Mediterranean Archaeology and Archaeometry, Vol. 7, No 1, pp. 41-51

DEVITRIFICATION BEHAVIOUR OF CORRODED GLASS: FOUR CASES STUDY

Ramadan Abd-Alla

Conservation department,
Faculty of Archaeology,
Cairo University, Cairo, Egypt.

E-mail: rmdnabdalla@yahoo.com

Received: 12 - 10 - 2006
Accepted: 20 - 12 - 2006

ABSTRACT

This paper focuses on the devitrification behaviour and recrystallization mechanism of archaeological glass. It also aims to reveal the fact concerning this phenomenon as a deterioration process associated with glass corrosion. Many archaeological glasses attributed and dated to the early Islamic period in Egypt were collected and analyzed using XRD spectroscopy technique to identify the mineralogical composition and determine the crystalline phases present. A preliminary study by analytical scanning electron microscopy (SEM&EDX) allowed characterization of the elemental chemical composition of the underlying glasses and the neocrystallisation developed on their surfaces. Furthermore, the compositional phases and glass texture were also examined. According to the confirmed results obtained for four glasses, it can be concluded that the archaeological glass can be devitrified or partially recrystallize due to the corrosion process addition to the thermal effects. Many separated crystalline phases such as quartz, calcite, tosudite, jacopsite and calcium silicate were detected in the glass samples. This phenomenon considered one of the most dangerous deterioration aspects of corroded glass. So understanding it will assists the glass conservators in treating such corroded glass.

KEY WORDS: Glassy state, Recrystallization, Decomposition, Crystalline phases, Glass corrosion.

INTRODUCTION

The structure of glass was for many years a challenging area of research for physical chemists and now for archaeological conservators. Numerous geological and industrial researches were carried out to study the devitrification and phase separation of the natural and geological glasses but a concentrated study of archaeological glass has not been done. All the recent scientific studies confirmed that quartz glass is not crystalline at room temperature because the arrangement of interatomic bonds between silica (Si) and oxygen (O) required for the establishment of order is impeded; the viscosity of glass is so high at room temperature that millions of years would be required for it to crystallize. So when and how the archaeological glass can be devitrified or recrystallize? Answering and discussing this question is the main objective of this work as following:

It was stated that the chemical composition considered one of the main factors affecting the glass devitrification. Therefore, the terms glass former and modifiers define the respective roles of the main components of glass. The glass former (silica, SiO_2) has a three-dimensional crystal lattice. When heated, the crystal lattice breaks down into a melt and takes on the random configuration of a liquid. If the melt is cooled slowly, the molecules crystallize back into the same three-dimensional network in which they were arranged before melting. However, if a modifier added the melt is cooled rapidly without allowing crystallization to occur, the molecules of the melt set into a glass. The product then has an irregular, three-dimensional network of silicon and oxygen atoms, within which the modifiers atoms are entrapped. The modifier atoms usually sodium and potassium, lower the melting temperature of glass to about 700 °C. The modifier also reduces the viscosity of the glass when liquid, and alters the coefficient of expansion of the solid. It also diminishes the chemical durability of the glass by increasing its solubility in water, and increase the tendency of glass to decompose. Stabilizing compounds are thus added to the melt in the form of alkaline-earth oxides: lime or magnesia. These decrease the solubility of soda and potash glasses, improve their chemical durability and/or prevent crystallization. The alkaline-earth oxide content also determines the hardening range, and hence the period during which glass can be shaped. Oxides such as those of aluminum and iron are intermediates, and enter glass in either a forming or modifying position, having intermediate bond strengths. Alumina improves the chemical durability and reduces the tendency of glass to crystallize during forming operation. The usual composition of soda-lime glasses is approximately 75 percent silica, 15 percent soda, and 10 percent lime (Goffer 1980, Newton and Davison 1989 and Abd-Alla 2006)

As mentioned above, to prevent decomposition and deterioration of glass, a balance of silica and modifiers is required; it is represent a difficult and complex problem of all ancient glass. Too much soda makes the glass easily corroded, even by water. Too much lime gives it a tendency to devitrify or recrystallize and makes it susceptible to weathering. Excess alumina raises the softening temperature of the glass although it improves the chemical durability and reduces the tendency of glass to crystallize during forming operation. Unfortunately, the ancient glassmakers were obliged to add much amount of soda and lime on the glass batch, so the produced glasses almost have exfoliated compositions.

