



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title:
Effect of Mn reducing treatment on integrity of glass corrosion bodies
proposal p26444

Experiment number:
EC602

Beamline:
ID19

Date of experiment:
from: 30/04/2010 to: 03/05/2010

Date of report:
1/9/2010

Shifts:
9

Local contact(s):
Lukas Helfen

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Simone Cagno – University of Antwerp*

Gert Nuyts – University of Antwerp*

Koen Janssens – Universiteit Antwerpen

Simone Bugani – University of Bologna*

Kristel De Vis – Artesis Hogeschool Antwerpen

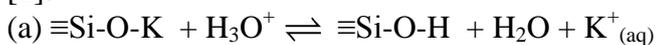
Joost Caen – Artesis Hogeschool Antwerpen

Report:

Introduction

Upon weathering, historical glass samples may turn brown-black due to the precipitation of Mn-containing-bodies within the superficial leached-out glass. This type of alteration is treated by restorers with mildly Mn-reducing agents. The purpose of the experiment was that of performing absorption tomography imaging of corroded glass samples before and after treatment. The aim is to assess the effectiveness of the treatment and verify whether it has no deleterious effects on the structure apart from removal of the dark colour.

Weathering of (historical) glass is a multi-step physico-chemical transformation of which the first phase is driven by diffusion of mobile cations (such as K^+ , Na^+) and their replacement by protons in the silica network [1]:



followed by diffusion of Mn-ions (present as Mn^{2+} and/or Mn^{3+} in the original glass [2;3] towards the voids and formation of (b) brown-black precipitates, containing more oxidized Mn species, e.g.:



This leads to the formation of an interfacial layer of leached-out glass of significantly lower density than the original glass. With increasing thickness (a few to 10s of μm), the stress across the interface between this gel layer and the glass interface becomes too high, causing a lamella of leached-out glass to physically crack off, thus exposing a new surface of the original glass. By a succession of such events, stacks of μm -thin lamellae of leached-out glass interspersed with voids, are formed, e.g. in the form of hemispherical corrosion bodies.

Due to interference phenomena, the multilayered material can obtain an iridescent aspect when the inter-lamellar voids are not water-filled. The Mn-precipitates, located in the cracks and voids within the alteration layer, give to the glass surface an unwanted dark appearance, particularly noticeable in figurative stained windows. This type of alteration is treated by restorers with mildly Mn-reducing agents such as hydroxylamine (NH_2OH) (see Figure 1).

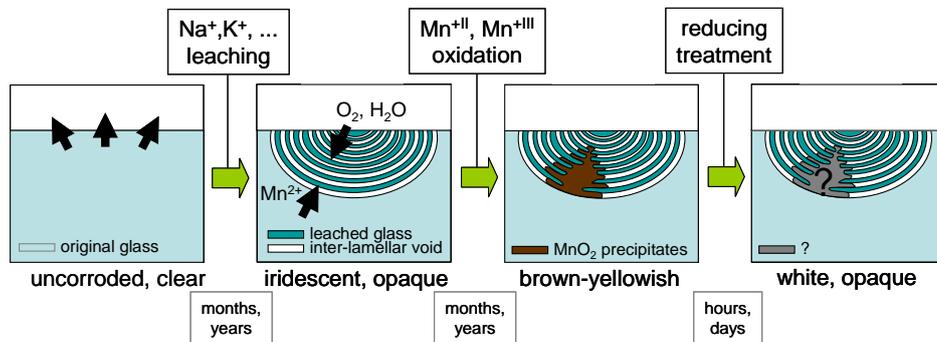


Fig. 1. Multi-step corrosion of historical glass, leading to discoloration; conservation treatment.

Up to now, no study involving SR-CT has been performed on Mn-bodies in historical glass. Only an experiment of visualization, on particularly corroded samples, was done by Schalm et al [4], by means of a table-top CT. In the present experiment we applied CT to real-life conservation circumstances, in order to better explain the process and provide useful information for an optimal conservation/restoration of glass.

Preparation

In this part of the experiment, we investigated the structural effects of the use of a reducing treatment by visualizing changes in the structure/porosity of the multilayered stacks via (nano)tomography, before and after in situ treatment of the same glass fragments.

The historical (stained) glass samples that were examined originated from the Canterbury Cathedral (U.K.). These glass samples date to the 14th century and have suffered corrosion in wet environment (groundwater), for 3-4 centuries.

