



# WP13 BUSINESS MEETING

Lisbon, 04/09/2013

# WELCOME.

- 10:10 – 10:20 Welcome, Introduction of the meeting and News
- 10:20 – 10:45 Activity of Working Groups. New topics
- 10:45 – 11:05 Challenges for localized corrosion and inhibition in sour systems, Rolf Nyborg, IFE
- 11:05 – 11:30 Experience with the Direct Assessment methodology, Patrizia Fassina, ENI
- 11:30 – 11:45 Coffee Break**
- 11:45 – 11:55 Nominating the new WP13 chairman
- 11:55 – 12:15 Pitting in four-point bend specimens: what is the significance?, Gareth Hinds, NPL
- 12:15 – 12:45 NACE TM0177 method A: an update, J. Kittel, IFP-EN, C. Taravel- Condat, Technip
- 12:45 – 13:00 AOB & Closure of Meeting**

# AN EFC DOCUMENT ON THE CORROSION MONITORING MANAGEMENT?

# PROPOSAL

- Issue an EFC document dealing with management aspects of Corrosion monitoring activities in the oil and gas production facilities (internal and external?),
- We might start from a new Cefracor document but excluding the description of methods and selection criteria (done in other standards), i.e. avoiding un-necessary overlaps,
- Including the follow-up of chemicals' injection and of periodic pigging within monitoring activities

# OVERALL SCOPE OF WORK



- Why? Objectives
- Who? Organisation – Responsibilities
- How? Selection – Program – implementation
- What to do with? Monitoring system – Data management
- So what? Analysis - Alarms – KPIs – Management of anomalies...

## NEXT STEPS...

1. Is it useful? Who's interested?
2. Translate the Cefracor document
3. Agree on the scope and table of content
4. Look for a writer?.

# PRACTICAL GUIDELINES (FOR NON SPECIALISTS)?

# PRACTICAL GUIDELINES FOR NON-SPECIALISTS

- Short synthetic guidelines, ideally 2 pages, no more than 4. Visual.
- Mostly focused on good practices: *What to do, what not to do and why*
- Particularly for our contractors, sub-contractors and operations, e.g.:
  - Welding of SS
  - Painting maintenance
  - Pressure testing
  - Removal of coupons and probes
  - Etc...
- Possibly in collaboration with Energy Institute or something equivalent.
- Also short educational pages on critical corrosion issues?
- Any real interest? If yes, do we look for contracted writers?



# Challenges for localized corrosion and inhibition in sour systems

Rolf Nyborg, Attila Palencsár, Jon Kvarekvål

Institute for Energy Technology (IFE)

Kjeller, Norway

# Background

- Particular problems for inhibition in sour systems
- Based on experiences from:
  - IFE JIPs 1998-2011: KIP I and II, KPP I and II, KSG, KLOC
  - single-client projects, sweet and sour
    - performance testing
    - method development
    - fundamental studies
- Parallels between mitigation options in sweet and sour systems
- → Improvement (knowledge, method, cost, environment...)

# Background

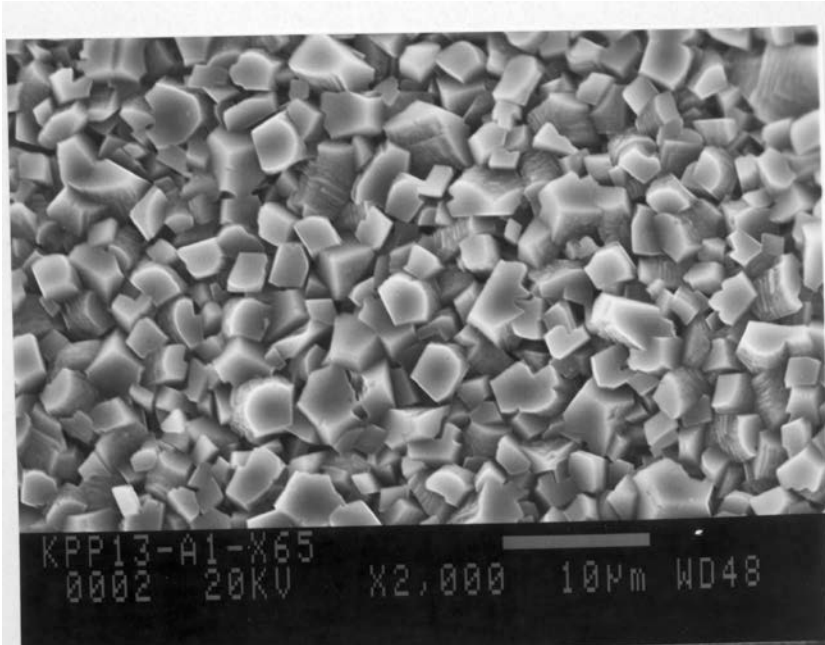
- Lack of understanding of the H<sub>2</sub>S/CO<sub>2</sub> pitting corrosion mechanisms has made it difficult to develop efficient prediction and mitigation methods
- Need to further increase the understanding of H<sub>2</sub>S/CO<sub>2</sub> corrosion
  - Build on previous JIPs and other recent studies
- Parameters for further study proposed
  - Possibly critical for initiation and propagation of localized corrosion
  - Effects have not yet been clarified or quantified

# Previous H<sub>2</sub>S corrosion research at IFE

- Small amounts of H<sub>2</sub>S (0.5-1.5 mbar) studied in KSC-V JIP (1995-1998)
- Somewhat higher H<sub>2</sub>S levels (20 mbar) studied in KPP-2 (1999-2001)
- High H<sub>2</sub>S levels (0.5-5 bar) main topic in KSG (2002-2007)
- Very high H<sub>2</sub>S levels (1-20 bar) studied in KLOC (2007-2011)
  - Continued in ongoing JIP KLIC (2012-2016)
- Numerous proprietary projects on sour corrosion (baseline, corrosion inhibition, pH-stabilisation)

# pH-stabilization – CO<sub>2</sub>

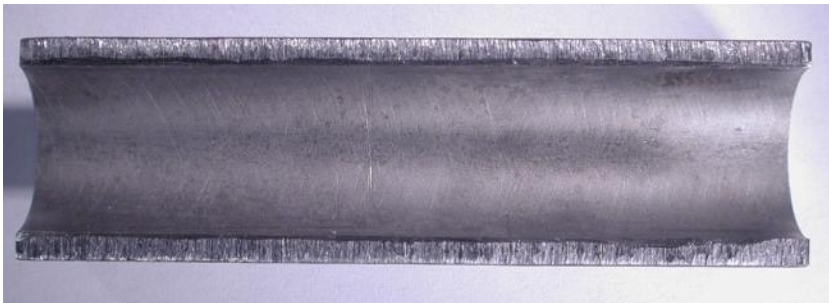
- Dense, adherent, well protecting FeCO<sub>3</sub> films are typical
- Corrosion usually uniform, very low rates



1 bar CO<sub>2</sub> and 40 °C in a 50 wt% DEG, pH 6.5 (NaHCO<sub>3</sub>), flow 1.5 m/s,  
5 weeks, **CR 0.013 mm/y**

# pH-stabilization – H<sub>2</sub>S/CO<sub>2</sub>

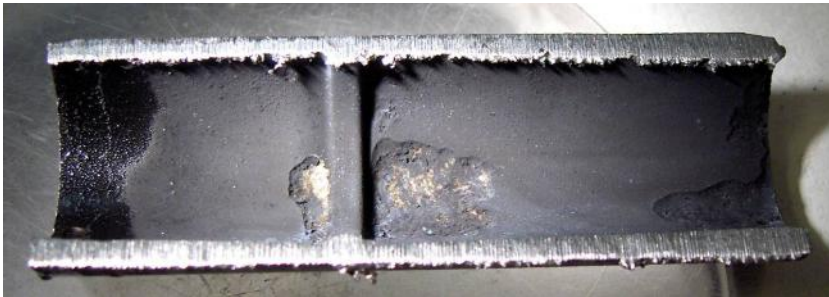
- FeS films are most typical
- Various possible outcomes depending on parameters



avg. CR 0.37 mm/y



pH 7-5-7, MEG 50-0-50 wt-%, avg. CR 0.39 mm/y



obstacle, avg. CR 0.25 mm/y



stagnant, avg. CR 0.22 mm/y

ALL: 60°C, 5 bar CO<sub>2</sub>, 0.5 bar H<sub>2</sub>S, pH 7, flow velocity 1 m/s, 50 wt% MEG, 29 days

# Inhibition – CO<sub>2</sub>

- Corrosion usually uniform, very low rates possible



inhibited

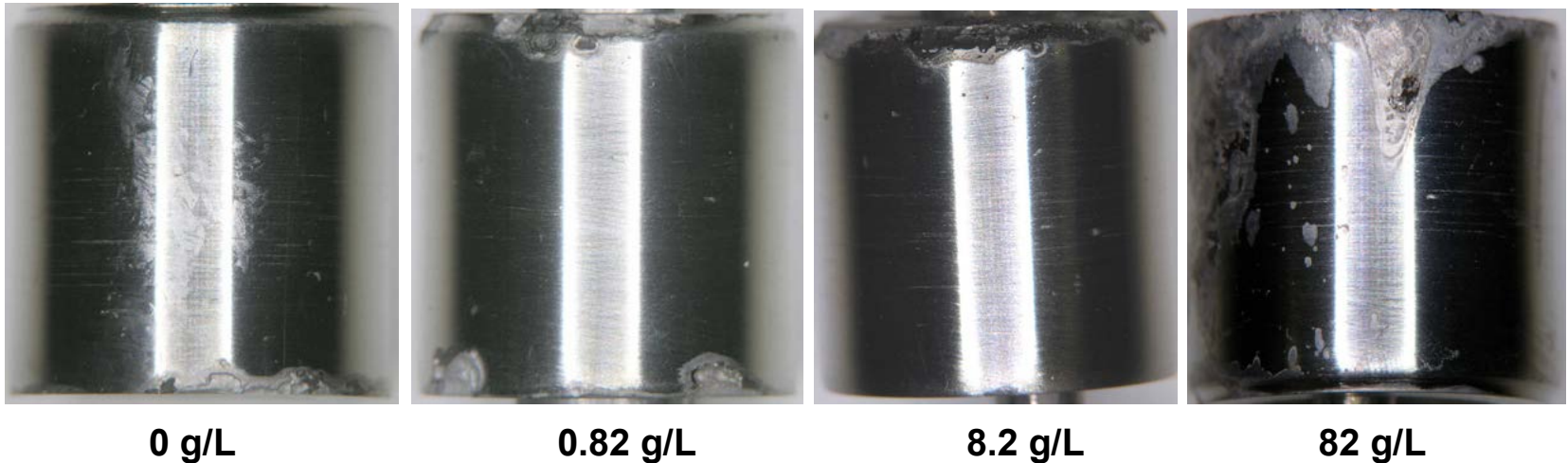


not inhibited

60°C, 0.8 bar CO<sub>2</sub>, 20 mmol NaOH (pH ~6.4, 50 wt% MEG, 0.82 g/L NaCl)

