



Decay processes of silicate glasses in river and marine aquatic environments



T. Palomar^{a,b,*}, I. Llorente^b

^a Dpto. de Conservação e Restauro and Research Unit VICARTE-Vidro e Cerâmica para as Artes, Campus de Caparica, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal

^b Centro Nacional de Investigaciones Metalúrgicas (CENIM), Consejo Superior de Investigaciones Científicas (CSIC), Ave. Gregorio del Amo 8, 28040 Madrid, Spain

ARTICLE INFO

Article history:

Received 24 March 2016

Received in revised form 31 May 2016

Accepted 5 July 2016

Available online 15 July 2016

Keywords:

Glass

Corrosion

River water

Marine water

ABSTRACT

To characterize the degradation mechanisms of silicate glasses in river and marine aquatic environments, soda-lime silicate, potash-lime silicate and lead silicate glasses were submerged during 300 days in synthetic marine and river solutions. The alteration was characterized through optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDS) and atomic force microscopy (AFM). The results of this induced alteration showed that the degradation mechanism is directly connected to the chemical composition of glass. In soda-lime silicate glasses the degradation proceeds in a two-step mechanism: firstly hydration and fissure development occurs, and secondly fissures grow and pits are formed. Lead silicate glass forms simultaneously pits and a recurrent alteration layer. Potash-lime silicate glasses forms stratified gel layers, which are easily detached. The potash-lime silicate glass was the least durable under aquatic conditions. Samples submerged in simulated marine water were altered faster than those submitted to river water.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The most significant property of silicate glasses concerns its chemical durability. It is directly related with the chemical composition of the glass and the stability and distribution of its chemical bonds. Low content of alkaline oxides generates a compact structure which increases the chemical durability of the glass. The presence of alkaline ions with low ionic radius ($\text{Li}^+ < \text{Na}^+ < \text{K}^+$) and the replacement of alkaline ions by Ca^{2+} or Mg^{2+} also induces a high structural packing of the glass and increases its chemical durability [1].

Degradation of silicate glasses can occur by different mechanisms which depend on the glass (chemical composition, defects and surface irregularities) and its environmental conditions (concentration of aggressive species, humidity and temperature). The principal factor for glass degradation is the environmental water content. Water is involved in all degradation mechanisms because it can produce the hydrolysis of the glass bonds (1). The hydrolysis favours the opening of the glass network and the diffusion of water molecules through the glass. Its consequence is the formation of a degradation layer called silica gel layer [1].

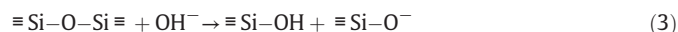


In aqueous media, the degradation mechanisms usually present two stages [2]. In the first stage, water induces the ion exchange of alkaline

ions ($\text{M}^+ = \text{Na}^+, \text{K}^+$) from the glass surface by the protons (H^+) from the water (2). The consequence of this reaction is the formation of hydroxyl ions (OH^-) which increase the pH of the aqueous surrounding of the glass.



In the second stage, the basic species break the oxygen bridge bonds (3) and induce irreversible disruptions on the glass network. The accumulation of negative charges in the glass surface increases the repulsion forces which tend to open the glass network. This opening promotes the reaction of water molecules with terminal groups which progressively raise the pH in the aqueous surrounding of the glass (4) and increase its degradation [2,3]. This mechanism prevails when $\text{pH} > 9$.



The mechanism in aqueous media has been confirmed for the alteration of historical stained glass windows due to the action of the rain and the mist [4–6]. However the studies focused on the degradation of silicate glass in natural aquatic media are scarce and most of them are archaeometrical characterizations of historical glass objects from different locations, among them, the shipwrecks in the coast of Kaş (Turkey) [7], the coast of Embiez (France) [8], the seabed of Grado lagoon (Italy) [9–11], the harbour of Lerwick (UK) [12], the coast of Hastings (UK) [12] and the coast of Murcia (Spain) [13–15]. The majority of the artefacts

* Corresponding author.

E-mail address: t.palomar@fct.unl.pt (T. Palomar).

Table 1
Chemical composition of model glasses analyzed by XRF.

	Chemical composition (wt%)			
	RA	VA	MA	CA
Na ₂ O	18.05	15.70	1.14	4.95
MgO	1.34	1.05	2.49	–
Al ₂ O ₃	3.40	2.25	3.21	0.14
SiO ₂	67.14	71.57	47.78	53.79
P ₂ O ₅	0.01	0.01	3.37	0.01
K ₂ O	1.30	0.76	19.16	8.20
CaO	7.25	8.46	22.63	0.06
TiO ₂	0.07	0.09	0.04	–
Cl [–]	–	–	0.04	–
MnO	0.46	–	–	–
Fe ₂ O ₃	0.93	0.06	0.08	–
SrO	–	–	0.01	0.03
ZrO ₂	0.01	0.01	–	0.08
Sb ₂ O ₃	–	–	–	0.57
BaO	0.03	0.03	0.05	2.60
PbO	–	–	–	29.57

Table 2
Salts used for the preparation of 250 ml of synthetic river [17] and marine water [18].

