Glass depolymerization in the process of long-term corrosion: A study of deteriorating semiopaque turquoise glass beads using micro-FTIR spectroscopy

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Abstract
Nowadays, a problem of historical beadworks conservation in museum collections is actual more than ever because of fatal corrosion of the 19th century glass beads. Study of the beads at different stages of glass corrosion using FTIR was carried out in the attenuated total reflection mode in the range from 200 to 4000 cm\(^{-1}\). We have observed glass depolymerization in the degraded beads, which is exhibited in domination of the band peaked at \(\sim 1000\) cm\(^{-1}\). We conclude that the simplification of the glass structure during its long-term degradation at room temperature may be explained within the thermal-fluctuation theory of materials fracture. We consider glass depolymerization, caused by the internal stress and decreasing the glass strength, as an essential corrosion mechanism of strongly stressed glass. We have also revealed shifts of two major absorption bands to low-frequency range (\(\sim 1000\) and \(\sim 775\) cm\(^{-1}\)) compared to ones typical for amorphous SiO\(_2\) (\(\sim 1100\) and \(800\) cm\(^{-1}\), respectively) connected with Pb\(^{2+}\) and K\(^+\) appending to the glass network. The presence of a weak band at \(\sim 1630\) cm\(^{-1}\) in all the spectra is attributed to the adsorption of H\(_2\)O. After annealing of the beads, the latter band disappeared completely in less deteriorated samples and significantly weakened in more degraded ones. Based on that we conclude that there is molecular water adsorbed on the beads. However, products of corrosion (e.g., alkali in the form of white crystals or droplets of liquid alkali) were not observed on the surface.

1. Introduction

The appearance of glass beads was inseparably associated with origin of glass in the third millennium BC and further development of its manufacturing technology [1, 2]. A short time later, Asia and Egypt—the main centers of glassmaking—began using opaque glass for making different articles including adornments. Before long, such things had become an important attribute in different rituals and ceremonies and played a huge role in life and culture of many countries and nations, as they represented power and wealth of their owners. In addition, such eminent works of art were essential objects for global trade expansion and were shortly spread throughout the world.

Therefore, the glass beads items had been the important part of humanity’s everyday life since the early ancient times, but only in the mid of the 18th century the real flourishing of beadwork art began. Although, this period was rather short and lasted only until the end of the 19th century, a lot of artworks were created. In this period, the craft was extremely fashionable and popular in Europe, where the main centres of glassmaking manufacture were concentrated in Murano (Italy) and Bohemia (in the present-day Czech Republic) [3, 4]. In addition, it was very important in North America, where American Indians used glass beads to decorate their clothing, religious objects, and functional tools and created unique style of work with glass beads [5]. In Russia,
Beaded embroidery was especially loved throughout the whole 19th century. Both professional embroiderers and women of all walks of life created beaded items. Such enthusiasm was connected with several reasons. Firstly, development and the beginning of industrial-scale production of glass seed beads in the glass-making centres led to decreasing the cost. Then, the total number of varieties of glass beads, differing in size, color and shape (round, faceted, multi-layered, transparent, cloudy, opaque, opalescent, etc.), exceeded a thousand. As a rule, 20 to 30 varieties of glass beads were used for embroidering a beadwork.

That is why the majority of museums in Europe, North America and Russia possess numerous exhibits, fully or partially comprised of beadworks, for instance, decorations, reticules (figures 1(a), (b)), different household items and even beaded pictures, as large as a few meters, with different plots [7, 8].

Nowadays, the museum curators, conservators and restorers faced with a problem of preservation of historical beadworks from museum collections. It is an actual issue because of pernicious corrosion of the 19th century glass beads. There are many reports in the literature suggesting the glass corrosion, glass disease, or crizzling, i.e. chemical processes occurring on the surface of glass at high humidity, as the main cause of the destruction of glass [9–11]. Koob distinguishes five main stages of the corrosion process [12].