Prior to the experiments at ESRF, samples of the same type (prepared in pillar-like shapes suitable for tomography) have been scanned by means of table-top absorption tomography (Skyscan, 3.4 μm resolution) to establish the general shape and position of the corrosion bodies. The resolution available with table-top CT was enough to distinguish the Mn-bodies within the glass, but insufficient for discerning fully the topographic detail. Additionally, an in-depth study (SEI, BEI, elemental maps, calculation of Mn-concentrations) of the polished surfaces has been performed with SEM/EDX on the same samples.

The experiment

During the experiment the treatment by means of hydroxylamine was tested, at concentration of 5% w/w. The treatment was monitored in a semi-continuous way: the samples were first placed into the solution in order to react, after a chosen time (30 minutes) they were removed and measured with absorption tomography (19 kV), using a resolution of 0,7 μm . After measurement the samples were returned into the solution for further treatment. 4 glass fragments were used, which differ in Na₂O (0-3%), K₂O (12-18%) and CaO (17-27%) content. A few tomograms, representing subsequent treatment steps, are shown in figure 2.

In all the samples the manganese removal is visually confirmed by the disappearance of the high density areas (manganese-containing bodies). It is the first time that the removal of Mn-bodies in historical glass can be visualized in 'real-time', thanks to SR-CT. The removal appears to be quick, but it is not complete in the maximum tested time (270 min). It has to be taken into account that the semi-continuous nature of the treatment also affects the speed of removal.

The Mn-removal can also be visualised by plotting the volume fraction taken up by the manganese inclusions as a function of the treatment time. For example the manganese removal in sample C2, is visualized in Figure 3 (blue curve). It is clear that more than 50% of the total volume is removed within the first hour of treatment, on a longer time the speed tends to level off, with an undissolved fraction remaining.

Another way of visualizing the removal is to 3D-render the inclusions (thresholding the attenuation coefficient) and compare how their volume and shape change with the passing of time, this is shown in Figure 4 for sample C2.

An important disadvantage of the treatment could be visualized in this experiment: an expansion of the leached layer (altered glass) is caused by the hydroxylamine solution. Water is indeed an important glass-alteration factor, and probably the corroded and fissured nature of the analyzed glass fragments accelerated the weathering. This is clearly shown in Figure 6 for the sample C10: the darker (low density) area noticeably expands over the tested treatment time.

In a chosen volume the expansion of the leached layer can be shown by plotting the volume fraction representing the leached layer in function of the reaction time. The evolution of its solution-driven extension

can be seen in figure 3 (red curve). In the same graph the volume fraction of healthy glass is also plotted (green curve).

