## Appendix 1

## List of participants

#### Participants EFC WP15 meeting 3<sup>th</sup> May 2018 Dalmine (Italy)

NAME	SURNAME	COMPANY	COUNTRY	
Al Musharfy	Mohamed	ADNOC Refining Research Center	UNITED ARAB EMIRATES	
Arzuffi	Mirko	Amec Foster Wheeler	ITALY	
Bignardi	Riccardo	Rina Consulting	ITALY	
Bour Beucler	Valerie	Nalco Champion	FRANCE	
Claesen	Chris J	Nalco Champion	BELGIUM	
Coppola	Tommanso	Rina Consulting	ITALY	
Corradini	Raffaele	Techint Engineering	ITALY	
Cozza	Ricardo	Saras	ITALY	
De Landtsheer	Gino	Borealis	BELGIUM	
de Marco	Marco	Istituto Italiano della Saldatura	ITALY	
Divido	Luigi	Rina Consulting	ITALY	
Escorza	Erick	Tenaris Dalmine	ITALY	
Farina	Carlo	CEFIT Corrosion Consultant	ITALY	
Fersini	Maurizio	Allied Fittings	ITALY	
Fullin	Luna	Tenaris Dalmine	ITALY	
Gabetta	Giovanna	Eni	ITALY	
Ghidini	Andrea	Sices Group	ITALY	
Kus	Slawomir	Honeywell	UK	
Lombardo	Paolo	Isab	ITALY	
Lucci	Antonio	Rina Consulting	ITALY	
Madeddu	Enrico	Sartec	ITALY	
Manganini	Diego	Sices Group	ITALY	
Marcolin	Giacomo	Tenaris Dalmine	ITALY	
Merlini	Paolo	Tenaris Dalmine	ITALY	
Millefanti	Mirko	Sices Group	ITALY	
Monnot	Martin	Industeel	FRANCE	
Poldi	Matteo	Eni	ITALY	
Ropital	François	IFP Energies nouvelles	FRANCE	
Russo	Emanuele	Eni R&M	ITALY	
Sentjens	Johan	Temati	NETHERLANDS	
Smith	Ali	Rina Consulting	ITALY	
Spaghetti	Alessandra	Sandvik	ITALY	
Suardi	Edoardo	Sarlux	ITALY	
Suleiman	Mabruk	ADNOC Refining Research Center	UNITED ARAB EMIRATES	
Tabaud	Frederic	BP RTE	NETHERLANDS	
Tarantino	Sebastian	Sitech	NETHERLANDS	
Torella	Raffaele	Rina Consulting	ITALY	
Van Rodijnen	Fred	Oerlikon metco	GERMANY	
van Roij	Johan	Shell Global Solutions International B.V.	NETHERLANDS	
White	Calum	KAEFER Isoliertechnik GmbH & Co. KG GERMANY		

## Appendix 2

### **EFC WP15 Activities**

## (F. Ropital)





e WP15 spring m	eetings :
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)



ROPEAN FEDERATION OF CORRESSON	cweb.org/Working+Parties	COrrosion Atlas Web page s/WP+Corrosion+in+the+Refinery+Industry/WP+15+Refinery+Corrosion+Atlas.html				
	Search 33	EUROPÄISCHE FÖDERA TION KORBOSON EUROPÄISCHE FÖDERA TION KORBOSON FEDERATIONE UROPEENNE DE LA CORROSION FEDERATIONE UROPEENNE DE LA CORROSION				
	Who we are	Welcome > Working Parties > WP Corrosion in the Retinery Industry > WP 15 Retinery Corrosion Alias				
	EFC Membership	EFC Working Party 15: Corrosion in the Refinery Industry				
	Working Parties					
	WP Corrosion and Scale inhibition	WP 15 REFINERY CORROSION ATLAS				
	WP Corrosion by Hot Gases and	Un this page you will into some corrosion failure cases from the retinery and process industries.				
	Combustion Products	These documents are only given for information and do not engage EFC.				
	WP Nuclear Corrosion WP Environment Sensitive Fracture	Failure case n°1: High temperature corroeion of a first stage reactor of a hydrocracking unit				
	WP Surface Science and Mechanisms of Corrosion and	Pailure case nº2: Chloride stress corrosion cracking of a H2S stripping tower in a hydodesulturisation unit				
	WP Corrosion Education	Failure case n*3: Creep and cracks in a hydodesulfurisation unit				
	WP Physico-chemical Methods of Corrosion Testing	Failure case nº4: Chloride stress corrosion cracking of mounting hardware in a FCC				
	WP Marine Corrosion	Failure case n*5: Metal dusting corroeion of a furnace tube in reforming unit				
	WP Microbial Corrosion	Failure case n°6: Sufficition in an atmospheric distillation unit				
	WP Corrosion of Steel in Concrete					
	WP Corrosion in Oil and Gas	Failure case n°7: HF stress corrosion cracking in an alkylation unit				
	WP Coalinos	Failure case n°8: Carbonate stress corrosion cracking in an FCC unit				
	WP Corrosion in the Refinery industry					
	WP 15 Refinery Corrosion Atas CUI Restricted Web Page	If you would like to add other failure cases, you can complete the enclosed file and send it to Francois Ropital email: francois ropital@itpen.fr				
	WP Cathodic Protection					
	WP Automotive Corrosion					







#### Appendix 3

## THOR<sup>TM</sup> 115 – New ferritic steel with improved

#### oxidation and sulfidation resistance

(L. Fullin)



EFC – WP15 Spring Meeting 2018

Dalmine – May 3<sup>rd</sup>, 2018



L. Fullin – Product Engineer

G. Marcolin – Product Manager

## Agenda

Introduction Metallurgy and properties Special tests Steam Oxidation Sulfidation and NAC HGO Hydrotreating Pilot Plant Chlorides Manufacturing experience Conclusions





#### Agenda



#### Introduction

Metallurgy and properties Special tests Steam Oxidation Sulfidation and NAC HGO Hydrotreating Pilot Plant Chlorides Manufacturing experience Conclusions



#### Introduction – New Tenaris Grade

**10-years development** 

R&D and Industrial Validation Market needs investigation

Cooperation with Universities, Laboratories and Normative Groups

Multicultural team

## Agenda

Introduction Metallurgy and properties Special tests Steam Oxidation Sulfidation and NAC HGO Hydrotreating Pilot Plant Chlorides Manufacturing experience Conclusions



#### **Metallurgy and Properties**

Design

Tenaris worked on the development and qualification of a new martensitic steel for high temperature applications with enhanced oxidation resistance.

- Improved steam oxidation resistance vs. 9Cr grades
- Creep properties better than grade 91
- Friendly in manufacturing and welding

#### Composition

С	Mn	Si	Cr	Ni	Cu	Мо	Al	V	Nb	Ν
0.1	0.4	0.4	11.0	< 0.2	< 0.15	0.5	< 0.02	0.2	0.04	0.05



#### **Metallurgy and Properties**

Microstructure
Thor<sup>™</sup> 115 microstructure consists of tempered martensite.
Cr-Ni balance limit enforced to prevent formation of δ ferrite.





(MPa)∖(°C)	550	575	600	625	650
New Gr.91 Cl. 1	98.5	75.5	54.3	36.8	24.0
New Gr.91 Cl. 2	102	78.2	57.6	39.2	25.1
Thor 115	108	85.0	63.3	45.3	29.8



#### **Metallurgy and Properties**

Physical properties

As a ferritic steel, Thor presents smaller thermal expansion and better thermal conductivity with respect to austenitic grades.





## Agenda

Introduction Metallurgy and properties Special tests Steam Oxidation Sulfidation and NAC HGO Hydrotreating Pilot Plant Chlorides Manufacturing experience

Conclusions



#### **Steam Oxidation**

- Steam oxidation testing performed by Oak Ridge National Laboratory
- Furnaces holding specimens (600, 625, 650 °C) fluxed with steam from ultra-high purity water.
- Testing duration 11,000 h (about 460 days)
- Specimens removed from furnaces every 500 h for the measurement of mass loss as a function of time.

Rate of oxidation in Thor is similar between 600 and 650 °C, thanks to the higher amount of available Cr for diffusion to the surface, forming a compact protective oxide (spinel) layer at higher temperature.



#### **Steam Oxidation - Field experience**

#### HRSG test loop Installed and running since May 2015.



Superheater steam is extracted from an existing vent and reheated inside a Thor circuit up to 615 °C.

Scale thickness at the inner tube surface after 2,421 h.



#### **THOR™115** in Downstream



## Chemistry identified as suitable for Refining corrosive environment

- Chemical composition in the middle of Ferritc and Stainless families
- Identification of fields of application of those materials
- Study of THOR behavior to understand strengths and weaknesses coming from Ferritic Steels and Stainless Steels



#### **Special tests: Sulfidation and NAC**



- Pilot Plant in VeneziaTecnologie
- No TAN decrease for degradation
- Comparative tests
- Tests in naphthenic and sulphidic environment
- Expected trends confirmed after weight loss analysis at different H<sub>2</sub>S contents

## Special tests: HGO hydrotreating pilot plant

- Tests performed at ARRC in Abu Dhabi
- HGO Hydrotreating
- 2 cycles, 1 month each
  - ➢ cycle A at 390°C
  - cycle B at 420°C
- Comparative tests and temperatures to stress corrosion kinetics:
  - First cycle stimulatingFeS layer formation
  - Second cycle boosting T
- Lower weight loss of Thor 115





#### Special tests: HGO hydrotreating pilot plant



- Calculated corrosion rate unchanged between first cycle and after the 2 cycles
- Higher stability of protective layer

## **Special Tests: Chlorides**





#### Tests carried out in CSM laboratories. Pitting morphology observed on THOR and SS:

- Diffuse shallow pits on THOR surface (depth  $\approx 6 \,\mu$ m)
- Deep localized pits on SS (depth  $\approx 60 \ \mu m$ )

## **Possible advantage in critical-defect** failure modes



## Agenda

Introduction Metallurgy and properties Special tests Steam Oxidation Sulfidation and NAC HGO Hydrotreating Pilot Plant Chlorides Manufacturing experience Conclusions



#### **Pipes and Tubes**



Trial heats successfully cast

Seamless pipes and tubes rolled covering Grade 91 feasibility

Main applications

- Boiler tubes (HRSG, heat exchangers, ...)
- Steam lines
- Furnace pipes (cracking furnaces, reformer interheater tubes, ...)
- Process Pipes (Vacuum Circuit, Hydroprocessing, Visbreaking, ...)



