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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.

ESRF	**Experiment title:** Effects of Mn-reducing treatments on the integrity of glass corrosion bodies	**Experiment number:** EC768
Beamline: ID19	**Date of experiment:** from: 28/4/2011 to: 3/5/2011	**Date of report:** 12/09/2011 *Received at ESRF:*
Shifts: 15	**Local contact(s):** Dr. Alexander Rack	

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Report:

Introduction

Upon weathering, historical glass samples may turn brown-black due to the precipitation of bodies of highly oxidized Mn (Mn^{4+}-Mn^{6+}) within the superficial leached-out glass. Weathering of (historical) glass is a multi-step physico-chemical transformation involving (a) leaching of mobile cations from the glass (replacement by protons), leading to the formation of stacks of μm-thin lamellae of leached-out glass interspersed with voids [1],

(a) $\equiv\text{Si-O-K} + H_3O^+ \leftrightarrow \equiv\text{Si-O-H} + H_2O + K^+_{(aq)}$

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.:

(b) $Mn^{2+} + \frac{1}{2}O_2 + H_2O \leftrightarrow MnO_2\downarrow + 2H^+$

This type of alteration is treated by restorers with mildly Mn-reducing agents such as hydroxylamine (NH_2OH). Such a treatment can be effectively monitored by means of absorption tomography and Mn-K edge XANES imaging (see report EC602).

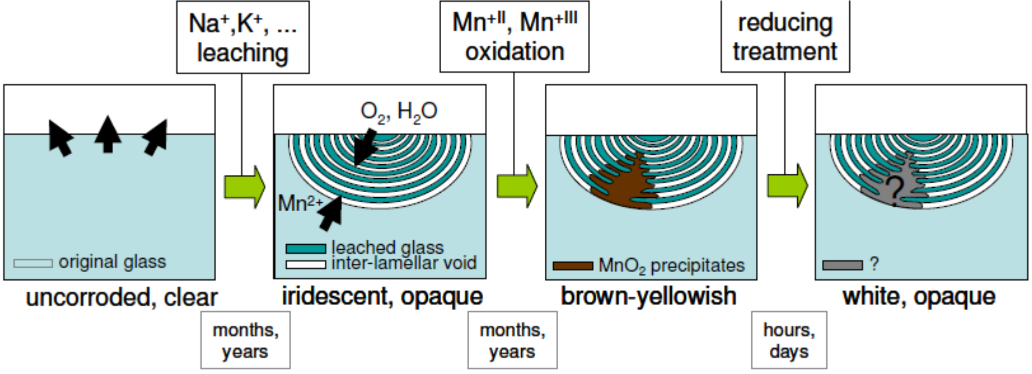


Figure 1 The different steps leading to the formation of Mn-browning and its restoration

However, also the gradual increase of the leaching damage inflicted by the NH_2OH-solution to the healthy parts of the historical glass could be clearly visualized, highlighting the dangers associated with this method of restoration. The aim of the follow-up experiment is to compare the effect of other reducing solutions with that of hydroxylamine in order to optimize the balance between desired and unwanted effects. In the previous experiment we had demonstrated how the Mn contained in the Mn bodies was in an oxidized form (see Report EC602 and reference 4) and how the treatment with NH_2OH, after an initial reduction of the oxidized Mn, was succesful in solvating the Mn following an exponential decay (see report EC602 and reference 4).

Experiments EC768 presents a novelty for what concerns the experimental approach, in order to minimize the loss of time for sample mounting/handling and resembling much more the real conservation circumstances.

Preparation

In the current experiment, more treatments were tested (Table 1), and in particular, as said before, a new approach was tried. In EC602 (ID19 part) the treatment was conducted in a discontinued way (several repetition of 30 min treatment in the solution, the measurement done on a ‘dry’ sample between two treatment periods). In EC768 the CT measurement were performed while the glass fragment was treated, kept in a fixed position in a plastic container (Fig. 2), thus performing “online” or real-time CT.

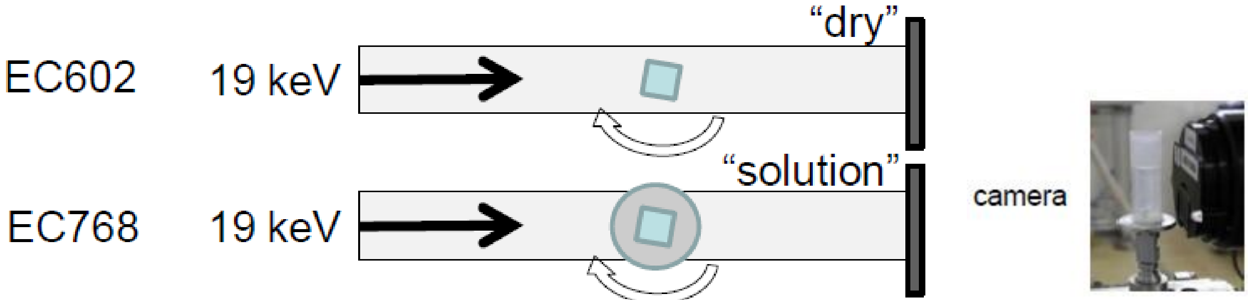


Fig. 2 Experimental setup of EC602 and EC768; on the right the sample can be seen immersed in the NH_2OH solution

