

# 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 via the User Portal:  
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

## Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

## Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

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.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.



<b>Experiment title:</b> <b>Investigation of Fe, Cr, Mn, Ni and Ce oxidation states to support vitrification of simulated high-iron radioactive wastes</b>		<b>Experiment number:</b> MA-4906
<b>Beamline:</b>	<b>Date of experiment:</b> from: 05/02/21 to: 09/02/21	<b>Date of report:</b> 13/12/21
<b>Shifts:</b>	<b>Local contact(s):</b> Paul Thompson	<i>Received at ESRF:</i>

#### Names and affiliations of applicants (\* indicates experimentalists):

Professor Paul Adrian Bingham

Miss Jessica Rigby

Mr James Eales

Dr Tony Bell

#### Report:

The proposed research directly supports operation of a world-leading facility under construction at the US Waste Treatment Plant (WTP) at Hanford. Two direct feed melters to vitrify radioactive legacy wastes will be operational as early as 2022. Foaming occurs in the melters due to gas evolution from batch-to-glass reactions causing blockages of melter components and reducing operational efficiency. Foam behaviour must be predictable before the melters are operational. A complete study of Fe, Mn, Cr, and Ce in the high-iron high-level waste (HLW) feed (HLW-NG-Fe2) was undertaken to determine contributions from multivalent species to foaming behaviour during melting. The use of sucrose as a baseline foam reductant was compared with graphite and an Fe<sup>2+</sup> iron oxalate (FeC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O) raw material iron source.

The centroid positions and intensities of the pre-edge features obtained were plotted against the standard reference

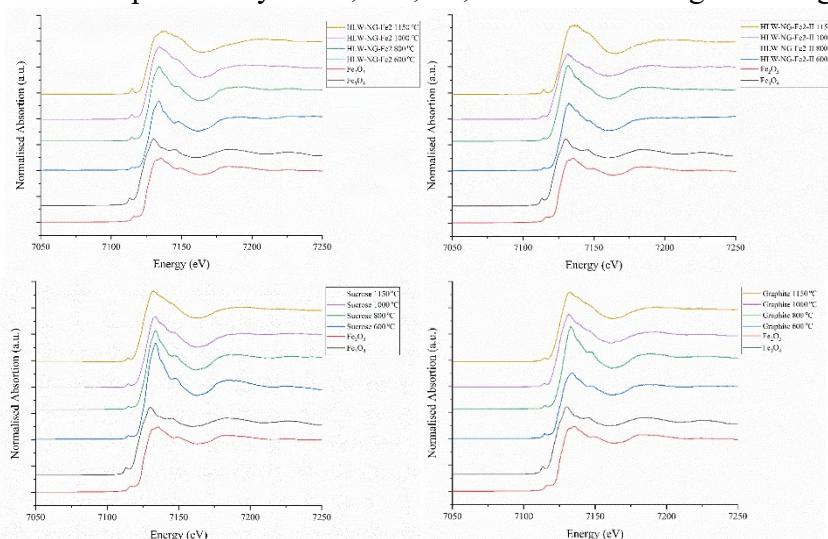


Figure 1 Fe K-edge XANES Spectra HLW-NG-Fe2, HLW-NG-Fe2-II, Sucrose and Graphite samples for 600, 800, 1000 and 1150 °C.

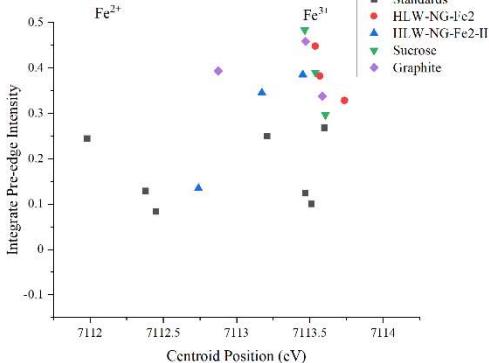


Figure 2 Integrated intensity and centroid positions of Fe K-edge pre-edge peaks for each of the 7 feeds.

materials to show the approximate oxidation state and coordination of each sample [32], since the spectra contains information on all of the iron in the sample, these plots display and average of all of the magnetic and paramagnetic iron in the samples. The integrated pre-edge intensity indicates the coordination state of the iron, where the higher intensities, approaching 0.3, are 4-coordinated and the lower intensities, around 0.1 are 6-coordinated Fe.

Ce L<sub>III</sub> and Cr K edge spectra were fitted to linear combinations of the standard reference materials using Athena, and the Mn K-edges were

fitted to a linear regression of the standards, the final fits for each sample are given in Figure 3.

