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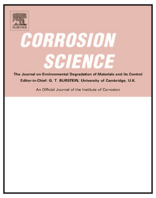

The effect of three luminescent ionic liquids on corroded glass surfaces – A first step into stained-glass cleaning

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ABSTRACT

Corrosion in medieval stained-glass represents a challenging issue in Conservation Science, being mainly composed by calcium salts. Model glass materials were produced and then subjected to an accelerated corrosion environment. Early stage glass corrosion layers observed were afterwards cleaned with luminescent ionic liquids (ILs). The effectiveness of the treatment was compared with Ethylenediaminetetraacetic acid solution and high levels of humidity, both of which have caused alterations on the glass surface. With the ILs, detectable morphological or chemical alterations were avoided and the gel-layer remains on the glass surface, indicating that these are a viable alternative to conventional cleaning methods.

1. Introduction

Medieval stained-glass is composed of a high concentration of alkaline and alkaline-earth ions, mainly potassium, calcium and sodium, and low contents of silica when compared with contemporary glass. The chemical composition of medieval glass is one of the main causes for its deterioration due to the reaction between the glass surface and water. In the presence of water, glass corrosion will occur with the formation of a hydrated layer and lixiviation of ions of Ca^{2+} and K^{+}. In the presence of pollutant agents, CO_2 and SO_2, corrosion crusts are formed at the surface. These crusts are composed of insoluble salts (such as calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$) and calcium oxalate (CaC_2O_4) and others) which are very difficult to remove from the glass surfaces.[1] This is an irreversible process that results in the permanent loss of the original glass once it is altered into corrosion crusts [2–5]. As this crust gets thicker, it alters the way light passes through the glass, degrading the effect of the stained-glass panel and thus its full appreciation.

A variety of mechanical and chemical cleaning methods is currently used in restoration practice with regards to this issue. The most commonly used mechanical methods include, among others, scalpels, bristle brushes and glass-fiber brushes; while the chemical methods range from the use of water (usually a solution of water:ethanol, 1:1 [v/v]) to organic solutions. However those that present a higher efficiency in removing the corrosion crusts are the same as those that may induce damage or long-term risks to the glass surface. These higher risk methods are the mechanical removal with the aid of a scalpel, that can scratch the glass surface, and the application of chelant agents, such as EDTA, weak acids and ionic resins, that may alter the pH of the surface or lead to the leaching of the surface, causing further degradation, for example [6–13].

Previous studies also describe the use of an excimer-laser operating at 248 nm for cleaning stained glass windows [6,8,10–13], with good results regarding the removal of corrosion crusts without damaging the glass surface or the gel-layer [8], which was confirmed by light microscopy, electron microscopy and infrared spectroscopy [6,8]. The conclusion of these studies was that this method could, indeed, be used for stained glass cleaning, although within limits. [8] However, this method does not seem to be as generally used nowadays as its promising results would suggest. This can be either due to the high equipment cost, the requirement of a qualified technicians, or the requirement of more extensive short and long-term tests.

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[1] Solubility products (K_{sp}, at 25 °C and zero ionic strength): $CaCO_3$ (calcite) = 4.5×10^{-9}, $CaC_2O_4 = 1.3 \times 10^{-8}$, $CaSO_4 = 2.4 \times 10^{-5}$ [1].

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The development of cleaning methods that are effective and harmless for the work of art but also less harmful to health and the environment are major concerns for conservators/restorers [6]. The idea that preceded this project was to design a cleaning material that could be easily controlled by the conservator, allowing restoration of the stained glass transparency but also leaving a thin corrosion layer of crystalline secondary phases that could act as a limiting factor to the progression of the alteration on the glass surface [14]. It is important to emphasize that any cleaning procedure should remove the corrosion deposits only as far as necessary to improve the transparency, without damaging the hydrated glass surface underneath.

Several different Ionic Liquids (ILs) were designed and tested for removing stained glass calcium corrosion crusts [15,16]. ILs in general were exhaustively studied and several applications in a variety of areas were developed in the last few years [16], including for usage in Conservation and Restoration, *e.g.*, of stained glass [15] and of paintings for varnish removal [17]. Previous studies have shown that the tested ILs were effective on the removal of corrosion crust on corroded historical samples composed of a mixture of calcium carbonate, calcium sulphate and calcium oxalate [15]. Their main action was to soften the corrosion layer, making possible its removal with the use of a cotton swab [15]. The final results showed an increase in the transparency of the glass, proving that the controlled partial removal of the corrosion crust was successfully achieved [15]. In this paper, the effect of the use of these developed luminescent ILs are described and compared with the alterations induced by high humidity levels and EDTA. At this stage, the aim of this work was to determine if these ILs are able to remove corrosion crusts and if there were any alterations – morphological and chemical – on the glass surface induced by the various cleaning materials, particularly through:

a) Comparison of the effects of each of the three different ILs – $[P_{6,6,6,14}]$[ANS] IL, $[C_5O_2MIM]$[ANS] and $[P_{6,6,6,14}]$[PyrCOO][2] – with the effect of EDTA deposition on the glass surface and with the effect of high relative humidity (RH);
b) Description of longer term effects (up to 16 weeks) of $[P_{6,6,6,14}]$[ANS] IL on the surface of un-corroded and artificially corroded model glass samples.

