Environmental degradation of Modern non-balanced glasses

Teresa Palomar, Alexandra Rodrigues

Abstract: Crizzling is an alteration pathology related to non-balanced glasses (high content of flux oxides and low content of stabilizer oxides), which can produce an intense damage such as transparency losses, appearance of drops on the surface or cracking. In this study two case studies (outdoor and indoor environment) were presented. The main alteration agent for these glasses was the water (rain, condensation and environmental humidity). In the outdoor environment, the rain washed away the [OH\(^{-}\)] ions formed during the alteration; however, the exposure to cyclic conditions accelerated its alteration rate. In the indoor environment, early stages revealed to consist of an alkali leaching that concentrates on the surface, on specific areas, that were related to water adsorption and consistent with the weeping phenomenon. Cracking and flaking of the surface represents a later stage, occurring specifically in unbalanced compositions.

Keywords: Glass, crizzling, natural environment, degradation mechanism

Degradación ambiental de vidrios modernos no equilibrados

Resumen: El crizzling es una patología de alteración relacionada con vidrios no equilibrados (con elevado contenido de óxidos fundentes y bajo de óxidos estabilizantes), que puede producir graves daños como pérdida de transparencia, aparición de gotas en la superficie o fisuras. En este estudio, se presentan dos casos de estudio (ambiente exterior e interior). El principal agente de alteración de estos vidrios es el agua (lluvia, condensación y humedad ambiental). En ambiente externo, la lluvia lavó los iones [OH\(^{-}\)] formados durante la alteración; sin embargo, la exposición a condiciones cíclicas aceleró su velocidad de degradación. En ambientes interiores, se observó el estado inicial consistente en la lixiviación de los alcalinos a la superficie, en áreas relacionadas con la adsorción de agua y el fenómeno de weeping. La formación de fisuras y el desprendimiento de la superficie corresponden a un estado más avanzado que ocurre específicamente en composiciones no equilibradas.

Palabras clave: Vidrio, crizzling, ambiente natural, mecanismo de degradación

Introduction

Glass is usually related to a material with high chemical durability. However, its stability depends on the chemical composition and, therefore, the strength and distribution of the chemical bonds in the glass matrix.

Historical glasses are formed by a former oxide (SiO\(_2\)), flux oxides which decrease the melting temperature of the glass (Na\(_2\)O and K\(_2\)O), and stabilizer oxides which create bridges in the structure to increase the chemical stability (CaO and MgO). The presence of a low content of alkaline oxides, alkaline ions with low ionic radius (Li\(^+\) < Na\(^+\) < K\(^+\)) and the replacement of alkaline ions by Ca\(^{2+}\) or Mg\(^{2+}\) induce a high structural packing of the glass that favors their chemical durability (Fernández Navarro 2003). However, if the chemical composition of the glass is not balanced (high content of flux and low content of stabilizers), the chemical resistance decreases, accelerating the degradation rate. These low stable formulas can be due to an incorrect production technology, an over-purification of raw materials or a wrong batch formulation (Kunicki-Goldfinger 2003).

Another important factor for glass alteration is the environmental conditions. In outdoor environments, there are several factors that can react with the glass surface. The
most aggressive ones are rain, wind, pollution, and aerosols (Woisetschläger et al. 2000; Munier et al. 2002; Melcher and Schreiner 2005; Melcher et al. 2008; Gentaz et al. 2011; Lombardo et al. 2014; Palomar et al. 2018; Palomar et al. 2019). In an indoor environment, these alteration agents are minimized; however, high environmental humidity and volatile organic compounds (VOCs), mainly the formic acid from the wood of the furniture, can accelerate the alteration mechanism.

The non-balanced glasses are especially susceptible to be altered. Their fast degradation frequently produces transparency loss, color change, the appearance of drops on the surface, salts, alteration layers, cracking, peeling and fracture, among others (Kunicki-Goldfinger 2008). This process, denominated crizzling, has been observed in soda, potash, mixed-alkali and lead silicate glass with low content of CaO and MgO, and predominantly in glasses from the 17th to 19th centuries from Italy, UK, and Central Europe. The crizzling is a severe pathology on glasses, observed generally in indoor environments; however, it can be also produced in external environments.

The main objective of this study is to characterize the effect of two different atmospheres on historical unbalanced glasses. For that, two sets of historical samples from the Cathedral of Girona, Spain (outdoor environment) and Museu Nacional de Arte Antiga (MNAA), Portugal (indoor environment) were characterized and compared.

**Characterization techniques**

The glass samples studied were characterized by the following techniques: optical microscopy (OM), X-ray fluorescence (XRF) spectrometry, and micro energy dispersive XRF, besides visual inspection.