# Inhibition – H<sub>2</sub>S / CO<sub>2</sub>

- Susceptibility to localized corrosion under many circumstances
- Often problems with electrochemical measurements
- Experiments susceptible to artifacts – difficulties in interpretation



60 °C, 0.1 bar CO<sub>2</sub>, 1 bar H<sub>2</sub>S, 50 wt% MEG, pH 6,  
300 ppm inhibitor, varying NaCl



# Inhibition

$\text{CO}_2$	$\text{H}_2\text{S} / \text{CO}_2$
Applicability/Feasibility	
<p>well documented, validated in lab and field</p> <ul style="list-style-type: none"><li>• Very low corrosion rates possible</li><li>• Many formulations</li></ul> <p>Glycol – positive impact</p> <ul style="list-style-type: none"><li>• Reduces <math>\text{CO}_2</math> corrosion rates</li><li>• Often better performance with increasing pH</li><li>• Allows lower dosage</li></ul>	<p>well documented often more difficult than sweet systems</p> <ul style="list-style-type: none"><li>• Very low corrosion rates possible</li><li>• Susceptibility to local attacks</li></ul> <p>Glycol – negative impact</p> <ul style="list-style-type: none"><li>• inhibition more difficult than in sweet systems</li><li>• performance loss with increasing pH and salinity</li><li>• localized attacks; galvanic effects, mechanisms not fully understood</li></ul>

# Inhibition

<b>CO<sub>2</sub></b>	<b>H<sub>2</sub>S - CO<sub>2</sub></b>
<b>Testing</b>	
well established variety of methodologies exist	some methods from sweet systems adaptable more complex, lack of comprehensive guidelines additional methodology needed for problem areas
<b>Understanding</b>	
fundamentals, mechanisms, failure modes well understood	gaps exist in understanding failure mechanisms, especially related to localized corrosion

# Inhibition

<b>CO<sub>2</sub></b>	<b>H<sub>2</sub>S - CO<sub>2</sub></b>
<b>Problems</b>	
<p>Deposits (UDC)</p> <ul style="list-style-type: none"><li>• typically inert deposits (sand, debris)</li><li>• parasitic inhibitor consumption</li><li>• block inhibitor access to steel surface</li><li>• create conditions for galvanic corrosion</li><li>• <b>robust test methodology exists</b></li></ul> <p>underdosage - pitting high temperature glycol regeneration</p>	<p>Deposits (UDC)</p> <ul style="list-style-type: none"><li>• <b>much more severe</b> than in CO<sub>2</sub>-corrosion</li><li>• inert (sand, debris), conductive (iron sulfide), reactive (sulfur)</li><li>• parasitic inhibitor consumption</li><li>• block inhibitor access to steel surface</li><li>• enhance galvanic corrosion</li><li>• accelerated general corrosion</li><li>• severe localized corrosion</li></ul> <p>localized corrosion more often an issue presence of glycol chemical compatibility (e.g. sulfur solvents)</p>

# Concluding remarks

- Many aspects of inhibition in sour media need to be better understood
  - Localized corrosion
  - Effects of deposits
  - Galvanic effects
  - Effects of glycol
- Interactions, effects and inhibitor failure modes need to be investigated
  - identify aspects critical to adequate inhibitor efficiency
  - identify safe operating windows if they exist
  - identify limits of applicability if they exist
- Need to improve/develop methods and equipment

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# Internal Corrosion Direct Assessment Eni's Experience

EFC meeting, Estoril 2013

eni

## NACE SP Direct Assessment: Introduction

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This standard practice formalizes a **methodology** to assess internal and external corrosion for onshore and offshore pipelines and other piping systems.

NACE DA methodology is a structured process that combines pre-assessment, indirect inspection, detailed examination, and post-assessment to evaluate the effect of predictable pipeline integrity threats such as internal corrosion.

The goal of DA is to identify locations with the greatest likelihood of corrosion, and its influencing factors such as water content, flow regime, liquid (i.e. water) holdup, flow velocities, temperature changes, and pressure changes.

These locations, assessment sites, shall be exposed and examined.



## Applicable Normative

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- NACE LP-ICDA SP-0208-2008: **Liquid Petroleum** Internal Corrosion Direct Assessment Standard
- NACE DG-ICDA SP-0206-2006: **Dry Gas** Internal Corrosion Direct Assessment Standard
- NACE WG-ICDA TG-305: **Wet Gas** Internal Corrosion Direct Assessment Standard
- NACE MP-ICDA TG-246: **Multiphase** Flow Internal Corrosion Direct Assessment Standard (DRAFT)
- NACE SCCDA SP-0204-2008: **Stress Corrosion Cracking** Direct Assessment Standard
- NACE ECDA SP-0502-2010: **External** Corrosion Direct Assessment Standard



# Direct Assessment Process and Tasks

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Direct Assessment is a four steps process. All four steps must be performed to complete the direct assessment successfully.

## ▪ **Step 1 – Pre-Assessment**

- Pipeline regions definition.
- Data collection (historic and current): pipeline design and operating data, fluid composition, bathymetric profile and pipeline route, failure history, chemical treatments, etc..

## ▪ **Step 2 – Indirect Inspection**

- Selection of indirect inspection tools (flow assurance tool, corrosion models, etc.).
- Corrosion assessment (wall thickness loss prediction).
- Selection of inspection sites (point with the greatest likely of internal corrosion).

## ▪ **Step 3 – Detailed Examination**

- Performing inspection based on priority inspection sites wall thickness readings).

## ▪ **Step 4 – Post Assessment**

- Analysis of the collected data.
- Analysis of the effectiveness of the DA
- Establish corrosion monitoring and mitigation strategies
- Determine re-assessment interval





## Direct Assessment: WHY?

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- Considering the several oil and gas projects of the last decades, a widespread pipeline network (onshore and offshore) have been developed.
- Today many of those pipelines are approaching their design life.
- The requalification process leads to the life extension of the pipeline operating life.
- **In addition, many of those pipelines are not able to undergo in-line inspection (ILI) by smart pigs.**

**How perform inspection and integrity assessment ?**



# ENI's Experience

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1. **Gas Condensate Offshore Pipeline (WG-ICDA)**
2. **Multiphase Onshore Pipeline (MP-ICDA)**



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# Eni's Experience: WET GAS-ICDA (Case 1)

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## Offshore pipeline $\approx$ 25km long

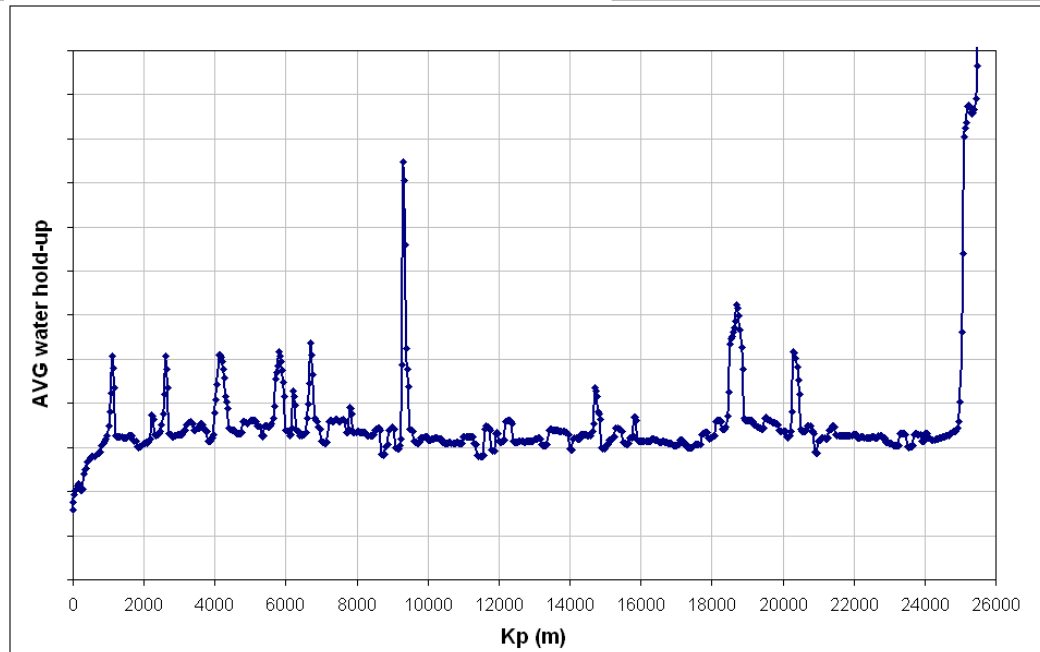
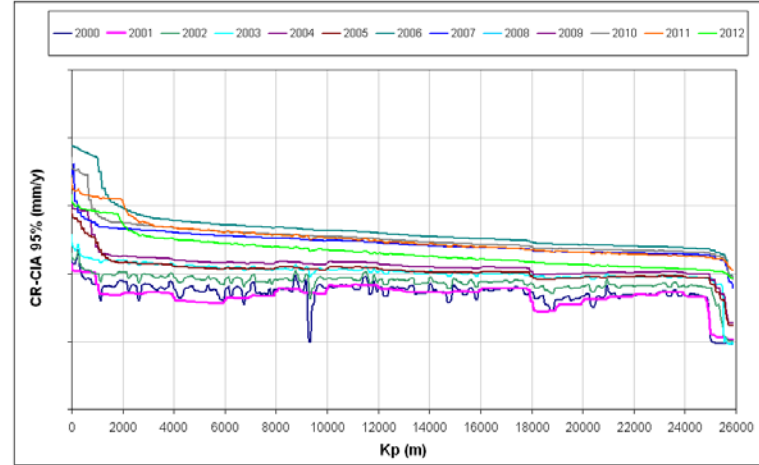
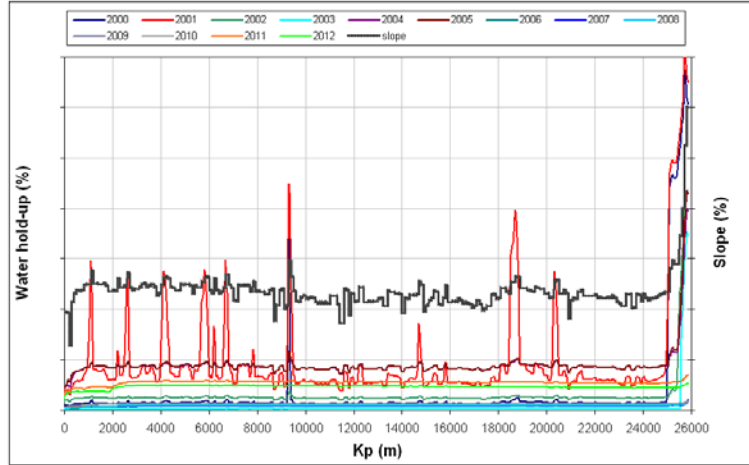
### ACTIVITIES PERFORMED