#### Thor<sup>™</sup>115: Manufacturing experience

Piping component	Manufacturer
Tubes NPS 1 to 4 in	Tenaris Silcotub
Pipes NPS 6 to 24 in	Tenaris Dalmine
Forged Flanges	Officine Melesi
Forged and Bored Pipes	Tenaris Dalmine / Simas
Fittings	Allied Fittings









- Process parameters equal to the ones used for grade 91
- Full mechanical characterization, with satisfactory results



## Agenda

Introduction Metallurgy and properties Special tests Steam Oxidation Sulfidation and NAC HGO Hydrotreating Pilot Plant Chlorides Manufacturing experience Conclusions





#### **Thor Achievements**

- Improved steam oxidation resistance vs. 9Cr grades
- **Creep properties** better than new grade 91 class 1 and 2
- Microstructurally stable (delayed formation of Zphase, no Laves phase)
- Friendly in manufacturing and welding
- Sulfidation resistance increased against P9
- **Different failure** mode in Chlorides environment vs Austenitic SS

#### Next steps

- Thor<sup>TM</sup>115 in API 530 and API 560 for furnaces
- Test loops in refineries





# Thank you



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## Appendix 4

## Testing of a material under HDT condition of a

## refinery

(M. Suleiman)

## Material Corrosivity Evaluation Under Simulated Hydrotreating Condition

By: Dr Mabruk Issa Suleiman



## Introduction

- Objective & Methodology
- Exposure Tests
- Test coupons prior to exposure
- Operational conditions trends
- Test coupons after exposure
- Results & Discussion
- Summary

## Crude Classification Based on API Gravity & Sulphur



# Refining


#### **Process Flowchart of a Refinery** the second Fuel Gas Amine Treating Refinery Fuel Other Gases H<sub>2</sub>S Claus Sulfur Plant - Sulfu - LPG Gas Processing Merox Treaters H<sub>2</sub>S from Gas Butanes Sour Water Stripper Gas Gas $H_2$ H2 Light Isomerate Isomerization Hydrotreater Plant Naphtha Gas H<sub>2</sub> Gas H<sub>2</sub> Distillation Heavy Reformate Catalytic Hydrotreater Reformer Naphtha Blending Pool 62 identified damage Gas H<sub>2</sub> Jet Fuel Atmospheric Jet Fuel Crude Merox Treater and/or Kerosene Kerosene Oil mechanisms Hydrocracked Gasoline H<sub>2</sub> Gas

CO2

Hydrogen

Synthesis

H<sub>2</sub>



Finished products are shown in blue -Sour waters are derived from various distillation tower

Air

Diesel Oil

Atmospheric

Light Vacuum

Gas Oil

Heavy

Vacuum

Gas Oil

Vacuum Residuum

Asphalt

Blowing

Gas Oil

Evacuated non-condensibles

> Distillation /acuum

Atmospheric

Bottoms

Hydrotreater

Gas Oil

Gas

ŧ

Natural Gas

Steam

- reflux drums in the refinery The "other gases" entering the gas processing unit
- includes all the gas streams from the various process units

### **MOST COMMON MECHANISMS**

S.N	DMN	Damage Mechanism	Inspection technique	Suitable material	% Location
1	1	Sulfidation	Visual, UT, and RT	5 & 9 Cr, or austenitic stainless steel depending on wt% S	9.5
2	2	Wet H2S Damage (Blistering/HIC/SOHIC/SSC	UT, DPT, MP, RT, AET	Low sulfur CS, Stress relieving	7.5
4	4	High temp H2/H2S Corrosion	UT, DPT,RT	Austenitic stainless steel	2.4
3	5	Polythionic Acid Cracking (NACE Standard RP0170)	UT, DPT, Metallography	Thermally stabilized 347 SS, alloy 20, alloy 625	2.9
4	6	Naphthenic Acid Corrosion	UT RT, and VI,	Austenitic stainless steel with higher Molybdenum content.	7.2
5	7	Ammonium Bisulfide Corrosion	UT ,RT IRIS, EC	300 Series SS, duplex SS, aluminum alloys and nickel base alloys	8.1
6	8	Ammonium Chloride Corrosion	RT or UT stream monitoring	Alloys 400, duplex SS, 800, and 825, Alloys 625 and C276 and titanium	4.6
7	9	HCI Corrosion	automatic ultrasonic scanning methods or profile RT	Alloy 400, titanium and some other nickel base alloys	4.3
8	10	High Temperature Hydrogen Attack	UT using a combination of velocity ratio and backscatter , &VI, metallography	To satisfy API 941, and use of SS cladding and weld over lay.	3.7
12	20	Erosion / Erosion-Corrosion	IR UT, RT, and corrosion coupons	Higher molybdenum containing alloys	6.3
13	22	Amine Cracking	WFMT or ACFM	API RP 945, Use solid or clad stainless steel, Alloy 400 or other corrosion resistant alloys in lieu of carbon steel	6.6
14	23	Chloride Stress Corrosion Cracking	UT, DPT, EC, Metallography	Carbon steels, low alloy steels and 400 Series SS, and nickel based alloys	5.5
19	45	Amine Corrosion	UT,VT, corrosion coupons	300 , 400 series SS	4.9

### **Material Selection for the Service life**

Components Design life	Years
Pressure vessels, reactors, exchangers and towers	30 Years
Exchanger tube bundles	10 Years
Non-removable trays and internals	30 Years
Tanks	30 Years
Heater tubes	100,000 Hours
Compressor Cases	20 Years
Piping Process	30 Years
Piping Utilities	30 Years
Pumps	30 Years
Replaceable trim and internals for pumps	4 Years minimum

