# Appendix 1 List of participants

# Participants EFC WP15 meeting 14<sup>th</sup> April 2011 Paris (France)

NAME	Company	Country		
Stein Brendryen	Statoil	Norway		
Martin Richez	Total	France		
Valerie Beucler	Nalco	France		
Stefano Trasatti	University Milan	Italie		
Edoardo Guerrini	University Milan	Italie		
Alain Pothuaud	GE Betz	France		
Claudia Laverte	GE	France		
Johan van Roij	Shell	Netherlands		
Fernando Bonilla	Vallourec	France		
Hennie de Bruyn	Johnson Mattey	United Kingdom		
Rachel Mansfield	Johnson Mattey	United Kingdom		
Carmelo Aiello	Consultant	Italie		
Ridha Yahyaoui	Axens	France		
Michel Munier	Axens	France		
Francois Weisang-Hoinard	Outokumpu	France		
Pascale Vangeli	Outokmupu	Sweden		
Johan Sentjens	Temati	Nertherlands		
Grzegorz Sielski	Sandvik	Poland		
François Ropital	IFP Energies nouvelles	France		

# Appendix 2

# **EFC WP15 Activities**

(Francois Ropital)



# Welcome to the EFC Working Party Meeting "Corrosion in Refinery" WP15

# Paris 14 April 2011



EFC WP15 Spring meeting 14 April 2011 Paris France

AGENDA EFC Working Party 15 Corrosion Refinery Industry Meeting 9h30-10h00 Welcome and WP15 Activities (F. Ropital) next Eurocorr sessions and workshops, collaborations with NACE publications, other points 10h00-10h45 Corrosion of sour gas unit treatment Opportunity of duplex use in the amine units, for CO2 treatment (F. Weisang-Hoinard, P. Vangeli Otokumpu) Revision of the EFC n° 46 "Amine unit corrosion in refineries" (F. Ropital) 10h45-11h00 Break 11h00-11h30 Mercury Corrosion and Removal form Refinery Streams (H. De Bruyn) 11h30-12h00 Naphthenic acid corrosion:an analytical approach (S. Trasatti) 12h00-12h30 Failure Cases - failure case of Dpcell Orifice flange for Hydrotreater unit (C. Aiello) EFC WP15 Spring meetinfailure case from the audience

EMPLA FERRAL PERSON DE CAMBONIO DE CAMBONI	AGENDA EFC Working Party 15 Corrosion Refinery Industry Meeting	
13h30-14h15	Corrosion under insulation Presentation "CUI and coatings" (Johan Sentjens - Temati) Revision of the EFC CUI guideline n° 55	
14h15-14h45	New stainless steels Sandvik SAF 2707HD heat exchanger tubes for demanding application in crude oil refinery (Grzegorz Sielski )	
14h45-15h15	Water treatment 3D Trasar for boiler technology (V. Beucler Nalco)	
15h15- 15h45	Monitoring Corrosion Monitoring system can help refinery plant to process opportunity crude by monitoring the corrosion rate to control inhibitor, to improve both plant versatility and profitability ( Claudia Lavarde -A. Pothuaud $GE$ )	
15h45 EFC WP15 Spring m	Other topics of discussion from the audience End of the meeting. neeting 14 April 2011 Paris France	3



# Presentation of the activities of WP15

# European Federation of Corrosion (EFC)

- Federation of 31 National Associations
- 20 Working Parties (WP)
- Annual Corrosion congress « Eurocorr »
- Thematic workshops and symposiums
- Working Party meetings (for WP15 twice a year)
- Publications
- EFC NACE agreement (20% discount on books price)
- for more information <a href="http://www.efcweb.org">http://www.efcweb.org</a>

EFC WP15 Spring meeting 14 April 2011 Paris France



## EFC Working Party 15 « Corrosion in Refinery » Activities

# Who is an EFC member

To be an EFC member you (individually or your company, university) has to be member of one of 31 national EFC "member societies". Your company or university can now also an affiliate member.

#### For example:

in Norway: Norsk Korrojonstekniske Forening

in France: Cefracor or Federation Française de Chimie

in Germany: Dechema or GfKORR

in UK: Institute of Corrosion or IOM or NACE Europe

in Israel: CAMPI or Israel Corrosion Forum

in Poland: Polish Corrosion Society

You will find all these information on www.efcweb.org or in the EFC Newsletter

## Benefits to be an EFC member:

- 20% discount on EFC Publications and NACE Publications
- -reduction at the Eurocorr conference

-access the new EFC web restricted pages (papers of the previous Eurocorr

Conference) via your national corrosion society web pages

EFC WP15 Spring meeting 14 April 2011 Paris France



# **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 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

EFC WP15 Spring meeting 14 April 2011 Paris France



## Presentation of the activities of WP15

News from European Federation of Corrosion (EFC)

The start of February 2011 has brought a change at the European Federation of Corrosion (EFC) with the appointment of a new Scientific Secretary/Public Relations officer.

**Juliet Ippolito** will now succeed Dr. Paul McIntyre who held this position for the past 14 years.



EFC WP15 Spring meeting 14 April 2011 Paris France

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EFC Working Party 15 « Corrosion in Refinery » Activities http://www.efcweb.org/Working+Parties-p-104085/WP%2B15-p-104111.html

Chairman: François Ropital Deputy Chairman: Hennie de Bruyn

The following are the main areas being pursued by the Working Party:

#### Information Exchange

Sharing of refinery materials /corrosion experiences by operating company representatives.