The **assessment procedure** consists of the following activities:

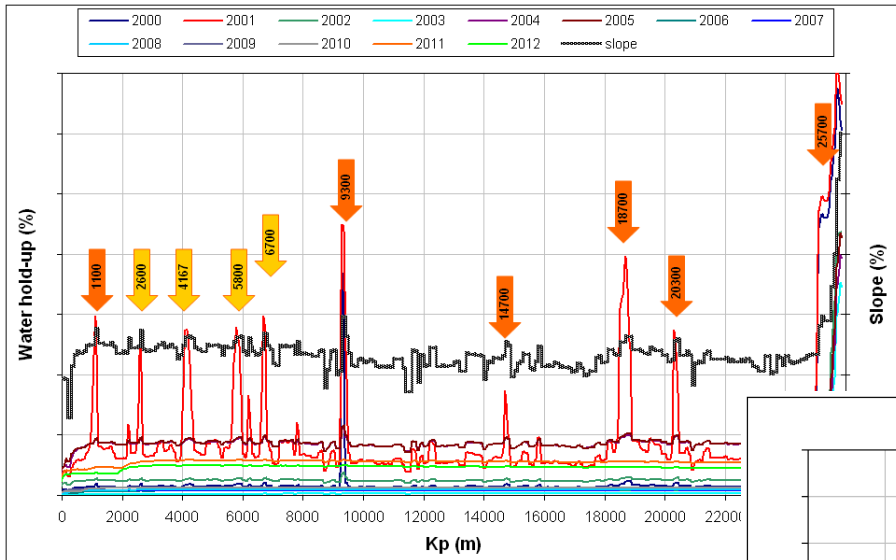
- **Activity 1 - Data gathering (PRE-ASSESSMENT)**: design and operating data, fluid composition, geometric characteristics and maintenance/inspection/repair data.
- **Activity 2 - Flow assurance and corrosion study (INDIRECT INSPECTION)** : identification of the most critical zones along the pipeline in which the flow conditions are such as to onset the corrosion attack. Operating data, pipeline bathymetric profile, pipeline characteristics and fluid properties are input data.
- **Activity 3 - Inspection (DETAILED EXAMINATION)**: planning and execution of wall thickness measurements in the critical zones (inspection points or assessment sites) previously identified by the activity 2.
- **Activity 4 - Inspection results analysis, corrosion assessment review and integrity assessment (POST ASSESSMENT)**: comparison of the measured wall thickness losses (activity 3) with those predicted in the activity 2. Based on the inspection data, a corrosion model tuning may be necessary.



# WET GAS-ICDA (Case 1) – Flow Assurance & Corrosion Assessment



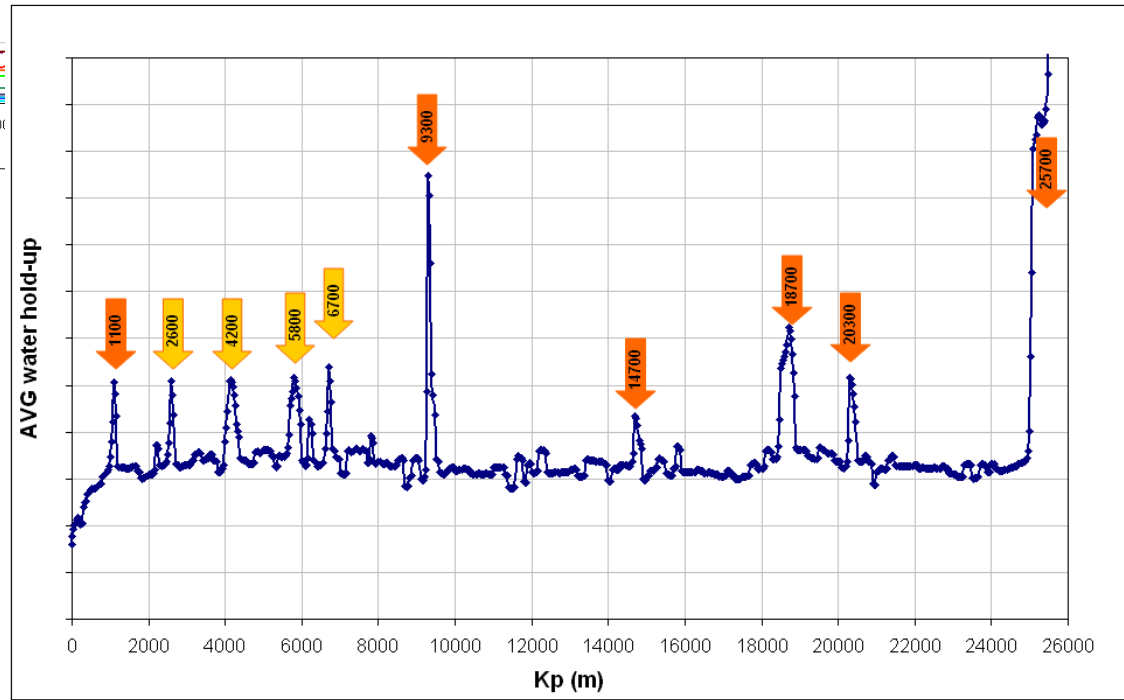
# WET GAS-ICDA (Case 1) – Inspection Sites Selection



Minimum n°6 assessment sites according to NACE WG-ICDA SP for a pipeline 25km long.

The final number of assessment sites is a agreement between economical and technical aspects.

Kp (m)	Remarks
1100	Mandatory
9300	Mandatory
14700	Mandatory
25700	Mandatory
18700	Mandatory
20300	Mandatory
25700	Mandatory
2600	Optional
4200	Optional
5800	Optional
6700	Optional



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## Eni's Experience: Multiphase - ICDA (Case 2)

- Pipeline not operative for most of the time
- Inspection sites selection is based on slope considerations only



# Conclusions

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- **For a reliable application, need of pipeline data over the operative life (historic and current data).**
  - Inspection points selected by current data only are not representative (e.g. corrosion inhibition treatment downtimes)
- **Inspection sites selection needs an accurate pipeline bathymetric profile and route.**
  - Aliasing of the true pipeline profile.
- **Corrosion model may need calibration after inspection.**
  - Predicted wall thickness losses over the operative life may not fit with the measured ones
- **The assessment sites identification may be not feasible for smooth or regular pipeline profiles (no preferential zones of water accumulation).**
  - Flow pattern constant along the pipeline → no liquid accumulation points → constant corrosion likelihood along the profile.



# Discussion

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- **Operators Experience on Direct Assessment Methodology?**
  - **Is DA methodology reliable?**
  - **Is the DA accepted by authorities for pipeline requalification?**
  - **Is DA applicable as stand-alone method for requalification?**





# Pitting in four-point bend specimens – what is the significance?

Dr Gareth Hinds  
Electrochemistry & Corrosion Group  
National Physical Laboratory



# NACE 4pb standard test

## Status at NACE meeting (Mar 2013)

- Draft standard v2 discussed at WG 085F meeting.
- New NACE TG formed: TG 494
- Standard to be developed as stand-alone document.

# NACE 4pb standard test

Update at Eurocorr meeting (Sept 2013)

- Finite element analysis undertaken by NPL shows that the current flexural 0.2% offset calibration method in 4 pt bend testing overstrains and overstresses the specimen.
- Consensus to use uniaxial tensile calibration data to set the longitudinal strain on each four-point bend specimen.
- This still slightly overstresses the specimen but this is unavoidable and in any case provides a conservative test.
- The force required to achieve a given strain will be greater if there is friction at the rollers. However, provided the friction is modest and the specimen is strain gauged to ensure the desired strain is achieved this will not affect the results.