Salt	Mass (g)	
	River water	Marine water
NaCl	–	29.8332
Na ₂ SO ₄	–	5.0423
KCl	–	0.8909
NaHCO ₃	0.1444	0.1798
KBr	–	0.1179
B(OH) ₃	–	0.0336
MgCl ₂ ·6H ₂ O	0.1347	13.2427
CaCl ₂	–	1.4124
CaSO ₄ ·2H ₂ O	0.1444	–
KHCO ₃	0.0257	–

were soda-lime silicate glasses and lime silicate glasses with low content of alkaline oxides. The high stability of these glasses induced a low degradation rate which favoured their preservation, even since Roman times. Nevertheless, most of them presented a whitish or iridescent surface layer with irregular morphology and low content of Na₂O and K₂O (approximately 5 wt%) and a high content of SiO₂ and Al₂O₃ [16].

Carmona et al. studied the degradation of model glasses in a marine synthetic media [17]. The study demonstrated that the degradation rate depended on the glass composition and the temperature of the media. The glasses presented alteration pathologies such as pits, craters,

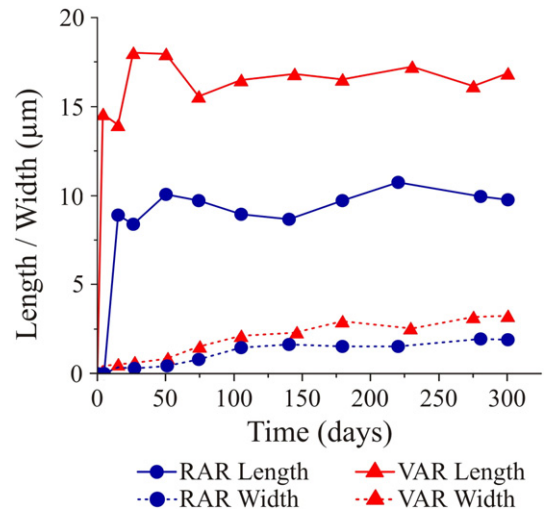


Fig. 2. Representation of pits average length and width from RAR and VAR glasses as a function of the experiment time.

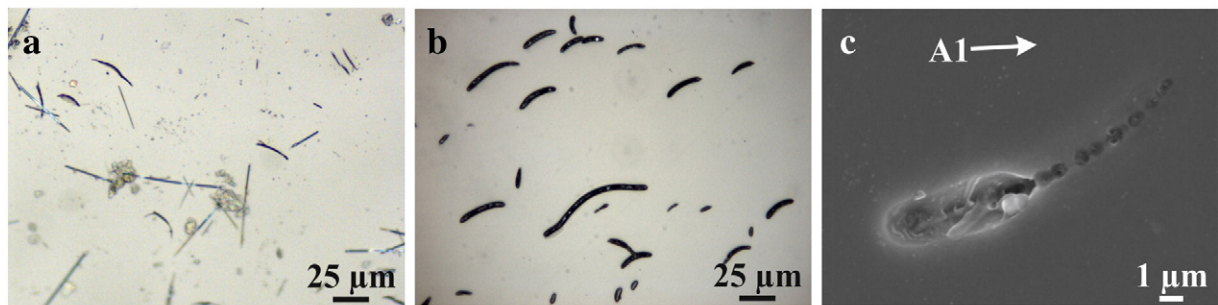
alteration layers and deposits of salt. The degradation layers were enriched in SiO₂ and MgO, which can be attributed to deposits of salts from the synthetic seawater. The hydrolytic attack on the glass surface also produced an increase in the pH of the aqueous media.

The aim of this study is to characterize the alteration mechanisms and degradation rate of soda-lime silicate, potash-lime silicate and lead silicate glasses in river and marine aquatic environments by submerging glass slices in synthetic marine and river media. This research will be especially useful for researchers who work with glasses exposed to natural aqueous media and for conservators and restorers who work with historical glasses from shipwrecks.

2. Experimental

2.1. Glass samples

Four model glasses were formulated and melted in the laboratory following the composition of the main representative historical glass types (Table 1). Glasses RA and VA were soda-lime silicate glasses. RA glass, similar to Roman glasses, contained a low percentage of Fe₂O₃ and MnO which reproduced the impurities of the raw materials. VA glass presented higher contents of SiO₂ and CaO, according to modern conventional window glasses. Glass MA was a potash-lime silicate glass with similar composition to medieval glasses and glass CA was a



Analysis	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO
A1	10.9	2.1	3.7	70.5	1.2	11.7

Fig. 1. Images of VAR glass altered in synthetic river water. a) OM image of fissures after 50 days. b) OM image of pits after 300 days. c) SEM image (×2500) of a pit after 300 days. The attached table shows the results of the EDS microanalysis (wt%).

Download English Version:

<https://daneshyari.com/en/article/1480187>

Download Persian Version:

<https://daneshyari.com/article/1480187>

[Daneshyari.com](https://daneshyari.com)