When a glass of an exfoliated composition reacts with water or an aqueous solution, chemical changes occur at the surface and may then spread to the whole of the glass, depending on a number of factors especially the composition of the glass, the pH of the liquid and the glass surface. The surface of glass is highly influential in the effect of the weathering process which occurs on it. Wely (1975) points out that a surface is a defect itself, because all surface ions are in a state of incomplete coordination. Surface area is an important factor in the corrosion of glass, as the amount of constituents released during decomposition is proportional to exposed surface area. As the ratio of surface area to volume (*SA/V*) of the leaching solution increases, there is an increase in the extraction of silica. This dissolution of the silica network causes alkali to pass into solution, and reduces the thickness of the surface gel (Newton 1989).

The addition of lime (CaO) to binary silicate glass is known to increase the durability. If lime (CaO) is added to the glass in increasing amounts to 10 mol per cent there is a rapid decline in soda extraction owing to the increasing stability of the surface gel. The stability is due to the presence of CaO increasing the coupling of the vibrational modes of the silica non-bridging oxygen modifier bonds to the bridging of the Si-O-Si network. It would be expected that the replacement of one (Ca^{2+}) ion by two protons (H^+) would have the same effect as replacing two (K^+) ions from the network, but in the latter case, a much more porous layer is formed. If the lime content is increased above 15 mol per cent, the weathering resistance starts being drastically reduced and glass are in rather poor condition. However, studies carried out by Cox *et al.* (1979) and Newton (1975-1989) showed that the glasses contained a high amount of lime (above 15 mol per cent) or magnesia (above 6 mol per cent) tended to behave differently from those which contained less than this amounts, even when compared on a molar basis, and it was subjected that microphase separation or devitrification was occurring at these levels.

As previously mentioned, when glass is in contact with water or moisture, the alkali metal ions (R^+) are slowly leached out to be replaced by protons (H^+) from the water. Not only are fluxing ions leached from the glass network by water, so are any colouring metals ions present. At the same time the insoluble salts and oxides are deposits on the glass surface, here the glass and weathering crusts become obscured by encrustations of insoluble salts. These may be especially prevalent where excess lime in glass is leached out, to be deposited as a whitish deposit on the surface or within decayed layers of the glass forming a continuous matrix. Furthermore, when the alkali metal ions (R^+) of glass surface were leaching out, the remaining silica-enriched film could have acted as a protective film which prevented the glass from further weathering (Meiguang *et al.* 1987 and Abd-Alla 2005) .The surface layer losses its glassy nature and characteristic refractive index and so appears dull or iridescence. Badly decayed glass may survive only as a chalky mass of silica gel and be somewhat difficult to identify as glass. At some advanced cases of deterioration and corrosion, phase separation and/or devitrification may be occurring (Jiazhi and Xianqiu 1986; and Cronyn 1990).

The second cause of glass devitrification is attributed by virtually all authors to the nature of the thermal treatment of molten glass during manufacture. When molten glass is cooled the randomly distributed molecules will endeavour to adapt a less configuration, more like those of crystals

(Newton 1989; Shelby 1997 and Belhadji et al. 2005). However, an alternative three-dimensional structure forms because the viscosity of the glass and the presence of network modifiers hinder the process. The silica networks, which form at high temperatures, cause the melt to have a high viscosity so that the molecules do not have time to form themselves into crystal lattices before cooling. However, when network modifiers are added, they have the effect of considerably lowering the viscosity and thus there are opportunities for new types of crystals to form. According to Newton (1989), a glass with a molar composition of 16% Na_2O, 10% CaO and 74% SiO_2 can form crystals of devitrite ($Na_2O.3CaO.6SiO_2$) which grow at a rate of 17 $\mu m\ min^{-1}$ at a temperature of 995°C. Thus at 11000C (below the liquidus temperature) there was extensive devitrification especially when the amount of lime is high. Devitrivite does not occur in nature as a mineral.