# NACE 4pb standard test

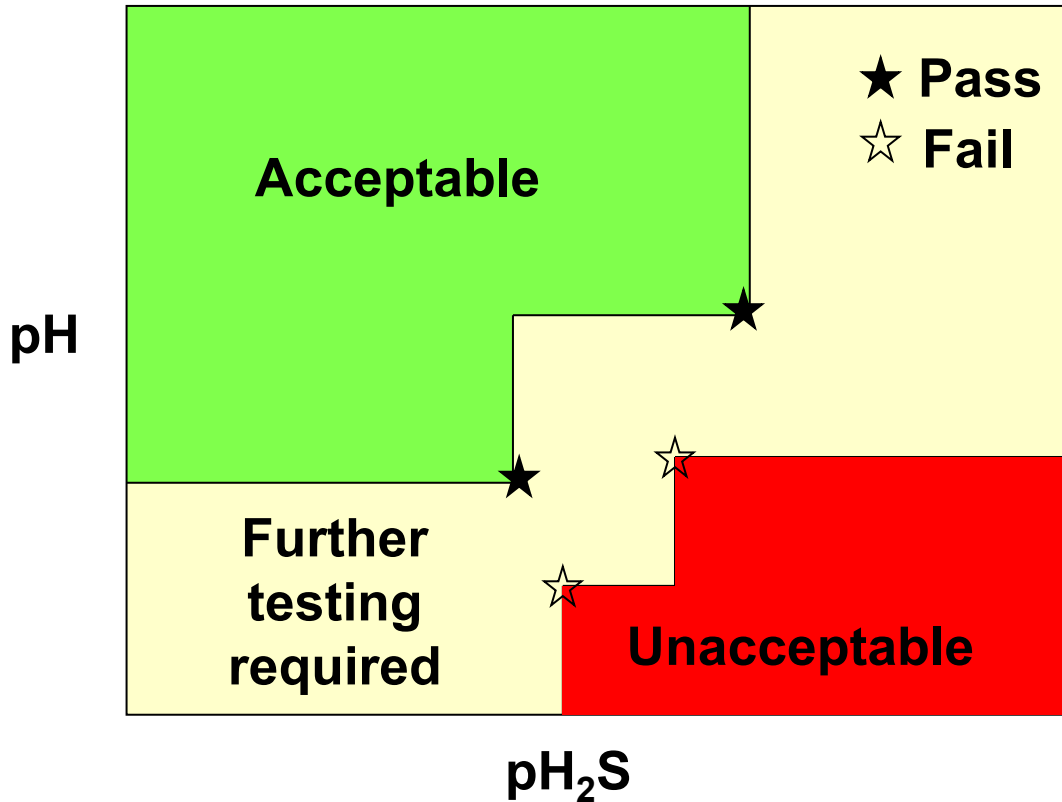
Revision (Sept 2013)

- Draft standard v3 generated in response to FE analysis and distributed to sub-group for review.
- Comments received from Phil Dent in particular (with excellent table specifying solution chemistry and its control for different standards) and a slightly modified version recirculated.
- Final revision and distribution to all NACE TG 494/WG 085F members in November.
- Discussion at NACE 2014 meeting.

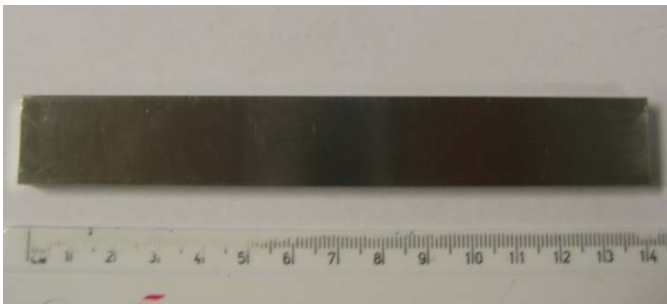
# Issue for discussion

- Four-point bend tests are commonly used in material qualification test programmes.
  - Test duration is typically 30 days
  - Acceptance criteria defined by end user – some tolerance of pitting in the absence of any cracking is not unusual
- Recent work at NPL investigating the effect of surface condition on SCC of 316L SS has highlighted a time dependence of the pit-to-crack transition.
- This raises concerns about test duration and how to deal with the observation of pitting in such tests.

# Test conditions



- Conditions designed to be just within the pass domain for 316L SS
- Test conditions: 110 °C, 1% H<sub>2</sub>S, 50,000 ppm Cl<sup>-</sup>, pH 4.5
- Effect of welding simulated by heat tinting in air
- Two different Ra values



**Untreated**



**1 h heat tint (800 °C)**

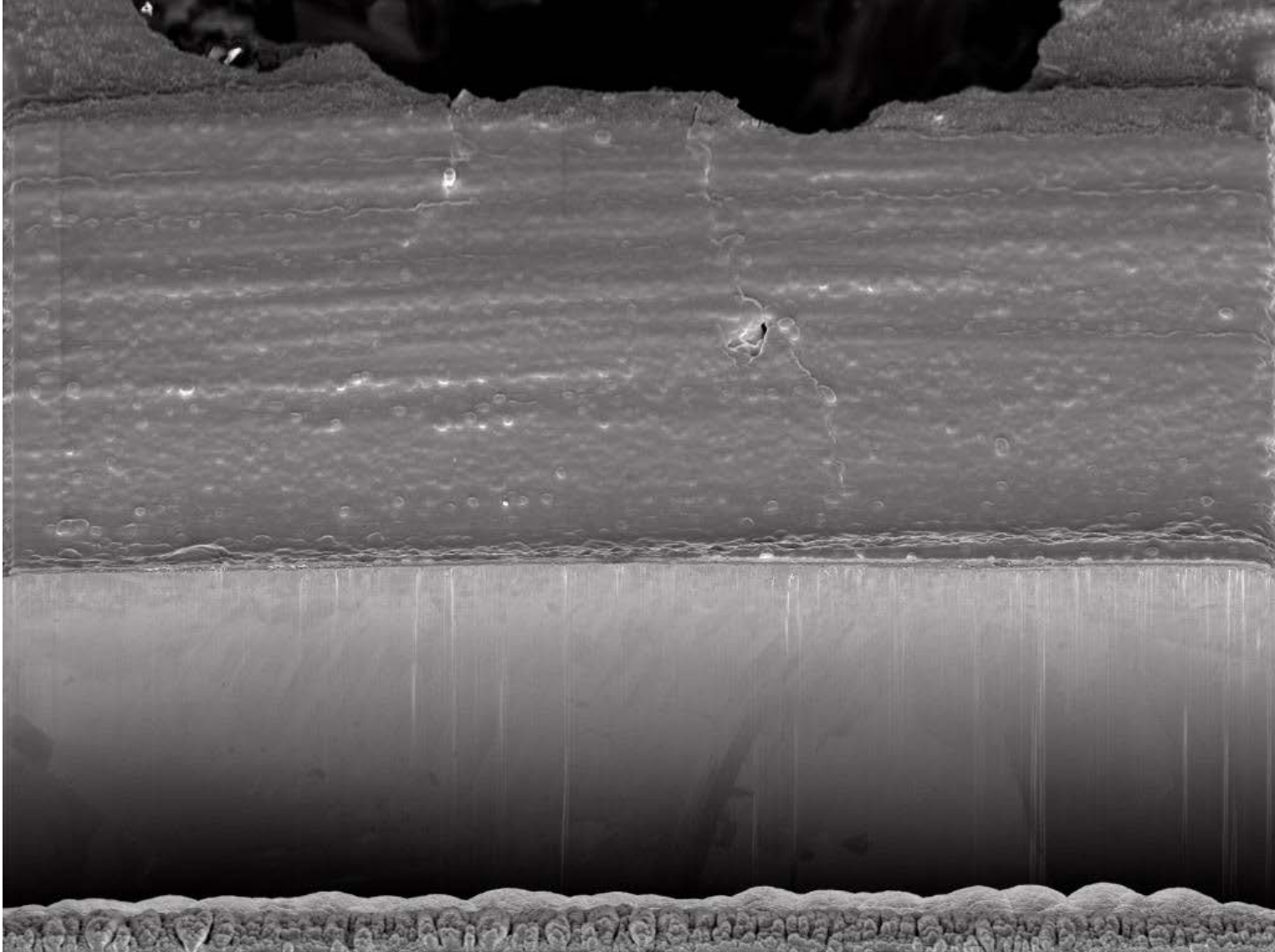
# 4pb Test Results

Duration	Heat tinted	R <sub>a</sub> (μm)	Pitting	Cracking
30 days	No	0.2	Yes	No
			Yes	No
		0.8 – 1.0	Yes	No
			Yes	No
	Yes	0.2	Yes	Yes
			Yes	No
		0.8 – 1.0	Yes	No
			Yes	No
90 days	No	0.2	Yes	No
			Yes	No
		0.8 – 1.0	Yes	No
			Yes	No
	Yes	0.2	Yes	Yes
			Yes	Yes
		0.8 – 1.0	Yes	Yes
			Yes	Yes

- Maximum pit depth (~ 60 μm) did not change appreciably from 30 days to 90 days
- Undercutting lateral growth of pits is a factor in the pit-to-crack transition

# FIB

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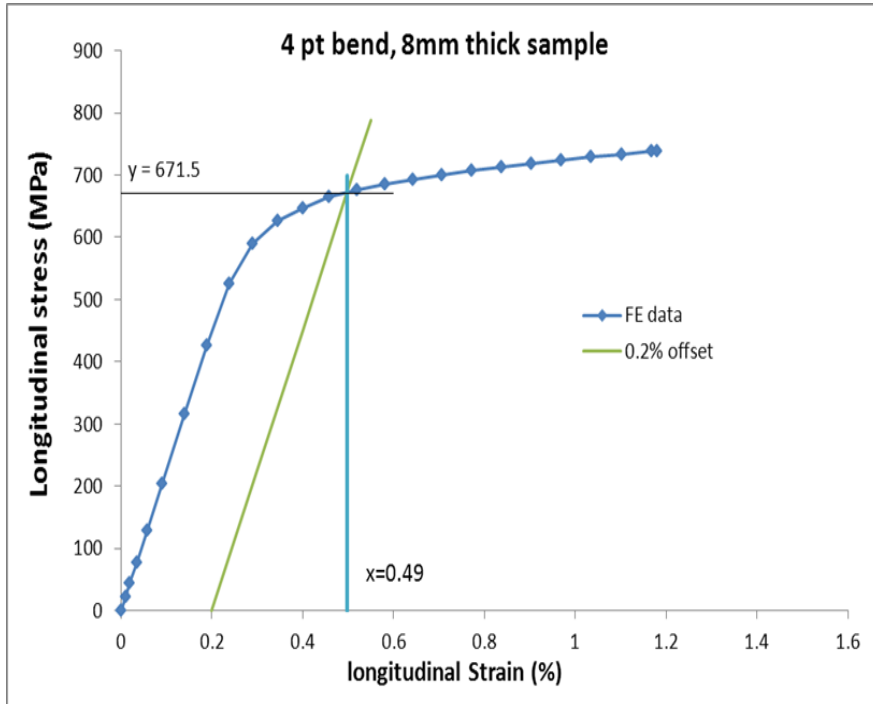