#### Forum for Technology

Sharing materials/corrosion/protection/monitoring information by providers

#### Eurocorr Conferences

#### WP Meetings

One WP 15 working party meeting in Spring,

One meeting at Eurocorr in September in conjunction with the conference,

#### <u>Publications - Guidelines</u>

EFC WP15 Spring meeting 14 April 2011 Paris France



#### Publications from WP15

• EFC Guideline n°40 « Prevention of corrosion by cooling waters » available from http://www.woodheadpublishing.com/en/book.aspx?bookID=1193

Update in relation with Nace document 11106 "Monitoring and adjustment of cooling water treatment operating parameters" Task Group 152 on cooling water systems

• EFC Guideline n° 46 on corrosion in amine units http://www.woodheadpublishing.com/en/book\_aspx?bookID=1299

•EFC Guideline n° 42 Collection of selected papers http://www.woodheadpublishing.com/en/book.aspx?bookID=1295

•EFC Guideline n° 55 Corrosion Under Insulation http://www.woodheadpublishing.com/en/book.aspx?bookID=1486



- •Future publications : suggestions ?
  - best practice guideline to avoid and characterize stress relaxation cracking?

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## EFC Working Party 15: Future objectives of the group

How to manage our working party meetings / Eurocorr sessions

#### · Eurocorr Sessions

- √Implements of Eurocorr sessions or workshops with other WP and NACE (a workshop can be on a topic without formal presentation)
- ✓ Implication of young corrosion students, PhD at Eurocorr session with a dedicated poster session

#### . Working Party Meetings

- √ Future topics of task forces
- ✓ Facilitating student trainings outside their countries in our companies
- ✓ Presentation of UE funding projects in our area (if they are)
- √ Collaboration on Standard

<u>Increase the collaboration with NACE</u> exchange of information on our activities - joint Eurocorr sessions

EFC WP15 Spring meeting 14 April 2011 Paris France



## EFC Working Party 15 plan work 2010-2012

- . Collaboration with Nace : exchange of information
- "NACE TEG 205X information exchange -corrosion in refineries"
- . Sessions with other EFC WP at Eurocorr (2011 in Stockholm, 2012 in Istanbul, 2013 Estoril-Portugal) on which topics?
- · Update of publications
  - · CUI quideline
  - · Amine acid gas treatment plants
- $\boldsymbol{\cdot}$  New Publications: best practice guideline to avoid and characterize stress relaxation cracking ?
- · Education qualification certification

EFC WP15 Spring meeting 14 April 2011 Paris France



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#### Eurocorr 2011

Stockholm 5-8 September 2011

Authors will be informed by mid April and the program will be on Website

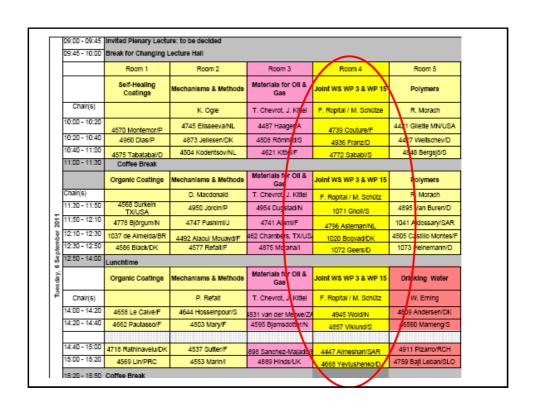
Monday 5 September: Refinery corrosion session

<u>Tuesday 6 September</u>: Joint workshop WP 3 + 15 on the high temperature corrosion in the refinery and process industries

Wednesday 7 September: annual WP15 working party meeting

http://www.eurocorr.org

09:00 - 0						
09:20 - 0	9:45					
09:45 - 1	0:30					
10:30 - 1	1:00 Coffee Break					
	Room 1	Room 2	Room 3	Room 4	Room 5	
	Sol-Gel Coatings	Mechanisms & Methods	TEG374X on Sour Service	Refinery Industry	Environment Sensitive Fracture	
Chair		Mol/NL	T. Chevrot, P. Budrak	F. Ropital	V. Olden	
11:00 - 1	TOE DIGGGGGG	4867 Marcus/F	4464 Settoon, 7X/USA	1066 Eaton, USA	4 52 Takal/J	
11:20 - 1	4000 El l'idecia E	4953 Neff/F	4637 Theb ult/F	4417 Cyprlano/BR	444 3 Olden/N	
11:40 - 1		4528 Schwind/S	4725 Koba ashl/J	4931 Claesen/B	4884 Yayodzinskyy/FIN	
12:00 - 1			418 Mannan WW/USA	4567 Lagad, TX/USA	4844 Zamanzade/D	
월 12:20 - 1		4904 Ott/CH	4538 KIn ura/J	4641 Candido/BR	1030 Nyhus/N	
8 12:40 - 1	4:00 Lunchtime					
12.40 - 1 de de de	Self-Healing Coatings	Mechanisms & Methods	EFC WP 18 / NACE TEG374X on Sour Service	Refinery Industry	Environment Sensitive Fracture	
Chair(s)		Marcus/F	T. Chevrot P. Badrak	F. Ropital	K. Wolski	
14:00 - 1	4:20 4472 Benfer/D	1035 Volovitch/F	4736 Moderer/A	4574 Höbing/S	4956 .ange/N	
14:20 - 1	4:40 4479 Yekehtaz/D	4468 Fredriksson/S	48 3 Fallahmohammadi/I	4434 van Rodijnen/D	4942 Unterumsberger/D	
14:40 - 1	5:00 4639 Forsén/FIN	4784 Starosvetsky/IL	4876 Bolzoni/I	4422 Groysman/IL	4426 A Rable/UK	
15:00 - 1	5:20 4632 Mol/NL	1052/1053 Macdonaid, PA/USA	4607 He/S	4513 Adeleke, TX/USA	480 Durit/F	
15:40 - 1	6:00 4688 Cho/ROK	4581 Boelen/NL	4861 Weinig/A	4456 Renner/D	483 Feser/D	
16:00 - 1	6:30 Coffee Break					
	Self-Healing Coatings	Mechanisms & Methods	EFC WP 13 NACE TEG374X on Sour Service	Refinery Industry	Envirorment Sensitive Fracture	
Chair(s)		Fushimi/J	T. Chevrot, P. Badrak	F. Ropital	V. olden / K. Wolski	
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16:50 - 1	4459 Galdaint	4783 Krieg/D	4941 Chambers, TC/USA	1036 HirsVFIN	VP 5 Business Meeting	
17:10 - 1	4869 Kartsonakis/GR	4742 Klemm/D		1946 Venkatesh, TX/US#	WP 5 Business Meeting	
time to b	e con General Assembly					
time to b	e con manual and the cost	. Hall of Dischbolm with D		he City of Stockholm and	December 199	