Figure 1. (a) A view of a beaded reticule and (b) an area on another beaded reticule of the 19th century, collection of the Museum of A. S. Pushkin in Moscow; both photographs were taken before restoration (the scale in panel b is given in cm): arrows marked with the letters ‘v’ show the voids where turquoise glass beads have been lost; at the same time, the areas embroidered with beads of other colors are in fairly good condition, and the beads themselves remain transparent and well-preserved; (c) a photograph of damaged beadwork on the reticule shown in the panel (a): arrows numbered from 1 to 4 show examples of historical turquoise beads at different stages of destruction surrounded by the intact ones; the arrow 5 indicates a modern blue bead replacing the lost historical turquoise one (the former is larger and more transparent); (d) corroded (cracked, discolored and crumbled) and mechanically damaged turquoise seed beads from a beaded museum exhibit of the 19th century obtained during its restoration (the beads are shown unwashed).
hydrated alkali appears on the glass surface and glass becomes hazy. A characteristic feature of this stage is formation of droplets of liquid alkali on the glass surface (at high room humidity, usually above 55% RH) or alkali in the form of white crystals (at low humidity, usually under 40%). Then glass begins to crack and eventually this process becomes more and more aggravated, cracking goes deep into glass until the beads completely break up into separate fragments (the fifth stage of degradation process). However, restorers noticed that the one kind of beads—translucent turquoise lead-potassium ones—is subjected to destruction more intensively. Significantly, on the same sites of the embroidery both damaged and well-preserved turquoise beads are observed (figure 1(c)). Therefore, we suggest that often not only crizzling, but mostly other processes (figure 2) affect their appearance and state.

In the previous works, we established that formation of micro and nanocrystallites of orthorhombic KSnSbO4 (KSS) in glass matrix (figures 2(e)–(g)), which arise during glass melting and bubbling, is one of the main causes of deteriorating of turquoise glass seed beads [7, 8, 14, 16]. We concluded that KSS precipitates and their clusters gave rise to internal stress (likely, tension) causing strain (likely, tensile one) in the glass bulk. In course of time, it leads to the conspicuous 'internal corrosion' of glass resulted from its slow fracturing and gradual formation of a network of cracks [7, 8, 15].

Another reason of degradation of translucent turquoise beads also relates to the process of their manufacturing [7, 8, 16]. Recently, we have discovered that seed beads of many kinds are composed of two regions of different glass [7, 8]. We have observed an internal core of the initial glass, often cracked due to KSS precipitates, and a crust coating the core (a shell) and consisting of re-fused glass that appeared due to tumble finishing at elevated temperature (figures 2(a)–(d)). The re-fused glass layer obviously differs in the composition of silicate units from glass of the core. Additionally, its specific volume differs from that of the core: it is larger or smaller than the specific volume of the core depending on the cooling rate of a bead after tumbling. At any rate, an interfacial domain between the core and the shell is always highly stressed in beads that are subject to shell

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**Figure 2.** SEM SE and BSE images of several turquoise bead glass samples demonstrating domains of original and re-fused glass—cores (1) and shells (2)—and colonies of KSnSbO4 (KSS) crystallites in glass (3): (a) and (b) segments of fragmented beads from the same exhibit; (c) an unusually fragmented bead showing details of its interior region; (d) sand-like particles of a bead after complete breaking; (e) to (g) KSS colonies causing the internal stress and glass fracture (for more details, see [7, 14]).

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4 We identified the crystalline inclusions observed in turquoise bead glass as orthorhombic KSS (CAS No. 132 265-14-6, PDF-2 card No. 00-045-0323) using x-ray powder analysis of the crushed glass samples [7, 15, 14] and electron backscatter diffraction (EBSD) on individual crystals directly in glass [7]. In both cases, the elemental composition of the crystallites was determined by EDX microanalysis.
forming (highly likely, in ones made of relatively fusible glass). As a consequence, a fracture eventually arises at
the core–shell interface [7], which accelerates the bead fragmentation [8].

Thus far, we have explored the unstable beads mainly using various scanning electron microscope (SEM)-
based techniques. Recently, we have presented our Raman study of the 19th century turquoise beads at different
stages of degradation and demonstrated substantial changes of the glass structure at the late stages of corrosion,
as well as its changes depending on depth in subsurface layers of a degraded glass grain [17]. Besides, we have
determined for the first time the characteristic Raman bands of orthorhombic KSS [14, 17].

