

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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

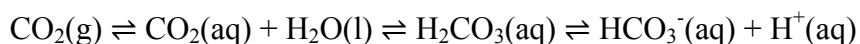
- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you 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 characterisation of oilfield corrosion scale	Experiment number: 28-01-1033
Beamline: BM28	Date of experiment: from: 19/02/2014 to: 22/02/2014	Date of report: 17/09/2014
Shifts: 9	Local contact(s): Oier Bikondoa	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): G. R. Joshi* , K. Cooper* , J. Lapinski* , D.L. Engelberg* , R. Lindsay* <i>Corrosion and Protection Centre, University of Manchester, UK</i>		

Report:

Within the oil and gas industry, internal corrosion of carbon-steel due to CO₂-saturated solutions, commonly known as sweet corrosion, is of widespread concern. On this basis, significant effort has been applied to gain mechanistic insight into this phenomenon, which is driven by the dissolution of CO₂ in H₂O to form an acidic solution; i.e.



The resulting aqueous phase species stimulate corrosion primarily through supplying reactants for the cathodic process, i.e. H₂(g) evolution. Iron dissolution (Fe(s) → Fe²⁺(aq)) occurs at anodic sites. Solid corrosion products may also appear as a consequence of these various processes, with their formation dependent upon a range of parameters, e.g. pH and temperature. If adherent to the carbon steel substrate, such solids can significantly reduce the rate of corrosion, and so are integral to material sustainability.

Typically, CO₂ induced corrosion scales on carbon steel are simply labeled as FeCO₃. Experimental data, however, indicate that these scales can be more complex, e.g. Fe₂(OH)₂CO₃ and Fe₃O₄ have also been reported as scale components. One ongoing concern about such scale characterization is that most studies are undertaken *ex situ*, i.e. following removal of the substrate from solution. This procedure may induce scale modification, and so *in situ* characterization is clearly a more desirable approach. The aim of the beam time was to progress this topic through *in situ* grazing incidence x-ray diffraction (GIXRD) of a sweet corrosion scale formed on X65 pipeline steel.

In situ GIXRD was undertaken employing synchrotron radiation (SR) from beam line BM28 (XMaS). For these measurements, a custom-made electrochemical-cell (E-cell), allowing both GIXRD and electrochemical corrosion rate monitoring, was mounted on the diffractometer stage. A photon energy of $h\nu = 15 \text{ keV}$, and an incidence angle (α_i) of 3° were used for data acquisition.

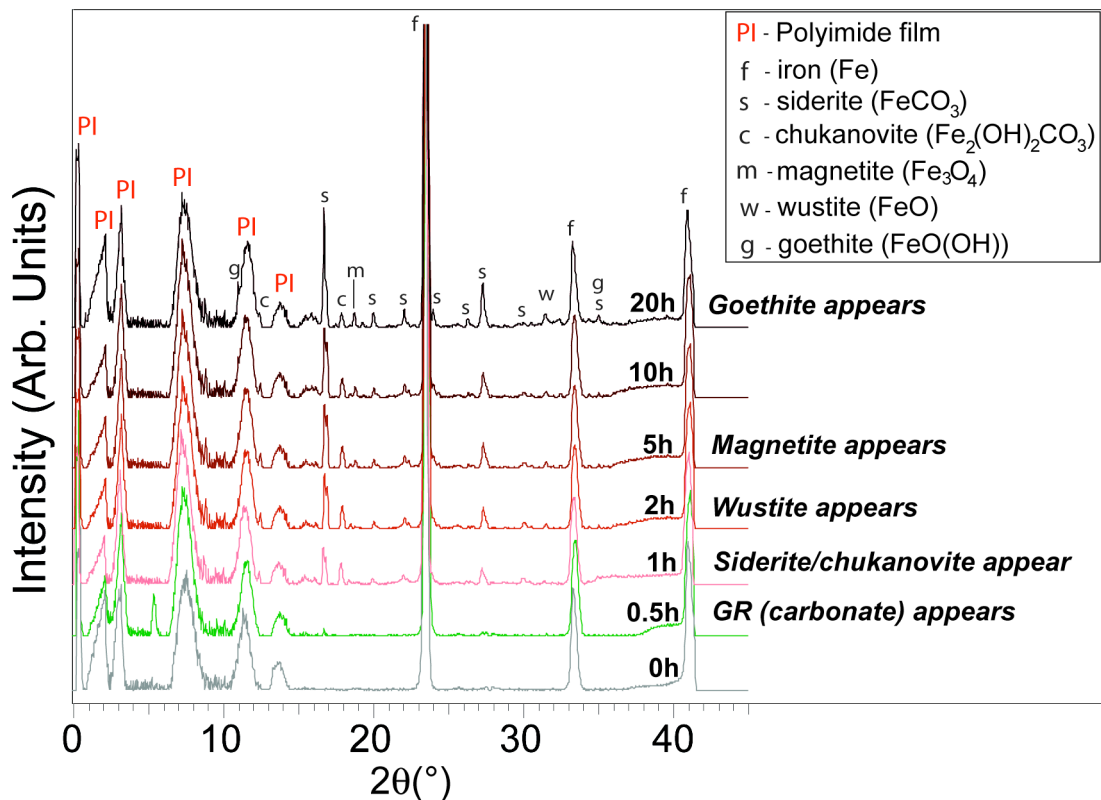


Figure 1: Series of diffractograms, acquired as a function of immersion time, from X65 sample immersed in CO₂-saturated 0.1M NaCl solution (pH = 6.8, T = 80°C) for a total of 20 h. All of the plots are normalized to the intensity of the peak at 2θ = 23.6°.

Figure 1 displays a series of diffractograms from the X65-steel sample immersed in CO₂-saturated 0.1M NaCl solution (pH = 6.8, T = 80°C) for 20 h. The bottommost plot is that of the polished substrate, acquired prior to immersion. Three peaks, located at 23.6°, 33.5° and 41.2°, can be attributed to originate from the bulk of the substrate, i.e. they are due to α-Fe. Features at low values of 2θ (~ 0° - 14°) can all be assigned to scattering from the polyimide film. Following 0.5 h of immersion an additional, quite intense peak appears at 5.5°, which can be assigned to the presence of a carbonated green rust (Fe₆(OH)₁₂CO₃). This feature is not apparent in the diffractograms acquired after immersion for 1 hour, being replaced by peaks assigned to siderite (FeCO₃) and chukanovite (Fe₂(OH)₂CO₃). Subsequently, the intensity of the siderite peaks increases. Given that the initial development of this phase coincides with a reduction in corrosion rate (not shown), it is suggested that this siderite scale likely makes a significant contribution to controlling substrate corrosion. Besides the carbonate components, peaks attributed to wustite (FeO), magnetite (Fe₃O₄), and goethite (FeO(OH)) appear, after 2 h, 5 h and 20 h of immersion, respectively. Currently, we suspect these phases are due to dissolution of some O₂ into the CO₂-saturated solution, although Fe₃O₄ has been reported to be an intrinsic constituent of sweet corrosion scale.

A preliminary report of this work has been submitted for publication in the proceedings of the NACE Corrosion conference (March 2015).