## Information:

Future conferences related to refinery corrosion

·5-8 September 2011

EUROCORR 2011 Stockholm, Sweden Website: <u>www.efcweb.org/Events</u>

•20-24 November 2011

18th International Corrosion Congress (ICC) Perth, WA, Australia,

•18-22 March 2012

CORROSION 2012/NACE Salt Lake City Website: www.nace.org

·20-25 May 2012

High Temperature Corrosion and Protection of Materials - Les Embiez (F)

•9-13 September 2012

EUROCORR 2012 Istanbul Turkey Website: <a href="https://www.efcweb.org/Events">www.efcweb.org/Events</a>

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# **Appendix 3**

Opportunity of duplex use in the amine units for  $CO_2$  treatment

(F. Weisang-Hoinard, P. Vangeli Otokumpu)



# **Stainless in Amine treatments**

2011 April14 EFC(Paris)

www.outokumpu.com

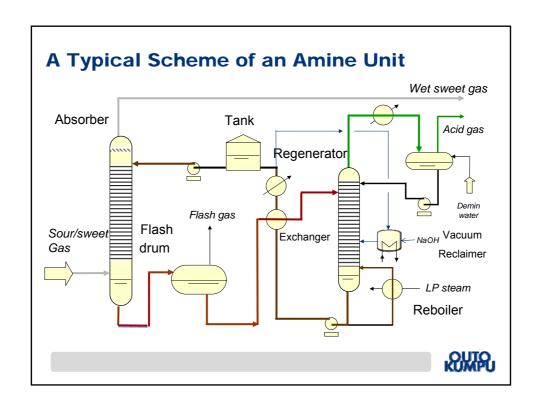
# **Amine treatment: Gas treatment**

- Use in refineries and CO<sub>2</sub> Capture
- CO<sub>2</sub>& H<sub>2</sub>S Absorption/ desorption
- Different types of Amines:
- MEA, DEA, MDEA & ....
- 2 wow in refineries:
  - · Sour & sweet environments
  - H<sub>2</sub>S from 30ppm to 50%
- CO<sub>2</sub> Capture/ low H<sub>2</sub>S content

2 (Total pages) | April 14, 2011 | Speaker information







# **Amine Unit Corrosion: Key Factors**

- · type of amine & concentration
- Amine loading
- Temperature
- Oxygen Entry
- Design



 $MEA > DEA \ge MDEA pH - Conductivity pH$ 

Thermal activation HSS

Velocity Turbulences



- → Uniform weight loss corrosion
- → Erosion corrosion
- → Amine stress corrosion cracking

4 (Total pages) | April 14, 2011 | Speaker information





# **Wet Acid Gas Corrosion: Key Factors**

- Flue gas composition /Inadequate scrubbing
- Inadequate design
- Too low gas flow rates
- CO<sub>2</sub> content in treated gas



Amine wall wetting/Condensation Water accumulation Condensation in the treated gas lines



- → Uniform weight loss corrosion
- → Hydrogen cracking (HIC, SSC...)

5 (Total pages) | April 14, 2011 | Speaker information



## **Main Corrosion Areas: Sweet Gas unit**

Absorbeur:

**Bottom** Erosion/Corrosion Head Acid gas corrosion **Rich Amine lines:** 

Degasing Erosion/corrosion

Rich/lean amine HEX:

Stress corrosion cracking Regenerator:

Head

**Erosion Corrosion** Acid gas outlet/condensor wet acid gas corrosion Bottom uniform corrosion

Reboiler:

Uniform corrosion **Lean Amine lines:** 

> HSS turbulence Erosion/Corrosion

6 (Total pages) | April 14, 2011 | Speaker information





# **Corrosion Resistance applications**

Upgrade Bottom of Absorber & Top of Regenerator with 304/316



Allows high intensity operation and debottlenecks

Are duplex grades an alternative to 300 serie?

Erosion/corrosion resistance CO2/CI- corrosion HSS corrosion resistance Costs

7 (Total pages) | April 14, 2011 | Speaker information



# **Chemical Composition and Properties**

Outokumpu	EN	ASTM	Cr	Ni	Мо	N	PRE*	$R_{p0.2}^{**}$	
LDX 2101®	1.4162	S32101	21.5	1.5	0.3	0.22	26	450***	Lean Duplex
2304	1.4362	S32304	23	4.8	0.3	0.10	26	400	Duplex
LDX 2404™	1.4662	-	24	3.6	1.6	0.27	33	480	Lean Duplex
2205	1.4462	S32205	22	5.7	3.1	0.17	35	460	Duplex
2507	1.4410	S32750	25	7	4	0.27	43	530	Super Duplex
4307	1.4307	304L	18.1	8.1	-	-	18	200	Austenitic
4404	1.4404	316L	17.2	10.1	2.1	-	24	220	Austenitic
4432	1.4432	316L	16.9	10.7	2.6	-	25	220	Austenitic
4439	1.4439	317LMN	17.3	13.7	4.1	-	33	310	Austenitic
904L	1.4539	N08904	20	25	4.3	-	34	220	Austenitic
254 SMO®	1.4547	S31254	20	18	6.1	0.20	43	300	Super Austenit

