GRAZING INCIDENCE FLUORESCENCE EXAFS AND NEAR EDGE SPECTROSCOPY FOR CORRODED GLASS SURFACES

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GRAZING INCIDENCE FLUORESCENCE EXAFS AND NEAR EDGE SPECTROSCOPY FOR CORRODED GLASS SURFACES

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Abstract

EXAFS at grazing incidence with fluorescence detection has been used to investigate the local atomic structure around uranium at the surface of borosilicate glasses. Structural changes have been observed as a result of leaching in water at 100°C. These indicate that uranium migrates to the surface to form island structures in a surface layer which, subsequently, peels off to reveal fresh surface for further corrosion.

Glass surface corrosion induced by water is a subject of increasing scientific and technological interest, particularly in view of concern about an accidental release of radioactive products from vitrified nuclear waste /1/. Fluorescence EXAFS at grazing incidence is proving to be a particularly useful tool for the surface investigation of changes in the atomic neighbourhood of a radioactive waste metal, especially as the wet state can be maintained during measurements.

A description and some theoretical background of this technique can be found in the literature /2,3/.

The samples (U-glasses) were borosilicate glasses (53.7 SiO₂, 16.7 B₂O₃, 21 Na₂O, 5.6 Al₂O₃, in weight percentage), with 3% UO₂. As reference samples, U metal, an uranyl compound and UO₂ were used. The glass was prepared at Stazione Sperimentale del Vetro, Murano, Italy, by melting of the mixture in air within a platinum crucible. This procedure ensures an oxidizing environment.

The uranium concentration in the glass was scanned by an electron microprobe and no evidence was detected for any inhomogeneities. Glass slabs were optically polished to better than ½10 but, after leaching, a porous microstructure was observable in the surface, probably the result of the formation of a hydrated gel layer. Leaching was performed dynamically under a flow of boiling water at 100°C in a Soxhlet apparatus. X-ray measurements were made immediately after leaching, thus the samples were still in the "wet" state. An increase of the pH value of the leachant was measured after leaching, indicating the dissolution of alkaline products from the glass surface. X-ray measurements were made on the wiggler EXAFS station 9.2 of The Synchrotron Radiation Source at the Daresbury Laboratory. Typical fluorescence intensities at grazing incidence at the L_{III} edge of uranium are reported in Fig.1.

Measurements were made at an angle incidence of half the critical angle for total external reflection at the surface of a borosilicate glass. With this geometry, the
penetration depth probed by the incident beam is expected to be about 50 Å in the unleached glass. As may be seen more clearly from the insert, there is an increase in the fluorescence intensity with leaching time, pointing to an increase in the uranium concentration at the surface. Detailed total reflection measurements give some evidence for the generation of a surface layer whose critical angle for total external reflection is less than that of the bulk glass, i.e. the layer has a lower electron density.

![Fig. 1. Near edge fluorescence at grazing incidence at the U LIII edge. In the insert, ΔI is the step height and I is the intensity of pre-edge scattering.](image)

From the results shown in Fig. 1, there is clear evidence for saturation in the increase of U fluorescence intensity after 100 h. Accordingly, short leaching times of 15', 30' and 90' were chosen for EXAFS measurements. Fluorescence EXAFS spectra were recorded for leached and unleached samples at one half of the critical angle for total external reflection. Reference compounds were measured from powders using the transmission geometry. Least squares fits to k3 weighted data were obtained using the curved wave program EXCURVE available at Daresbury Laboratory /4/. In order to accurately determine phase shifts and back-scattering amplitudes for U-O and U-U pairs spectra, the reference compounds mentioned earlier were accurately fitted to their crystallographic radial distribution functions. Fig. 2 shows the comparison between experiment and theory for uranyl-fluoride-fluor ammonium. As in other uranyl compounds, the nearest neighbour octahedral oxygen shell is split into two subshells (2:4). The structural parameters are summarized in the insert. No U-U correlations are detectable for this molecular structure. UO2, on the other hand, has the fluorite structure with 8 nearest neighbour oxygens and 12 nearest neighbour uranium. Both shells are readily resolved in EXAFS as we have found for other fluorite oxides /5/. The U-O distance and Debye-Waller factors were 2.41 Å and 0.003(5) Å^2. For U-U correlations the corresponding values were 3.89 Å and 0.005(0) Å^2. The more

