Effect of marine aerosols on the alteration of silicate glasses

Teresa Palomar[a,b,c,*], Anne Chabas[d], David M. Bastidas[c], Daniel de la Fuente[c], Aurélie Verney-Carron[d]

[a] Higher Education Institution of Glass, Spanish Glass Foundation, The Royal Glass Factory of La Granja, Pº Pocillo, 1, 40100 La Granja de San Ildefonso, Segovia, Spain
[b] Research Unit VICARTE "Vidro e Cerâmica para as Artes", Campus de Caparica, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal
[c] Dept. Surface Engineering, Corrosion & Durability, National Centre for Metallurgical Research (CENIM), CSIC, Ave. Gregorio del Amo 8, 28040 Madrid, Spain
[d] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris-Est et Université Paris Diderot, 61 avenue du Général de Gaulle, 94010 Créteil Cedex, France
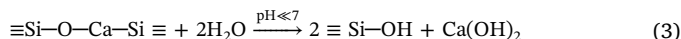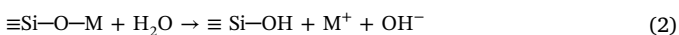
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ABSTRACT

This work is focused on the effect of marine aerosols on soda-lime, potash-lime and lead silicate glass samples. Two kinds of tests were carried out, the first one under laboratory controlled condition during 36 days to evaluate the alteration of glass surface by NaCl aerosols, and the second one in a marine atmosphere in Cabo Vilano (Galicia, Spain) for up to three months. Both tests showed similar results. NaCl aerosols acted as condensation nuclei in high humidity environments favoring the lixiviation of the alkaline and alkaline-earth ions from the glass surface and the solubilization of atmospheric gases (CO_2, SO_2).

Marine aerosols could also accelerate the corrosion attack inducing the loss of the surface hydrogen bonds and the opening of the network accelerating the corrosion mechanism. Results also confirmed that high humidity favored the alteration of the glass surface and the formation of new crystalline phases. Soda-lime silicate and lead silicate glasses were the most durable ones, whereas potash-lime silicate glass presented a fissured alteration layer due to the hydrolytic attack of the surface. New crystalline phases including chlorides, carbonates and sulfates were detected on the glass surfaces which can be related to marine aerosols, environmental particles and the reaction of the cations lixiviated from the glass with the atmospheric gases.

1. Introduction

Stained glass windows are the historical glasses the most affected by atmospheric degradation because they are located as part of the facade of the buildings daily submitted to wet and dry deposition. They are affected by soiling, which concerns the deposit of soot particles and soluble salts over the glass surface. These deposits can be anthropic, biogenic, terrigenous or marine [1], and can generate a loss of transparency and an increase of the roughness and the hygroscopicity of the surface [2].

Stained glass windows also undergo chemical alteration. The water retained by the glass surface can induce the hydrolytic attack of the glass by the breaking of the siloxane bonds (Eq. (1)) and the lixiviation of the alkaline ions (Eq. (2)). In acid environments, the lixiviation of alkaline-earth ions can also occur accelerating the degradation rate of the glass (Eq. (3)) [3–6].

$$\equiv Si-O-Si \equiv + H_2O \leftrightarrow 2 \equiv Si-OH \tag{1}$$

$$\equiv Si-O-M + H_2O \rightarrow \equiv Si-OH + M^+ + OH^- \tag{2}$$

$$\equiv Si-O-Ca-Si \equiv + 2H_2O \xrightarrow{pH \ll 7} 2 \equiv Si-OH + Ca(OH)_2 \tag{3}$$

As consequence of the hydrolytic attack, the altered areas present a high content of silanol groups (Eqs. (1)–(3)) which can polymerize between them to form a porous network enriched in SiO_2 (Eq. (1)) [7]. The diffusion of environmental water molecules is favored in these areas, and they can react with the bulk glass to form pits or degradation layers [3,8–11].

Dealkalization produces also the accumulation of OH^- groups in the altered areas (Eqs. (2), (3)), which can transform the hydrolytic attack into a basic one. This basic attack accelerates the breaking of the siloxane bonds and the dissolution of the glass structure accelerating the alteration rate, mainly at pH > 9 (Eq. (4)) [12,13].

$$\equiv Si-O-Si \equiv + OH^- \rightarrow \equiv Si-OH + \equiv Si-O^- \tag{4}$$
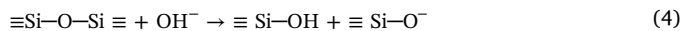
Tensions between altered and unaltered areas can generate fissures, cracks and craters [14,15]. Additionally, the ions leached during the hydrolytic attack can react with atmospheric gases (CO_2, SO_2, NO_x) to form deposits over the surface and inside the cracks (Eqs. (5), (6)) [16–19]. The most common deposits are carbonates (calcite) and

sulfates (gypsum and syngenite) [20–24].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (5)$$