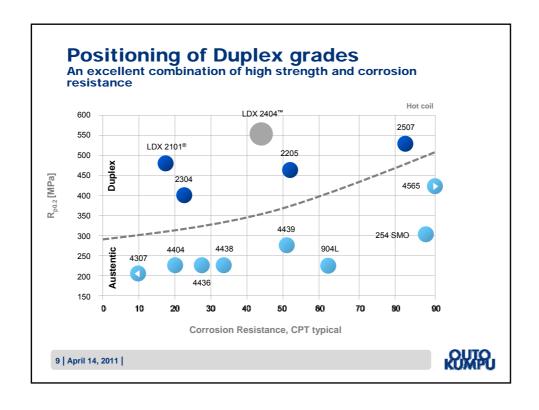


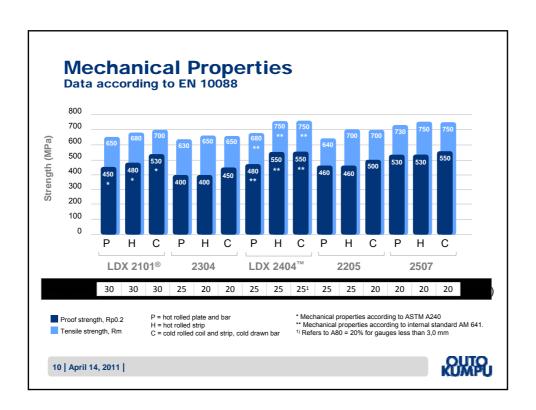


<sup>\*</sup> PRE = %Cr + 3.3x%Mo + 16x%N

\*\* [MPa] Hot rolled plate, min values at 20°C according to EN 10088

\*\*\*Not yet in EN 10088, Rp0.2 according to ASTM A240



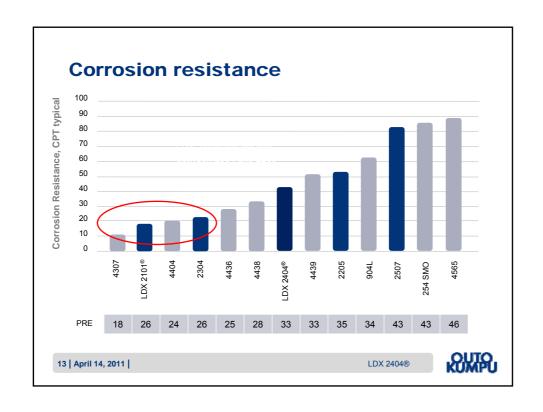


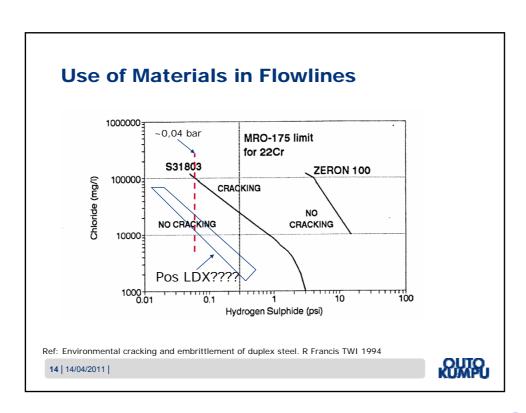


# CO2 corrosion resistance depending of Cr level To a supplied of Cr level To supplied to the autoclave. (3.0MPa CO2 at 25°C, test duration 06hr, flow velocity 2.5 m/s) CO2 corrosion resistance depending of Cr level To a supplied of Cr level To a supplied of Cr level To supplied of Cr level To steels at 150°C in the autoclave. (3.0MPa CO2 at 25°C, test duration 06hr, flow velocity 2.5 m/s) To total pages) | April 14, 2011 | Speaker information

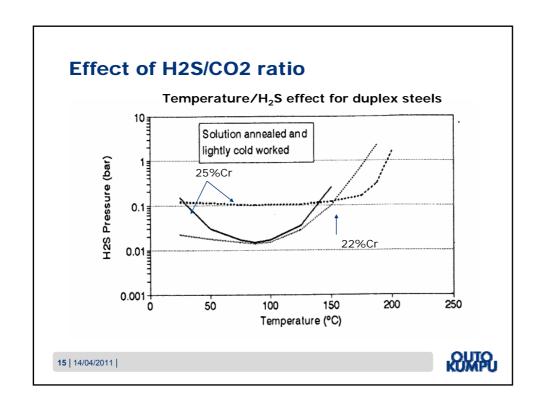
# Corrosion resistance to HSS Amine degradation & heat Stable salts: Formate, acetate, oxalate, Chloride, sulfate & phosphate in acidic conditions Duplex has equal or better corrosion resistance as 304/316 \*\*Tourned of Neuron of Lamely inpy for Type, NML and JIML, Independent Diagram of 6.1 many of anyy for Alley Solf and Transmit Acids Acid Alley Solf and Transmit Acids Acid Acid Alley Solf and Transmit Acids Acid Acid Alley Solf and Type SML and JIML, Informatical Alley SML and JIML, Informat

