MINUTES OF MEETING

EFC Working Party no 13 Corrosion in Oil and Gas Production
WP meeting held during Eurocorr 2003.

Date/place: Budapest / 2. October 2003

Minutes:

Welcome, News and Confirmation of the Agenda

The Use of Inhibitors in Oil and Gas Production
Jim Palmer gave a status for the new document:
The document is review by The Institute of Materials and only minor corrections were required. A new section on "guidelines for the prevention, control and monitoring of preferential weld corrosion" is proposed. The document is expected to be published early 2004.

Jim Palmer gave a presentation of the results from a JIP undertaken by CAPCIS, TWI and IFE on weld corrosion. Rapid failures have been observed with weld metal containing 1% Nickel. Generally low chloride waters (condensed water) gave low galvanic effects. Most corrosion inhibitors will reduce localized weld corrosion, but some corrosion inhibitors led to preferential weld corrosion that was not present prior to injection of the inhibitor. For low concentrations the weld could be anodic, but when the inhibitor concentration was increased, the weld turned cathodic. Splitting of the weld into a ZRA set up was an effective method to study these effects. Based on the findings from this JIP it is recommended that checking for potential preferential weld corrosion should be a part of a qualification programme for corrosion inhibitors.

J-L Crolet commented that some inhibitors are very sensitive to the potential and an anodic polarization could reveal if a particular inhibitor is sensitive to this effect. A. Turnbull proposed that an anodic polarization could be undertaken to define the safe potential "domain" for an inhibitor.

It was generally agreed that J. Palmer should include a section on this in the new EFC document.

A. Turnbull referred to the galvanic anodic dissolution method that NPL use to identify the likelihood of preferential weld metal corrosion. The relevant paper is in British Corrosion J, 2002, Vol 37, No 3, 182-193. Title is "Evaluation of techniques for measuring corrosion activity of carbon steel welds". Authors are Nimmo, et al.

Status of case histories document
Liane Smith asked everybody to send cases that could fit into the document. If there are already cases published in the open literature, she wanted references to these publications.

It was agreed that the document should only contain cases with CRA's, i.e. all types of stainless steels and nickel alloys. In principle all types of "equipment" could be covered

("down hole", well heads, piping, manifolds, vessels, pumps, flowlines, heat exchangers, instruments etc.)

A common format for all cases will be defined. References will be given, but the company that experienced the failures should not be mentioned. It was proposed to make the document WEB based. L. Smith will look into this, but in the mean time cases should be sent directly to her.
Thierry Cassagne presented recent failures due to stress corrosion cracking of duplex process piping. One case with internal (no oxygen) cracking down stream a LCV in a sweet condensate line due to very high chloride content and high temperature. Another case with external cracking at the outlet of a filter was presented.

Corrosion in CO_2 Service

Yves Gunaltun gave a presentation on Top of line corrosion (TOLC). Several cases with TOLC were described. TOLC can occur due to condensation of water in the upper part of the pipeline in stratified flow regime. Common for all cases was a high content of organic acids. Corrosion control in such systems requires special methods as traditional film forming inhibitors continuously injected cannot reach the upper part of the pipe in a stratified flow. Methods that have been used are injection of MDEA to neutralize the organic acids and batch treatment with film forming inhibitors. For new pipelines, heat insulation of the pipeline can be an effective method to eliminate TOLC. TOLC can give initial corrosion rates in the order of 10-15 mm/year, but the corrosion rate will normally stabilize at approximately 0.5 mm/year after 6-12 months.

Yves Gunaltun gave a presentation on an initiative taken by some oil companies to develop an international standard/guideline on CO2 corrosion prediction. The motivation for this work is the large discrepancy between existing models as published by IFE. Selection of the model to be used in a specific project can thus influence the materials selection. The aim for this work is to give guidance on how prediction shall be carried out to avoid the discussion about what model to be used and the effect of various parameters. This means that effect of important parameters such as water wetting and protective scales must be defined, which will give strong guidance on what models to be preferred.

