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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 scaling across a weld-joint	**Experiment number**: 28-01-1125
Beamline: BM28	**Date of experiment**: from: 29/10/2015 to: 3/11/2015	**Date of report**: 27/05/2016
Shifts: 15	**Local contact(s)**: Oier Bikondoa	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Within the oil and gas industry, internal corrosion of carbon-steel due to CO_2-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 CO_2 in H_2O to form an acidic solution; i.e.

$$CO_2(g) \rightleftharpoons CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$
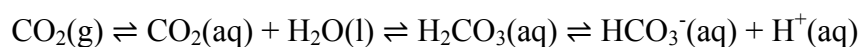
The resulting aqueous phase species stimulate corrosion primarily through supplying reactants for the cathodic process, i.e. $H_2(g)$ evolution. Iron dissolution ($Fe(s) \rightarrow Fe^{2+}(aq)$) occurs at anodic sites. Solid corrosion products may also appear as a consequence of these various processes, 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. One specific area of interest is that of weld-joints, as such areas can be highly vulnerable to failure due to increased sweet corrosion rates. There, however, remains incomplete understanding of the mechanisms leading to this phenomenon, including the impact of local variations in scaling.

Typically, CO_2-induced corrosion scales on carbon-steel are labelled as siderite ($FeCO_3$). However, these scales are almost certainly more complex. For example, a recent in situ grazing incidence x-ray diffraction (GIXRD) study conducted by our group at XMaS [1] has shown that whilst the primary scale component on a pipeline carbon-steel (X-65) was siderite ($FeCO_3$), chukanovite ($Fe_2(OH)_2CO_3$) was also present. In addition, a so-called green rust carbonate ($Fe_6(OH)_{12}CO_3$) was apparent during the early period of immersion. The aim of this beam time was to undertake similar *in situ* measurements from an X-65 pipeline steel weld joint. Utilising the well-defined synchrotron radiation (SR) beam spot, GIXRD scans of each region of the weld-joint (i.e. fusion zone (FZ), heat affected zone (HAZ) and base metal (BM)) were possible, facilitating analysis of scale composition across the weld as a function of immersion time.

The *in situ* GIXRD was undertaken employing 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 $h\nu = 15$ keV, and an incidence angle (α_i) of 3° were used for data acquisition.
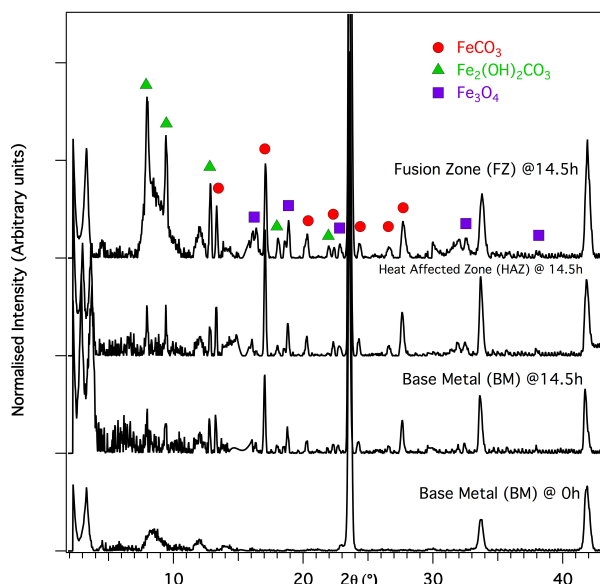
Figure 1: Diffractograms from the FZ, HAZ and BM regions of an X-65 weld-joint sample, acquired *in situ* after 14.5 h of immersion in CO$_2$-saturated deionised water (pH = ~ 4, T = 80°C). Data acquired from the BM region immediately following immersion are also plotted (all three regions looked identical at this point). All of the plots are normalized to the intensity of the Fe peak at 2θ =23.6°.
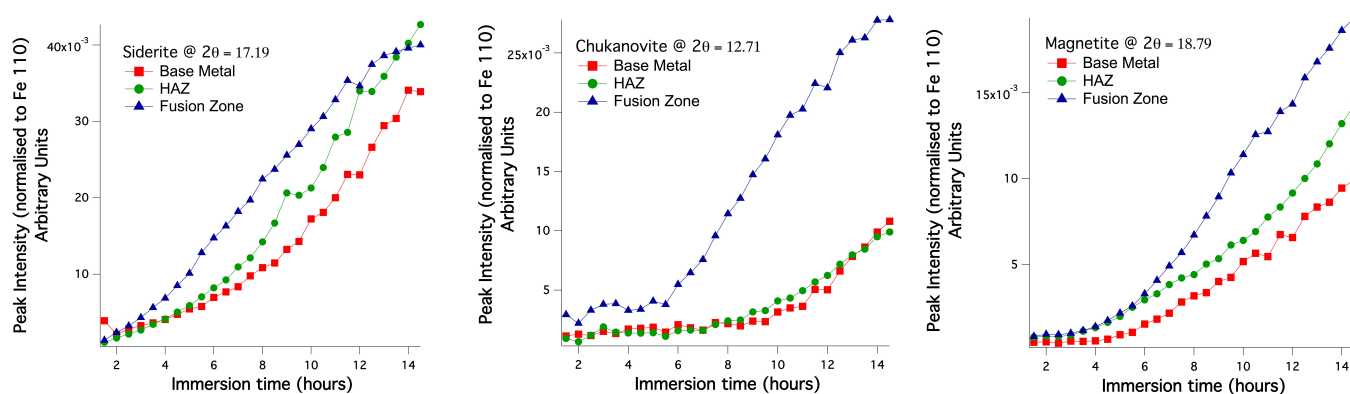

Figure 2: Plots of (selected) diffracted peak intensities for siderite (left panel), chukanovite (middle panel) and magnetite (right panel) as a function of immersion time. Data were acquired from the FZ, HAZ, and BM regions of an X-65 weld joint sample immersed in CO$_2$-saturated deionised water (pH = ~ 4, T = 80°C) for a total of 14.5h.

Figure 1 displays diffractograms from the FZ, HAZ and BM regions of an X-65 weld-joint sample, acquired *in situ* after 14.5 h of immersion in CO$_2$-saturated deionised water (pH = ~ 4, T = 80°C). The bottommost plot in this figure was acquired from the BM region directly after immersion (0 h); all three regions displayed a similar profile at 0 h. The peaks located at 23.6°, 33.5° and 42.1° are attributed to the substrate bulk (α-Fe). Other features at low 2θ values can be assigned to the polyimide film that was used as an X-ray transparent window in the E-Cell. Annotation indicates that siderite (FeCO$_3$), chukanovite (Fe$_2$(OH)$_2$CO$_3$), and magnetite (Fe$_3$O$_4$) are present on all three weld regions after 14.5 h of immersion, although their relative proportions vary with region, suggesting that local substrate variation influences scaling. We note that the appearance of Fe$_3$O$_4$ is somewhat unexpected, and may be a result of X-ray induced radiolysis (further work is required to verify this hypothesis). Figure 2 displays plots of diffracted peak intensities as a function of immersion time for each corrosion product on the FZ, HAZ, and BM regions. These data provide insight into temporal scale evolution. For example, there appears to be an induction period of ~ 6 h prior to significant chukanovite scale growth, after which it grows most rapidly on the WZ region. Further analysis/interpretation of these data is underway.

References
1. *G. Joshi et al, NACE Corrosion 2015, NACE International, Dallas, 2015, Paper No. 5674*