Appendix 1

RINA Activities

(A. Lucci)

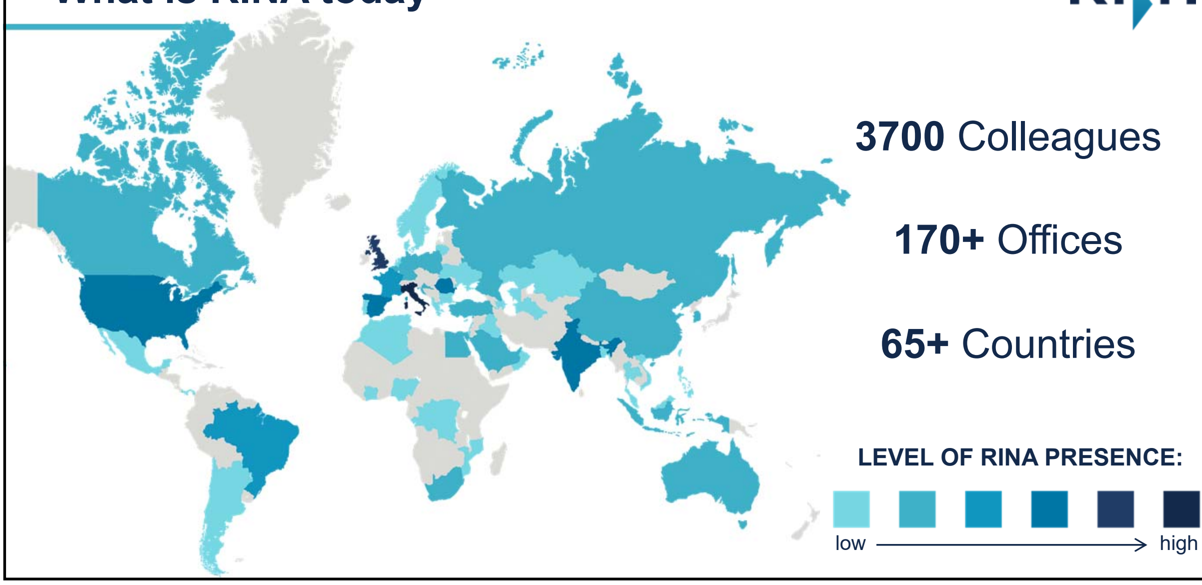
Competence and Experience

OVER 150 YEARS OF EXPERIENCE

RINA provides a wide range of services across the Energy, Marine, Certification, Transport & Infrastructure and Industry sectors through a global network of 170 offices in 65 countries.

RINA is a member of key international organisations and an important contributor to the development of new legislative standards.

What is RINA today

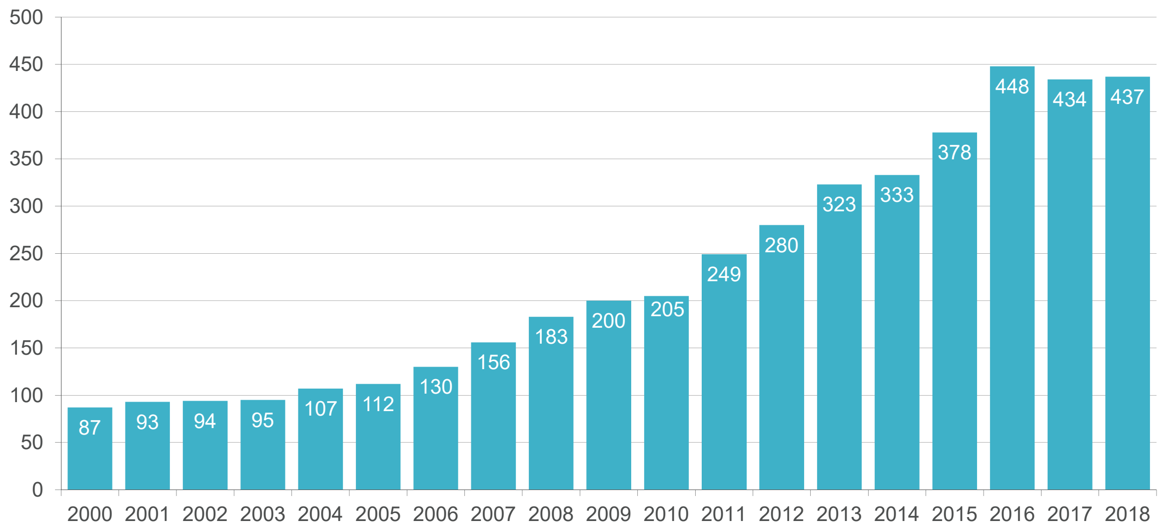


3700 Colleagues

170+ Offices

65+ Countries

REVENUES TURNOVER (millions of euro)



Our markets

ENERGY

ENERGY - OIL & GAS

SERVICES

- Geosciences
- Environment, HSE & Permitting
- Logistics
- Advanced Numerical Simulation
- Pre-FEED, FEED & Detail Design
- Project Management Consulting
- Operation & Maintenance Engineering
- Asset Integrity Management
- On Site Assistance
- Construction & Commissioning Management
- Inspection, Expediting and Material Management
- Vendor Qualification and Auditing
- QA/QC and Site Supervision
- Asset Classification or Certification

MARINE

SERVICES

- Classification and Statutory Services
- Certification of Material, Product & Personnel
- Marine Technical Advisory Services
- Training for crews and ship operators

TRANSPORT & INFRASTRUCTURE

SERVICES

- Studies, Conceptual Design & Feasibility
- Design Services
- PMC / Construction Supervision
- Technical Advisory
- Asset Integrity Management (AIM+)
- Environmental Impact Assessment
- Operation and Maintenance
- Decommissioning
- Logistics and Supply Chain
- Railway Certification & Testing
- Design Verification
- Site Supervision
- Technical Inspection on Buildings, Infrastructure & Railways
- Energy & Sustainability Audits in Real Estate
- Green Building Certification
- PPP - Public Private Partnership and PF - Project Finance Independent Verification

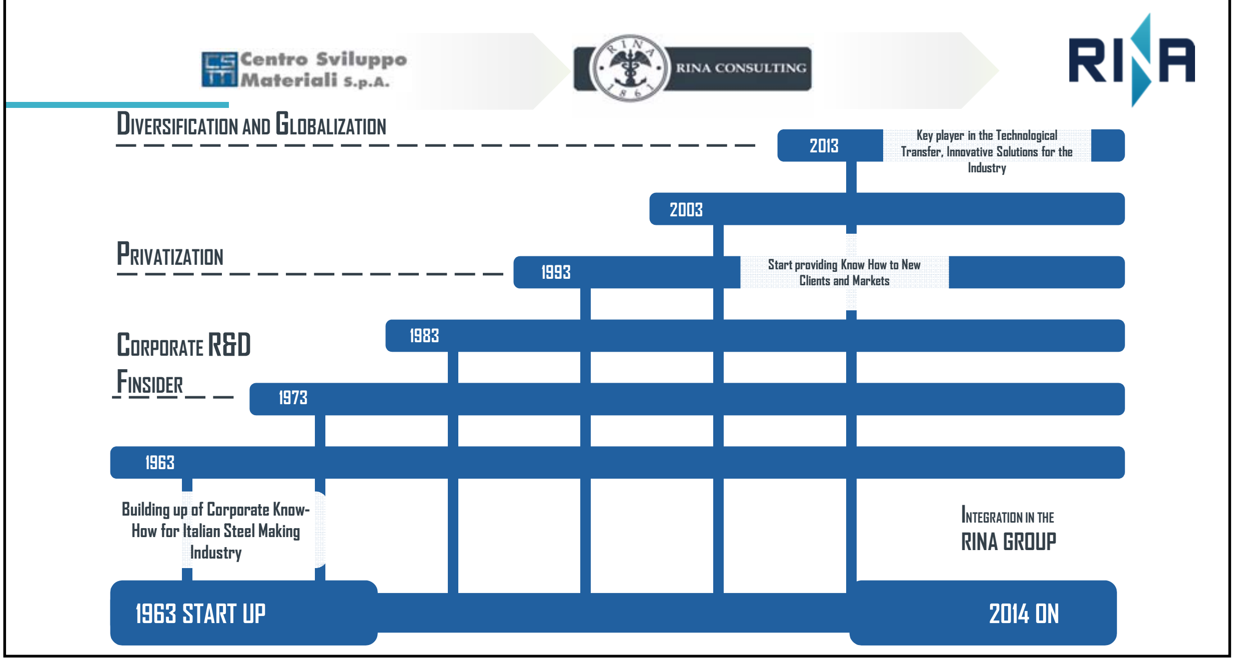
INDUSTRY

Materials, Technology & Innovation

SERVICES

- Innovation & Business Strategy
- Product Design & Engineering
- Materials and Product Development
- Manufacturing Process Innovation& Smart Manufacturing
- Material Selection & Qualification
- Product & Process Sustainability
- Fitness For Services
- Engineering Critical Assessment (ECA)
- Life Cycle Assessment
- Performance Assessment
- Condition Assessment & Forensics

CSM Overview



INNOVATION CHAIN

RINA

MATERIAL DEVELOPMENT
- Alloys Design for new materials at higher performance
- Alloy Design for Powders for Additive Manufacturing
- New special coatings

PROCESS DEVELOPMENT
- Steelmaking & Casting & Rolling & Forging
- Additive Manufacturing
- Heat treatment & Surface conditioning
- Welding and Joining

PRODUCT DEVELOPMENT
- Net shape and near net shape products
- Semi-products
- Coatings
- Flat, Long Products and Tubes
- Application Engineering
- Prototyping

CROSS – CUTTING TECHNOLOGIES
- Through process approach
- L2/L3 Control Systems
- Tailor made tools Customized sensors
- Technological DB

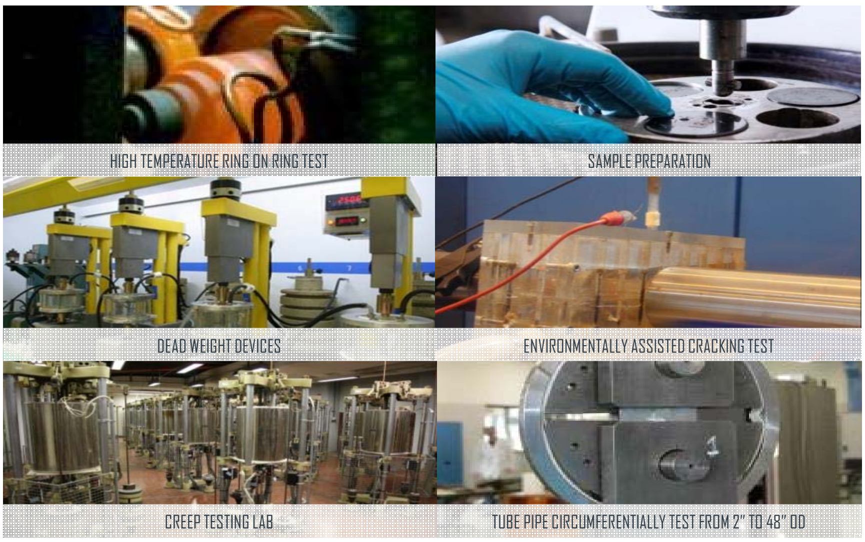
ENVIRONMENTAL SOLUTION
- Solid Waste Valorization
- Water Management
- Emission Reduction
- Energy Recovery

KEY ENABLING TECHNOLOGIES:

Nanotechnology, Advanced Materials, Advanced Manufacturing, Information and Communication Technology

INDUSTRY
LABORATORIES

RINA



Integrity Plan

RINA

Material Performance, standard, inspection strategy, at risk assets identification.

- Material Selection & Corrosion Assessment
- Engineering Critical Assessment (ECA)
- FFS (Fitness-For-Service)
- Failure Analysis
- Welding (WPS & WPQR)
- Creep, Fatigue, fracture mechanics,
- Corrosion mechanism evaluation
- Special Solutions for HSE
- RBI (Risk Based Insp.)
- QRA (Quantitative Risk Assessment)
- RAM (Reliability, Availability, Maint.)
- SIL (Safety Integrity Levels)
- RCM (Reliability Centered Maintenance)
- …

Inspection and Surveys

RINA

Inspection and survey to determine equipment/asset status.

- NDT Engineering
- Inspection
- Regulatory Compliance
- SHM (Structural Health Monitoring)
- NDT Examination
- Failure Analysis
- Testing
- …

Data Analysis

Inspection results analysis, interpretation and implications

- IDA (intelligent Data Analysis)
- LCA (Life Cycle Analysis)
- PoF (Probability of Failure)
- PM (Probability Modeling)
- Degradation Mechanism
- HSE Modelling
- …

Recommendation

Data Management, Feedback, and Plan Update

- Data Management
- Feedback and plan update
- Life cycle extension design
- Serviceability Design
- Material Selection Review
- Integrity Operating Window
- …

Appendix 2

List of participants

Participants EFC WP15 meeting 10th April 2019 Roma (Italy)

NAME	SURNAME	COMPANY	COUNTRY
Al Musharfy	Mohamed	ADNOC Refining Research Center	UNITED ARAB EMIRATES
Atzeri	Giuseppe	SARLUX	ITALY
Arduini	Barbara	Eni	ITALY
Bhamji	Imran	TWI	UK
Bour Beucler	Valerie	Nalco Champion	FRANCE
Corradini	Raffaele	Techint Engineering Construction	ITALY
de Freitas Barbosa	Gustavo Simiema	KAEFER Isoliertechnik GmbH & Co. KG	GERMANY
De Landtsheer	Gino	Borealis	BELGIUM
de Marco	Marco	Istituto Italiano della Saldatura	ITALY
Del Ferraro	Walter	Versalis stabilimento di Mantova	ITALY
Faraone	Nicola	Voestalpine Böhler Welding GmbH	ITALY
Fersini	Maurizio	Allied Fittings	ITALY
Fischbacher	Peter	Emerson Automation Solutions	ITALY
Fullin	Luna	Tenaris Dalmine	ITALY
Giodafatto	Ugo	CND Service	ITALY
Kawakami	Tadashi	Nippon Steel Cooperation European Office	GERMANY
Kawana	Kosuke	Mitsui & Co Ltd	JAPAN
Koller	Swen	Holborn Europa Raffinerie GMBH	GERMANY
Kuehn	Michael	PPG Protective & Marine Coatings	UK
Leone	Antonino	Eni	ITALY
Lombardo	Paolo	Isab Lukoil Company	ITALY
Loyan	Sophie	Total	FRANCE
Lucci	Antonio	Rina Consulting	ITALY
Madeddu	Enrico	Sartec	ITALY
Miranda	Michele	ENI	ITALY
Monnot	Martin	Industeel	FRANCE
Onodera	Yoichi	Mitsui & Co Ltd	JAPAN
Rehberg	Thomas	KAEFER Isoliertechnik GmbH & Co. KG	GERMANY
Rigodanze	Luca	Versalis stabilimento di Mantova	ITALY
Rodriguez Jorva	Javier	CEPSA	SPAIN
Ropital	François	IFP Energies nouvelles	FRANCE
Rothwell	John	TWI	UK
Smith	Ali	RINA Consulting - CSM S.p.A	ITALY
Suardi	Edoardo	SARLUX	ITALY
Suleiman	Mabruk	ADNOC Refining Research Center	UNITED ARAB EMIRATES
Van Rodijnen	Fred	Oerlikon metco	GERMANY
van Roij	Johan	Shell Global Solutions International B.V.	NETHERLANDS
Wassink	Casper	Eddyfi Technologies	FRANCE
Zabbia	Marco	Istituto Italiano della Saldatura	ITALY
Zlatnik	Ivan	MITSUI & Co Deutschland	CZECH REPUBLIC

Appendix 3

EFC WP15 Activities

(F. Ropital)

EFC Working Parties

http://www.efcweb.org

- WP 1: Corrosion Inhibition
- WP 3: High Temperature
- WP 4: Nuclear Corrosion
- WP 5: Environmental Sensitive Fracture
- WP 6: Surface Science and Mechanisms of corrosion and protection
- WP 7: Education
- WP 8: Testing
- WP 9: Marine Corrosion
- WP 10: Microbial Corrosion
- WP 11: Corrosion of reinforcement in concrete
- WP 12: Computer based information systems
- WP 13: Corrosion in oil and gas production
- WP 14: Coatings
- WP 15: Corrosion in the refinery and petrochemistry industry
  (created in sept. 96 with John Harston as first chairman)
- WP 16: Cathodic protection
- WP 17: Automotive
- WP 18: Tribocorrosion
- WP 19: Corrosion of polymer materials
- WP 20: Corrosion by drinking waters
- WP 21: Corrosion of archaeological and historical artefacts
- WP 22: Corrosion control in aerospace
- WP 23: Corrosion reliability of Electronics

- Task Force on Corrosion in CO_2 Capture Storage (CCS) applications
- Task Force on atmospheric corrosion

Presentation of the activities of WP15

European Federation of Corrosion (EFC)

- Federation of 29 National Associations
- 21 Working Parties (WP) and 1 Task Force
- Annual Corrosion congress « Eurocorr »
- Thematic workshops and symposiums
- Working Party meetings (for WP15 twice a year)
- Publications

for more information http://www.efcweb.org

EFC Working Party 15 « Corrosion in Refinery » Activities

http://www.efcweb.org/Working+Parties-p-104085/WP%2B15-p-104111.html

Chairman: Francois Ropital   Deputy Chairman: Johan Van Roij

Information Exchange – Forum for Technology
Sharing of refinery materials /corrosion experiences by operating company representatives (ie corrosion atlas).
Sharing materials/ corrosion/ protection/ monitoring information by providers

Eurocorr Conferences : organization of refinery session and joint session with other WPs (2018 Krakow-Poland, 2019 Seville-Spain, 2020 Brussels-Belgium)

WP Meetings
One WP 15 working party meeting in Spring,
One meeting at Eurocorr in September in conjunction with the conference,

Publications - Guidelines

Education – qualification – certification
List of "corrosion refinery" related courses on EFC website ?
Proposal of courses within Eurocorr ?

EFC Working Party 15 « Corrosion in Refinery »

List of the WP15 spring meetings :

10 April 2003	Pernis - NL (Shell)
8-9 March 2004	Milan -Italy (ENI)
17-18 March 2005	Trondheim- Norway (Statoil)
31 March 2006	Porto Maghera - Italy (ENI)
26 April 2007	Paris - France (Total)
15 April 2008	Leiden -NL (Nalco)
23 April 2009	Vienna - Austria (Borealis)
22 June 2010	Budapest - Hungary (MOL)
14 April 2011	Paris - France (EFC Head offices)
26 April 2012	Amsterdam - NL (Shell)
9 April 2013	Paris - France (Total)
8 April 2014	Mechelen - Belgium (Borealis)
14 April 2015	Leiden -NL (Nalco)
26 April 2016	Paris - France (Total)
13 April 2017	Frankfurt - Germany (EFC Head offices)
3 May 2018	Dalmine - Italy (Tenaris)
10 April 2019	Roma - Italy (Rina CSM)

Publications from WP15

• EFC Guideline n°40 « Prevention of corrosion by cooling waters » available from http://www.oxbowbooks.com/oxbow/working-party-report-on-control-of-corrosion-in-cooling-waters.html

•EFC Guideline n° 55 Corrosion Under Insulation *A second revision is in progress by a task forve*

•EFC Guideline n° 46 on corrosion in amine units *A revision is in progress by a task force*

•Future publications – task forces :

- best practice guideline on corrosion in sea water cooling systems (joint document WP9 Marine Corrosion and WP15). A task force started
- best practice guideline to avoid and characterize stress relaxation cracking ?

WP9-15 Best practice guideline on corrosion in sea water heat exchangers systems

1- Introduction **M. Suleiman** (chapter leader)
2- Main seawater heat exchangers systems and other uses, **M. Suleiman** (chapter leader)**,** V. Bour-Beucler (contributor)
3- Seawater environment: aggressivity, living organisms, deposits and scale formation, pretreatment **A.M. Grolleau** (chapter leader) . M. Suleiman
4- Different forms of corrosion in sea water heat exchangers systems (galvanic, crevice, erosion…) **A.M. Grolleau** (chapter leader), F. Ropital
5- Biocide treatments (chlorination) – how they can affect the corrosion resistance **V. Bour-Beucler** (chapter leader) A.M. Grolleau, P. Bleriot
6- Corrosion and scale inhibitors **P. Bleriot (**chapter leader)
7- Corrosion tests **A.M. Grolleau** (chapter leader)
8- Materials used **A. Surbled** (chapter leader)
8.1- Carbon steels and coating and concrete A. Surbled F. Dupoiron
8.2- Stainless steels D. Thierry, A.M. Grolleau A. Philipp
8.3- Nickel base alloy D. Thierry, A.M. Grolleau , A. Philipp
8.4- Copper alloys A.M. Grolleau
8.5- Aluminium, Titanium alloys A. Surbled F. Dupoiron
8.6- Plastics , composites, non metallic J.M Daubenfeld, M. Suleiman
9- Corrosion protection **J.Z. Zhang** (chapter leader)
9-1 Material selection to avoid galvanic corrosion J.Z. Zhang
9-2 Coatings J.Z. Zhang
9-3 Corrosion control by use of cathodic protection A.M. Grolleau, J.Z. Zhang
10- Maintenance and tube cleaning **F. Dupoiron** (chapter leader) J.Z. Zhang A. Surbled,
11- Control and monitoring, inspection techniques **A. Surbled** (chapter leader)

EFC EUROPEAN FEDERATION OF CORROSION

WP15 Corrosion Atlas Web page

http://www.efcweb.org/Working+Parties/WP+Corrosion+in+the+Refinery+Industry/WP+15+Refinery+Corrosion+Atlas.html


EUROPÄISCHE FÖDERATION KORROSION
EUROPEAN FEDERATION OF CORROSION
FEDERATION EUROPEENNE DE LA CORROSION

Search

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Welcome > Working Parties > WP Corrosion in the Refinery Industry > WP 15 Refinery Corrosion Atlas

Who we are
EFC Membership
Working Parties
WP Corrosion and Scale Inhibition
WP Corrosion by Hot Gases and Combustion Products
WP Nuclear Corrosion
WP Environment Sensitive Fracture
WP Surface Science and Mechanisms of Corrosion and Protection
WP Corrosion Education
WP Physico-chemical Methods of Corrosion Testing
WP Marine Corrosion
WP Microbial Corrosion
WP Corrosion of Steel in Concrete
WP Corrosion in Oil and Gas Production
WP Coatings
WP Corrosion in the Refinery Industry
WP 15 Refinery Corrosion Atlas
CUI Restricted Web Page
WP Cathodic Protection
WP Automotive Corrosion

EFC Working Party 15: Corrosion in the Refinery Industry

WP 15 REFINERY CORROSION ATLAS

On this page you will find some corrosion failure cases from the refinery and process industries.

These documents are only given for information and do not engage EFC.

Failure case n°1: High temperature corrosion of a first stage reactor of a hydrocracking unit

Failure case n°2: Chloride stress corrosion cracking of a H2S stripping tower in a hydodesulfurisation unit

Failure case n°3: Creep and cracks in a hydodesulfurisation unit

Failure case n°4: Chloride stress corrosion cracking of mounting hardware in a FCC

Failure case n°5: Metal dusting corrosion of a furnace tube in reforming unit

Failure case n°6: Sulfidation in an atmospheric distillation unit

Failure case n°7: HF stress corrosion cracking in an alkylation unit

Failure case n°8: Carbonate stress corrosion cracking in an FCC unit

If you would like to add other failure cases, you can complete the enclosed file and send it to Francois Ropital email: francois.ropital@ifpen.fr

EFC WP15 Spring meeting 10 April 2019 Roma - Italy

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EFC EUROPEAN FEDERATION OF CORROSION

Eurocorr 2019 Congress

Seville Spain 9-13 September 2019

Authors will be informed by the end of April

Refinery corrosion session on Thursday and Friday 12th 13th September full days- to be confirmed-

Annual WP15 working party meeting during Eurocorr on Wednesday 11th September – May be also face to face taskforce meetings on CUI and amine units guidelines
-to be confirmed -

EUROCORR The European Corrosion Congress

https://eurocorr.org/EUROCORR+2019.html

8

Information :
Future conferences related to refinery corrosion

8-13 September 2019
EUROCORR 2019 Seville Spain

15-19 March 2020
CORROSION 2020 NACE Conf Houston Texas

6-10 September 2020
EUROCORR 2020 Brussels Belgium

19-23 September 2021
EUROCORR 2021 Budapest Hungary

Look at the Website: www.efcweb.org/Events

EFC WP15 Spring meeting 10 April 2019 Roma - Italy

9

Appendix 4

Recent lean amine (alkaline) stress corrosion cracking experiences

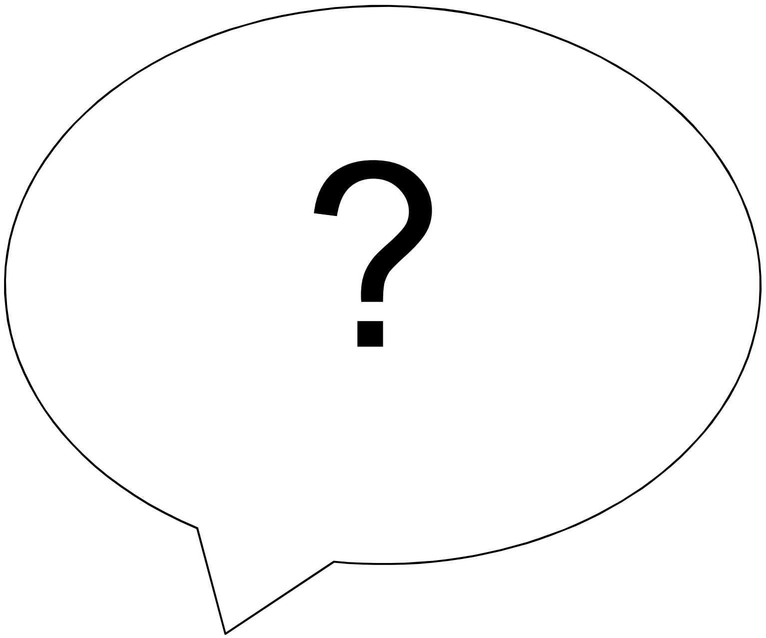
(S. Loyan)

TOTAL RECENT LEAN AMINE CRACKING REX

Sophie LOYAN (TOTAL Refining & Chemicals)

EFC WP15 Spring meeting– April 2019

ALKALINE STRESS CORROSION CRACKING - ASCC



ALKALINE STRESS CORROSION CRACKING - ASCC

Passive surface
+
Film rupture mechanism under plastic strain
+
Rapid repassivation

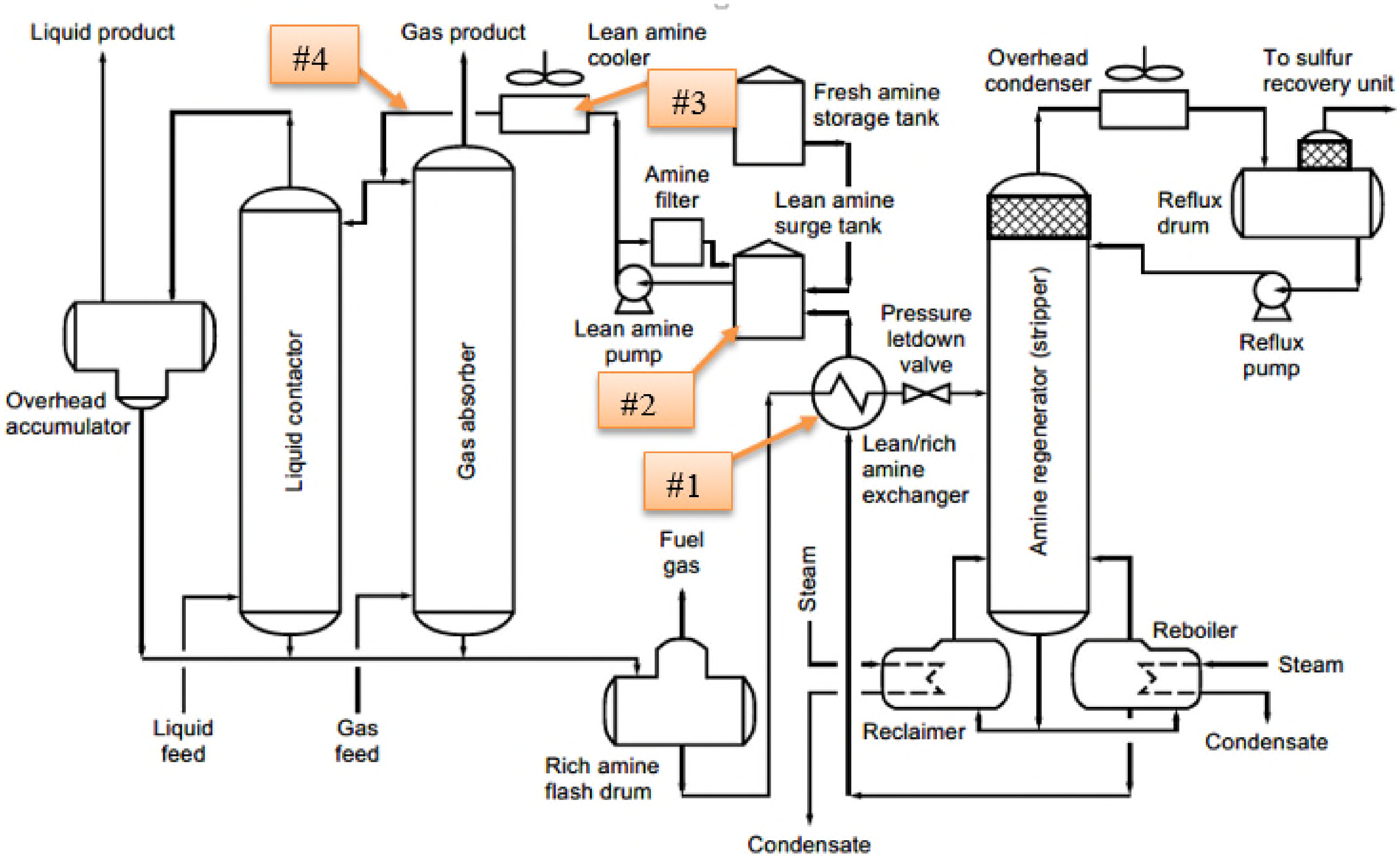
SCC found in lean MEA & DEA at potentials between – 600 & - 800 mVsce

Intergranular cracking at potentials near active/passive transition

<u>Influence factors </u>for SCC in amine solution :

- Type of amine
- Concentration of amine solution
- Temperature of metal
- Tensile stress level
- Chemistry of the solution (no ASCC in fresh amine or with strongly sulfidizing environment).

AMINE UNIT : ASCC REX

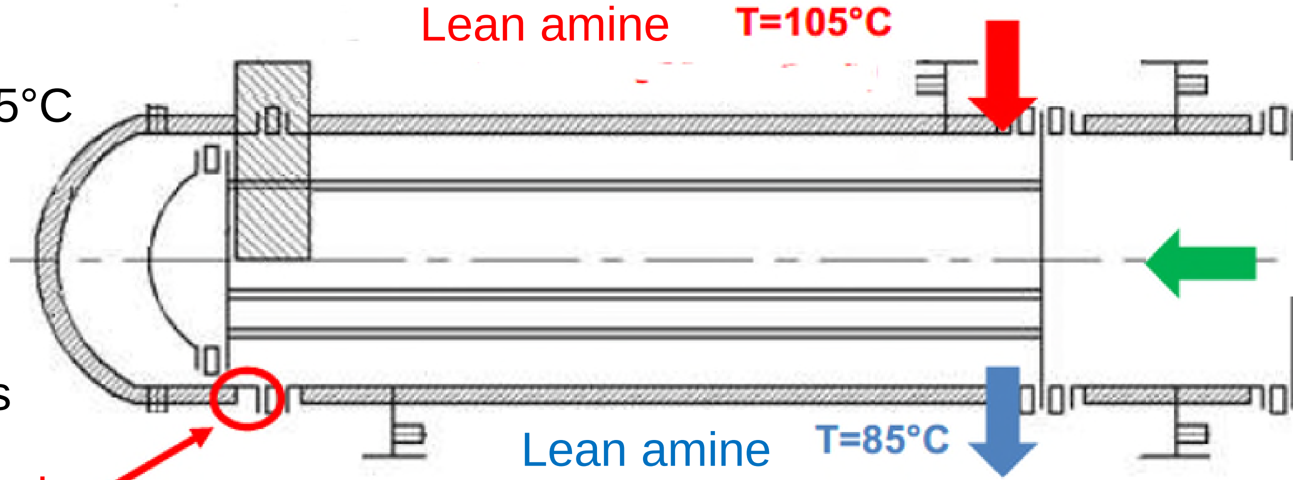


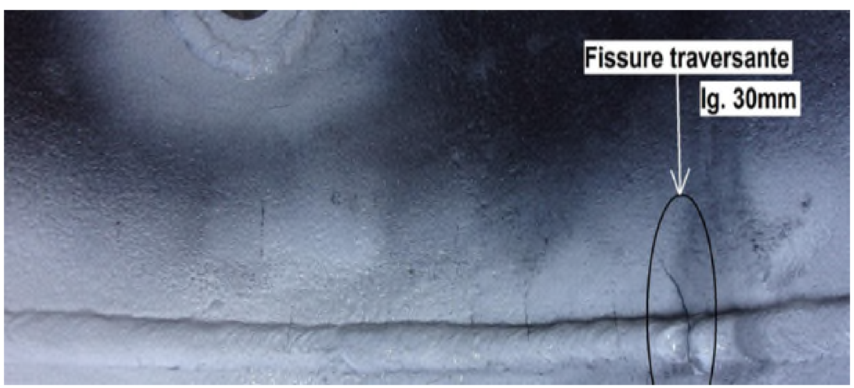
1 : LEAN/RICH AMINE HEAT EXCHANGER

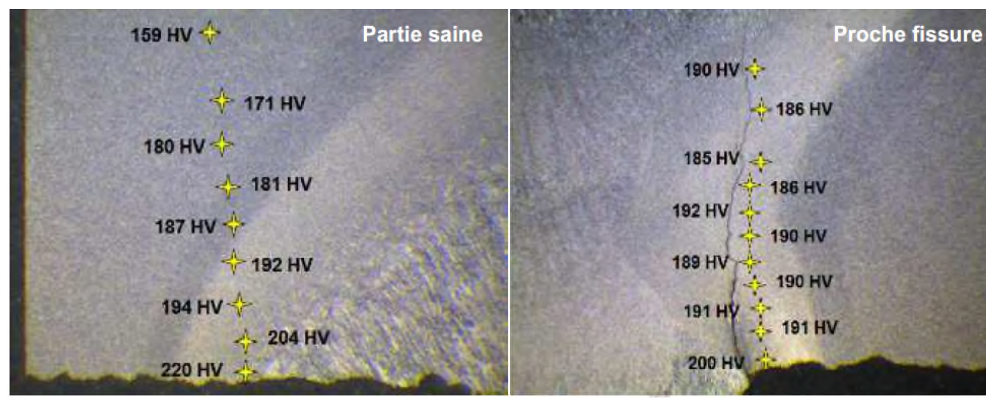
ASCC : LEAN/RICH AMINE HX

FCC unit
DEA 25-28%
P : atmospheric
T in/out 105°C/85°C

CS PWHT
Insulated
12 mm thick
Lifetime 45 years







Micro hardness : Hv0.1

ASCC : LEAN/RICH AMINE HX

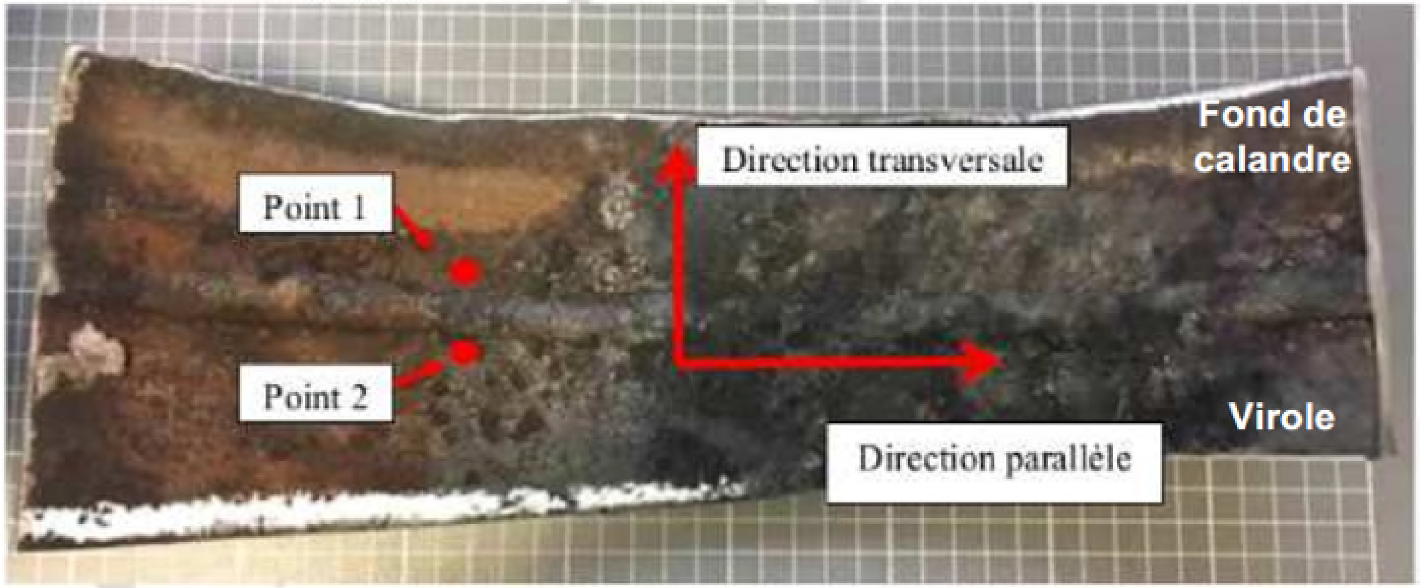


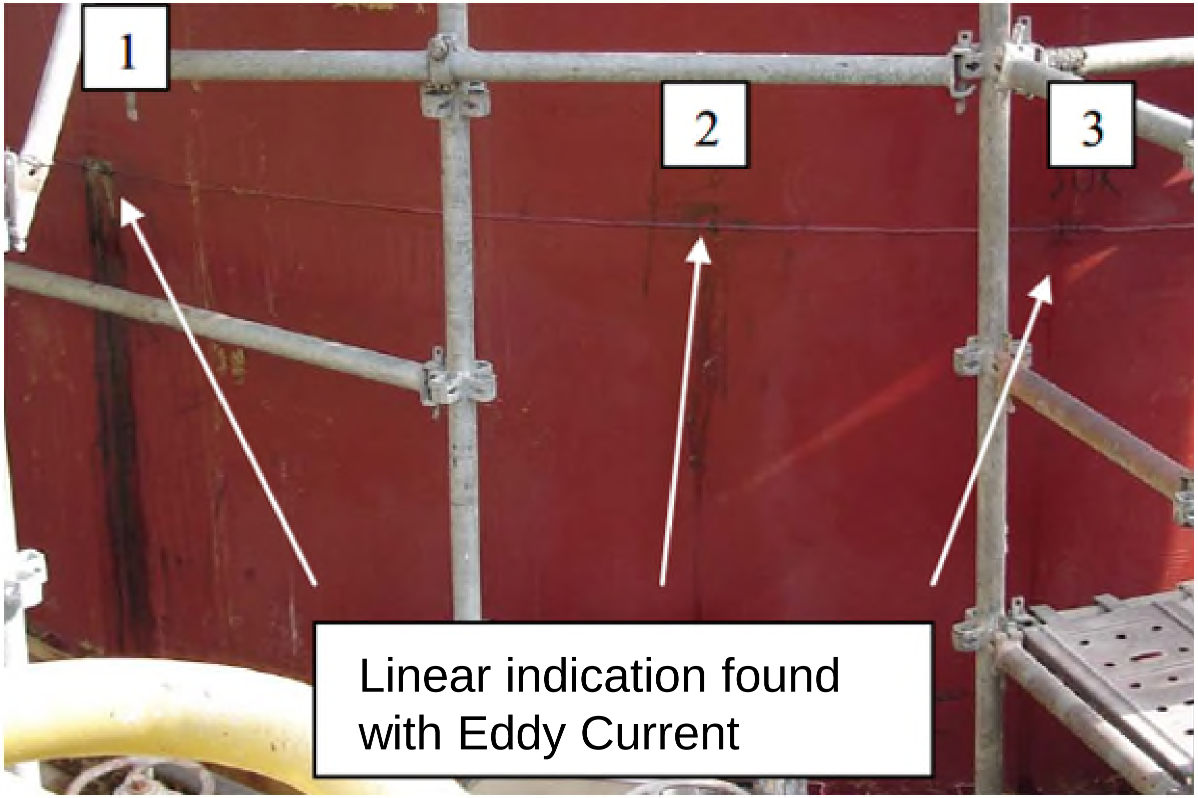
Figure 9 : localisation des mesures de contraintes résiduelles

	Contraintes parallèles (MPa)	Contraintes transversales (MPa)
Point 1	98	-17
Point 2	42	-62

Tableau 1 : Résultats des analyses de contraintes résiduelles orientation donnée par rapport au cordon

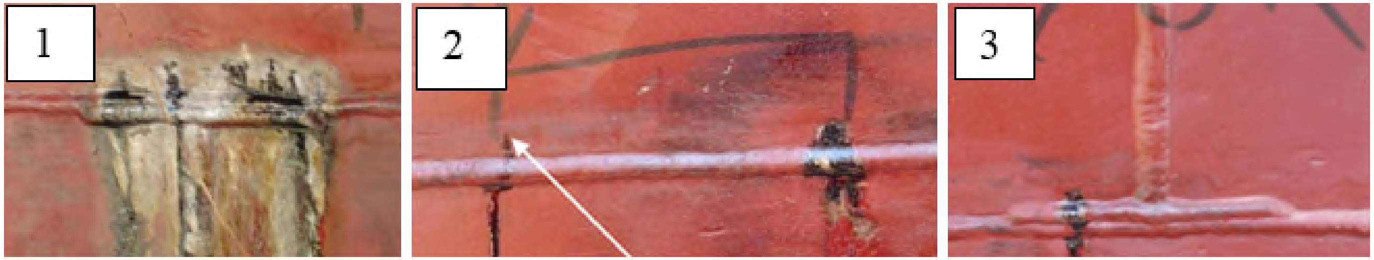
2 : LEAN AMINE TANK

ASCC : LEAN AMINE TANK

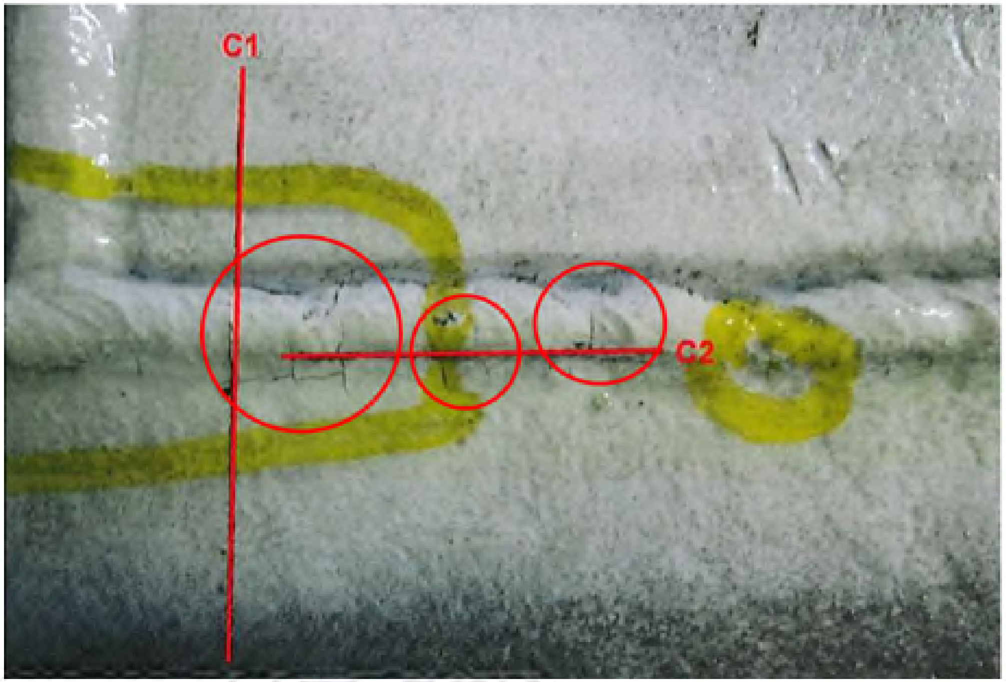


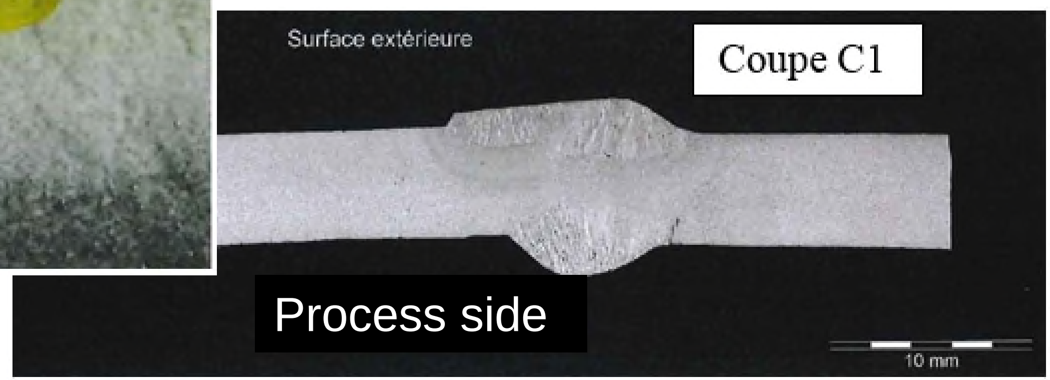
FCC unit
DEA 25-28%
P : atmospheric
T : 78°C

