Minutes of meeting
WP13 Corrosion in oil and gas production

Lisboa, 7 September 2005

Welcome, News and Confirmation of the Agenda

The Chairman announced that the draft minutes from the meeting at EUROCORR 2004 were available on the EFC website. He requested that any comments on the minutes should be sent to him within one month of the meeting. After that the minutes would be made final and put on the website.

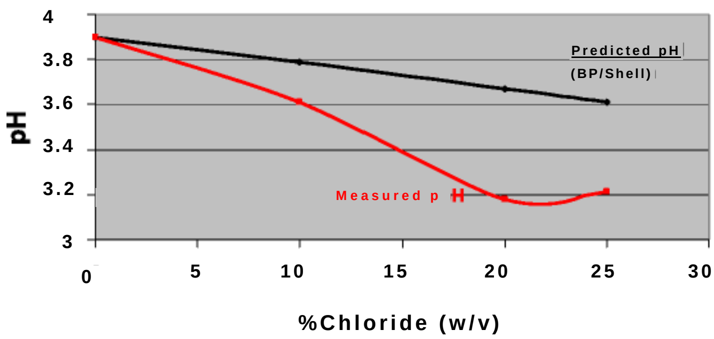
ANTIKOR from Russia, represented by Dr. Alexandr Muradov, had again kindly offered to sponsor a prize for the best oral presentation by a young author in the Oil and Gas session at the conference. This was the third time that ANTIKOR had sponsored the prize. Among several good candidates, Delphine Zuili of Technip, Paris, was selected as the winner. She had presented, in an excellent way, some failures of AISI 316L austenitic stainless steel due to SSC. These data were of great value in connection with ISO 15156. Dr. Muradov presented the prize and warmly congratulated the winner.

Corrosion Aspects of CRAs in Oil and Gas Production in the Absence of Hydrogen

Chairman: Chris Fowler

pH measurements versus modelling in high chloride conditions

R. Francis presented a comparison of measured and calculated pH. For high chloride and low pH conditions they had found a significant discrepancy between what was measured and what was predicted by most of the prediction tools and curves from ISO 15156-2, as shown below.



In the discussion that followed there were some comments related to the accuracy of pH measurements for the actual conditions, but R. Francis commented that the manufacturers of the pH probe confirmed that measurements under these conditions are valid when the probe is calibrated correctly. There were also comments that high chloride and low pH is a non-existent combination, but this does not change the fact that measurements and models give different results. R. Francis explained that measurements were undertaken under just a few conditions and that they had no indication of discrepancies for other conditions. It was a generally agreed that this had to be sorted out and a task force consisting of the following volunteers was proposed:

Alan Turnbull, Sytze Huizinga, Arne Dugstad, Stein Olsen, Roger Francis (Must be checked !).

This group shall evaluate this and come back with a recommendation for the next meeting at EUROCORR 2006. Possible changes to EFC16/17 will be included. See items later in the minutes.

The influence of chloride dilution on the propagation of stress corrosion cracking

T. Cassagne presented a study on crack propagation. An investigation had been undertaken to establish whether existing SCC cracks would propagating if the chlorides were removed from the electrolyte and whether the crack would continue to propagate if chlorides were introduced to the electrolyte. A loop test was undertaken with 316L tubes and external TIG welds to generate residual stresses. The environment was 35 % $MgCl_2$ at a temperature of $90 < T < 100$ °C and included a heat flux.

The test programme consisted of 3 phases:

Phase 1: Crack initiation and propagation (3 days)
Phase 2: Chloride dilution (1 week and 40 days)
Phase 3: Chloride injection (3 h and 2 days)

Monitoring of crack propagation was undertaken by acoustic emission (AE). The results showed that crack propagation stopped when the electrolyte was diluted and the chloride content went down (< 20 ppm Cl^-), but the same cracks re-initiated when the chlorides were introduced again. These results correspond to cracks with depths < 1 mm, but a 1 mm deep crack in 316 piping is already considered a deep crack. The practical consequence of these results is that washing and removal of chlorides from the environment can be a method to stop crack propagation for already existing cracks.