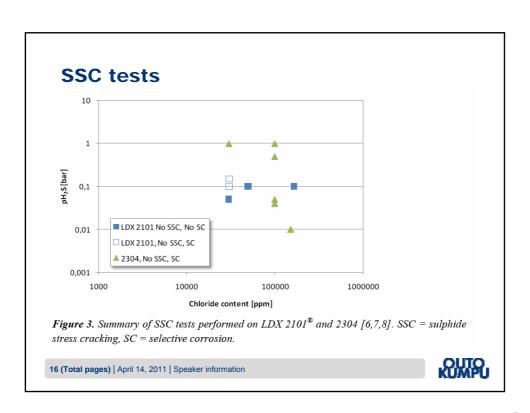




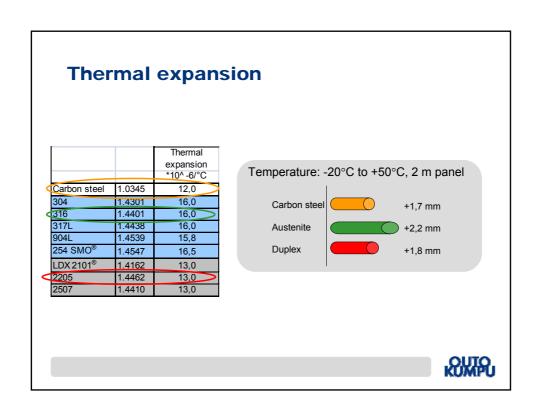


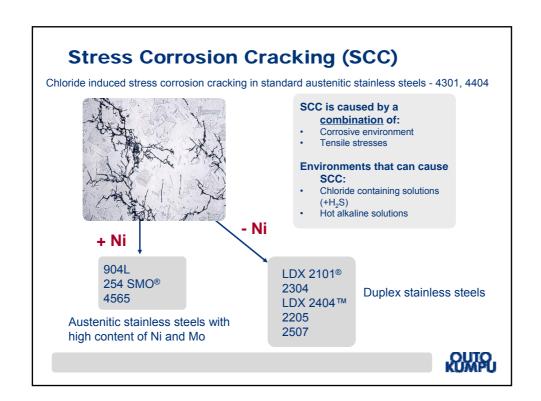




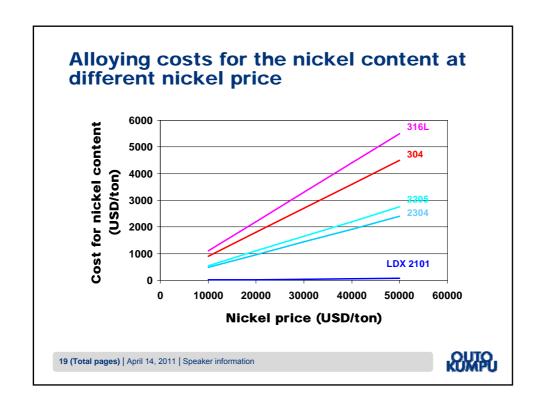


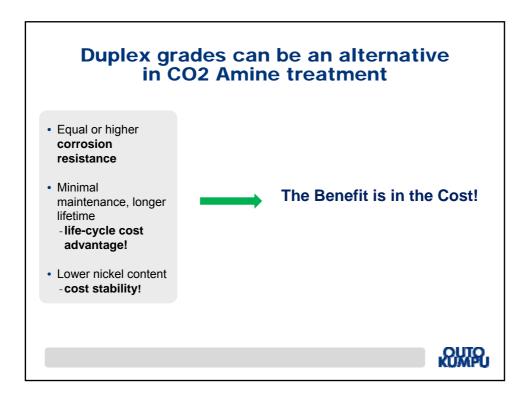
















# Thank you!

Activating Your Ideas
Contact: francois.weisang-hoinard@outokumpu.com
www.outokumpu.com





# **Appendix 4**

Corrosion and Removal form Refinery Streams

(H. De Bruyn, R. Mansfield Johnson Matthey

Catalyst)