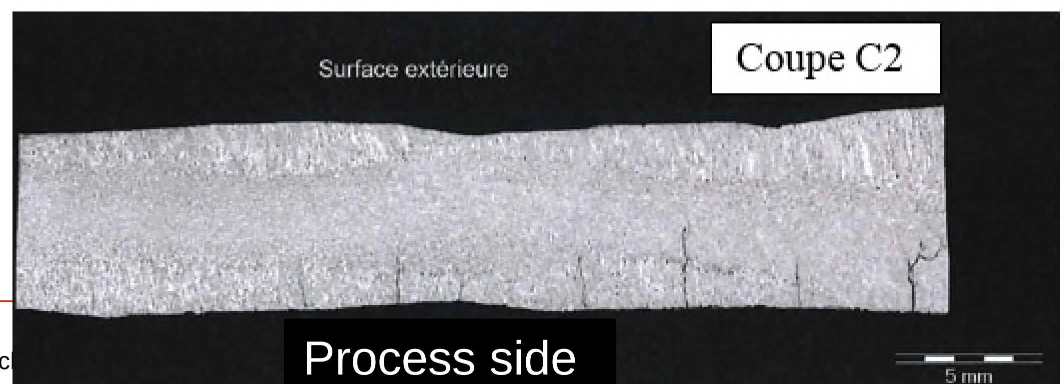
CS PWHT
Insulated
6 mm thick
Steam coil in the bottom (1,5 barg)
Lifetime 15 years



ASCC : LEAN AMINE TANK





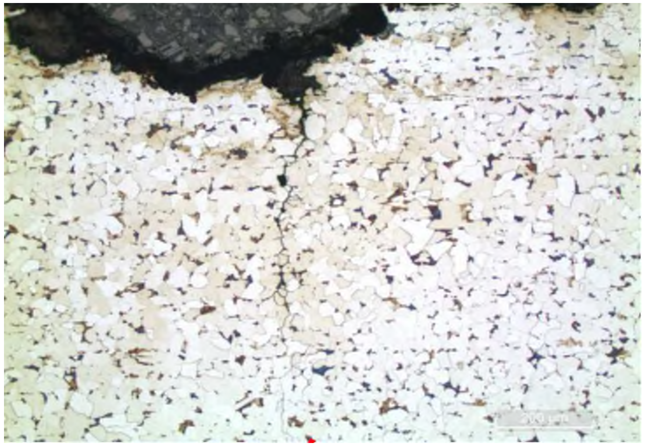


3 : AIR COOLER (EXPANDED JOINT)

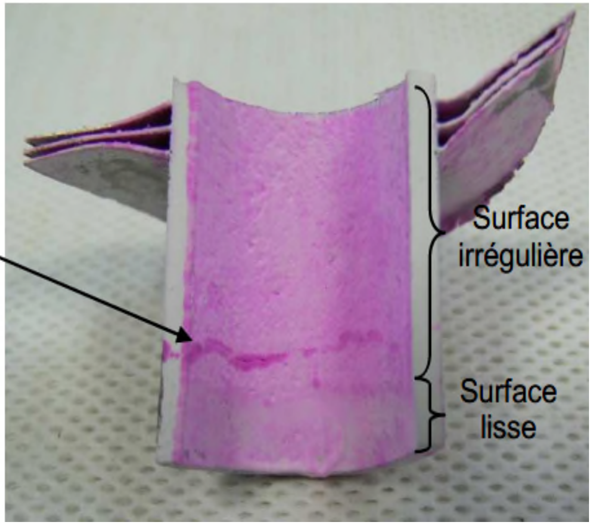
ALKALINE STRESS CORROSION CRACKING - ASCC

HDS unit
DEA 25 %
P : 11 barg
T in/out: 55-70°C/35-55°C

CS expanded jointed
2,4 mm thick; 25,4mm diameter
Lifetime 35 years



crack

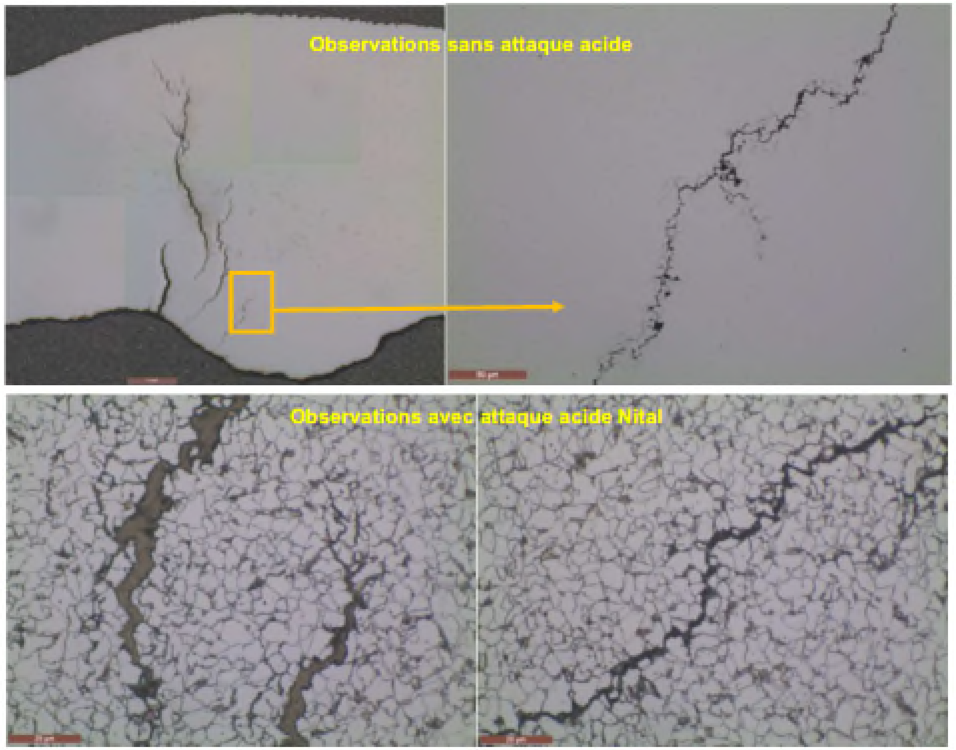


4 : LEAN AMINE PIPING

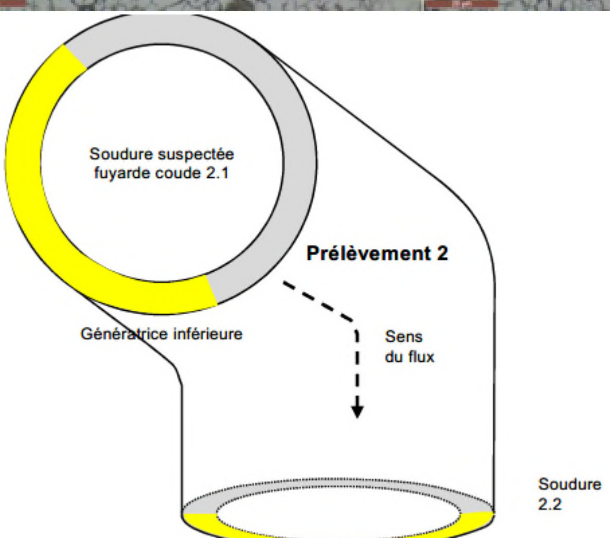
HDS unit
DEA 30 %
P : 10 barg
T: 50-70°C

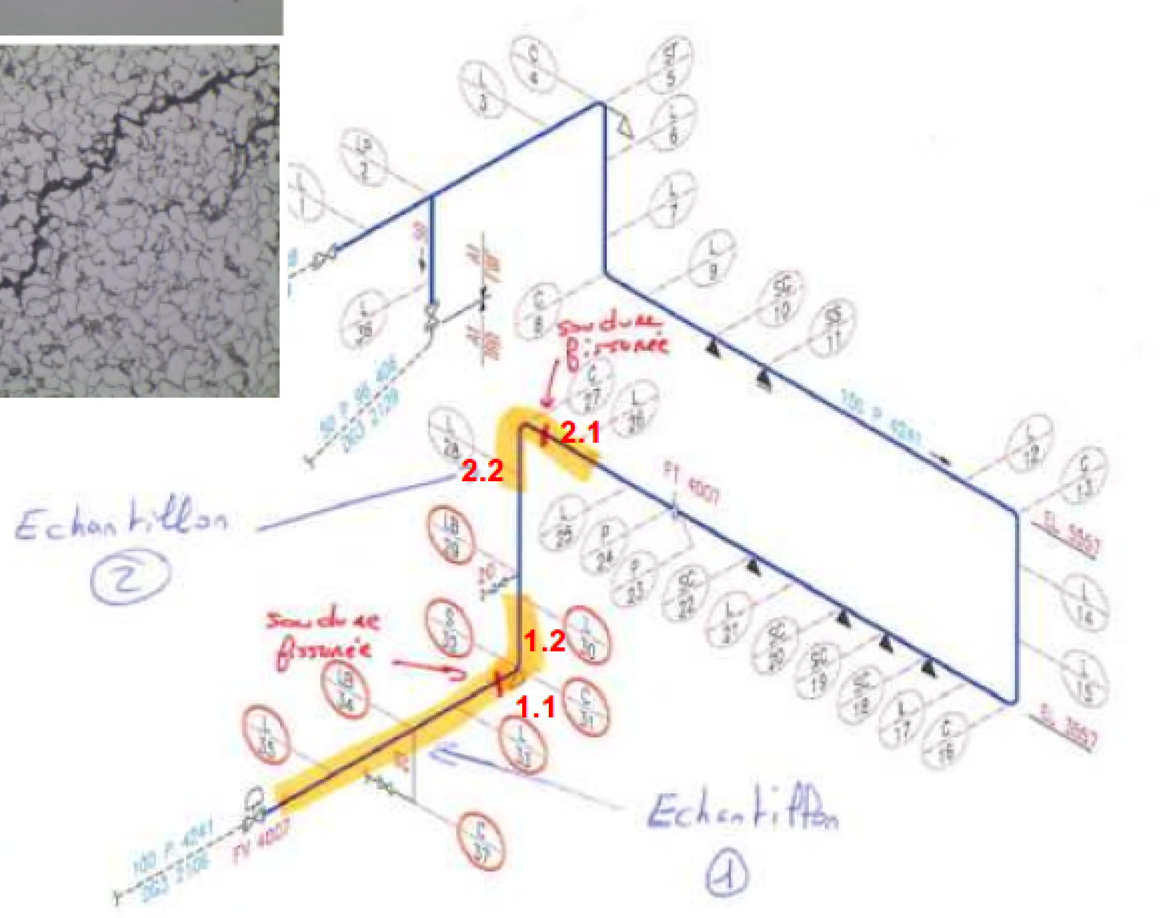
CS PWHT
6 mm
Insulated + steam traced (with 3,5barg saturated steam)
Lifetime 46 years

ASCC : PIPING



	Echantillon 1.1		
	Pied de cordon	1mm du pied de cordon	Métal de base
Contraintes (MPa)	61	35	-77





MAIN TAKEAWAYS

- All TOTAL ASCC REX in lean amine were with DEA solution (not with MDEA)
- Leak = pinhole difficult to find/identify – absence of thickness loss
- Every kind of CS pressure vessel or piping can be concerned
- Original PWHT is not a guarantee to avoid ASCC
- Hardness measurement are not representative to residual tensile stress
- Effect of temperature **++**
- Quality of lean amine solution in the mechanism ? Effect of decommissioning for shutdowns with steam out ? Quality of DEA ?

RECOMMENDATIONS

- Inspection plan should also focus on PWHT equipment & piping for lean amine cracking detection.

- For manufacturing:
  - ✓ **PWHT quality for a good stress relieve efficiency**
  - ✓ Respect rules of the art (welding, joint expansion).
  - ✓ Use Stainless Steel taking into account technical and economical reasons

Appendix 5

Permasense monitoring for amine units

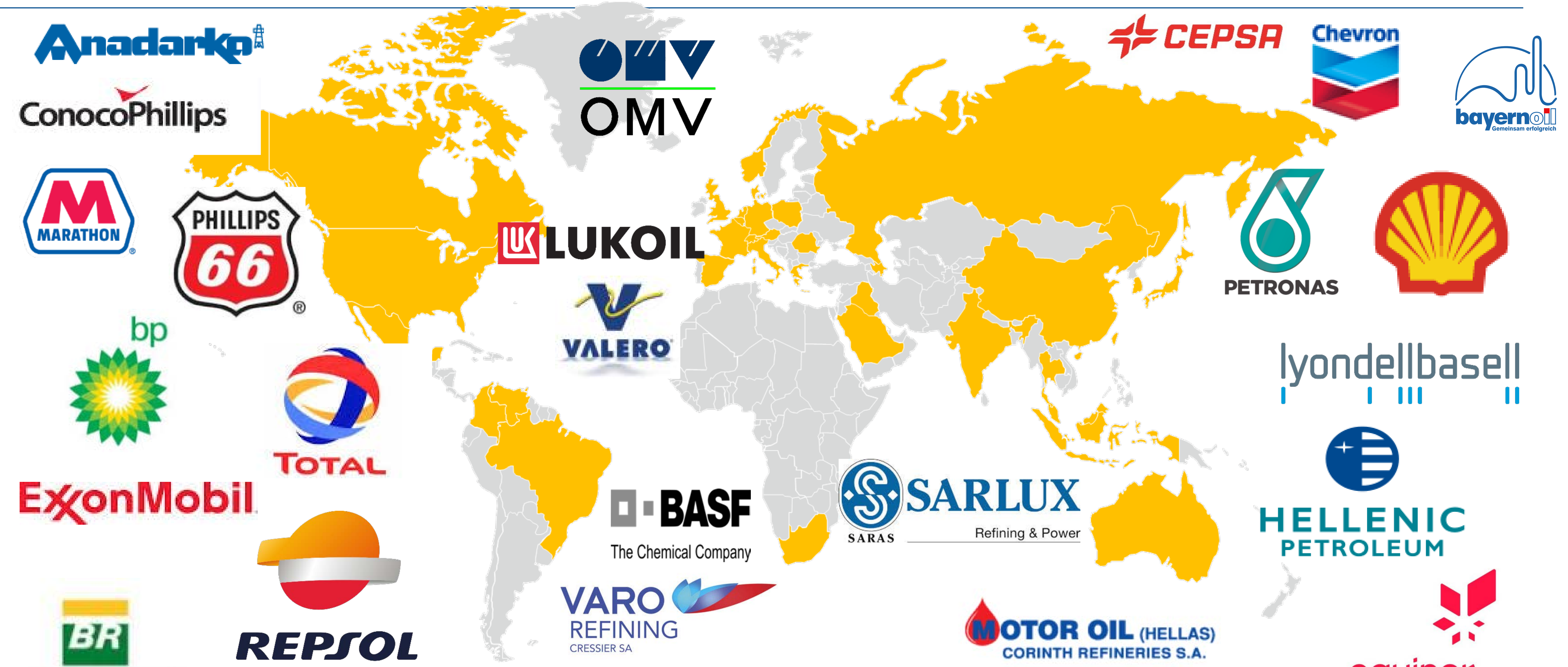
(P. Fischbacher)

Permasense Non-Intrusive Corrosion & Erosion Monitoring Solutions

EFC WP15 Corrosion Refinery Industry 10th April 2019 Meeting

PETER FISCHBACHER – PETER.FISCHBACHER@EMERSON.COM

Global Experience to-date



>20,000 sensors in >185 facilities in >40 countries

>18 million wall thickness measurements delivered to desk, >170 million operating hours

Permasense Applications

Opportunity Feedstock – real time online corrosion data, effective & efficient asset integrity management. Utilizing feedstock of different quality.

Increased Productivity – continuous, increased production rates & facilitate decision to increase productivity

Process Optimization – root cause analysis to minimise or even eliminate process attributed corrosion including material selection, to maximise production uptime

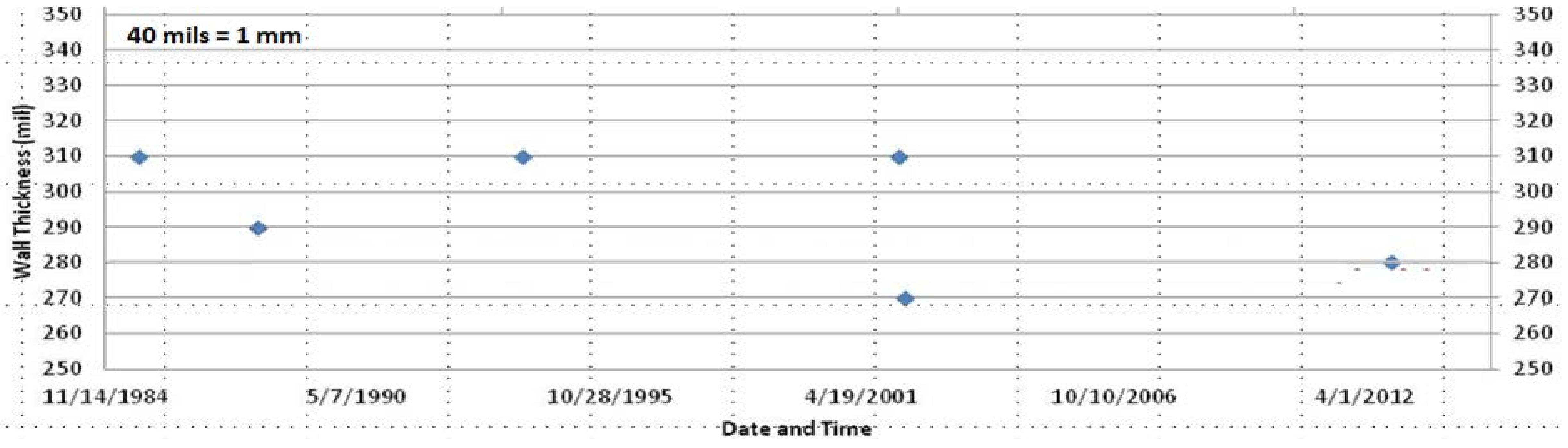
Extended Equipment Life Span & Planned Shutdown – understanding of corrosion behaviour to implement self regulation asset management system, determine planned shutdown period

Unmanned Operations / Reduction of OPEX – to minimise human intervention especially to hazardous, inaccessible area or unmanned platform resulting in improved safety & reduction of operational cost

Treatment Optimisation - monitor effectiveness of chemical injection, optimise chemical consumption & minimise inevitable corrosion

Traditional Corrosion Monitoring Approaches

- **Intrusive (ER probes)**
  - Fast response to changes in corrosion risk (if real time data delivery is given)
  - Maintenance headaches
  - Indirect measurement
- **Manual UT inspection**
  - Good snapshot of current equipment integrity
  - Very infrequent and poor repeatability, safety issues at high-temperatures
  - Normal UT measurements get confused by internal roughness

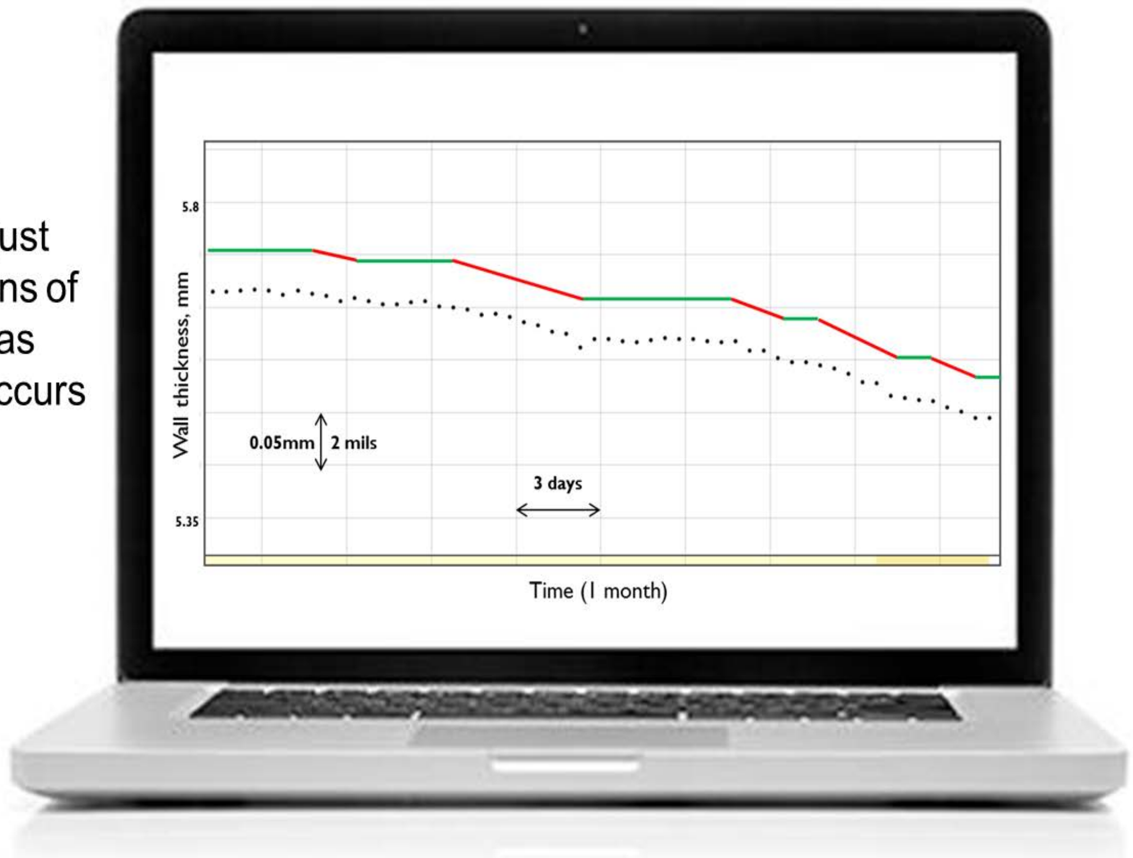


permasense
Experts in remote monitoring solutions

Best Quality and Frequency of Thickness Measurements

- **Fast Response to Corrosion and/or Erosion by using Permasense**
  - Outstanding measurement repeatability affords detection and measurement of ≈ 10 microns of metal wall loss
  - Regular data delivery (e.g. every 12 hours) allows detection of corrosion or erosion events within days
  - **Exceptional tool to service Maintenance & Inspection with corrosion monitoring & improve plants profitability!**

Measure just 10s microns of wall loss, as the loss occurs



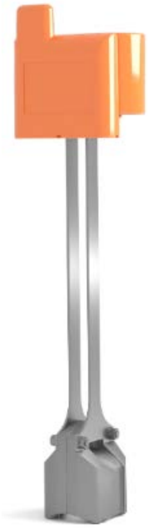
EMERSON

Non-Intrusive Sensors for Any Location, Operating at Any Temperature

ET210

ET310

ET410



WT210

	ET210	ET310	ET410	WT210
Temperature Range	Up to 120°C (250°F)	Up to 200°C (320°F)	Up to 300°C (518°F)	Up to 600°C (1100°F)
Measurement Technique	Ultrasound – EMAT			Ultrasound - Waveguide
Battery Life	Up to 9 Years			
Hazardous Area	Class 1 div 1 / Zone 0			
	Sharing WirelessHART infrastructure – all data viewed in DataManager at desk			

EMAT-based sensor specifications

permasense
Experts in remote monitoring solutions

PERMASENSE QUALITY DATA

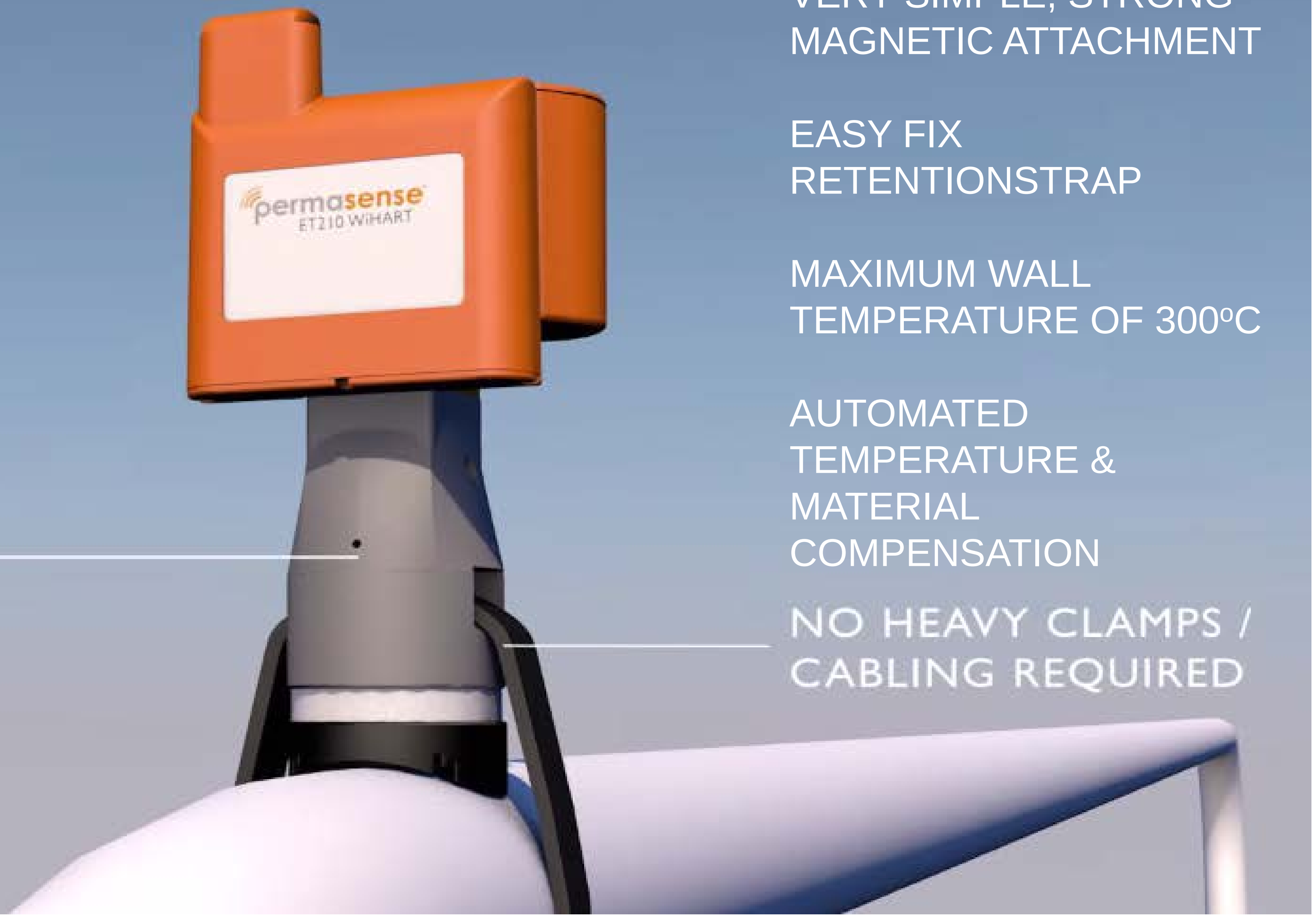
INTRINSICALLY SAFE SENSORS

ULTRA-LOW POWER CONSUMPTION: up to 9 year battery life

NON-INTRUSIVE

NO NEED TO REMOVE EXTERNAL COATINGS (up to 1000 micron)

WirelessHART TECHNOLOGY



VERY SIMPLE, STRONG MAGNETIC ATTACHMENT

EASY FIX RETENTIONSTRAP

MAXIMUM WALL TEMPERATURE OF 300ºC

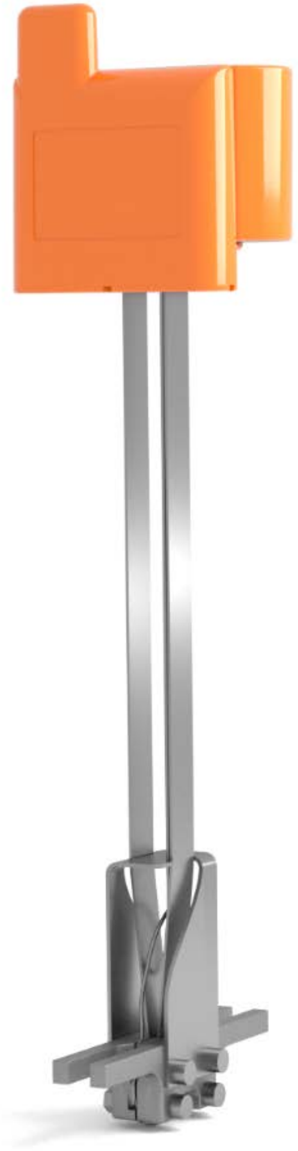
AUTOMATED TEMPERATURE & MATERIAL COMPENSATION

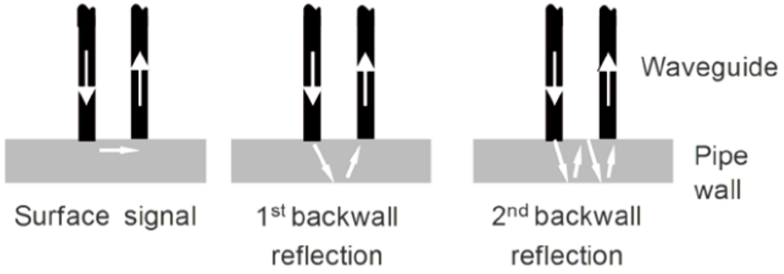
NO HEAVY CLAMPS / CABLING REQUIRED

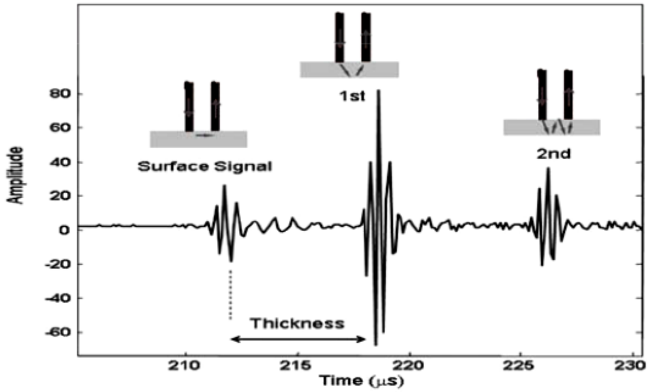
EMERSON

WT Technology - unique high temperature capability

- **Based on established ultrasound technology**
  - Unique waveguide transducer
  - Permanent installation
- **Install anywhere**
  - Temperatures up to 600 C (1100°F), e.g. refinery crude unit pipework
  - Temperatures down to -180 C (-292°F), e.g. LNG plants
  - Intrinsically safe (Class1 Div1)
- **Data to Desk**
  - WirelessHART
  - 7-9 Year battery life
  - Remotely adjustable data acquisition rate
  - Automated temperature and material compensation
  - Unique and patented processing to eliminate internal surface roughness effects and detect onset of corrosion activity





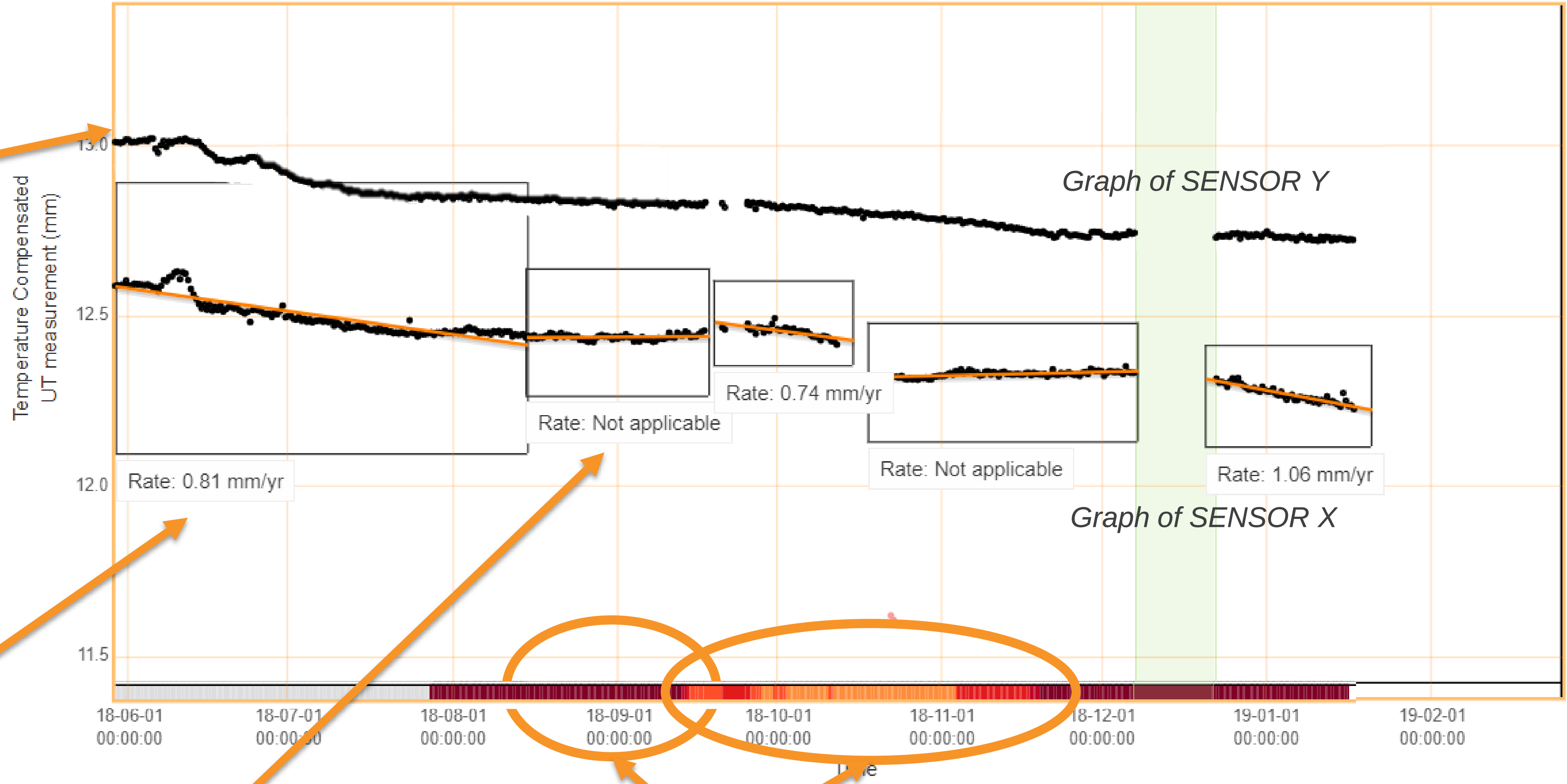


Typical signal and wave path from the sensor.

permasense
Experts in remote monitoring solutions

Permasense Wall Thickness Trend Evaluations

Similar corrosion trend – corroborating data brings confidence



What happened here?

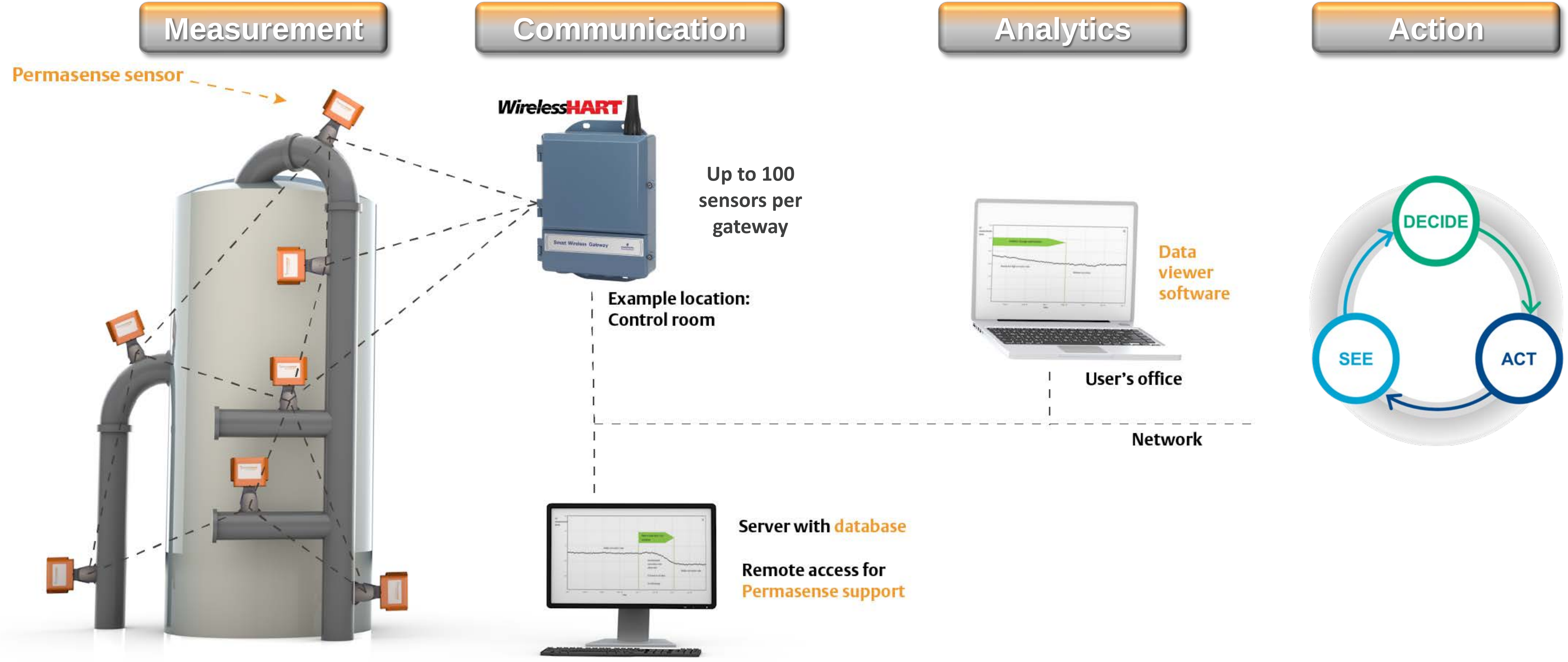
That did not happen here?

PSI shows less internal activity. Crude slate change? Inhibitor increase? Sulphur Content?

EMERSON.

permasense
Experts in remote monitoring solutions

System Overview – Real Time Asset Health Data to Desk



Easily installed, on-line. Typical size system installed in 3-4 days.

EMERSON

Refinery Case Study Amine Unit Corrosion Monitoring

EMERSON

Overview of Corrosion Issues in Amine Units

- Corrosion in amine units can be divided in two types
  - Wet acid gas corrosion of carbon steel from the reaction of CO2 and H2S with iron through a thin liquid film;
  - Amine solution corrosion of carbon steel in the presence of aqueous amine
- Key variables for assessing amine unit corrosion
  - Acid gas loading
  - Velocity and wall shear stress
  - Temperature
  - Impurities and heat stable amine salts
  - CO2 to H2S ratio
  - Choice of amine type

Averaged corrosion rates for carbon steel

Velocity [ft/s]	H2S loading as molar ratio to MEA 0.2	0.4	0.6	0.8
0	0	0	1	1
20	8	12	12	12
40	12	14	16	20
60	13	16	20	43
80	16	18	25	66

dark green	< 5 mpy
light green	5 - 10 mpy
yellow	10 - 15 mpy
orange-yellow	15 - 20 mpy
orange	20 - 50 mpy
red	> 50 mpy

Figure above shows the predicted variation of corrosion rates for carbon steel with amine acid gas loading and velocity. This shows that, as would be expected, high rich amine H2S loading combined with high velocity results in higher corrosion rates.