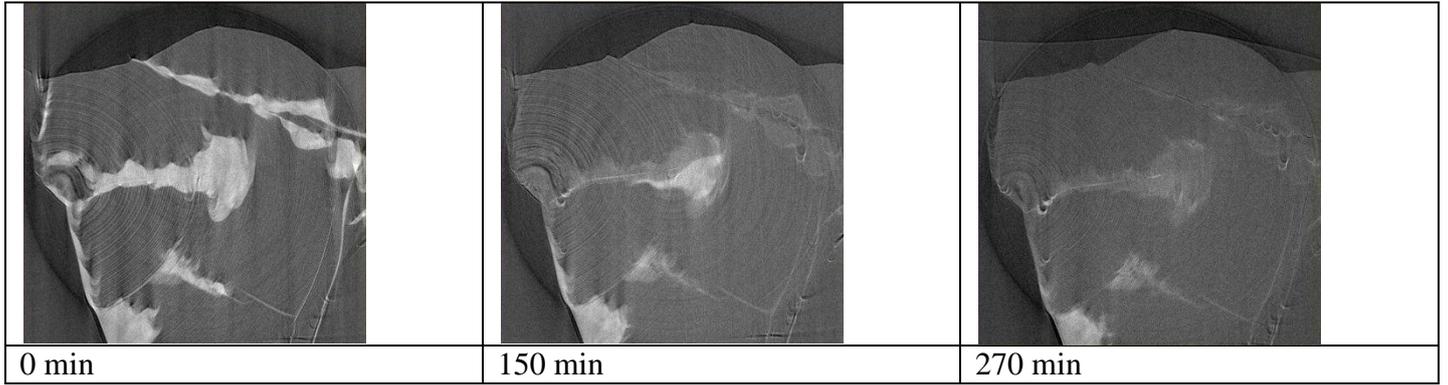


Figure 2. Sample C2: tomograms collected at different treatment times

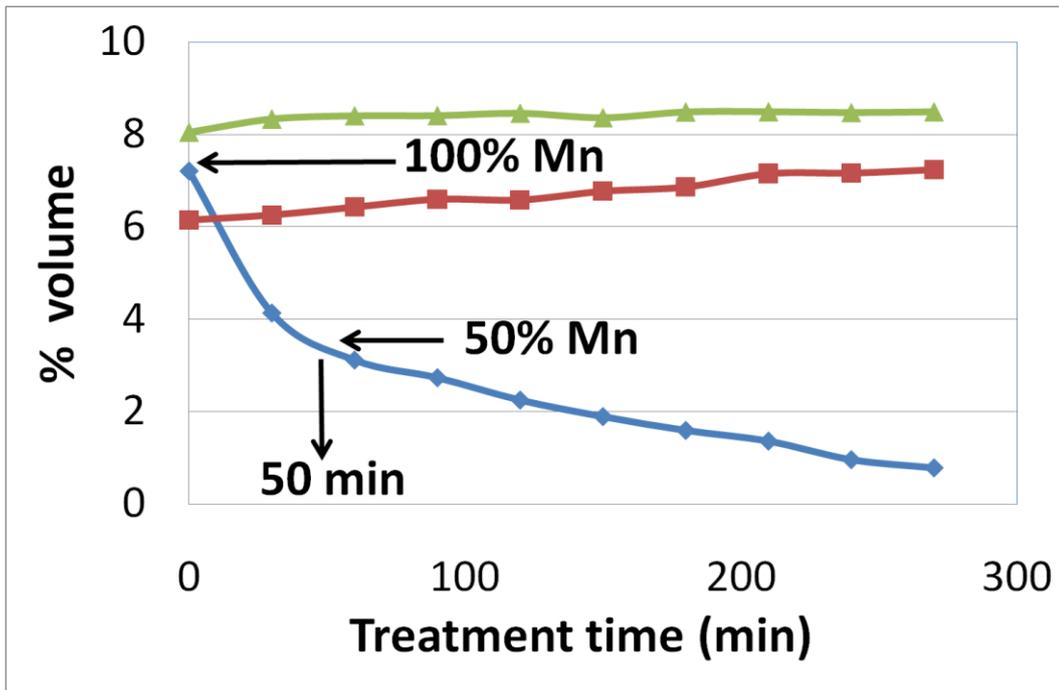


Figure 3. Plot of the Mn-bodies (blue), leached layer (red) and healthy glass (green) volume as a function of the treatment time. Leached layer volume is divided by 2, healthy glass volume is divided by 10.

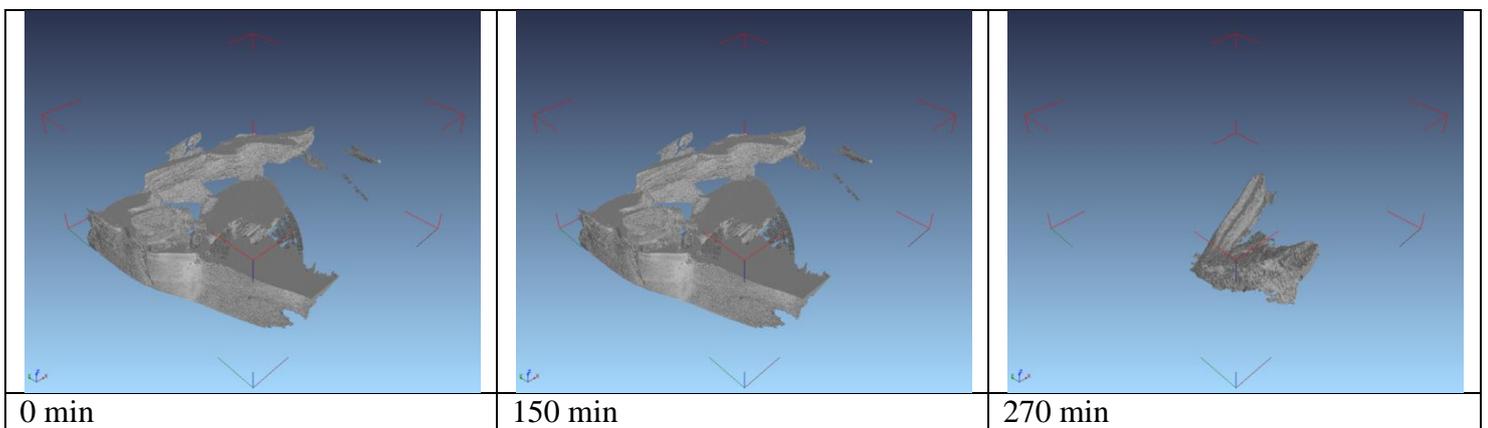


Figure 4. 3D-rendering of the Mn-bodies at different treatment times for sample C2