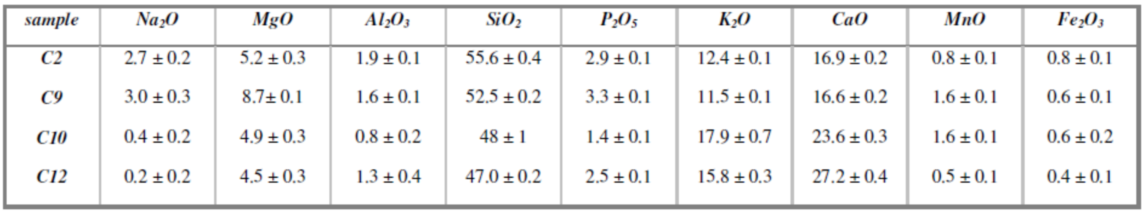
NH_2OH	NH_2OH + EDTA	$C_6H_8O_7$
0.2%; 0.5%; 1%; 1% + KCl, NaCl	1% + KCl, NaCl	1%; 5%

Table 1 Tested treatments (% w/w)

In the part of the experiment done at ID19, we investigated the structural effects of the use of a reducing treatment by visualizing changes in the structure/porosity of the multilayered stacks via high resolution tomography, during the *in situ* treatment of the same glass fragments (from 0 to 280 minutes).

The historical (stained) glass samples that were examined originated from archaeological excavations done at Sidney Sussex College, Cambrige (U.K.). These glass samples date to the 14th century and have suffered corrosion in wet environment (groundwater), for at least 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 calculated composition of the historical fragments is that of a non-durable medieval potash-lime glass (Table 1).

Moreover, experimental altered glass fragments were prepared by corroding in a controlled environment sensor glass (Fraunhofer M1.0 [5]) and immersing it in a 1M solution of $MnCl_2$ in order to facilitate Mn precipitation.



sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	Fe_2O_3
C2	2.7 ± 0.2	5.2 ± 0.3	1.9 ± 0.1	55.6 ± 0.4	2.9 ± 0.1	12.4 ± 0.1	16.9 ± 0.2	0.8 ± 0.1	0.8 ± 0.1
C9	3.0 ± 0.3	8.7± 0.1	1.6 ± 0.1	52.5 ± 0.2	3.3 ± 0.1	11.5 ± 0.1	16.6 ± 0.2	1.6 ± 0.1	0.6 ± 0.1
C10	0.4 ± 0.2	4.9 ± 0.3	0.8 ± 0.2	48 ± 1	1.4 ± 0.1	17.9 ± 0.7	23.6 ± 0.3	1.6 ± 0.1	0.6 ± 0.2
C12	0.2 ± 0.2	4.5 ± 0.3	1.3 ± 0.4	47.0 ± 0.2	2.5 ± 0.1	15.8 ± 0.3	27.2 ± 0.4	0.5 ± 0.1	0.4 ± 0.1

Table 2 Composition of the Sidney Sussex College fragments [4]

Results

The sensor glass did not prove to be a suitable support for CT imaging of Mn-precipitation, at least in its present conditions: the precipitates could only be observed on the immediate surface and no dendrites, as reported in literature [6], were observed. Thus we concentrated on the historical glass.

The continuous nature of the treatment allowed to performe real time imaging of the Mn-removal, however, a drawback we experienced was the decreased transmission due to the attenuating volume of the solution + holder. The decreased transmission resulted in blurrier images, as can be discerned from the two tomograms from EC602 and EC768 in Figure 3.

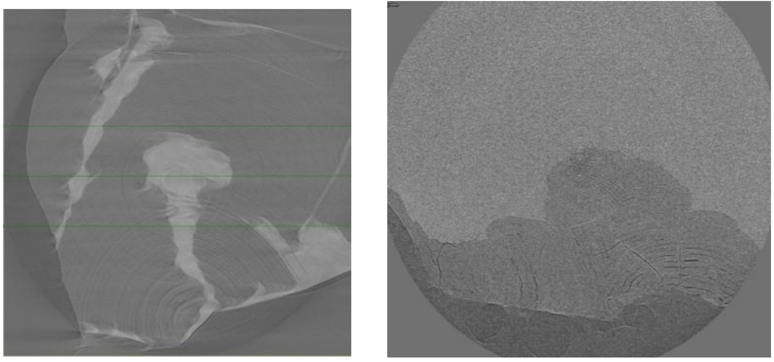


Fig 3 A tomogram from EC602 (left) and EC768 (right)