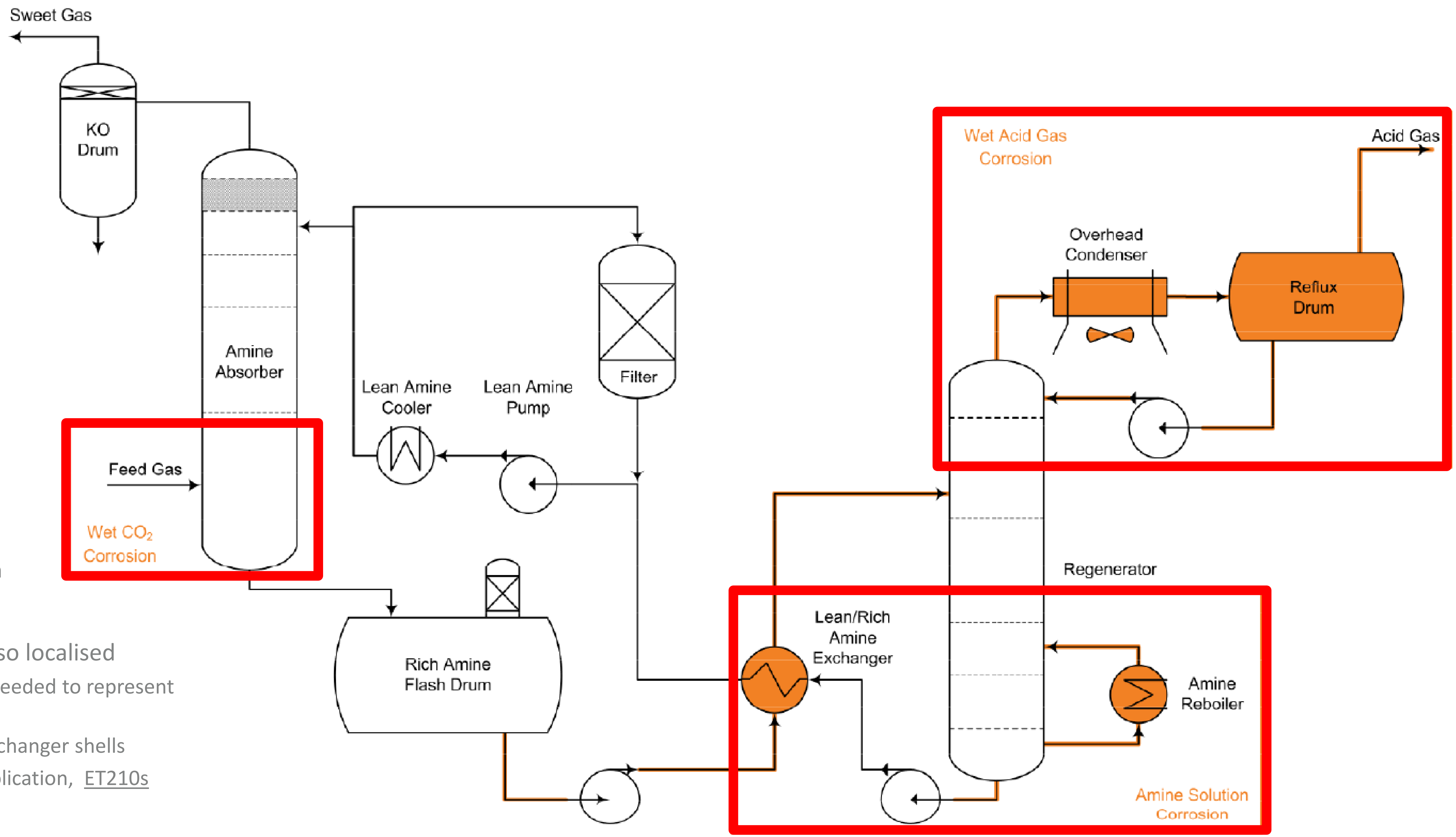
Amine Unit Process Overview

Corrosion issues

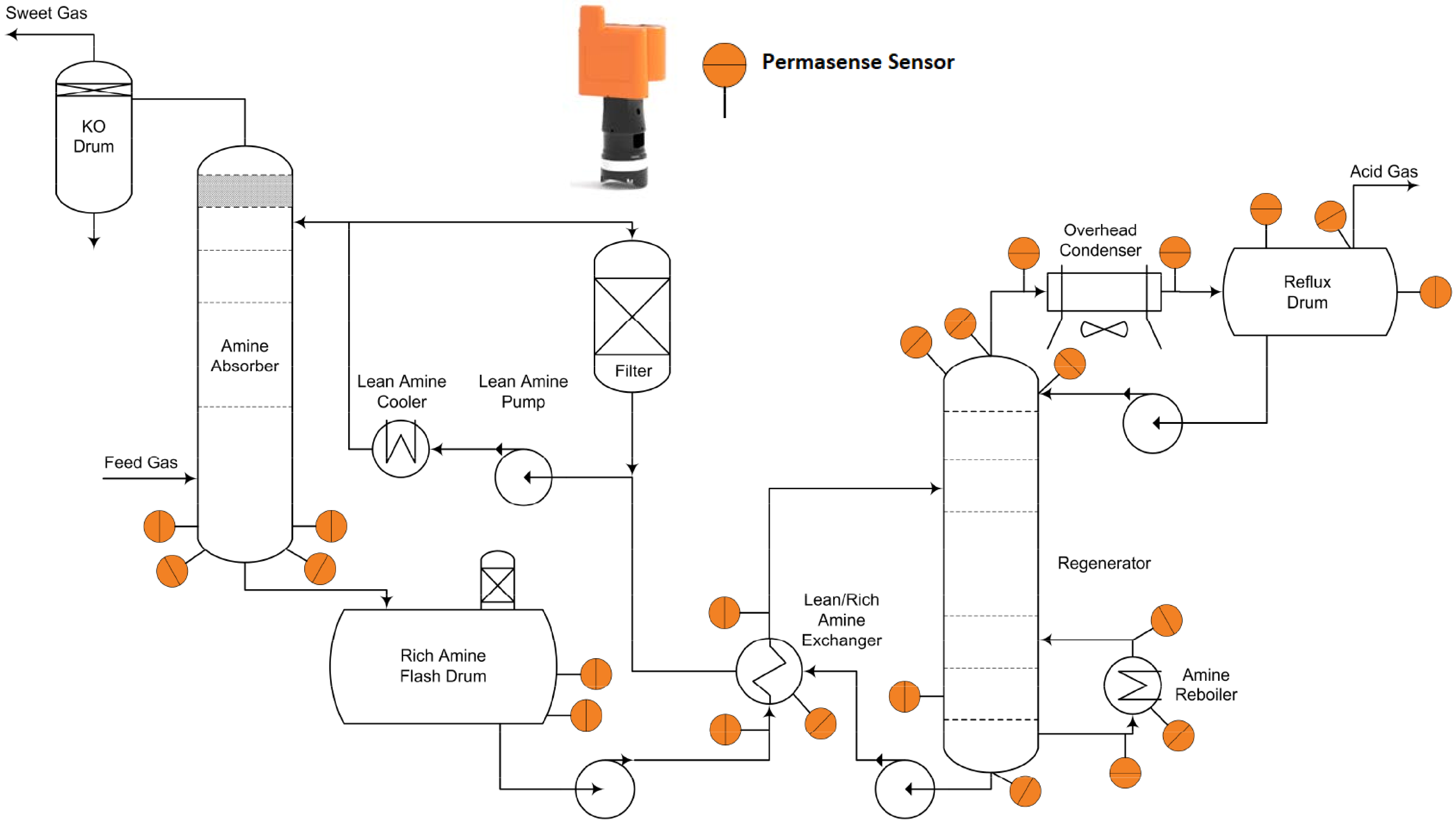
- High gas loading
- Heat stable salts
- Amine degradation
- Oxygen contamination

Corrosion is uniform and not so localised

- Fewer measurements needed to represent entire system
- Elbows, bends, tees, exchanger shells
- Lower temperature application, ET210s



Permasense Solution for Amine Units

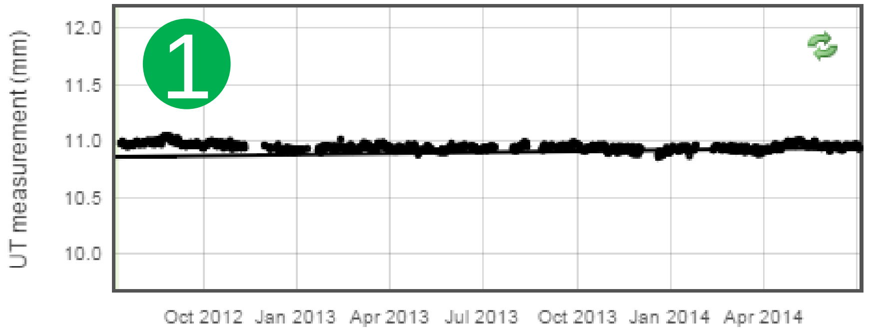


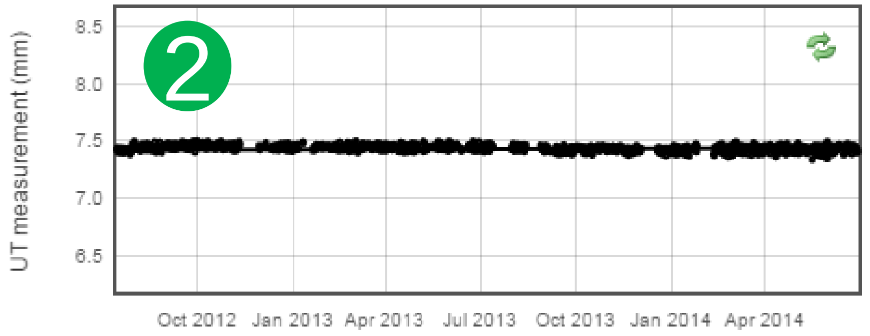
Permasense Solution for Amine Units

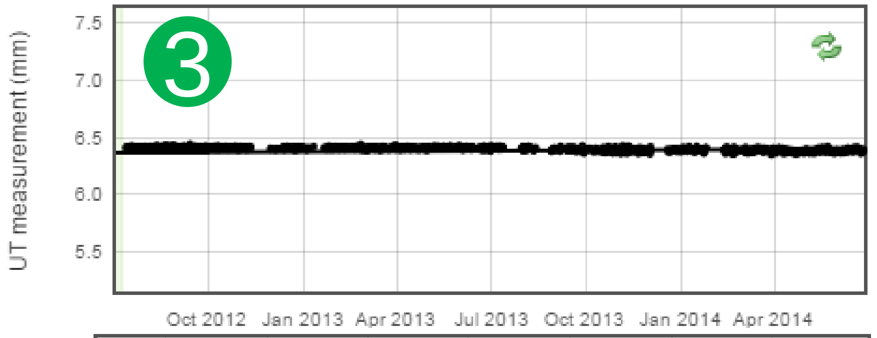
- Continuous wall thickness measurement sensors are ideally suited to monitor corrosion in the highest risk areas of amine units

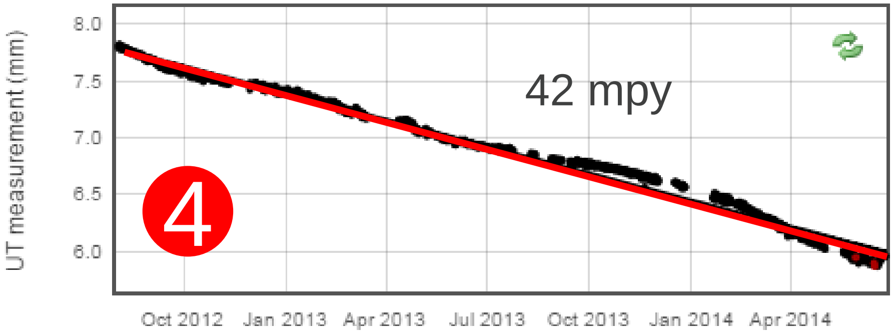
- The monitoring data enables engineers to
  - Reliably determine if corrosion is taking place
  - Supporting the management of unit integrity between planned shutdowns
  - Understanding the correlation between corrosion rates and process conditions
  - Optimizing corrosion monitoring prevention & mitigation measures

Case Study: Preventing Unplanned Outages – Amine unit





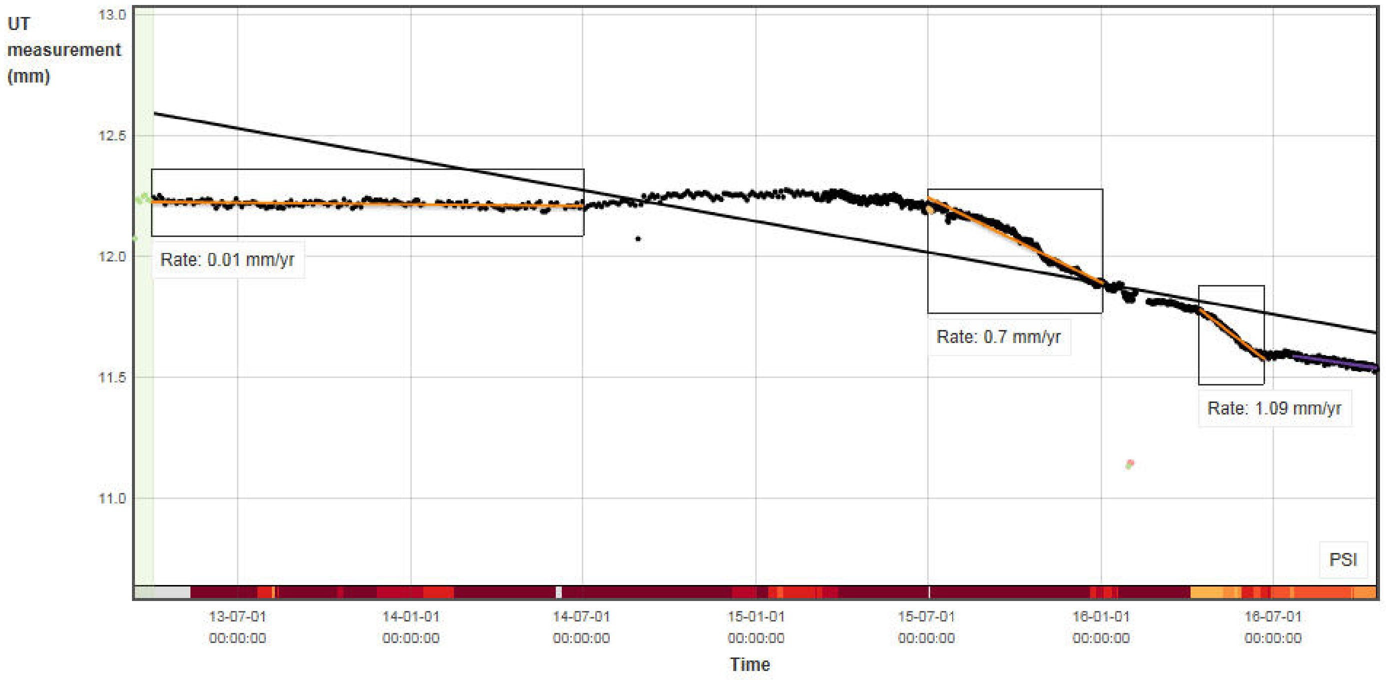




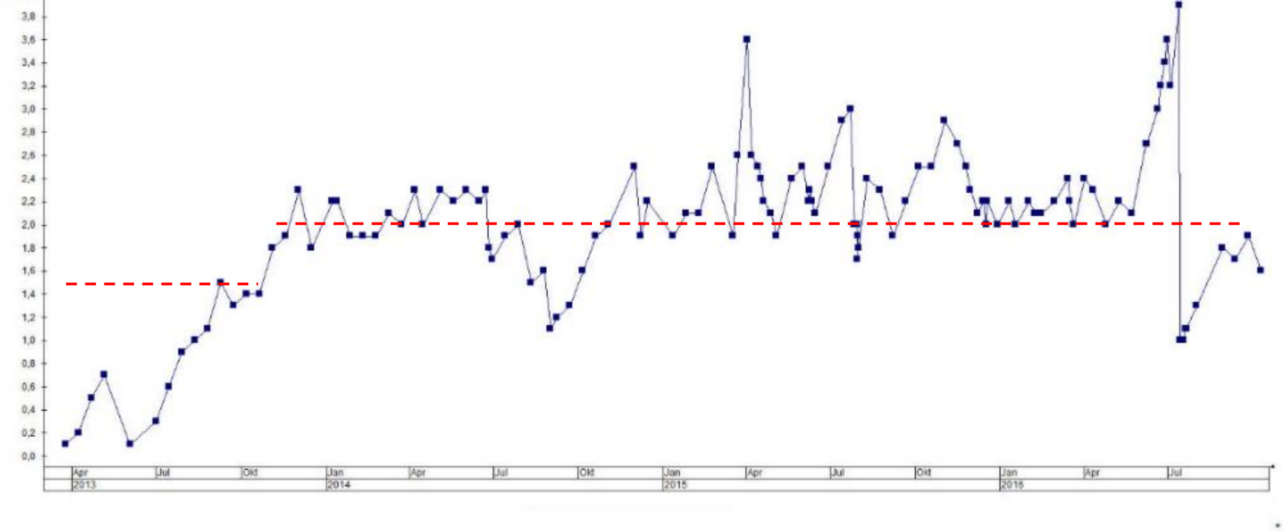
- Refinery with four amine absorber / regeneration trains
- All similarly configured, all stainless steel – corrosion NOT expected
  - Much faster and **unexpected** corrosion in train 4
    - 1 year to retirement even in stainless !
  - High CO_2 content feed due to preferential routing of FCC off-gas to train 4
  - Carbonic acid attack mechanism
  - Feeds redistributed to dilute effect of CO_2 corrosion across trains and extend run length

Early warning & enable decision making on process optimization to extend equipment life span

Case Study: Amine Regenerator – Process Optimization



Heat Stable Salt Content



- Historically controlled amine dump/top-up to heat stable salts level of ≤1
- Opex savings from fewer amine changes – targeted 1.5, then 2
- Reboiler outlet corrosion monitored
- Rising corrosion rate trend over time corresponding to increasing heat stable salts content
- Trade-off operating cost saving against equipment replacement cost

Commercial Impact of Amine Unit Shutdowns

- The commercial impact of an amine system outage on a given plant will depend on the type of plant, its specific configuration and the feed quality, but is often significant

- Amine units often operated at significantly higher processing rates and amine H2S loading
  - This causes limits in the flexibility that the processing facility has to shut down the amine system for repairs in the event of a corrosion-induced leak, as the risk of H2S gas evolution

- Without storage for rich amine, the facility is forced to limit the H2S load on the amine system by, for example:
  - Change of feedstock (heavy, high sulphur crudes changed to light, lower sulphur, and more expensive feeds),
  - Reduced production rate (lower natural gas feed rate to a gas processing platform or onshore plant)
  - Change of production mode (yielding high sulphur, raw gas oil to storage for

Appendix 6

Use of new sensor techniques to detect CUI

(G. De Landtsheer)

Corrosion Under Insulation (CUI)
Can we avoid it by using sensors?

Can data collection under insulation be a step-change for the future, in real-time monitoring of degradation effects?

Gino De Landtsheer,

Senior Group Expert Piping & Valves

Borealis

Department: Asset Technology

Division: Discipline engineering & Technical solutions(Piping & Valves)

BOREALIS

Keep Discovering

Introduction – current situation

- The industry is desperate to find a solution to avoid CUI, and to have control about the possible risks that can be related to CUI.
- Large budgets are spend to inspect plants and since a 100% visual inspection is still the most reliable method, it results in large inspection budgets and time consuming activities
- In the past 2-3 years some pilots with resistive sensors came in the picture, and some tests were performed in the field by different owner-operators, but results were rather poor of quality
- Recently a capacitive sensor was introduced to the market, and Borealis is now in a review/testing phase to determine the capabilities for real-time monitoring of damage & degradation effects under the insulation

Data monitoring under insulation

⇨ What are the main targets / properties of this sensor concept?

- Fully automated, autonomous concept
- Data-driven
- Real-time, continuously 24/7 monitoring
- Non-intrusive installation (on the existing insulation)

It can:

- Inspect passive equipment (static/piping)
- Detect moisture
- Evaluate risk zones
- Predict corrosion

Based on data evaluation, it will:

- Detect leaks
- Detect Corrosion Under insulation

Data monitoring under insulation
Present status of developments

⇨ Moisture & CUI sensor patent granted

– Moisture: electrical capacitive measurement based
– CUI: electro-chemical impedance spectroscopy based

⇨ Moisture & leak detection sensor available for pilot tests

- Borealis is now installing a small sensor network at a pre-defined location in the Beringen (B) plant
- Monitoring will be during a timeframe of at least 2 years
- Other pilots are already installed at Sitech Chemelot site (Geleen NL) / Oil & gas Technology centre Aberdeen (UK)

Data monitoring under insulation
Possibilities – moisture ingress

Risk-based Analysis

- Human based – costly

Non-accessible items

- Very high extra cost
- Equipment taxometry

Thermal losses

- No insulation
- TipCheck

Data monitoring under insulation
Possibilities – Leak detection

Major leaks

- Easy to detect – Drop in pressure
- Unexpected

Small Leaks

- Hard to detect
- Long-term problems
    - Operational losses
    - Corrosion Under Insulation (CUI)
    - Structural instability

Data monitoring under insulation
Possibilities – Corrosion Under Insulation

- Root cause = moisture
- Invisible
- Adhoc detection
- Costly removal of insulation
- Significant operational, safety and economic challenge

Data monitoring under insulation Solutions

Past & Present

- Removal of insulation
- Expensive / human based
- Discrete mapping / Risk Based Inspection (RBI)
- Ad-hoc inspections

New sensor solutions

- Mounting outside of the cladding
- Automated / data based
- Complete 360° detection
- Detection over a complete segment
- Continuous monitoring (24/7)

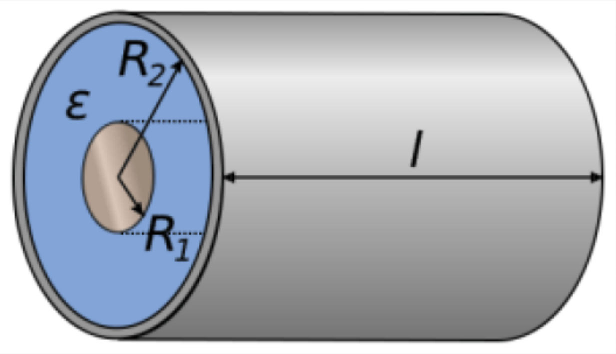
Data monitoring under insulation
Technical

senspro
Data Under Insulation

TECHNICAL

Electrical Capacitive measurement

- ε_r Air = 1
- ε_r Water = 78,5



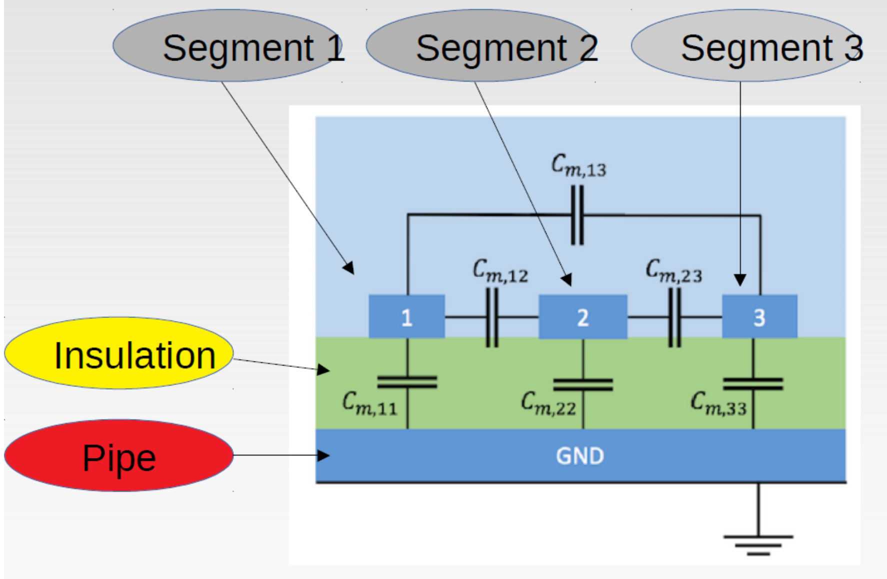
$$C = \frac{2\pi \epsilon_0 \epsilon_r L}{\log_e\left(\frac{R_2}{R_1}\right)} F$$

Data monitoring under insulation
Technical

TECHNICAL

Mutual capacitance

- Cladding interrupted
- Segmentation
- Cladding restored



Data monitoring under insulation
Technical

OVERVIEW

End-to-end Solution

- Sensor
  (on cladding)
- Gateway
  (on premise)
- Data Analytics
  (cloud)
- Control Cockpit
  (user)

PATENTED

Data monitoring under insulation
Technical

iSensPro
Data Under Insulation

SENSOR

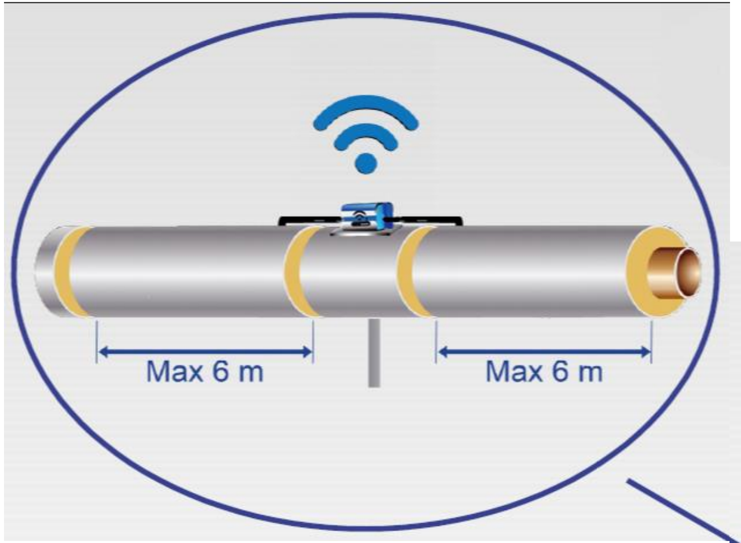
PATENTED

iSensPro Sensor

- Movement
- Surface temperature
- Moisture & Leakage
- Corrosion (Q1-Q2)

Features

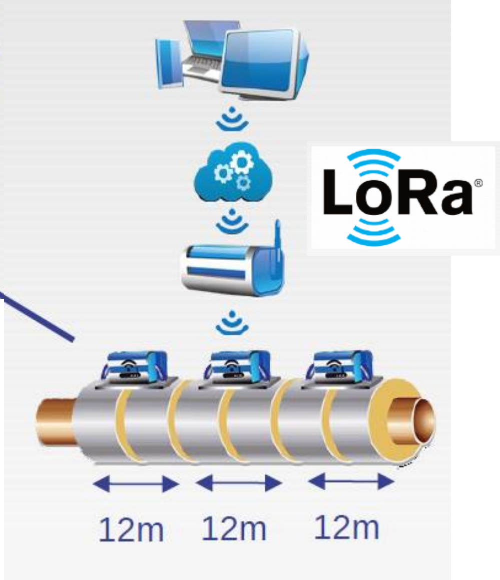
- Battery +3 year
- Solar cell
- ATEX pending
- GPS (optional)
- Noise (optional)



- ✓ Mounted on outside of cladding
- ✓ Non-intrusive
- ✓ Continuous monitoring 24/7
- ✓ Automated data-based
- ✓ Complete 360° detection
- ✓ 1 sensor per support (practical)

Cloud Coms

iSensPro Gateway
- Wired, WiFi, GPRS



Data monitoring under insulation
Technical

CLOUD

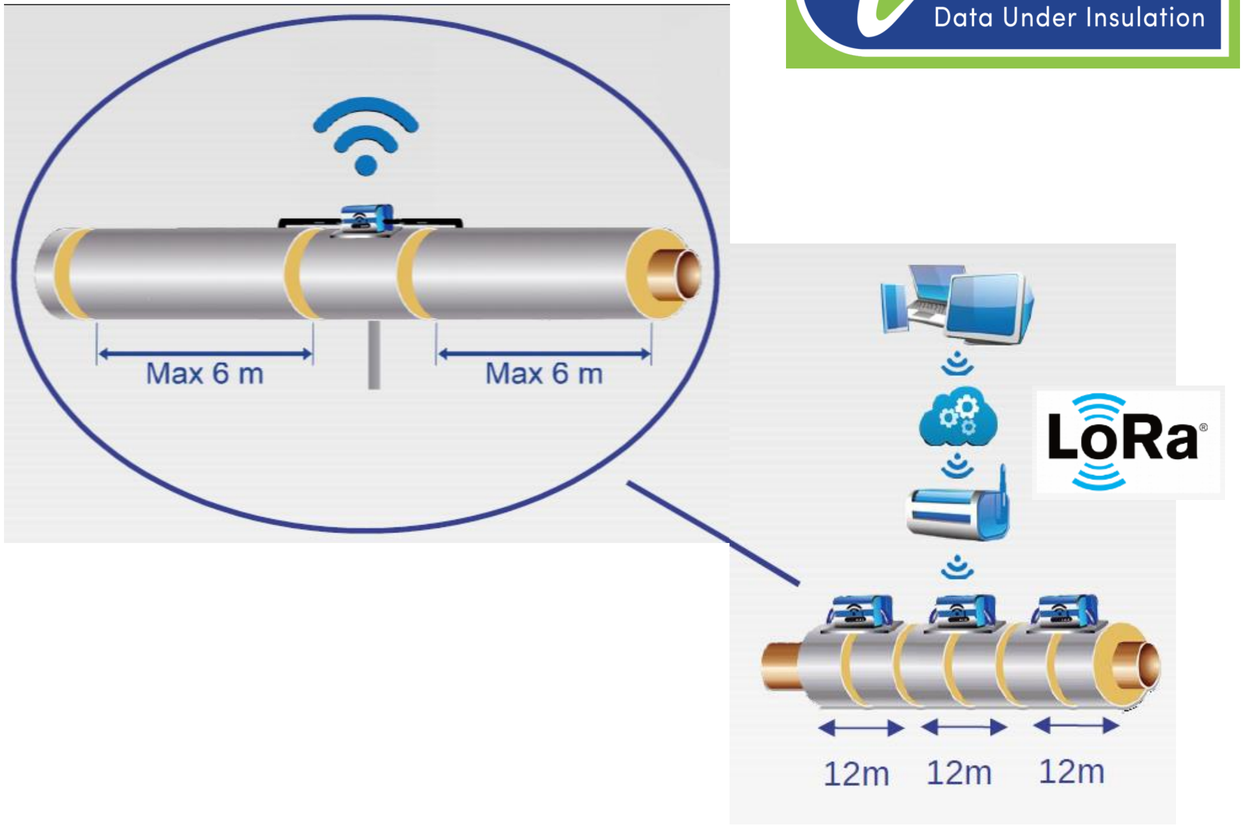
Data Analytics

HOW?

- Operational Inputs (localisation, weather,…)
- Machine Learning
- Customised Analytics

WHAT?

- Alert Generation
- Root Cause Analysis
- CUI (coating degradation)



Data monitoring under insulation
Asset management

Control Cockpit

HOW ?

- Data vault (pull)
- E-mail (push)
- iSensPro Smartphone App (demo)

WHAT ?

- Alerts & Status

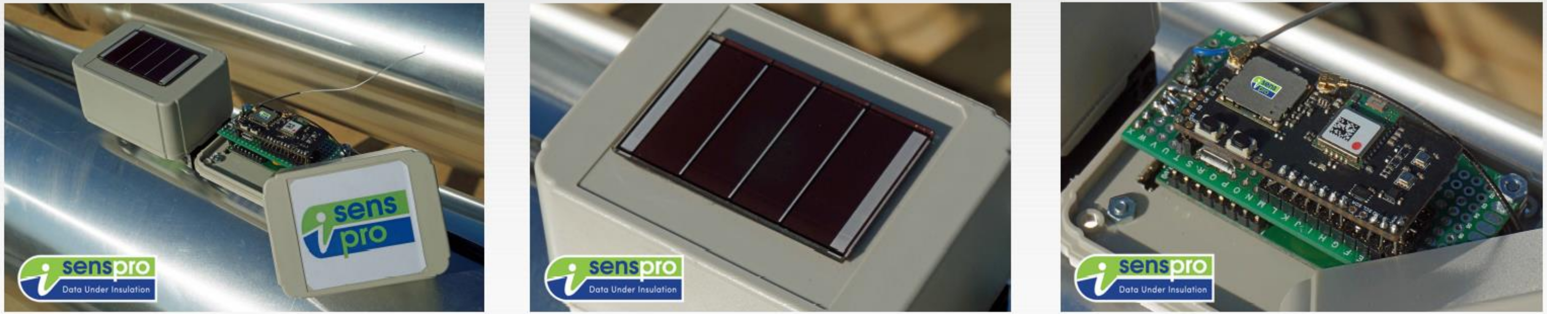
BOREALIS

Data monitoring under insulation
Practical view

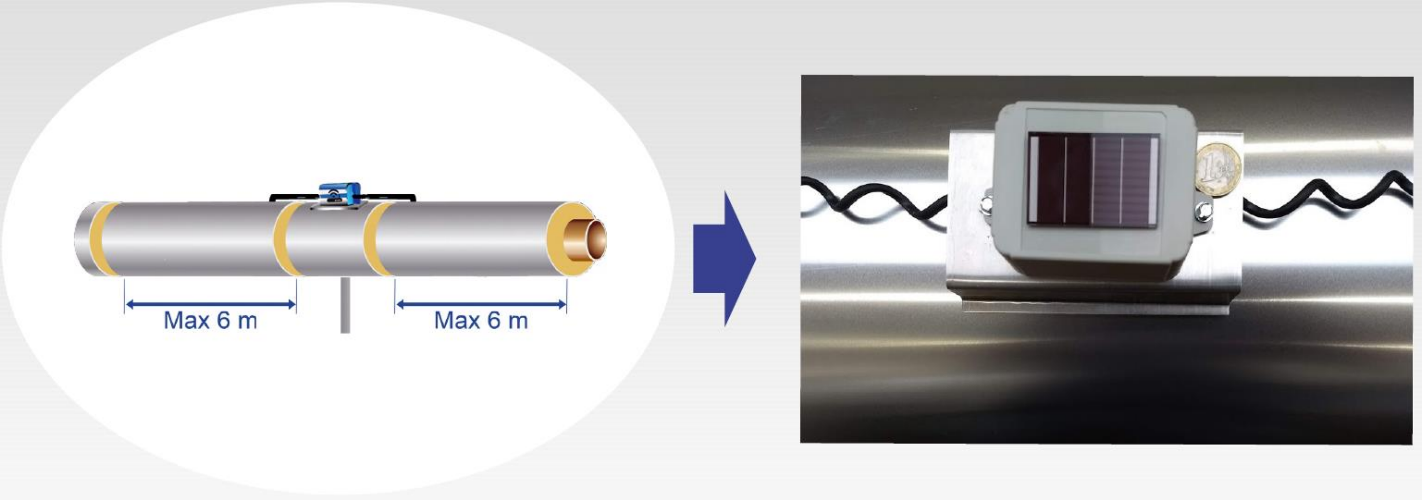
Monitor Data Under Insulation

Movement, Surface Temperature, Moisture, Corrosion (2019Q1)

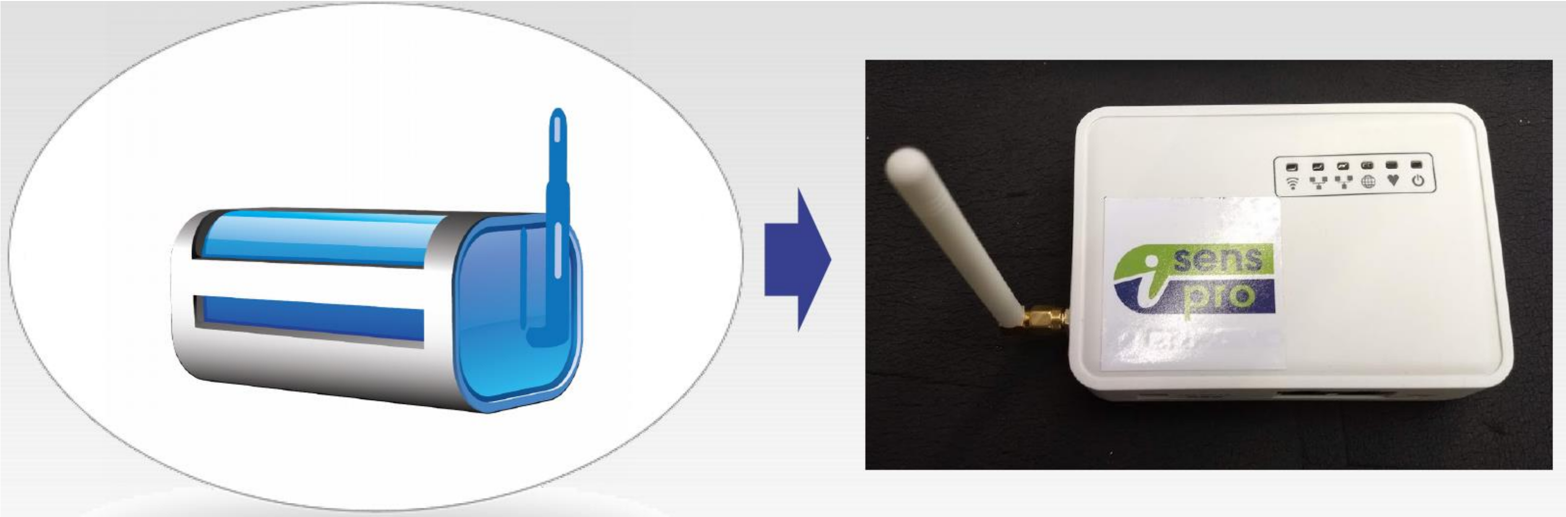
- Easy to install, mounted on outside of cladding
- Non intrusive, complete 360° detection
- Continuous monitoring, 24/7, automated data driven



Data monitoring under insulation
Practical view



Data monitoring under insulation
Practical view



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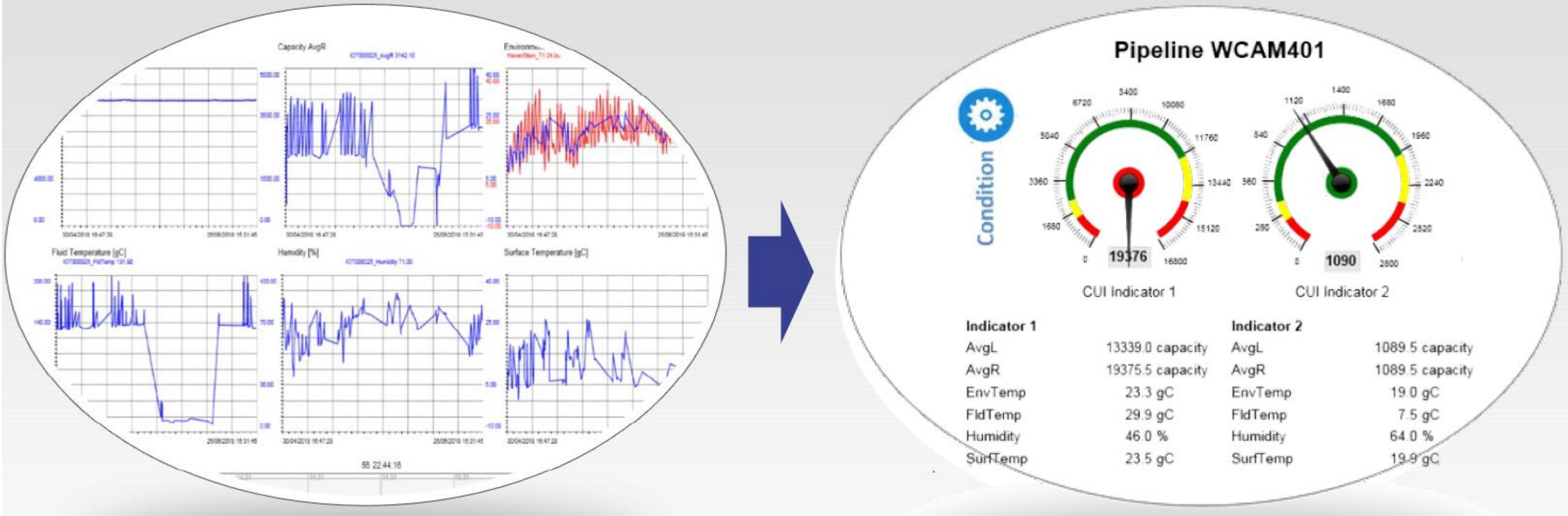
Data monitoring under insulation
Practical view



BOREALIS

Data monitoring under insulation
Advantages

senspro
Data Under Insulation

Non Intrusive
No need to remove insulation

Continuous Monitoring
Automated inspection & detection

Complete Detection
Measure 360° from outside on cladding

Predict & Mitigate
Pro-active data-based maintenance

Compatible with IoT
Smartphone, Tablet, all major platforms

DATA UNDER INSULATION
CUI

Data > Knowledge > Action
Make your maintenance team pro-active

Appendix 7

New array sensor for Pulsed Eddy Current Corrosion testing

(C. Wassink)


Eddyfi Technologies
PULSED EDDY CURRENT ARRAY (PECA)
CASPER WASSINK

Contents

ABOUT US

- GLOBAL PRESENCE - OFFICES IN 7 COUNTRIES
- MORE THAN 1000 UNITS IN THE FIELD
- SUPPORTING CLIENTS IN OVER 70 COUNTRIES
- CREATION IN 2009 WITH PEOPLE OF 30 YEARS OF EXPERIENCE IN NDT
- MORE THAN 30% OF OUR EMPLOYEES IN R&D

History of PEC

PULSED EDDY CURRENT TESTING OF FERROMAGNETIC MATERIALS

- Reinvented in the early1990s by ARCO for CUI inspection in the Prudhoe Bay field
  - Patent granted, lapsed in 2010
- Adopted by Applus RTD and Shell
  - Commercially available from 1998
  - RTD-INCOTEST and Shell PEC
  - Little technology development
- Both Shell and Applus RTD discontinued PEC development around 2015
- Three new equipment vendors and increase in technology development since 2016
  - Eddyfi - Lyft
  - Maxwell NDT – PECT
  - TUV Rheinland Sonovation – Sonopec

Lyft - Pulsed Eddy Current Reinvented

WHY USE PULSED EDDY CURRENT

Electromagnetic inspection technology is used to detect defects and corrosion in ferromagnetic materials.

Provides a relative wall thickness measurement through liftoff:

- Non-metallic pipe protection (concrete, composite wraps, coatings, and more)
- External corrosion product
- Corrosion under insulation (CUI)
- Marine growth

PEC is a versatile inspection solution!

Eddyfi Technologies

Lyft - Pulsed Eddy Current Reinvented

WHY USE PULSED EDDY CURRENT

CUI - Corrosion under insulation

- PEC inspects through insulated structures, protected or not with weather jacket
- Supports aluminum, stainless or galvanized steel weather jackets
  - – Inspects wall thickness up to 100mm (4 in)
  - – Supports liftoff/insulation/coating thickness up to 300 mm (12 in)

Eddyfi Technologies is proud to offer the first standard Pulsed Eddy Current Array (PECA) solution dedicated to improve inspection productivity for CUI and CUF applications!