Egil Gulbrandsen gave a presentation on the effect of acetic acid. The acetic acid inhibits the anodic reaction in a CO2 environment, but at the same time it is a cathodic reactant. This means that the acetic acid will give an increased risk for localized corrosion. The acetic acid will also reduce the effect of the protective scales. It is presently not possible to quantify the effect of acetic acid on the CO2 corrosion rate.

Carbon Steel in H_2S Service

Trond Rogne gave a presentation with the title: "Is hardness always a reliable parameter to assess resistance to SSC? Hardness requirements for backing steel for clad steels".
SINTEF has undertaken SSC testing of a steel with a YS of 808 MPa and a hardness of 28.5 HRC. The same steel was also tested after annealing that reduced the YS to 621 MPa and the hardness to 18 HRC. When tested at 100 mbar H2S and pH 4 the steel cracked in both conditions, even when the hardness was 18 HRC. This is in contrast with EFC and NACE that recommends use of C-steel in sour service when the hardness is below 22 HRC.
L. Smith commented that the cracks were shallow and not typical for a material that is sensitive to SSC. Shallow pits/cracks are normally found in all materials due to the

combination of high stresses and a very corrosive environment and all indications less than 0.5 mm in depth are normally disregarded. Annealing of the specimen may also create residual stresses that may influence the results. Based on the uncertainties with respect to preparation of the specimens and the appearance of the pits/cracks, it was concluded that these results did not clearly contradict EFC/NACE with respect to hardness requirements and resistance to SSC. However, there are some cases where materials with acceptable hardness values have failed in laboratory testing. Many companies will thus not only rely on hardness values, but testing will be undertaken for critical components.

SINTEF has undertaken testing for Statoil to study the need for hardness requirements for backing steel for clad vessels for sour service. The background is the need in the industry to use high strength backing steels to save weight and cost. Testing has been undertaken with backing steel with 808 MPa YS and a hardness of 28.5 HRC. The cladding was a 309SS with a hardness below 200 HV10. FPB specimens were made and all C-steel surfaces were covered to avoid exposure. For some of the specimens, defects were made to simulate imperfect clad layers. For some specimens also CP was simulated by polarization as some vessels are protected by anodes. Two environments were used:
100 mbar H2S at pH 4 to simulate condensed water and 100 mbar H2S at pH 5.5 and 5% NaCl to simulate formation water.

The conclusions from the test simulating condensed water were:

- Carbon steel clad with stainless steel that has defects penetrating down to the base material is not resistant to hydrogen cracking in the actual sour H2S environment. Cathodic protection to the Zinc potential (-1050 mV SCE) has a similar effect and enhance cracking.
- Polarising C-steels to the Zinc potential (-1050 mV SCE) in sour service environments (pH < 5) lead to high production of hydrogen, rapid consumption of anodes and a high risk of hydrogen related cracking. Under these conditions CP should not be used.
- The long time test (100 days) at 100 mbar H2S / CO2 and ambient temperature also revealed a hydrogen crack through half of the clad material for one of the specimens. This is probably a consequence of the low potential of the specimen through the test, which was below the hydrogen reaction line, and shortcoming of only one clad layer

The conclusions from the test simulating formation water were:

- No cracking found in clad samples without defect and under cathodic protection
- Cracking found in bottom of defects

"Hydrogen permeation through steel membranes in sour media for the different nodes of EFC 16 diagram" by S. Duval. This was also presented at the Eurocorr conference and for details, it is recommended to read the paper. There was some discussion after the presentation and the main comments were related to the thickness of the membranes used for the permeation studies.

Corrosion Resistant Alloys in H_2S Service

N Amaya gave a presentation with the following title: "Intergranular SCC in supermartensitic steels – the effect of welding method". SMI has carried out a study to investigate the susceptibility for intergranular SCC for weldments made by GMAW and GTAW. Their results showed that the weldment made by GTAW did not crack in as welded conditions, but the weldments made by GMAW required a PWHT at 630 degrees C for 5 minutes to resist intergranular SCC.