# **ACTIVE SULPHUR**



~~~~~	***************************************
S,Th	Sulphides, Thiols
DS, T	DS, Thiophenes
Ar-S	Aryl-sulphides
BT	Benzothiophenes
NBT	Naphtenic-Benzothiophenes
DiBT	Di-Benzothiophenes
NDiBT	Naphtenic-di-Benzothiophenes
Bnaph	Benzo-Naphthothiophenes
NBNaph	Naphthenic-Benzo-Naphthothiophenes
DiNaph	DiNaphthothiophenes

(1200 ppm) is less corrosive than the one having (590 ppm) due to the Presence of active Sulphur in several





## SOME EXPERIENCE WITH MERCAPTAN-SULFIDIC CORROSION

Site	Metallurgy	Feed Composition	Corrosion rate	Location
Singapore	CS A106	Laminaria and others	>1 mm/yr	CDU furnace
Canada	Carbon steel	Condensate	1.6 mm/yr	Main fractionator furnace tubing and column
UK	CS	Mixture of crudes	0.6 mm/yr	Hydrocracker reboiler circuit
Germany	CS	Blend crudes	0.5	HGO draw line
NewZealad	P5 (5Cr-1Mo)	Blend crudes		Furnace tube charge heater
Japan	P5 (5Cr-1 Mo)	Blend crudes		CDU /HVU
Saudi Arabia	CS A106	Arab light	0.9 mm/yr	CDU furnace
UAE	CS & P5 (5Cr-1 Mo) & P9	Condensate	>1 mm/yr	Re-boiler( heater) & Charge heater tubes

### **Sulfidation corrosion**

- **Wastage of the wall**
- **1800**
- With the advent of FCC , coking, and Hydroprocessing
- A function of temperature, the total sulfur the types of sulfur, the type of stream,
- □ above (230 °C).
- Set of curves
- **Prediction** is an elusive **technical challenge**.



#### **Location of Sulfidation Corrosion**

- Sulfidation corrosion can occur wherever sulfur compounds are present in a hydrocarbon stream and the temperature exceeds approximately 230 °C.
- H2-free sulfidation occurs in the hotter areas crude, vacuum, coker, visbreaker, and hydroprocessing feed and distillation sections.
- H2/H2S corrosion most commonly occurs in hydroprocessing
- Organic acids







### **PRACTICAL GUIDELINES**

- **1. Existing Units and Components**
- 2. Materials Selection Guidance
- H2-free Services
  - Carbon steel for temperatures up to (275 °C). Use fully killed steels to assure silicon content > 0.10 wt %.
  - > 5Cr-0.5Mo for temperatures between (275 °C and 325 °C).
  - > 9Cr-1Mo above (325 °C).
  - 300 Series SS can also be used to virtually eliminate sulfidation corrosion.



### **PRACTICAL GUIDELINES**

#### H<sub>2</sub>/H<sub>2</sub>S Services

- With high mole % H2S at metal temperatures above 260 °C), 300 Series SS are the preferred choice.
- Low ally steel may be used for lower severity services, such as naphtha and kerosene Hydrotreaters with lower mole % H<sub>2</sub>S levels,

#### **Other considerations**

- Heater Tubes
- Linings or Cladding
- Piping Components
- Scaling
- Specification Break
- PMI Program
- Materials Operating Envelope (MOE)



### **Material Corrosivity Evaluation**

- □ ARRC was requested test a new alloy was developed by M/s Tenaris namely Thor<sup>™</sup>115 in comparison to P5 and P9.
- ARRC simulated real refinery conditions in a pilot plant unit that was specially modified
- Actual feedstock and operating conditions used in refineries









### **TEST OBJECTIVES & METHODOLOGY**

#### **OBJECTIVES**:

- To test new alloys and compare with P5 and P9 in a H<sub>2</sub>S environment at certain temperatures (390°C and 420 °C):
- Prepare coupons and determine corr. rate estimation in line with ASTM G1 and ASTM G4, wherever applicable.
- Exposing the coupon samples to H<sub>2</sub>S in the range of 9000 – 12000 ppm



Figure 10: Schematics of process unit with stream numbers

lesting conditions				
Process	Feed	<b>Testing environment</b>	Testing condition	
Hydro treatment	Heavy Gas Oil (HGO)	H <sub>2</sub> S: approx. 1.1% H <sub>2</sub> : 98% – 99%	Pressure: 40 to 57 bar Reactor Temp: Max 400 °C Coupon Test Chamber Temp: 390/420 °C	



- The three tested materials were designated material numbers, shown in Table 2.
- □ Each material had 4 coupons, labeled A through to D

Material	Material number	Coupons
Р5	1	1A, 1B, 1C, 1D
P9	2	2A, 2B, 2C, 2D
Thor™ 115	3	3A, 3B, 3C, 3D



### • FIRST 30 DAYS **DURATION** □30 days **TEMPERATURE** □390°C □ FEED FLOW RATE Average: 20.3 cc/hr □ PRESSURE (=H<sub>2</sub> partial pressure) Average: 56.9 bar

#### EXPOSED COUPONS LAYOUT IN TEST CHAMBER

- TOP HOLDER
  - 1A

Test 1

- 2A
- 3A
- MIDDLE HOLDER
  - 1C
  - 2C
  - 3B
- BOTTOM HOLDER
  - 1B
  - 2B
  - 3C

T boost to 420°C to establish clear comparison at different T severities

Test 2

- SECOND 30 DAYS
  - DURATION
    - 30 days
  - TEMPERATURE
    - 420°C
  - FEED
    - HGO
  - FEED FLOW RATE
    - Average: 19.0 cc/hr
  - PRESSURE (=H<sub>2</sub> partial pressure)
    - Average: 57.0 bar

- EXPOSED COUPONS LAYOUT IN TEST CHAMBER
  - TOP HOLDER
    - 1A
    - 2A
    - 3A
  - MIDDLE HOLDER
    - 1D
    - 2D
    - 3D
  - BOTTOM HOLDER
    - ∎ 1B
    - 2B
  - 3C

## **COUPON GROUPS**

Table 3: Coupon terminology					
Middle helder					
		۲ <b>۲</b>			
	Coupon Tag number	Naming			
st 1	1C	Test 1 (390°C) coupons			
Tes	2C				
	3B				
	Top holder				
N	Coupon Tag number	Naming			
<b>1</b> 0	1A	Test 1&2 coupon, or Full run			
est	2A	coupons (Top holder)			
Ĕ	ЗА				
	Middle holder				
	Coupon Tag number	Naming			
it 2	1D	Test 2 (420°C) coupons			
Les	2D				
'	3D				
	Bottom holder				
	Coupon Tag number	Naming			
82	1B	Test 1&2 coupon, or Full run			
st 1	2B	coupons (Bottom holder)			
He	3C				

### Surface Prepared And Cleaned New Coupons Before Exposure





#### Test 1: H<sub>2</sub>S concentration and temperature trends



Test 2: H<sub>2</sub>S concentration and temperature trends

Coupons after Test 1 upon retrieval. From L to R: Top holder; Middle holder and Bottom holder



Coupons after Test 2 upon retrieval. From L to R: Top holder; Middle holder and Bottom holder.



### **Corrosion rate results**

- Corrosion rate plots were made for:
- Test 1 coupons exposed at 390°C
- Test 2 coupons exposed at 420°C
- Average corrosion rates for the full run coupons (Test 1 & 2)
- Comparison of corrosion rates for materials in Test 1, Test 2 and Full run

In order to visualize and compare each material's corrosion rate, specific marker colors and shapes were assigned.

Material	Material number	Marker
Р5	1	
Р9	2	
Thor ™ 115	3	



#### Comparing corr. rates of Test 1, Test 2, and Full run (Test 1 & 2) coupons

Tested materials not anticipated to be used for these exposure conditions

Summary

- Merely to obtain a comparative results in a short time period
- The actual corrosion rate values are relevant to the specific test conditions only
- The desired objective of the tests is to rank material performances
- Materials 3 have better resistance to sulfidic environments compared to materials 1 and 2.

#### Appendix 5

#### Material selection for heat exchanger tubes in

#### oil refineries

#### (A. Spaghetti)

### OIL REFINERY SANDVIK HIGH PERFORMANCE MATERIALS





### OIL REFINERY 5 TYPE OF PROCESSES:

#### 1. Distillation

- Atmospheric
- Vacuum

### 2. <u>Conversion</u>

- Decomposition
- Unfication
- Reforming
- 3. <u>Treatment</u> (various)
- 4. <u>Blending</u> of HC fractions and additives
- 5. Others



# CDU – OVERHEAD CONDENSER



### **CORROSION RISKS**

- Pitting and crevice corrosion
- HCl (dewpoint) corrosion
- Salt residues in crude oil → under deposit corrosion
- Solid deposits of ammonium chloride (→ under deposit corrosion) ← injection of ammonia to neutralize
- Increased use of sour crude  $\rightarrow H_2S$
- Stress Corrosion Cracking
- Microbiological Induced Corrosion



### PITTING AND CREVICE CORROSION



	SAF 2507®	SAF 2707 HD™
Max crevice temp	40°C	70°C
Min flow rate	1 m/s	1 m/s
Max tube wall temp	60°C	90°C

Value for SAF2507<sup>®</sup> and SAF2707HD<sup>™</sup> in seawater.

Critical pitting temperature measured in modified G48A and "Green death". Critical crevice corrosion temperature obtained in testing with a crevice specified in the MTI-2 procedure.

5

### PITTING AND CREVICE CORROSION



CCT = critical crevice temperature G 48 B CPT = critical pitting temperature G 48 A

\*Based on more than 20 years practical experience

### HYDROCHLORIC ACID CORROSION

7



### SALT RESIDUALS AND SOLID DEPOSITS

- Hydroxides, carbonates, sulfates, nitrates ad phosphates have an inhibition effect on pitting, but then can form deposits → under deposit corrosion
- Pitting resistance is impaired by stagnant solutions
- High flow rate of chloride containing water in tubular heat exchanger will keep the surface clean both from deleterious species at pitting sites and from fouling which could otherwise reduce heat transfer
- Flow rate below 1 m/s should be avoided

### **SOUR CRUDES**

#### LOW PH AND/OR HIGH CHLORIDES CONCENTRATION



Hydrogen Embrittlement (ferrite) Low Temperature (SSC)

Metal corrodes and  $H^+$  is reduced to  $H_2$ 

Two  $H_2$  can migrate on the surface and leave the metal as  $H_2$ 

H<sup>+</sup> can be absorbed into the metal

HS<sup>-</sup> and S<sup>-</sup> retard H<sup>+</sup> recombinations



Stress Corrosion Cracking (austenite) High temperature

H<sub>2</sub>S promotes formation metal sulphides on the metal on the SS surface

Non passivating surface layer

Promote growth of pitting and crevice corrosion

Lead to SCC of austenite (induced by chlorides)

### STRESS CORROSION CRACKING

#### INDUCED BY CHLORIDES

- Autoclave
- 100 bar
- 8 ppm O<sub>2</sub>
- Load = proof strength
- NaCl-solution
- 1000h (6 weeks)


### NACE MR0103 MATERIALS RESISTANT TO SULFIDE STRESS CRACKING IN CORROSIVE PETROLEUM REFINING ENVIRONMENT

- Aims at refinery application
- Controlled environment
  - Low salinity
  - Low  $H_2S$
  - Controlled pH
- Material qualification is based on alloy composition and hardness

1.3.5.1.1 The high-pH sour environments differentiate refinery sour service from the oil and gas production sour environments covered by NACE MR0175/ISO 15156, because many wet sour streams in production also contain carbon dioxide and hence exhibit a lower pH. Another major difference is that chloride ion concentrations tend to be significantly lower in refinery sour services than in oil production sour services.