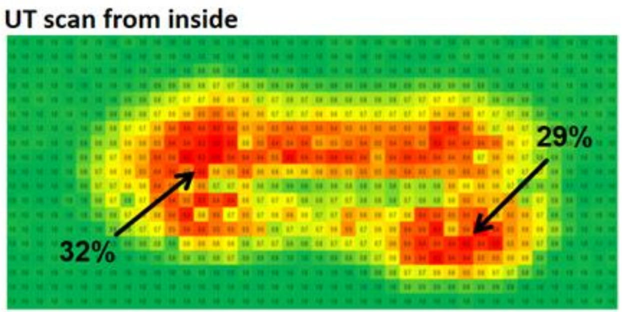
Eddyfi Technologies

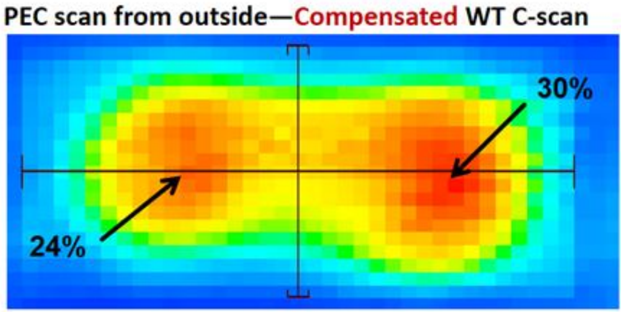
Lyft - Pulsed Eddy Current Reinvented

WHY USE PULSED EDDY CURRENT

Scab and blistering

- PEC measures the remaining thickness of conductive material, not the corrosion product layer





Eddyfi Technologies

Lyft - Pulsed Eddy Current Reinvented

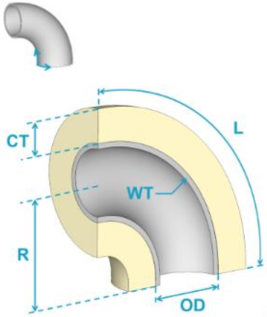
WHY USE PULSED EDDY CURRENT

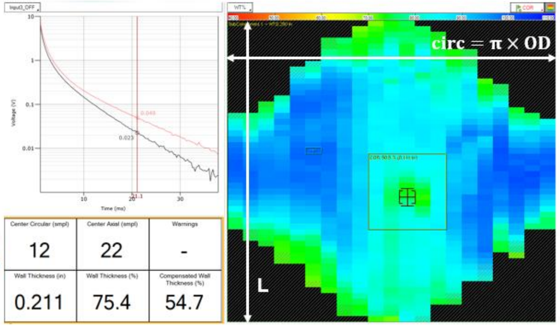
CUF - Corrosion under Fireproofing and Concrete

- PEC measures remaining wall thickness through concrete, polymer coating, metallic mesh and reinforcing bar

FAC - Flow accelerated corrosion

- PEC is suitable for measuring corrosion in elbows and other limited access areas

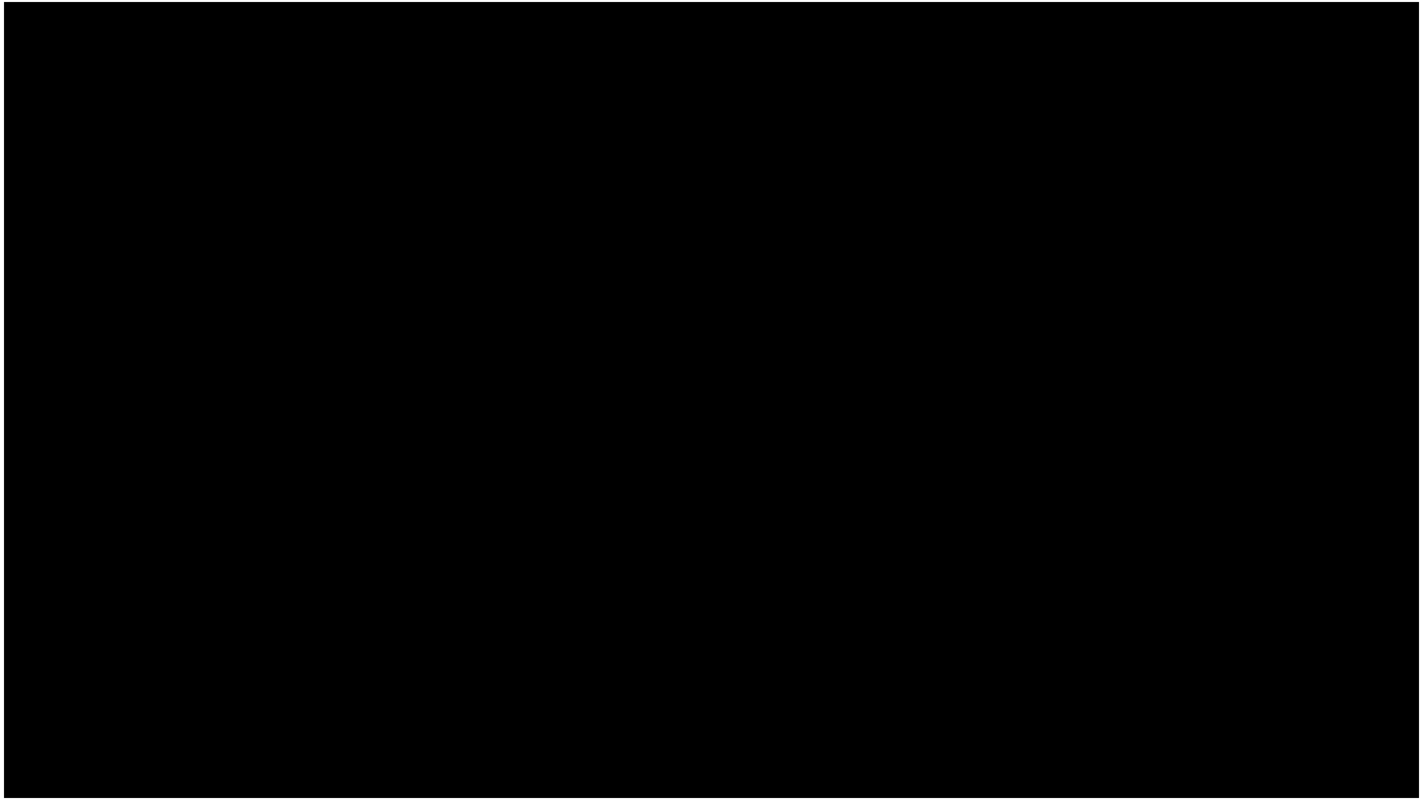




PEC Working Principles

Lyft - Pulsed Eddy Current Reinvented

PEC WORKING PRINCIPLES



Lyft - Pulsed Eddy Current Reinvented

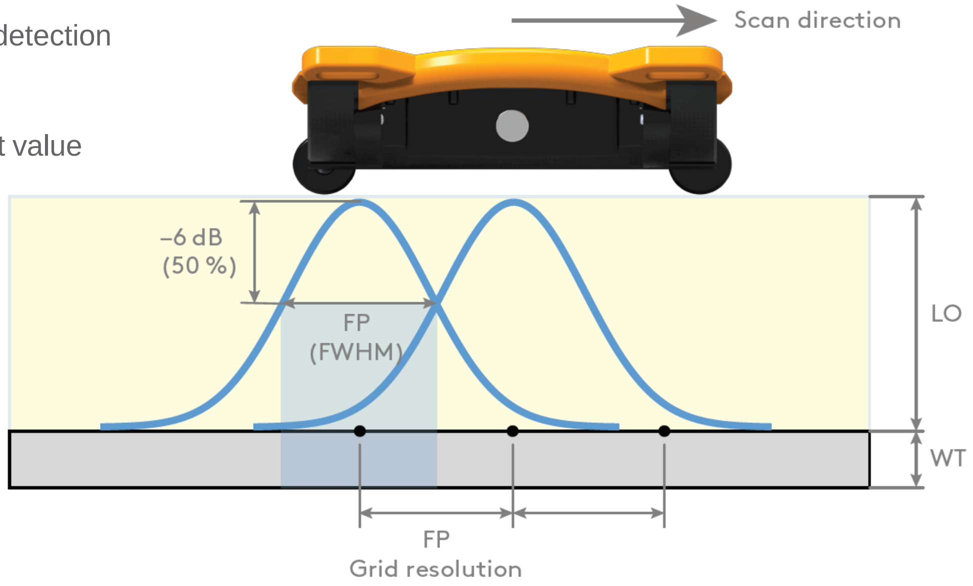
PEC WORKING PRINCIPLES

The footprint represents the surface area seen by the probe

- Used to set the scan grid resolution required for the detection of the smallest detectable defect
- Minimum detectable defect size depends on footprint value

Footprint value changes with:

- Probe size
- Liftoff or Coating/Insulation thickness
- Component wall thickness
- Diameter of the inspected pipe



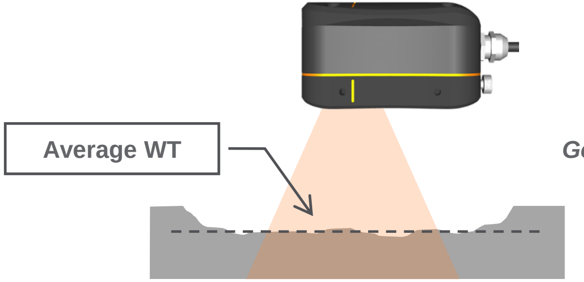
Lyft - Pulsed Eddy Current Reinvented

PEC WORKING PRINCIPLES

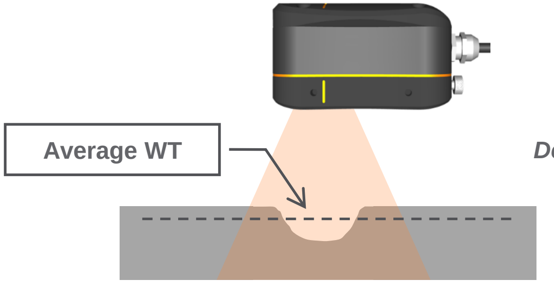
Average wall thickness measurement impact

- Defect larger than the averaging area
  = sizing accuracy +/- 10%
- Defect smaller than the averaging area
  = undersizing

The thicker walls around the indication influence the averaging calculation



Good sizing accuracy



Defect undersizing

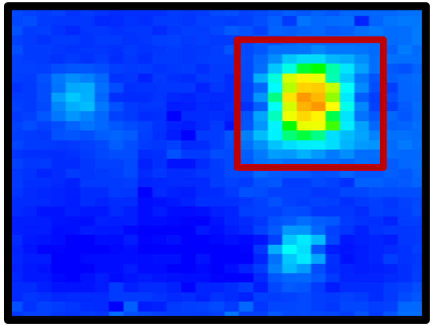
Eddyfi Technologies

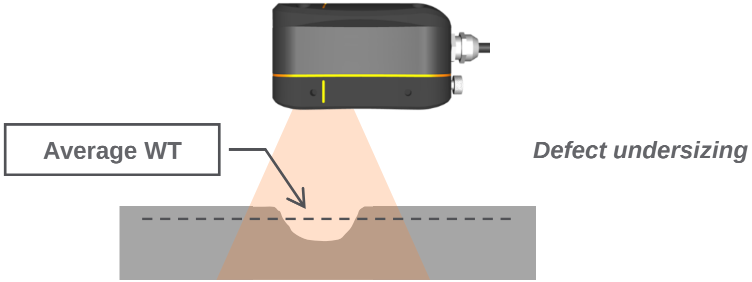
Lyft - Pulsed Eddy Current Reinvented

PEC WORKING PRINCIPLES

Lyft uses a compensated wall thickness (CWT) sizing tool against the undersizing effect of PEC

- Isolate defect contribution
- Calculate a compensated wall thickness value
- Brings back sizing accuracy for defect smaller than the probe averaging area to +/- 10%





Lyft - Pulsed Eddy Current Reinvented

PECA INSPECTION SOLUTION

Standard Pulsed Eddy Current Array (PECA) solution dedicated to CUI and CUF applications

Six elements, large coverage probe :

- Ensures 457 mm (18 in) single-pass coverage
- Integrated locking mechanism to adjusts to pipe OD from 152 mm (6 in) total including insulation, up to flat surface
- Spring loaded wheels for smooth acquisitions over buckles and uneven surfaces.
- Minimizes gridding time with Grid-as-u-go™

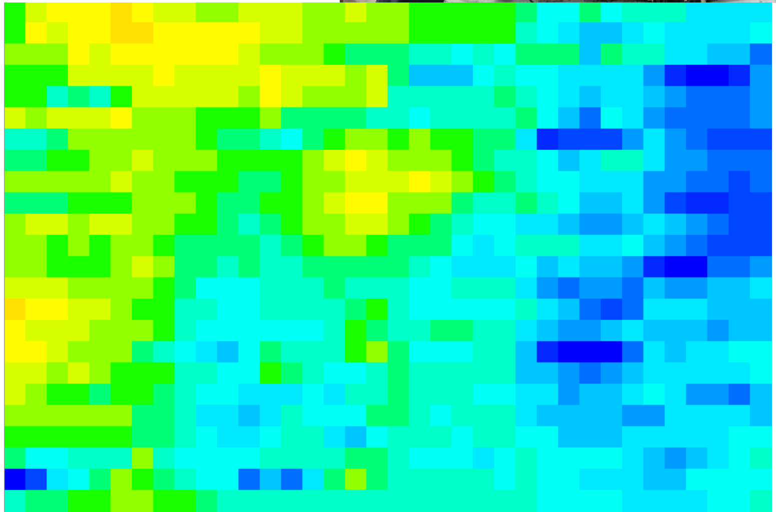
Improves overall inspection productivity up to 10 times when compared to inspections with mono-element PEC

Inspection productivity improvements

Actual Scan Examples

SECTION OF A FIRE-PROOFED VESSEL SKIRT

- ✓ Wall thickness: 13 mm
- ✓ 25 mm thick fireproofing including welded wire mesh
- ✓ Scanned area: 3 m x 2 m
- ✓ PECA in dynamic mode
- ✓ Preparation and scan completed in about 5 minutes
- ✓ 3 areas of interest found with around 40% wall loss

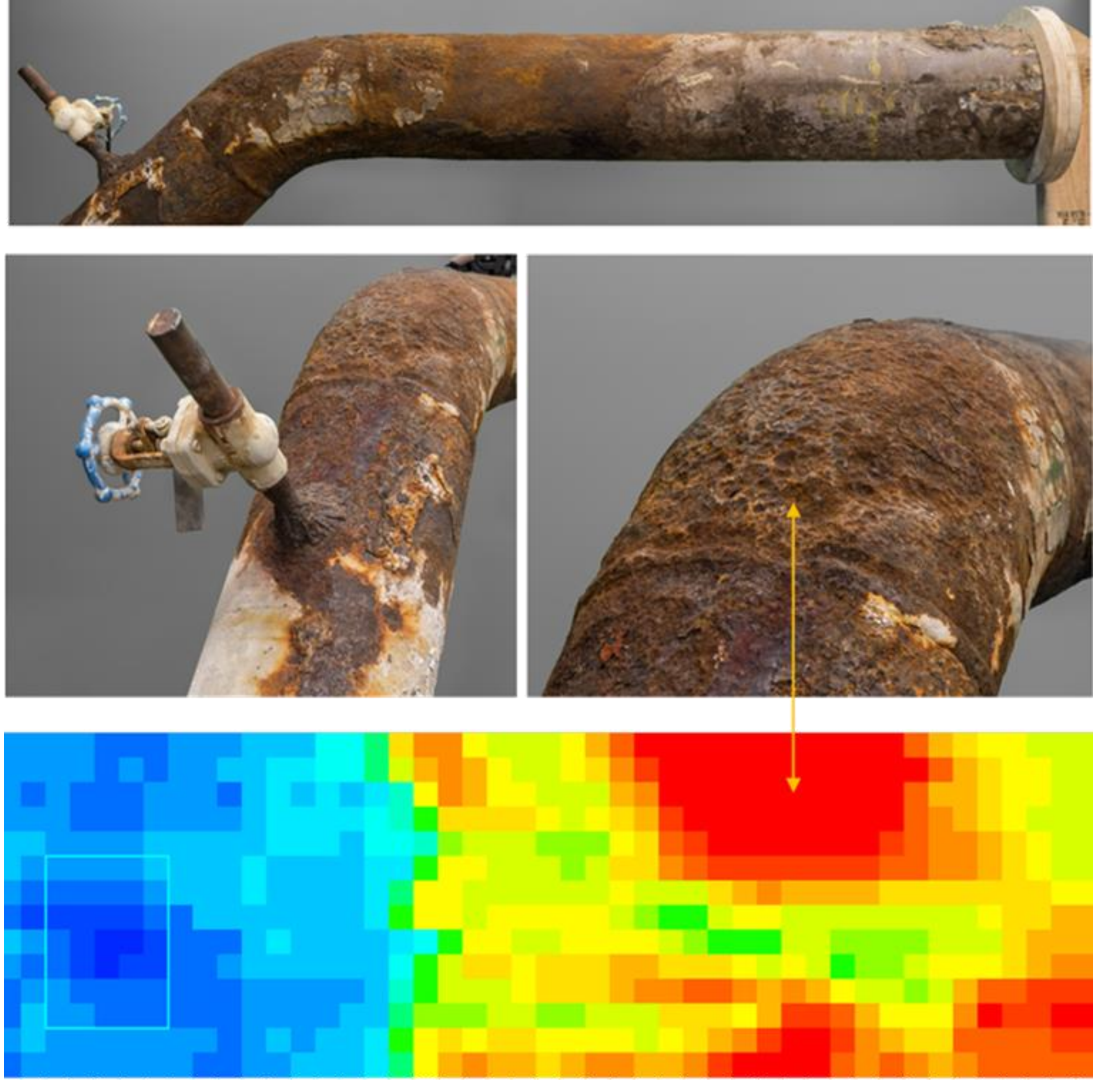


Eddyfi Technologies

Actual Scan Examples

FIELD EXTRACTED PIPE/ELBOW

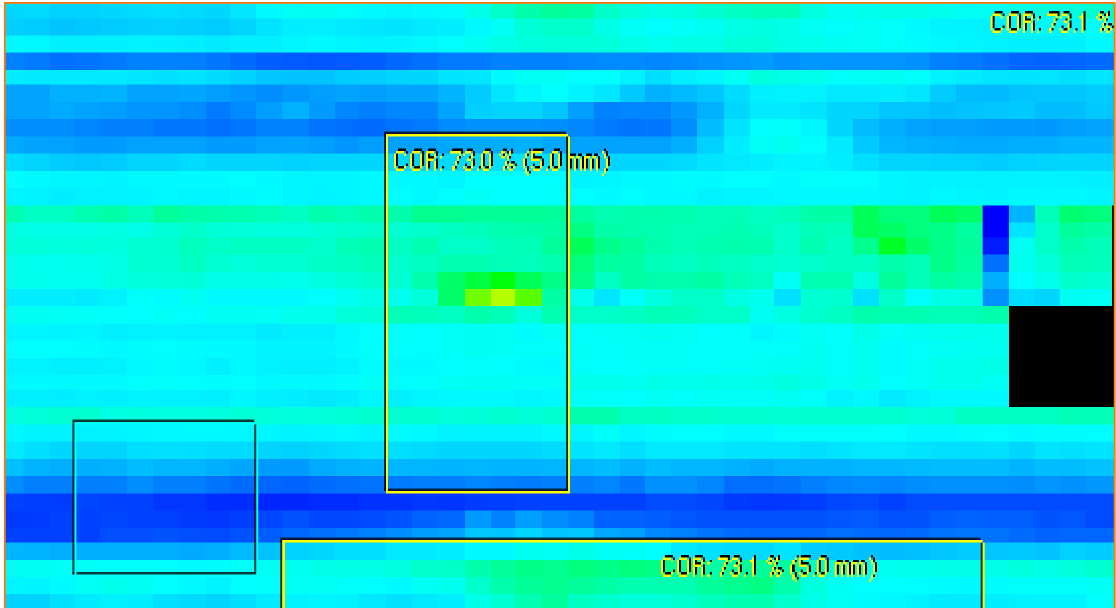
- ✓ 1.5 m pipe/elbow section
- ✓ 200 mm OD schedule 40
- ✓ 25 mm of insulation
- ✓ PECA in dynamic mode
- ✓ Full coverage in **3 passes**
- ✓ **Completion in less than 2 minutes including preparation**



Actual Scan Examples

CLOCKSPRING WRAPPED PIPELINE

- ✓ 2 m long section of a wrapped pipeline
- ✓ 760 mm OD, 6.8mm WT
- ✓ 25 mm of clock spring repair wrap
- ✓ PECA in dynamic mode
- ✓ Full coverage in 6 **passes**
- ✓ **Completion in less than 10 minutes including preparation**



Bilfinger/Eddyfi LYFT CUI trial: 4-8 June

Participants:

- Marco Michele Sisto (Eddyfi, Canada)
- Scott Westwater & Nathan Kershaw (Bilfinger)

Equipment:

- Eddyfi LYFT (medium probe) & system x 2
- New LYFT array (PECA) x 1

Pipes scanned:

- L pipe assembly 1 (SS clad): 100mm insulation
- 4 x 3m straight pipes: 100mm insulation

Pipes not scanned:

- L pipe assembly 2 (galvanised cladding) (outside of spec. of special probe).

All test samples scanned with both single probe and array

- All scanning was dynamic

CUI trial duration c. 3.5 days

Test assemblies & pipes – after welding & insulation

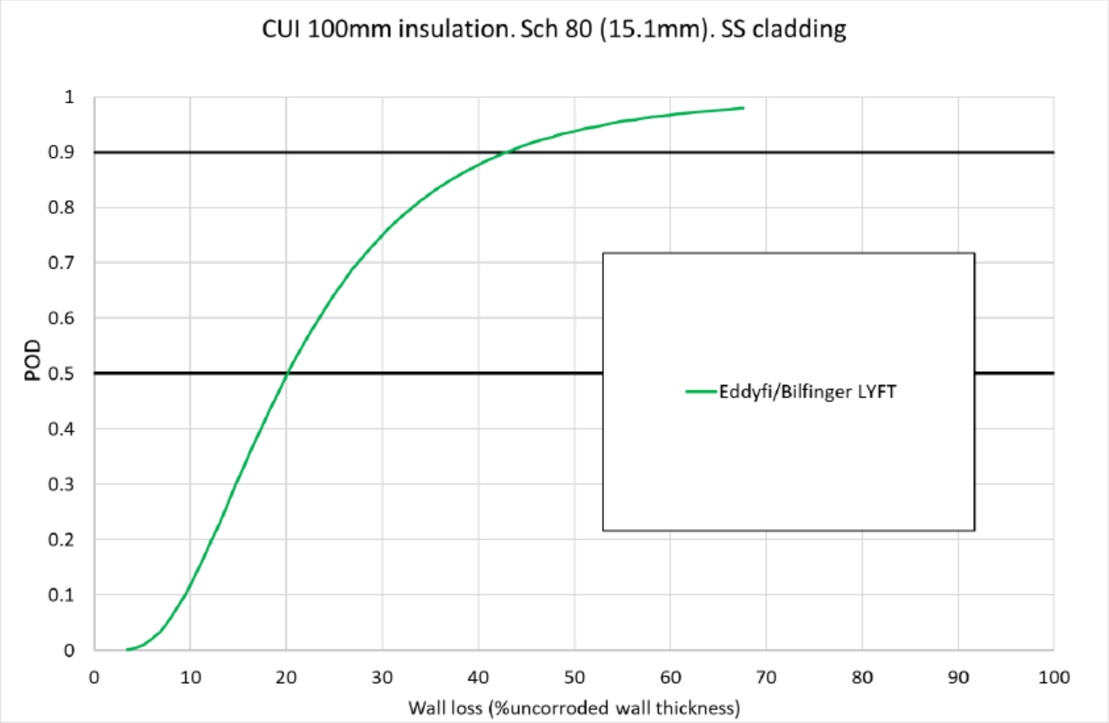
HOIS
Advancing NDT in Oil & Gas

LYFT trial - Provisional results of POD and false-call analysis: sch 80 SS clad pipes

Total number of false calls: 0

POD curves show:

- Gradual rise with %wall loss
- 20% wall loss gives a POD of 0.5
- 43% wall loss gives a POD of 0.9



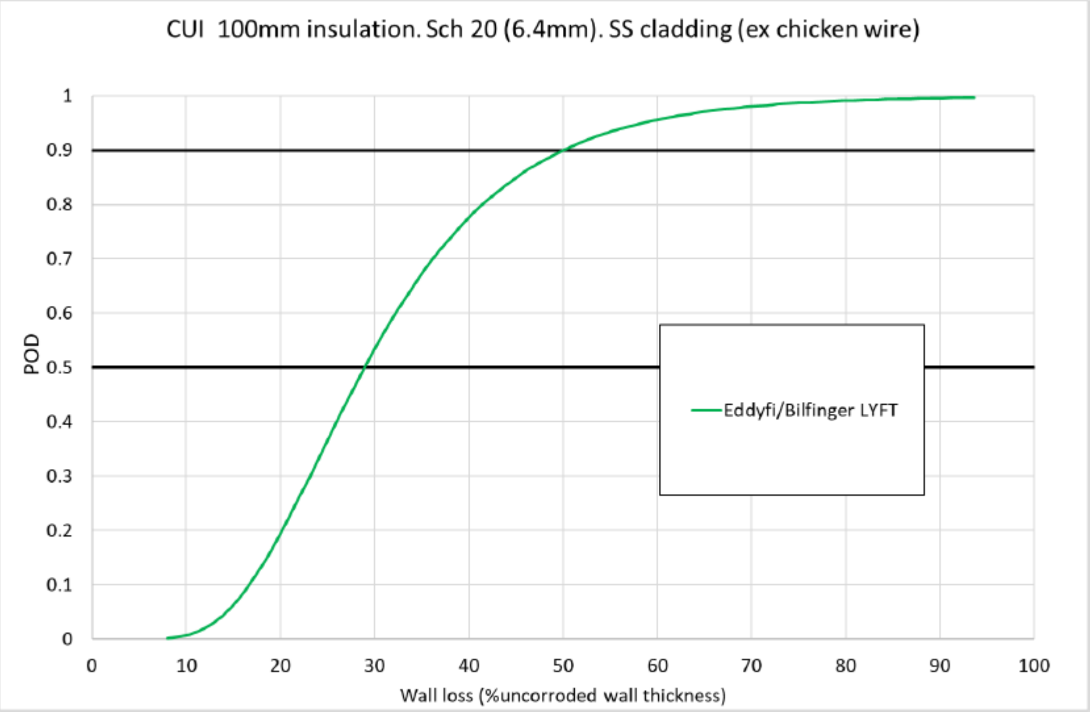
HOIS
Advancing NDT in Oil & Gas

LYFT trial - Provisional results of POD and false-call analysis: sch 20 SS clad pipes (excluding chicken wire)

Total number of false calls: 2

POD curves show:

- Gradual rise with %wall loss
- 29% wall loss gives a POD of 0.5
- 50% wall loss gives a POD of 0.9



HOIS
Advancing NDT in Oil & Gas

Lyft - Pulsed Eddy Current Reinvented

ADVANTAGES OF USING PECA TECHNOLOGY

- High productivity with array technology and high resolution dynamic mode
- Provides a relative wall thickness measurement through liftoff
- Inspects through various types of coatings/insulations
- Not affected by surface preparation
- Detects OD and ID corrosion
- In-service inspections, no need to remove insulation
- Safe, no hazard

Eddyfi Technologies

Grid-As-U-Go™

Real time

Dynamic scan

10x speed

Regular scan

10x speed

Appendix 8

High Temperature Hydrogen Attack management within Total

(S. Loyan)

HTHA MANAGEMENT WITHIN TOTAL

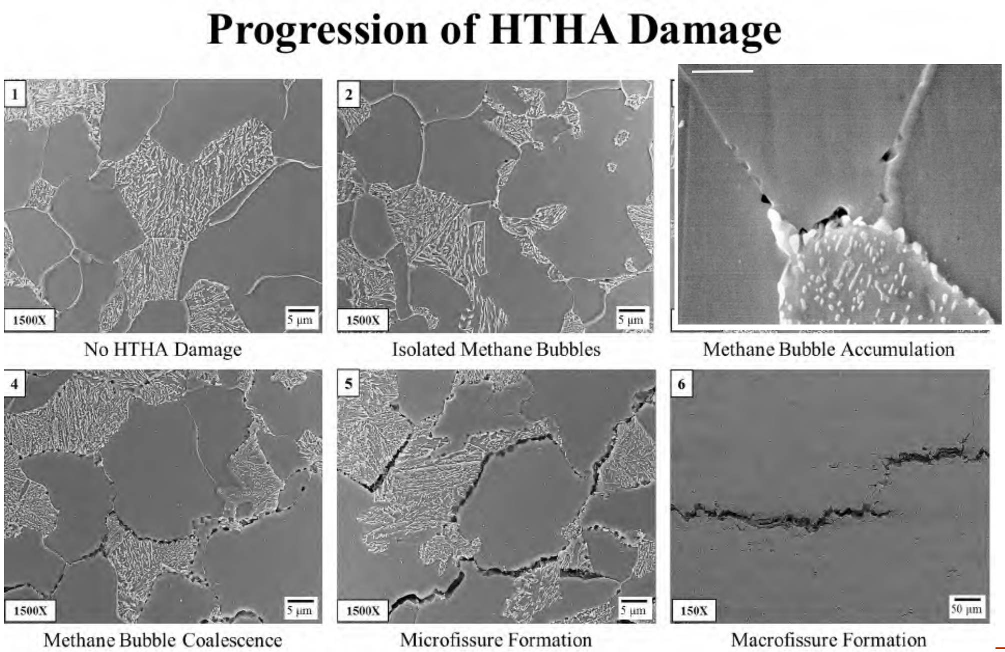
Sophie LOYAN (TOTAL Refining & Chemicals)

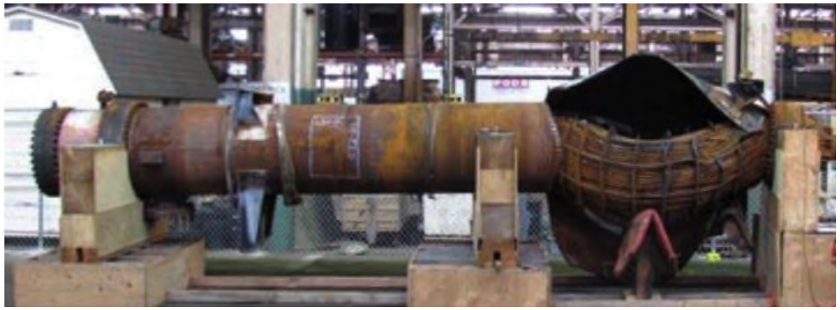
EFC WP15 Spring meeting– April 2019

Confidential

HTHA MECHANISM AND DAMAGES

- High Temperature Hydrogen Attack on CS (Carbon Steel), C-0.5Mo, and Cr-Mo alloys
- Time mechanism dependent = ageing
  - ⇒ Incubation time (no observable microstructure modification observable)
    - ⇒ Loss of steel mechanical properties
      - ⇒ Micro-cracks
        - ⇒ Rupture





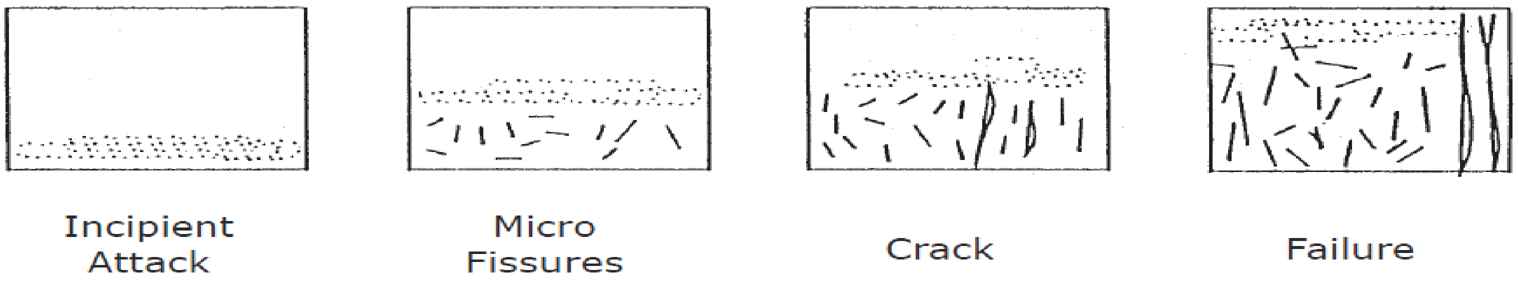
TESORO 2010 – 7 casualties

HTHA MECHANISM AND DAMAGES

Mechanism :

At T > 204 °C (400°F) and ppH2 > 5,5 bar (80 Psi) :

- Starting by dissociation of molecular hydrogen : $H_2 \rightarrow 2H$
- H diffusion into the steel (and if any through the clad)
- Reaction of decarburization: Fe_3C (carbides) + 4H → 3 Fe + CH_4



HTHA – A CHALLENGING DEGRADATION

- Non homogenous damage
  - Welds (HAZ and WM)
  - Base metal
  - Influence of stresses

- HTHA mechanism is **time dependent** = ageing

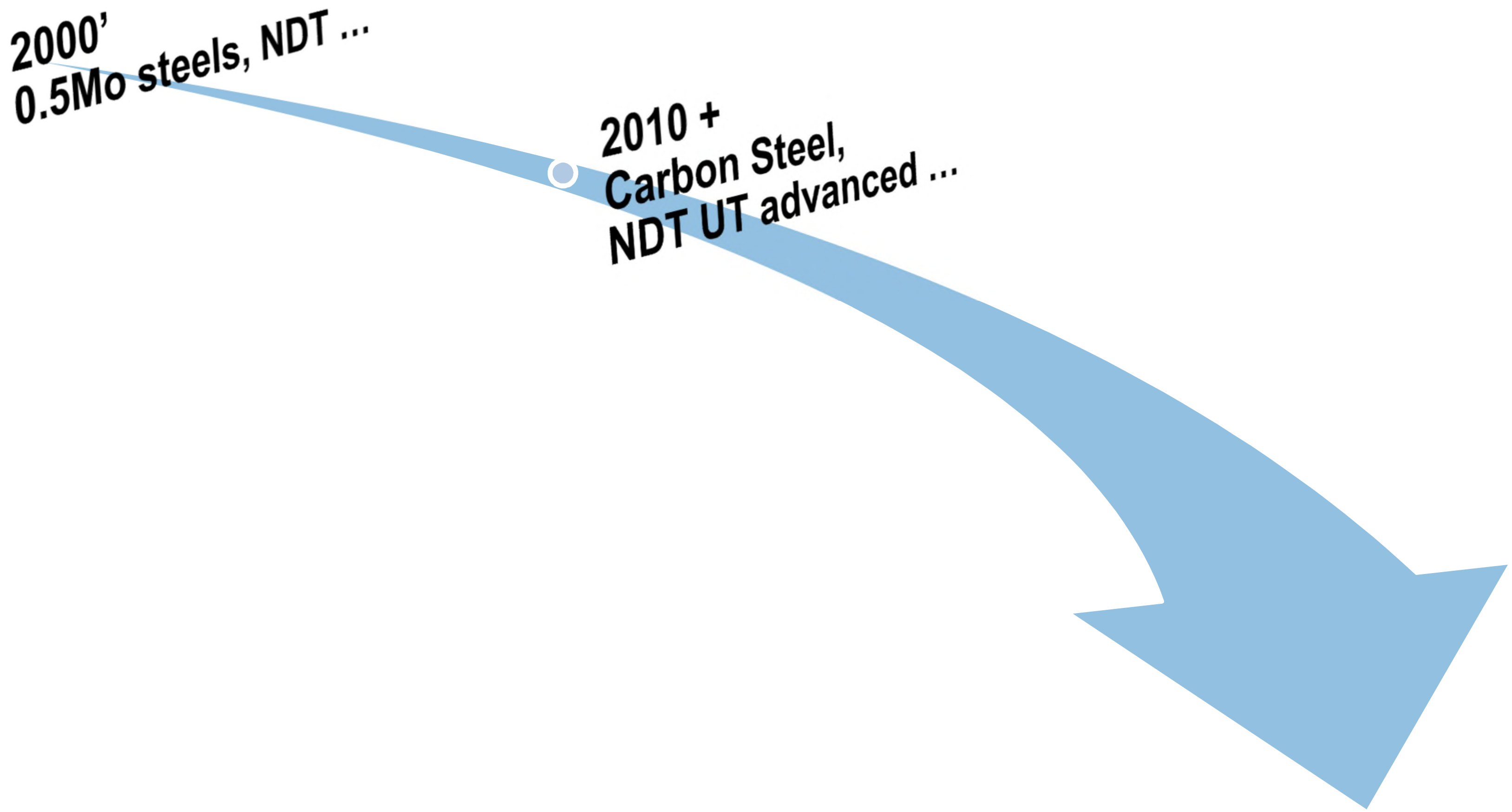
- Observable microstructure modifications only after **incubation time**

- **Detecting degradations** associated with HTHA is very **challenging**

- So far, **no Fitness for service model validated**:
  - Mechanical properties function of degradation extend unknown
  - Kinetic unknown

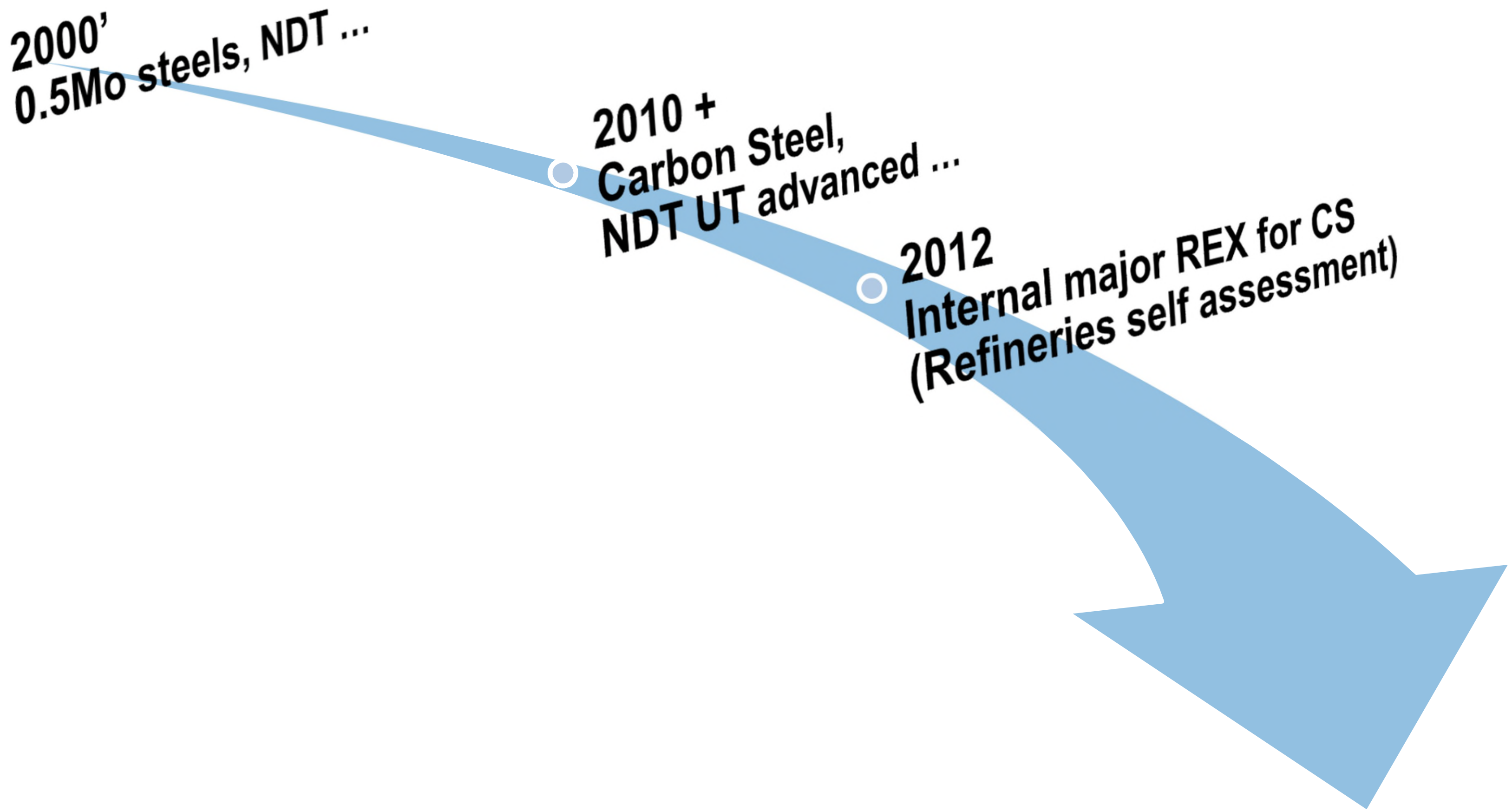
  ⇒ **No possible Fit for purpose justification in case of HTHA detection**
  ⇒ **Repair not guaranted**

2000'
0.5Mo steels, NDT …

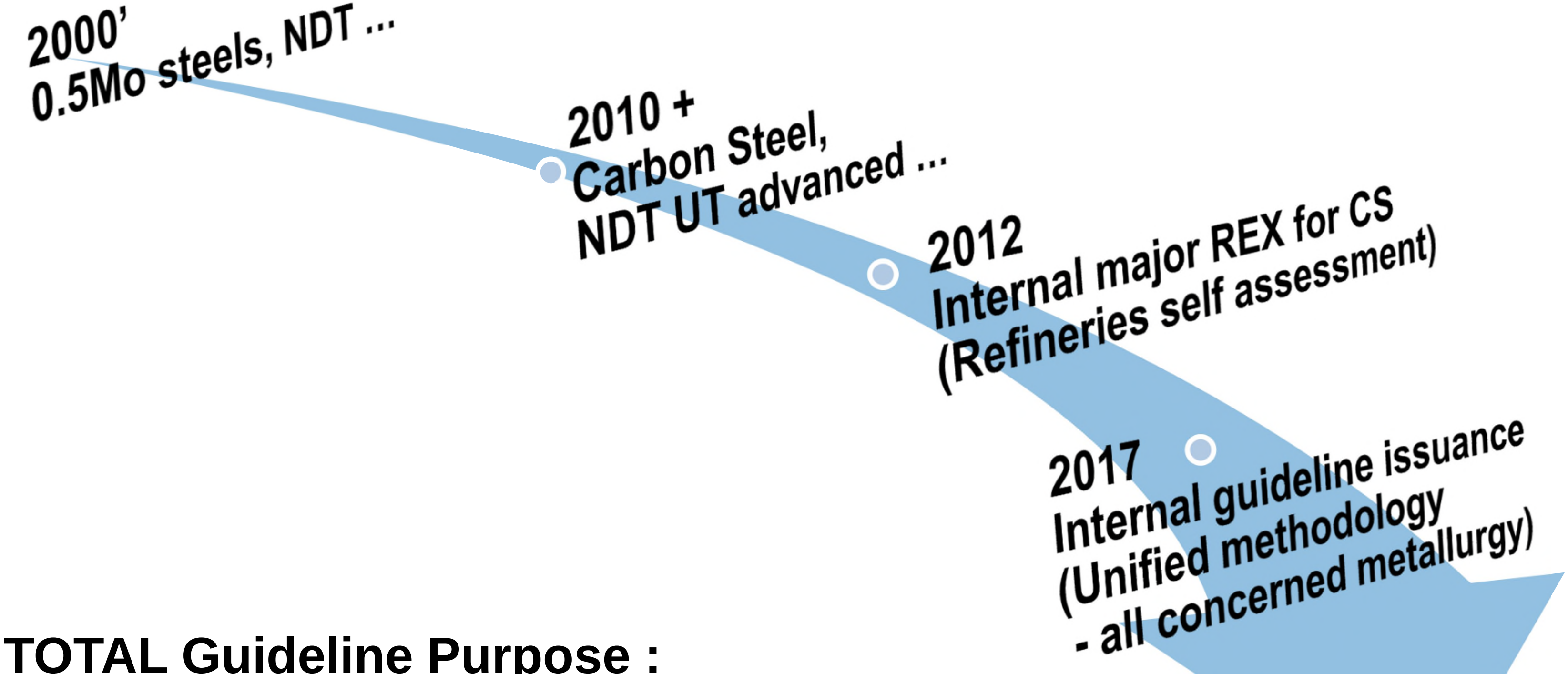

2000'
0.5Mo steels, NDT ...
2010 +
Carbon Steel,
NDT UT advanced ...