In the discussion that followed there was reference to other studies where it was shown that cathodic protection (CP) also will stop the propagation of cracks.

The HISC programme

Roy Johnsen presented the work undertaken by SINTEF, DNV and TWI on Hydrogen Induced Stress Cracking (HISC). This is a programme focused on cracking of stainless steels due to hydrogen from cathodic protection. The background for starting this work, which is sponsored by several oil companies and steel manufacturers, is failures that have occurred with both supermartensitic and duplex stainless steels. The objective of the programme is to develop relevant test methods for qualification of materials and to develop guidelines to avoid HISC from CP for new installations. Fundamental studies on hydrogen charging and transport in steels are currently being undertaken. In addition, cracking experiments are being undertaken to study surface breaking vs embedded defects. The first draft guideline has been prepared for duplex stainless steels. Part of the work involves Finite Element analyses to evaluate the effect of residual stresses. Results from a full scale test at TWI will also be re-analysed.

As part of the fundamental work, an open workshop on hydrogen in steels will be organised in Oslo on 15 November 2005. For further details, please contact Roy Johnsen.

The Use of Inhibitors in Oil and Gas Production
Chairman: Jim Palmer

<u>A new downhole monitoring tool</u>
K. Spicer presented information about a new downhole monitoring tool developed by CAPCIS. As surface monitoring options, LPR/ER is misleading and coupons give cumulative results. None of the current downhole inspection options are suited for optimisation of the inhibition, such as callipers, Flux Leakage, Ultra Sonic or Electrical Resistance.
The objectives were to develop a real time, rapid response measuring device that is exposed to the downhole environment and behaves as tubing.

The wireline deployed tool was based on existing EN and LPR surface equipment.
Specifications: 8,000 psi, 125 °C. 3 mild steel electrodes simulate the completions.
The tool was configured for LPR and EN in high water cut wells. The LPR outputs, general corrosion rate in real time and the EN data are presented as colour coded pitting and instability. The EN data distinguish local and general corrosion. Additional real time temperature, pressure and vibration sensors were installed on the tool as well.

The successful operation of the tool was reported and LPR and temperature profiles were recorded. The tool gave a rapid response from the EN that made it possible to distinguish between local and general corrosion. The inhibitor effectiveness was studied.

Further work is required to define the operating envelope and an inhibitor optimisation trial will be undertaken.

<u>Field monitoring strategy for corrosion inhibitor optimisation</u>
M. Swidzinski showed a slide where performance of High Sensitivity Probes was compared with Existing Technologies. The RPCM consists of full thickness ring pairs that can give fast response, but good temperature compensation is required. Side streams are very useful, but LPR and high sensitive ER can give very different results. The LPR can give significantly lower corrosion rates due to scaling of the probes. A general recommendation is to get an online system where all data are recorded and displayed online. Periodic measurements in a side stream are also recommended for verification of the online measurements.

On questions about the field experience with the Ceion system, M. Swidsinski replied that the hardware worked successfully, but the software routines for temperature compensation needed refining.

<u>Field optimisation of corrosion inhibitors to mitigate localised corrosion</u>
(G. Winning). Normally pipelines fail due to localized corrosion while most monitoring techniques can only detect general corrosion. The localized corrosion can be as pitting or crevice corrosion. Traditionally corrosion evaluations are focused on general corrosion by use of monitoring techniques such as LPR or ER. Inhibitor optimization requires faster methods for detection of localized corrosion. The only technique that can offer this is EN in combination

with LPR. This is relevant for water injection and flowlines and downhole tubing. An aquifer water injection system was described where the general corrosion was measured to be insignificant by use of LPR, but the tubing failed due to corrosion. A new field data equipment based on LPR, HD and ECN was used to monitor the system online. The equipment could detect a high pitting activity and made it possible to optimise the inhibition as the equipment gave a fast response. Several products could be tested and a product able to stop pitting corrosion could be identified.