In 1977, Kny and Nauer have claimed that devitrification might occur in cold glasses although thousand of years may be required for this to occur. They also claim to have found microcrystallites of the order of 20 nm in size in ancient glasses. So according to Newton and Kny, the differences between the two cases of devitrification are that in the true devitrification in the first case the total chemical composition remains unaltered. The composition will change locally as crystals separate from the base glass, but no atoms are added or subtracted which were not already in the glass. Whereas the second case of devitrification means that the glass are partially or completely decomposed and the chemical composition are altered due to loss of some alkaline compounds and encrustation of a new mineralogical deposits on the glass surface during corrosion process.

According to the research work carried out by Brill (1987), it was confirmed that if the unpurified plant ashes soda "the another alkali source in glass containing primarily sodium and potassium carbonate" were purified by leaching and recrystallization, the magnesium (except for any in the form of chloride) would have been separated out along with the other insoluble components, such as the calcium, aluminum, phosphorus, iron, etc. Examination and analysis of three corroded glasses unearthed at Yangzhou carried out by Jiazha and Xianqiu (1986) revealed that there are longstrip crystals in all glasses, and [beta $BaSi_2O_5$], [$PbCO_3$], [$Pb_5\ (Pb_4)_3$ OH] and [$5PO.P_2O_5.SiO_2$] are the main crystal phases. Kawano *et al.* (1997) reported neoformation of clay minerals as hydration products of volcanic glasses. XRD analysis performed by Karakas and Kadir (2000) indicates that the volcanic glasses contain halloysite, kaolinite, illite, smectite, quartze, minamite and jarosite. An experimental study carried out by Munier *et al.* (2002) to evaluate the atmospheric factors influencing the formation of neocrystallisations on low durability glass exposed to urban atmosphere indicates clearly that the nature of the glassy substrates is not the main factor influencing sulphates, nitrates and chlorides formation process but depend essentially on atmospheric parameters acting in the same way on all types of glasses. Belhadji *et al.* (2005) also reported that the aging effect is probably necessary in order to increase or decrease the crystallization rate of the glass.

Archaeologists and glass conservators have, however used the term devitrification in quite a parallel connection to mean *loss of vitreous nature of glass.* In this case the glass has weathered or corroded, due first to loss of alkali followed by loss of other constituents and finally the creation of a silica gel. In this case the chemical composition has changed. From his point of view, Newton (1989) has been mentioned about this use of the term *devitrification* that this use therefore, is ambiguous, especially as some forms of weathering can take place without any apparent loss of vitreous nature. For example, the surfaces of all ancient glasses are de-alkalized and can be said to consist of a *hydrogen glass* instead of the usual *alkali glass* yet their surfaces can remain shiny and vitreous although marked chemical changes have taken place. Therefore, he recommended that the term devitrification should in future be restricted to the description of the formation of crystals from the melt. Therefore, in this study, by using various analytical methods we examine the devitrification as structural and morphological alterations of archaeological glass, which frequently are associated with its corrosion process and reflect its chemical decay.

EXPERIMENTAL

Analysed glasses

Many archaeological glasses of different typology and colors excavated from the ruins of Al-Fustat: the archaeological Islamic site in Egypt, have been collected, cleaned and prepared for chemical analysis. They were excavated from damp soil, so most of them are completely corroded and subjected to intensive chemical decay (Fig. 1). According to the date determined by archaeologists, all of them were made locally at the same site in the beginning of early Islamic period (2ndAH/ 8thAD). For the XRD measurements, the glass samples were prepared in fine powder form, whereas just small samples were required for EDX analysis and the microscopic examination. It should be noticed that the explanation of analyses and examinations will restricted only to the results of four corroded glasses as cases study, in which some crystal phases were detected. They are shown in figure 1 and marked from left to right by G.1, G.2, G.3 and G.4.