2000'
0.5Mo steels, NDT …

2010 +
Carbon Steel,
NDT UT advanced …

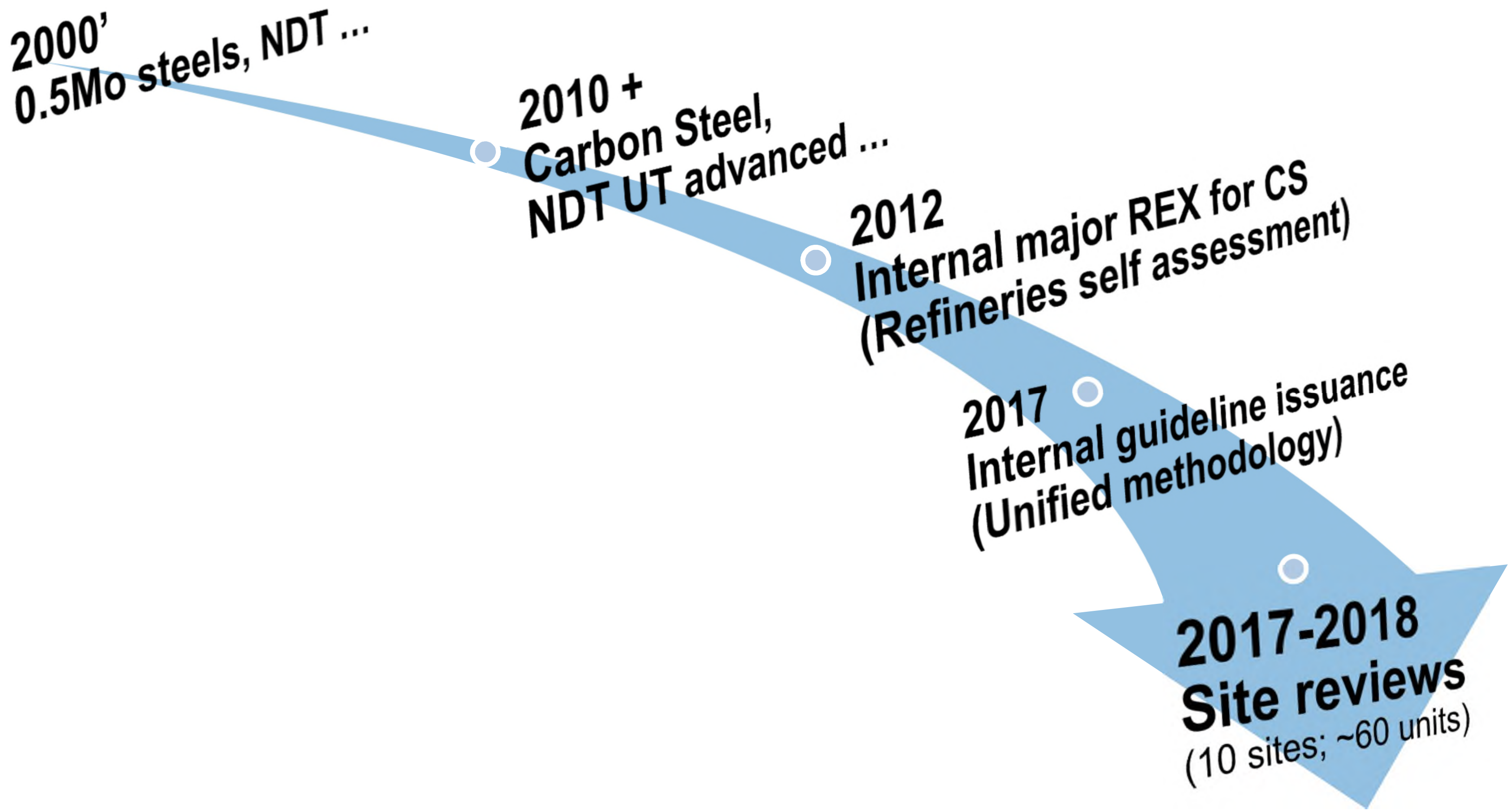

2000’
0.5Mo steels, NDT …
2010 +
Carbon Steel,
NDT UT advanced …
2012
Internal major REX for CS
(Refineries self assessment)

TOTAL



➢ **TOTAL Guideline Purpose :**

- To indicate a methodology for taking inventory of equipment and piping that might be subject to HTHA
- Rank equipment and piping function of HTHA severity based on Nelson Curves
- Define the inspection plans function of HTHA severity
- Give criteria for replacement

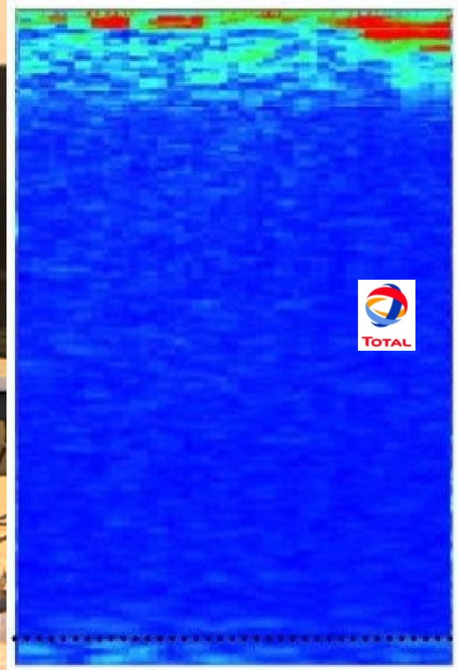

2000'
0.5Mo steels, NDT …
2010 +
Carbon Steel,
NDT UT advanced …
2012
Internal major REX for CS
(Refineries self assessment)
2017
Internal guideline issuance
(Unified methodology)
2017-2018
Site reviews
(10 sites; ~60 units)

SITE REVIEWS KEY LEARNINGS

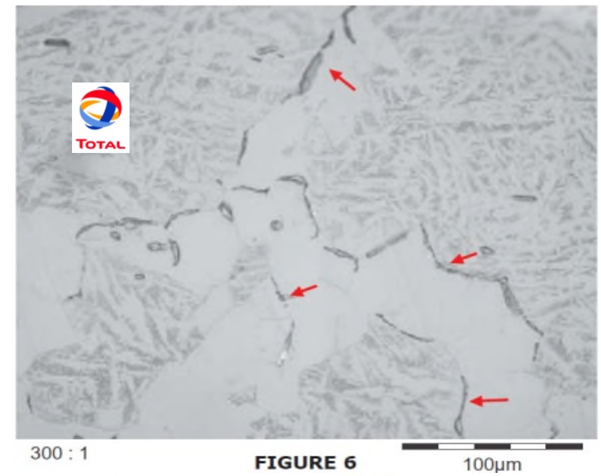
- Time consuming (organization, preparation, onsite meetings, report)
- Multi-skilled team essential (corporate + refinery)
- Difficulties for a comprehensive inventory :
  - Identifying (max) process conditions on some location => process simulations necessary (T/pH2 evalutation)
  - Evaluating transient phases impact
  - Digging into history / modifications
  - Looking @ specific areas (HX by-pass, spec break …)
- To be done at least 2 years ahead of a major TA
- Inspection / replacement strategy to be discussed with management
- Replacement = opportunity to take some samples for on-going/future work (NDT early detection; FFS; repairs)

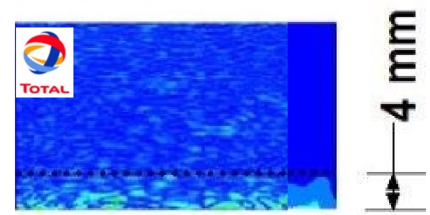
NEW UT TECHNIQUES DEVELOPMENTS

Block 3A



Linear PA 0°





TFM

Méthodes 2010

Méthode 2017

High frequency TOFD; PAUT / TFM

OUR CONCERNS

Inventory :
Modifications: modified P/T; equipment re-location ?
Time effect ? On very old units?

NDT /Inspection:
Early detection ?
Damage quantification ? Morphology ?
UT criteria ? Reference blocks ?
Operators certification ?
RBI approach ?

In case of HTHA detection:
FFS ?
Repairs ?

THANK YOU FOR YOU ATTENTION

QUESTIONS ?

HTHA = SAFETY ISSUE

WE ARE STILL OPEN TO DISCUSS WITH EVERYBODY ON ALL HTHA CONCERNS

SOPHIE.LOYAN@TOTAL.COM

CHARLES.LENEVE@TOTAL.COM

Appendix 9

Stress relaxation cracking : a design or metallurgical issue

(M. De Marco)

ISTITUTO ITALIANO DELLA SALDATURA
Il Gruppo

Stress Relaxation Cracking (SRC), a design or metallurgical issue?

M. De Marco

Weldability is…

…the capacity of a material to be welded

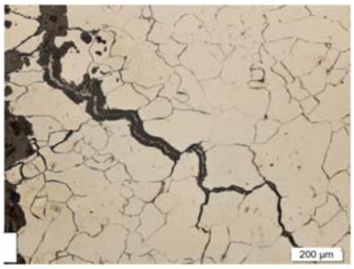
- ✓ under fabrication conditions imposed into a specific, suitably designed structure
- ✓ to perform satisfactorily in the intended service

By ignote at American Welding Society (AWS)

2

INTRODUCTION

- Stress relaxation cracking can occur **during fabrication or in service**
- Cracking of a metal due to stress relaxation during PWHT or service at elevated temperature – **500÷750 °C**
- Often observed in **welded joints of heavy wall sections** → weldability issue!
- Affected materials low alloy steels , 300 series SS, nickel based alloys as 800/800HT



Many names for the similar problem

Fabrication	In Service
Reheat cracking	Stress relaxation cracking
Stress relief cracking	Creep embrittlement cracking
Stress relaxation cracking (SRC)	Stress induced cracking
	Stress assisted grain boundary oxidation (SAGBO) cracking

- Appears the term **"creep"…**
- Then, SRC is a creep related failure?
- Someone can say Yes; it happens at relatively high temperature where **creep dominates mechanisms of fracture**
- Corrosion? No, it's not primarily related to corrosion; some oxidation occurs at crack side during propagation.

Susceptible materials

Alloy designation	Type	Composition
A508, Class 2	Steel forging	0.6Mo, 0.40Cr, 0.25C
A514, Grade F	Steel plate	0.5Mo, 0.5Cr, 0.05V, 0.15C
A517, Grade F	Steel plate	0.50Mo, 0.5Cr, 0.15C, 0.003B
A533, Grade B	Steel plate	0.5Mo, 0.20C
A710 (HSLA-80, HSLA-100)	Steel plate	2.0Ni, 0.5Cr, 0.5Mo, 1.0Cu, 0.05C
F/P22	Steel forging/plate	2.25Cr–1.0Mo–V
Type 347	Stainless steel	18Cr–11Ni–0.6Nb–0.04C
Type 321	Stainless steel	18Cr–10.5Ni–0.4Ti–0.04C
Alloy 800H	High-alloy SS	21Cr–32Ni–0.4Ti–0.4Al–0.1C

- Also 304 and 316 susceptible, especially in the "H" versions
- This presentations will focus on "austenitic" alloys

800HT> 347>800H>321>304>316

5

When?

- Fabrication: During PWHT
- Early in service: 200÷2000 hrs
- Mature: > 10000 hrs (more known as creep embrittlement ?)

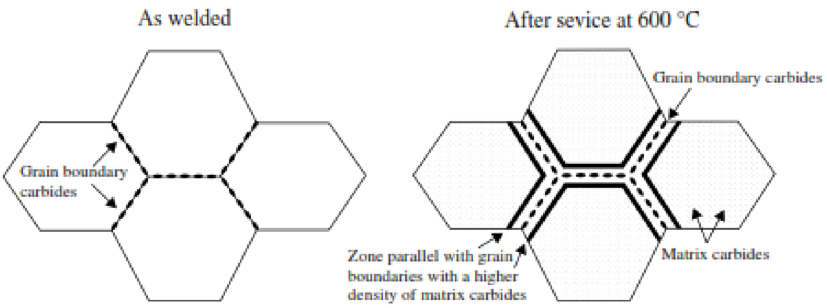
Complex matter

- **Many factors** interrelated in RCA
- Not corrosion related! Primarily mechanical induced.
- The high temperature environment induce typical oxidation phenomenon at crack side

6

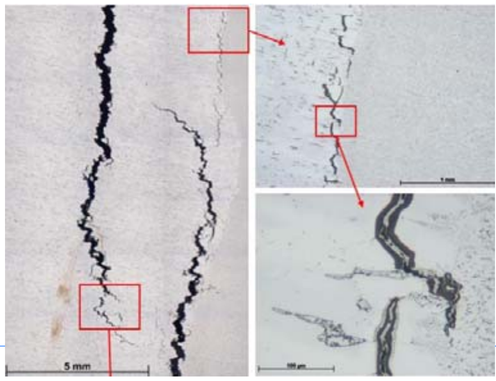
The metallurgical side of SRC

- Local **lack of high temperature (500-750 °C) ductility** of weld zones (WM, HAZ) due to age hardening effects
- Local low high T ductility due to
  - **Large intergranular carbides** (M_{23} C_6) surrounded by Precipitation Free Zones-PFZ
  - **Fine intragranular carbides** (NbC, TiC) precipitated out at dislocations that strengthen the grain interiors
- Coarse grain materials (<4 ASTM E112) more susceptible.

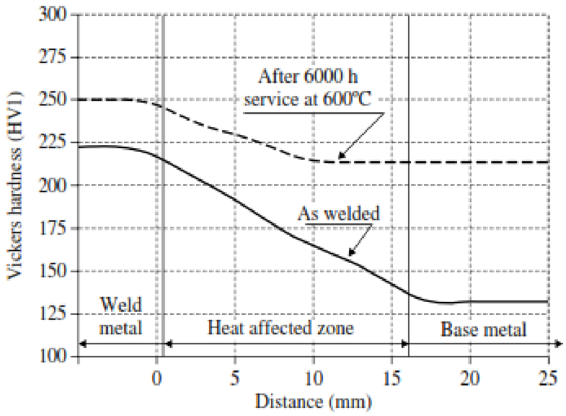


Appearance

- Cracks almost always confined to **WM and HAZ**
- Cracks at **grain boundaries**
- Cracks **normal to pipe surface**
- Little or no evidence of deformation
- On cracked grain boundaries, a **metallic rich filament** can be recognized incapsulated in an oxide layer (if cracking was in service)



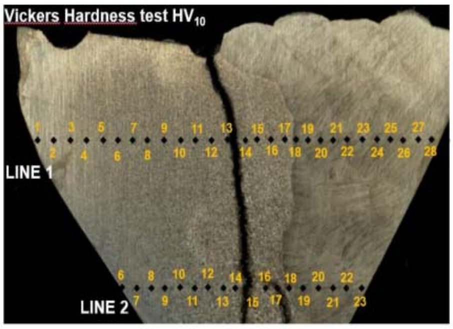
"**Age hardening**" effect can induce hardness level greater than the one typically found in annealed austenitic materials

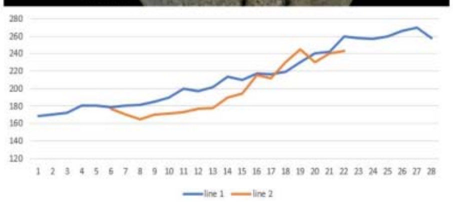


Alloy 800H after service @ 600 °C

Real Case

- Parent Material AISI 321H, consumable E347
- Piping system 70 mm thick butt weld failure
- Crack in HAZ
- 650 °C , 2000 hrs

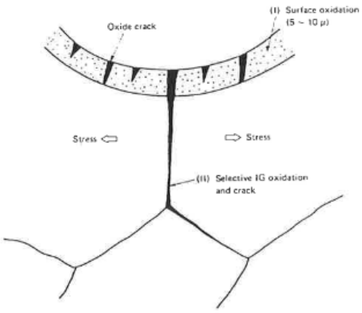




Real Case

AISI 321H failed at 650 °C

Metallic filament (iron rich)



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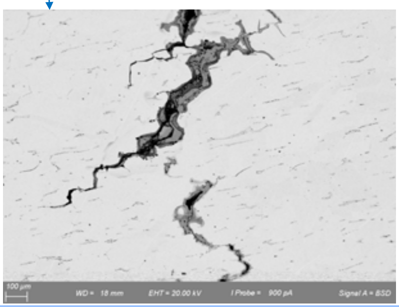
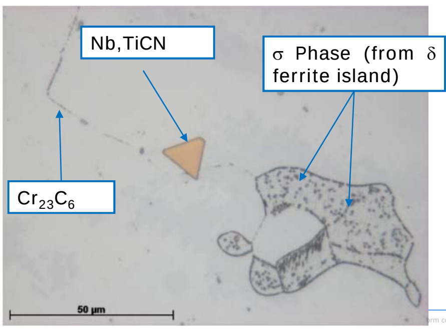
- SRC is **grain boundary related mechanism**
- Presence of sigma phase can promote the phenomenon?
- Real case on 321H heavy pipe weld (1200 hrs @ 600 °C)
  - Some step wise propagation at crack tip
  - Presence of scattered sigma phase at grain boundaries
  - Secondary influence?
  - Further reduction in HT ductility?





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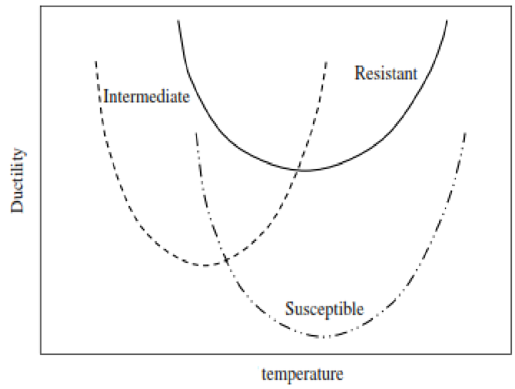
But…

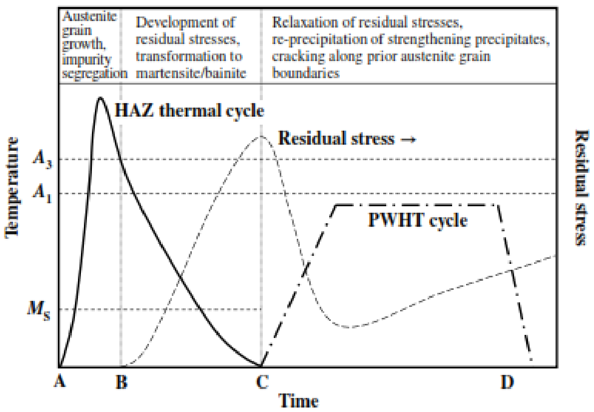
…a local stress/strain field must be present that can highlight the local lack of HT ductility

- Ductile **strain relief cannot occur** (high temperature brittleness?)
- Local relaxation as small as **0,1 %** can induce SRC in susceptible weldments



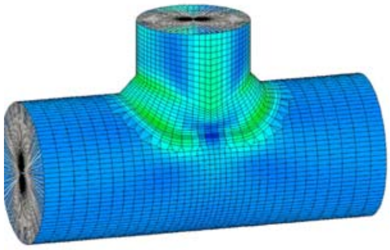
SRC during PWTH

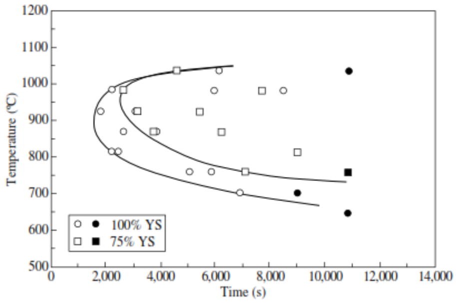
- Relaxation of residual stresses from welding
- If time of carbides precipitation overlaps with relaxation effect at temperature, cracks can occur; the relaxation cannot be accommodated
- It depends on **thermal gradient** (heavy section worse!)



SRC during Service

- Weld zones loaded during service
  - Thermal loads
  - Mechanical loads
  - Cyclic service





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Recent cases analyzed by IIS
Austenitic SS 321H, 304H

- Mainly due to
  - ✓ Weld located in **high stress/strain area** (bending moment, severe displacements, local strain effect, thermal load during start-up/shutdown)
  - ✓ Presence od **start-up/shut-down cycles**
  - ✓ Natural susceptibility to SRC of **"as welded"** (No PWHT) parent materials
  - ✓ Not optimal **fabrication practices** (e.g. welding, installation, fit-up)
    - ✓ Weaknesses of fabrication specifications (no knowledge of SRC)
  - ✓ Weaknesses in the **design** ?

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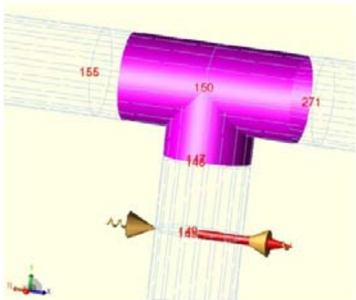
The Design Team

- For sure it should have a **metallurgical / material engineer** (real construction with real materials are not a simple purple model!)
  - Material selection!
  - Material and fabrication requisitions!
- **Verify local stress / strain** (FEA in most critical area with "primary + secondary + peak" stresses)
- Consider the **lower possible allowable stresses** and limit as much as possible **local strains**.
- Locate as much as possible **field welds in low stress locations**.
- Specify the optimal **support systems.**



- Some Engineering company/End-users specifications contain indications/recommendations for the design team.
- And the codes?

- **Asme II Part D Note G5 (Table 1A)**

G5 Due to the relatively low yield strength of these materials, these higher stress values were established at temperatures where the short-time tensile properties govern to permit the use of these alloys where slightly greater deformation is acceptable. The stress values in this range exceed 66⅔% but do not exceed 90% of the yield strength at temperature. Use of these stresses may result in dimensional changes due to permanent strain. These stress values are not recommended for the flanges of gasketed joints or other applications where slight amounts of distortion can cause leakage or malfunction. For Section III applications, Table Y-2 lists multiplying factors that, when applied to the yield strength values shown in Table Y-1, will give allowable stress values that will result in lower levels of permanent strain.

- **ASME B31.3 Note 8 of Table 302.3.5 (weld joint strength reduction factor)**

(8) Certain heats of the austenitic stainless steels, particularly for those grades whose creep strength is enhanced by the precipitation of temper-resistant carbides and carbonitrides, can suffer from an embrittlement condition in the weld heat affected zone that can lead to premature failure of welded components operating at elevated temperatures. A solution annealing heat treatment of the weld area mitigates this susceptibility.

PWHT or NO PWHT?...this is the problem

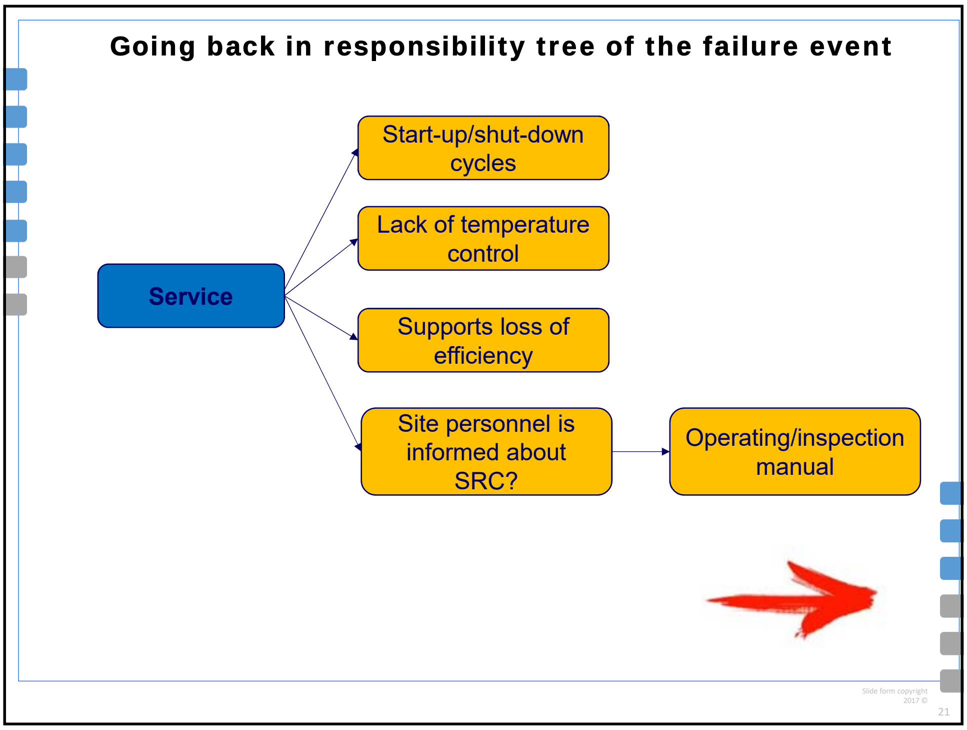
- Sometimes required by code for Pressure Vessel (e.g. 800 H/HT for service T> 540 °C).
- **Stress relief effect and controlled precipitation of carbides**.
  - Increase in reliability in High T service of SRC susceptible materials.
- 900 °C for 1.5÷4 hr can be an optimal solution, easily applicable to stabilized alloys (321, 347, 800H/HT).
- Solution annealing (e.g. 1050 °C) can be difficult in practice.
- DANGER! **PWHT** can induce **SRC during PWHT** (stress relaxation overlaps carbide strengthening precipitation), especially in heavy sections (> 25 mm).
  - Control the thermal gradient
  - Easier in shop PWHT, difficult in field PWHT
- Execution of PWHT shall be evaluated by **risk / benefit analysis**

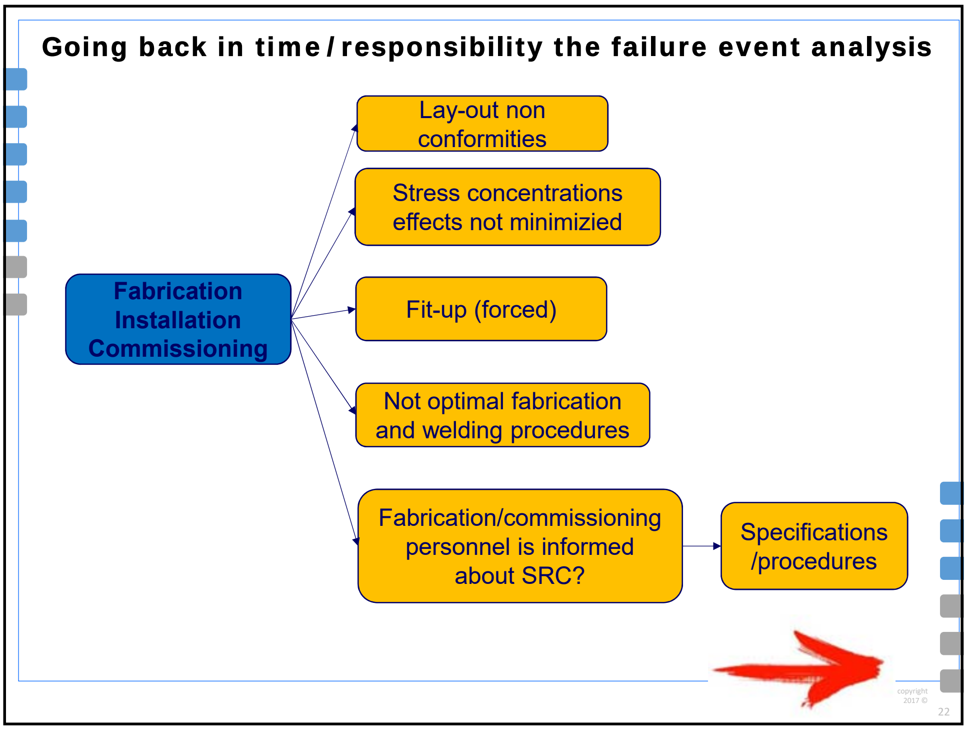
Going back in the physical causes analysis

Mode of fracture → Intergranular in HAZ or WM with oxidation and metallic rich filament

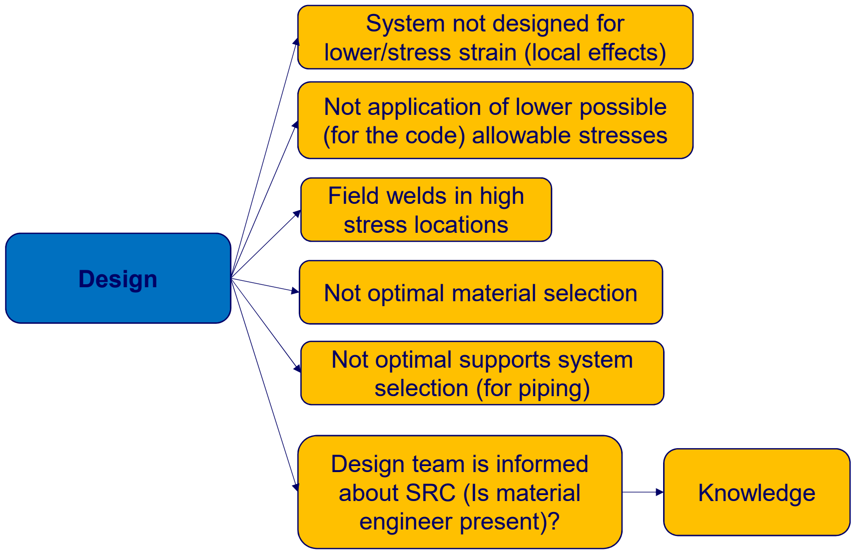
Mechanism of fracture → SRC

Physical causes → Susceptible material Lack of HT ductility at high T in WM and HAZ + (AND) Stress/strain field


Going back in responsibility tree of the failure event
Service
Start-up/shut-down cycles
Lack of temperature control
Supports loss of efficiency
Site personnel is informed about SRC?
Operating/inspection manual


Going back in time / responsibility the failure event analysis
Fabrication Installation Commissioning
Lay-out non conformities
Stress concentrations effects not minimizied
Fit-up (forced)
Not optimal fabrication and welding procedures
Fabrication/commissioning personnel is informed about SRC?
Specifications /procedures

Going back in time / responsibility the failure event analysis



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Thanks for your attention

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Appendix 10

Biodetergent as part of the cooling water system treatment to have a better legionella control

(V. Bour-Beucler)

Biodetergent as part of the cooling water system treatment to have a better legionella control

Rome 2019 April 10th
Valerie Bour Beucler Nalco Champion

Agenda

- Introduction
- Bacteria and cooling water systems
- Biofouling and its effects
- Biodetergent an important part of the cooling water system treatments
- Case study of a new cooling system in the North of Europe.
- Conclusion

What do Microbes Need to Grow ?

- Essential elements
  - C, N, P, S
  - *Sources*: leaks, air-borne contamination, make-up water, and product components, etc.

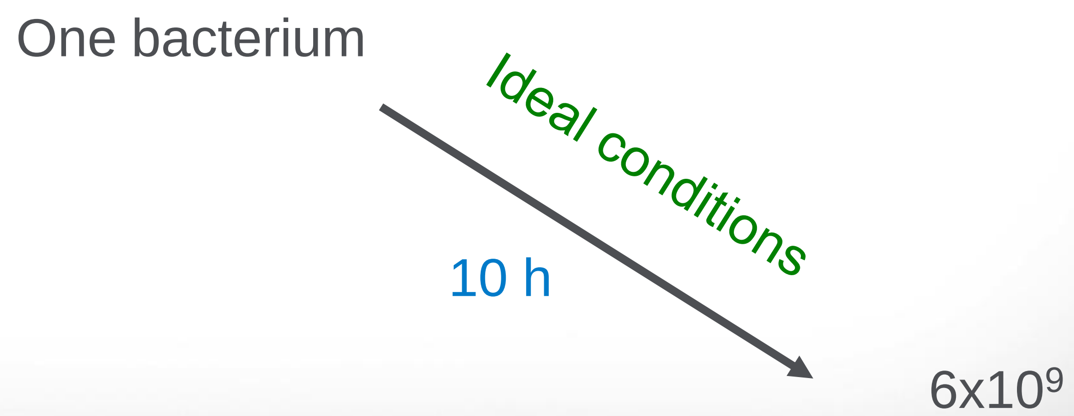
- Suitable conditions
  - Temperature: 10 - 50 ° C (50 to 125 ° F)
  - pH: 3 -10
  - Oxygen for aerobes
  - Sunlight for algae
  - Deposits to limit Oxygen for anaerobes

- All these conditions are present in our cooling water systems

Bacteria and Legionella could grow very fast in a cooling water

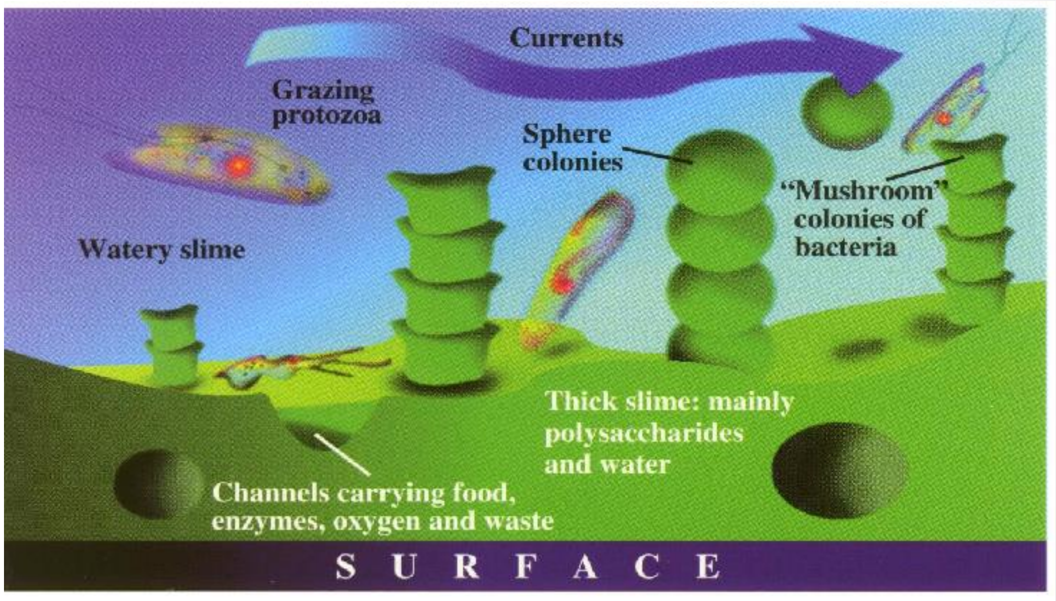
If a cooling system is non treated properly and left with the right conditions of growth, bacteria can grow rapidly and cause problems

- In the lab, bacteria replicate in 20 min



Biofilm

All organisms earlier discussed do not live in the water system individually, but together form an ecosystem, which is called biofilm



Biofilm – where 90% of the microbes Live

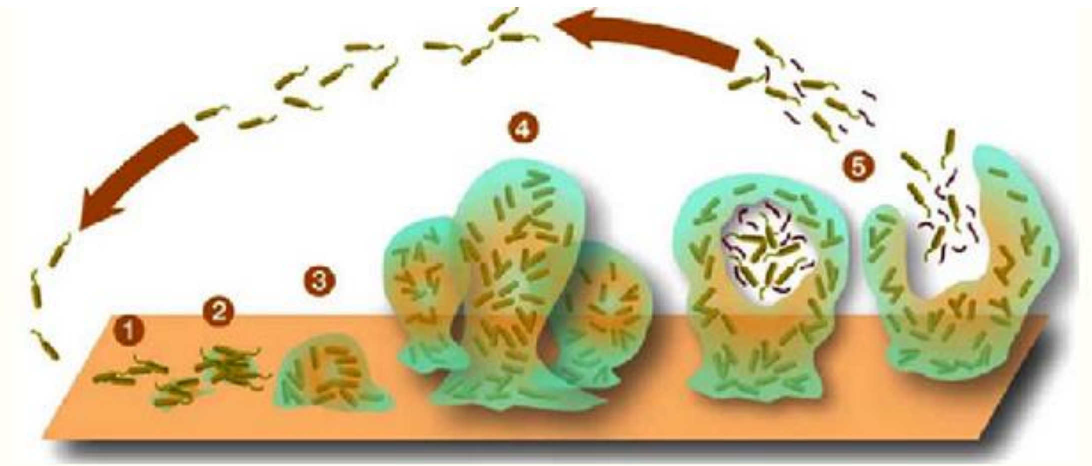
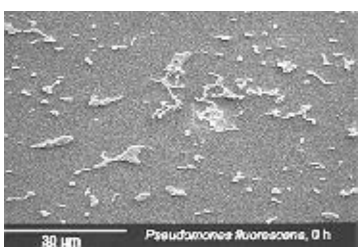
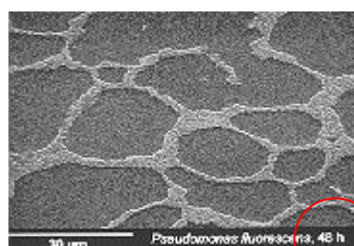


Fig. 1: The biofilm life cycle. 1: individual cells populate the surface. 2: extracellular polymeric substance (EPS) is produced and attachment becomes irreversible. 3 & 4: biofilm architecture develops and matures. 5: single cells are released from the biofilm.



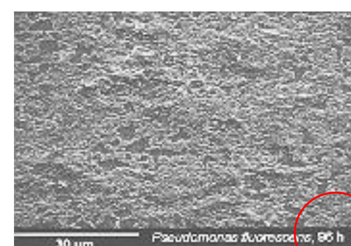
1. Cells & aggregates begin to attach

(minutes)



2. Microcolonies merge

(hours)



3. Biofilm is covering full surface

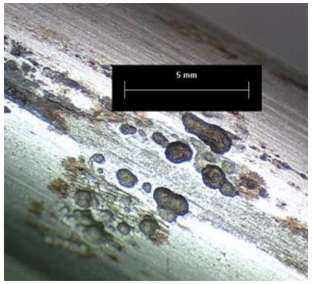
(days)

How Does Biofilm Affect your Operation?

- Fouling: Energy Losses

Deposit	Thermal Conductivity (W/mK)
Calcium Carbonate	2.26 - 2.93
Biofilm	0.63

- Microbially Influenced Corrosion:
  - Premature Equipment Replacement
  - Unscheduled Maintenance or Downtime



- Health and Safety Related Issues: Legionella

Biofilm Increases Fill Fouling

- Loss of cooling efficiency
- Production capacity reduction
- Cooling tower failure
- Tower fill replacement
- Tower capacity derating
- Health-related concerns

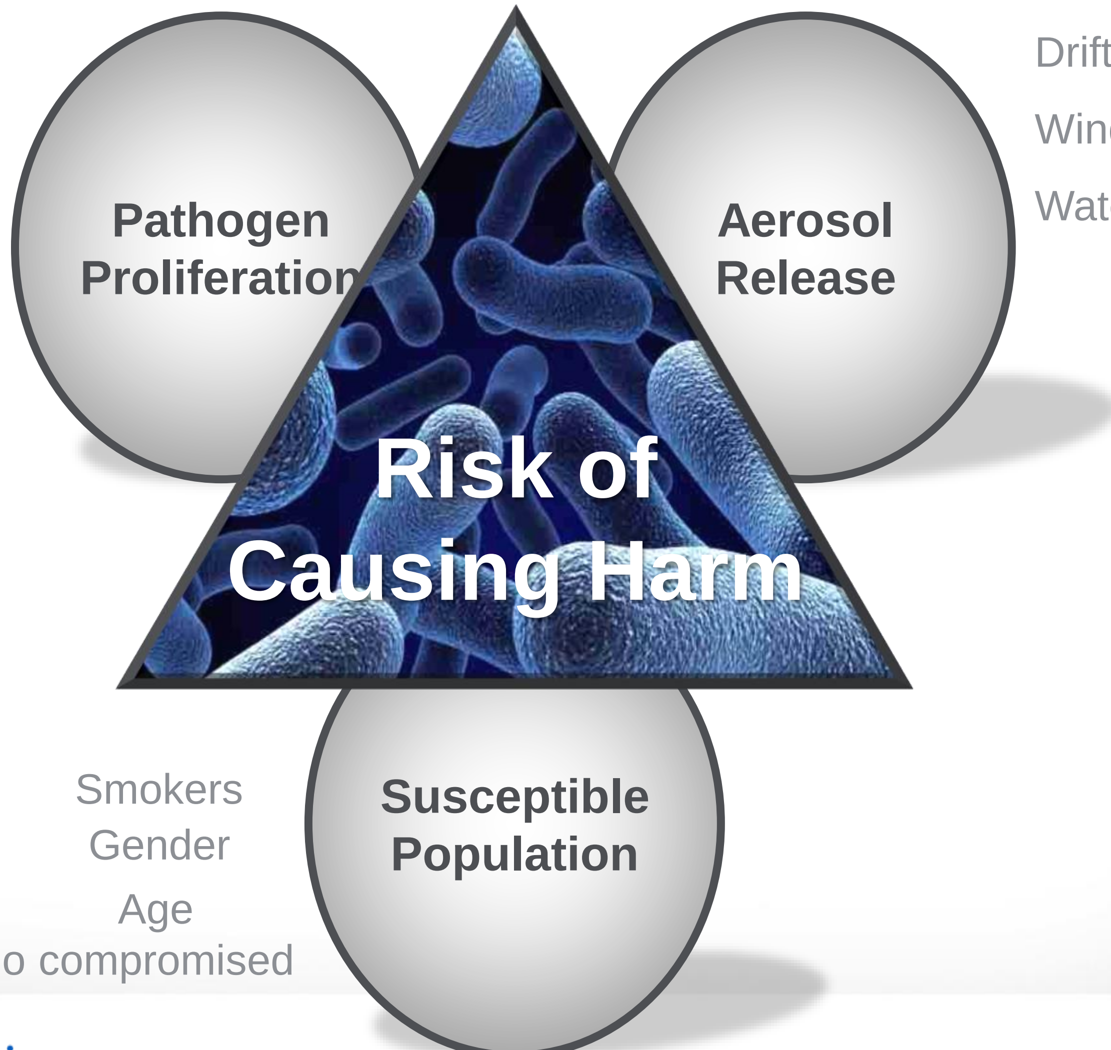
Conditions that increase risk of causing harm

Stagnation

Biofilms

Deposits

Biocides



Drift Eliminator efficiency

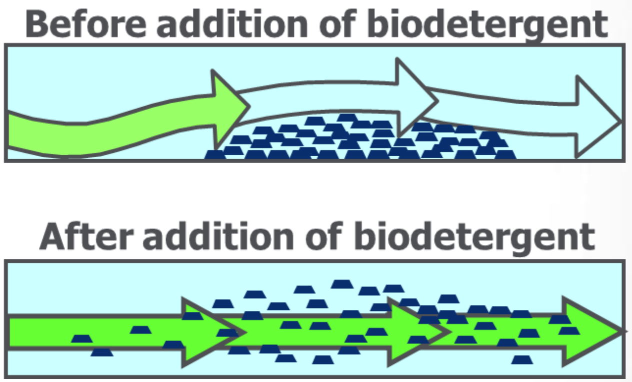
Wind

Water Flow

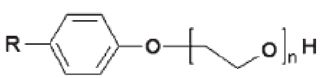
Smokers
Gender
Age
Immuno compromised

Biodetergents as part of the cooling water system treatments

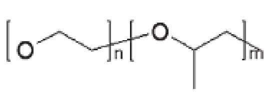
- Surface-active chemicals
- No biocidal characteristics on their own, should be associated with biocides
- Prevent micro-organisms from attaching to surfaces
- Accelerate detachment of a biofilm by loosening the slime matrix



Nonionic Surfactants



Alkylphenol Ethoxylate
(R = 8-12 and n = 5-10)



Ethylene Oxide/Propylene Oxide Copolymer (n = 2-60, m = 15-80)

Biodetergent combined to biocide will kill a part of the bacteria present in the biofilm and will clean cooling water surfaces and reduce biofilm

Case study of a new cooling water system

- New cooling water system (start up and passivation done successfully)
- No biodetergent injection planned (owner decision)
- Cooling system of small size (300 m3 of volume) without acid injection
- All organic treatment, controlled by 3D Trasar
- Oxidizing biocide with bromine and free chlorine residual controlled by chlorometer
- Shock dosage of non oxidizing biocide
- ATP check weekly, Microbio analysis 2 par month and Legionella analysis monthly

New cooling water system in North of Europe

- After some months of running (less than 1 year)

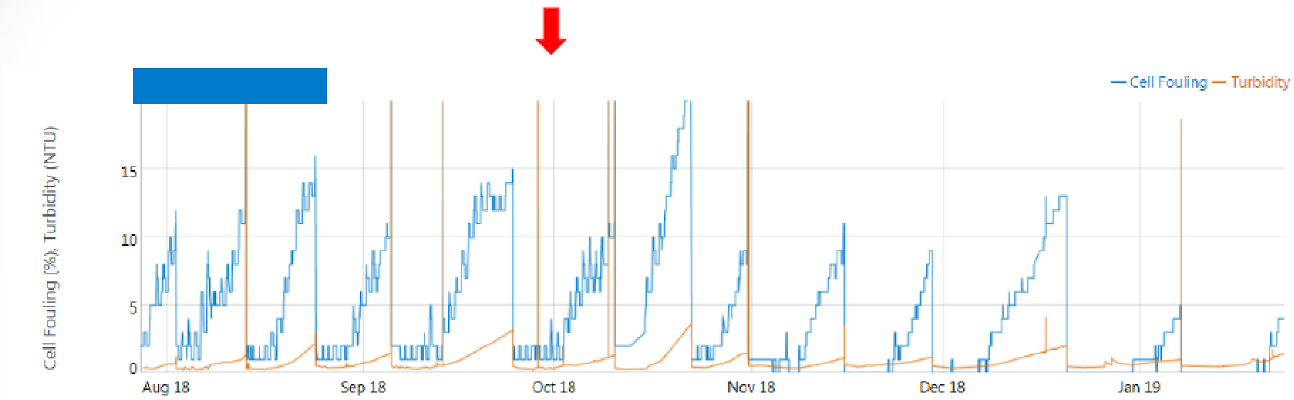
System assurance – KPI’s

KPI's	KPI set	unit	KPI result	% on target	remarks
Corrosion					
mild steel corrosion (coupon)	< 1,0	mpy	x	x	no coupons available
iron	< 1,0	ppm Fe	0,12	100%	
MS (localized corrosion)	no		x	x	no coupons available
Scaling/fouling					
Ryznar Index	> 3,6		3,83	100%	
Oil/grease	<300	ppb	x	x	
visual inspection corrosion coupons	no		x	x	no coupons available
flow drop since TA	< 5%	%	1,1%	x	15/01/2019: 2590 m^3/h 19/09/2017: 2620 m^3/h
Microbio inhibition					
Microbiology	<10.000	CFU/ml		100%	
SRB	< 1	CFU/ml		100%	
legionella	< 1000	CFU/ l		75%	8000 CFU/L 4/09 20000 CFU/L 2/10
Enviromental					
AOX	< 0,8	ppm C			excluded from contract
online TOC	< 20	ppm C	10,35	100%	average value AI945203

- Legionella amount < 1000 CFU/l since mid-October!
- 5x positive Legionella, 2x above spec.

