Study of glass decay by X-ray Absorption Spectroscopy

M. Abuín, A. Serrano, M. A. Villegas, J. Llopis, J. Chaboy, M.A. García, N. Carmona.

October 2012, Burgos, Spain
1.- Introduction

2.- Main objective

3.- Experimental method

4.- Results

5.- Summary
All glasses undergo decay phenomena

- Chemical composition
- Environment


M. García-Heras et al., Construcc. 53,270 (2003) 21-34
Chemical analyses & decay diagnosis are essential ... Why?

- Complete historical knowledge.
- Optimize restoration and conservation procedures.
- Improve preservation strategies.

Museum of the Royal Glass Manufactures of La Granja (Segovia).
18th century bottle exhibited in a showcase.
Study the degradation state of historical glasses by XAS

Outside of stained glass windows from León cathedral.
Absorption of an x-ray s → continuum transitions are around XAS possibilities.
X-Ray Absorption Spectroscopy: XAS

Useful for non-crystalline and highly disordered materials... like glasses.

- Strongly sensitive to:
  - oxidation state
  - coordination number

Used to determine:
- coordination number
- atomic distances.

Multiple Scattering

Single Scattering

Room Temperature
In air

Strongly sensitive to:
- oxidation state
- coordination number

Energy (eV)
XAS main advantages

- sensitive to low concentrations
- spatially resolved
- gives complementary information – from the macroscopic to nanometer level
- versatile method
- non-destructive and non-invasive
**But ... which are the indicators of decay?**

Metal transition ions, colloids inside the glass.

Colour: Electronic transitions of d → d orbitals fall into VIS-NIR range.

and... s → p transitions fall into XAS range!!!

- **Mn (6.5 KeV) K-edge.**
- **Fe (7.1 keV) K-edge.**
- **Cu (8.9 keV) K-edge.**

**Cross section.**

*Glass of León Cathedral .13th C.*

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorbance (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>

**IFEFFIF Package: Athena**
- coloured original glasses
- broken fragments impossible to be relocated

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colour</th>
<th>Date</th>
<th>Provenance</th>
<th>Image</th>
<th>Weathered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me-14</td>
<td>green</td>
<td>1st C. BC</td>
<td>Archaeological site of Mérida</td>
<td></td>
<td>yes</td>
</tr>
<tr>
<td>Le-13</td>
<td>blue</td>
<td>13-14(^{th}) C.</td>
<td>León cathedral</td>
<td></td>
<td>no</td>
</tr>
<tr>
<td>Le-19</td>
<td>blue</td>
<td>13-14(^{th}) C.</td>
<td>León cathedral</td>
<td></td>
<td>yes</td>
</tr>
<tr>
<td>To-5</td>
<td>red</td>
<td>15(^{th}) C.</td>
<td>Toledo cathedral</td>
<td></td>
<td>no</td>
</tr>
<tr>
<td>Mi-3</td>
<td>red</td>
<td>15(^{th}) C.</td>
<td>Miraflores chartreuse</td>
<td></td>
<td>yes</td>
</tr>
<tr>
<td>Vi-2</td>
<td>red</td>
<td>18(^{th}) C.</td>
<td>Spanish stained glass windows</td>
<td></td>
<td>no</td>
</tr>
<tr>
<td>Re-1</td>
<td>green</td>
<td>18(^{th}) C.</td>
<td>Spanish stained glass windows</td>
<td></td>
<td>no</td>
</tr>
</tbody>
</table>
The three original red glass fragments under consideration show diverse degree of deterioration.
Relation between the absorption edge energy and oxidation state of glass samples at the Cu k-edges at all analyzed glass samples (reference compounds are marked by red colour).
EXAFS results: Cu

Cu-Cu

Cu-O

FT-Magnitude

R (Å)

foil Cu
Cu₂O
CuO

FT-Magnitude

R (Å)

Le_13
Le_19
Mi_3
Re_1
To_5
Vi_2
XANES & EXAFS results: Cu

Historical green glass sample.

Relation between the absorption edge energy and oxidation state of glass samples at the Cu k-edges at different positions of sample.
XANES results: Mn

All samples have very homogeneous spectra.

The absorption edge of all glass sample is located at energies between the absorption edges of MnO and Mn$_2$O$_3$ reference compounds.
Relation between absorption edge energy and oxidation state of glass samples at the Mn k-edges (reference compounds are marked by red colour).

All glasses seem to have Mn ions in oxidation states between +2 and +3.
Spectra of all glass samples show a small pre-peak at low energy side of the absorption edge.
Relation between absorption edge energy and oxidation state of glass samples at the Fe k-edges (reference compounds are marked by red colour).

Degraded surfaces present higher oxidation level than unaltered ones.
• These results prove the utility of XAS techniques in the study of glass decay.


• To establish a relationship between the molecular environment of the glass chromophore and the degradation state of the glass surface.

• XAS main advantages: element selective, sensitive to low concentrations, spatially resolved, gives complementary information at nanometer level, versatile method, non-destructive and non-invasive.

• This is an on-going project and there are still some open questions...
Acknowledgements

Spanish Ministry of Economy and Competitiveness and Consejo Superior de Investigaciones Científicas.

**SMEC Project** FIS-2008-06249, **Geomaterials Program** S2009/MAT-1629 and Comunidad de Madrid project **NANOBIO MAGNET** S2009/MAT-1726

**BM25-Spline** staff.

*N. Carmona* acknowledges the FSE-MEC, **Ramon y Cajal Program** RYC-2007-01715.

*A. Serrano* acknowledges CSIC (**JAE Program**) for pre-doctoral fellowships.

*M. Abuin* acknowledge Campus of International Excellence (**PICATA Program**) for pre-doctoral fellowships.
X-ray absorption studies of manganese valence and local environment in borosilicate waste glasses

David A. McKeown *, Wing K. Kot, Hao Gan, Ian L. Pegg

Vitreous State Laboratory, The Catholic University of America, 620 Michigan Ave, N.E., Washington, DC 20064, USA

Received 22 August 2002; received in revised form 29 April 2003

Abstract

X-ray absorption data were collected and analyzed to characterize the manganese environments in borosilicate glass formulations to be used for immobilization of nuclear wastes. Mn can become a significant constituent in some radioactive wastes, because of the use of Mn-compounds in waste pretreatment processes. Sixteen borosilicate glasses were investigated, which were synthesized to simulate the Mn environments in the anticipated waste glasses, where MnO concentrations range from 0.4 to 13.6 wt%. The X-ray absorption near edge structure (XANES) for all glasses investigated indicate that most of the manganese within these samples is divalent. The extended X-ray absorption fine structure (EXAFS) analysis results for the glasses show average Mn–O distances near 2.07 Å, coordination numbers between 4.3 and 5.2, and large first-shell Debye–Waller factors. The EXAFS findings indicate that Mn$^{2+}$ in borosilicate glass is most likely within a distribution of environments that include 4- and 5-coordinated sites. EXAFS data and fitting results also show that the average manganese environments in these glasses are statistically invariant with respect to composition as well as to synthesis conditions.

© 2003 Elsevier B.V. All rights reserved.
Fig. 2 VIS absorption spectra of: a) red glasses Mi-3, To-5 and Vi-2; and b) green glasses Me-14 and Re-1 and blue glass Le-13.