# Mercury removal Johnson Matthey Catalysts



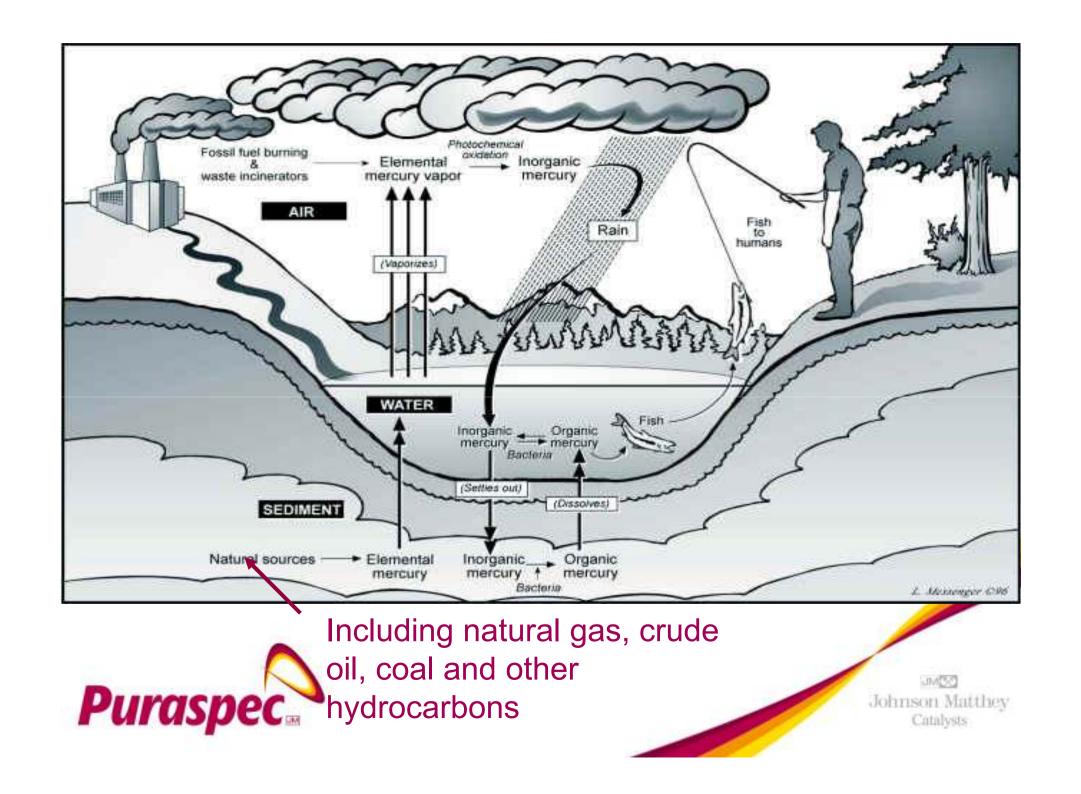
JM**©** Johnson Matthey Catalysts

# Mercury – A Refinery Issue?

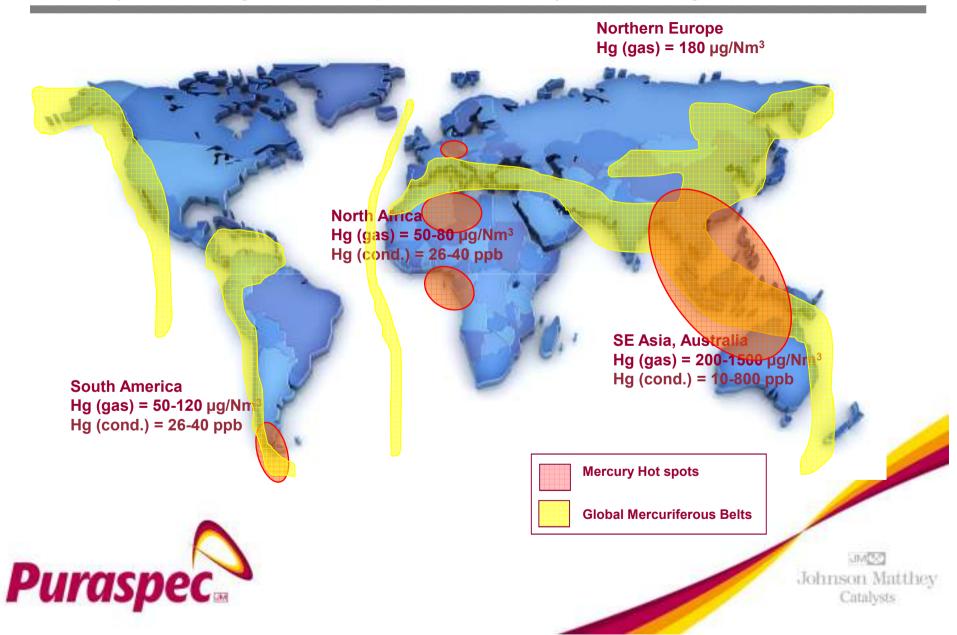
- Where is mercury containing crude oil found?
- Why remove mercury?
- Mercury Distribution
- PURASPEC<sub>JM</sub>







# Mercury belt and global hot spots for mercury in oil and gas reserves



# Why Remove Mercury?

- Poisoning of catalysts in downstream plants
- Emission of mercury to atmosphere
- Exposure of workers to mercury
- Economical Issues
- Corrosion of process equipment





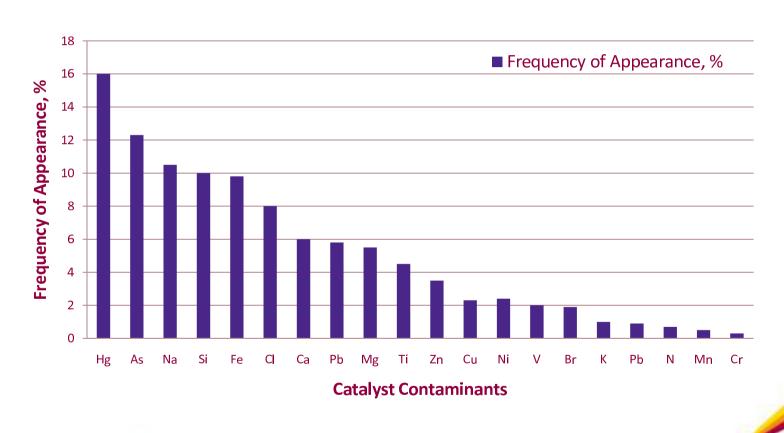
# Poisoning of downstream catalysts

- Pt and Pd are particularly prone to Hg poisoning
- React to form a 1:1 amalgam i.e. PtHg or PdHg that is stable at the low temperatures <150°C</li>
  - Ethylene Production:
  - 2000 ppm have been found on the top of 0.05% palladium acetylene hydrogenation catalyst
  - Hg can be driven off by heating above 150 to 200 °C but this accelerates sintering and loss of active surface area.





# Selective Hydrogenation Catalyst Poisons



JIM SC

Johnson Matthey Catalysts



# **Exposure of Workers**

- Hg is known to be toxic
- Volatility combined with lack of smell makes Hg very dangerous
- In 2005, the European Union Scientific Committee on Operational Exposure Limits recommended a tightening Hg limits to
  - 0.02 mg/m3 for the 8 hour time weighted exposure (TWA) limit;
  - 0.01 mg/litre in blood samples.
- Adsorption/desorption on steel surfaces
  - Plant contaminated with Hg potentially pose significant risks to workers opening equipment up for maintenance and similar work
    - Inspection of refinery process equipment
    - Welding repairs
      - » Hg vapours are generated
  - Mercury can be absorbed through the skin, by inhalation and if swallowed through digestion.



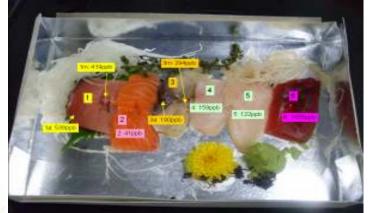


# Emission of mercury to atmosphere

- Methyl mercury is a very toxic form of mercury found in aquatic systems where it concentrates in predatory fish
- United Nations Environmental Protection, UNEP
  - Examples of maximum allowed or recommended levels of mercury (Hg) in fish
- Maximum allowed/recommend levels in fish US:
  - 1.0 mg/kg (ppm)

Puraspec...

