

## 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.



	<b>Experiment title:</b> In Situ electrochemical studies of carbon dioxide interaction with carbon loaded iron and mixed iron-nickel sulfide using XAS	<b>Experiment number:</b> 26-01-987
<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 11-Sep-2013 to: 16-Sep-2013	<b>Date of report:</b> 03-Jan-14
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dipanjan Banerjee	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Prof Nora De Leeuw, Utrecht University, Netherlands</b> <b>Dr Mariette Wolthers, Utrecht University, Netherlands</b> <b>Miss Husn-Ubayda Islam*, University College London, UK</b> <b>Dr Katherine Holt*, University College London, UK</b> <b>Dr Nathan Hollingsworth*, University College London, UK</b> <b>Miss Anna Roffey*, University College London, UK</b> <b>Miss Siti Zakaria*, University College London, UK</b>		

## Report:

### Outline

The aim of this beamtime was to further understand the structural changes that occur to a catalytically active iron sulfide system in an electrochemical environment. The focus of investigations were two samples consisting of carbon loaded greigite ( $\text{Fe}_3\text{S}_4$ ) and violarite ( $\text{FeNi}_2\text{S}_4$ ) particles obtained through solvothermal decomposition of dithiocarbamate complexes. The reaction that supposedly occurs on the greigite surface is the assisted conversion of  $\text{CO}_2 + \text{H}_2$  to  $\text{HCOOH}$  and other organic species, while violarite surface is passive.

### Aim

Our understanding thus far is based on previous beamtime experiments that suggest a gradual transformation of the greigite surface to another species which corresponds to changes in catalytic activity. Previous EXAFS has shown that EXAFS data of dry greigite consists of 40% bulk and 60% surface using this technique. A study was therefore performed to discover interaction of the electrochemical environment with the carbon loaded greigite and violarite in a range of pH's, both with and without the presence of carbon dioxide and over at least 2 voltometric cycles. Modifications to the cell setup allowed acquisition of higher quality XAS which allowed us to probe the EXAFS region. Particular attention was given to increasing time, and to standard iron species in dry and solute environments.

### Results

All electrochemical cycles of greigite have two possible outcomes. Most commonly, the surface transforms to an oxyhydroxide, less commonly, dissolved iron(III) species overwhelm the XAS spectra. The latter has occurred only a few times and seemingly at random. The most likely reason is that the setup is not as constant as we would like, particularly with regards to the thickness of electrolyte layer between window and drop coated electrode – this is a major source of discrepancy that occurs during cell setup between runs. The more

common process is the formation of iron oxyhydroxide. This process occurs at different rates, according to linear combination fitting, depending on pH and to potentials in the cycle, and in correlation with production rates when carbon dioxide is present. Violarite spectra demonstrate the stability of the structure in the electrochemical cycle.