Effect of biofouling

Cell fouling 3Dtrasar



- 15/10: 20 000 CFU/L Legionella → ¼ chock Biocide
- 17/10: Start dosing 1 liter injections N73550 2 x /d + extra ATP monitoring → OK
- 18/10: Start dosing 2 liter injections N73550 2 x /d

→Significant decrease of cell fouling
→Same impact seen on cleaning grids

→ Relation between biocide upsets and cell fouling

Conclusion

- Biodetergent introduction help to minimise fouling
- Biodetergent should be considered as a best practices associated to the biocides to have microbio under control
- Even new cooling system outside from process leak can suffer from bio growth and biofouling increase particularly if no biodetergent has been dosed continuously.

Appendix 11

Stress corrosion cracking of stainless steels under insulation

(S. Koller)

SCC of stainless steel under insulation

HOLBORN EUROPA RAFFINERIE GMBH

MEA-Regenerator (stripper)

Build in 1979

Material:

1.4541-X6CrNiTi18-10 (AISI 321) – 10 mm

Dimension:

Hight: ≈ 17 m, Ø = 2020 mm

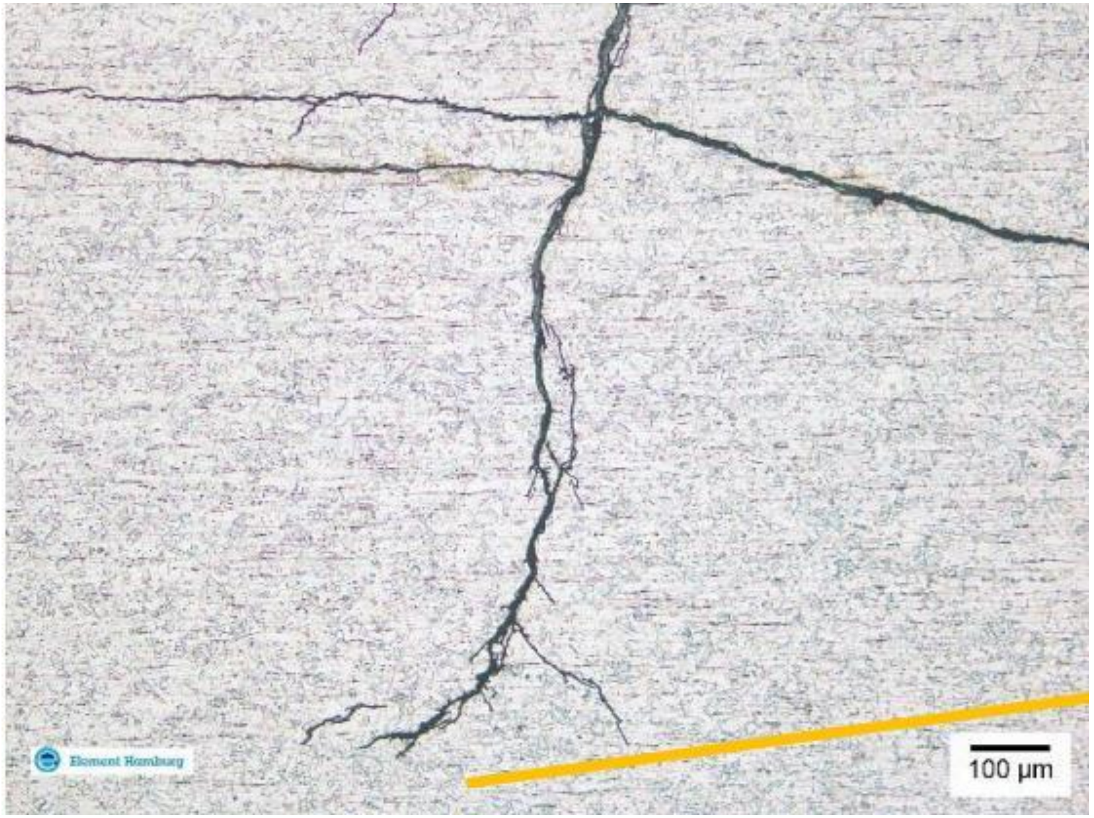
Operating (design) conditions:

P_{max} = 3,5 bar, T_{max} = 160 °C

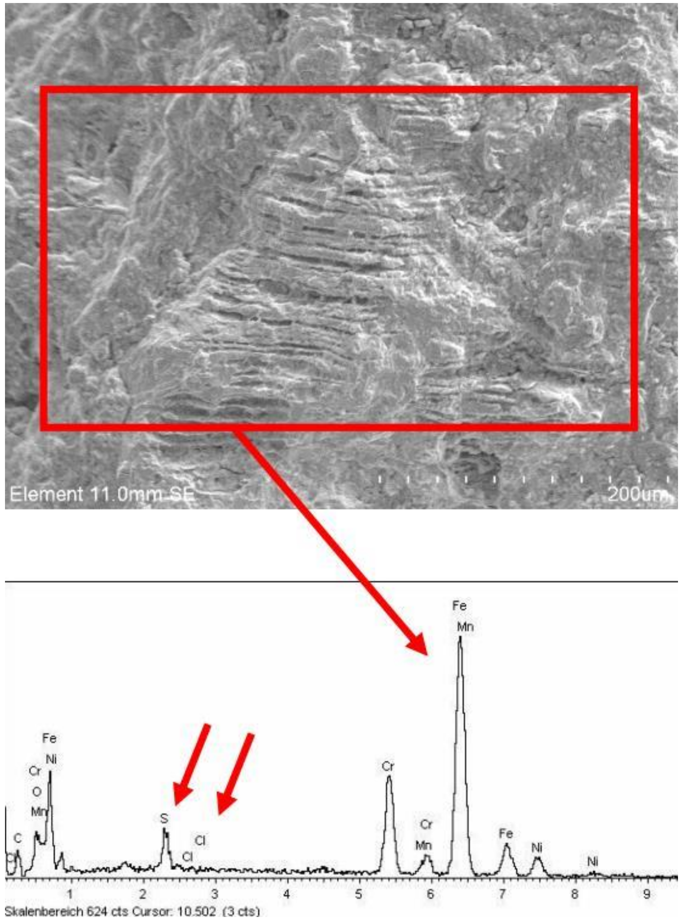
MEA-Regenerator with removed insulation

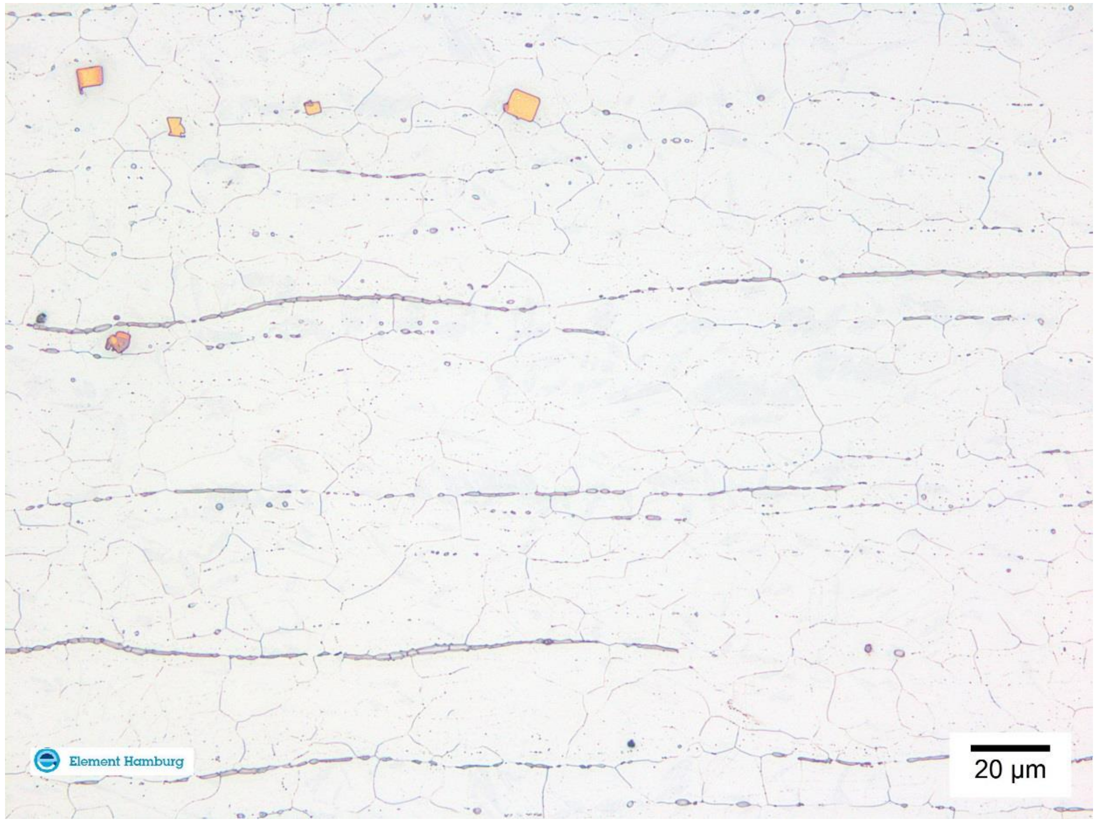
Crack indication after PT

Laboratory examination

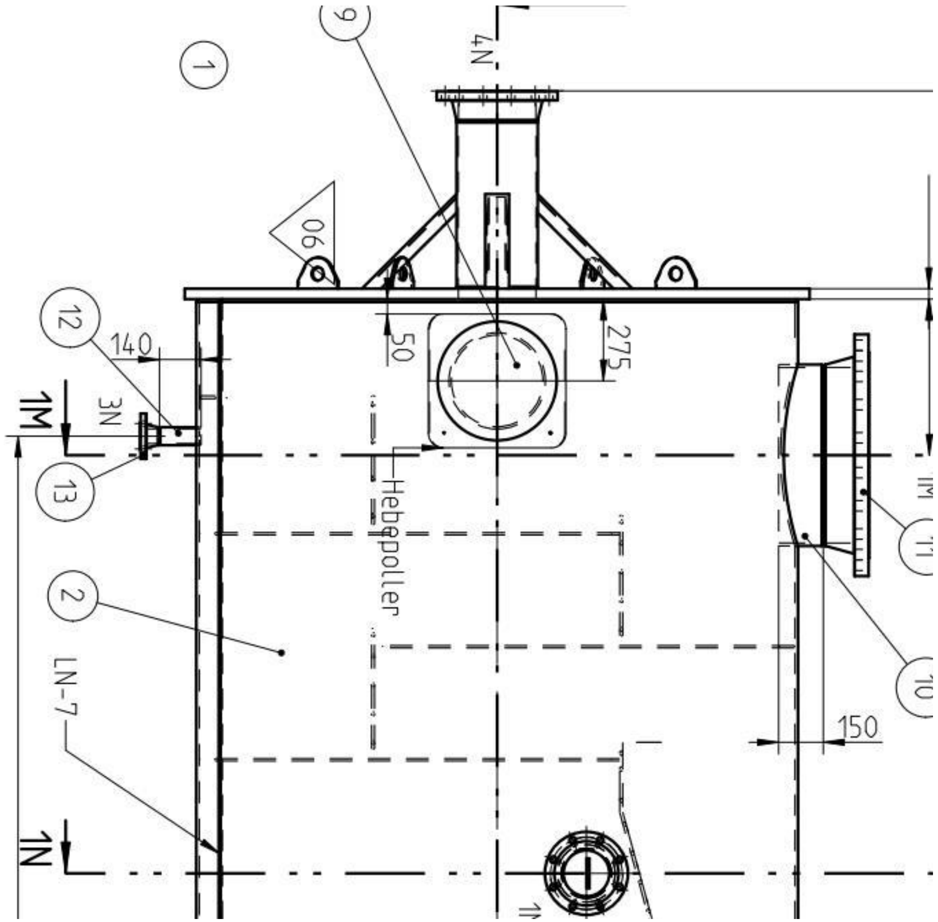


Laboratory examination





Renewed tower



Result

If you have old insulated stainless steel equipment, take care of it!

Appendix 12

Influence of ferrite content on Sulfide Stress Corrosion of duplex stainless steel

(M. Monnot)

Working Party 15, April 10th 2019

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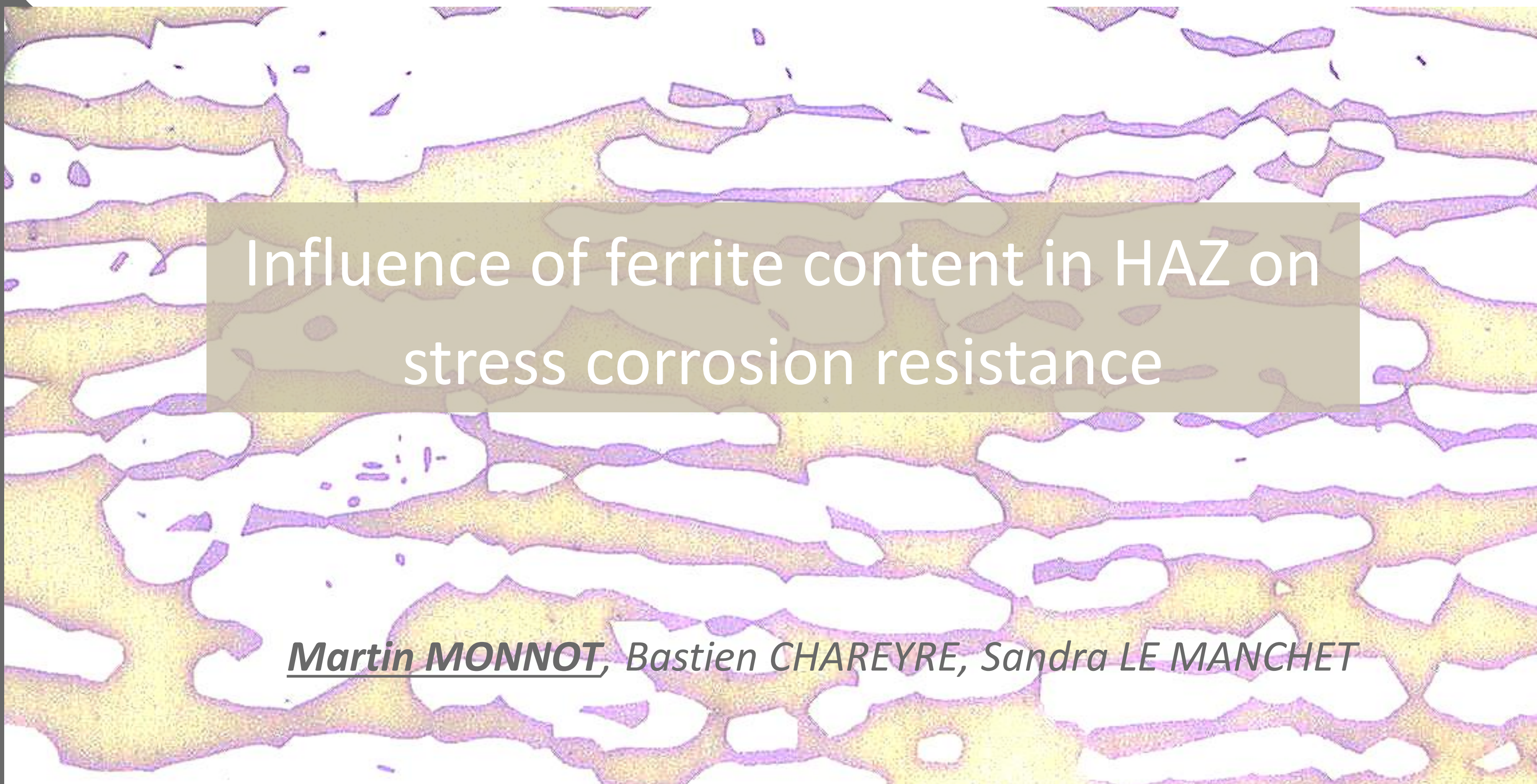

Influence of ferrite content in HAZ on stress corrosion resistance

Martin MONNOT, *Bastien CHAREYRE, Sandra LE MANCHET*

Introduction

- Duplex stainless steels are widely used for various application (Refinery application for example). The microstructure contains 35%-55% ferrite to combine high mechanical and good corrosion resistance.
- Several standards limit ferrite content in Heat affected zone (HAZ) of duplex stainless steel to 65% or 70%. Failures due to chloride stress corrosion cracking attributed to a too high ferrite content in the weld have thus been reported.
- Nevertheless, it is still unclear what is the ferrite content limit to affect significantly corrosion resistance properties.
- The aim of the present study is to quantify the effect of ferrite content on stress corrosion resistance in sour environment

Outlines

- Material and methods
- Preparation of Gleeble specimens
- Stress corrosion susceptibility

Material : Duplex grade UR™ 2205

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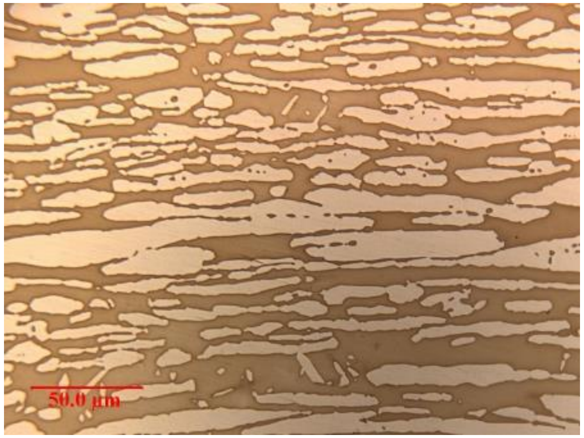
Grade	C	Ni	Cr	Mn	Si	Mo	N	PREn*
UR™ 2205	0.022	5.63	22.18	1.69	0.43	2.75	0.128	**33**

Grade	AYS		UTS		El %
	MPa	ksi	MPa	ksi	
UR™ 2205	550	80	655	95	25

**PREn = Cr + 3.3 Mo + 16 N*



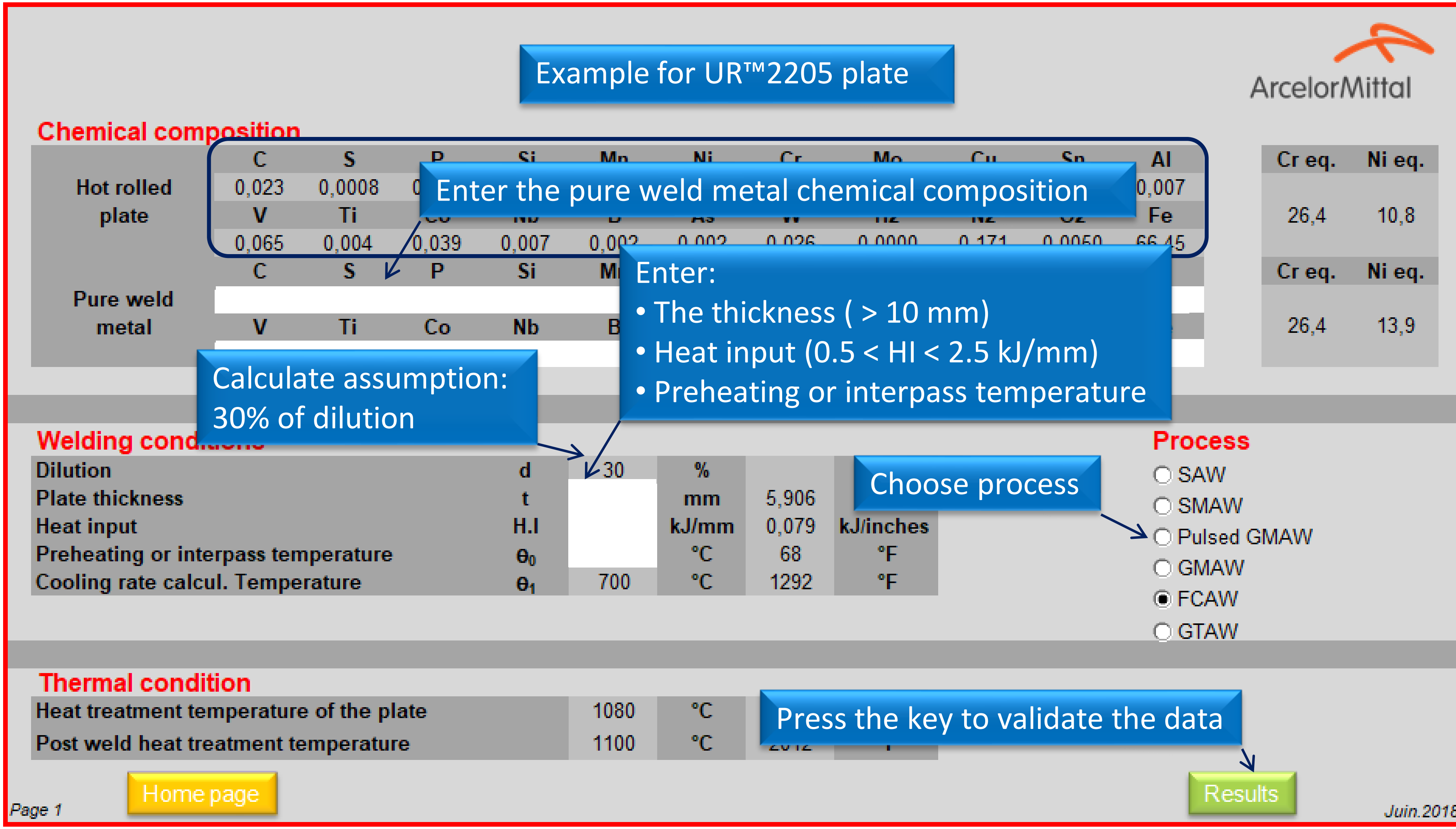
Typical microstructure of UR™ 2205

Methods

- **Test method: Slow Strain Rate Traction (SSRT)**
  - Solution : 100 g L^{-1} NaCl, 0.5 bar H_2S, pH=4.5, 90°C
  - Reference environment : Glycerine at 90°C
  - Strain rate : 10^{-6} s^{-1}

Preparation of Gleeble specimens

Prediction with Formulinox



Preparation of Gleeble specimens

Prediction with Formulinox

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Weld metal chemical composition with 30% of dilution

Chemical composition

Weld metal	C	S	P	Si	Mn	Ni	Cr	Mo	Cu	Sn	Al
	0,028	0,004	0,021	0,477	1,527	7,922	22,349	3,010	0,043	0,001	0,008
	V	Ti	Co	Nb	B	As	W	H2	N2	O2	Fe
	0,055	0,003	0,012	0,002	0,001	0,000	0,008	0,000	0,156	0,002	64,37

Thermal Cycle

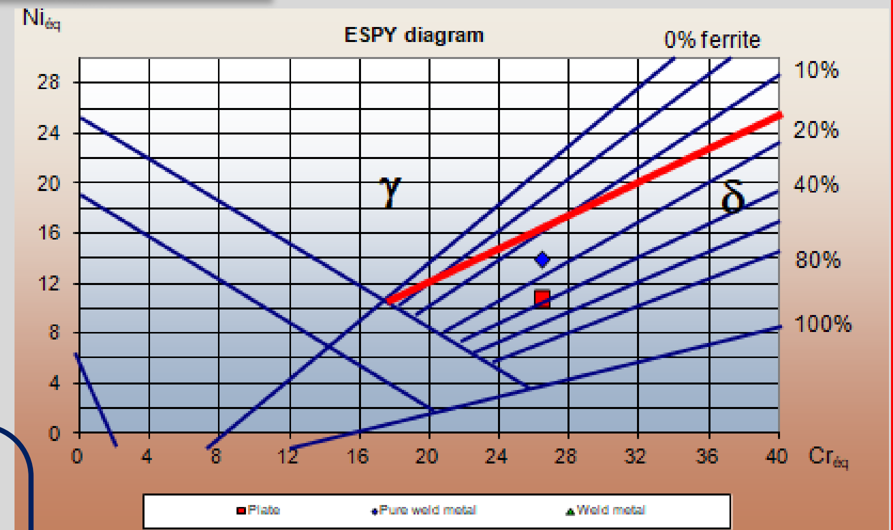
Cooling rate at

Microstructure (ferrite %, risk of hot cracking…)

…. nitrogen solubility 0,29 %

Microstructure

ESPY ferrite	22	%
ESPY ferrite	22	FN
Primary solidification type	delta	
Risk of hot cracking	low	
Risk of hydrogen embrittlement	no	
As welded		
Plate ferrite %	52	%
Weld metal maxi. ferrite%	35	%
Maximum ferrite% in HAZ	69	%
Solution annealed		
Weld metal ferrite %	30	after H.T 1100°C
Plate ferrite %	54	after H.T 1100°C



Weld mechanical properties

Maximum hardness in HAZ	269	Hv
Maximum hardness in weld m…	[illegible]	Hv
Hardness in weld metal (avera…		
Weld metal U.T.S. (+20°C)		
Weld metal Y.S.0,2% (+20°C)		
Ductile fracture at -50°C in we…		yes
Ductile fracture at -50°C in weld metal (sol. annealed)		yes

Possibility to chose five test temperatures for CVN

Plate mechanical properties

Plate CVN (YX) at	20	°C	166	J	122	ft-lb	
Plate U.T.S.(+20°C)	T.D.	624	L.D.	629	MPa	91	Ksi
Plate $YS_{0,2\%}$(+20°C)	T.D.	424	L.D.	428	MPa	62	Ksi

PREN (weld metal)	35			
Weld metal CPT (as welded)	22	°C	72	°F
PREN (plate)	35			
Plate CPT	39	°C	102	°F

Corrosion properties ASTM G48A

Page 2 Juin 2018

Preparation of Gleeble specimens

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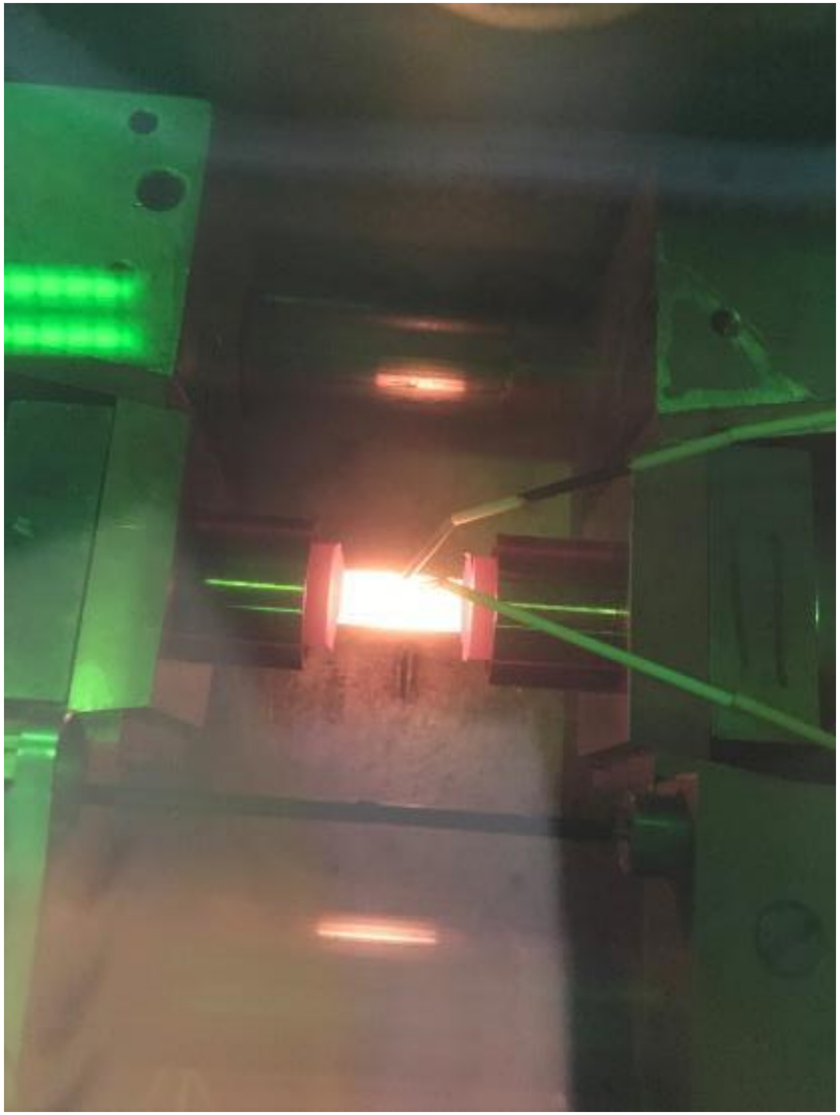
- **Thermal cycle:**
  - Increase of temperature to 1300°C
  - Cooling rate : 1°C/s or 57°C/s
- **Specimen size** : 11 x 11 x 110 mm

Gleeble specimen allows to have HAZ microstructure on the whole calibrated zone

Remark: Gleeble specimen does not take into account the fact that weld microstructure is heterogenous



Preparation of Gleeble specimens

Ferrite content

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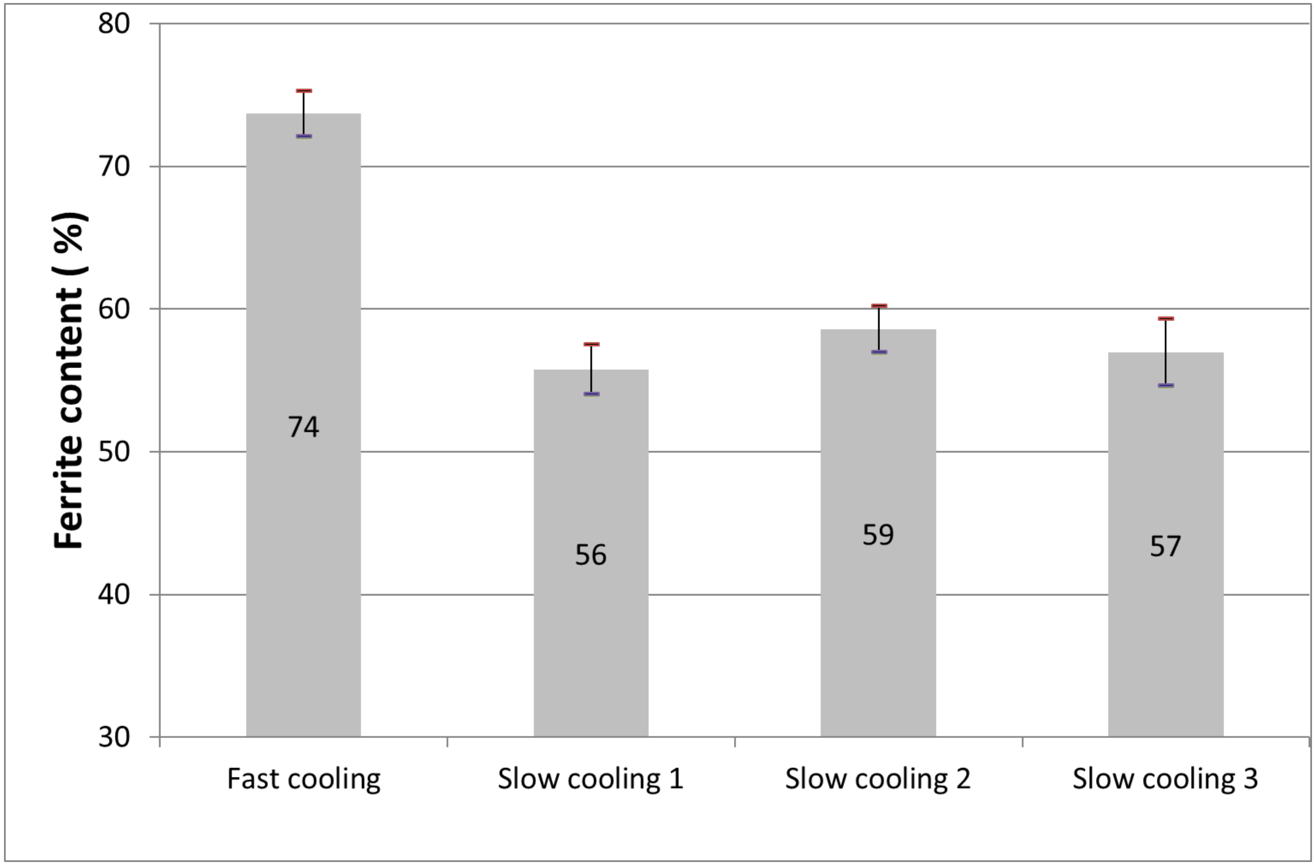
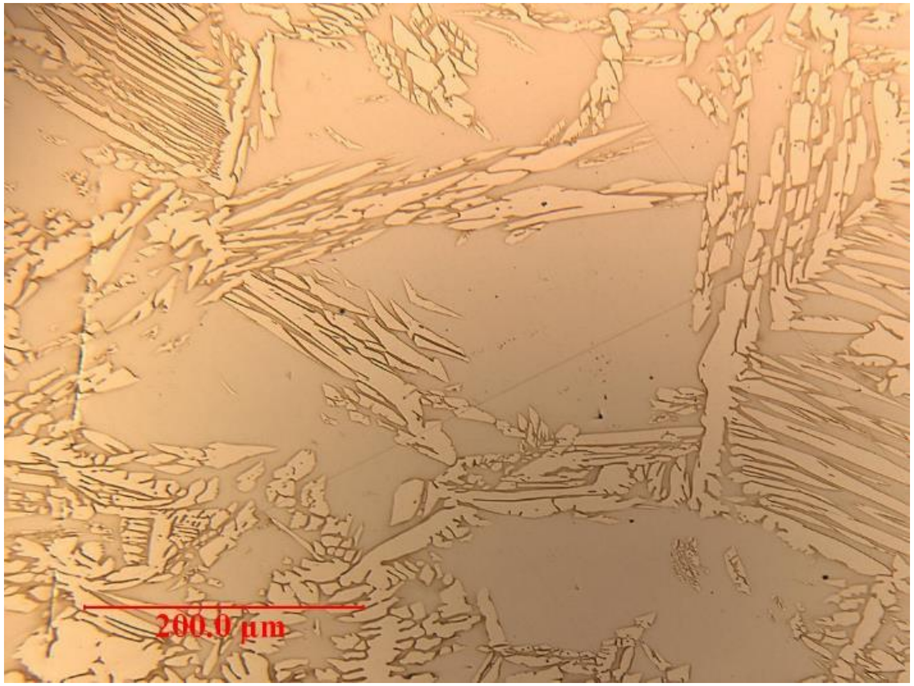


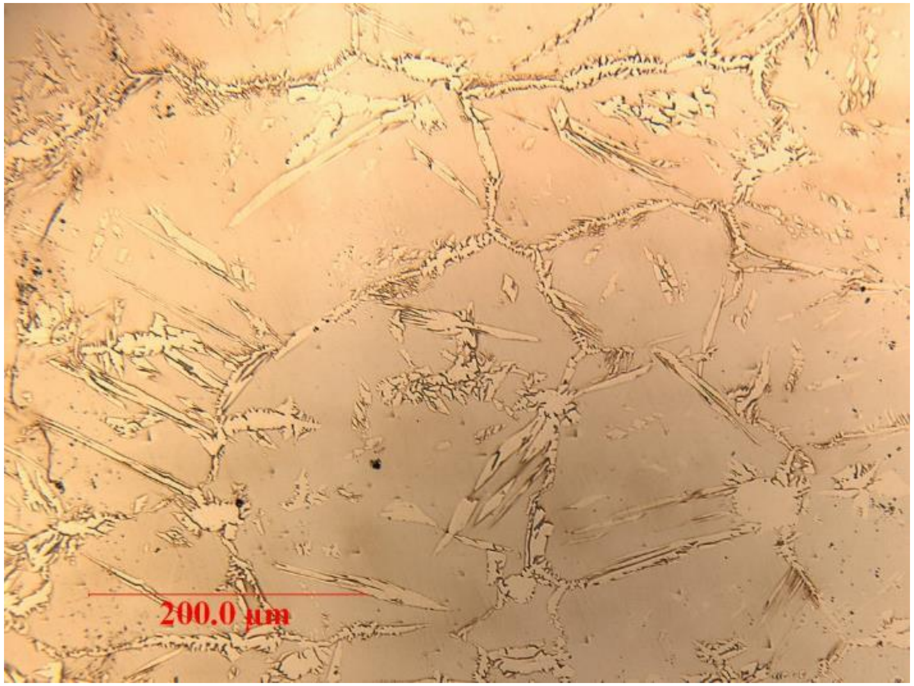
Ferrite content in function of cooling rate

Gleeble specimens with UR™ 2205 allows simulation of HAZ with ferrite content between 58% and 74%.
Ferrite content in accordance with Formulinox calculations

Preparation of Gleeble specimens

Microstructure





Microstructure of Gleeble specimen : slow cooling (left), fast cooling (right)

Microstructure morphology is similar to the microstructure observed on real welds

Stress corrosion susceptibility

SSRT curves

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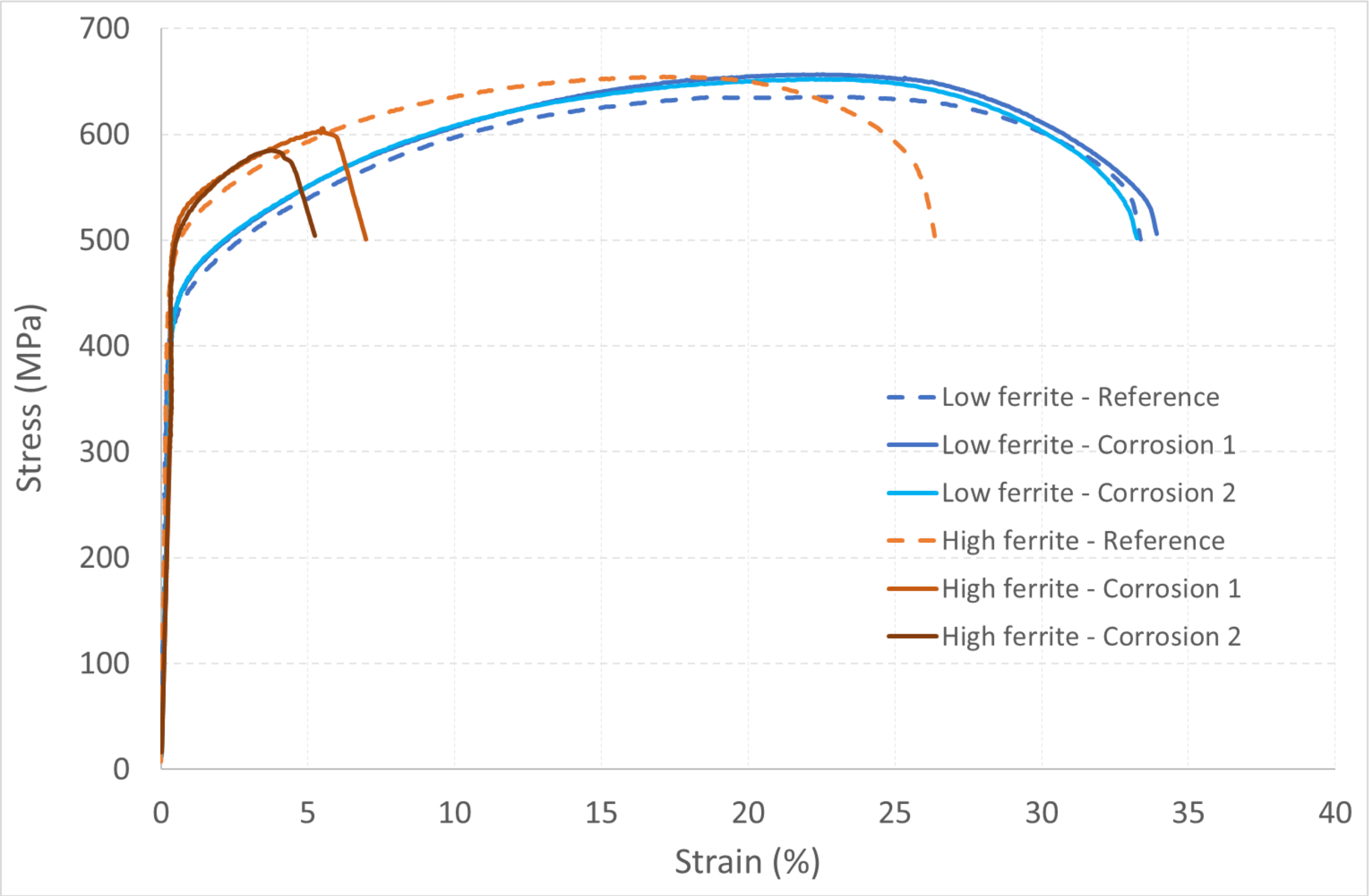
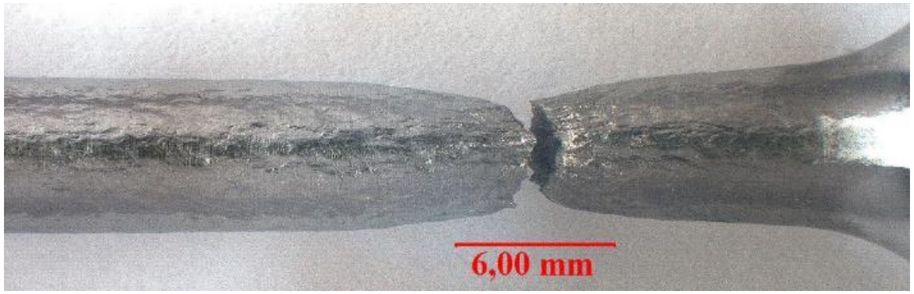


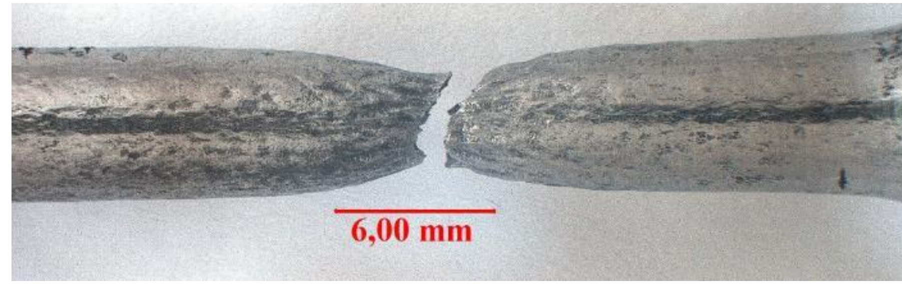
SSRT curves in 100 g L^{-1} NaCl, 0.5 bar H_2S, pH=4.5, 90°C

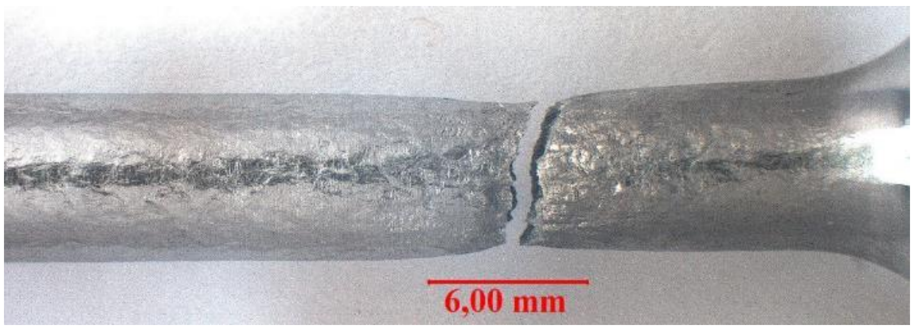
- No stress corrosion susceptibility for ferrite content around 58%
- High stress corrosion susceptibility for ferrite content around 75%

