Minutes of meeting
WP13 Corrosion in oil and gas production

Maastricht 25. September 2006

Welcome, News and Confirmation of the Agenda

The draft minutes from the meeting at Eurocorr 2005 were accepted.

The Use of Inhibitors in Oil and Gas Production

Chairman: Jim Palmer

US perspective on inhibitor selection in comparison with the EFC39, Mike Joosten, ConocoPhillips

Main conclusions from the presentation:

- Acceptance criteria for corrosion inhibitors depend on the specific physical or design characteristics of the production system.
- The corrosion inhibitor must be compatible with all chemicals, produced fluids, and injection system materials.
- Testing has proven to be a good indicator of inhibitor performance under operating conditions.
- Preliminary screening tests are required. Both high and low shear testing are required to understand chemical performance.
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ConocoPhillips (COP) works mostly in conformity with EFC testing protocols, however, it was noted that COP does not pre corrode samples before lab testing.

Other key points with respect to COP selection protocols are as follows:

- COP ranks inhibitors based on results from a variety of test methods, mainly dynamic and loop tests
- COP uses dose response and inhibitor partitioning results between oil and water to recommend an optimum inhibitor concentration in the field
- COP evaluates the effect of solids (sand, clay, corrosion products, scale, etc.) on the inhibitor performance and MIC activity
- COP uses field trial results as the final decision criteria for inhibitor choice in existing fields
- COP works interdependently with the chemical suppliers

Testing procedures,
Rolf Nyborg IFE

Kjeller Inhibitor Project Phase II is a JIP executed by Institute for Energy Technology in the period 2001-2004. It was funded by 10 international companies: Aramco, ChevronTexaco, Clariant, ConocoPhillips, ENI Agip, Nalco, M-I Production Chemicals, Norsk Hydro, Statoil, and Total. An adjoining project on effect of emulsions was partly funded by The Research Council of Norway.
The objective of the JIP was to develop test methods and equipment that address critical factors for inhibitor performance.
It was proposed by the JIP Steering Committee to disseminate the test protocols developed in the project to facilitate and standardize corrosion inhibitor testing concerning new and important factors that have not been addressed in existing tests and standards. An EFC document was considered by the Committee as suitable way of dissemination and IFE was requested to pursue this option.

Existing oilfield corrosion inhibitor test protocols are:

- ASTM G170.01a Standard Guide for Evaluating and Qualifying Oil Field and Refinery Corrosion Inhibitors in the Laboratory
- ASTM G184.06 Standard Practice … Rotating cage
- ASTM G185.06 Standard Practice … Rotating Cylinder Electrode
- NACE- T-1D-8 / NACE T-1D-34

In general much focus on flow aspects, less on chemical interactions with the produced fluids and solids.

Protocols proposed for EFC publication:

- Test of CO_2 corrosion inhibitor performance in the presence of suspended solids
- Guidelines for the assessment of clay in produced fluids
- Test of CO_2 corrosion inhibitor performance under sand deposits
- Test of CO_2 corrosion inhibitor performance on pre-corroded carbon steel with iron carbonate film

Example: Test of CO_2 corrosion inhibitor performance under sand deposits

Description:

- Test of inhibitor performance on carbon steel specimens covered by sand, with and without galvanic coupling to bare steel surface
- Galvanically coupled specimen: represents area near edge of sand
- Specimen without galvanic coupling: represents area deep in the sand layer

Test cases considered:

- Sand before inhibitor (sand deposition with inadequate inhibition)
  Inhibitor before sand (sand deposition with adequate inhibition)

Test apparatus: Glass cell with dedicated specimen holder unit
Corrosion measurements:

- Galvanically coupled LPR (EIS, sweep optional), inspection, pit depth

The JIP partners must approve formally that the procedures can be published by EFC. The procedures can be published as a "green book" or alternatively the procedures can be posted on the WP13 home page. This has been accepted by STAC as an option.
Action: Rolf Nyborg to get the approval by the end of the year and notify Jim Palmer.

The following group volunteered to go through the procedures and make a proposal to the WP13 regarding publishing before next meeting in Freiburg.
Jim Palmer, Thierry Cassagne, Stein Olsen, Milan Bartos, George Winning
Action : Make a proposal before the next WP13 meeting, (J. Palmer responsible).

