

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>

Reports supporting requests for additional beam time

Reports can 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: In situ Electrochemical Study of Iron and Iron-Nickel Sulfide reactivity towards Carbon Dioxide using X-Ray Absorption Spectroscopy	Experiment number: 26-01-947
Beamline: BM26A	Date of experiment: from: 16-May-2012 to: 19-May-2012	Date of report: 19-Jul-2012
Shifts: 9	Local contact(s): Sergey Nikitenko Dipanjan Banerjee	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr Mariette Wolthers* , Utrecht University, Netherlands Husn-Ubayda Islam* , University College London, UK Prof. Gopinathan Sankar* , University College London, UK Dr Katherine Holt* , University College London, UK Dr Nathan Hollingsworth* , University College London, UK		

Report:

The aim of this beamtime was to perform in situ electrochemical studies on mixed iron and nickel sulphides using x-ray absorption spectroscopy. A full characterisation of structural changes and surface binding, as a function of potential, in deoxygenated and CO₂ rich electrolyte was proposed.

Good quality data could be collected up to 10 A⁻¹ but not further – this was most likely as a result of scatter from electrolyte between the working electrode and the cell window. Further development of the set up will attempt to overcome this issue. XANES data and first shell EXAFS were collected.

In the experimental method, between 5 and 10 scans were taken at each potential after changes in spectra had stopped. Some changes were gradual rather than instantaneous – it was found that carbon loaded materials were much more receptive to potential changes than the pure systems – an expected result due to the increased contact of particles to a conductive medium.

We concentrated on pyrrhotite (Fe₇S₈), greigite (Fe₃S₄) and violarite (FeNi₂S₄) since these are materials whose surfaces have been extensively modelled by our group in recent months; our present understanding of surface hydration and CO₂ binding on these materials will hopefully correlate with the experimental results found on this beamtime.

Figure 1 shows the XANES region of carbon loaded pyrrhotite over a range of potentials. In a deoxygenated pH7 buffer, the edge is seen to shift towards higher energies and white line intensity increases. These are classic signs of oxidation of the Fe centre and change in coordination. Further analysis of the data must be performed in order to deduce species being oxidized and those being reduced. The same experiment with a CO₂ rich buffer solution produced strikingly different results, including the shift of the edge to lower energies at a strongly negative potential, and the decrease in white line intensity at negative potentials followed by an increase when positive.

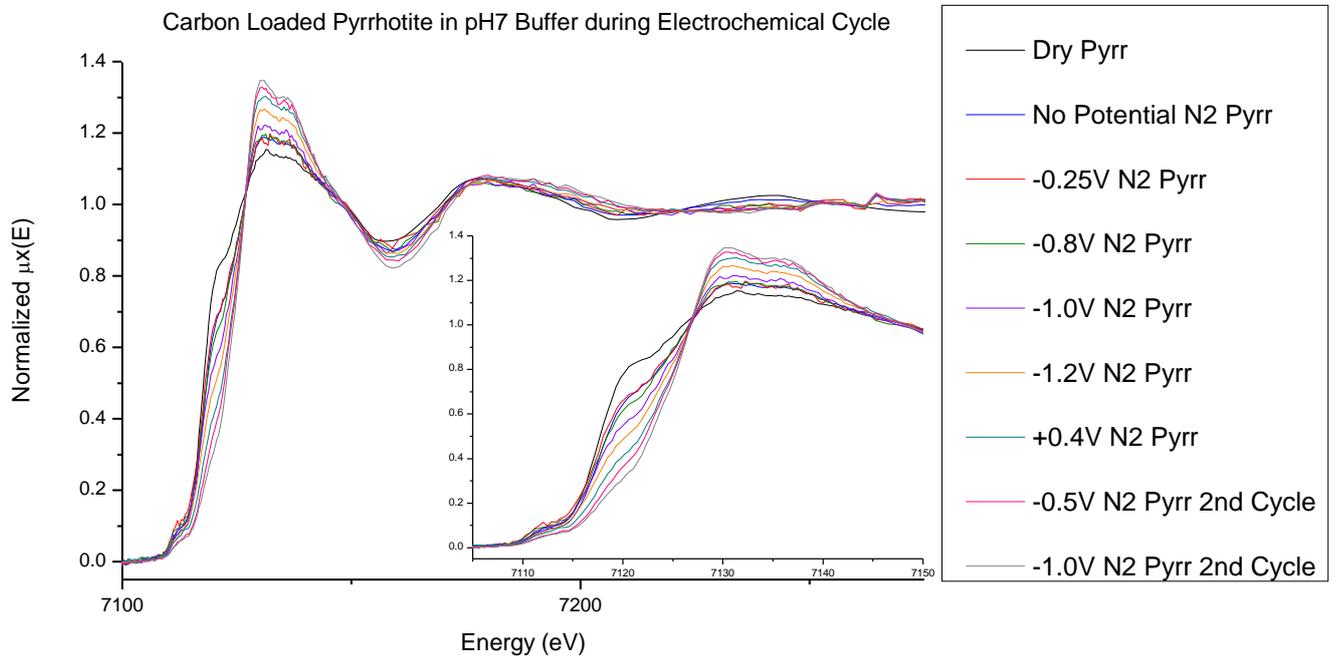


Figure 1: XAS spectra of carbon loaded pyrrhotite in a pH7 buffer in the electrochemical cell over a range of potentials.

The results are of purely surface changes and it is therefore an encouraging observation that the changes in XANES spectra between potentials are significant – it suggests that the synthesized particles have a large enough surface to bulk ratio to be able to determine surface changes from standard fluorescence measurements. The quality of data produced from the cell is also much better than expected and there are considerations for expanding the use of the set up for other systems.