<u>New EFC publication on procedures for testing of corrosion inhibitors</u>
A. Dugstad presented results from a JIP where test protocols for inhibitor testing were defined. These are procedures not related to flow, but to other parameters that can consume the inhibitor and reduce the inhibitor performance. Parameters that were studied were:

- Effect of suspended solids in the fluids on CI performance
    - Depletion of inhibitor by adsorption onto solids
    - How to assess the amount of solids in produced fluids
- Effect of oil-in-water emulsions on CI performance
    - Depletion of inhibitor by adsorption on the oil-water interface
- Effect of sand deposits on CI performance
    - Inhibition under sand deposits
    - Sand aggregation in presence of surface-active inhibitors
- Effect of corrosion product films ($FeCO_3$) on CI performance
- CI performance at low water cut (Effect of o-w partitioning)

All these protocols are made such that tests can be undertaken in relatively simple equipment and no sophisticated or expensive equipment is required.

The steering committee in this JIP has asked IFE to make these protocols available and is offering this to EFC as a possible new "Green book". This was discussed in the WP and there were no negative comments to this. IFE will discuss this in the JIP and make a proposal to be presented and discussed during EUROCORR 2006.

Status of case histories document Chairman: Liane Smith

S.Olsen reported on behalf of L. Smith. The objective was to study if a "Green book" on failure cases related to O&G could be made. L. Smith offered to lead this work and formats and examples were made and presented during EUROCORR 2003. After EUROCORR 2004 a website was made where people could put in the information. However, no cases have been reported, and it is concluded that such book cannot be made at this point due to lack of data and interest among the WP members.

Carbon Steel in H_2S Service
Chairman: Liane Smith. Chris Fowler acted as chairman.

<u>HIC acceptance criteria.</u>
There is a discrepancy between EFC16 and ISO 15156 regarding HIC acceptance criteria. The criteria in ISO are copied from an existing ISO standard and are slightly less conservative than EFC16. The recommendation is to change the criteria in EFC16 to be in line with ISO as ISO according to the ISO rules must be in accordance with other ISO standards.

<u>CAP hardness requirement.</u>
Another subject discussed in the ISO 15156 meetings on 3 September was the cap hardness

criterion for C-steels that are protected by CP. In EFC16 it is stated: “If hydrogen exit from the external surface is impeded (e.g. by CP) then the hardness of the cap should not exceed the limits stated for the root”. This was copied into the ISO 15156-2 (Table A.1). In reality very few companies follow this and no documentation has been found to support this. In fact the only way to study this is to do a full ring test with H_2S environment inside and seawater and CP on the outside. The suggestion is to take this out of EFC16.

It was noted that in ISO 15156 Jim Skogsberg had sought information related to this restriction and it may be balloted for change. By way of background, TWI had published initial results from a JIP to demonstrate relaxation of cap hardness for sour service was acceptable at the time of EFC 16 development. Later work was published demonstrating that even with external CP these relaxations could remain, but this knowledge was not incorporated into the standard so far.

Reference to latter paper is: Richard Pargeter from EUROCORR 2000

<u>Materials subject to significant straining</u> (e.g. by pipe reeling) shall undergo straining prior to testing. The need for stating this in EFC16 and EFC 17 shall be evaluated.

<u>New edition of EFC 16 ?</u>
Before next meeting during EUROCORR 2006 a proposal for changes in EFC 16 and 17 will be proposed. For EFC 16 the above points will be included.

For both documents it shall be evaluated if the procedures for buffering and start up of cracking tests shall be changed according to points proposed by J-L Crolet and discussed during EUROCORR 2003.

Corrosion Resistant Alloys in H_2S Service
Chairman: Chris Fowler

<u>Testing with elemental sulphur</u>
During last WP meeting in 2004 a task force was formed to make a proposal for test methodology in S containing environments. No proposal is yet made.

R. Kane made a presentation based on a Survey Conducted by InterCorr from 1996. Information was gathered from “Steel-Iron Test Specification of the Institute for Iron and Steel (VDEh), Germany” December 1995 DRAFT; Current Status is not known and must be checked.
Comments were also solicited from J.B. Hyne, Professor of Chemistry, University of Calgary
Basically, elemental sulphur can exist in the three distinct conditions:

- The elemental sulphur is physically dissolved in the medium
- The elemental sulphur forms a separate solid phase
- The elemental sulphur forms a separate liquid phase

For S dissolved in the medium there is no contact between elemental sulphur and the test specimen. The sulphur vaporizes on heating and dissolves into the test environment.
There is no temperature limitation, but at high temperature this will simulate a condition of

sulphur under-saturation.