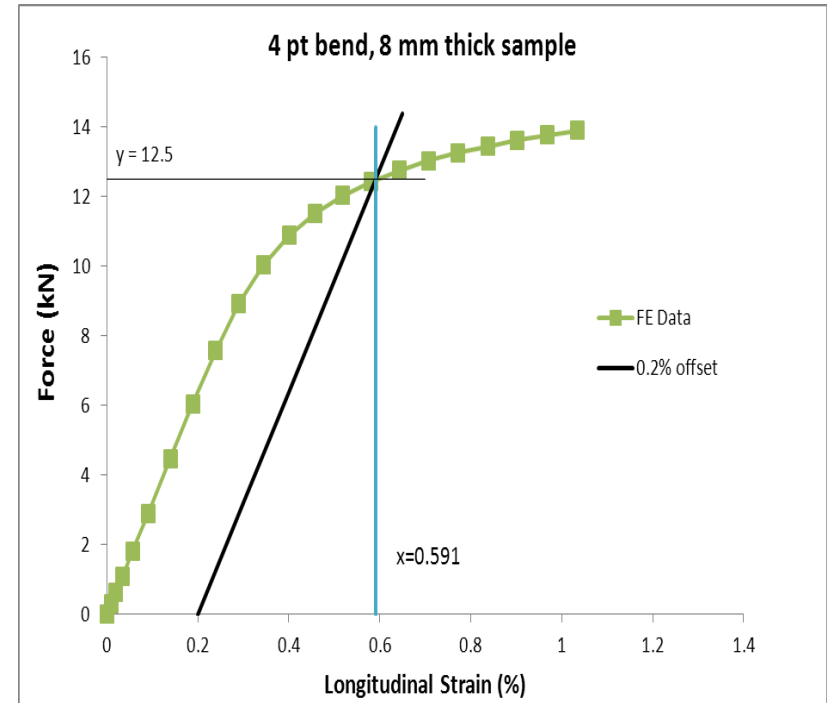
# NPL perspective

- Under conditions in which pitting is known to be the precursor to cracking, the observation of even shallow pitting in four-point bend testing of CRAs should be deemed a failure.
- Time dependence of pit to crack transition - 30 day standard test may not be sufficiently conservative.
- Discussion...

# FE analysis



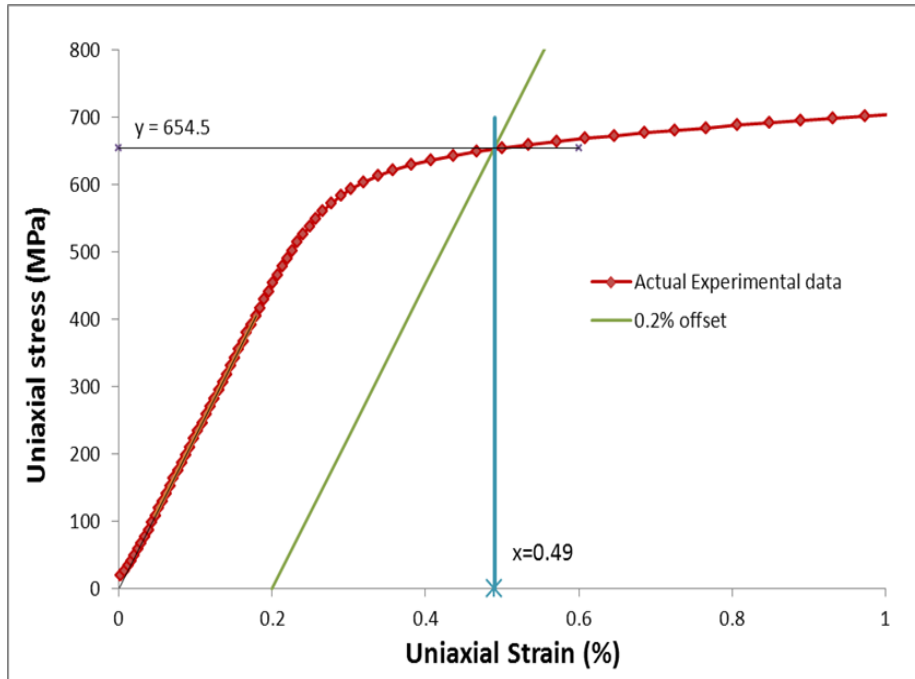
Calculated stress-strain on tensile surface indicating total strain of **0.49%** at 0.2% plastic strain



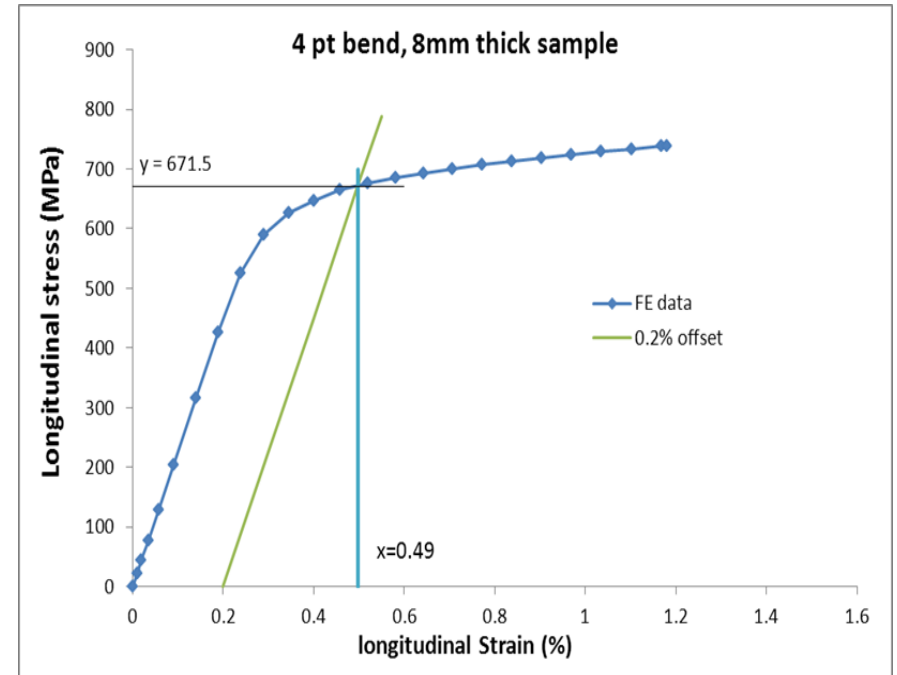
Calculated force-strain on tensile surface indicating total strain of **0.59%** (0.3% plastic strain) using 0.2% offset method.

- 0.2% offset method in 4 pt bend testing overstrains and overstresses the specimen
- use uniaxial tensile data to set total strain (longitudinal) for 4 pt bend specimen

# FE analysis



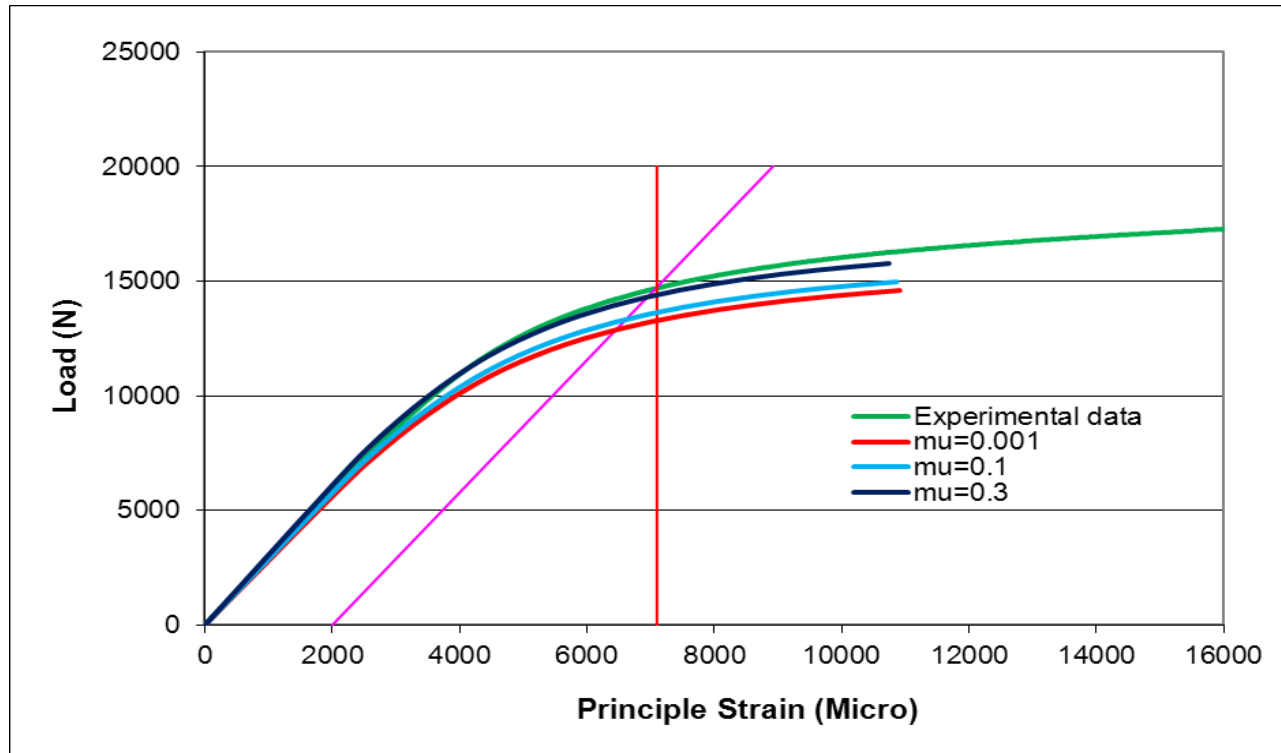
Experimental uniaxial tensile test data



Calculated stress-strain on tensile surface of 4 pt bend specimen.