This paper presents the results of the Fourier-transform infrared (FTIR) spectroscopy study of historical
turquoise glass beads. Since the vibrational spectroscopy is a powerful method for investigation of glasses, we
have focused on the structural characterization of beads at different stages of corrosion (intact, severely cracked
with color alteration, fragmented) and its relationship with the elemental composition.

FTIR spectroscopy is widely used for properly understanding of the changes in physical properties of
different types of silicate glass, in particular, for lead oxide based glasses since they have been applied in optical
and optoelectronic devices. Generally, such research works are devoted to studying of binary silicate glasses
[19–21] and much less of ternary systems [22–24].

In contrast to predetermined composition of the above-mentioned glasses, the variable content of historical
seed beads is very complicated and includes both glass-forming substances (processed vein quartz, or another
silicate raw material, which usually have different impurities (see, e.g., [25]), pearl ash5 or potash, calcium
carbonate, lead-containing components), and diverse technological additives (fluxes, oxidizing agents, fining
agents, colorizing, decolorizing or opacifying agents).

2. Samples, methods and equipment

2.1. Techniques and equipment

FTIR spectroscopy analysis was performed using a LUMOS microscope (Bruker) in attenuated total reflection
( ATR) mode with Ge ATR crystal. Experiments were carried out in spectral range from 600 to 4000 cm−1 at a
spectral resolution of 4 cm−1 (routine 64 scans were made). The beads were fixed on indium holders with little
push (hardness of indium is 1.2 Mohs’ scale). This procedure was chosen in view of the complex geometric shape
of glass beads and their fragments, fragile condition of samples at some stages of deteriorating, and necessity in
further exploration of samples by other analytical methods.

FTIR spectra of some glass beads were recorded between 100 and 600 cm−1, using a Vertex 70v (Bruker) in
ATR mode with diamond ATR crystal. The spectral resolution was 4 cm−1, the number of scans was 64.

Elemental compositions of all samples were analyzed using a M4 TORNADO micro-x-ray fluorescence
(micro-XRF) spectrometer (Bruker). It is equipped with a polycapillary lens, which enables focusing the tube
radiation and concentrating it in a spot of about 25 μm in diameter. The x-ray detector is a silicon drift detector
with a 30 mm² active area and energy resolution of about 145 eV. The presence of vacuum sample chamber
permits identifying light elements that is very important for glass exploration, as Mg, Al, Si, K, and Ca are
significant glass components and influence its properties.

Scanning electron microscopy (SEM) studies were performed using Vega-II XMU (Tescan) and Mira 3
XMU (Tescan) microscopes. As a rule, SEM images are demonstrated in both secondary electrons (SE) and
backscattered electrons (BSE) in this article.7

2.2. Samples

Samples of cloudy turquoise glass beads at different stages of destruction were taken during the restoration of
secular beaded articles of the 19th century from museum collections of Russia (examples of specimens are
shown in figure 3(a)). Transparent white and green, and semi-opaque yellow beads were also subjected to study
because of differences in their elemental and molecular composition apart from the turquoise glass ones
(figure 3(b)).

The surface of dirty glass beads was initially examined to determine the main contaminants, which appeared
to be organic compounds and could be the traces of handling, organic pesticides, or organic solvents which were
used in previous restoration. Then, before all experiments, samples were washed with high purity isopropyl
alcohol ([C3H7OH] > 99.8 wt. %) at 40° C for 20 minutes in a chemical glass placed into an ultrasonic bath
(ν = 40 kHz, P = 120 W) [14]. Sample washing was repeated before every experiment.

5 Recently, IR absorption bands of orthorhombic KSS have also been determined; they are presented in [18].

6 An impure product obtained by partial purification of potash from wood ashes.

7 Complementary pairs of SEM SE and BSE images are shown since SEM operating in the former mode represents mainly the substance
elemental composition (i.e. its density), while operating in the latter mode it renders mainly the spatial relief, whereas both types of the
information are usually required to correctly interpret data obtained using SEM.
All the samples were characterized using micro-XRF analysis following the procedure described in [7].