Carbon Steel in H_2S Service

Chairman: Liane Smith

Acceptance criteria for HIC testing (EFC16 vs. ISO 15156), Liane Smith

Difference between EFC 16 and ISO 15156 summarised below.

- The solution chemistry is the same, but referenced docs are not.
- The testing temperature is different and could differ by 6 degrees (23 °C is typical for HIC testing, no-one knows where the 25 °C came from).
- CTR, CSR values are different, but not considered to be so significant that it demands an immediate new edition of EFC16.
- The relaxation of CSR in EFC16 to 5% is considered to be valuable for heavy section steel and so it would be useful to retain.

	EFC WP 13	**ISO15156-2**
Test solution	NACE TM0284 (low pH, solution A)	NACE TM0177-96 Environment A (5 w% NaCl + 0.5 w% CH3COOH)
Temperature	23 ± 2 ºC	25 ± 3 ºC
Acceptance criteria	CLR ≤ 15 % CTR ≤ 3 % CSR ≤ 1.5 % (5% if all cracks are within the centre segregation zone and there is no crack face separation > 0.1mm	CLR ≤ 15 % CTR ≤ 5 % CSR ≤ 2 %

- Discussion raised question of whether results evaluation is per specimen section, or average of 3 faces per specimen, or average of 9 faces of all 3 specimens. This can significantly affect the results.

Conclusion

Bring these comments to the attention of the ISO maintenance panel, requesting that they may resolve the small differences and reach a definitive description which EFC16 will then copy.

Acoustic emission detection of HIC
M. Renaud gave a presentation on the use of Acoustic Emission to detect HIC appearance during testing. The technique seemed to be able to distinguish the formation of FeS and the onset of HIC as discrete events. The technique is useful for investigating mechanistic issues.

External cap hardness requirement with CP, Liane Smith.
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 ISO15156-2 (Table A.1).

There were a few cases where the relaxation in hardness (to 275Hv) has been allowed on offshore sour pipelines subject to CP. In reality many girth welds may exceed the 248Hv at the outer cap and are inevitably exposed to CP if immersed.

There are no known failures, but experience is not perhaps long enough or well enough documented.

TWI (Stuart Bond) has been requested to submit a ballot to the Maintenance Panel of ISO15156 to remove the restriction preventing relaxation of external weldment hardness when the component is subject to external CP. A draft ballot has been prepared and will soon be submitted, any data to further support this case would be most welcome (stuart.bond@twi.co.uk).

There are today discrepancies between ISO 15156-2 and EFC16. ISO has defined a region 0. More important is the fact that the hardness requirements in region 1 and 2 are different. In these regions ISO allows only for hardness relaxation for specific components and there is no difference between root and cap. For ISO the CP problem is thus only related to conditions that fall within Region 3.

The general consensus of the meeting was to relax the CP comment for Region 3. Another issue is the discrepancy between ISO and EFC in Region 1 and 2. This was not discussed in detail.

Any change of EFC16 would be delayed until ISO doc change to avoid constantly chasing updates. The aim would be to come in line with ISO 15156, but the final changes of EFC16 will be subject to discussion in the WP13.

Corrosion Aspects of CRAs in Oil and Gas Production in the Absence of Hydrogen
Chairman: Chris Fowler

Testing with elemental sulphur, Liane Smith
The current Appendix for EFC17 is a good general document but has too many varying parameters to be referenced for a specific test method. The range of possible forms of S makes the matrix of possible tests very broad. It was suggested to establish a test approach for

a) elemental sulphur in contact with the surface as the worst case
b) sulphur dissolved in hydrocarbon liquid (or sulphur solvent) which is the most frequently encountered condition.

Liane Smith cautioned that a single well tubing may exhibit all phases in one well depending upon the T profile, with sulphur dissolved in hydrocarbon at the bottom, precipitated sulphur at a higher depth and sulphur dissolved or distributed in the water/oil phase nearer the surface.

Chris Fowler informed that in NACE/ISO part 3 it is referring to EFC17. His recommendation was that testing procedures should be put in EFC17.

A group would try to get the first effort put together a protocol for the above two test approaches which may then be referenced by ISO.

The following group was formed, Chris Fowler, Gerit Siegmund, Russ Kane.
Action: Propose testing procedures with elemental sulphur to be presented at next WP13 meeting in Freiburg.