Analytical techniques

Investigation of the compositional phases and determination of the elementary chemical composition of the selected glass samples were performed by scanning electron microscopy attached with Energy dispersive X-ray spectroscopy (SEM with EDX). This technique has two advantages:

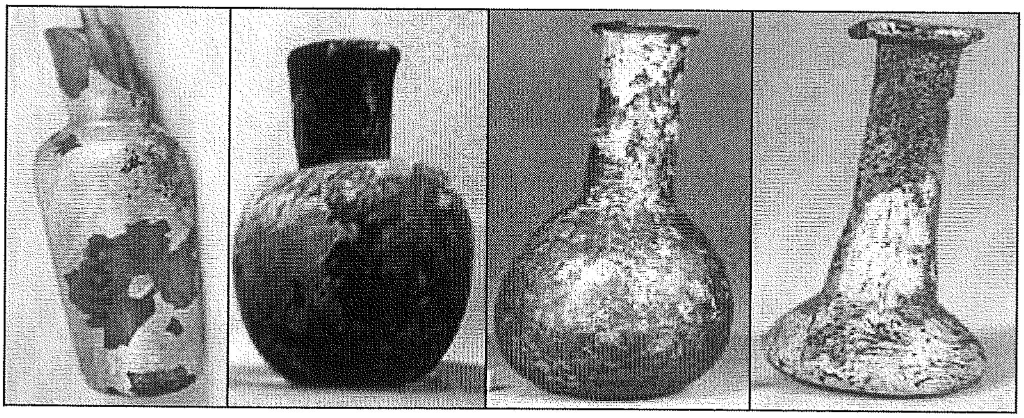

Fig. 1 Four corroded glass objects from the early Islamic period in Egypt, selected for analytical study.

its qualitative and quantitative determination and it just require a very small glass as a sample. Furthermore, SEM was effectively used to examine the glass texture and reveal any alteration of the glass and its corroded surface especially the aspects of devitrification, phase's separation and neocrystallization growth. An SEM equipment (model FEL Quanta 200) attached with EDX unit (model Philips XL30) with accelerating voltage 30 K.V, located at Department of Earth Sciences, Yarmouk University in Jordan was used. The samples were coated with amorphous carbon, and SEM was operated in backscattered mode, which is suitable for examining the compositional phases of glass material. Magnification 10X up to 400,000X and resolution for 3.5 nm.

The determination of mineralogical constituents and crystalline phases present in the glasses was carried out by X-ray diffraction spectrometry (XRD). Though glass is amorphous or non-crystalline substance, this technique can be employed especially to identify the crystalline phases of the corroded glass. 6000-Shimazu x-ray diffractometer with Cu K? radiation (1.543 A°) and operating in reflection mode, located at Faculty of Archaeology and Anthropology, Yarmouk University in Jordan was used. The scan range was 10 to 80° with a step size of 0.01°. A scanning speed of 0.01 min^{-1} and accelerating voltage of 40 K.V was used.

RESULTS AND DISCUSSION

EDX determinations

The chemical composition of both the original or underlying glass and its corroded surface was determined for the selected four glasses by EDX method. Analyses results given in Table 1 indicate that these glasses are identified as soda-lime-silica (Na_2O-CaO-SiO_2) glass, and characterized by low potassium and magnesium content. This composition indicates also that they are made with natron salt as a source of alkali. Furthermore, it is agreements with the results of recent studies of Brill (1999) and Henderson *et al.* (2004) about the chemical composition of the early Islamic glass in Egypt. Chemically, these glasses are completely decomposed due to attacking of the intensive deterioration factors especially water for long time in the ground. There is an obvious change in the compositions of the corroded glass surface in comparison with the original glass in the center, i.e., Na_2O and K_2O content decreases and SiO_2 increases.

The Al_2O_3 and Fe_2O_3 of the corroded surfaces also have increased, obviously due to the dissolution of other components of the glass, leaving an apparent enrichment of Al and Fe, which have very low solubilities. However, in the present cases, the outer corrosion crusts are chemically exfoliated, it seems generally to be rich in silica (SiO_2 avg. 79.03 %), rich in lime or calcium oxide (CaO avg. 7.57%) and poor of alkali (Na_2O avg. 5.08%; K_2O avg. 0.25%), whereas the underlying glasses are not, they relatively have chemical compositions similar to those of unaltered glasses from the same site and period. However, the original or unaltered glasses are generally characterized by their high amount of alkali (Na_2O avg. 13.13 %; K_2O avg. 0.75%) and moderate contents of silica (SiO_2 avg.74.29%), lime (CaO avg. 7.04%), magnesia (MgO avg. 2.30%) and alumina (Al_2O_3 avg. 2.54%).

Table 1: Chemical composition of glasses and their corroded layers obtained by EDX.