OM was carried out by a Leica MZ16 reflected light microscope equipped with a Leica DC300 camera for Girona samples. The microscopic documentation in the case of MNAA replica samples was carried out using a light microscope (Axioplan 2, Zeiss) with digital camera (Nikon DMX). The whole surface area was observed in order to identify surface features.

For Girona samples, semi-quantitative chemical analysis by XRF was carried out by a PANalytical Axios wavelength dispersed X-ray spectrometer equipped with a tube of rhodium of 4 kW and 60 kW. Analytical determinations were undertaken through the standard-less analytical software IQ+ (PANalytical) based on fundamental parameters from synthetic oxides and well-characterized natural minerals. In addition, Sheffield glass nos. 7 and 10 (Society of Glass Technology) are commonly used as internal routine control standards. Powder samples (1 g approx.) for bulk XRF analysis were prepared by grinding body glass fragments, with their most external surfaces removed by polishing, in an agate mortar. After that, pressed boric acid pellets were made, using a mixture of n-butylmethacrylate and acetone (10:90 wt. %) as binding medium. This methodology agrees with the recommendation of the Corpus Vitrearum for the stained-glass analyses.

For MNAA glassworks, the analyses had to be done in situ in the museum, by non-invasive techniques such as portable micro-X-ray fluorescence (µ-EDXRF). The analyses were therefore achieved using a portable spectrometer ArtTAX 800, Bruker (Billerica, MA, USA). It operates with a molybdenum (Mo) X-ray source, focusing polycapillary lens and electro-thermally cooled xFlash (Si drift) detector, with 170 eV resolution. The accurate positioning system and polycapillary optics enabled a small area of primary radiation (70 µm) at the sample. The excitation and detection paths can be purged with helium to allow the detection of low Z elements down to aluminium. Spectra were acquired under the following conditions: voltage 40 kV, intensity 0.6 mA and live time of 360 s. Helium purging was used to allow the determination of elements down to aluminium. Each glass was analysed in (at least) three different areas. Quantitative analyses were carried out with the WinAXIL program, making use of spectra obtained from glass standards (A, B, C, and D from Corning Museum of Glass, Corning, NY, USA). All CMOG glass standards were used to validate the quantitative procedure.

In-depth characterization of the corrosion processes were obtained with the production and use of replica samples, with similar composition to the historical materials. The methodology used for this study was adopted in VICARTE (Glass and Ceramics for the Arts) Research Unit since 2012 (Rodrigues et al. 2014), where through historical techniques – by blowing and fire-polishing the surfaces – they become as close as possible to the real historic ones. This revealed to be an important factor for the understanding of the alteration of these surfaces in the initial state, hence the composition of the glass surface is considered, as well as the chemistry of surface layers formed during the glass samples production.

**Case Studies**

—*Crizzling in an outdoor environment: Cathedral of Girona*

The stained-glass rose window “La Asunción de la Virgen María” (“Assumption of the Virgin Mary”) is located in the west façade of the Cathedral of Girona since the 18th century. According to some documents from the cathedral, their glasses were imported from Venetia (Italy) (Palomar et al. 2011; Palomar 2013).

All the analyzed samples presented an advance state of alteration on their external surface. They showed several fissures and crystalline deposits inside some cracks [figure 1 a]. Even, the accumulation of deposits raised the dealkalinized areas that caused their detachment [figure 1 b]. The morphology of the cavity, with conchoidal form,
pointed out that the detachment was mechanical instead of chemical, where the alteration front use to be continue or semispherical (Palomar 2018). It was also observed new fissures inside some cavities as result of the recurrence of the degradation process. The cracked surface presented a high content of SiO$_2$, result of an advanced state of dealkalinization, with crystals of K$_2$SO$_4$ [figure 1 c]. The formation of this salt was due to the reaction of the K$^+$ ions leached from the glass and the SO$_2$ from the polluted environment. K$_2$CO$_3$ was not detected because it has a higher solubility in aqueous solutions than K$_2$SO$_4$ (Palomar et al. 2017).

Regarding the surfaces exposed to the indoor environment, the surface of the sample G1 was completely fissured, as the outdoor surface, instead of the other three glasses that showed a net of aligned pits [figure 2 a and b]. This uncommon pathology could also be related to the same alteration mechanism but in a lesser degree. The humidity and condensation inside the building produced the dealkalinization process. The tensions between the silica gel layer and the bulk glass were liberated forming fissures. In this indoor environment, the fissures can trap the condensed humidity creating a stationary state inside them. The basic species formed inside the fissures as result of the alkaline attack caused the dynamic breakage of the glass, which forms the aligned pits (Palomar and Llorente 2016).