Using uniaxial total strain data to achieve 0.2% plastic strain in 4 pt bend still overstresses the specimen a little but unavoidable

# FE analysis – friction effect



The force required to achieve a given strain will be greater if there is friction at the rollers. However, provided the friction is modest and the specimen is strain gauged to ensure the desired strain is achieved this will not affect the results.

# **CEFRACOR (French Federation of Corrosion)**

*President: Marcel ROCHE*

## **Oil & Gas and Chemical Industries Committee**

*Chairman: Jean KITTEL*

### **Working Group 5 – Environmental Cracking**

*WG Lead: H. Marchebois → C. Taravel-Condât, N. Désamais, V. Ligier*

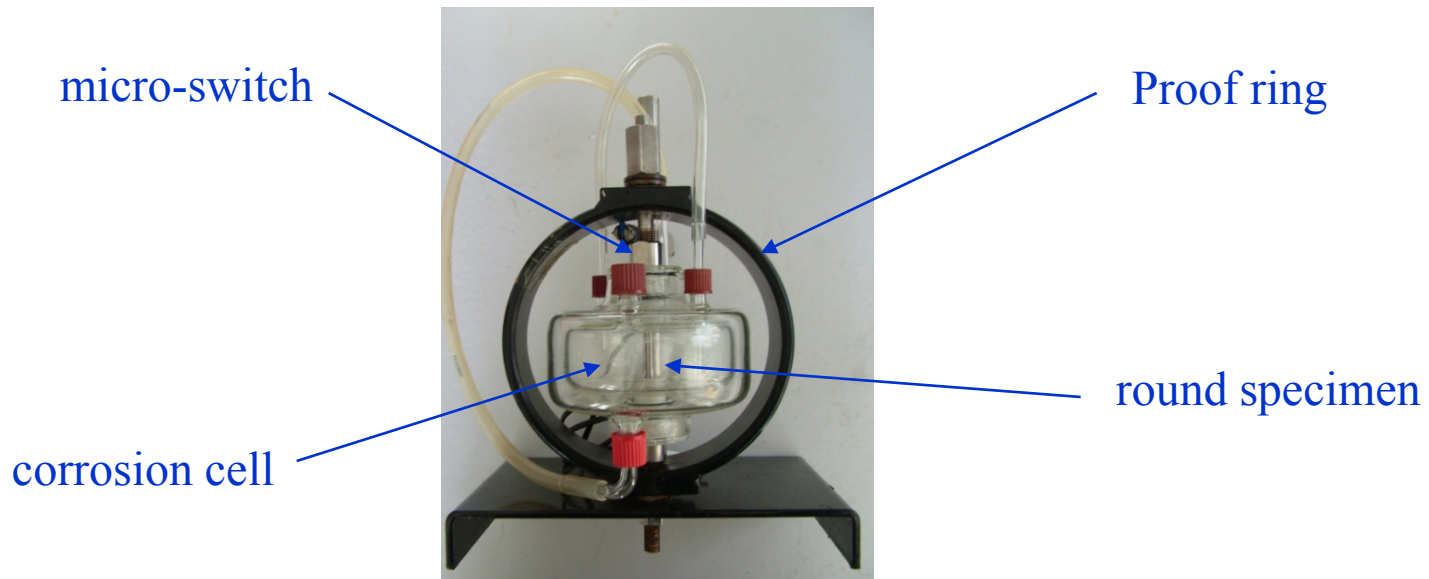
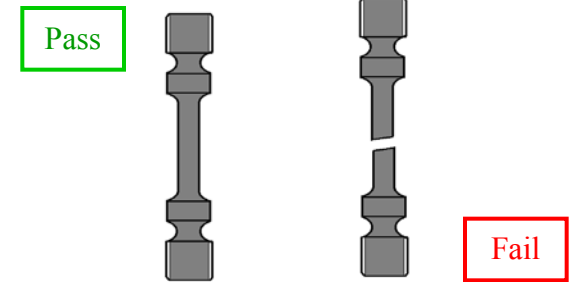
#### **2011-2013 activities on NACE TM0177 Method A**

- Current testing methods vs. recommendations
- How to reduce variability of results ?
- Most relevant parameters

# NACE TM0177 Method A: Basics

## ►► Uniaxial Tensile test

- *NACE TM0177-05 Method A*
- *Standardized test in the O&G industry*
- *Critical test seen as a reference*



Test is stopped after 720 hours (1 month) if no failure/secondary crack has occurred

# *Can Method A test be better controlled?*

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2.2.7 EC test results can show statistical variability. Replicate testing may be needed to obtain a representative value characterizing resistance to EC.

*from NACE TM0177-2005*

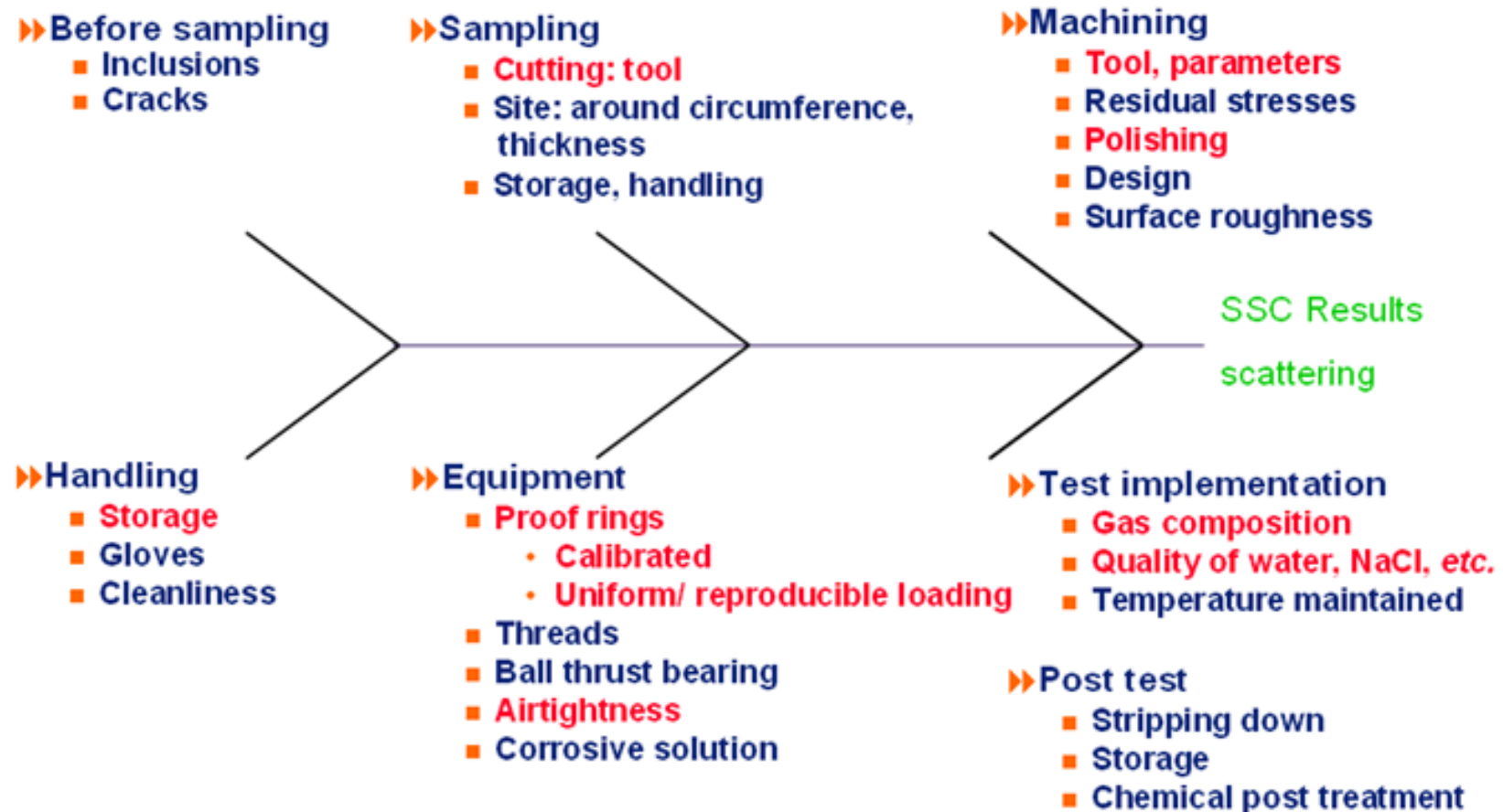
**Variability induced:  
by the SSC mechanism vs. by the test procedure?**

➔ Objectives: to identify the most influent parameters that may induce experimental scattering

# Influent parameters that may affect the SSC test result

## ►► Identification of parameters that may induce exp. variability

– Exemple of an Ishikawa diagram that has been defined and discussed





## **Methodology used:**

- What is specified in the standard ?
  - Is it sufficiently detailed ?
  - Is it adapted to current practices ?
  
- How could this parameter affect the results ?
  - Identification of relevant publications
  - Share of unpublished experience of participants
  
- What are actual « best practices » ?
  
- Could we do better ?
- Do we need further investigations to conclude ?

