



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: <i>In situ</i> characterisation of sweet oilfield corrosion scaling as a function of salinity	Experiment number: 28-01-1144
Beamline: BM28	Date of experiment: from: 06/07/2016 to: 12/07/2016	Date of report: 29/09/2016
Shifts: 18	Local contact(s): Oier Bikondoa	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): M. Al-Kindi* , K. Cooper* , J. Andrews* , D.L. Engelberg , R. Lindsay* <i>Corrosion and Protection Centre, University of Manchester, UK</i>		

Report:

Internal corrosion of oilfield facilities fabricated from carbon steel due to the presence of CO₂ dissolved in the aqueous phase of the produced fluids (oil/gas/water) is of huge concern, and much effort is expended to keep it under control. A lack of mechanistic insight into relevant corrosion phenomena, however, is restricting progress in this area to largely empirically based advances. One key, missing ingredient is detailed knowledge of potentially protective CO₂-induced (sweet) corrosion scales formed on carbon steel in oilfield environments. The aim of this study was to address this issue through elucidating the nature of such scales *in situ* with grazing incidence X-ray diffraction (*GIXRD*), as well as probing the kinetics of their nucleation/growth. More specifically, we have focused on the impact of aqueous phase salinity, which varies significantly with oilfield geology, and is known to influence both scale composition and kinetics.

Typically, sweet corrosion scales on carbon steel are labelled as siderite (FeCO₃). However, these scales are almost certainly more complex. For example, a recent *in situ 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 (FeCO₃), chukanovite (Fe₂(OH)₂CO₃) was also present. In addition, a so-called green rust carbonate (Fe₆(OH)₁₂CO₃) was apparent during the early period of immersion.

Concerning sweet corrosion/scaling as a function of aqueous phase salinity, our research group has been exploring this topic, employing electrochemical measurements in tandem with *ex situ* scale characterisation techniques. We have examined the corrosion of polycrystalline Fe in CO₂-saturated NaCl_(aq) solutions (0 M - 1 M), and found that increasing NaCl_(aq) concentration can retard the growth of the corrosion scale, as well as modifying the scale composition, i.e. in 0 M NaCl solution both siderite and chukanovite were found to be scale components, whereas only siderite was identified in 0.01 M - 1 M NaCl solutions. The goal of the current work was to gain further insight into the impact of NaCl_(aq) on scale growth mechanisms through *in situ GIXRD* to probe the evolution of the scales as a function of time in the presence/absence of NaCl_(aq) (0 M/1 M). Two specific questions, pertinent to the mechanism of sweet scale formation, we wished to address through these *in situ* measurements were:

- (i) *Does chukanovite form as a precursor to siderite in the presence of NaCl_(aq)?*
- (ii) *Does the occurrence of green rust carbonate [4,5] depend upon the presence of NaCl_(aq)?*

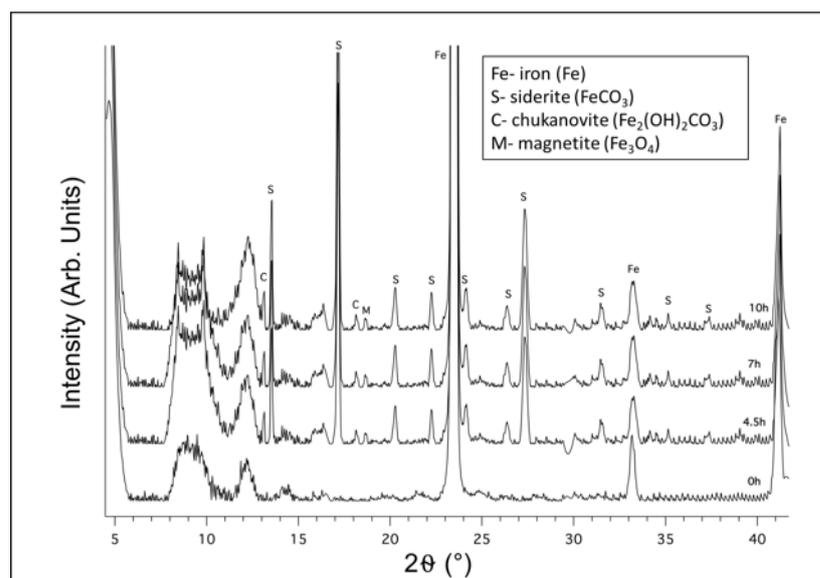


Figure 1: A series of diffractograms, acquired *in situ* as a function of immersion time, from a polycrystalline Fe sample immersed in CO₂-saturated 0 M NaCl solution (pH = 6.8, T = 80°C). All of the plots are normalised to the intensity of the peak at 2θ ~ 24°.

In situ GIXRD measurements were undertaken employing synchrotron radiation 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 displays a selection of diffractograms, acquired *in situ* as a function of immersion time, from polycrystalline Fe immersed in CO₂-saturated 0 M NaCl solution; pH = ~ 6.8, T = 80°C. The bottommost plot is that of the polished substrate, acquired prior to immersion. Three peaks, located at ~ 24°, ~ 34° and ~ 41°, 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 kapton film that was used as an X-ray transparent window in the E-Cell. After 4.5 h of immersion siderite (FeCO₃), chukanovite (Fe₂(OH)₂CO₃), and magnetite (Fe₃O₄) are all present on the Fe surface (as indicated by the annotation on the figure), and persist up to the last measurement shown at 10 h. The presence of chukanovite is consistent with the previous *ex situ* measurements, where this phase was also apparent at 0 M concentration of NaCl.

Unfortunately, no measurements with 1 M NaCl solution were performed due to a beam line failure (shutter started to leak), which significantly curtailed our beam time (~ 2 days were lost). Given this issue, further time is required to complete these measurements, and another application will be submitted.

References

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