- US EPA reference dose: 0.1 μg methylHg/kg body weight per day
- 60 kg person tolerable intake = 0.006 mg Hg/day
- Tuna shown = 1.06 mg/kg
- 5.7 grams of tuna would be equivalent to maximum tolerable level for 1 day



Analysis & photo of sashimi from Singapore restaurant courtesy

Johnson Matthey Catalysts

# **Economical Issues**

- Discounted crude available to refineries which have a mercury treatment strategy in place
- Asian Open-Spec Naphtha reveals potential value
  - "Friday, Jun 26, 2009:
  - SINGAPORE (Dow Jones). Asian open-spec naphtha market participants said Friday they plan to test the mercury content of more grades to protect the interests of end-users.
  - Japanese and South Korean petrochemical producers, which are major receivers of open-spec naphtha, recently voiced concerns over high mercury content, considered a contaminant that can damage plants".
- Increased regeneration/replacement of catalysts
- Disposal of contaminated equipment





# Corrosion LME (Liquid Metal Embrittlement)

- Liquid Metal Embrittlement (LME) is a form of environmental cracking: molten metals in contact with specific alloys
- Change in the fracture mode (ductile to brittle)
- Failure due to LME: instantaneous or it may take place after some time
- Presence of stress is necessary. The stresses may be tensile, shear or tortional in nature, but not compressive.
- Tensile stress contributes to crack propagation rates.
- Cracking under load can be extremely rapid such that cracks may pass through the wall thickness within seconds of contact with the molten metal.
- Very small quantities, even a few micrograms of the low melting point metal, are sufficient to cause LME.





# Corrosion LME (Liquid Metal Embrittlement)

- Liquid metal embrittlement can occur in a variety of alloy and molten metal combinations
- Well known combinations:
  - Aluminium & aluminium alloys mercury
  - Austenitic stainless steel zinc
  - Copper alloys mercury
  - Alloy 400 (Monel) mercury
  - High Strength Steels Cadmium, Lead
- Different theories
  - Commonly accepted that the molten metal diffuses along grain boundaries
  - Weakens inter-atomic bonds
  - Cracking frequently develops along grain boundaries





#### Corrosion – LME (liquid metal embrittlement)







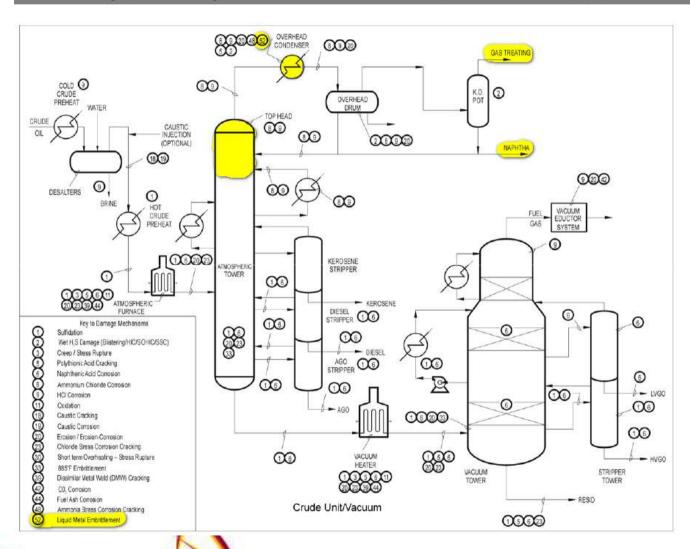
#### Corrosion LME (Liquid Metal Embrittlement)

- Hg can induce corrosion and can lead to failure of equipment items
- Hg only (no co-action of air, H<sub>2</sub>O)
- Hg diffuses into grain boundaries
- Weakens structure such that cracks develop along boundaries rapid
- LME affects:
  - Aluminium alloys
  - Copper-base alloys
  - Monel 400
  - Titanium alloys





## API 571 – Damage Mechanisms Affecting Fixed Equipment in the Refinery Industry



Puraspec.

API 571 indicates only the overhead condensers in a crude unit as a potential area for liquid metal embrittlement.

Hg will also affect Monel 400 in an atmospheric column top, as well as equipment in the gas treating units.

Hg can concentrate in naphtha streams, posing significant problems for downstream ethylene cracking units (cold separation section where aluminium is used extensively.



#### Corrosion - Amalgam Corrosion

- Elemental Hg forms amalgams with various metals
  - Al, Cu, Brass, Zn, Cr, Fe and Ni
- Damage to the stable oxide layer required before amalgamation can occur
- Mechanism is self-sustaining when water and air is present
- Example:
  - Hg + Al = Hg(Al)
  - $Hg(AI) + 6H_2O = AI_2O_3.3H_2O + H_2 + Hg$
- Presence of amalgams in refinery process equipment my render the materials susceptible to other corrosion mechanisms (organic acids, sour water, etc.)