Oxides (Wt. %)	**(G. 1) Corroded glass bottle**		**(G. 2) Corroded glass vessel**		**(G. 3) Corroded glass flask**		**(G. 4) Corroded glass bottle**	
	Original glass	*Corroded surface*	*Original glass*	*Corroded surface*	*Original glass*	*Corroded surface*	*Original glass*	*Corroded surface*
SiO_2	71.76	77.43	73.55	78.02	75.92	79.62	75.94	81.07
Na2O	14.72	5.13	13.41	6.12	12.07	5.18	12.31	3.92
CaO	6.87	7.19	7.79	8.32	6.73	7.36	6.80	7.42
K2O	0.86	0.31	0.76	0.11	0.61	0.28	0.77	0.31
MgO	1.33	2.46	1.43	2.06	1.05	1.74	1.10	1.45
Al2O3	2.83	4.02	2.65	2.20	2.55	4.06	2.13	4.09
Fe2O3	0.76	2.53	0.52	1.38	0.50	1.12	0.47	1.02
MnO	0.81	0.85	0.60	0.79	0.57	0.64	0.52	0.72
Total %	100	100	100	100	100	100	100	100

XRD determinations

XRD analyses were carried out on both partially and completely corroded glass samples. The results given in Table 2 and Figures 2 -5 reveal that the original or underlying glasses are quite amorphous and still having its glassy nature, whereas the outer surfaces and their corroded crusts are devitrified and loss its characteristic glassy nature. Initial growth of crystalline phase of hydrated calcium silicate ($Ca.5SiO_3.5.xH_2O$) was detected in sample G.1. Completely growths of crystalline phases of calcite ($CaCO_3$) and quartz (SiO_2) were confirmed in sample G.2, which perfectly cleaned from any soil deposits to avoid any existence of them from soil. Tosudite [$(K, Ca)\ 0.\ 8Al_6$ $(Si, Al)\ 8O_{20}$ $(OH)\ 10.\ 4H_2O$] is the main crystal phase presented in the sample G. 3. The XRD of the corroded layer of the sample G. 4 shows that calcite ($CaCO_3$) is the main crystal phase, and there are certain amounts of Jacobsite ($MnFe_2O_4$), calcium silicate (Ca_2Si) and hydrated calcium iron aluminum silicate (Ca_2FeAl_2 (SiO_4) (SiO_2O_7) $(OH)2.H_2O$) crystals as well.

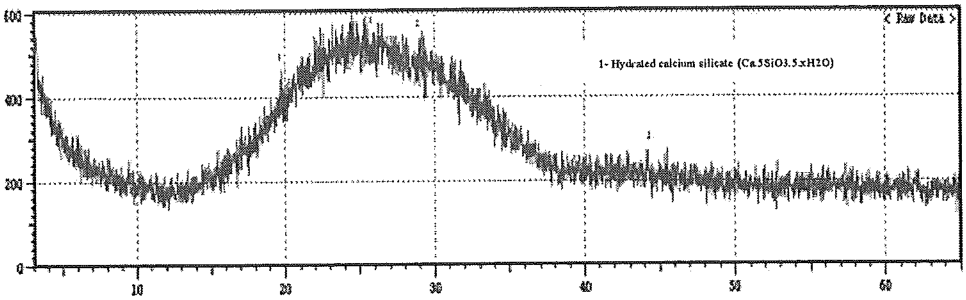

Fig. 2 XRD pattern of sample G. 1 showing the initial growth of crystalline phases.

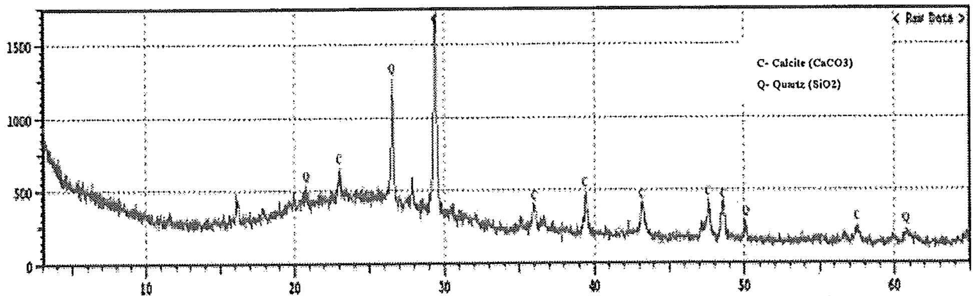

Fig. 3 XRD pattern of sample G. 2 showing the completely growth of crystalline phases.