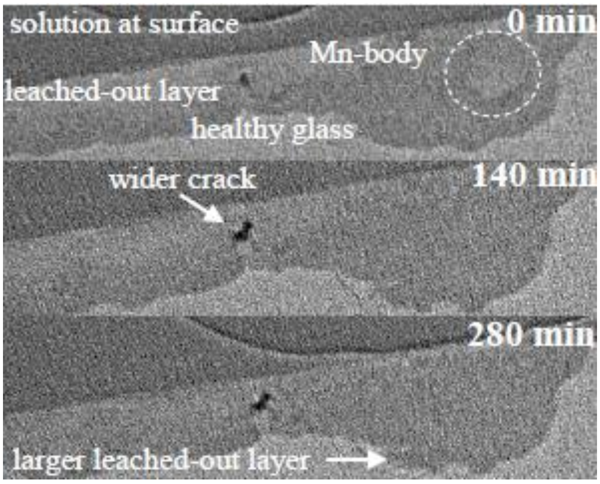


Fig 4 tomograms of the same sample/area at different periods of treatment with $C_6H_8O_7$ 5%

As a consequence of the lower transmission achieved, not all the treatments could be equally evaluated yet, even though in many cases the Mn-removal was visible (Fig 4).
The treatment for which the removal was proved were the more concentrated ones, i.e. citric acid 5%, Hydroxylamine 1%, EDTA + Hydroxylamine 1% (additioned of KCl, NaCl), by means of which already a relevant amount of Mn is removed in the first part of the 4 hours of treatment that have been tested (Fig 5).
The speed of removal in the small volume marked in Fig 5 is shown by the biplot in Fig 6. The treatment appears to be effective quickly: all the Mn appears to be removed from the selected volume in little more than 2 hours.
In Fig 5 it can also be observed how little leaching damage is done to the original glass, thanks to the presence of 5% KCl and NaCl in the treating solution.
On the other hand, the less concentrated solutions did not prove to be effective, and no or very little Mn-removal could be observed at the end of the 4 hour treatment (Fig.6).

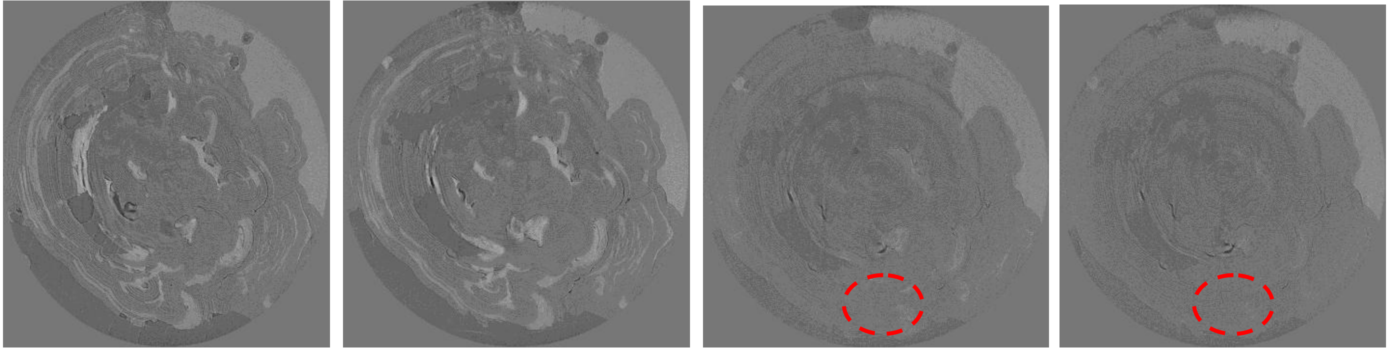


Fig 5 Sample C2 before treatment, after 4h of EDTA treatment, after 1h and 2h NH_2OH treatment (+KCl and NaCl). It is visible how non-MnO_2 precipitation is removed by EDTA, while in 2 hours the hydroxylamine effectively removes the Mn-bodies. No leaching damage can be observed.