## NACE MR0103

#### MR0103-2012

#### 2.8 Duplex Stainless Steel Materials

2.8.1 Wrought and cast duplex stainless steel products shall be in the solution-annealed and liquid-quenched condition. Tubing shall be rapidly cooled by liquid quenching, or by air or inert gas cooling to below 315 °C (600 °F). The ferrite content shall be 35 to 65 vol%. Aging heat treatments to increase strength and/or hardness are prohibited because of the formation of embrittling phases.

2.8.1.1 The hardness of grades with PREN ≤ 40% according to Equation (1) shall not exceed 28 HRC.<sup>(10)</sup>

2.8.1.2 The hardness of grades with PREN > 40% according to Equation (1) shall not exceed 32 HRC.<sup>(10)</sup>

2.8.2 Welding of Duplex Stainless Steels

2.8.2.1 Fabrication and repair welds in all wrought and cast duplex stainless steels shall be produced using a welding procedure qualified by performing the following tests on specimens taken from the WPQT coupon(s):

2.8.2.1.1 A hardness survey shall be performed in accordance with Appendix C. The average hardness shall not exceed 310 HV, and no individual reading shall exceed 320 HV.

2.8.2.1.2 Metallographic ferrite measurements shall be performed in accordance with ASTM E562.<sup>19</sup> The average ferrite content in the weld deposit and HAZ shall be within the range of 35 to 65%, with a relative accuracy of 10% or lower.

2.8.2.1.3 Technical considerations for qualification of welding procedures for duplex stainless steels are included in Appendix D (nonmandatory).

## MICROBIOLOGICAL INDUCED CORROSION

#### WITH CHLORINATION

- Corrosive environment
- Pitting corrosion is a common problem in stagnant seawater
- Cl<sub>2</sub> is an oxidant commonly added to seawater exchangers to mitigate against biofouling
- Cl<sub>2</sub> increase the electrochemical potential
   ⇒ increase the severity of the environment
   ⇒ pitting corrosion

#### WITHOUT CHLORINATION

- Active microorganisms stick to the surface
- Reduced heat transfer and risk for crevice corrosion (Microbiological Induced Corrosion "MIC")

## **CHLORINATION**

- Cl<sub>2</sub> is an oxidant commonly added to seawater exchangers to mitigate against biofouling
- Cl<sub>2</sub> increase the electrochemical potential → increase the severity of the environment → pitting corrosion



# HYDRODESULFURIZATION

# HYDROTREATING

«PROCESS TO CATALYTICALLY STABILIZE PETROLEUM PRODUCTS BY CONVERTING OLEFINS/AROMATICS TO PARAFFINS OR REMOVE OBJECTIONABLE ELEMENTS FROM PRODUCTS OR FEEDSTOCKS BY REACTING THEM WITH HYDROGEN»





# COMMON CORROSION RISKS



# **COMMON CORROSION RISKS**

### Chlorides

- SCC of low-alloyed stainless steel grades like 304 and 316
- Pitting corrosion at stagnant conditions and high chloride content
- Crevice corrosion if there is risk for fouling
- H<sub>2</sub>S
  - Hydrogen embrittlement of ferritic materials
  - Chloride induced corrosion

- Ammonium compounds
  - Under deposit corrosion
  - Ammonium salts can cause erosion on soft material
- Polythionic acid
  - Can cause "stand still corrosion"
- Solid deposits (expecially ammonia salts)
  - Can cause erosion of tube ends leading to leakage



# MATERIAL SOLUTION

- Good Sandvik SAF 2205®
  - -Widely used in refineries
- Better Sandvik SAF 2507®
  - -Improved resistance to chloride induced localized corrosion and SCC
- Best Sandvik SAF 2707 HD<sup>™</sup>
  - -Excellent resistance to chloride induced localized corrosion and SCC
- For higher temperatures (> 300°C)
  - -Sanicro<sup>™</sup> 28 and Sanicro<sup>™</sup> 41
  - –Offer very good H<sub>2</sub>S resistance and excellent SCC resistance



# SANICRO<sup>TM</sup>28 ADVANTAGES IN REFINERIES APPLICATIONS



# THE SANICRO<sup>™</sup> FAMILY

- <u>SA</u>ndvik <u>NI</u>ckel <u>CRO</u>mium
- % Ni > 8: the structure is fully austenitics
- Other alloy elements make materials «multi-purpose»

#### Most used SANICRO in refineries

Grade	С	Si	Mn	Р	S	Cr	Ni	Мо	Cu	Ti
SANICRO™ 28	≤0,020	≤0,6	<2,0	≤0,025	≤0,010	27	31	3,5	1,0	
SANICRO™ 41	≤0,030	≤0,5	0,8	≤0,025	≤0,010	20	38,5	2,6	1,7	0,7



### **GENERAL CORROSION**



- Isocorrosion diagram for Sanicro<sup>™</sup> 28, 904L and ASTM 316L, in deaerated sulphuric acid
- The curves represent a corrosion rate of 0.1 mm/year (4 mpy)



### GENERAL CORROSION



 Isocorrosion diagram for Sanicro<sup>™</sup> 28 in sulphuric acid containing 2000 ppm chloride ions at a corrosion rate of 0.1 mm/year (4 mpy)



#### **GENERAL CORROSION**



 Isocorrosion in hydrochloric acid. The curves represent a corrosion rate of 0.1 mm/year (4 mpy).



### PITTING CORROSION



 Critical pitting temperature (CPT) at +400 mV SCE for different alloys in synthetic seawater (3% NaCI), at different pH values

PRE = % Cr + 3.3 x % Mo + 16 x % N

SANDVIK

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#### STRESS CORROSION CRACKING

 Results of stress corrosion cracking tests on different steel grades in 40% CaCl<sub>2</sub>, at 100 °C (210 °F), pH = 6,5



## LABORATORY TEST CONDITIONS: R&D



- Sanicro<sup>™</sup> 28 laboratory sour test result. All specimens stressed to 100% of yield strength.
- pH 2.9
- (1) 5% NaCl (30,000 ppm Cl<sup>-</sup>)
- (2) 15% NaCl (90,000 ppm Cl<sup>-</sup>)

Sanicro<sup>™</sup> 28 can be used safely at high H<sub>2</sub>S partial pressures and temperatures without any corrosion

# SANICRO<sup>™</sup> 28: WHEN & WHY?

- Sanicro<sup>™</sup> 28 is suitable in special demanding applications:
  –heat exchangers with temperatures above 250 °C
  –Alternative to Alloy 825 (Sanicro<sup>™</sup> 41)
- Sometimes refinery conditions are high in H<sub>2</sub>S and with low pH
  - –Duplex or super duplex should not be used
  - –Sanicro<sup>™</sup> 28 suitable material choice



# DISCUSSION

- H<sub>2</sub>S in itself is not corrosive for stainless steel, due to its weak acidity and dew point
- In combination with a low pH and/or high chloride concentration it can enhance hydrogen absorption which can lead to hydrogen embrittlement of ferrite phase and/or sulphide stress cracking (SSC)
- According to NACE MR0175-ISO 15156-1:2003, Sanicro<sup>™</sup>28 is categorized as solid solution nickel based alloy group 4c and is recommended for any application under the conditions described by Table 2
- In an H<sub>2</sub>S environment, Sanicro<sup>™</sup> 28 in cold worked condition showed excellent resistance to stress corrosion cracking / sulphide stress corrosion attack



# SUMMARY

- Sanicro<sup>™</sup> 28 is a high end material exhibiting very good corrosion resistance and mechanical properties
- Sanicro<sup>™</sup> 28 has:
  - Worse resistance towards chloride induced localised corrosion than super duplex and 6Mo austenitic grades
  - Better resistance towards chloride induced localised corrosion than 2RK65 (904L)
  - Better resistance towards H<sub>2</sub>S containing environments than super duplex grades
- NACE MR0175 should not be used for material specifications for refinery applications, introducing NACE MR0103 (material qualification is based on alloy composition and hardness)



# THANKS FOR THE ATTENTION

Alessandra Spaghetti Global Technical Marketing Sandvik Materials Technology

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#### Appendix 6

#### **Corrosion during water washing of CDU**

#### overheads

#### (M. De Marco)



### Is Water washing in CDU overhead always beneficial?

M. De Marco

#### INTRODUCTION

- CDU overhead corrosion control can be a very challenging job
- Corrosion by acid condensate (HCI and other inorganic and organic acids)
- Fouling by salts (acidic) and corrosion products (UDC)
- For overhead corrosion and fouling to occur HCI vapor has to:
  - Dissolve in water condensate
  - React with ammonia vapor and form ammonium hydrochlorides salts
  - React with liquid organic neutralizers and form neutralizer hydrochloride salts
  - Penetrate existing corrosion deposits on metal surface
  - Penetrate existing corrosion inhibitors film



- CDU overhead corrosion mitigation starts from crude feed to the Unit.
  - Crude tank settling
  - Desalting
  - Caustic addition
  - Overhead control as injection of inhibitors, neutralizers and water washing
  - Monitoring of Key Performance Indicators (KPIs as pH, Chlorides, Iron, etc.) and Operating Windows (OWs)
  - Inspection strategies
  - Metallurgical upgrades to CRA (the right one!)



- In general water wash injection into overhead systems should not be necessary if the crude charge is properly desalted ( < 3,5 ppm salt) -> Overhead water condensate with Cl<sup>-</sup> < 20 ppm.</li>
- No ammonium chloride and/or neutralizer hydrochloride salts are likely to form as long as the dew point exceeds 110 °C (safety margin often applied).
- The principal objective of water injection is to
  - remove deposits of salts and corrosion products (crude no longer properly desalted or increasing frequency of desalter upset).
  - scrub some of the salt-forming contaminants from the overhead vapor before they have a chance to react.
  - raise the pH at the aqueous dew point, which occurs at the point of water injection.
- NOTE: Water injection can dilute also HCI but even an optimistic ten fold dilution corresponds in any case to high and unacceptable corrosion rate.
- NO matter how well planned and implemented, water injection by itself is non substitute for other OVHD corrosion control measure.

#### • WW quantity

- 5-15 % of total overhead vapor rate.
- the volume of water required to bring the atmospheric tower overhead stream to the aqueous dew point plus some free excess water (10-25 %).

#### • WW quality

- <u>Recycled Water from the atmospheric tower overhead drum</u> is a common source. locally available, air-free (oxygen contamination can accelerate corrosion). In addition to low oxygen content, other characteristics of good wash water include low solids content and relatively neutral pH
- <u>BFW</u>, although costly (oxygen free).
- <u>Stripped sour water</u> (low in oxygen and, with good sour water stripper operation, low in NH<sub>3</sub>, H<sub>2</sub>S and acids).
- Fresh water such as well water, surface water, raw water, cooling water, and cooling tower blowdown <u>are not normally considered good</u> water sources because they contain oxygen.