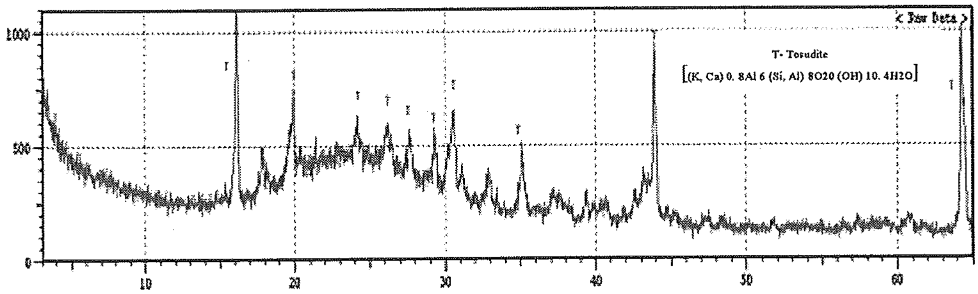

Fig. 4 XRD pattern of sample G. 3 showing the completely growth of crystalline phases.

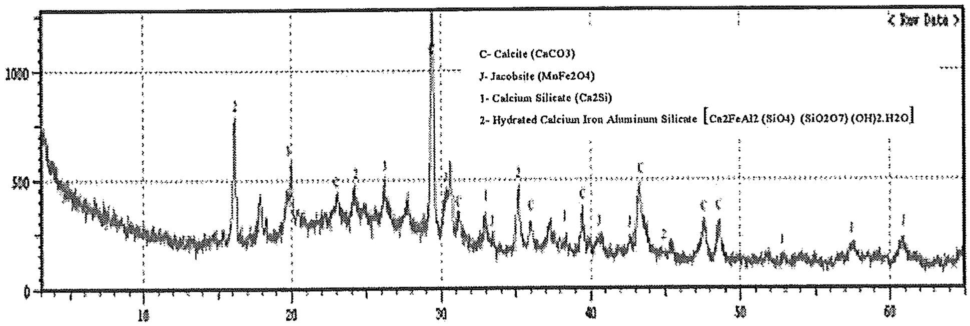

Fig. 5 XRD pattern of sample G. 4 showing the completely growth of crystalline phases.

Table 2. Mineralogical composition and crystalline phases present in the glass samples obtained by XRD.

Sample No.	Crystalline phases	Formula	Card No.
G. 1	Hydrated Calcium silicate	Ca.5SiO3.5.xH2O	(33-306)
G. 2	Calcite	CaCO3	(5-586)
	Quartz	SiO2	(46-1045)
G. 3	Tosudite	[(K, Ca) 0. 8Al 6 (Si, Al) 8O20 (OH) 10. 4H2O]	(46-1463)
G. 4	Calcite	CaCO3	(5-586)
	Calcium Silicate	Ca2Si	(3-798)
	Jacobsite	MnFe2O4	(10-319)
	Hydrate Calcium Iron Alum. Silicate	[Ca2FeAl2 (SiO4) (SiO2O7) (OH) 2.H2O]	(36-437)

Fig. 6: Backscattered electron image of sample G. 1 showing the fractures and dissolution voids of devitrified area of corroded surface.

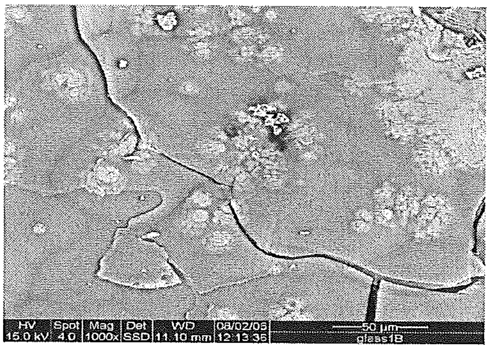

Fig. 7: Backscattered electron image of sample G. 2 showing neoformation of calcite phase in fractures of corroded and cracked surface.