Stress corrosion susceptibility

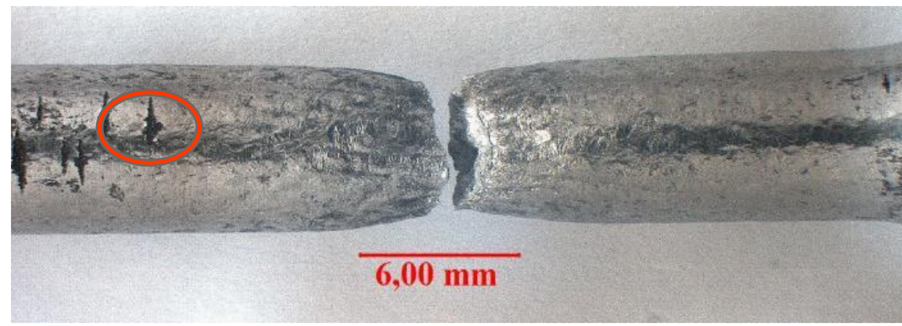
Low ferrite content







SSRT specimen in glycerin

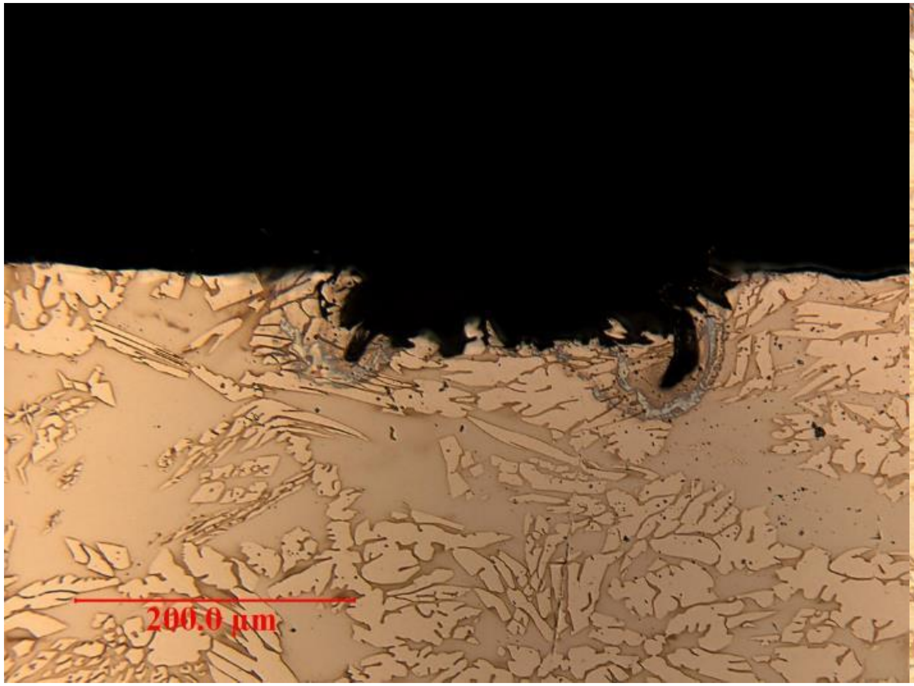


SSRT specimen in corrosive environment

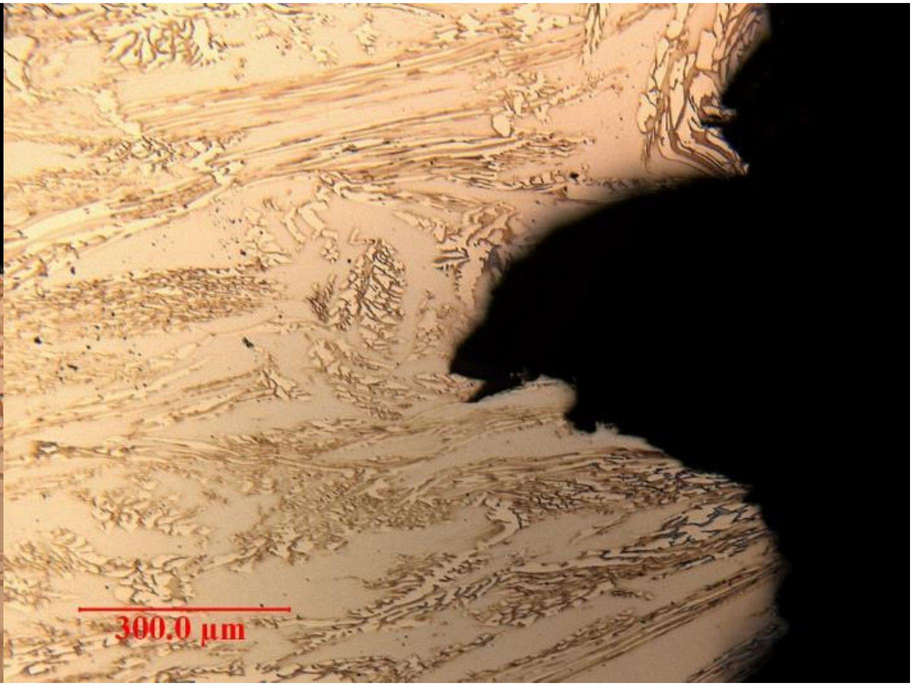
A_{corr}/A_{ref}	Z_{corr}/Z_{ref}
1.02	1.07

- Failure is anisotropic
- Small corrosion sites
- No loss of mechanical properties

Stress corrosion susceptibility
Low ferrite content



Corrosion site on calibrated zone



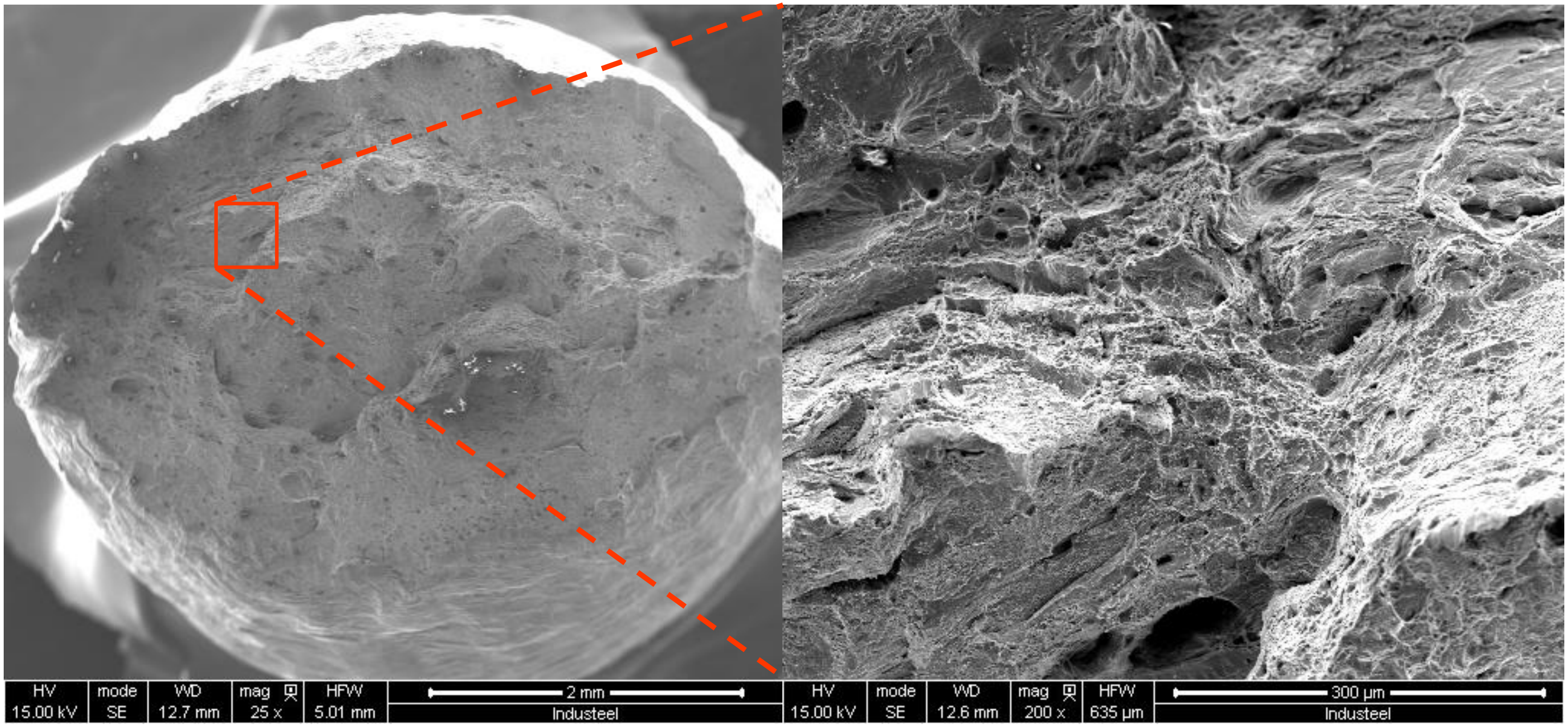
Cross section of fracture surface

- Corrosion sites corresponds to superficial selective dissolution of ferrite
- Fracture surface seems to be ductile

No crack initiation observed and superficial dissolution

Stress corrosion susceptibility

Low ferrite content

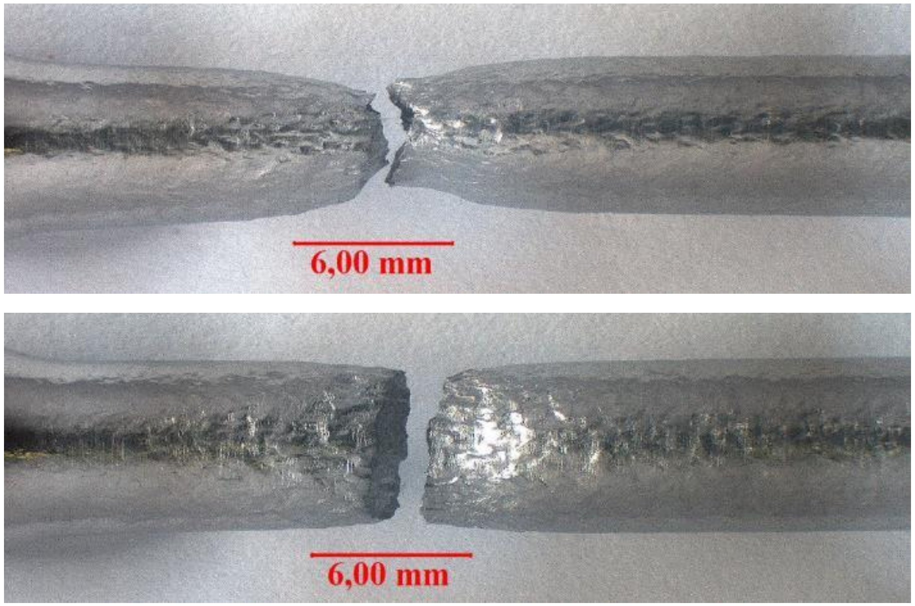


- Fracture surface is anisotropic due to the microstructure (rolling direction)
- Fracture surface is fully ductile

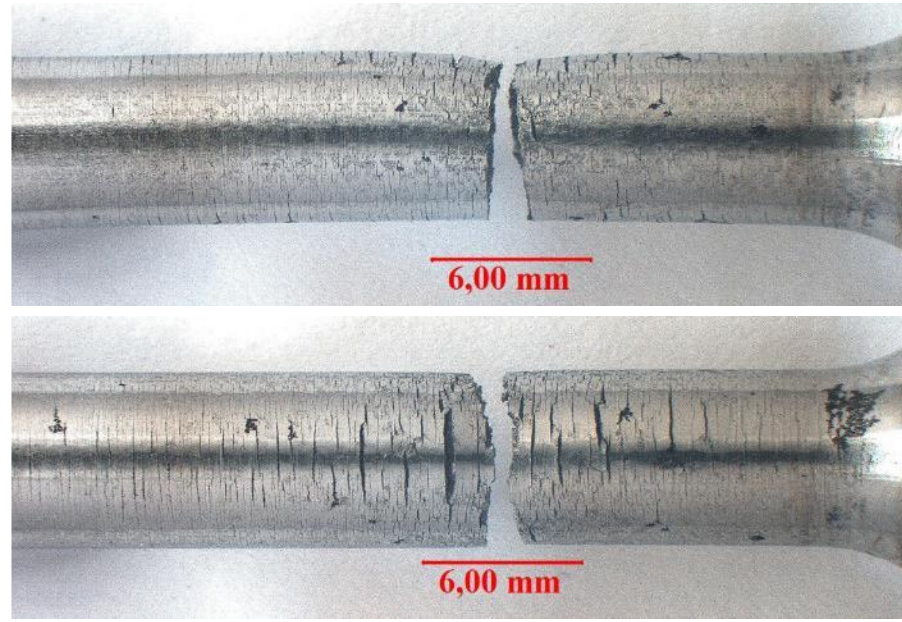
No sensitivity to stress corrosion have been observed though macroscopic and microscopic characterizations

Stress corrosion susceptibility

High ferrite content



SSRT specimen in glycerin



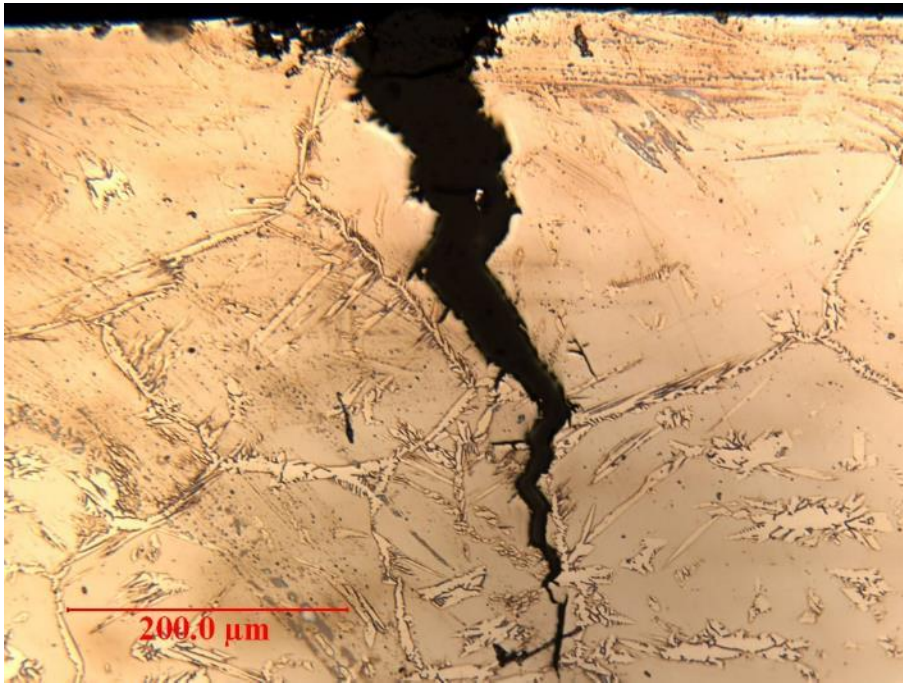
SSRT specimen in corrosive environment

A_{corr}/A_{ref}	Z_{corr}/Z_{ref}
0.31	0.18

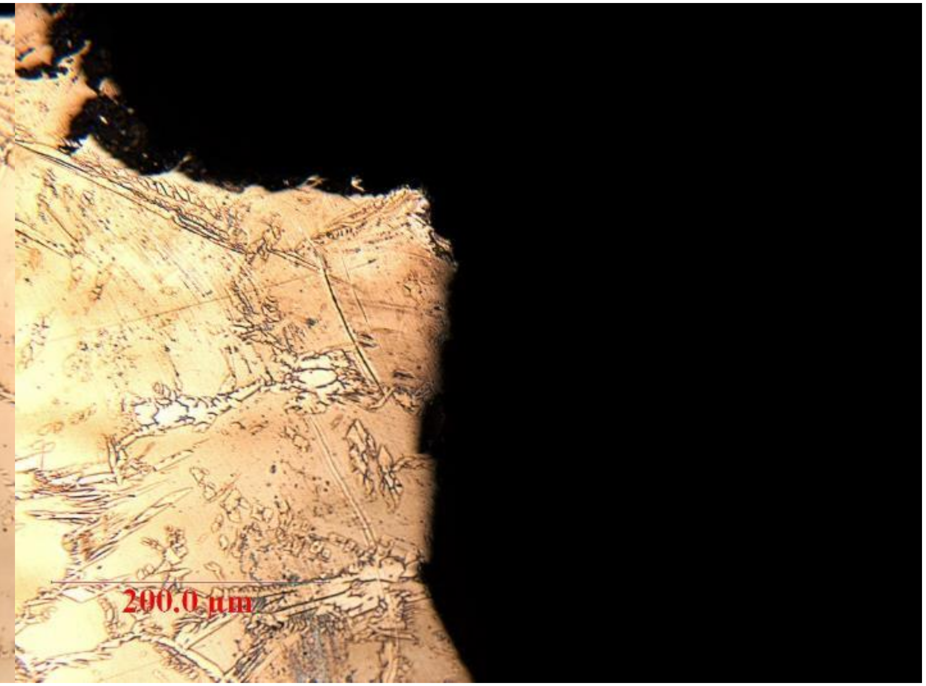
- Failure is anisotropic
- Multiple secondary cracks
- High loss of mechanical properties

Stress corrosion susceptibility

High ferrite content



Secondary crack on calibrated zone

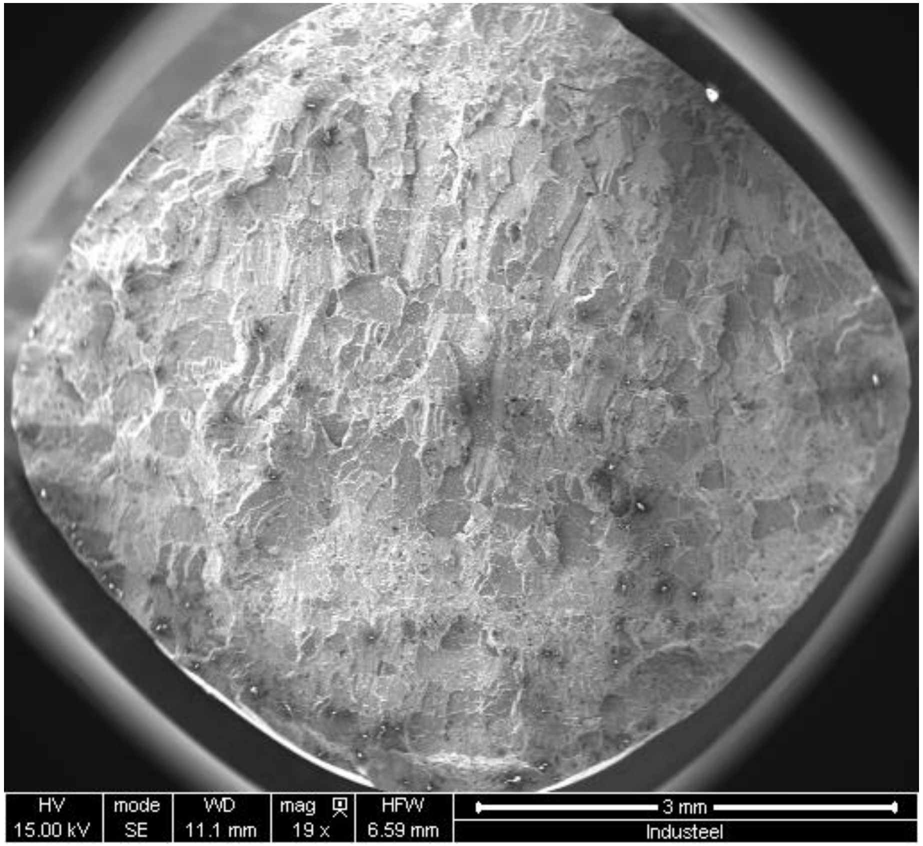


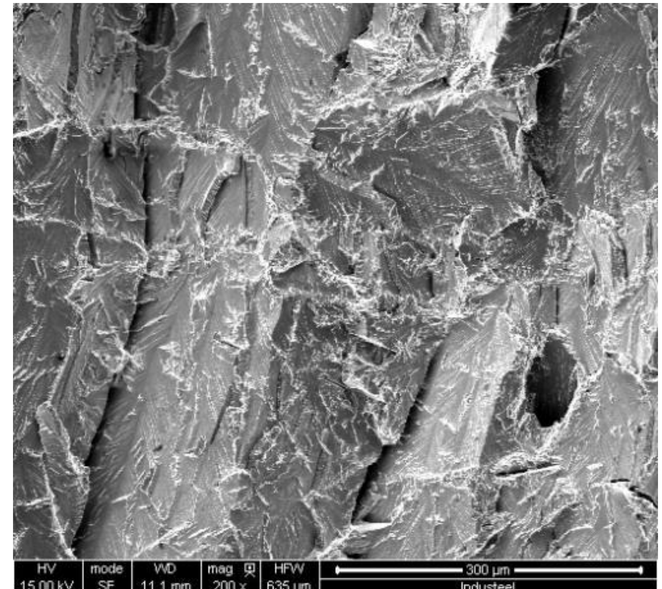
Cross section of fracture surface

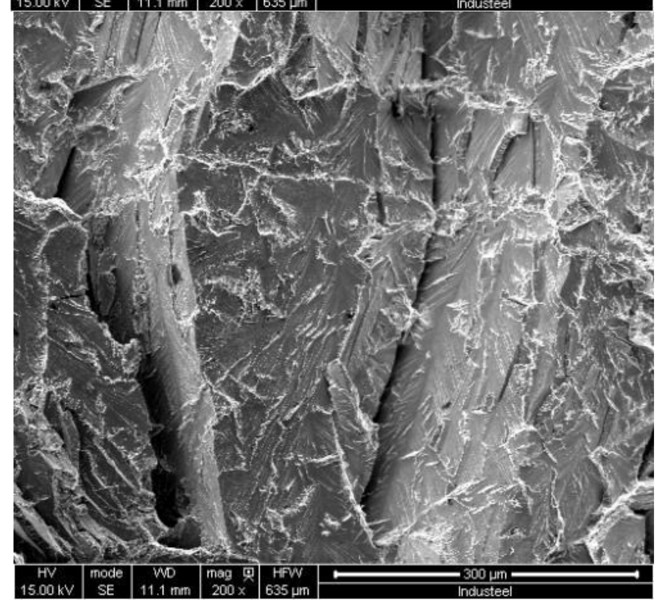
- Secondary cracks are transgranular and quite deep
- Fracture surface seems to be brittle

Brittle failure and transgranular secondary cracks

Stress corrosion susceptibility
High ferrite content







- Fracture surface is fully brittle

High sensitivity to stress corrosion have been observed though macroscopic and microscopic characterizations

Conclusions

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- Influence of ferrite content in HAZ has been characterized thanks to Gleeble specimens. It allows a homogeneous and reproducible ferrite content on a large surface.
- Formulinox is an interesting tool to predict welds properties
- High ferrite content (74%) is clearly more sensitive to stress corrosion than low ferrite content (58%). Failure mode on SSRT tests is brittle for high ferrite content.
- Restriction on maximal ferrite content in HAZ can be adequate for some application. Moreover, guidelines for welding duplex have to be carefully followed.

Appendix 13

Unusual cracking in stripper section of HDS Units

(M. De Marco)

ISTITUTO ITALIANO DELLA SALDATURA
Il Gruppo

Unusual cracking in Stripper section of HDS Units

M. De Marco

INTRO

In refinery assets corrosion evaluation & management sometimes people should …

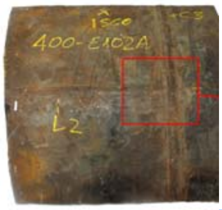
2

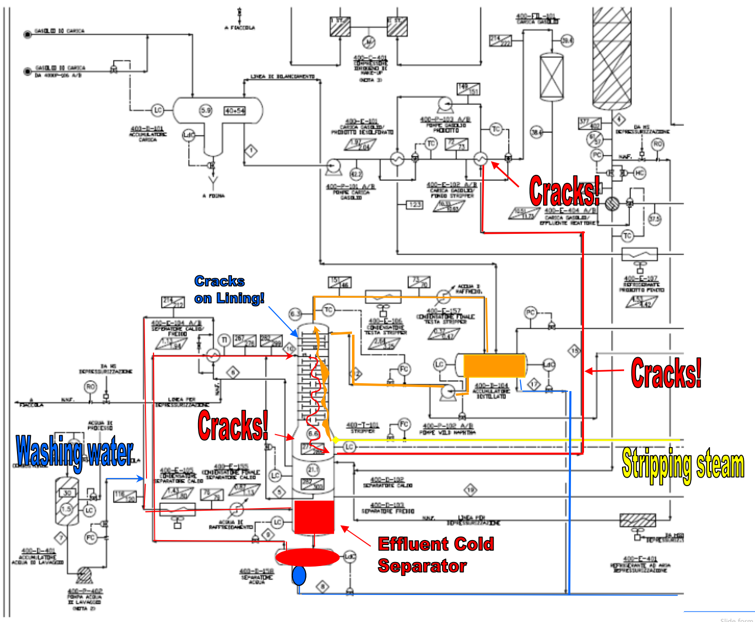
INFO

Some failure events occurred in the gas oil stripping circuit of the HDS Unit

- **2014** : plate taken from the shell of the **stripped product cooler HX** with through thickness cracks at a weld
- **2016**: n° 2 samples taken from **line form stripper column to product cooler** with cracks at weld.
- **2016**: n° 2 plates from **stripper column bottom** with cracks at weld.

NOTE:
In last years discontinuous service of the Stripper circuit





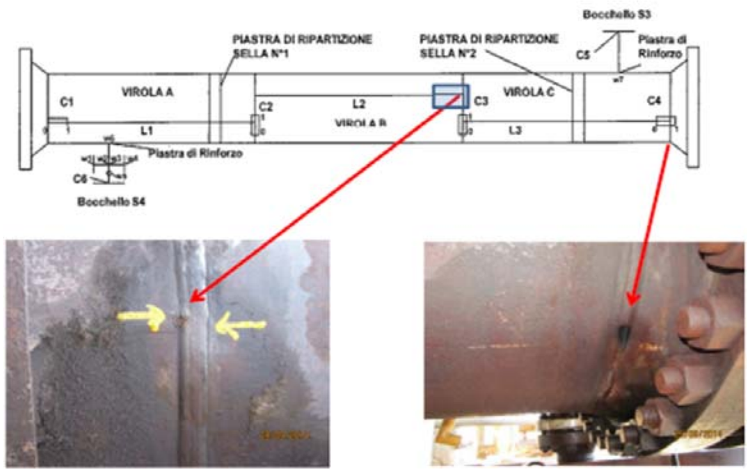
Case 1 - Stripped gas oil cooler

- In the shell side, the stripper bottom fluid (stripped gasoil) is cooled at the expense of the feed to the reaction circuit
- HX is the first exchanger after the column that cools the bottom stripped product
- During normal service, the shell side operating conditions are characterized by a inlet temperature of 277 °C and a pressure of 6.6 barg; at outlet T ≅ 220 °C and P≅ 6.1 barg

	Shell side		*Tube side*	
Design pressure	135 psi	9,5 kg/cm^2	685 psi	48,2 kg/cm^2
Test pressure	243 psi	17,1 kg/cm^2	1124 psi	79 kg/cm^2
Design temperature	580 °F	304,4 °C	450 °F	232.2 °C
Flow	Stripper Bottom		Feed	

5

Localization of the cracks

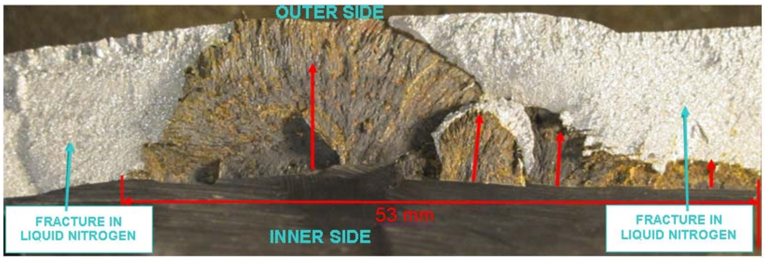


6

Fractographic Examination

Crack initiation zone on the shell inner side and presence of a layer of adherent and compact deposits, black - brown colored, on the whole surface of the fracture

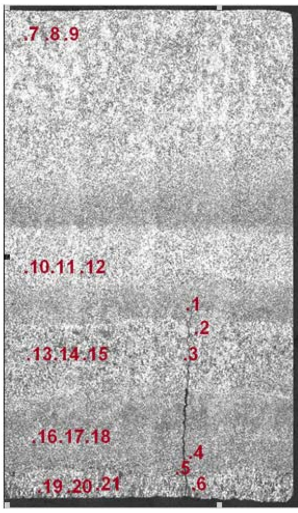
Elliptical and irregular morphology ("terraces"), characterized by multiple propagation fronts, not homogeneous, on different planes



7

Microhardness $HV_{0,3}$

No anomalies revealed as high hardness zone close to the crack (typical critical max value can be 248 HV)

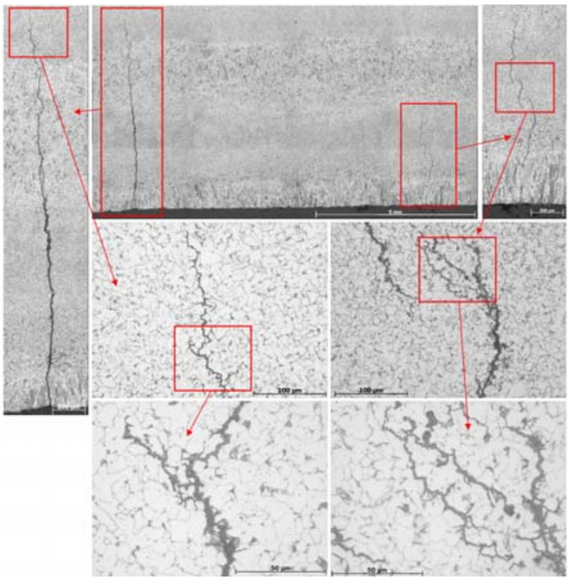


Posizione	$HV_{0,3}$
1	153
2	165
3	169
4	173
5	179
6	188
7	181
8	162
9	160
10	150
11	145
12	146
13	177
14	166
15	165
16	163
17	163
18	171
19	181
20	184
21	175

8

Micrographic examination

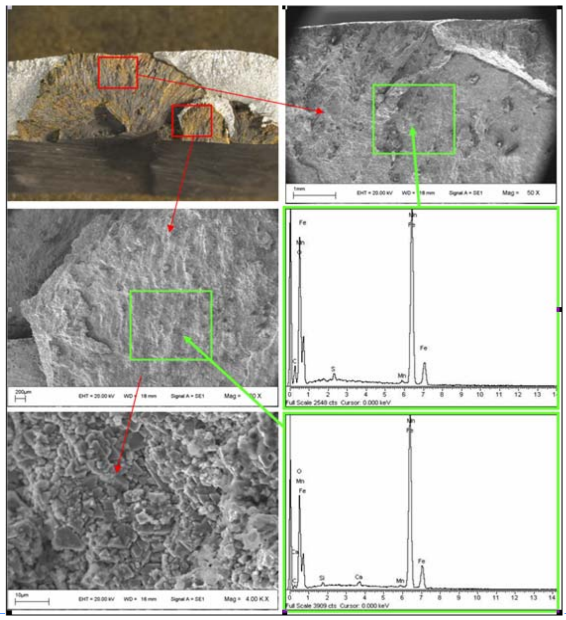
- ✓ Branched intergranular cracks with deposit inside
- ✓ Mainly intergranular propagation
- ✓ No anomalies in the metallographic structure
- ✓ No generalized and/or localized corrosion phenomena
- ✓ No original imperfections ascribed to the weld



9

SEM + EDS examination

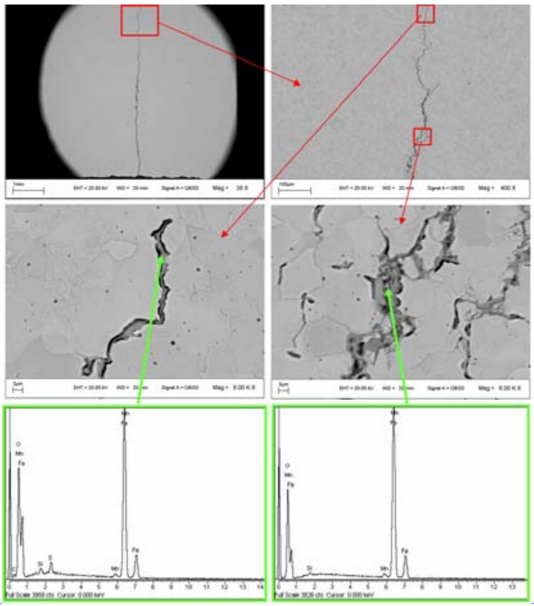
- ✓ Presence of oxides and element attributable to base material
- ✓ Traces of S and Ca



10

SEM + EDS examination

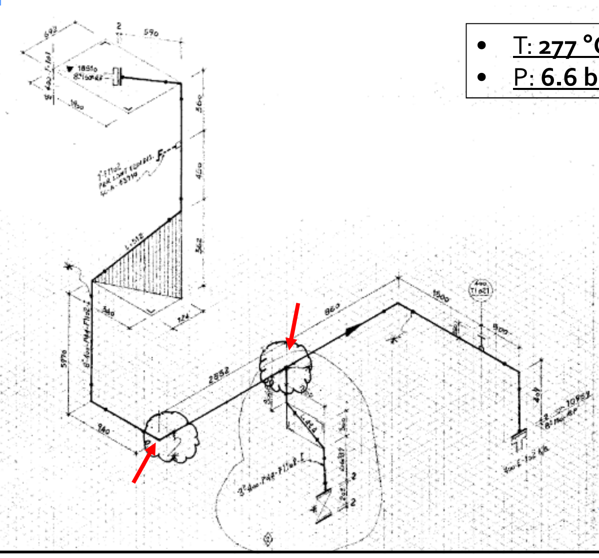
- ✓ Presence of oxides and element attributable to base material
- ✓ Clearly visible intergranular propagation
- ✓ Traces of S

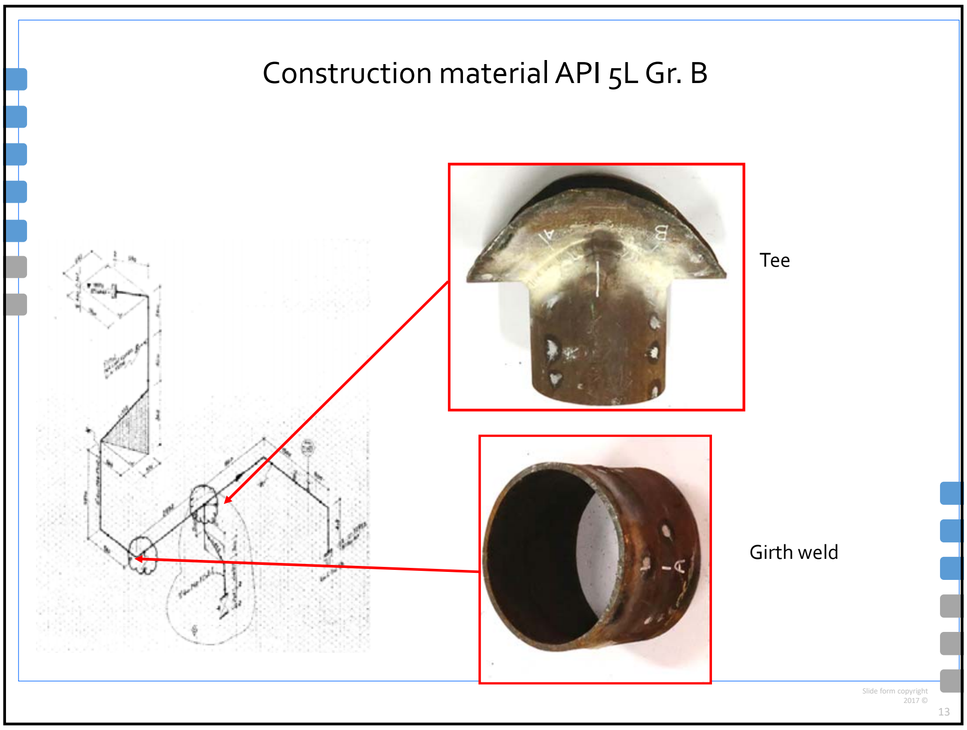


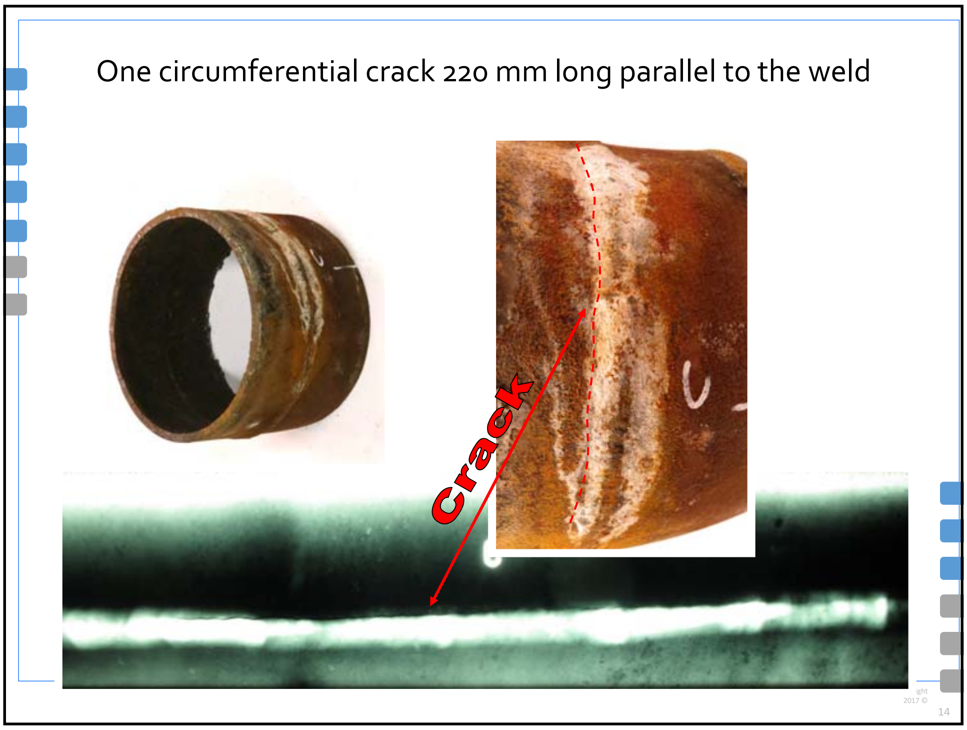
Case 2 – Stripper to HX line

Outlet piping of the stripped gasoil from stripper bottom to E102A shell side

- T: 277 °C
- P: 6.6 barg;

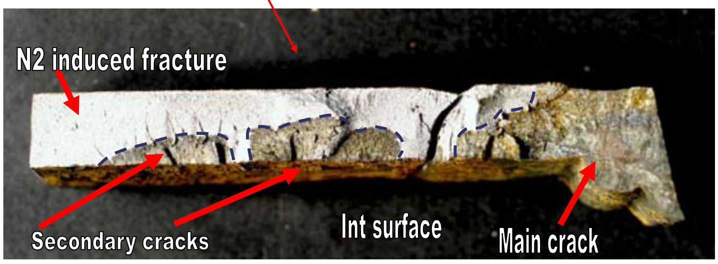



Construction material API 5L Gr. B
Tee
Girth weld
13


One circumferential crack 220 mm long parallel to the weld
Crack
14

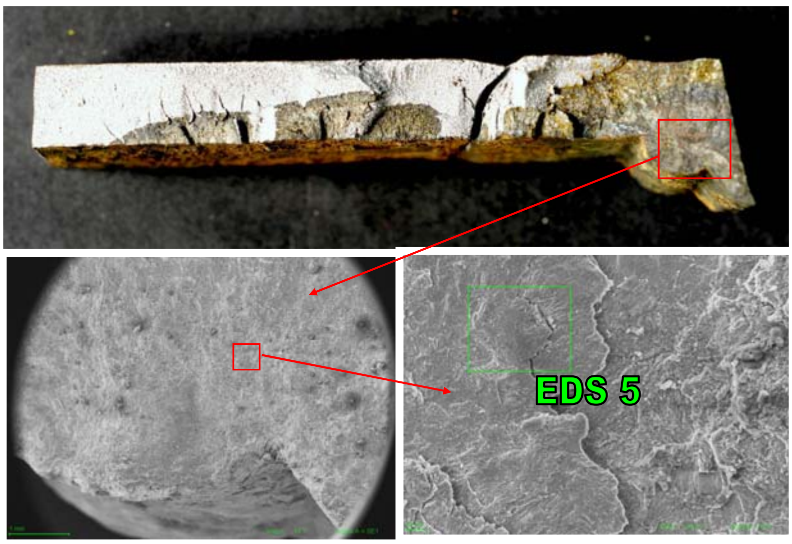
SEM + EDS examination

- Irregular "terrace like" fracture surface with dark deposits
- Pseudo-elliptical shape



15

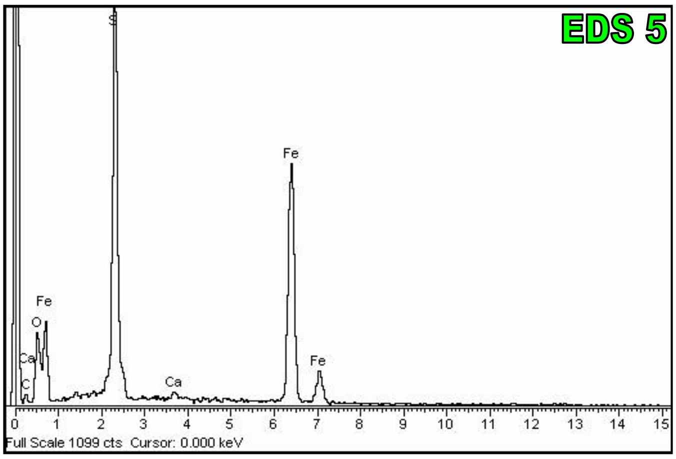
SEM + EDS examination



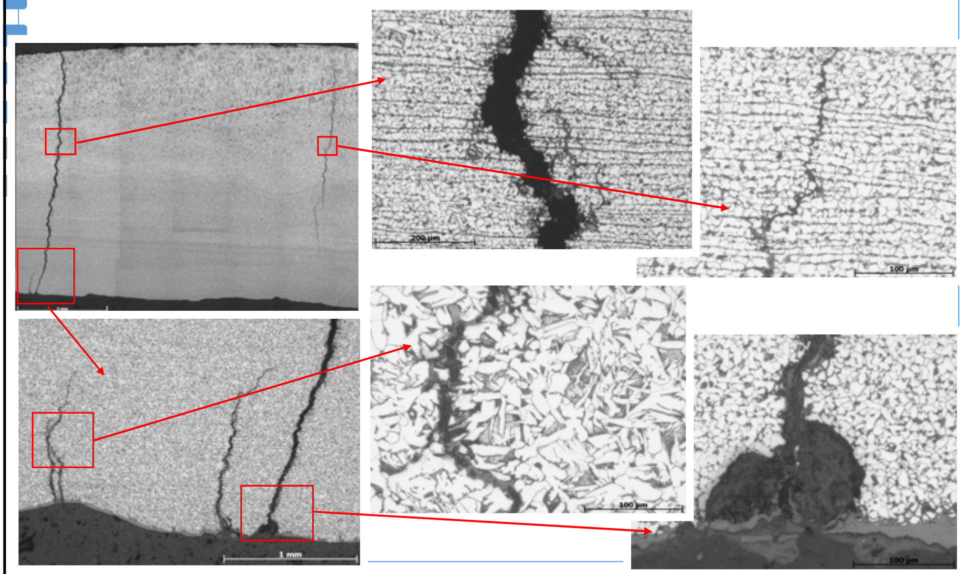
16

SEM + EDS examination

Elements from base material + Surfur + Calcium

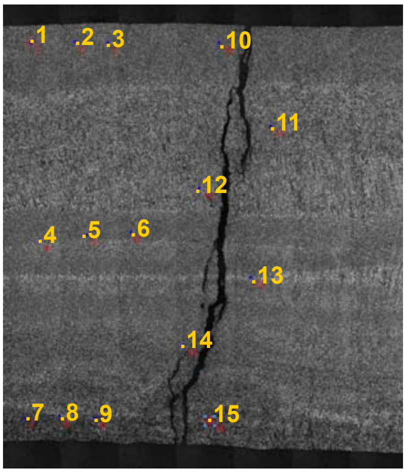


Branched cracks with inner deposits and intergranular propagation.