- WW injection point
  - <u>Atmospherics tower overhead line</u> -> for maximum contact time, scrubbing and effect on dew point.
  - <u>Close to the inlet of the overhead condenser</u> bundles -> for maximum distribution to the banks



#### • Problems with WW

- Previously dry components can become wet and in certain cases experience acid corrosion (especially if insufficient water is injected).
- Dissolved air (O<sub>2</sub>) can induce corrosion.
- Impingement problems in high velocity area (usual limits of wet stream in OVHD 9-15 m/s) -> elbows, change in flow direction, inlet area of HEs.
- Not proper distribution of WW in HEs parallel banks.
- Process issues -> heat balance in HEs

#### **CASE HISTORY #1**

- Overhead condenser CDU unit
- Corrosion phenomena of tubes close to inlet nozzle
- Corrosion close to impingement plate
- Water washing implemented on the vapour line ahead since last 2 years
- Water used -> water from SWS
- Corrosion increased in the last 2 years (bundle installed in 2016)
- Injection of neutralizer and inhibitor on the vapour line





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#### EDS Analysis on external surface



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#### Section of a corroded tube



Actual configuration-> Impingement plate itself can cause a restriction -> not sufficient clearance



Better configuration-> Sacrificial solid rods (also possible to increase nozzle diameter)



• CONTROL INJECTION RATE AND QUALITY OF WASHING WATER!

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#### CASE HISTORY #2

- Overhead condenser CDU unit (AIR COOLER)
- Corrosion phenomena of Plate at outlet section (flow discharge of relevant tubes)
- Water washing implemented on the vapour line at each AC bank
- Water used -> demineralized BFW (not deaerated)
- Mixed metallurgy for tubes in different banks (duplex + CS)
- Injection of neutralizer (MEA + MOPA) and inhibitor on the vapour line







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#### pH, Chlorides and Iron in the OVHD accumulator



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#### Other issues with the aircoolers

Grooving corrosion on the tubesheet at outlet of tubes (only with SS tubes, no with CS tubes)



Organic fouling at AC inlet Box (asphaltenes rich)



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#### DISCUSSION

- Heavy impingement corrosion of plate.
- Organic fouling plug some tubes -> increased velocity in plug free tubes
- WW -> BFW with 5 ppm O<sub>2</sub> -> not deaerated
- CONTROL INJECTION RATE, INJECTION POINT AND QUALITY OF WASHING WATER, ALSO CONSIDERING HEAVY ORGANIC FOULING (PLUGGUNG OF SOME TUBES)

## Appendix 7

## Advancement of the development of a

## methodology to characterize Stress Relaxation

## Cracking

## (M. Monnot)



# Advancement of our development of a methodology to characterize Stress Relaxing Cracking on welded stainless steels

03/05/2018

Martin MONNOT

# Introduction

- ArcelorMittal
- Reheat Cracking and Stress Relaxation Cracking are damage mechanisms occurring in equipments from many industries combining both high stresses and high temperatures.
- <u>Reheat Cracking (RHC)</u> is commonly associated to Carbon & CrMo(V) steels, and is generally a problem occurring during fabrication (PWHT after welding) of the equipment
- WED

Example of a RHC Crack in a HAZ of a CrMoV low alloy steel

Stress Relaxation Cracking (SRC) is commonly associated to austenitic alloys, such as 300 series and nickel base alloys occurring during service of the equipments.



Example of a SRC Crack in a HAZ of a 347H austenitic stainless steel

# First methodology

- 4 points bending test: •
  - Welded samples (HAZ) with seam
  - Dimensions: 140 x 40 x 4 mm \_







Grade	Stress applied	Deflection (mm)	Temperature (°C)	Holding time	Cracks number
304LN	>> 120% YS	5	650	500 h	No cracks
			600		
		3	600		
347H	>> 120% YS	5	650		
			600		

# Second methodology

- U-bend test: •
  - Welded samples (HAZ) with seam
  - Dimensions: 140 x 40 x 4 mm





Weld in transverse direction

Weld in longitudinal direction

## Is the metallurgical state adequate to initiate SRC?

## Microstructure after ageing



• Precipitation state after ageing under the weld seam



> Intergranular precipitation first, transgranular precipitation then

## Influence of precipitation on hardness

• Use of micro hardness instrument (weight of 0.010 kg<sub>f</sub>)

Mark in grain

Mark at grain boundary









## Hardness after ageing 600°C/500h



Decrease of hardness with differences between grain and grain boundary

## Third methodology



- No cracks on previous set-up, probably because of :
  - Thickness of plates: 4 mm is too thin
  - Welding process: weld seam induced HAZ too small
  - Precipitation and stress relaxation kinetics mismatch



- ✓ U-bend set-up : strain around 10%
- ✓ Specimen 15 mm thick
- ✓ Welding process : GMAW through all thickness
- Sensitization before straining

On going tests in order to optimize sensitization before straining



# THANK YOU FOR YOUR ATTENTION !

Please feel free to share questions or remarks

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## **Appendix 8**

## Non-destructive inspection through insulated

#### systems

(B. White)

Minutes of EFC WP15 Corrosion in the Refinery and Petrochemical Industry 3 May 2018

# Non-Destructive Inspection Through Insulated Systems

KAEFER

Tenaris University, Dalmine, May 3<sup>rd</sup> 2018 Calum White





# KAEFER worldwide





## Our turnover in Euros





Our diverse and dedicated team





## Accreditation



INSPECTION BODY No. 8689

# DNV·GL

Certificate No: AOSS0000AKZ



THE BRITISH INSTITUTE of NON-DESTRUCTIVE TESTING



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# Corrosion Under Insulation (CUI)

#### How CUI is caused

- In order to have CUI, you must have an insulation system installed on a pipeline or vessel
- > Water penetration allows oxygen corrosion to occur. This can happen due to: Rain water
   Deluge systems
   Process liquid spillages
   Condensation



> Further contamination, primarily chlorides and sulfates from the environment or insulation can speed up the process dramatically



# **Corrosion Under Insulation (CUI)**

- > CUI is generally categorised into one of four categories:
  - 1. Low temperature (cold or cryogenic conditions)
  - 2. Sweating service (operating below the dew point)
  - 3. High temperature (above ambient temperatures)
  - 4. Cyclic temperature (alternating)
- Special consideration regarding dew points is required depending on location
  - Figure 1 –
    EFC No. 55: CUI Guidelines





# CUI – The Problem

- > Hidden threat due to insulation & cladding
- > No form of insulation is immune
- > Inspection technology difficult, or at least slow and very costly
- > >80% CUI occurrences in piping
- > 40 to 60% of pipe maintenance costs are caused by CUI
- > Approximately 10% of the total maintenance budget is spent repairing damage from CUI
- > <u>NACE SP0198</u>-2010 & <u>EFC 55</u>: CUI can occur up to 175°C
- > CUI rates ~20 times greater than atmospheric corrosion rates may occur

Carbon steel: -4 °C to + 175 °C: Risk of CUI (highest risk area: +60 °C to +120 °C)

Stainless steel: +50 °C to +175 °C



# Non-Destructive Testing (NDT)

#### > Conventional Techniques

- > Volumetric:
- > Ultrasonic Testing (UT)
- > Radiographic Testing (RT)

- > Surface:
- > Magnetic Particle Testing (MT)
- > Dye Penetrant Testing (PT)
- > Eddy Current Testing (ET)
- > Visual Testing (VT)



# New Technologies in NDT

#### > CUI Inspection – Inspect without removing insulation means considerable savings for the owner

#### > OpenVision

- > Portable fluoroscopic (RTR) low voltage X-ray inspection tool
- Capable of inspecting through cladding and insulation
- > Can image the pipe wall surface, showing areas of potential CUI or contaminated insulation

#### > Eddyfi Lyft

- > Pulsed Eddy Current (PEC)
- Induces powerful magnetic force into the test item through cladding and insulation
- Can evaluate average remaining wall thickness over an area



# **OpenVision**

> Handheld or mounted low voltage X-ray scanning device







# What does CUI look like?







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# **OpenVision**

## **Main Benefits**

- > Real time data acquisition
- > Capable of inspecting through most insulation and cladding
- > Also capable of locating welds
- > Fairly low radiation intensity
- > No isotope (can be turned off)
- > Performed in a two man team
- Roaming safety barriers reduce exclusion site zone




### **OpenVision**

### **Main Limitations**

- > <u>Radiation</u> Although relatively low energy, there is still a radiation danger. Depending on energy used, differing exclusion zones may be recommended
- > Requires the use of classified workers
- > High operator dependency (working on automated analysis)
- > Access restrictions Require 360° access for full coverage





## **OpenVision in Action**





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> Pulse Eddy Current (PEC) System





7 14.05.2018 NDT Through Insulated Systems

#### > How it works

- 1. Emission phase (the pulse): Probe injects magnetic fields that penetrate and stabilise in the component thickness.
- 2. Cut-off phase: Magnetic field emission is stopped abruptly, which induces strong eddy currents in the component.
- 3. Reception phase: Receiver measures the decay of the eddy currents as they diffuse into the material thickness.





#### > Main Benefits

- Can detect remaining wall thickness of material through insulation and cladding, including galvanised cladding
- > Very portable equipment
- > Very safe, zero exclusion zone required
- > Can be performed online





#### > Main Limitations

- > Screening tool, provides relative measurement
- Unable to discriminate near-side and far-side defects
- > Impossible to detect small pitting