Limits for AISI 316, Stuart Bond TWI
TWI is currently undertaking a JIP to establish safe environmental limits in terms of pH_2S, chloride, temperature and pH for 316L material. The testing is undertaken both on solid and clad material. Testing is performed according to ISO15156 procedures and the results will be used in a ballot to ISO/NACE to extend the limits for AISI316. Testing will include a typical formation water and condensed water environment with pH_2S up to 10 bars and temperature up to 120° C.

Corrosion in CO_2 Service
Chairman: Rolf Nyborg acting for Arne Dugstad

Prediction of CO2 corrosion, proposal for a new document, R. Nyborg, IFE.
In the EFC WP13 meeting in Trondheim 1997 it was agreed that IFE should propose a JIP for evaluating available CO_2 corrosion prediction models against operation experience with the aim to reach to a commonly agreed practice for CO_2 corrosion prediction.

IFE started a JIP on this in 1998 and this has been running in three phases with about 15 participating companies, the third phase will be finished in 2007.

The various models can give very different results and the main differences between the models were:

- Prediction of oil or water wetting
- Effect of corrosion product films

The grouping of the models was as follows:

- Conservative or non-conservative models:
    - Very conservative models: de Waard, Hydrocor, Cassandra
    - Conservative models: Norsok, ECE
    - Non-conservative models: KSC Model, Lipucor, Predict, ….
- Effect of protective corrosion films
    - Weak effect: de Waard, Hydrocor, Cassandra, ECE
    - Moderate effect: Norsok, Lipucor, KSC Model
- Effect of oil wetting:
    - No effect: Norsok, Cassandra, KSC Model
    - Large effect: de Waard, Hydrocor, ECE, Lipucor, Predict

In parallel to the JIPs at IFE a group of people from the operators was formed with the aim to develop a guideline document for CO_2 corrosion prediction. The group was chaired by Yves Gunaltun from Total.

A 17 pages draft document with the title "Guideline for Corrosion/corrosivity Prediction in Oil and Gas Production Systems" has been prepared by this operators group. The objective of the document is to:

- Produce international guideline for CO2 corrosion prediction in design of oil and gas facilities
- Provide engineering companies, contractors and suppliers with guidelines for corrosion prediction during design

There is an appendix that lists some of the models that have been subject to evaluation and are listed as possible reference models. The operators decided to submit the draft document for consideration as an EFC "Green Book" or it can be posted on the EFC web.

The following group of people will go through the document and give their recommendations to the WP13 members.
Rolf Nyborg (chair), Steve Turgoose, C.de Ward, J. Bradburn, Milan Bartos.

Action: To present a recommendation to the WP13 meeting in Freiburg

pH measurements versus modelling in high chloride conditions, Rolf Nyborg IFE
This was a subject raised in the meeting in 2005.

IFE has compared the pH calculations reported with BP and Shell models in 2005 with the MultiScale model and found less than 0.02 pH unit difference at 250 g/L NaCl. The conclusion is that model error is not a likely cause of the reported difference.

IFE has undertaken pH measurements in their lab. The equipment used was a standard double junction, combination pH (glass) electrode and the solutions made from distilled water and technical grade NaCl. These measurements gave pH values very close to the predicted values. The deviating data reported in 2005 were thus not reproduced. The deviation thus seems not to be general, and may be caused by factors relating to electrode, test solution or test protocol. No obvious error source was established by the present investigation.

There was not time to discuss the conditions for the different measurements in detail. This should be discussed between the labs that have done the measurements.

***Action**: Compare conditions for the different pH measurements in order to try to explain the differences, report at next WP13 meeting (Egil Gulbrandsen, Chris Fowler, Roger Francis).*

Corrosion Resistant Alloys in H2S Service
Chairman: Chris Fowler

Evaporation of formation water - chemistry and SCC, Alan Turnbull, NPL
The background for the work was data from Shearwater development.
"Inside to outside" cracking of 22 Cr DSS was reported by Huizinga et al, Corrosion' 05.

Chloride SCC occurred @ 140 °C and there were residual stresses associated with welds and doubler plate at leak site. The failure was unexpected but associated with concentration of salts due to evaporation and complete evaporation to dryness would not have occurred.