This different mechanism is directly related to the chemical composition of the glasses. All of them were potash-lime silicate glasses with a high content of K$_2$O (~23 wt. %), SiO$_2$ (~65 wt. %), and relatively low content of CaO (~ 5 wt. %) [table 1]. However, small differences in their proportions are responsible for their different degree of alteration. The sample G1 has a higher ratio of alkaline oxides and silica ([K$_2$O+Na$_2$O]/SiO$_2$ = 0.42) and the highest ratio between the potash and the calcium oxides (K$_2$O/CaO = 4.72). This relatively higher content of alkaline oxides introduced several points of reticular discontinuity that promote hydration and surface dealkalinization, accelerating the degradation process.

<table>
<thead>
<tr>
<th>Analyzes</th>
<th>Na$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>SO$_2$</th>
<th>Cl</th>
<th>K$_2$O</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.6</td>
<td>1.9</td>
<td>84.2</td>
<td>1.6</td>
<td>0.3</td>
<td>4.9</td>
<td>6.4</td>
</tr>
<tr>
<td>A2</td>
<td>6.7</td>
<td>--</td>
<td>5.3</td>
<td>40.3</td>
<td>--</td>
<td>47.8</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 1.- Chemical composition of the stained glasses from the Cathedral of Girona

Samples | Chemical composition (wt%)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na$_2$O</td>
</tr>
<tr>
<td>G1</td>
<td>2.26</td>
</tr>
<tr>
<td>G2</td>
<td>2.20</td>
</tr>
<tr>
<td>G3</td>
<td>1.41</td>
</tr>
<tr>
<td>G4</td>
<td>2.16</td>
</tr>
</tbody>
</table>

—Crizzling in an indoor environment: Museu Nacional de Arte Antiga (Portugal)

The glass objects in Museu Nacional de Arte Antiga (MNAA), Lisbon, Portugal, presented a high variability of compositions. The case study of the group of glassworks collected by Ferdinand II of Portugal is an especially valuable one. This collection represents a chronology which spanned many centuries, as well as multiple and widespread European production centers (Rodrigues and Martinho 2015). The glass objects with unbalanced compositions in this case were selected from 17th and 18th century productions, both Na- and K-rich compositions from the Venetian (or façon de Venise) and Bohemian types.
These unbalanced compositions exposed to an indoor environment presented signs of alteration. Museum objects, both with high Na₂O and K₂O content, evidenced weeping and crizzling of the surfaces (figure 3 a-d).

The observations made under OM [figure 4 a and b] revealed that in the early stages (1 year exposure), the formations on the surface were consistent with the weeping phenomenon, which often precedes the crizzling (Koob, 2006). This occurred to both Na-rich and K-rich glass types, although to different extents. No crizzling was observed in these early stages.

Due to the impossibility to observe these glasses under the OM, or to perform more invasive analyses, some compositions similar to analyzed glasses were replicated [Table 2] and aged under museum-like conditions (45%, 55%, 65% and 75% RH and room temperature) for the understanding of the early stages of the alteration processes.

It seems that the cracking and flaking of the surface represents a later stage in an indoor environment, occurring specifically in unbalanced compositions. Moreover, crizzling was also more visible after washing, such as it was in the case of MNAA1079vid [figure 3 b]. When no run-off occurs (indoor environment), the alkaline species can still be partially retained in the alteration layer (Alloteau et al., 2017). If some run-off occurs or if the surfaces are washed, leached and probably even partially retained alkali is removed from the surface. The µ-EDXRF analyses performed on the surface of MNAA1079vid and MNAA1043vid clearly evidence a decrease in the alkaline species concentration, and an increase in silica (to around 80 wt. %, which could not have been the original glass composition) [table 3].

**Figure 3.** a) Weeping (droplets on the surface, left) and crizzling (cracking of the glass, right) on object MNAA1074vid, a Na-rich glass; b) crizzling on object MNAA1079vid, a Na-rich glass; c) weeping phenomenon on MNAA1009vid, probably K-rich glass; d) crizzling phenomenon on MNAA1043vid, a K-rich glass with PbO.

**Figure 4.** OM analyses to the MNAA replica materials aged over 1 year. a) Na1 glass; b) K1 glass.

### Table 2. Chemical composition of the glassworks and replica materials from MNAA, Lisbon.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n=3)</td>
<td>Na₂O</td>
</tr>
<tr>
<td>MNAA1079vid</td>
<td>13.8*</td>
</tr>
<tr>
<td>Na1</td>
<td>17.2</td>
</tr>
<tr>
<td>Na2</td>
<td>14.8</td>
</tr>
<tr>
<td>MNAA1043vid</td>
<td>–</td>
</tr>
</tbody>
</table>

* - both Na2O and MgO, obtained through µ-XRF semi-quantification. /** - includes addition of PbO / n.d. - not detected / § - replica materials were produced taking into consideration that the historic glass surfaces analyzed were depleted in alkali and enriched in SiO₂, as can be seen in the analyses in Figure 1.