- > Undersizes flaws smaller than the averaging area of the probe
- > Edge effect near metallic structures
- > Impossible to detect through hole defects









### Holistic CUI Package

KAEFER is working towards offering a full inspection package, tailored to clients' needs.

- > 1. Visual inspection to identify areas of high risk
- > 2. Screening technique using site suitable method (OpenVision or PEC) to determine presence of CUI
- > 3. Deinsulation
- > 4. Inspection (VT, UT)
- > 5. Reinsulation





### **Current Operations**

KAEFER is providing a CUI inspection service for clients in Australia:

- > Operations have been progressing since 2016
- > Very positive feedback from clients
- > We want to acknowledge the successful outcomes from the KIPS "open vision" work completed in A station units in recent months. The inspections identified corroded pipes and failed hangers which have since been replaced, mitigating potential safety breaches as well as minimising risk of unplanned outages. In addition, KIPS also identified corrosion at locations where we considered to be least susceptible to CUI. We have now incorporated the KIPS open vision method in our inspection strategies for pressure piping and hangers, and now aiming to utilise rope access. Many thanks. THE

Adrian Fidel

Mechanical Engineer - Boilers, Gas & Renewables Engineering

AGL Torrens



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### **Appendix 9**

### **Sulfide Stress Corrosion Cracking on dissimilar**

#### 625/carbon steel welds

(M. De Marco)



SSC cracking of a dissimilar welding in gas piping

M. De Marco

### INTRODUCTION

- CRAs are widely applied in Oil& Gas industry in order to guarantee corrosion and SCC resistance in very harsh environments (H<sub>2</sub>S, CO<sub>2</sub>, Cl<sup>-</sup>, MIC, various organic and inorganic acids...).
  - Standard and Special stainless steels
  - Nickel alloys
  - Copper alloys
  - Titanium alloys
  - ...
- Sulfide Stress Cracking (SSC) is one of the most insidious damage mechanisms that must be considered during design, construction and operation of components in O&G industry.



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#### **CASE HISTORY #1**

- ISO15156/NACE MR0175 parts 2 and 3 cover respectively the requisitions to resist to SSC phenomena of Carbon/low alloy steels and CRA.
- EFC publications 16 and 17 cover respectively the requisitions to resist to SSC of Carbon/low alloy steels and CRA.
- Many end-users and engineering company specifications outhere



#### SSC failure case history

- Gas treating plants.
- 2" valve made of Carbon Steel (CS) welded to CS pipe.
- Operative conditions
  - T: 61 °C
  - P: 55,7 barg
  - H<sub>2</sub>O: 0,37 % mol (close di dew point)
  - $ppH_2S$  : 1,76 barg
- In order to avoid damage to non metallic components in the valve during PWHT (commonly applied on CS in sour service) the weld was realized by 625 alloy filler (E-NiCrMo-3) with previous buttering on both pipe and valve side



Slide form copyright 2017 © • HV10 hardness on the joint showed values in accordance with sour service requirements.



- But...
- ...after 60 days in operation the valve failed at dissimilar weld -> circumferential crack.
- NOTE: analysis of deposits on internal surface showed indications of water condensate and sour environment

![](_page_159_Picture_3.jpeg)

![](_page_159_Picture_4.jpeg)

- Crack path along the fusion line.
- Macroscopically the crack does not seem a typical SCC phenomena

![](_page_160_Picture_2.jpeg)

- Microscopically the scenario changes totally.
- Crack path along the fusion line, with corrosion products inside
- Partially Mixed Zone (PMZ) of dissimilar welding
- Chemical composition gradients induce the formation of martensitic structure.

![](_page_161_Picture_4.jpeg)

Small crack along FL at dissimilar welding in the joint on the other side of the valve (apparently sound)

Locally branched with corrosion product inside.

![](_page_162_Picture_2.jpeg)

![](_page_162_Picture_3.jpeg)

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- Microhardness profile across fusion line in cracked dissimilar welding.
- Hardness peaks with very high values
- MATERIAL SUSCEPTIBLE TO SSC IN WET SOUR SERVICE

![](_page_163_Figure_3.jpeg)

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- Dissimilar welding between CS and nickel alloys induces the formation of Type II grain boundaries parallel to fusion line with high energy -> weak point for crack nucleation
- High hardness induced in PMZ by chemical gradients increases the susceptibility to Hydrogen cracking.
- SSC is cause by Hydrogen -> hardness critical factor in Hydrogen induced fracture
- Normal hardness measurements carried out during weld qualification cannot put in evidence this narrow critical zone.

![](_page_164_Figure_4.jpeg)

2017 ©

• In presence of corrosive electrolyte (chlorides, low pH), galvanic corrosion at fusion line can increase the hydrogen charging effect of sour environments

![](_page_165_Picture_1.jpeg)

![](_page_165_Picture_2.jpeg)

- NACE TM 0177 SSC test con sample taken from sound weld
- 2 of 3 specimens fractured after 720h
- Not fractured specimen with small cracks and signs of corrosion on CS side
- Fracture very similar the one occurred in service!

![](_page_166_Picture_4.jpeg)

# CAN PWHT MITIGATE THE CRACKING SUSCEPTIBILITY OF DISSIMILAR WELD IN SOUR SERVICE?

- PWHT induces carbon migration to PMZ with high hardness values.
- PWHT cannot relive hardness peaks in dissimilar weld CRA/CS.
- Welded joint still remains susceptible to SSC in environments that can sustain the damage mechanism.

![](_page_167_Figure_4.jpeg)

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#### Appendix 10

### **Opportunity Crude Processing and Optimized**

### **Blend Management with Crude Corrosivity**

### **Prediction System**

(S. Kus)

![](_page_169_Picture_0.jpeg)

Dr. Slawomir Kus EFC Meeting Dalmine Opportunity crude processing and optimized blend management with crude corrosivity prediction system

![](_page_169_Picture_3.jpeg)

![](_page_170_Picture_0.jpeg)

- 1. Opportunity crudes processing benefits and threats
- 2. Crude blending approach and corrosion
- 3. Crude corrosivity prediction model development and outcomes
- 4. Blending and crude corrosivity prediction static approach
- 5. Real time blending / prediction / monitoring

6. Summary and Q&A

![](_page_170_Picture_7.jpeg)

## **Opportunity crudes – benefits to refinery**

- Reference crude oils prices (WTI, Brent etc.) increasing since mid of 2016
- Discount for e.g. Heavy Canadian Crude (WCS) typically varies from 13\$ to 25\$/bbl
- 13M\$ of theoretical additional income for refinery – when processed a single, mid-size tanker of heavy crude (c.a. 1M bbl or 160,000m<sup>3</sup>)

![](_page_171_Figure_4.jpeg)

## **Opportunity crudes – danger to refinery**

- Opportunity crudes have different corrosion characteristics than traditional light and sweet feedstock
- High conc. of naphthenic acids and organic sulphur compounds
- Dominant damage mechanisms:
  - Sulfidic corrosion
  - Naphthenic acids corrosion

#### <u>Affected equipment:</u>

- Crude heater and transfer lines
- Bottom of CDU (>220°C) and respective side cut lines
- Atmospheric residue transfer
- Major part of vacuum column especially side cut lines (VGO, MVGO, HVGO etc.)
- Vacuum residue transfer lines

![](_page_172_Figure_12.jpeg)

![](_page_172_Picture_13.jpeg)

## **Crude blending approach and corrosion**

![](_page_173_Figure_1.jpeg)

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THE POWER OF CONNECTED

## Crude blending approach and corrosion

![](_page_174_Figure_1.jpeg)

THE POWER OF CONNECTED

## **Crude Corrosivity Corrosion Prediction model development**

#### **Crude Corrosivity JIP Phase 1**

- Dec 2006 June 2010
- 200+ high temp autoclave tests
- 8 steels and alloys tested (CS, 5Cr, 9Cr, 12Cr, 304, 316, 317, 904)
- Experiments at T ranged from 230 to 370°C)
- Synthetic Crude Oils with TAN values of 1, 3, 5.5
- Sulfur simulated using H2S additions  $(0.5\% \div 5\% H_2S/N_2)$
- WSS values ranging from 0.1 to 135 Pa
- Experimental Duration (48 or 168h)
- · Benchmarking with sponsorsupplied vacuum gas oils selected with various characteristics (TAN/active S)

### Crude Corrosivity JIP Phase 2

- Jan 2013 Dec 2017
- Addressed data gaps in the Phase I program
- Generated in-depth understanding of the role of active sulphur species, and corrosion in low acid content conditions
- High WSS tests (20 tests, WSS) up to 1000Pa) using special HOFL (hot oil flow loop)
- 210 high temp autoclave tests
- Upgrade of Phase I Prediction Model
- Benchmarking with sponsorsupplied VGO & AGO with various TAN/active S

Crude Corrosivity JIP Phase 3

- Q2-Q3 2018 (JIP Phase III) planned commencing)
- Further expand capabilities in corrosion prediction including:
  - high velocity and multiphase flow across a range of wall shear stresses.
  - conditions with high temp,
  - impact of broader range of naphthenic acid species,
  - create fundamental models for expressing active sulphur and naphthenic acid corrosivity based on principals for molecular and empirical modelling.
- JIP is still open for participants

![](_page_175_Picture_28.jpeg)

### **Corrosion prediction of blended crude – static approach**

![](_page_176_Figure_1.jpeg)

#### For field case description see NACE paper 2018-11381

### **Crude Assay Corrosivity Database**

#### Database

Crude Assay Database						Comments	5			
General Information										
Reference										
Drigin										
Region	Centr	al Asia								
Sample Date	7/22/	2009								
Assay Date										
Issue Date										
Deservation Name	11. Ba	Units Whole Crude		Atmospheric Cuts				Var		
Upromotor Nomo	Units									
Parameter Name	Onita	MINIC CIUDE	atmcut1	atmcut2	atmcut3	atmcut4	atmcut5	vacuumcut1	vacuumcut2	
IBP	°C	mole crude	atmcut1 50	atmcut2 100	atmcut3 150	atmcut4 200	atmcut5 250	vacuumcut1 300	vacuumcut2 350	
IBP EBP	°C		atmcut1 50 100	atmcut2 100 150	atmcut3 150 200	atmcut4 200 250	atmcut5 250 300	vacuumcut1 300 350	vacuumcut2 350 400	