"Possible artefacts in artificial acetate buffering and CO_2 corrosion prediction" by JL Crolet. For details the reader is referred to paper no 140 to be presented at the NACE conference in 2004 in New Orleans. Only a very short summary is given here. There are some issues that will have an impact on EFC 16/17 and ISO 15156. If the pH is adjusted to the required value without saturation of the test gas, a major pH shift can occur (for higher pH values > 4) when the test gas is introduced.
For the higher pH values (pH>4.6), the buffer strength of the proposed acetate buffer (4 g/l NaAc + HCl/NaOH) is low and much lower than the natural buffer with bicarbonate in the system. It is not recommended to use reduced buffer as proposed for the supermartensitics.
S. Olsen presented a proposal how this WP should deal with this new information with respect to need for immediate or later revisions of the EFC 16 and 17. The proposal was as follows:

Consequence for testing of C-steel - EFC 16
JL Crolet:

- NaAc buffer has limited capacity for pH> 4.6 OK
- Avoid the need for pH measurements with the solution saturated with the test gas !
- For high pH (pH> 4.6) there is a limited need for buffer as iron sulphides limits the corrosion rate !
- Recommendation:
  Use the 4 g/l NaAc buffer for pH < 4.6
  Use NaHCO3 for pH>4.6 and calculate the required concentration (natural buffer)

Proposal to WP for EFC 16:

- Normally testing undertaken at ambient temperature
- If you follow EFC as it is today, including pH adjustment with the test gas, it is basically OK

Discussion:

- Don't we need a strong buffer at high pH ? Probably not due to protective sulphide scales.
- Should we avoid the need for pH adjustment with the solution saturated with the test gas ? For checking and adjustment during the test period, pH must be checked with the test gas anyway for high pH !!!!

Recommendation:

- No immediate need to change the EFC 16!
- JL Crolet's proposal is better than the existing procedure!
- Must be discussed during the next meeting

Consequences for testing of CRA's - EFC 17
JL Crolet:

- No need for a strong buffer! OK
- Avoid the need for pH measurements with the solution saturated with the test gas!
- 0.4g/l NaAc for SMSS can lead to depassivation (not confirmed)
- Recommendation:
  For pH<3.9 adjust the pH by use of HCl to the required level!
  For pH>3.9 use NaHCO3 and calculate the required concentration (natural buffer)

Proposal to WP for EFC 17
Testing can be undertaken at all temperatures that limits the use of acetic buffer and natural buffer at ambient test pressure. If testing is undertaken in autoclaves, a full simulation is recommended

Recommendation:

- No immediate need to change the EFC 17!
- JL Crolet's proposal is better than the existing procedure!
- Must be discussed during the next meeting

"Loading of specimens"by Chris Fowler.
BODYCOTE has conducted testing of 13% Cr supermartensitic SS in a full ring test and in FPB small scale testing. Specimens that cracked in the FPB testing did not crack in the full ring test. In a full ring pipe the specimen is restrained and residual stresses are maintained. In addition stesses are also applied in the hoop direction. This same discrepancy between full ring and small scale testing has also been observed for testing of C-steel. In EFC 16 or 17 there are no guidance given on dimensions of the FPB specimens. Based on this experience it is recommended to use as large specimens as possible for FPB testing.

Is there a need for a new edition of EFC 17 (16)?
The conclusion from the discussion was that there was no immediate need for new editions. New items to be discussed for new editions are dimensions of test specimens and details on testing of 13% Cr supermartensitics.

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

"Implementation of a new CP design for supermartensitic stainless steel pipelines", by Svein Eliassen, Statoil. This was also presented as a plenary lecture during the Eurocorr conference and the reader is referred to that paper for details. Statoil has undertaken a detailed study to make a robust CP design for subsea flowlines made of 13% Cr supermartensitic SS. The background was hydrogen induced stress cracking of existing flowlines. This cracking had occurred at the anode attachments due to extreme local stresses and coating defects due to penetration by the anode grounding cable. The new design recommended for new flowlines is based on the new ISO 15589-2. No anodes are connected directly to the 13% Cr pipe material, but only on anode spools made of clad material. By doing this, it is still possible to apply "full polarization" by use of aluminum anodes.
L. Smith commented that reduced polarization will eliminate the risk for hydrogen induced stress cracking from CP. Even if this will require a more complex CP design using other types of anodes and isolation joints, this can be an attractive alternative if included in an early stage of a project.