The Shell approach was as follows:

- Use thermodynamic model to predict chemistry of evaporated solution at different levels of water loss
- Conduct FPB and spring-loaded C-ring tests in predicted environment simulating mainly 84% water loss but with slightly lower levels also to determine threshold concentration/water loss level

The main results were:

- Threshold for cracking in absence of oxygen associated with loss of water of 78%
- Oxygen increases susceptibility - lowers threshold water loss at which cracking would occur

NPL has tried to reproduce the results.
The assumption was that as water evaporates, salts precipitate and soluble salts, such as $MgCl_2$, remain in solution.

Chemical analysis of salts supports the qualitative trends of the model, but quantitatively, the model is relatively poor in critical region of high water loss and high concentration. This is consistent with the view that thermodynamic modelling of multi-species solution at very high concentrations is still a challenge. Testing should thus focus on experimentally determined chemistry.

The test conditions were: T=140 °C; 1.8 bar CO_2

84% water loss solution (208300 ppm Cl^-) and 93% water loss solution (272100 ppm Cl^-)
Stresses:
0.2% plastic strain at 84% water loss
0.2%, 0.35% and 0.55 % plastic strain at 93% water loss

The NPL study was unable to reproduce the SCC in oxygen-free environments reported by Shell, as no cracking occurred in the tests.

There was no time for a thorough discussion, but there is a need to clarify what is technically correct. T. Cassagne from Total informed that their test results were in line with the NPL study – no cracking without oxygen. Statoil has undertaken testing with AISI 316 in oxygen free sweet environment with cracking.

A group of people will meet to try to sort out the discrepancy and report to WP13 in Freiburg.
Action: S. Olsen

Hydrogen Embrittlement of Ferrous Materials, Mioara Elvira Stroe, Cebelcor
The data were from her PhD thesis (2005) at Université Libre de Bruxelles (ULB) and CEBELCOR.

The main purpose was to

- get a better understanding of HE mechanism
- find a more appropriated test method

The work was focused on HE of supermartensitic stainless steels (SMSS) and electrochemical charging of hydrogen. The model" Hydrogen Enhanced Localised Plasticity" (HELP) was the basis.
In steps from HELP to embrittlement:

1. H diffuses and concentrates around dislocations
2. H shields the interactions between dislocations
3. under dynamic loading: material segregation into ductile and hard zones
4. redistribution of stress over a reduced cross section
5. failure

The following table describes alternative test methods:

Test	Fracture	Advantage	Disadvantage
SSRT	Ductile	Dynamic Slow	High strain
RSSRT	Mixte	Dynamic Realistic strain	Plastic strain limited in time
SW RSSRT	Brittle	Dynamic Realistic strain Long time	

The conclusions from the work were:

- slow dynamic plastic strain : key factor
- good agreement theory – experimental
- SW RSSRT – more appropriated

Future work should focus on

- segregation into ductile and brittle zones
- applicability of SW RSSRT to other materials

Hydrogen Induced Stress Cracking (HISC) - Duplex stainless steel under cathodic protection –effects of microstructure, Gro Østensen Lauvstad, SINTEF.
The background for the ongoing JIP was given. Several HISC related failures have occurred on different materials.

The final phase of the JIP HISC3 will be undertaken in 2007. A Recommended Practice DNV-RP-F112, "Design of stainless steel subseaequipment exposed to cathodicprotection"- has been issued as draft version and is available on the net (http://www.dnv.com/technologyservices/qualinno/services/technicalstandards.asp).

General remarks regarding test methods for HISC:
•Constant load -> critical stress
•Constant bending/deflection -> critical CTOD/CMOD
•Effects of cold creep
–Constant load > constant deflection
–JIP HISC 2: Singe Edge Notch Tension (SENT)
•Slow strain rate (SSR)
–General information on susceptibility to hydrogen embrittlement
–Screening test –not to be used for design
The ongoing work has concluded that specific test methods should be applied to quantify the susceptibility to HISC. More details will be presented later.

CTOD testing of forged and HIP materials show the following:

- CTODcrit(HIP) > 0.06
- CTODcrit(forged) > 0.02

This confirms the strong dependence on microstructure (austenite spacing).

The final stage of the JIP will focus on use of a proposed test method on different grades and materials and the DNV RP will be updated based on these results.

NEXT MEETING
Next meeting will be in connection with Eurocorr 2007 in Freiburg 9.to 13. September.