3. Experimental results and interpretation

3.1. Micro-XRF spectroscopy

The chemical composition of all historical glass bead samples was studied by micro x-ray fluorescence analysis. As far as XRF is non-destructive and non-invasive method of elemental analysis [26], it allows one to analyze these samples using other methods.

The results of elemental analysis of some samples are presented in the table 1; they show the distinction in the ratio between the main components and technical additives in the beads of different colors.

These data have shown that lead-potassium glass PbO–K2O–SiO2 with small content of Cu and Sb was mostly used for turquoise beads manufacture.8

Investigation of the samples at all stages of destruction indicates that the qualitative elemental composition of glass is the same with small deviations of several elements (e.g., P, S, Ni). Most likely, they are the part of uncontrolled impurities of the main components (for instance, it could be connected with different impurities of the used quartz raw material [25] or the elemental composition of pearl ash, which depends on the species of plant [30]). Copper is likely a chromophore of the turquoise glass beads [31].

For transparent and green glass beads production, lead-potassium glass was also used, yet the ratios between Pb and K contents of the samples differ: in the transparent glass beads, the contents of Pb and K are close, whereas the green ones show a high level of Pb and very low content of K (table 1). The yellow glass beads are made of lead glass PbO–SiO2 (potassium content is insignificant).

3.2. Micro-FTIR spectroscopy

Infrared spectroscopy is widely used in the studies of vitreous and polymorphous crystalline modifications of silicon dioxide SiO2. It was determined that all of them are mainly characterized by the presence of two absorption peaks in the region from 600 to 1700 cm⁻¹: a strong and wide peak at 1100 cm⁻¹ assigned to stretching vibrations of the Si–O bond and a weak wide peak at 800 cm⁻¹ assigned to the bending vibrations of the Si–O bond [32–34].

FTIR spectra of the turquoise glass seed beads at different stages of deterioration [13, 15] are presented in figure 4. A strong and wide band in the region from 820 to 1250 cm⁻¹ and weak bands in region from 650 to 820 cm⁻¹ are observed in all spectra. Two major absorption bands are seen in the spectra to be shifted to low-frequency range (~1000 and ~775 cm⁻¹) compared to ones typical for amorphous SiO2 (~1100 and ~800 cm⁻¹, respectively). This effect is associated with adding of supplementary components (in this case, lead and potassium), changing the glass structure and, consequently, its infrared spectrum [24, 35].

8 It is worth to notice that some samples of the similar deteriorating turquoise beads contain sodium along with potassium [16, 27–29]. Recently, we also revealed samples of turquoise beads made of Na2O–K2O–SiO2 glass, which are also characterized by the presence of KSS crystals in glass bulk and the analogous pattern of destruction.
Table 1. The results of elemental analysis of samples of turquoise (A1 to A7 and B1 to B3), transparent (B4), green (B5), and yellow (B6) glass seed beads (figure 3), at.%