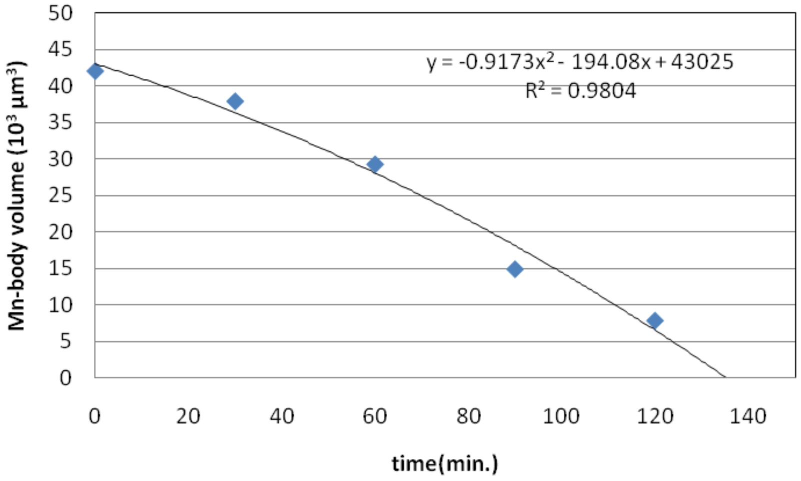


Fig 6 biplot showing the speed of Mn-removal by NH_2OH (volume marked in red in Fig 5, deeper in the sample). After 60 min approx. 50% of Mn is removed from the selected volume; after approx. 140 min all Mn is removed.

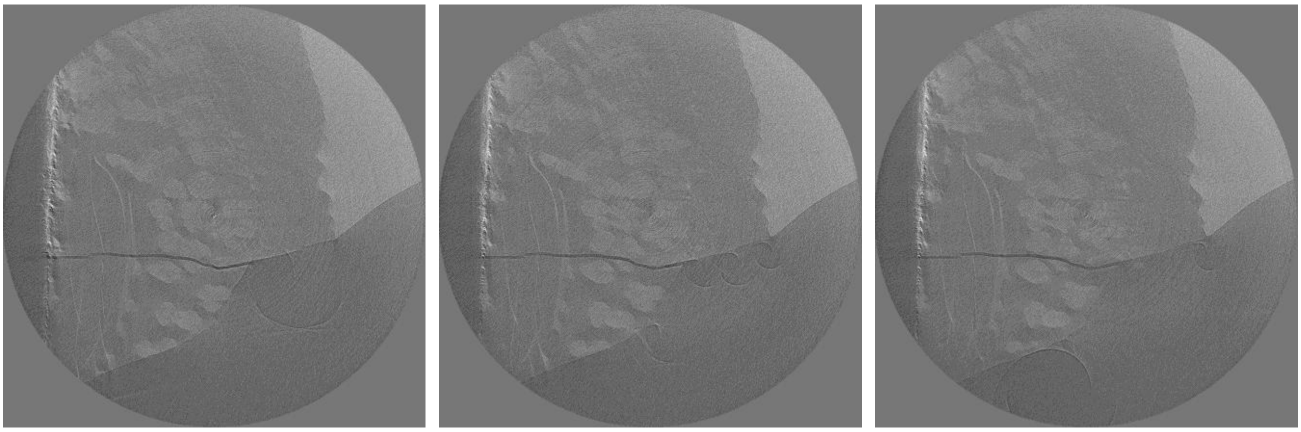


Fig 6 Sample C10 treated with 1% citric acid at 0, 140 and 260 min. No Mn-removal is observed

Conclusion and future

Experiment EC768 proved for the first time that it is possible to perform real-time CT on the treated sample while it is immersed in the reducing solution. As mentioned before the evaluation of the results is still ongoing, however we can already list some preliminary conclusions.

First of all we experienced that a lower concentration of hydroxylamine (1%) than in EC602 is sufficient to remove a great part of the Mn-bodies; lower concentrations (0.5-0.2%) did not work, thus we believe to be close to the critical concentration. Then we proved that citric acid is also successful in extracting Mn from the Mn-bodies, albeit to a lesser extent and at a higher concentration (5%) than hydroxylamine. Finally, the addition of potassium and sodium salts to the treating solution appears to be an effective way to prevent leaching.

However, in order to investigate a closer replica of the real conservation conditions, we would need to perform the experiment in a different way, with the treatment supported by methil-cellulose gel, entering the glass from the altered surface only, as it happens in the restoration of large stained glass windows. Moreover, a number of questions have to be completely answered, e.g. what is the minimum treatment time and concentration, or what is the best way to reduce the leaching damage. In order to answer these questions and to test the effectivenesso of the gel-supported conservation treatment, proposal p28872 has been submitted, as a continuation of experiment EC768.

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] Cagno S, Nuyts G, Bugani S, De Vis K, Caen J, Cotte M, Helfen L, Reischig P, Janssens K (2011) Evaluation of manganese-bodies removal in historical stained glass windows via SR-µ-XANES/XRF and SR-µ-CT, J. Anal. Atom. Spectr. accepted. [5] H.Römich, Evaluation of protective glazing systems**,** e-Preservation Science 1 (2004) 1-8. [6] Anaf W, Study on the formation of heterogeneous structures in leached layers during the corrosion process of glass, Ceroart (2010) Horizons, hors-série