# Specific analysis of few parameters ranked as « most important »

## ►► Specimen preparation

- **The use of current machining tools (carbide or ceramic tools) not in line with NACE criteria anymore**, *i.e.* « in machining operations, the final two passes should remove no more than a total of 0.05 mm (0.002 in.) of material »?
- **How to perform the polishing ?**
  - Manual mechanical polishing (long./transverse) *vs.* automated polishing
  - Electrolytic polishing (only acceptable on CS) *vs.* mechanical polishing
- **Roughness** ( $R_z + R_a$  instead of only  $R_a$ ) – frequency of the checking – 0.81  $\mu\text{m}$  in NACE Std. instead of 0.2  $\mu\text{m}$  in EFC 16
  - » A lot of paper on the topic « effect of residual stresses »: mainly on SCC/stainless steel (1969 to 2011)
  - » Role of the machining residual stresses on the SSC resistance of carbon steel evaluated acc. to NACE TM0177 Method A, Mendibide *et al.*, 2012

# *Specific analysis of few parameters ranked as « most important »*

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## ►► Applied Stress

- Stress measurement - « Bending stress error » *cf.* API WG 1055 / ASTM E1012 or torsion effect
  
- Calibration of sustained loaded proof-ring (variability *vs.* calibration method)
  
- Applied stress *vs.* SSC susceptibility for non standard size specimen (function of test environment, material, *etc.*)
  - » The Initiation Of Surface Preparation On Stress Corrosion Cracking Of Stainless Steels In High Temperature Water, Matsushima *et al.*, 1978
  - » Effect Of Surface Conditions On The Probability Distribution Of Stress Corrosion Cracking Failure Times Of Type 304 SS, Shibata *et al.*, 1985
  - » Improved understanding of test variables in the NACE tensile test, Bosch *et al.*, 2009
  - » NACE TM0177 method A uniaxial tensile testing: learnings from investigations on test procedure, Marchebois *et al.*, 2009

## ▶▶ Influence of pH

- CO<sub>2</sub> / H<sub>2</sub>S vs. N<sub>2</sub> / H<sub>2</sub>S - pH "drift/shift" = f(pH, P<sub>H<sub>2</sub>S/CO<sub>2</sub></sub>, buffer, etc.)
- Influence of buffering
  - » The effect of buffered solutions in corrosion testing of alloyed 13 Cr martensitic stainless steels for mildly sour applications , Drugli *et al.*, 1999
  - » Use and misuse of laboratory tests, Cayard *et al.*, 2000
  - » Use and abuse of acetate buffering, Crolet *et al.*, 2004
  - » Development of a C125 high strength low alloy steel for octg: ssc mapping in slightly sour environment, Marchebois *et al.*, 2008
  - » For a better control of pH drift when testing SSC in Fitness-For- Purpose conditions, Augustin *et al.*, 2009

# Important parameters to be checked

## ►► Influence of dissolved oxygen

- Degasing with N<sub>2</sub> vs. CO<sub>2</sub>?
- 20 mn degasing (see TM0177) does not seem to be enough for large vessels or low P<sub>H<sub>2</sub>S</sub>?  
O<sub>2</sub> concentrations max and min values? (gas quality dependant at high pressure in autoclave)
- To specify a maximum residual oxygen content as defined in the NACE FPB draft document (lead A. Turnbull), *i.e.* 50 ppb max. for carbon steel grades lower or equal to 80 ksi, and 10 ppb max. for higher grades and CRAs
  - » The role of trace amounts of oxygen on the corrosivity of H<sub>2</sub>S media, Crolet *et al.*, 1991
  - » CO<sub>2</sub> / H<sub>2</sub>S Corrosion Under Wet Gas Pipeline Conditions In The Presence Of Bicarbonate, Chloride, And Oxygen, Lyle *et al.*, 1998
  - » Use and misuse of laboratory tests, Cayard *et al.*, 2000
  - » Corrosion Consequences of Oxygen Entry into oilfield brines, Martin *et al.*, 2002
  - » Effect of oxygen on aqueous sour corrosion systems, Palencsar *et al.*, 2009
  - » Sulfur Corrosion Due To Oxygen Ingress, Boivin *et al.*, 2011
  - » Effect of O<sub>2</sub> and temperature on sour corrosion, Song *et al.*, 2011
  - » Some confidential lab. studies discussed off-record...

# *Important parameters to be checked*

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## ▶▶ **Acceptance criteria**

- There are no big issues to check the SSC susceptibility but to distinguish « cracks » and « pits » (multiple indentations homogeneously distributed on the gauge length)
  - » Stress Corrosion Cracking of Low Strength, Low Nickel Steels in Sulfide Environments , Dunlop, 1978
  - » The effect of low H<sub>2</sub>S concentrations on welded steels, Pargeter, 2000

- ▶ **Need to share this work with EFC and NACE members**
  - Excel file summarizing all our work is available, and will be attached to the minutes of the meeting for everybody to comment
  
- ▶ **Publish a short paper on the topic summarizing the important parameters to be controled**
  
- ▶ **If required, to discuss a potential update of the Std./guidelines**

# O<sub>2</sub> contamination during SSC/HIC tests



C Taravel Condat

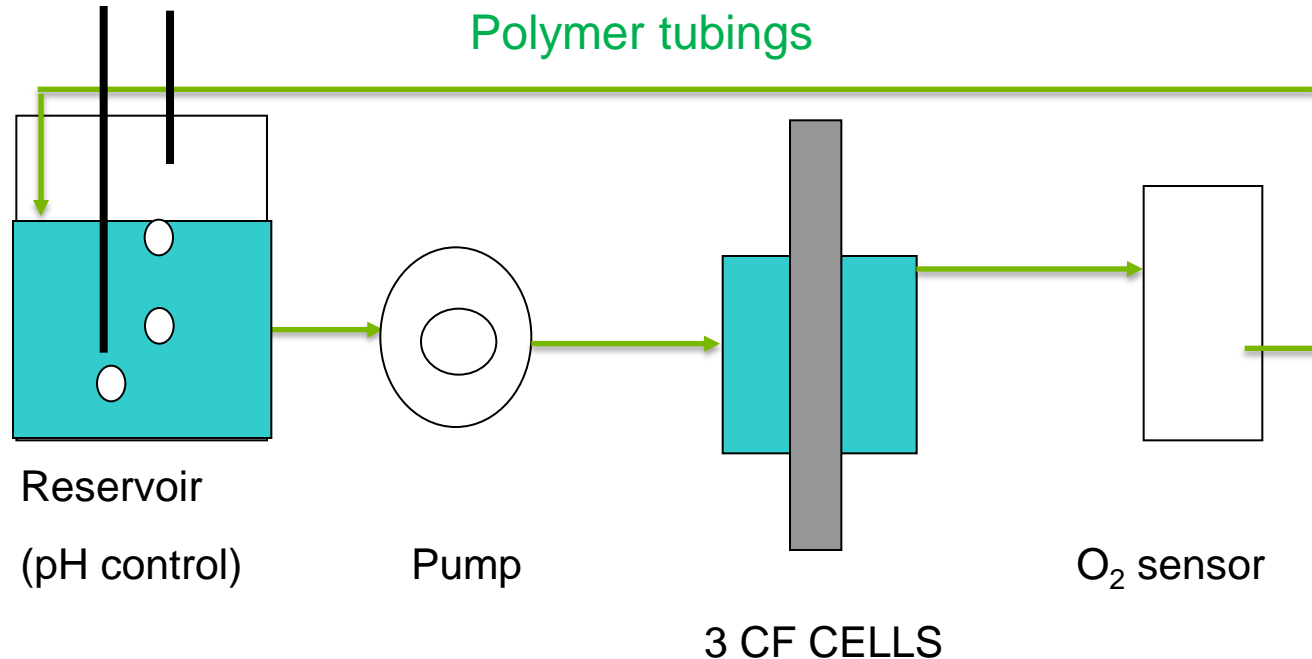


# Deaeration during SSC/HIC tests

- **Test NACE SSC/HIC under H<sub>2</sub>S requires deaeration**
- **TM0177/TM0284 NACE standards : no limit value specified**
- **NACE standards: for tests at 1 bar H<sub>2</sub>S. Now more and more tests are done in fit for purpose conditions at very low p<sub>H<sub>2</sub>S</sub> (mbars) and constant pH.**
- **Standart deaeration still ok for fit for purpose tests at low PH<sub>2</sub>S ?**
- **What is the influence of O<sub>2</sub> contamination on SSC and HIC**