IBP Field (in Weight)	°C °C wt%	100	atmcut1 50 100 6.52	atmcut2 100 150 11.956	atmcut3 150 200 14.362	atmcut4 200 250 12.488	atmcut5 250 300 17.08	vacuumcut1 300 350 4.191	vacuumcut2 350 400 18.84	
IBP Yield (in Weight) Yield (in Volume)	°C °C vt% vol%	100 100	atmcut1 50 100 6.52 8.48	atmcut2 100 150 11.956 13.91	atmcut3 150 200 14.362 17.68	atmcut4 200 250 12.488 13.83	atmcut5 250 300 17.08 17.58	vacuumcut1 300 350 4.191 4.1	vacuumcut2 350 400 18.84 17.76	
IBP EBP Yield (in Weight) Yield (in Volume) Crude Fraction	°C °C wt% vol%	100 Crude Oil	atmcut1 50 100 6.52 8.48 Select Crude Fracti	atmcut2 100 150 11.956 13.91 Select Crude Fracti	atmcut3 150 200 14.362 17.68 Select Crude Fracti	atmcut4 200 250 12.488 13.83 Select Crude Fracti	atmcut5 250 300 17.08 17.58 Select Crude Fracti	vacuumcut1 300 350 4.191 4.1 Select Crude Fracti	vacuumcut2 350 400 18.84 17.76 Select Crude Fr	
IBP EBP Yield (in Weight) Yield (in Volume) Crude Fraction H2S Level (Active Sulfur)	°C °C wt% vol%	100 100 Crude Oil Select Sulfur Level	atmcut1 50 100 6.52 8.48 Select Crude Fracti Select Sulfur Level	atmcut2 100 150 11.956 13.91 Select Crude Fracti Select Sulfur Level	atmcut3 150 200 14.362 17.68 Select Crude Fracti Select Sulfur Level	atmcut4 200 250 12.488 13.83 Select Crude Fracti Select Sulfur Level	atmcut5 250 300 17.08 17.58 Select Crude Fracti Select Sulfur Level	vacuumcut1 300 350 4.191 4.1 Select Crude Fracti Select Sulfur Level	vacuumcut2 350 400 18.84 17.76 Select Crude Fr Select Sulfur Le	
IBP EBP Yield (in Weight) Yield (in Volume) Crude Fraction H2S Level (Active Sulfur) Total Sulfur	°C °C wt% vol% wt%	100 100 Crude Oil Select Sulfur Level 2.92	atmcut1 50 100 6.52 8.48 Select Crude Fracti Select Sulfur Level 0.00388	atmcut2 100 150 11.956 13.91 Select Crude Fracti Select Sulfur Level 0.0606	atmcut3 150 200 14.362 17.68 Select Crude Fracti Select Sulfur Level 0.0219	atmcut4 200 250 12.488 13.83 Select Crude Fracti Select Sulfur Level 0.197	atmcut5 250 300 17.08 17.58 Select Crude Fracti Select Sulfur Level 1.55	vacuumcut1 300 350 4.191 4.1 Select Crude Fracti Select Sulfur Level 2.95	vacuumcut2 350 400 18.84 17.76 Select Crude Fri Select Sulfur Le 3.28	
IBP EBP Yield (in Weight) Yield (in Volume) Crude Fraction H2S Level (Active Sulfur) Total Sulfur Mercaptan Sulfur	oC oC wt% vol% wt% ppm	100 100 Crude Oil Select Sulfur Level 2.92 0.0015	atmcut1 50 100 6.52 8.48 Select Crude Fracti Select Sulfur Level 0.00388 0.00383	atmcut2 100 150 11.956 13.91 Select Crude Fracti Select Sulfur Level 0.0606 0.00498	atmcut3 150 200 14.362 17.68 Select Crude Fracti Select Sulfur Level 0.0219 0.00438	atmcut4 200 250 12.488 13.83 Select Crude Fracti Select Sulfur Level 0.197 0.00269	atmcut5 250 300 17.08 17.58 Select Crude Fracti Select Sulfur Level 1.55 0.00159	vacuumcut1 300 350 4.191 4.1 Select Crude Fracti Select Sulfur Level 2.95	vacuumcut2 350 400 18.84 17.76 Select Crude Fr Select Sulfur Le 3.28	

#### **Crude/side cuts corrosivity comparison**

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	1111							
C	Couda							
alysis Analysis MPS Comparis	on Matrix							
Anshirir								
Analysis								
			Analyze	Done				
Select Crude Assay	Select Crude Assa	ay Blended Crude						
Test Crude	SideCut Name	Crude Fraction Pre	ssure (nsin) Temperatu	ire (°F) Nanhthenic Acid Tyn	e Use TAN/NAT TA	AN Value (mo/o) NA	T Value (mo/o) H2S Lev	els (Act
	LIN	A Nachtha	95.09	450.00 Turna	A TAN	1.05	1.00	
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Blended Crude	AD:	5 Diesei	85.28	зоо.оо туре	A NAT	1.50	1.20	
	LVC	D LVGO	85.28	556.18 Type	A NAT	4,00	3.00	
	AGC	D AGO	85.28	650.00 Type	A NAT	4,54	2,50	
	HVC	D HVGO	85.28	700.00 Type	A NAT	4.67	3.50	
	<							1
160 > 140			Blended Cr	ude 1				
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160 (60 120 22 20 20 20 20 20 20 20 20			Blended Cr	ude 1				
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160     140       140     120       38     60       0     MOC:       Carbon Steel     ✓       SideCut: HNA     ✓       100     66       100     66       100     ✓       100     5///>10       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0       100     0 <t< td=""><td>MOC: Carbon SideCut: AGO</td><td>iteel V MOC</td><td>Blended Cr : Carbon Steel V 2ut: ADS Blended C</td><td>MQC: Carbon Steel v SideCut: LVO</td><td>MCC: [ SideOut: H</td><td>Carbon Steel 💌</td><td>MOC: Carbon St SideCut: VRS</td><td></td></t<>	MOC: Carbon SideCut: AGO	iteel V MOC	Blended Cr : Carbon Steel V 2ut: ADS Blended C	MQC: Carbon Steel v SideCut: LVO	MCC: [ SideOut: H	Carbon Steel 💌	MOC: Carbon St SideCut: VRS	
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![](_page_177_Picture_5.jpeg)

8

## **Crude corrosivity mapping**

#### Side-cut corrosivity mapping

![](_page_178_Figure_2.jpeg)

#### **Sensitivity Analysis**

![](_page_178_Figure_4.jpeg)

![](_page_178_Picture_5.jpeg)

### **Corrosion prediction of blended crude – real time approach**

![](_page_179_Figure_1.jpeg)


# Summary

- Refiners <u>now</u> have ability to make informed decisions about crude blends to process and blends to avoid
- It is now possible to validate current metallurgy (CDU/VDU) versus different blends and identify crude fractions to avoid
- On-line, real time integration of blending data and corrosion prediction allows for faster, quantitative evaluation of NAP Acids corrosion and Sulphidation phenomenon
- New data on effects of sulfur in crude and sulphidation, provides a paradigm shift, allowing use of carbon steel under certain combinations of medium sulfur and high TAN conditions
- New insights correlating role of NAP acids in determination of corrosion rate in crude fraction will enable handling of high TAN crudes
- Increase operating margins and work with opportunity crudes with consequent improved profitability

# Appendix 11

# **Corrosion under pipe supporting**

### (S. Tarentino, G. de Landtsheer)

### <u>Corrosion Under Pipe Supports (CUPS)</u>

⇒ Risk Assesment, Detection,& Repair

Corrosion Under Pipe Support strategy needs to be seen as part of the CUx inspection strategy (CUx = CUI + CUPS + CUL+CUF+...)

Sebastian Tarantino, Senior Integrity Engineer Sitech Services (NL)

Gino De Landtsheer, Senior Group Expert Piping & Valves Borealis

Project & Technical Support (PTS) Division: I-PMO & Engineering





**Part 1: Introduction** 



### Introduction

#### → Why thinking about CUPS strategies?

- Recent incident in Geleen (NL), causing a fire, was a trigger to investigate inspection strategies
- CUPS was not yet recognized as a possible safety factor
- → Scope:
  - Definition of guidelines for inspections, maintenances strategies, lifting procedures for pipes
  - Definition of parameters to perform a dedicated risk assessment

#### → Stakeholders:

Sitech Services, Borealis, DSM, Chemelot Chemical Site (NL)

#### → Necessary actions:

- Check & evaluation of possible existing CUPS strategies in the industry
- Preparation of specifications and procedures, fit for purpose in our operational plants
- Definition of risk rating tool, to allow a decision making process, when to take the necessary actions



### Part 2: Results of ongoing actions



### **CUPS – Damage & Degradation Mechanism**

Progressive undercutting of paint



Localized wall loss

on pipe



#### $\rightarrow$ Introduction:

- Cause of external corrosion failures on above-ground piping in aging facilities
- This document applies to all carbon steel, low allow steel and stainless steel piping.
- Main risk are that CUPS is:
- It is not easily visible
- May be under estimated

#### $\rightarrow$ Target:

Implementation of a CUPS strategy, that can be independent but preferable integrated in a general CUx strategy.

#### $\rightarrow$ Parameters taken into consideration / probability assessment:

 $\begin{array}{l} Probability \\ forton \end{array} = P_{AC} \ \times \ P_{PF} \ \times \ P_{PM} \ \times \ P_{WT} \ \times \ P_T \ \times \ P_{YSP} \ \times \ P_{YSC} \ \times \ P_{ST} \ \times \ P_{SM} \ \times \ P_{Pad.M} \end{array}$ 

Prob. Factor	Description
P <sub>AC</sub>	Atmospheric condition
P <sub>PF</sub>	Piping failure
P <sub>PM</sub>	Piping material
P <sub>WT</sub>	Piping wall thickness
P <sub>T</sub>	Process temperature

Prob. Factor	Description
P <sub>YSP</sub>	Years in service (piping)
P <sub>YSC</sub>	Years in service (coating)
P <sub>ST</sub>	Support type
Р <sub>ѕм</sub>	Support material
P <sub>Pad.M</sub>	Pad material





#### → Parameters taken into consideration / probability assessment:

Probability Ranking	Consequence Value
5	> 28
4	12 – 28
3	5 – ≤12
2	2 – ≤5
1	≤ 2

#### → First lessons learned:

- Formula too complex simplified version to be created
- Probability weight of the different parameters was questioned
  - Few experience about aging towards CUPS
- CUPS should part of the overall CUx Consequence Assessment exercise, taking care about:
  - Safety and health impacts
  - Environmental impacts
  - Economic impacts



#### → Replacement assesment:

- In order to evaluate which piping shall be replaced, a procedure linked to the history of the piping and the risk value of the piping supports, for each line, is developed :
  - 3 or more incidents in the same line, related or not to piping supports, or
  - 30% or more of the piping support with a risk value equal to "High", or
  - 50% or more of the piping support with a risk value equal to "Medium High"
- Remaining wall thickness < 50% of the nominal thickness = Replacement!



Note: (evaluation parameters still under discussion)

#### → Non Destructive Examinations (NDE):

#### EMAT techniques / comparison:

- Verkade technique  $\Rightarrow$  good results  $\leq 60^{\circ}$ C (due to improves sensor design)
- Normal EMAT techniques are possible in a broader temperature range, but not as accurate

Evaluation of possible techniques:

- Visual
- EMAT technology (Electro Magnetic Acoustic Transducers)
- RT (not easy!)





#### → Prevention of CUPS:



- Use of pipe shoe shall be mandatory in new design and evaluated in retrofits.