Elemental S as solid phase provides for intimate contact of the elemental sulphur with the test specimens. Temperature limitation of ~ 110 °C, below which the mechanical suspension of solid sulphur particles may settle out. This simulates a condition of sulphur super-saturation. Melting point of sulphur is 119 C at which point the sulphur becomes a molten liquid and not a solid phase.

For testing with a separate liquid S phase the temperature must be above the melting point of sulphur (i.e. > 119 °C). The amount of sulphur in the test environment should be at least 0.1 to 10 percent by weight (i.e. 1 to 100 g / L) mixed into the test environment. The amount depends on the nature of the production environment and amount of sulphur (i.e. phase behaviour).

It was decided to keep the same group of people (C: Fowler, R. Kane, G. Schmitt, G. Siegmund and L. Smith). A proposal for test methods will be made before EUROCORR 2006.

<u>Deficiency of the strain gauging formula in EFC</u>
C. Fowler reported on a possible deficiency in the strain gauging formula in EFC17 A7.7 that is believed to give conservative values. Based on some in-house work at Bodycote, the existing formula is believed to overestimate the applied strain by 9 %. A group was formed to look into this and make a proposal for changes if required. The group consists of the following persons: A. Turnbull, C. Fowler, S. Bond, R. Francis, S. Huizinga, S. Olsen.

<u>New edition of EFC17?</u>
Before the next meeting during EUROCORR 2006 a proposal for changes in EFC 16 and 17 will be made. For EFC 17 the two points mentioned above (testing with S and straining formula) will be included. In addition, the following two points discussed under EFC16 shall be included:
- straining of specimens prior to testing and buffering procedure.

<u>Other:</u>
C. Fowler informed that testing of supermartensitic materials under borderline conditions (high H_2S) has shown that testing at 7 °C can be more severe than testing at ambient temperature. More details on this will be published later.

<u>New NACE group on Corrosion issues on welded CRAs</u>
S. Bond, who is chairing this group under STG32 advised the remit and planned activities for this group, and sought additional members and input. Several sub-groups were formed during the first official meeting during CORROSION 2005. The next meeting will be at NACE CORROSION 2006. The intention is to produce a draft summary report that will include Technology Gaps by Q4 2006 or Q1 2007

Corrosion in CO_2 Service

Chairman: Arne Dugstad
<u>An update of EFC 23?</u>
A. Dugstad asked for volunteers to participate in a review and update of EFC23. There was not a good response to this request. A. Dugstad will contact some people directly to see if this can be undertaken. The outcome of the work will be reported at next WP meeting in 2006.

Top of line corrosion, challenges and need for better understanding
A. Dugstad gave a general presentation of parameters involved in TOL and the challenge to understand in order to be able to predict TOL corrosion rates. He referred to a paper presented at the EUROCORR by TOTAL. IFE is currently undertaking a JIP on this subject.

Other

Corrosion fatigue TWI
Much remains to be learnt about the corrosion fatigue performance of materials in oil & gas applications. TWI had compiled data from a several pieces of work demonstrating the significant reduction in fatigue life which occurred when exposed to seawater with CP:

Duplex, superduplex & supermartensitic SS have higher crack propagation rates in 3 % NaCl, seawater with cathodic protection & sour brine compared to air.
Crack propagation in 12 % Cr supermartensitic stainless steel HAZ in seawater with cathodic protection at -1100mV was up to seven times faster than in air.
Crack propagation in a 22 % Cr duplex stainless steel simulated HAZ microstructure in 3 % NaCl at 15 °C was up to a factor of seven times higher than in air

Industry is presently studying such issues in particular for steel catenary risers in sweet, mild sour and sour conditions, and as such it is a hot topic for the oil & gas offshore sector.