# Technip Experience : Corrosion Fatigue tests

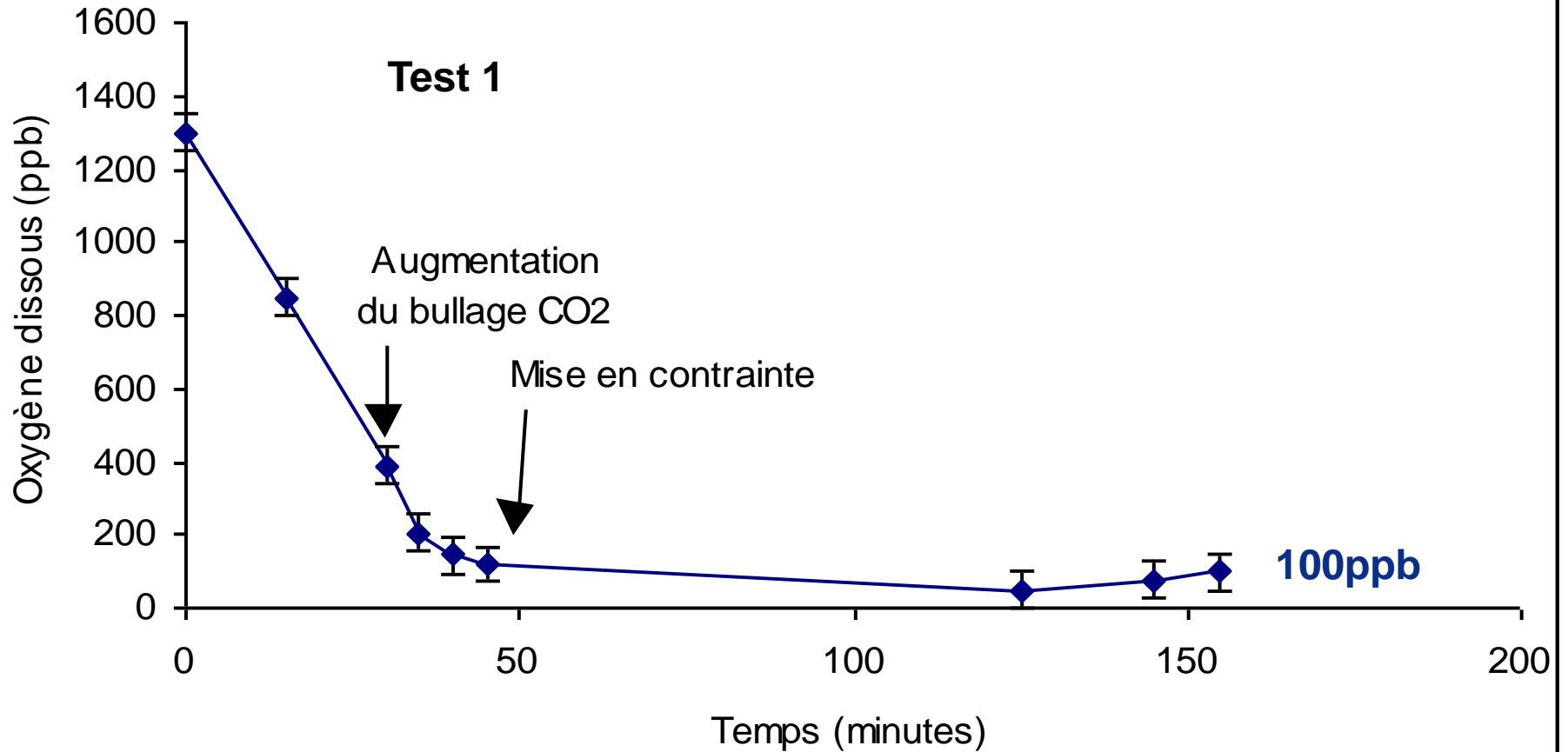
## ▪ Experimental device (principle)



- Degassing of the reservoir for 1 night (N<sub>2</sub>)
- Purging of the circuit for 20 minutes
- Circulation of the deaerated solution during 20 minutes
- CO<sub>2</sub> saturation in the reservoir according to NACE flowrate

# Case 1

## ■ CO<sub>2</sub> N45 , tubing Norprene



# Summary of different configurations

Test	Gas	Tubing	N2 bag	Oxygen level	Remarks
1	CO <sub>2</sub> N45	Norprène	No	100 ppb	
2	CO <sub>2</sub> N45 then N48	Viton	Pump	48 ppb then 35 ppb	
3	CO <sub>2</sub> N48	Viton	Pump, cell, O2 sensor	27ppb	
4	CO <sub>2</sub> N48	Viton	Pump, cell, O2 sensor	0.4ppb	Saturated in iron
5	90%CO <sub>2</sub> 10% H <sub>2</sub> S	Norprène	No	17.5ppb	

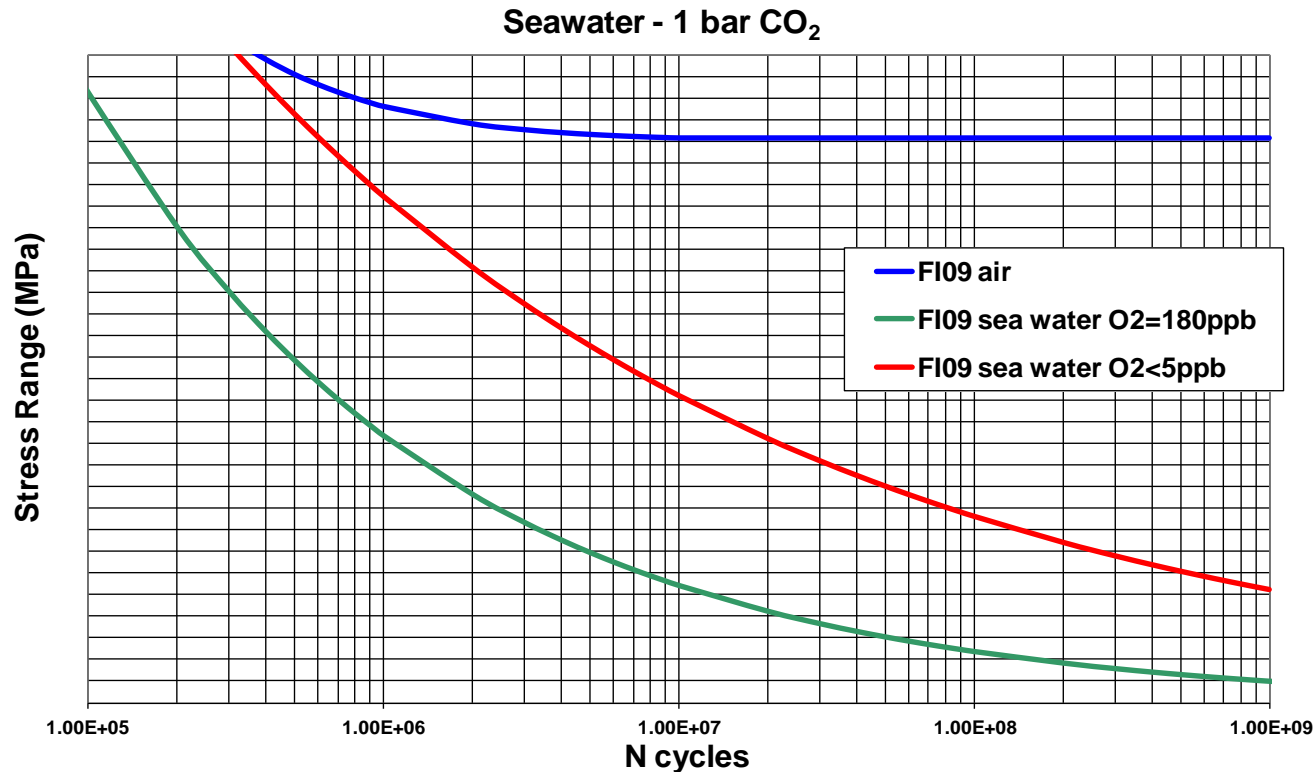
# Discussion/Conclusions

- Polymer tubings may be source of continuous O<sub>2</sub> contamination. Viton much less permeable to O<sub>2</sub> than Norprene.

Nature of polymer	Permeability O <sub>2</sub>
VITON	1
NORPRENE	10

- Reduction of length of polymer tubings AMAP → decrease of O<sub>2</sub>
- O<sub>2</sub> contamination at pump
  - Viton + N<sub>2</sub> bag around pump reduces O<sub>2</sub> level by a factor 3
- Use of pure CO<sub>2</sub> (N48) instead of N45
- Strong CO<sub>2</sub> bubbling can compensate O<sub>2</sub> entry (but high consumption of gas)
- **Although those improvements, O<sub>2</sub> > 10 ppb**
- **H<sub>2</sub>S** and Steels consume O<sub>2</sub>

# Effect of O<sub>2</sub> contamination on FC



Today CF tests are done in N<sub>2</sub> box or using Stainless steel tubings and autoclaves to reach O<sub>2</sub> < 5 ppb  
Nace tests are done using generally polymers tubings.

# How to reach 10 ppb O<sub>2</sub> in a NACE test and why?

- Draft document FPB (A Turnbull) : Max residual oxygen 50 ppb for CS grades < to 80 ksi, **10 ppb max. for higher grades and CRAs**
  - ➔ **10 ppb O<sub>2</sub> is a challenging target**
- O<sub>2</sub> influence on SSC and HIC
  - O<sub>2</sub> reacts with H<sub>2</sub>S. For fit for purpose tests at low ppH<sub>2</sub>S, it may reduce the severity of the environment.
  - measurement of H<sub>2</sub>S content in the solution to know if H<sub>2</sub>S level is kept constant during the test . Use technics adapted to low ppH<sub>2</sub>S.
  - O<sub>2</sub> increases Corrosion rate ➔ increase of SSC?
- O<sub>2</sub> must be measured without H<sub>2</sub>S and steel (consumption)
  - ➔ blank test in a same testing configuration with CO<sub>2</sub> (duration 1 month)
- Limit AMAP length of polymers tubings and choose tubing material with low permeability to O<sub>2</sub> . Steel tubes are the best solution to reach low level of O<sub>2</sub> (<10 ppb).

## NACE TM0284

Trace oxygen impurities in the purge gas are much more critical than water impurities if nitrogen (or other inert gas) is continuously mixed with the H<sub>2</sub>S to obtain a lower partial pressure of H<sub>2</sub>S in the gas and hence a lower H<sub>2</sub>S concentration in the test solution. Oxidation products could accumulate, resulting in changes in corrosion rate and/or hydrogen entry rate (see the paragraph below on Reasons for Exclusion of Oxygen).

Obtaining and maintaining an environment with minimum dissolved oxygen contamination is considered very important because of significant effects noted in field and laboratory studies:

(1) Oxygen contamination in brines containing H<sub>2</sub>S can result in drastic increases in corrosion rates by as much as two orders of magnitude. Generally, the oxygen can also reduce hydrogen evolution and entry into the metal. Systematic studies of the parameters affecting these phenomena (as they apply to environmental cracking) have not been reported in the literature.

(2) Small amounts of oxygen or ammonium polysulfide are sometimes added to aqueous refinery streams in conjunction with careful pH control near 8 to minimize both corrosion and hydrogen blistering. The effectiveness is attributed to an alteration of the corrosion product.

In the absence of sufficient data to define and clarify the effects of these phenomena on environmental cracking, all reasonable precautions to exclude oxygen shall be taken. The precautions cited in this standard minimize the effects of oxygen with little increase in cost, difficulty, or complexity.





# Thank you