- The crevices at the pipe surface and their ability to trap water must be eliminated.
- As a secondary concern, metal-to-metal contact should be eliminated if possible.
- The solution should allow easy maintenance and inspection of the pipe at the support point.
- The system must provide complete support to the piping system.
- It must be applicable to new construction and retrofits



### **Pipe Lifting Procedure**

#### → Introduction:

- Due to lifting, forces/stresses in axial and radial direction will arise in the pipeline. Those forces/stresses will increase if;
  - The lifting height increases, or
  - The distance between the supporting columns or the "arched length" (see Annex 1) increases, or
  - The diameter of the pipeline increases.

#### → Target:

Creation of a typical calculation set-up, which acts as guidance to serve the users in the decision process when to lift and how to lift

#### → Risk Assessment:

Risk assessment shall be an integral part of the supply of lifting equipment;



### **Pipe Lifting Procedure**

#### → Lifting Tools:

- Cranes
- Fixed Lifting Beams
- Special Tools
  - Pipe Rack Jack
  - Hydraulic Pipe Lifting







### **Pipe Lifting Procedure**

#### → Categorization:

- On-Stream Lifts:
  - Consequence ranking  $\leq 3$
  - Process temperature ≤ 60°C
  - Acceptable stress calculations
- Shutdown Lifts:
  - Consequence ranking  $\geq$  3
  - Process temperature  $\geq$  60°C
  - Not acceptable stress calculations

For both cases, it is mandatory to perform a risk assessment and a lift plan



### Appendix 12

# JIP proposal corrosion under insulation on

(J. Sentjens)



# **Southwest Research Institute**

**Corrosion under Insulation JIP** 

# Leonardo Caseres, Ph.D.

Senior Research Engineer Environmental Performance of Materials



# CUI JIP – Southwest Research Institute Research Objective and Goals

**Corrosion under Insulation JIP** 

- Determine the performance of coating/insulation systems applicable to CUI using the <u>framework of the TG516 test</u> <u>method</u>. This program will enable:
  - An accurate coating/insulation durability evaluation using two temperature regimes
  - High quality data to support the development/optimization of existing/new coatings and insulations
  - Make/revise recommendations for coating/insulation selection based on durability, define acceptance criteria and safe integrity operating window



# **NACE TG 516**

### Corrosion under Insulation JIP

Test Company	Single or multi Specimen testing CUI test	Reproducibility Demonstrated (Externally)*	Cyclic temperature (Range °C)	Immersion conditions or S <i>a</i> turated	Pipe Orientation	Insulation
Sherwin Williams	S	N	Y(Amb – 177°C)	S	N/A	Y
Hempel	S	N	Y(70-450°C)	S	V	Y
PPG	М	<b>?</b> <sup>2</sup>	Y(Amb – 250°C)	Ι	Н	N
Belzona	S	N	Y(70 – 150°C)	S	н	Y
International Paint	S	<b>Y</b> <sup>1</sup>	Y(Amb – 600°C)	S	V	Y
Juton	М	N	Y(Amb -500°C)	I	н	N
Statoilhydro	М	N	Y(Amb -140°C)	I	н	Y
Shell	s	N	Y(Amb – 191°C)	s	N/A	Y



# Test proposal stage

### **Corrosion under Insulation JIP**

- <u>Task 1</u>: Refine CUI-EM test procedure (in parallel with NACE TG516)
- <u>Task 2</u>: Selection of coatings and insulation combinations.
- Task 3: Testing
  - 70-175°F (20-80°C)
  - 70-400°F (20-200°C)
  - 70-600°F (20-315°C)
- <u>Task 4</u>: Develop durability predictions to make "more timely and better informed decisions on the selection of CUI coatings and insulation materials"





**Corrosion under Insulation JIP** 

# Leonardo Caseres, Ph.D.

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### **Appendix 13**

### **Experiences of MIC damage occurred under**

### non-operating conditions

(M. Arzuffi)



Microbiological Induced Corrosion

# Experiences of MIC damage occurred under non-operating conditions

EFC WP15 Spring Meeting 03 May 2018, Tenaris - Dalmine

# Introduction to Wood.



# Wood facts...





# Wood Italian office...





Engineering & Design

Studies Concept FEED Detailed Design Grassroot / Brown field



Build Procurement Construction Commissioning Start-up



Improve Modifications Upgrades Optimisation Project management PMC

Years experience (in Milan since 1957) **SUU** Currently ~800 employees +008

Plants and Process Heaters designed





# Background

MIC in Material Selection activity for refinery plants

# Background



A recent experience highlighted the importance of material preservation To avoid contamination and corrosion during fabrication & pre-commissioning activities

# Background







# Failure cases

Analysis and comparison of 3 failures over 20 years

# Fabrication History

	Case 1	Case 2	Case 3	
Component	H.E. U-bend Tube	180° Elbow - Fired Heater Radiant Coil	90° Elbow – Piping line	
Material	SS 321	A403 WP 347	A403 WP 304L	
Fabrication	SMLS Tubes bent & stress relieved	Wrought SMLS NPS 5 x 6.5 mm	Wrought SMLS NPS 8 x 9.6 mm	
History	Shop Hydrotest Delivering on site <b>PickI./Passiv./Rinsing</b> on TS Hydrotest ShellSide → FAILURE	Shop Hydrotest (horiz. pos.) Shipment (horizontal pos.) <b>Field hydrotest</b> (vertical pos.) NDE (RX) → FAILURE	Shop Hydrotest Sea shipment (heavy storm) Site Bevelling (ends left open) Site hydrotest → FAILURE	
Layout	Fabrication History – Case 1 (U-Tube)	Fabrication History - Case 2 (Coll Ebow)   Image: Coll Coll Coll Coll Coll Coll Coll Col	Fabrication History – Case 3 (Piping Elbow)	



# Fabrication History – Case 1 (U-Tube)





# Fabrication History – Case 2 (Coil Elbow)



# Fabrication History – Case 3 (Piping Elbow)





# Fabrication History – Case 3 (Piping Elbow)


### Defect analysis

	Case 1	Case 2	Case 3
Defect	Defect analysis – Case 1 (U-tube)	Defect analysis – Case 2 (Coil Elbow)	<image/>
Position	Intrados	Intrados	Extrados
Туре	Through hole	Deep occluded pit	Through hole
Morphology	Occluded cavern pit, needle shaped walls, small starting hole (Ø ~0.5 mm)		
Notes	Most corr. indication on the 6h lines	Traces of stagnant water (elbow full of water)	Traces of stagnant water (water pool)

### Defect analysis – Case 1 (U-tube)



### Defect analysis – Case 2 (Coil Elbow)



### Defect analysis – Case 3 (Piping Elbow)











### Defect analysis – Case 3 (Piping Elbow)



### Defect analysis

	Case 1	Case 2	Case 3
Pit nucleation	(Not identified)	Non-homogeneous grain dimension (due to bending)	High residual stress (weld HAZ)
Corrosion products	Brown reddish deposit crown around internal hole	Brown reddish deposit haloes around internal hole	Brown reddish deposit around external hole, discoloration on inner surface
	Chlorine, Phosphorus	Sulphur	Sulphur, Chlorine
Other defects	Small pitting & local depassivation	Elongated cavities & holes	Small isolated & rounded pits
	Similar defects in similar location $\rightarrow$ onset of same type of corrosion as main defect		
Notes	All corr. indication where water pool was likely		
Corrosion phenomenon	Severe Localized corrosion (now deemed to be MIC)	MIC	MIC
Promoting environment	High conc. Residual Chlorine	Contaminated stagnant water	Contaminated stagnant water
Water source	Surface chemical treatment	Field Hydrotest	Not yet fully clear.





### Lessons Learnt

Awareness and attention to fabrication, pre-commissioning and non-operating conditions

### Possible source of water & bacteria



#### Hydrotest operations (shop & field)

- Contaminated hydrotest water (Bacteria)
- Handling of water in contaminated facilities (Bacteria)
- Not fully reliable Drain & Drying method (Water)



#### Sea shipping

- Possible Sea Water entrapment (Water & Bacteria)
  - Missing or damaged openings protections
    - Improper handling or heavy storm



#### Storage & Erection operations (shop & field)

- Unprotected openings during storage and erection activities
  - Collection of debris in stored materials (Bacteria)
  - Carry-over of dirt and rain water (Water & Bacteria)



### Lessons learnt





**Appendix 14** 

#### Influence of fluorides leak on cooling system

corrosion (case study)

(V. Bour-Beucler)

## **Eurocorr WP15 Spring Meeting**

### Case study regarding fluorides leak in cooling water systems

Dalmine May 3rd



# Background

### Refinery in Middle East after turn around

- 4 recirculating cooling systems feed with reuse water (soft water with high level of chlorides and sulfates).
  - Stress conditions are make up water quality
- Start up without heat exchangers passivation
  - High soluble iron level (>15mg/L)
  - SRB spot measurements at 40



- Carbon steel heat exchangers and small part of copper alloys.
- Leak of fluorides in reuse water tank over 100 mg/L
  - Heat exchangers cleaning process side (alkylation)



# **Consequence and direct impact**

#### Carbon steel corrosion high increases

- several mm/an
- Fouling and deposit

Blowdown increase (water and treatment consumption)

- Economical impact
- Water limitation

Biofouling and mineral fouling in low velocity part of the system.

Overconsumption of anodic corrosion inhibitors (OPO4)



# Root causes analysis

- Unpassivated cooling water system and unpassivated heat exchangers
  - High level of iron
    - ACTIVE CORROSION
- Présence of fluorides
  - Iron fluoride formation and corrosion increase (agressive ions)
  - Iron oxide and iron fluoride fouling
  - Complexing cleaning solution process side (NTA) cooling water system impact (copper transportation)

### ▲ SRBs

- Growth in the deposit and localized corrosion formation
- Under deposit corrosion
- Biofilm growth non adapted oxidizing biocide



# Iron and fluorides follow up



CWS



Taking Energy Further<sup>™</sup> 5

# Heat exchanger tubes



#### Deposit with mainly iron fluoride







# Action plan

Replacement of reuse water by city water

- Blowdown to maintain low fluorides level
  - Fluoride <3mg/L</p>
- Critical heat exchangers shutdown and cleaning
- Reuse water Pre chlorination with chlorine dioxide (Purate system)
- Cooling system passivation with PSO (corrosion inhibitor).



# **CIO2** and corrosion



### Purate case study results



#### Figure 3: MED train C heat transfer coefficient improvement





Figure 2: Microbial and fungal counts in seawater system