Microhardness $HV_{0,3}$

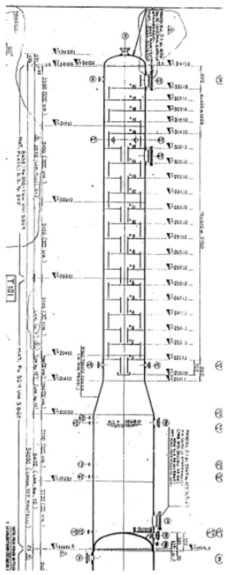
No anomalies revealed as high hardness zone (typical critical max value can be 248 HV)



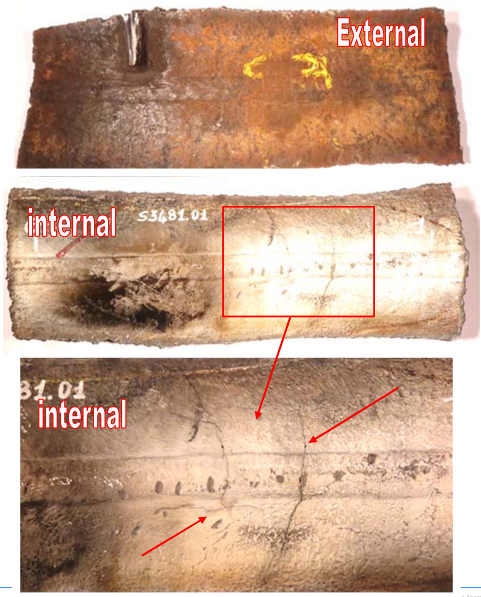
1	189
2	189
3	184
4	186
5	189
6	205
7	216
8	224
9	220
10	205
11	223
12	215
13	181
14	198
15	199

Case 3 - Plate from stripper column bottom

Construction material
Fe52.1 UNI 5869



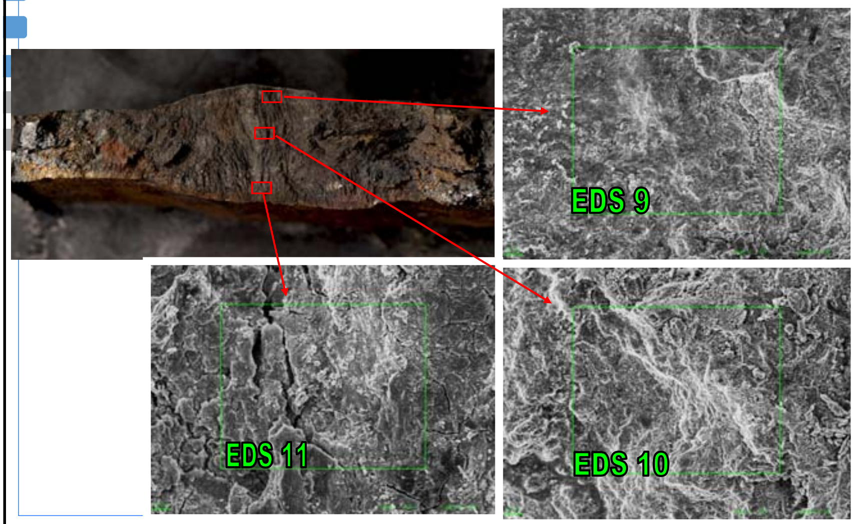
Internal Cracks transversal to the welds



21

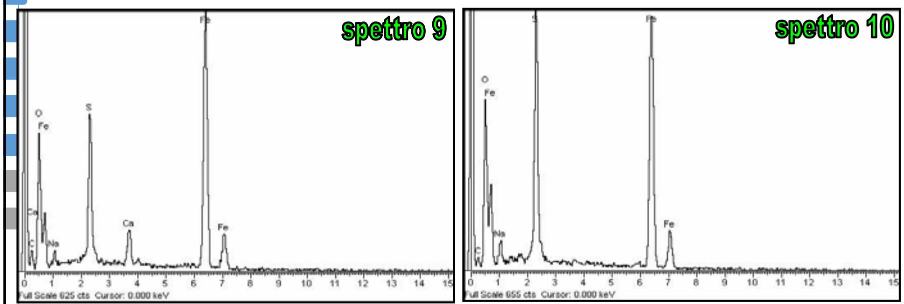
22

SEM + EDS examination



23

SEM + EDS examination



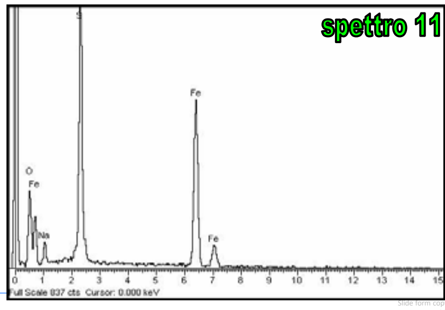
Elements from base material and high amount of **Sulfur**.

In addition →

In EDS 9 (close to external surface) presence of **Ca.**

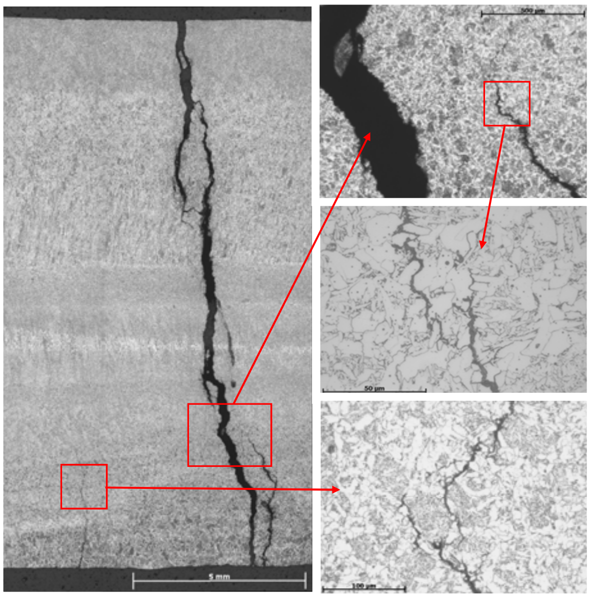
In EDS 10 presence of **Na**.

In EDS 11 presence of **Na**



24

Micrographic examination

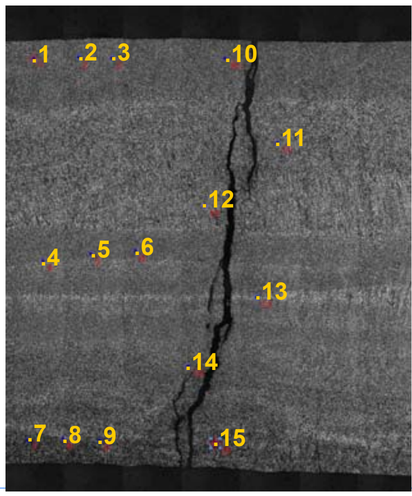


- Branched cracks with deposits inside (transversal to the weld)
- Starting from internal surface
- Intergranular propagation

25

Microhardness $HV_{0,3}$

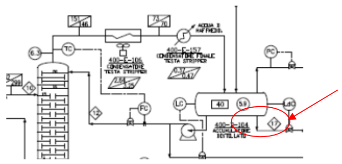
No anomalies revealed as high hardness zone (typical critical max value can be 248 HV)

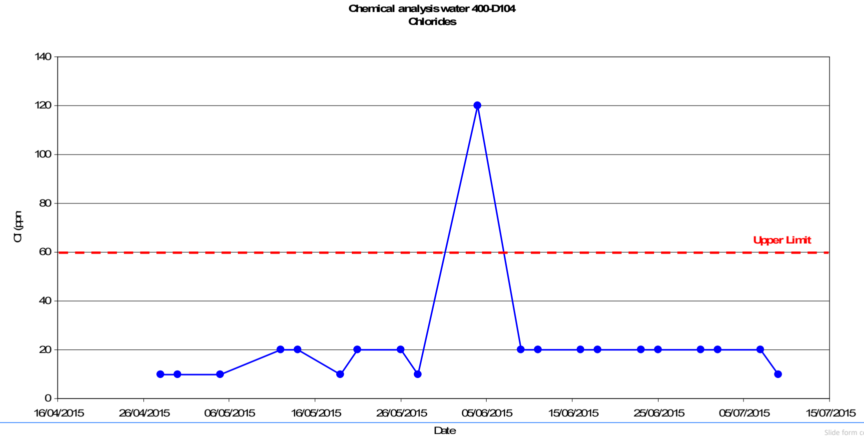


1	189
2	189
3	184
4	186
5	189
6	205
7	216
8	224
9	220
10	205
11	223
12	215
13	181
14	198
15	199

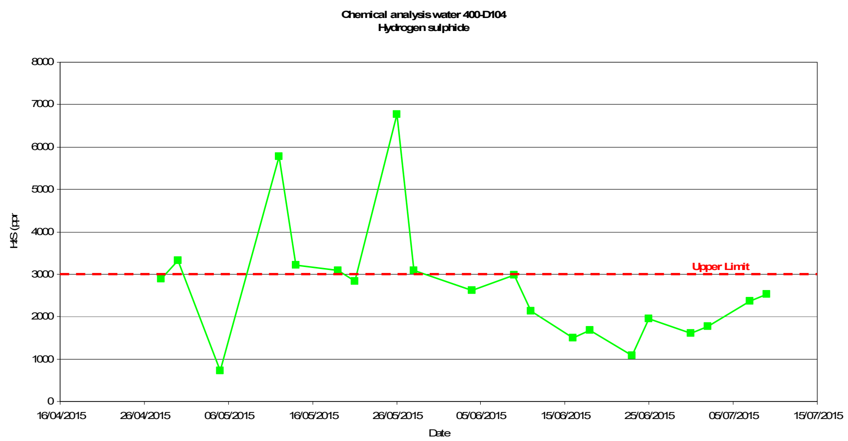
26

Stripper column overhead accumulator water

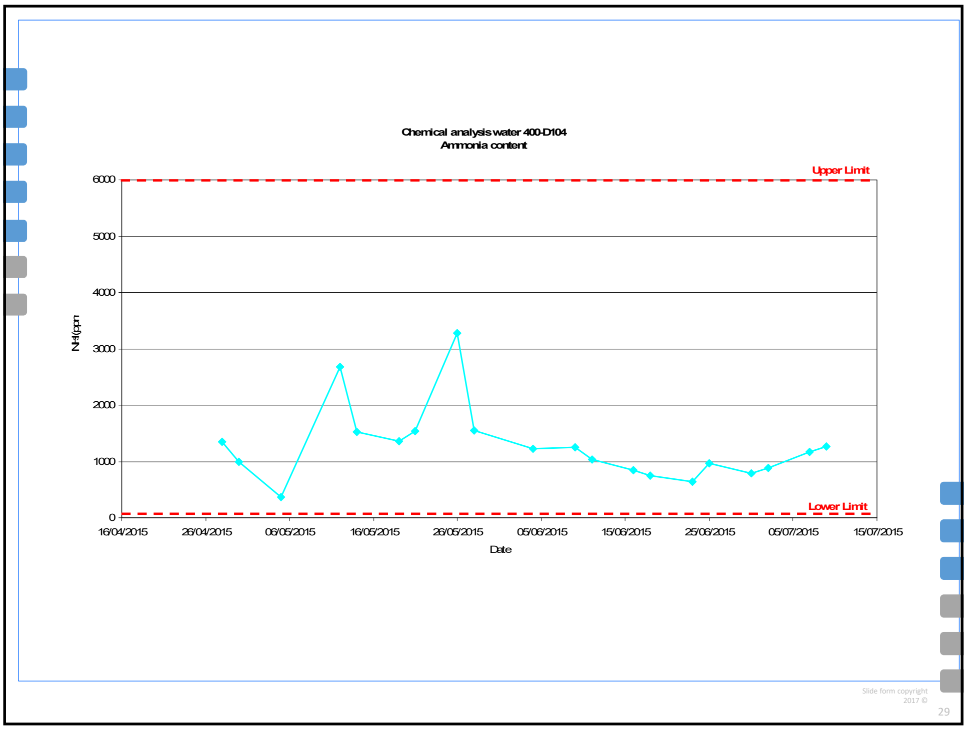




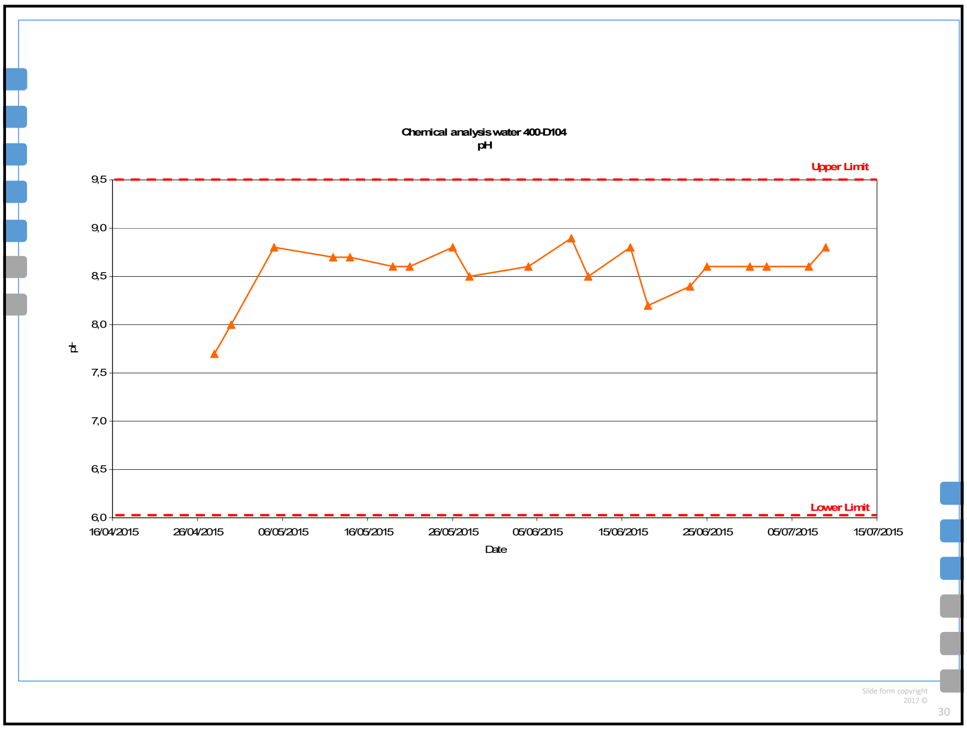
27



28

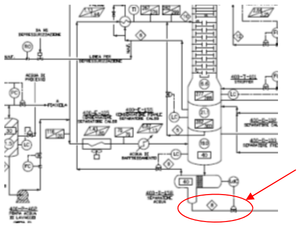


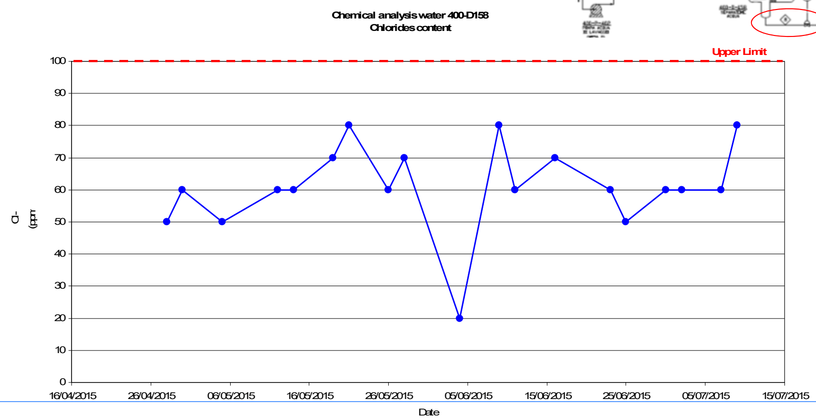
Chemical analysis water 400-D104
Ammonia content
Upper Limit
Lower Limit
6000
5000
4000
3000
2000
1000
0
16/04/2015
26/04/2015
06/05/2015
16/05/2015
26/05/2015
05/06/2015
15/06/2015
25/06/2015
05/07/2015
15/07/2015
Date
29



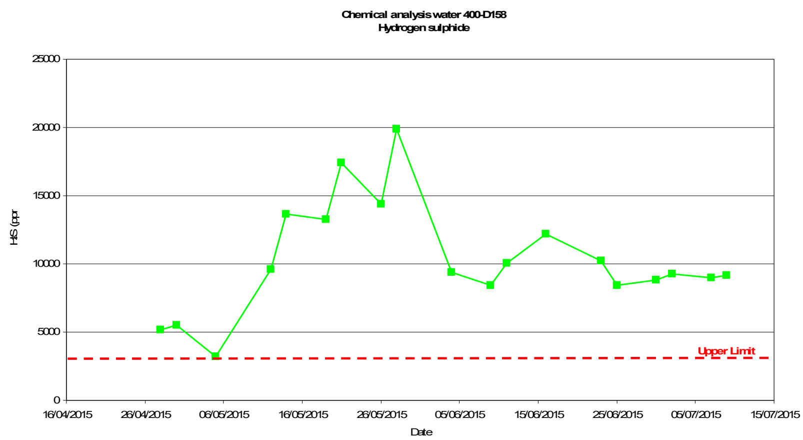
Chemical analysis water 400-D104
pH
Upper Limit
Lower Limit
9,5
9,0
8,5
8,0
7,5
7,0
6,5
6,0
16/04/2015
26/04/2015
06/05/2015
16/05/2015
26/05/2015
05/06/2015
15/06/2015
25/06/2015
05/07/2015
15/07/2015
Date
pH
30

Water collected from effluent cold separator

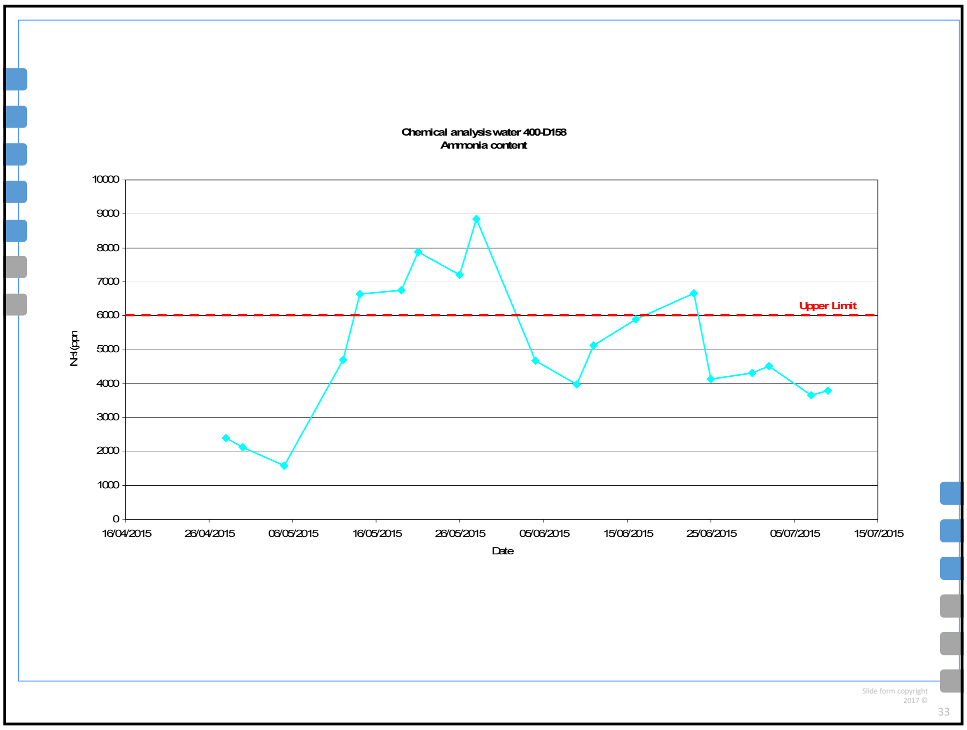




31



32


Chemical analysis water 400-D158
Ammonia content
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Upper Limit
16/04/2015
26/04/2015
06/05/2015
16/05/2015
26/05/2015
05/06/2015
15/06/2015
25/06/2015
05/07/2015
15/07/2015
Date
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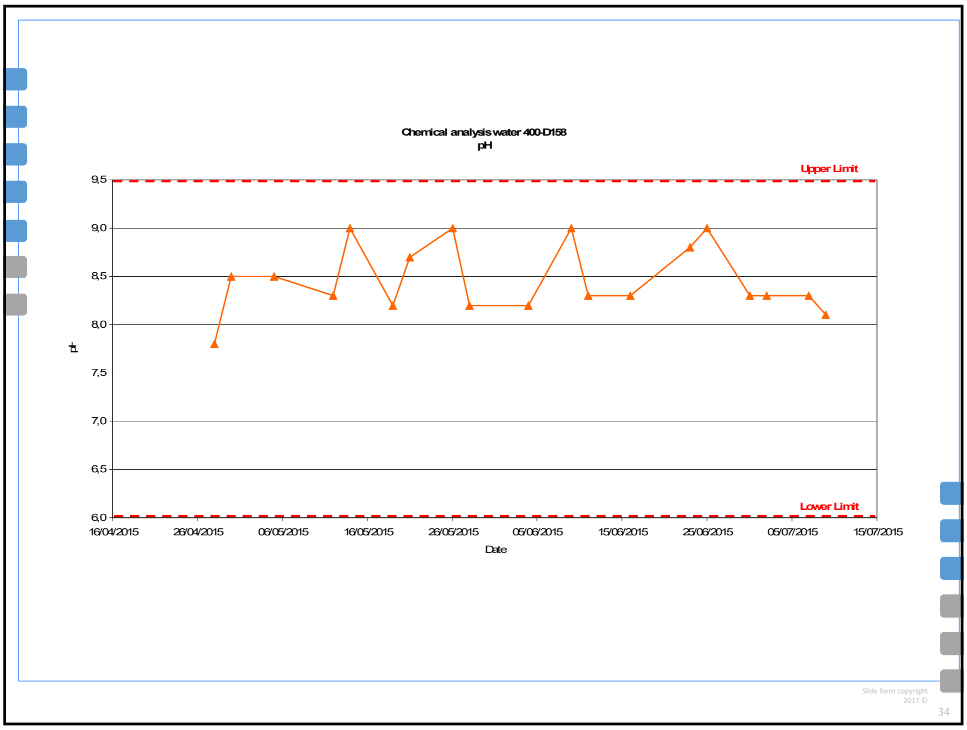
Chemical analysis water 400-D158
pH
9,5
9,0
8,5
8,0
7,5
7,0
6,5
6,0
Upper Limit
Lower Limit
16/04/2015
26/04/2015
06/05/2015
16/05/2015
26/05/2015
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15/06/2015
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15/07/2015
Date
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Findings

- The cracks affecting the samples investigated started from the inner surface of the component and were localized at welds, transversal to them with the exception of one case (pipe girth weld sample) where crack was parallel to the weld at weld toe.
- The crack surfaces had a macroscopic irregular appearance and propagated through the wall thickness with elliptical and "terrace shape" morphology with layer of brown deposits.
- Near the main through thickness cracks there were various smaller secondary cracks with the same morphology and parallel to them.
- In the micrographic sections the cracks were branched and with mainly intergranular propagation path with deposits inside.

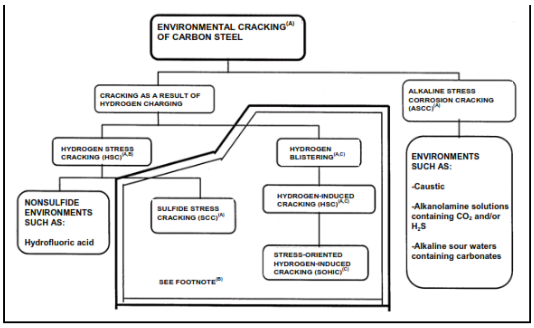
Findings

- The deposits found on the cracks surfaces and inside the cracks (in section) were composed mainly by elements from base materials and process fluid (iron, manganese, sulfur) and by exogenous elements ascribable mainly to an aqueous phase (calcium, magnesium, sodium, potassium, chlorine and, again, sulfur).
- No anomalies were found in the chemical compositions, microstructure and mechanical properties of analyzed materials.
- No welding imperfections were detected that could have been influenced the failure event occurred
- No high micro-hardness values were measured in correspondence with fissures that can lead to certain type of failure (low toughness, Sulphide Stress Cracking).
- No generalized and/or localized corrosion phenomena were detected in correspondence with the internal surface of the analyzed sample

- The morphology of the investigated damage can be associated to **Environmentally Assisted Cracking (EAC) phenomena.**
  - Such damage phenomena require the presence of static stresses (applied or residual) and/or low strain rate monotonic stresses (e.g. thermal transient) and a corrosive environment;
  - The standard operating thermodynamic conditions (277°C and 6.6barg) not congruent with the condensation of separated water phase, which, in any case, should be present in small quantities in that area of circuit (stripped gasoil).
  - Therefore in causes analysis, the possible and the most probable sources of origin and stagnation of separated water phase (non emulsified in the hydrocarbon) should be verified.

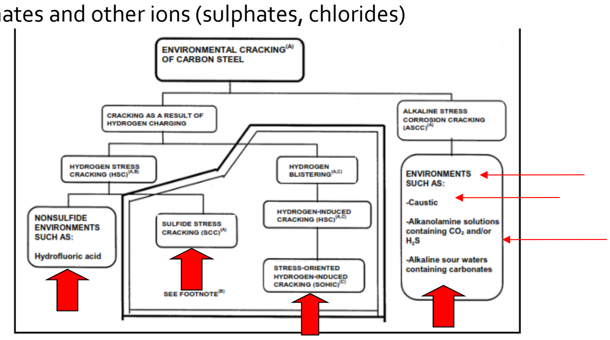
Temp	Pres	Specific Volume m3/kg		Sp. Internal Energy kJ/kg		Specific Enthalpy kJ/kg			Specific Entropy kJ/kg-K		Temp
°C	bar	vf x 10^3	vg	uf	ug	hf	hfg	hg	sf	sg	°C
180	10.022	1.1275	0.194	761.80	2583.2	762.93	2014.8	2777.7	2.1387	6.5849	180
200	15.539	1.1564	0.127	850.66	2594.8	852.46	1940.3	2792.7	2.3307	6.4314	200
220	23.179	1.1897	0.086	941.12	2601.9	943.88	1857.8	2801.7	2.5181	6.2852	220
240	33.443	1.2287	0.060	1033.58	2603.5	1037.69	1765.6	2803.3	2.7021	6.1429	240
260	46.887	1.2753	0.042	1128.80	2598.5	1134.78	1661.6	2796.4	2.8844	6.0010	260
280	64.118	1.3323	0.030	1227.96	2585.5	1236.50	1542.4	2778.9	3.0676	5.8561	280

- Considering the discontinuous service of the stripping circuit, the possible temporary accumulation of aqueous phase could be just the shutdown phases of the system and/or and non steady-state service.
- As support for the definition of the specific corrosive agents in the electrolyte which can induce EAC, the document NACE SP0472-2010 (Methods to prevent and control in service environmental cracking of carbon steel weldments in corrosive petroleum refining environments) can be used as a reference, as it considers the different possible scenarios for the phenomena of EAC on carbon steel in refinery plants.



(A) Refer to the *NACE Glossary of Corrosion-Related Terms*[11] for definitions (including *stress corrosion cracking*).
(B) The forms of environmental cracking included within the double lines are commonly referred to as wet H_2S cracking when they occur in wet H_2S environments.
(C) This form of environmental cracking can also occur in nonsulfide environments such as hydrofluoric acid.

1. HF: very improbable
2. SULPHIDE STRESS CRACKING: require high hardness (>248 HV) and has different morphology
3. WET H2S induced BLISTERING, HIC and SOHIC: has very different morphology
4. ALKALINE STRESS CORROSION CRACKING: similar intergranular morphology with branched cracks and deposit inside
   - Caustic
   - Amine with CO2 and H2S
   - Alkaline sour water (NH3 and H2S containing water with alkaline pH) with carbonates and other ions (sulphates, chlorides)



(A) Refer to the *NACE Glossary of Corrosion-Related Terms*[11] for definitions (including *stress corrosion cracking*).
(B) The forms of environmental cracking included within the double lines are commonly referred to as wet H_2S cracking when they occur in wet H_2S environments.
(C) This form of environmental cracking can also occur in nonsulfide environments such as hydrofluoric acid.

- **Alkaline process sour water**: NH3 and H2S from process (reaction circuit) ; process waters analyses showed an alkaline pH and high level of ammonia and hydrogen sulphide, with presence of chlorides.

- **Washing waters injected before cold separator**: can be cause ions contamination from dissolved salts
  - Mg, Ca, Na chlorides.
  - carbonates/bicarbonates.
  - sulphates.

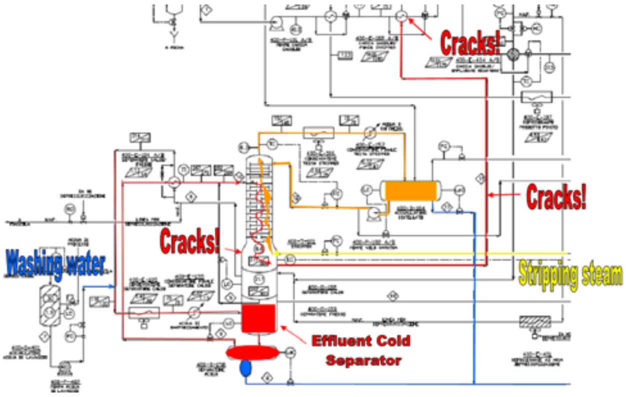
- **Washing waters** can introduce also **O2** in the process that increases susceptibility to EAC.

- **Stripping steam** can introduce alkalinity (depends on the water treatment in the steam generation) and carbonates

→ Discontinuous, non steady-state service of the circuit can cause water separation and accumulation.

→ Alkaline water with high pH, ammonia, H_2S, chlorides, carbonates, (Na-alkalinity ?), (Oxygen??) – EAC Active!

→ Start up and transient service cycle can cause fast heating, water evaporation , concentration of aggressive ions and thermal-transient stress/strain (slow strain rate) acting together with residual welding stresses



Thanks for your attention

Appendix 14

Analysis of Corrosion Damage in a Refinery Regeneration Circuit Tube

(A. Smith)

Analysis of Corrosion Damage in a Refinery Regeneration Circuit Tube

Ali Smith, Rina Consulting – Centro Sviluppo Materiali

EFC Working Party 15 Corrosion Refinery Industry Meeting
10th April 2019

Background (1)

- **Short description of problem:**
  - In last years a catalyst regeneration circuit had experienced internal corrosion damages, in particular in dead zones near valves.
  - In the last two years (2016-2018), the damage level has increased significantly.
  - A sample of tubing from the regeneration circuit has been made available for analysis.
- **Conditions**:
  - Tube in regeneration circuit used to transport gases to the catalyst.
  - Tube section of interest is near a valve where flow is experienced occasionally i.e. to introduce N_2 into circuit.
  - Other gases present from other parts of circuit can be C_2Cl_4, H_2, CO, CO_2, air, and sulphating agents.
  - Temperature in dead-leg is in range 100-400°C.
  - When N_2 not flowing temperature is below 100°C.

Background (2)

•**Material of construction:**

- ASTM A335 P11 (Low alloy carbon steel with Cr and Mo). Horizontal tube section. Diameter 4 inches and wall thickness of 8.56 mm.
- Tube is welded to a flange attached to a valve.

•**Service history:**

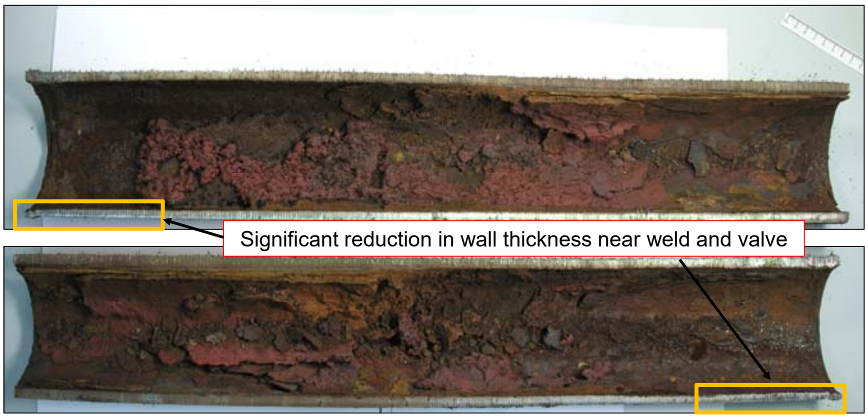
- Since 2016 the level of C_2Cl_4 added to the regeneration circuit has increased.
- Since 2016 the level of corrosion in the regeneration circuit has increased significantly.
- Service life of as-received tube section was 1 year.

Introduction

- The aim of the work is to establish the operating internal damage mechanisms for the tube section from the regeneration circuit.
- Laboratory analysis methods were discussed and agreed with the Refinery.
- The test activities performed are listed below:
  - Visual inspection
  - Analysis of any corrosion deposits via XRD and pH.
  - SEM-EDS of damage zones at surface.
  - Optical microscopy +SEM/EDS of damage after sectioning.
- Finally suitable recommendations were made to prevent such corrosion in the future.

RESULTS

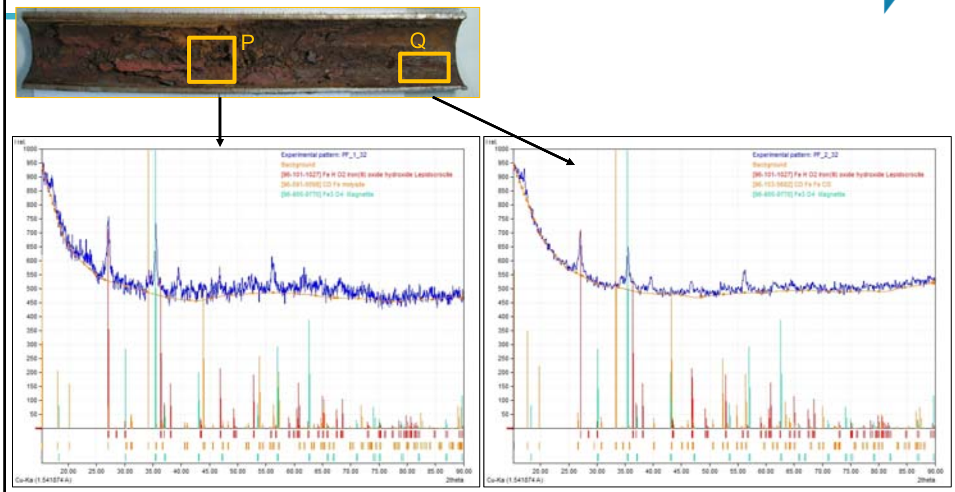
Visual inspection of dead-leg



- Inner surface shows thick deposits up around 10 mm thick.
- Deposits appear mostly red-brown.
- Wall thickness reduced the most near weld (squares).

Analysis of deposits by X-ray Diffraction

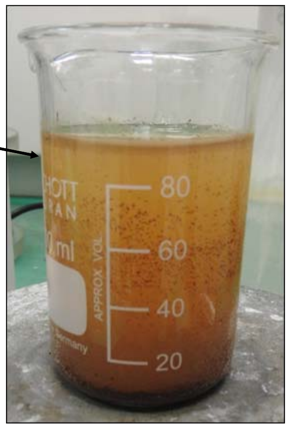
RINA



- Deposit in zones A and B are chemically similar:
- Zone P: FeO (OH) = 50wt%, Fe_3O_4 = 35wt%, $FeCl_3$ = 15%.
- Zone Q: FeO (OH) = 57wt%, Fe_3O_4 = 35wt%, $FeCl_3$ = 8%.

Analysis of deposit properties in tap-water

RINA



pH of tap water = 7.57.
pH of deposit in tap water after 1 hour = 3.01.

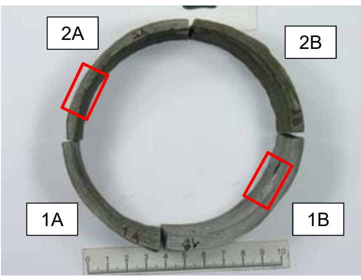
- Deposit appears to partially dissolve in tap water giving acidic pH.
- Low pH suggests hydrolysis of $FeCl_3$ (formation of hydroxide and H+).

Selection of zones for SEM-EDS and Metallography (1)

- Focus on girth weld area (where thickness of pipe wall was reduced):

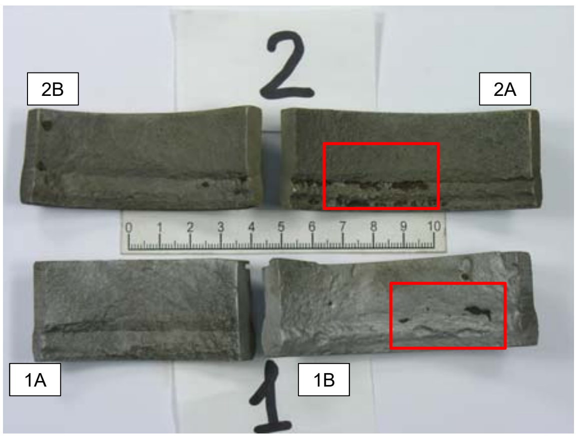
Zones 1 and 2 cut and then chemically cleaned

Selection of zones for SEM-EDS and Metallography (2)



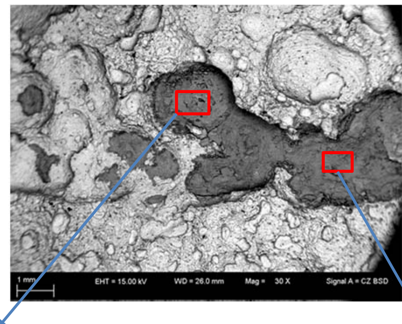
Zone 2A => area with minimum wall thickness (HEAVY DAMAGE).

Zone 1B => area at 180° to zone 2A (LIGHT DAMAGE).



Next slides focus on zone of heavier damage only (zone 2A).

SEM-EDS on surface of heavy damage zone

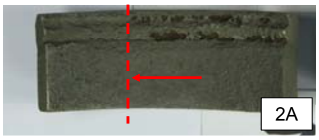


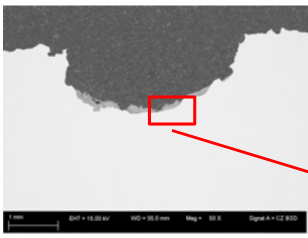
Element	Wt%
CK	23.47
OK	22.79
SiK	00.46
ClK	03.48
CrK	02.33
FeK	43.38
NiK	04.10

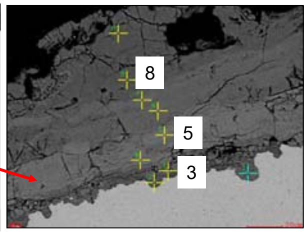
Element	Wt%
CK	11.23
OK	21.26
SiK	00.44
ClK	04.53
CrK	01.31
FeK	58.93
NiK	02.30

- Zone 2A reveals round corrosion sites of several mm in diameter in base and weld.
- SEM-EDS shows main elements as O, Fe, Cl.

SEM-EDS after sectioning at heavy damage zone







3

Element	Wt%
OK	06.21
SiK	00.99
CaK	00.42
CrK	01.40
MnK	01.05
FeK	89.94

5

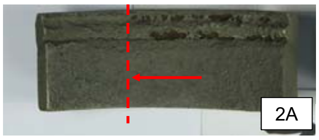
Element	Wt%
OK	22.22
MnK	01.73
FeK	76.05

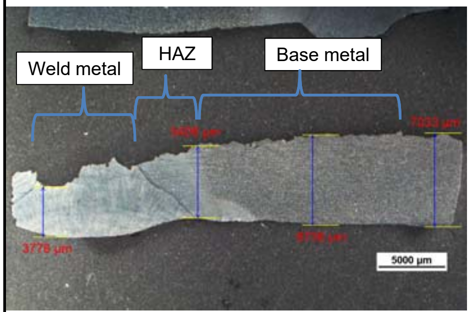
8

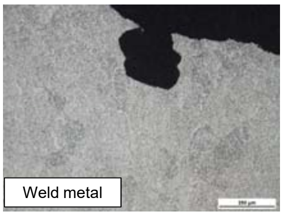
Element	Wt%
OK	26.47
SiK	00.51
ClK	04.35
MnK	01.93
FeK	66.74

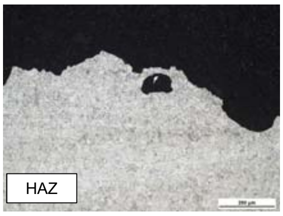
- Corrosion products in cross section contain O, Fe and Cl.

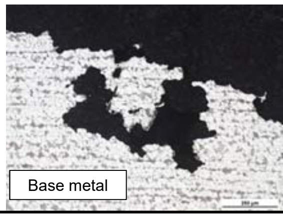
Optical microscopy
Section heavy damage











- Section reveals significant loss of wall thickness compared to original (8.56 mm original). Attack is more intense in weld zone (weld metal and HAZ).

Damage mechanisms
+ Recommendations

Summary of key results

RINA

- Corrosion products near and far from the girth weld were mainly iron oxide-hydroxide i.e. FeO (OH), magnetite i.e. Fe_3O_4, and $FeCl_3$.
- Preferential attack of the weld and HAZ occurred, extending in a continuous manner along a significant portion of the pipe circumference.
- The minimum wall thickness (3.8 mm) was located in the weld metal i.e. around 56% loss in wall thickness compared to the nominal tube thickness (base metal).

Proposed main damage mechanism: HCl acid dewpoint corrosion

RINA

- During the operation phase C_2Cl_4 decomposed and reacted with H_2 to give HCl gas. Considering the reported decomposition range for C_2Cl_4 of 400-800°C, it is highly likely that the perchloroethylene decomposed in a nearby line, where a higher temperature of 540°C can be reached.
- The HCl gas was transported to the cool dead-leg zone, where condensation of water vapour containing dissolved HCl occurred.
- The acid water droplets caused corrosion of the steel. The corrosion product ($FeCl_3$) formed via the reaction of iron with aqueous HCl under the presence of oxygen.
- Preferential attack of the weld probably could occur since the weld is usually more anodic with respect to the base metal (assume both in contact with fluid).

Other damage mechanisms: rusting

- The presence of water vapour, condensed water, and oxygen in the dead leg facilitated the formation of rust.
- The presence of magnetite (lower oxidation state of iron) suggests that initially a limited supply of oxygen was available.
- Over time and in the presence of water and oxygen, this was converted to iron oxide-hydroxide.

Recommendations

- Possible actions to mitigate HCl acid-dew point corrosion in the regeneration circuit:
- Reduce the amount of HCl by reducing (as far as possible) the amount of perchloroethylene introduced into the regeneration circuit.
- Implement/Maintain a regular NDT inspection program of all zones in the circuit where HCl acid-dew point corrosion is a risk, to detect and monitor local thinning of pipe walls .
- Consider use of corrosion resistant Ni base alloys for critical zones (requires a dedicated assessment e.g. costs, risks of inducing other damage mechanisms).