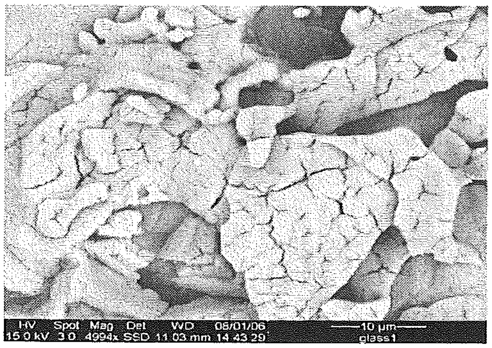

Fig. 8: Backscattered electron image of sample G. 3 showing neoformation of tosudite phase in fractures and dissolution voids of corroded surface, which losses its glassy nature.

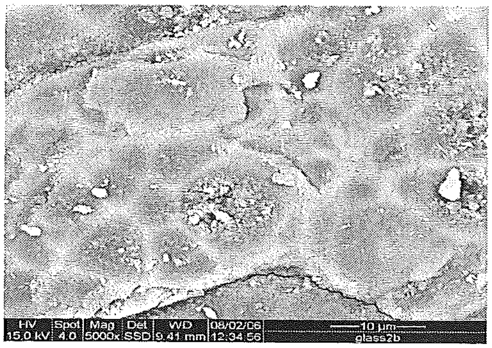

Fig. 9: Backscattered electron image of sample G. 4 showing neoformation of clay minerals phases deposited in fractures and pitted areas of corroded glass surface.

SEM observations

From SEM observation of the corroded glass samples, it can be seen that there are longstrip crystals in all of these glasses. Figs. 6-9 shows the backscattered electron images of them, from which we can find crystals containing calcium, silica, aluminum iron and manganese. In Fig. 3, we can also see that the edges of crystals began to be corroded. As it extended toward outer layer, SiO_2 crystals become smaller and lesser. This is why the corrosion layer shows sharp decrease in SiO_2 content.

Furthermore, the surfaces of all glasses seem to be inhomogeneous pitted, curviplanar, surface-planar and highly fractured forms. Most of these glasses were damaged and rich in dissolution voids and microcracks; the cracks often spread from the crystalline into the glassy area. Most crystalline areas often are much cracked. Addition to that, other aspects of sugar-like surface, flaking, and highly fissured nature of decayed crusts were also observed.

CONCLUSIONS

According to the results obtained by the qualitative and quantitative techniques (EDX &XRD) that followed by microscopic examination using SEM of four corroded glasses selected for experimental study here; it can be concluded that devitrification or recrystallization of ancient glass with no doubt is basically a fact of fusing and heat treatment, but it could be occur to the deteriorated glass especially those chemically are exfoliated and completely corroded. In this case, the devitrified glasses loss their glassy nature. Ratio and intensity of the crystalline phases depends on the rate of glass corrosion and damage state. Types and compositions of these separated phases are related to those of original glass and attacking solutions. Quartz, calcite, jacobsite, tosudite and calcium silicate hydrate are the common crystalline phases present in the analyzed glasses.

However, we are in accordance with all previous studies that devitrification is a fact of fusing. Some types of glass loss their glossy surface easier than others but most every glass will grow devitrification crystals if given enough time at high temperatures. On the other hand, the obtained results here suggest that crystal phases can form within the glass during its production which may result in corrosion of the glass melter *(flux)* and detrimentally affect the durability of the waste form. This phenomenon frequently is associated with glass corrosion, so it can be use the term devitrification in the conservation and archaeological studies to mean *loss of vitreous and/or glassy nature of the corroded glass, and also to describe formation of crystals due to chemical alterations and decomposition of the ancient glass* in a similar way to those resulted during fusing and heat treatment of unaltered glass. On the other hand, this phenomenon and its decay aspects considered on of the most dangerous factors affecting glass stability and durability. Therefore, glass conservators should be familiar with it during the treatment of corroded glass.

AKNOWLEDGEMENTS

This study was financially supported by the general directorates of XRD, EDX and SEM laboratories located at Yarmouk University in Jordan. The author is grateful to the anonymous referees for their critical reviews and suggestions.

REFERENCES

Abd-Alla, R. (2005) Evaluation of the impact of chelating agent (EDTA) on the treatment of weathered glass. T. Akasheh (ed.), *proceeding of The fourth international conference for Science & Technology in Archaeology and its Conservation*, 7- 11 December, The Hashemite University , El-Zarqa Jordan.