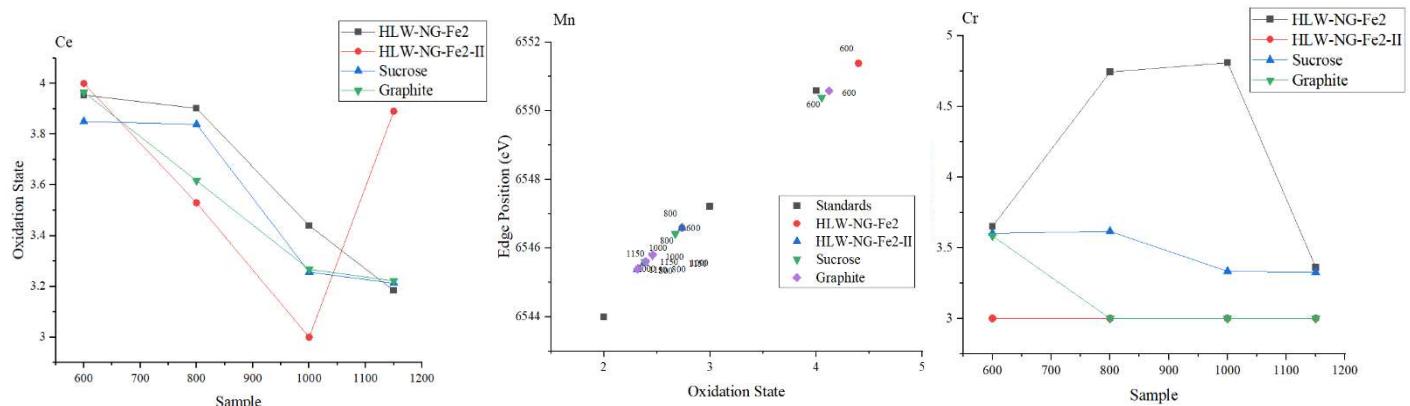


Figure 3 Integrated intensity and centroid positions of Fe K-edge pre-edge peaks for each of the 7 feeds.

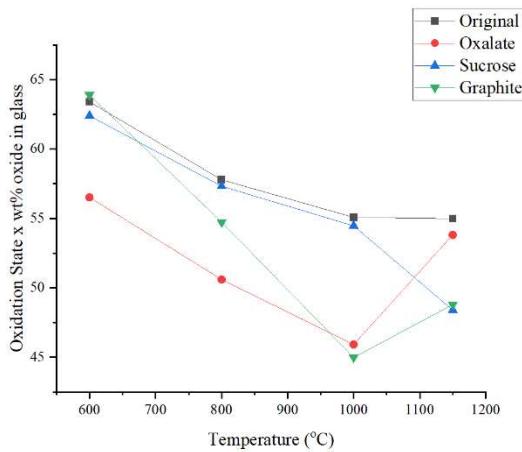


Figure 4 Sum of the oxidation state changes amongst all edges for each of the 7 feeds scaled by the amount of each element in the feed.

We have derived the amount of Fe, Mn, Cr, and Ce that are reduced during melting from the original oxidation state in the feed to the final oxidation state in the melt, for the HLW-NG-Fe2 feed. Overall, Mn reduces the most, by 1.44 oxidation states, i.e. a change from 4+ to 2.56+ as an average of all of the Mn in the final glass. This change theoretically contributes 5.25 g/kg of glass of evolved O<sub>2</sub>, and actually the oxidation state of the iron in the final glass remains 3+, therefore no net contribution to O<sub>2</sub> evolution comes from a change in Fe oxidation state. A reduction in Ce contributes a further 0.005 g of O<sub>2</sub> per kilogram of glass, and the final oxidation state of Cr is greater than the original, so oxygen consumption has occurred at a rate of

0.010 g/kg of glass, leaving the final total oxygen evolution due to these species at 5.201 g/kg of glass, none of which is from a change in Fe oxidation state. In summary of the O<sub>2</sub> evolved during melting of HLW feeds and the contribution to foaming behaviour, it is not sufficient to focus only on the behaviour of Fe<sub>2</sub>O<sub>3</sub>, despite it being the most abundant species. In this feed, particularly, Mn has a higher contribution to total evolved O<sub>2</sub>, and in fact the contributions of species present in very small quantities, Cr and Ce, become important at higher temperatures where gases can be trapped beneath a viscous melt. In combination with evolved gas analysis and feed expansion tests, the O<sub>2</sub> evolution will help to determine the optimal reductant for melting.