|       | Mg  | Al  | Si  | P   | S   | K   | Ca  | Mn  | Fe  | Ni  | Cu  | Zn  | As  | Sb  | Pb  | K/Pb |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| A1    | 38.41 | 0.91 | 19.07 | 0.98 | 0.21 | 3.71 | 0.06 | 0.28 | 5.49 | 30.88 | ~0.6 |
| A2    | 0.79 | 45.21 | 16.41 | 1.95 | 0.02 | 0.32 | 6.48 | 0.08 | 0.50 | 5.37 | 22.85 | ~0.7 |
| A3    | 0.67 | 46.60 | 0.09 | 12.50 | 2.63 | 0.07 | 0.38 | 6.51 | 0.07 | 0.53 | 5.09 | 24.86 | ~0.5 |
| A4    | 0.66 | 43.60 | 0.05 | 17.50 | 1.14 | 0.29 | 10.83 | 0.10 | 0.57 | 6.03 | 19.04 | ~0.9 |
| A5    | 0.77 | 47.69 | 0.06 | 10.80 | 0.94 | 0.01 | 0.27 | 0.03 | 8.75 | 0.10 | 0.37 | 7.31 | 22.75 | ~0.5 |
| A6    | 0.69 | 45.07 | 18.91 | 2.13 | 0.04 | 0.68 | 6.75 | 0.69 | 6.14 | 18.90 | ~1.0 |
| A7    | 0.66 | 43.60 | 0.05 | 17.50 | 1.14 | 0.29 | 10.83 | 0.10 | 0.57 | 6.03 | 19.04 | ~0.9 |
| B1    | 1.11 | 54.31 | 30.25 | 6.33 | 0.02 | 0.30 | 1.84 | 0.03 | 0.13 | 2.16 | 3.52 | ~8.6 |
| B2    | 1.04 | 68.80 | 16.19 | 0.59 | 0.01 | 0.19 | 0.02 | 6.29 | 0.08 | 0.30 | 1.57 | 4.22 | ~3.8 |
| B3    | 1.02 | 65.03 | 0.23 | 18.70 | 1.19 | 0.21 | 7.13 | 0.06 | 0.31 | 2.07 | 3.85 | ~4.9 |
| B4    | 1.91 | 71.04 | 14.08 | 1.27 | 0.10 | 0.12 | 0.03 | 0.02 | 1.04 | 9.31 | ~1.5 |
| B5    | 1.35 | 56.31 | 2.17 | 2.07 | 5.41 | 0.79 | 1.01 | 0.02 | 3.40 | 0.07 | 27.4 | ~0.08 |
| B6    | 1.54 | 52.72 | 0.07 | 7.03 | 0.22 | 2.37 | 0.10 | 0.71 | 0.20 | 0.04 | 0.54 | 0.98 | 33.48 | ~0.01 |
Analysis of the FTIR spectra (figure 4) reveals the following features. (i) An appreciable shift of the absorption band 1100 → ~1070 cm\(^{-1}\) and a less pronounced shift of the absorption band 800 → ~775 cm\(^{-1}\) is observed in the samples (A1) to (A3); it is also necessary to note the appearance a new peak above ~945 cm\(^{-1}\). (ii) For the samples (A4) to (A7), the shift of the band at 1100 cm\(^{-1}\) is more considerable, while the shape of the overall absorption band peaked at ~1000 cm\(^{-1}\) becomes less complicated. (iii) A weak absorption band at 716 cm\(^{-1}\) is observed in all spectra. (iv) A weak absorption band above 1630 cm\(^{-1}\), which is connected with the presence of water on the surfaces of beads [36], is also observed. After annealing of the beads at 300°C, the band disappeared completely in less deteriorated samples and became significantly weaker in more destroyed ones. Based on that we conclude that there is adsorbed molecular water on the glass beads surface.

The structure of silicate glasses is known to be dominated by discrete silicate units with short- to medium-range order, which define their physical and chemical characteristics [19]. In order to determine the structural units in wide absorption bands of complex shapes with several maxima, the deconvolution has been performed using Gaussian functions,\(^9\) and vibration frequencies have been analyzed (figure 5). The peak positions were found in the second derivative of FTIR spectra. According to the obtained results, the spectra of more corroded samples have fewer fit components than those of the intact ones. For example, ten or more fit spectral components are, as a rule, identified for well-preserved samples of turquoise glass beads (A1 to A3) in the range from 600 to 1300 cm\(^{-1}\) (Figure 5(a)) whereas deteriorated turquoise beads (A4 to A7) demonstrate only five components (figure 5(b)) with one dominating the others. The deconvolution results for well-preserved turquoise, yellow and green glass seed beads are characterized by more uniform distribution of components and intensity of fit peaks (figures 5(a), (c), (d)). Several strong absorption bands with a close intensity are usually observed in the spectra of these samples. For instance, three intense components with similar integral intensities (17.99, 18.55, and 15.83) are observed at 875, 982 and 1048 cm\(^{-1}\), correspondingly, in the green sample (figure 5(d)). The bands are assigned to paired tetrahedra (Si\(_2\)O\(_5\)\(^{−}\) or Q\(^3\)) in the Engelhardt’s Q-notation [37],\(^{10}\) chains (Si\(_2\)O\(_4\)\(^{−}\) or Q\(^2\)) and framework (SiO\(_2\) or Q\(^4\)) in compliance with the vibration frequencies [19]. Apart, in glass of strongly corroded turquoise beads and transparent glass beads, which are also prone to destruction, the main dominant component is observed at ~1000 cm\(^{-1}\) and ~1020 cm\(^{-1}\), respectively (figures 5(b), (e)). Absorption band at 1000 to 1020 cm\(^{-1}\) is characteristic to Si\(_2\)O\(_4\) chains (Q\(^2\)) when the non-bridging oxygen atoms are bonded to both alkali metal cations (K\(^{+}\)) and Pb\(^{2+}\) ions [23]. Thus, more corroded beads have more depolymerized glass structure in compliance with integral intensity of fit components (chains and paired tetrahedra, mainly).