Abd-Alla, R. (2006) The raw materials of ancient Roman glass in Egypt and Jordan: a comparative analytical study, *Adumatul*, vol.14, 23-31.

Belhadji, M., Ziani, N., and Mostefa, M. (2005) Phase separation and devitrification study of GeTeSb Chalcogenide glasses, *Chinese Journal of Physics*, vol. 43, 95-102.

Brill, R. (1962) A note on the scientists' definitions of glass, *Journal of Glass Studies*, vol.4, 127-138.

Brill, R. (1986) Chemical glass of some early Indian glasses. H.C Bhardwaj (ed.), *Archaeometry of glass*, proceeding of the XIV international congress on glass, 2-6 March, Indian Ceramic Society, New Delhi, 1-25.

Brill, R. (1999) *Chemical analysis of early glasses.* Corning museum of glass, New York.

Buyes, S. and Oakly, V. (1999) *The conservation and restoration of ceramics*, Butterorths, London.

Cox, G.A., Heavens, O.S., Newton, R.G., and Pollard, A.M. (1979) A study of the weathering behavior of medieval glass from York Minster, *Journal of Glass Studies* , vol. 21, 54-75.

Cronyon, J.M. (1990) *The elements of archaeological conservation*, TJ. Press, Rutledge.

El-Shamy, T.M., and Ahmed, A. (1977) Corrosion of some common silicate glasses by aqueous solutions. *Proceedings of the 11th International Congress on Glass, Prague, July*, Vol. III.

Goffer, Z. (1980) *Archaeological chemistry; a source book on the applications of chemistry to archaeology*, John Wily& Sons, New York.

Henderson, j., McLoughlin, S.D. and McPhail, D.S. (2004) Radical changes in Islamic glass technology: evidences for conservatism and experimentation with new glass recipes from early and middle Islamic Raqqa, Syria. *Archaeometry*, vol. 46, 439-468.

Jiazhi,Li., and Xianqiu,C. (1986) A study on west Han Pbo-BaO-SiO_2 glass and its corroded layers unearthed at Yangzhou, H.C. Bhardwaj (ed.), Archaeometry of glass, proceeding of the XIV International Congress on glass, March 2-6, 1986, New Delhi.

Karakas, and Kadir, S. (2000) Devitrification of volcanic glass in Konya volcanic units, *Turkish Journal of Earth Science*, vol. 9, 39-46.

Meiguang, S., Ouli, HE., and Fuzheng, Z. (1987) Investigation on some Chinese potash glasses excavated in Han dynasty tompes, in: H.C. Bhardwaj (ed.), *Archaeometry of Glass*, proceeding of the Archaeometry session of the XIV international congress on glass, The Indian Ceramic Society, New Delhi, 15-20.

Munier,I., lefevre,R. and Loson, R. (2002) atmospheric factors influencing the formation of neocrystallisations on low durability glass exposed to urban atmosphere, *Glass technology*, vol. 43C, 114-124.

Newton, R. and Davison, S. (1989) *Conservation of glass*, Butterworth and Co., London.

Paul, A. (1977) Chemical durability of glasses; A thermodynamic approach. *Journal of Material Science*, vol. 12, 2246-2268.

Pollard, A. and Heron, C. (1996) *Archaeological chemistry*, RSC press, Cambridge.

Rose, P., Ojovan, M., Hyatt, N., and Lee, W. (2004) Crystallization within simulated high level waste borosilicate glass, *Material Research Society, Symp.proc.* vol. 824, CC5.6.1- CC5.6.6.

Shelby, J. (1997) *Introduction to glass science and technology*, RSC press, Cambridge.

Shugar, A. and Rehren, Th., 2001, Formation and composition of glass as a function of firing temperature, *Glass Technology*, vol. 43C, 145-150. Proc. XIX int. Congr. Glass, Edinburgh 1-6 July.

Wely, W.A. (1975) Structure of sub-surface layers and their role in glass technology, *Journal of Non-crystal solids*, vol.19, 1-25.

Zarzycki, J. (1991) *Glasses and the vitreous state*, Cambridge university press, Cambridge.