GRAZING INCIDENCE X-RAY DIFFRACTION CHARACTERIZATION
OF CORROSION DEPOSITS INDUCED BY CARBON DIOXIDE ON MILD STEEL

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ABSTRACT
The paper reports the results of a feasibility study on the use of grazing incidence x-ray diffraction (GIXRD) and synchrotron diffraction (GISRD) for near-surface characterisation of corrosion deposits induced by CO2 action on the inner surfaces of mild steel pipelines carrying natural gas. The principal direction of the diffraction work, which forms part of a broader study, is to construct depth profiles of corrosion product phase distributions. Mild steel was corroded with a laboratory reactor in which the field corrosion conditions were simulated. GIXRD data for this preliminary study were measured with CuKα x-rays (\(\lambda = 1.542 \, \text{Å}\)), and the GISRD data with synchrotron radiation (\(\lambda = 1.750 \, \text{Å}\)) marginally lower in energy than the FeK-edge. The results show that the GIXRD at the stated wavelength, using either scanning detector optics or imaging plates, is promising for depth profile construction. It has been observed that GIXRD with imaging plates affords the possibility of conducting real-time GIXRD studies.

INTRODUCTION
Grazing incidence x-ray diffraction (GIXRD and GISRD) is being applied for near-surface characterisation of corrosion deposits formed on the internal surfaces of mild steel pipelines, which are used to deliver natural gas from offshore deposits in Western Australia. Corrosion control is the prime focus of the study. The CO2 component of the gas stream reacts readily with mild steel to produce corrosion deposits – notably siderite, FeCO3, as well as other candidate phases. This preliminary study was planned to evaluate the efficacy of using laboratory-source GIXRD for depth profile construction, and also to examine the value of using GISRD.

EXPERIMENTAL
The corrosion trial was conducted with Nippon mild steel, grade API 5L-B which has a certified wt % composition: 0.17% C, 0.18% Si, 0.55% Mn, 0.018% P, 0.004% S, 0.06% Cu, 0.01% Cr, 0.02% Mo, 0.01% V. A coupon of dimensions 20 x 10 x 1 mm was cut from the inner surface of a pipeline steel sample and then polished with diamond paste to a finish < 1 μm. The corrosion reactor trial was conducted with a 2 litre Parr autoclave apparatus containing 800 ml of...
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formation water' and 200 ml of oil, selected to match the environmental conditions applying to the Wandoo off-shore platform near the northwest coast of Western Australia. The exposure conditions simulated the production conditions: 50°C, CO₂ partial pressure of 3.4 bar, and with a total pressure of 21 bar made up with CH₄. The reactor was stirred continuously at 700 rpm for the test period - 14 days.

Diffraction data collection was planned assuming that the corrosion deposit would comprise a matrix of siderite, together with other phases deposited by sea water action. For planning purposes, penetration depths (PDs) were computed with a simple model, comprising siderite deposited on an α-Fe substrate, according to: 

\[ PD = \frac{2\alpha}{\mu} \]

for grazing incidence angle \( \alpha \) in radians and linear attenuation coefficient \( \mu \). While the formula should apply only to \( \alpha \) values above the critical angle for total external reflection, the measured diffraction data indicated that total external reflection is not observed with these deposits, presumably due to the non-uniform nature of the deposits. Figure 1 presents plots of PD versus angle \( \alpha \). The graphs show the importance of choosing a wavelength beyond that of the FeK absorption edge to provide a PD range of some 10 µm for an \( \alpha \) operating range of several degrees. An additional advantage of working beyond the edge is the reduction in fluorescence from the sample. The rationale for using synchrotron radiation in this study was to provide ready selection of wavelength whereas CuKα radiation had to be employed for the laboratory x-ray measurements. It is clear from these calculations that CoKα radiation could provide useful depth profiles with GIXRD, whereas in this case a Co-target tube was not available.

Figure 1. Calculated penetration depths for grazing incidence diffraction versus incidence angle - FeCO₃ matrix.
GIXRD asymmetric data were measured as follows with a Siemens D5000 diffractometer fitted with a grazing incidence attachment: Cu tube [type FL Cu 4KE] operating at 40 kV and 30 mA (Kα wavelength, 1.542 Å); parallel beam optics, incident beam divergence = 1°; diffracted beam divergence = 0.5° and 0.4° soller slits; receiving slit = 0.15°, post-diffraction graphite analyser; and NaI detector with pulse discrimination; 20 step size = 0.02°, time/step = 2 s.

Bragg-Brentano (symmetric-geometry) XRD data were measured to compare the GIXRD data with ‘conventional’ data. A Siemens D500 Bragg-Brentano diffractometer was employed as follows - Cu tube [type Fk60-04 CU] at 40 kV and 30 mA; fixed slit optics with incident beam divergence = 1°, receiving slit = 0.15°, post-diffraction graphite analyser; NaI detector with pulse discrimination; and 20 step size = 0.04°, time/step = 1 s.