This result agrees well with the Raman spectroscopy data. The appearance of an intense line of Raman scattering peaked at 980 cm\(^{-1}\) [17], usually associated with the Si\(_2\)O\(_4\)\(^{−}\) (Q\(^3\)) units, in the degraded turquoise bead glass evidences in support of the simplification of the glass structure in the course of its degradation and dominance of the silicate chain (Q\(^2\)) units in damaged glass.

The obtained data also correlate with the results of the FTIR study of turquoise glass beads in the far spectral region. The FTIR spectrum of a turquoise glass bead at the intermediate stage of destruction (A3) in the region from 100 to 600 cm\(^{-1}\) is presented in figure 5(f). The spectrum shows two absorption bands at 286 and 245 cm\(^{-1}\), assigned to Pb–O–Pb bonds in the [PbO\(_4\)] unit that confirm the presence of chains [22, 23]. Lead may act in

\(^9\) Since the studied absorption lines are inhomogeneously broadened, Gaussian functions are quite suitable for the deconvolution of the bands. The deconvolution using Voigt profiles gives nearly the same results.

\(^{10}\) See the description of the Q\(^n\) nomenclature in the next footnote.
glasses as a network former or as modifier of the SiO2 network [23]. The absorption band at 431 cm\(^{-1}\) is assigned to Pb–O–Si bonds that proves the presence of the [PbO\(_4\)] units in bead glass of this type [23]. In the sample A3, integral intensity of fit components assigned to sheets and framework ([PbO\(_4\)] units) has greater contribution compared to much more deteriorated samples A6 and A7.

4. Brief discussion

The observed simplification of the glass structure during its corrosion may reduce the glass strength and, hence, accelerate the generation of micro-discontinuities and microcracks in its bulk due to internal stress inherent to bead glasses prone to degradation [8]; additionally, depolymerization facilitates the growth of fractures. It was shown in [38] that the ultimate elastic strain experienced by glass at the instant of fracture is about 10% for glasses with a three-dimensional atomic structure (Q\(^4\)) and about 5% for glasses with a layered (Q\(^3\)) or chain (Q\(^2\)) structure. This fact is associated in that article with the decreased uniformity of the loading distribution over atomic bonds in less polymerized glasses. Thus, following [38], we have come to conclusion that the observed glass depolymerization is another reason for the bead glass corrosion.

The phenomenon of glass depolymerization may be understood taking into account the fluctuation mechanism of the fracture at atomic level [39]. The process resulting in fracture of a stressed solid is known to comprise a sequence of elementary random events of stressed atomic bonds breaking by local energy fluctuations. It may be assumed that local stresses in internally loaded glass result in, foremost, reducing atomic bond rupture barrier and decreasing the local energy fluctuation required for surmounting this barrier and breaking the bond, hence, increasing the rupture likelihood of a bond and accelerating the breakage of chemical bonds, first those that form three-dimensional (Q\(^4\)) silicate networks and then those that form two-dimensional (Q\(^3\)) ones due to excess stress, which is likely applied to them because of the non-uniform distribution of local loading among the atomic bonds. Once a bond has been broken and a local discontinuity has appeared, the load is redistributed among the neighbouring bonds additionally decreasing their rupture barrier and increasing the probability of their breaking due to lower magnitudes of required local energy fluctuations. In such a way, the process goes on until the structure decays to simpler ones.