<table>
<thead>
<tr>
<th>SHELL COORDINATION NUMBER</th>
<th>DISTANCE (Å)</th>
<th>DWF (Å^2)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1.85</td>
<td>0.0035</td>
</tr>
<tr>
<td>2</td>
<td>2.34</td>
<td>0.0045</td>
</tr>
</tbody>
</table>

Fig. 2. k^3 weighted experimental EXAFS (solid line) and fit (dashed line) for reference uranyl compound (uranyl-fluoride-fluor ammonium), using modified phase shifts from EXCURVE. Data were filtered to include the first two oxygen shells.
complex EXAFS spectrum of metallic uranium was also successfully fit out to 4 Å. In all cases, phase shifts and back-scattering amplitudes yielded interatomic distances correct to 1% or better, correct coordination numbers and realistic Debye-Waller factors. These parameters were used to fit the FLEXAFS spectra obtained from the glass surfaces. In order to avoid possible artifacts from Kiessig fringes that might be associated with the generation of a surface gel layer, the k-range was limited to 3 - 14 Å⁻¹.

Analysis of all the glass spectra revealed radial distribution functions with three major features: one due to U-O correlations and the other two to U-U correlations. These can be seen in Fig. 3 where results of two different leaching periods are shown. In particular, the first feature (U-O distances) consists of two main contributions reminiscent of an uranyl radical. The pair distribution function for the fit shown in Fig. 2 is also included in Fig. 3 (dotted curves), where the resemblance can be clearly seen. Indeed, the chemical shift for the $UL_{III}$ edge for the glass spectra is close to that for the uranyl reference as other authors have found /6/.

It is obvious from Fig. 3, however, that the radial distribution functions for the glass surface are more complicated than either of the oxide reference compounds. In order to analyse this, we used the procedure of subshell analysis, constructing the oxygen coordination sphere from several subshells with the same integrated coordination number. This is particularly appropriate for studying the distorted metal environments in many glassy and crystalline oxides /7/. From Fig. 3 it can be seen that compared to the uranyl reference, the second subshell around 2.3 Å is broadened in the glass spectra and is also skewed - tailing off to longer distances. Where U-U correlations are not seen in the uranyl reference compound, they are seen in the glass spectra and, indeed, can be modelled to a planar square lattice /8/ as proposed earlier by Knapp et al. /6/.

Fig. 3. $k^3$ weighted EXAFS experimental (solid line) and fitted (dashed line) spectra from leached U-glasses and their corresponding pair distribution functions. Experimental data are Fourier filtered from 1 to 5 Å. Leaching times in minutes are marked in the figure. Dotted curves on the right correspond to the pair distribution function for the uranyl reference compound from Fig. 2.
The two atomic distributions shown in Fig. 3 demonstrate that the local environment of uranium changes as corrosion advances. We have found the two U-U features become more prominent with leaching. This can be seen in Fig. 3 and also in Table I where the normalized weights of U-U (1) and U-U (2) are listed for different leaching times. This data suggests that in the initial build-up of uranium at the surface (Fig. 1), the uranyl-like complexes agglomerate into larger islands. A broadening of the U-O feature is also observed, indicating the oxygen environment may becoming more disordered with progressive corrosion. This would be expected, for instance, if the surface gradually became more hydrated. After 90' of leaching, however, a uranium environment reminiscent of the unleached polished surface is recovered (Table I). This behaviour is consistent with a peeling off of a surface layer, revealing fresh material for an aqueous attack.

<table>
<thead>
<tr>
<th>Leaching time</th>
<th>U-U (1)</th>
<th>U-U (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0'</td>
<td>0.3(7)</td>
<td>0.0(4)</td>
</tr>
<tr>
<td>15'</td>
<td>0.4(4)</td>
<td>0.1(3)</td>
</tr>
<tr>
<td>30'</td>
<td>0.8(4)</td>
<td>0.2(4)</td>
</tr>
<tr>
<td>90'</td>
<td>0.3(5)</td>
<td>0.1(4)</td>
</tr>
</tbody>
</table>

The present grazing angle spectroscopic results at the UL\textsubscript{III} edge indicates that the process of borosilicate glass leaching in water involves the migration of uranium to the surface with the complexing of uranyl-like centres, accompanied by the generation of a surface layer. This is, subsequently, shed with a total time cycle of between 30' and 90'.

References

8. G.N. Greaves (this conference).

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