A.Turnbull gave a presentation on cyclic SSRT. NPL research suggests little virtue in the application of the cyclic slow strain rate technique to evaluate the resistance to hydrogen embrittlement of work-hardening alloys such as SMSS. In testing of welded SMSS the cyclic

component of plastic strain was negligible after the first cycle as a consequence of work hardening, creep being the dominant plastic deformation mechanism. Analysis of the Shell data suggests that creep may be the primary factor in their particular tests also. The longer time for testing required in the cyclic slow strain rate test would be better used for conventional slow strain rate testing at lower strain rates or for constant load tests.

In the following discussion, S. Huizinga expressed Shell's view, that could be summarized as follows: There is a significant difference between the cyclic SSRT as performed at NPL and that which is part of Shell's qualificiation procedure for CRA. The latter cycles the load between 80 and 100% of the 0.2% proof stress, which is determined in situ, while NPL cycled between the proof stress and 2% plastic deformation. In Shell's case, the cyclic component in the strain extends over several cycles, at least in the data that were presented for duplex stainless steel. Nevertheless, NPL's conclusion that most of the plastic strain for the duration of the cyclic SSRT test is related to creep is correct. This observation puts the cyclic SSRT in proper perspective with respect to e.g. constant load and SSRT testing, but it does not disqualify the method for use in determining resistance against stress corrosion or embrittlement cracking of CRA.
There was a lot of discussion and it was recommended that this item was put on the agenda for the next meeting.

"Failure of a Super Duplex Stainless Steel HUB due to HISC from CP" by S. Huizinga. This HUB failed after 6-9 months in service. After retrieval, the failed HUB was investigated. Also the stresses applied on the HUB during operation were calculated. The HUB was not coated and no sigma phase was found in the microstructure. Even though a very high content of hydrogen was recorded that could indicate a failure due to hydrogen induced stress cracking, it was concluded that the main cause was extreme global loading.

Stein Olsen gave a short presentation on the need for new qualification methods for hydrogen stress cracking from CP. The recent field failures of duplex stainless steels have shown that materials regarded as "almost immune" to hydrogen stress cracking have failed under extreme conditions. If a qualification test should differ between immune or not immune, many materials used with success over many years would be excluded. The point made was thus that more refined qualification methods should be made that could be used for fitness for purpose testing. There was a short discussion that revealed that there was not much interest for this in the audience. This could be an item for the next meeting.

JL Crolet presented the "Multimedia Corrosion Guide". Detailed information can be found on this web site www.cdcorrosion.com . A presentation will be made by its editor Prof.S. Audisio (and J.-L. Crolet as surrogate speaker) in the computer session of Eurocorr 2004 in Nice, probably on Monday afternoon at 16:30 (to be checked on site).

Final remarks. It was a general opinion that the agenda for the meeting was too busy and that there was too short time for presentation and discussion of each item. This will be changed for the next meeting. There were also some comments on the date for the meeting and too long time between the Oil&Gas session in the conference and the WP meeting. Also there is a meeting held for the ISO 15156 where many people attend that could be interested in the WP meeting. This ISO meeting is normally held the weekend before the Eurocorr conference. So the recommendation is that the WP meeting should be held as soon as possible during the

Eurocorr week. Only the day for the Oil&Gas session must be avoided. This means that our meeting can coincide with the meetings in the refinery and the inhibitor WP.

S. Olsen has asked the organizer of the Eurocorr 2004 for a full day as early as possible in the week, and we have to wait for the decision.

Possible items for 2004
Corrosion fatigue of flexibles in sour environments
Problems related to mercury
Cyclic SSRT
Test method for hydrogen stress cracking from CP
Buffering for testing