11 We would like to remind to readers what the degree of glass polymerization means in terms of structural units. In a nutshell, it means the following: the less is degree of glass polymerization the simpler is the structure of most units that compose it. Silicate glass may be considered as a polymer substance composed by SiO\(_4\) tetrahedral monomers. The most polymerized glasses mainly consist of 3-D framework (SiO\(_2\)) composed of Q\(^4\) silicon-oxygen units (in the Q\(^n\) nomenclature, \(n\) designates a number of the SiO\(_4\) tetrahedrons attached to a chosen SiO\(_4\) node while Q means simply an abbreviation of the word ‘quaternary’ [37]) and 2-D sheets of hexagonal rings represented by Si\(_4\)O\(_{12}^n\) radicals [19] and composed of Q\(^n\) sites. The least polymerized glasses contain mainly paired tetrahedrons (Si\(_4\)O\(_{12}^2\)) composed of Q\(^2\) species and chains (Si\(_4\)O\(_{10}^3\)) of Q\(^3\) ones. In the intermediate case, hexagonal rings (Si\(_4\)O\(_{12}^4\)) of Q\(^4\) sites and double chains (Si\(_4\)O\(_{12}^5\)) made up of inner Q\(^4\) and outer Q\(^2\) sites are also present at considerable amounts.

12 I.e. increasing the bond breaking rate \(dN_b/\,dt\) where \(N_b\) is the total number of broken atomic bonds and \(t\) is the time.
Chains \((Q^2)\) and especially paired tetrahedra \((Q^1)\) appear to be more resistant to stress, presumably because of lower loading applied to bridging oxygen bonds in them. However, according to the considered model, glass consisting of them (and consequently containing less number density of bridging oxygen) should be less strong than close in composition but highly polymerized glass composed by the \(Q^4\) and \(Q^3\) species. Thus, in such a scenario, glass depolymerization caused by the internal stress, being a phenomenon that decreases glass strength, should be considered as an important degradation mechanism inherent to this type of glass corrosion.

It should be noted also that the characteristic dimensions \(a\) of light scatterers that we previously observed using Rayleigh scattering in glass of deteriorating turquoise beads (they are estimated as \(a \ll 150 \text{ nm}\) \([13]\)), the number density of which grows with the rising glass corrosion degree, coincide with the sizes of nucleating micro-discontinuities that, according to \([40]\), are typical defects emerging due to the aforementioned process at locations of shear and rotational strains. We presumably identify the observed light scatterers with this type of defects. The material destruction related to formation and growth of such microscopic defects is a kinetic thermal fluctuation process occurring throughout the entire period of material loading \([40]\), which lasts in the case of glass beads under the study for more than a hundred years. The merger of the micro-discontinuities and the formation of microcracks and then macrocracks is the only possible final phase of this process that ends by glass fracturing and bead fragmenting.

5. Conclusion

In the work, we make an effort to establish correlation between turquoise glass beads preservation, their elemental composition and changes of glass structure. For comparison, prone to destruction transparent white glass beads and well-preserved stable green and yellow glass beads are also objects of study.

Micro-XRF spectroscopy of samples has shown that lead–potassium PbO–K\(_2\)O–SiO\(_2\) glass with a small amount of Cu and Sb was used for turquoise beads manufacture. In addition to that, many uncontrolled impurities, which could be connected with different admixtures of main components and technical additives, were detected. FTIR study shows that more corroded beads have more depolymerized structure in compliance with integral intensity of fit components (chains \((Q^2)\) and paired tetrahedra \((Q^1)\), mainly). Such simplification of the glass structure may reduce the glass strength and promote the formation of new microcracks in its volume as well as the growth of existing ones.

Finally, we can conclude that the model of bead glass internal corrosion, previously proposed by us for explanation of the long-term process of the turquoise bead glass degradation at room temperature \([7]\), agrees with the commonly adopted thermal fluctuation theory of materials fracture. The simplification of the glass structure under internal stress during the long-term degradation of glass at room temperature also finds a realistic explanation within this theory.

We consider glass depolymerization, caused by the internal stress and decreasing the glass strength, as an essential corrosion mechanism of stressed glass of seed beads.

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