In the context of this work, the short-term effects refer to the cases in which the glass surface was submitted to each condition for 1–24 h, while the mid-term corresponds to a period of 7–28 days, and the longer-term effects to the tests in which the IL was in contact with the glass surface for up to 16 weeks.

2. Experimental

2.1. Production of glass samples, accelerated surface corrosion and ionic liquids synthesis

Model glass with a composition similar to those typically found in stained-glass from Mosteiro da Batalha [18,19] – the main example of international Gothic architecture in Portugal which also has the oldest examples of Portuguese stained-glass in the country, from the 15th century [20] –, was produced with laboratory reagents p.a. (SiO_2 and $CaCO_3$, Sigma-Aldrich; K_2O and P_2O_5, Panreac; MgO, BDH; Al_2O_3, Merck). Table 1 presents the chemical composition of the produced glasses.

The mixture of reagents was melted in an Al_2O_3 crucible at 1300 °C, over 24 h. The glass obtained was blown using traditional off-hand glass tools and techniques analogous to the production period of the historical stained-glass. The resulting roundels (discs) kept a fire-polished surface nearly identical to the historic glass production. The discs were annealed at 500 °C (for 4 h), which was followed by slow cooling (~20 h), and then they were cut into pieces with no further polishing. The pieces were cut using a diamond tipped glass cutter with the approximate dimensions of 1.5 cm^2. The model glass samples were then divided in six groups, as showed in Fig. 1.

2.2. Experimental design for the tests carried out on the glass samples

The purpose was to compare the effect of three ILs ($[P_{6,6,6,14}]$[ANS] IL, $[C_5O_2MIM]$[ANS] and $[P_{6,6,6,14}]$[PyrCOO]) and EDTA with the effect of a high level of humidity on the glass surface, from a short period (1 h) to a longer period of contact (28 days), in order to access the mid-term effect of these compounds.

The samples from group A were vacuum sealed immediately after the model glass has been produced and cut, in order to avoid at most any kind of alteration provoked by atmospheric conditions. Group B samples were placed in a desiccator with a stable, high RH between 85 and 90% at ~22 °C – these conditions were controled by placing silica gel in the desiccator, and monitored using a data logger. A drop of IL was deposited on the samples of groups C, D and E. After the due time, the ILs were removed using a swab impregnated with a solution of water:ethanol (1:1/v:v), and its complete removal was always controlled using a UV-light lamp (365 nm). For the group F samples, a solution of 3% EDTA + 3% NH_4HCO_3 in distilled water, pH 8.26 was used [6]; the samples were put in a closed plastic container and covered with the EDTA solution for durations ranging from 1 h to 28 days, then removed and rinsed with distilled water several times. All the samples were then cut, casted in epoxy resin and abraded with Micro-Mesh® sanding sheets, up to 16000 mesh, for the examination of the cross section.

The samples have been characterized before and after the cleaning treatment, to detect the presence of ILs residues and surface alterations, both morphological and chemical. The characterization was performed using microscopy techniques – such as Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) –, Raman microscopy and Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS), for elemental line-scan profiles.

Longer-term tests were also carried out, testing the long term effects (up to 16 weeks) of one of the ILs – the Trihexyltetradecylphosphonium 8-anilino-1-naphthalenesulfonic acid, ($[P_{6,6,6,14}]$[ANS]). For this set of experiments, a new model glass roundel was produced, following the same protocol as before. The experimental design for the long-term tests consisted in dividing the samples into two groups: a control group, vacuum sealed, and a group subjected to induced corrosion by having the samples immersed in distilled water for 3 months, each sample in a different container.

A drop of IL was deposited on 3 samples from each group, while a fourth sample was left without IL. The emission spectra were measured for all samples, in order to control the intensity of the emission of the IL over time. Upon the removal of the IL, using a swab impregnated with a solution of water:ethanol (1:1/v:v), its complete removal was always controlled using an UV-light lamp (365 nm) and emission spectroscopy. Then each sample was analysed to verify if there were any morphological and chemical alterations.

Optical microscopy images of surfaces of the non-corroded and corroded glass samples, before and after the cleaning procedure,

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[2] $[P_{6,6,6,14}]$[ANS] – trihexyl(tetradecyl)phosphonium 8-anilino-1-naphthalenesulfonic –, $[C_5O_2MIM]$[ANS] – 1-[2-(2-Methoxyethoxy)ethyl]-3-methylimidazolium 8-anilino-1-naphthalenesulfonic – and $[P_{6,6,6,14}]$[PyrCOO] – trihexyl(tetradecyl)phosphonium 1-pyrene carboxylate.

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