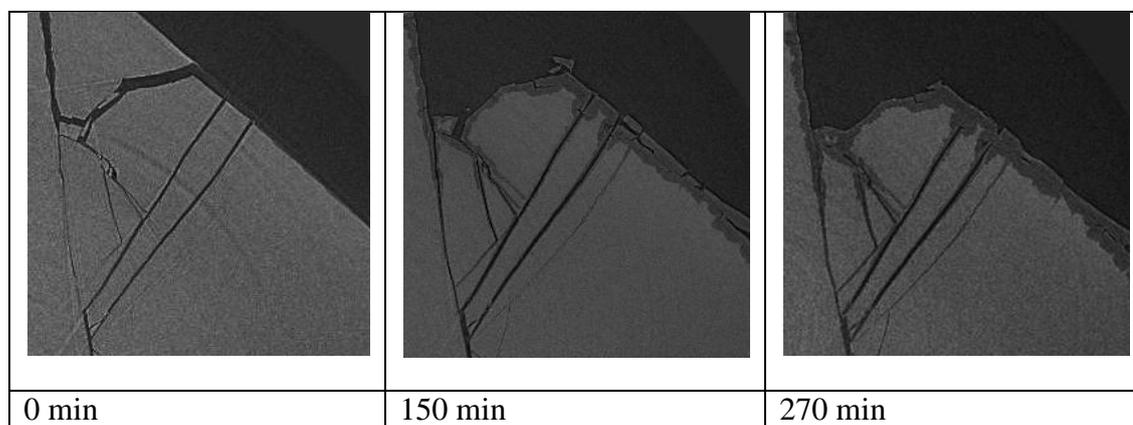


Figure 5. Detail of the leached layer for sample C10 at different treatment times

Conclusion and future

From these experiments we now know that the manganese is indeed removed from the inclusions, after its reduction. A number of conclusions can be drawn:

- a) The absence of material with a different attenuation coefficient than the surrounding glass, in the place where former Mn-bodies were located, points to a removal without re-precipitation of Mn in other forms.
- b) The tested time has never been enough to remove totally the Mn-bodies, probably due to the difficulty of penetration of the solution in the inner parts of the leached layer (also hindered by the embedding resin). The speed of removal is fastest in the first hour and then decreases. The effect of the interruptions and drying-out for the measurements has to be taken in account.
- c) On the other hand extended treatment time causes further alteration of the glass, namely extension of the Na- and K-leached layer. An optimum that balances maximal Mn-removal and minimal induced alteration ought to be found.

Further experiments need to be done, using different reducing-chelating agents (such as citric acid, EDTA, acetylacetone) with lower concentrations in order to minimize/prevent expansion of the leached layer. K- and Na-enriched solutions, in order to minimize the uptake from the glass, or pH-buffered solutions during could be possible way to overcome the problem and should be tested. Moreover, the production and weathering (e.g. exposition to acid/MnCl₂) of glass of controlled shape and composition could be a good and viable alternative to the historical glass samples used for this experiment tests.

With this aim, [proposal p26444](#) has been submitted, as a continuation of experiment EC602.

References

- [1] Newton, R.G., The weathering of medieval window glass, *J. Glass Studies*, 17 (1975) 161-168; Melcher, M.; Schreiner, M., *J. Non-Cryst. Solids* 352 (2006) 368-379. [2] Chalmin E., Farges F., Brown GE, A pre-edge analysis of Mn K-edge XANES spectra to help determine the speciation of manganese in minerals and glasses, *Contrib. Mineral. Petrol.*, 157 (2009) 111-126. [3] Quartieri S. et al., Fe/Mn XANES study of Ancient Roman Glasses, *Eur. J. Mineral.*, 14 (2002) 749-756. [4] Schalm, O. et al., Manganese staining of archaeological glass: the characterization of Mn-rich inclusions in leached layers and a hypothesis of its formation, *Archaeometry* (2010) accepted.