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \qquad (6)$$

Several works have assessed the influence of atmospheric conditions, especially climatic factors and pollution, on the degradation mechanism, either in real environments [2,25–28] or in climatic chambers [5,29,30]. These studies proved that high relative humidity and high concentration of gaseous pollutants accelerate the degradation rate of historical glasses. Moreover, soiling, deposited particles and chemical alteration can provide exogenous elements for secondary phases or change the local condition of water retention and the chemical composition of the water film [18]. The presence of salts increased the glass degradation by extending the time of wetness of the glass surface and forming saline solutions in the case of deliquescent salts [31]. However, the influence of the marine aerosols on atmospheric degradation of glasses is poorly studied. The deposition of saline particles from marine atmospheres is known to accelerate the degradation of historical stone materials [32–34]. In aqueous solution, other studies have demonstrated that the salts from seawater lead to increase the corrosion rate of quartz, silica [35–40] and silicate glasses [41,42]. The proposed mechanism points that alkaline cations in aqueous solutions were easily exchanged by protons from the silanol groups. Due to the steric hindrance, these bonds were situated perpendicularly to the surface, favoring the opening of the structure and, consequently, raising the degradation rate [35]. The same mechanism could occur with the deposit of marine aerosols on the glass surface because the alkaline chlorides (NaCl, KCl…) are the major contributors of marine aerosols, but the information about the effect of atmospheric salinity on glass degradation is scarce.

The alteration of glass is also dependent of its chemical composition. Generally, the most vulnerable glasses to the alteration are those with high content of alkali ions, mainly potassium, or low content of stabilizer ions, such as calcium or magnesium [43,44]. However soda-lime silicate glasses can also be altered by environmental factors [15,23].

Therefore, the main objective of this work is to assess the influence of NaCl particles, the principal marine aerosols, on the degradation of glasses with three different compositions: soda-lime silicate, potash-lime silicate and lead silicate glasses. Two experiences were developed, in laboratory and in a real environment. The laboratory tests were set up in order to evaluate the alteration of the glass surfaces caused by NaCl aerosols in temperate climates [45]. The laboratory results were compared afterwards with the glass alteration in the marine atmosphere of Cabo Vilano (Galicia, Spain), which is a more complex real environment.

This research will be especially useful to evaluate the conservation of historical stained glass windows located in places near the coast.

2. Experimental

2.1. Glass samples

Three model glasses were formulated in the laboratory following the composition of the main representative historical glass types (Table 1).

Glass NCS was a soda-lime silicate glass, similar to modern conventional window glasses [46]; glass KCS was a potash-lime silicate glass with similar composition to medieval glasses [47,48]; and glass PS was a lead silicate glass with high content of PbO, similar to crystal glass [49]. The raw materials were melted at 1450 °C, for the KCS and PS glasses, and 1550 °C, for the NCS glass, during 3 h and then annealed from 600 °C to environmental temperature during 6 h.

The obtained model glasses were cut in slices of $10 \times 10 \times 2$ mm and then polished using emery paper and an aqueous suspension of cerium oxide to obtain optical quality. Previous to the experiment, the samples were cleaned with ethanol to remove organic adsorbents or oily species in the surface which could affect the tests.

2.2. Laboratory corrosion tests

The laboratory experience was developed to evaluate the alteration of the glass surfaces caused by NaCl aerosols in temperate climates [45]. NaCl was deposited on the glass samples. For that, samples were placed inside the CIME corrosion chamber developed to simulate dry atmospheric deposition on materials [50]. A solution of 100 g/L NaCl was prepared and nebulized into CIME using an AGK 2000 (Palas®) collision-type atomizer equipped with a dryer system. To increase in a realistic manner the production of marine aerosol, 100 g/L NaCl only represents four times the concentration of this salt in seawater and three times its salinity [51,52].

Samples were then subject to different levels of relative humidity (RH): 100% RH, 23% RH, and cycles 100-23% RH, which represented the day/night cycle, and a constant temperature of 20 °C. Three samples of each glass (NCS1, KCS1, PS1) were placed in a sealed box whose bottom is filled with ultrapure MilliQ water to maintain the RH at 100%, three other samples (NCS3, KCS3, PS3) in a second box filled with a supersaturated saline solution of CH_3COOK used to fix the RH at 23% [53,54]. For cycles, three samples (NCS2, KCS2, PS2) were weathered for 2 days in the CIME chamber at a daily rate: 23% RH during 8 h and at 100% during 16 h. Then they were placed inside sealed boxes and switched manually following the same rate during the week and at 100% during the weekends. The experiment was carried out for 36 days.

2.3. Field exposure

A second kind of test consisted in the exposure of samples ($10 \times 10 \times 2$ mm) with the same chemical composition in a real marine atmosphere for up to three months in Cabo Vilano wind farm (Galicia, Spain). They were placed in vertical position unsheltered from the rain in a corrosion station located at 280 m to the shore. It was measured 643.51 mg / (m²·day) of chloride during the exposure period [55]; the atmospheric SO_2 content was negligible. Frequent heavy rainfall and high relative humidity levels were recorded at the test site, indicating prolonged times of wetness of the glass surface [56].

2.4. Characterization techniques

Glass samples were characterized by the following techniques: X-ray fluorescence spectroscopy (XRF), optical microscopy (OM), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS),

Table 1
Chemical composition of the glasses used in this study analyzed by semi-quantitative XRF and normalized to 100% (wt%).

Chemical composition														
Glass	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	K$_2$O	CaO	TiO$_2$	Fe$_2$O$_3$	ZnO	As$_2$O$_3$	Sb$_2$O$_3$	BaO	PbO
NCS	15.1	4.7	1.9	71.5	–	0.3	0.3	8.4	–	0.1	–	–	–	–	–
KCS	0.8	2.9	3.6	46.2	3.3	–	21.9	20.5	0.1	–	–	–	–	–	–
PS	8.6	–	0.3	60.9	–	–	5.0	0.1	–	–	1.2	0.4	0.9	3.3	15.4