### Table 3. Chemical composition of two very different areas of the surface of the glasswork MNAA1079vid.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n=1)</td>
<td>Na₂O</td>
</tr>
<tr>
<td>MNAA1079vid</td>
<td>Min. values</td>
</tr>
<tr>
<td></td>
<td>Max. values</td>
</tr>
</tbody>
</table>
Discussion

In both environments, water was the main alteration agent of the unbalanced glasses. The rain (outdoor environment), the condensation water and the high humidity (indoor and outdoor environments) favor the leaching of the alkaline oxides from the glass lattice by the hydrolytic attack (Reaction 1) and the ionic exchange (Reaction 2). As result, a hydrated surface layer and drops of alkaline hydroxide were formed on the surface.

\[ \Xi Si-O-Si + H_2O \leftrightarrow 2 \Xi Si-OH \text{ Reaction 1) } \]
\[ \Xi Si-O-X + H_2O \rightarrow \Xi Si-O-H + XOH (X: Na, K) \text{ (Reaction 2)} \]

In an outdoor environment, the rainwater can wash the leached ions (alkaline, alkaline-earth and hydroxyl ions) from the glass surface. The removal of hydroxyl ions favors the maintenance of a neutral pH in the glass surface (Palomar et al. 2019). In addition, during the drought periods, the alkaline ions leached from the glass can react with the atmospheric gases (CO\(_2\), SO\(_2\), NO\(_x\)), solubilized in rainwater to form crystalline deposits (Reaction 3) (Melcher and Schreiner 2006).

\[ 2K^+ + SO_4^{2-} + 2OH^- \rightarrow K_2SO_4 + H_2O \text{ (Reaction 3)} \]

In the indoor environment, the accumulation of the species [OH\(^-\)] in the surface can cause two different alteration mechanisms. In a humid environment, the hygroscopicity of the alkaline hydroxide (KOH and NaOH) can attract more water accelerating the ionic exchange and the hydrolytic attack (Reaction 1 and 2) (Rodrigues et al. 2018a; Rodrigues et al. 2018b) and, therefore, the advance of the alteration layer to the glass bulk. However, if the content of [OH\(^-\)] ions increases pH > 9, the siloxane bonds can be broken by the alkaline mechanism (Reaction 4). In both situations, the result is the formation of a thick alteration layer on the glass surface, and, in the worst scenario, it can produce the complete loss of the piece.

\[ \Xi Si-O-Si + OH^- \rightarrow \Xi SiOH + \Xi SiO^- \text{ (Reaction 4)} \]

If the altered glass piece is moved to an environment with lower humidity, the alteration layer could be fissured and cracked, favoring the detachment of the external layer (figure 1 b) and the drying of the surface drops. If salts are crystallized inside the fissures, they could force the cracks progression and the layer detachment.

In a more controlled and mild environment such as a museum, the evolution of the deterioration processes over time is dependent on the equilibrium (or fluctuations) of the humidity, temperature and its influence to a certain composition. On the other hand, the composition can be determinant for the reactivity with the water in the surrounding environment. This occurs since the hydration of the glass is much dependent on the alkali content (Reaction 2) and type (energies of complexation and hydration vary) (Alloteau et al., 2019). Due to the lack of washing away of the [OH\(^-\)] ions trapped in the H-bonding network (or of their precursor H\(_2\)O species H-bonded to non-bringing oxygens), a self-catalytic effect of the system towards hydrolysis can sometimes occur (Alloteau et al., 2019). This is enhanced if the alkali content is high, since H-bound species are found in the alkali vicinity. Moreover, if not followed by repolymerization or rearrangement of the structure – being some structure more prone to form a passivation layer than other –, the leaching of the alkali ions can likely contribute to the opening of the porosity of the network and/or to the entrance of more environmental water molecules attracted to the surface by the leached species.

Conclusions

Glasses with unbalanced composition (flux vs. formers and stabilizers) are very susceptible to environmental agents, mainly the water (rainwater, condensation, and humidity). The excess of alkaline oxides and the low percentage of calcium and magnesium oxides in these glasses favors the ionic-exchange mechanism between the environmental water and the alkaline ions from the glass, which favors the formation of a silica gel layer on the surface. In an indoor environment, alkaline drops are formed and they stay on the surface favoring the alkaline attack, capable of breaking the siloxane Si–O–Si bonds in the glass. However, in outdoor environment, the contact with the rainwater is higher but it also removes the basic species. The formation of salts in dry atmospheres is also dangerous since they can force the detachment of the external alteration layer.

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References


THICKETT, D., LEE, L. R. (2004). *Selection of materials for the storage or display of museum objects*, London: The British Museum


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