GISRD asymmetric data were measured at the Australian National Beamline Facility on Beamline 20B, Photon Factory, Tsukuba, Japan using the BIGDIFF instrument [ref 1] - Si(111) channel-cut monochromator set to deliver λ = 1.750 Å which is just below the FeK-edge; parallel beam optics with incident beam width = 50 μm. Data were acquired with 2 detection systems, (1) with a scanning NaI detector using a step width of 0.05° and 5 s/step; and (2) with Fuji imaging plates for a data collection time of only 15 minutes.

RESULTS AND DISCUSSION

Figure 2 shows a typical corrosion ‘blister’ on the surface of the coupon after exposure. Associated energy dispersive spectrometry (EDS) measurements indicated that these features are consistent with the formation of siderite. The corrosion deposit was shown to be of mean

Figure 2. Backscatter electron SEM images for blister features on the surface of corroded steel specimen.
thickness 7-8 µm using Bragg-Brentano x-ray attenuation data extracted from XRD patterns from a blank mild steel sample and the corroded specimen (see details of diffraction measurements following).

The Bragg-Brentano XRD pattern and the corresponding GIXRD pattern are given in Figures 3 and 4, respectively. In both patterns, the phase FeCO₃ (siderite) is clearly observed in addition to the α-Fe phase from the mild steel substrate. Siderite formation has been induced by CO₂ dissolved in the water flowing through the pipeline. Figure 3 also appears to indicate Fe₃C (cementite) peaks, presumably from the presence of cementite as a minor phase in the substrate, whereas the near-surface pattern in Figure 4 does not contain these features. By contrast, CaCO₃ (calcite) lines are definitely seen in the near-surface GIXRD pattern, apparently due to a reaction between the CO₂ and calcium ions which are also present in the water flowing through the pipeline; however, these calcite lines are not observed in the Bragg-Brentano data. The presence of C, O and Ca was confirmed by SEM-EDS elemental analysis. It is possible that that the aggregation of cementite in the corrosion deposits, which arises from this material being cathodic and less susceptible to corrosion relative to the surrounding steel matrix, is not prevalent in the grazing incidence plots because the surface layers undergo rapid aerial oxidation to amorphous oxides and hydroxides of iron upon removal of the specimen from the reactor apparatus. By contrast, the prominent calcite features in the GIXRD pattern are due to the phase developing on the surface.

Figures 5(a) and (b) show the GISRD results obtained with a scanning detector and with imaging plates, respectively. The imaging plate pattern in Figure 5(a) for α = 2° is incomplete due to a data processing problem. The two sets of GISRD data convey similar information, with the scanning detector patterns having superior statistics. As in the two GIXRD plots, the α-Fe and FeCO₃ features are prominent. However, the intense calcite peak (Ca100) noted in the GIXRD patterns is barely detectable in the GISRD plots (2θ = 33.5°) which may be due to the lower spread in grazing incidence angle with the GISRD optics resulting in the calcite grains being inefficiently detected. The line at 2θ = 39.5° was not identified.

It is evident in Figure 6, showing the ratio of peak counts for the siderite ‘100’ peak to the most intense peak for α-Fe versus PD, that the GISRD data are depth profile sensitive. It appears that the siderite features intensify when the PD depth approaches 2 µm. By contrast, the intensity ratios for siderite and α-Fe from the GIXRD plots do not show the same dependence which is consistent with the discussion above on the PD-α plots in Figure 1. It has been demonstrated that GIXRD at a wavelength beyond the FeK-edge can provide useful depth profile information. Also, it is possible that the GIXRD method will provide useful depth profile sensitivity with a Co-target tube.
Figure 3. Bragg-Brentano XRD pattern measured with x-ray tube and scanning detector. CuKα radiation (1.542 Å). The number associated with the symbol for each peak identifier is the PDF intensity value.

Figure 4. Grazing incidence XRD patterns measured with x-ray tube and scanning detector. CuKα radiation (1.542 Å). See Fig 3 for peak code description.
Figure 5(a). Grazing incidence SRD patterns measured with scanning detector - wavelength = 1.750 Å. See Fig 3 for peak code description.

Figure 5(b). Grazing incidence SRD patterns measured with imaging plates -. wavelength = 1.750 Å. See Fig 3 for peak code description.
Figure 6. Depth profile plots for the GIXRD, GISRD (imaging plates) and GISRD (detector scan) data. Plot of ratio [(intensity of ‘100’ line for siderite) / (intensity of ‘100’ line for α-Fe)] versus calculated penetration depth – see Fig 1.

CONCLUSION

It has been shown that –

- GIXRD at a wavelength beyond the FeK-edge can provide useful depth profile information.
- It is also possible that the GIXRD method will provide depth profile sensitivity with a Co-target tube.
- The most significant finding from the study was the observation from grazing incidence measurements with synchrotron radiation that imaging plate detection affords the possibility of real-time diffraction studies of corrosion processes.

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REFERENCE