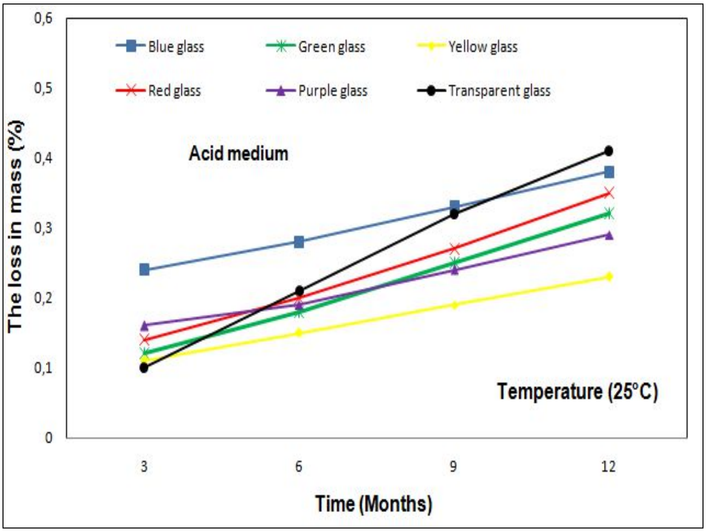

Figure 7. *The loss of mass as a function of time in the basic medium at room temperature [T = 25 ° C].*

Chemical structural Preacher: The idea that the aqueous corrosion of glass depends, among other things, the organization is commonly short allowed. Recall that the basic structural units of glass silicate SiO_4^{4-} tetrahedral are organized network more or less polymerized. In this scheme, any oxygen atom connecting two tetrahedral is termed bridging. Conversely, oxygen connecting a tetrahedron with a "modifier" ensuring electro-neutrality (Ca, Na element are classified as non-bridging oxygen.

[12-]Papadopoulos N , Drosou C, Influence of weather conditions on glass properties, Journal of the Chemical Technology and Metallurgy ,2012,p 429-439.

The relative importance of non-bridging oxygen reflects the importance of network outages Si-O-Si and therefore degradation of the vitreous material [13].

Conclusion

At the end of the work, the alteration of archaeological glasses Palace of Ahmed Bey Constantine it shows the following:

- The study was carried out mainly on the degree of damage (loss of mass), the morphology and the surface (transparency).
- Analysis of the chemical composition of archaeological glass is paramount to identify the historical and technical aspects of production, so the glasses Ahmed Bey Palace his typical glasses the transition period Medieval Renaissance in which the network forming oxide is SiO_2 60%. Silica is the major constituent of glasses are studying, it is highly soluble and contributes to the morphological reorganization gels.

However, sodium is highly soluble element is added to glass to compensate for deficits load. When in excess, it depolymerizes the glass, which has the effect of increasing the rate of weathering. It modifies the geometry probably covalent backbone, thereby facilitating the penetration of water, calcium is also a charge compensator which is soluble and increases the initial rate of alteration, since as the sodium, it depolymerizes the silica network and the average size increases might interatomic cavities.

[13-]El-Shamy T.M, Lewins J, Douglas R.W, The dependence of the pH of the decomposition of glasses by aqueous solution,Glass Technol ,1972, p 160- 165.

The study of behavior and aging of archaeological glass palace Ahmed Bey shows a degree of alteration more or less weak in neutral environments and acid, but it is important in the alkaline medium, while the degradation is proportional to the temperature and time for the various harsh environments.

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