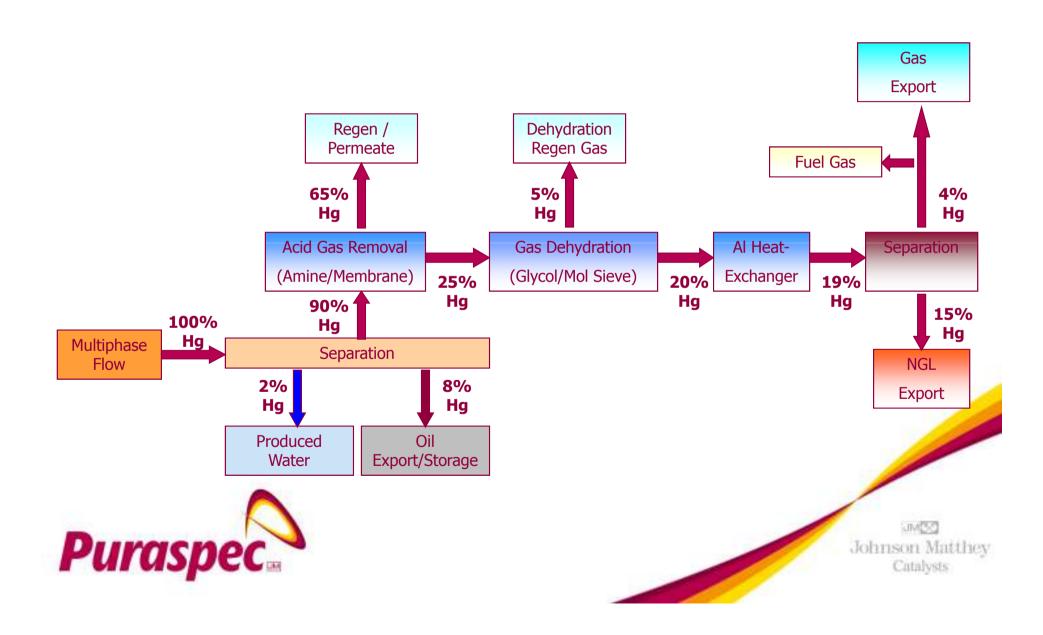
#### Corrosion - Amalgam Corrosion







#### Mercury distribution



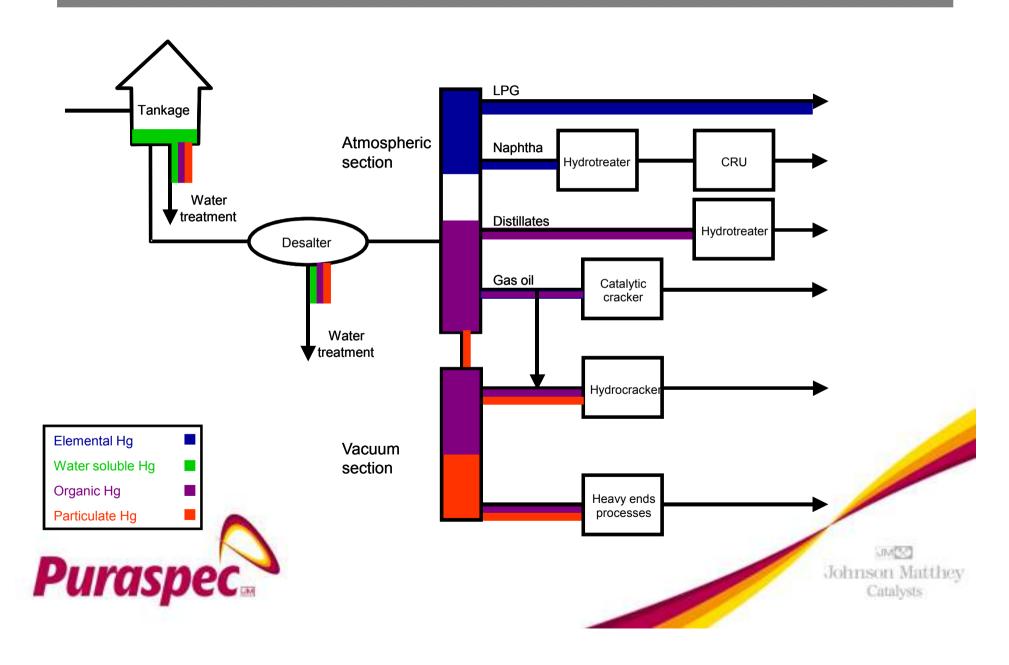
#### Mercury Compounds in Refinery

- Elemental mercury (Hg<sup>0</sup>)
  - Relatively volatile species, with a high vapour pressure, which will mainly transfer with the LPG & naphtha streams
- Ionic & Suspended Mercury
  - Mainly removed in desalting unit
  - Any residual suspended/particulate mercury which is found within lighter streams can be removed by physical separation
  - Any residual ionic/suspended Hg and "heavy" asphaltene Hg will exit with the bottom fractions from the atmospheric and vacuum units
    - > Bound within petroleum coke
    - > Can produce atmospheric emissions if used as boiler fuel
    - Recycle to FCC and transformed to elemental Hg
- Organo-mercury
  - Hydrotreaters will convert most species to elemental form (Hg<sup>0</sup>)

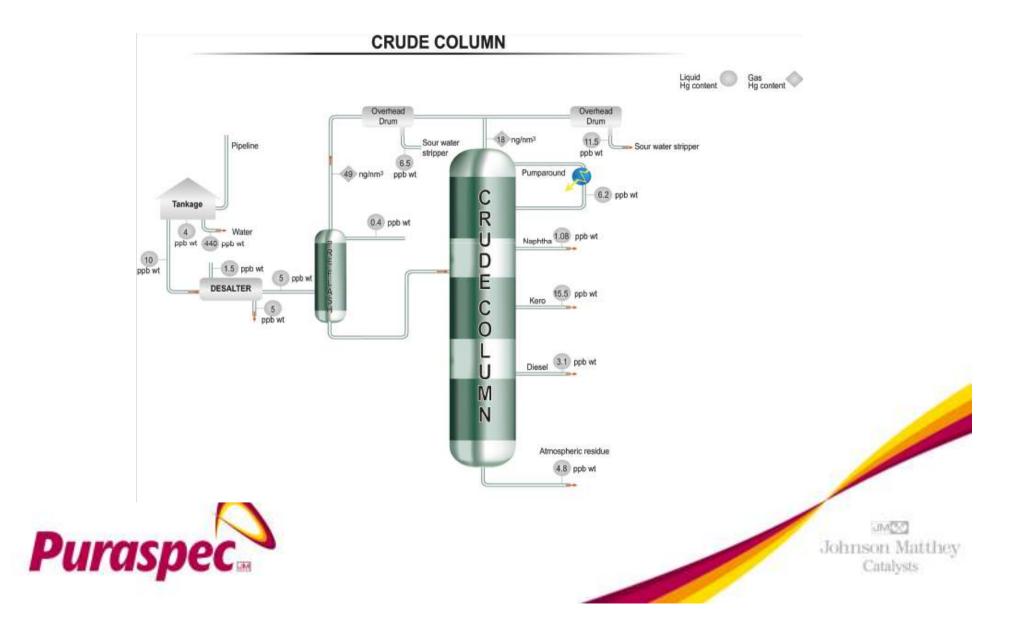




### Mercury Transport in Refineries



#### Mercury Distribution in Crude Column



#### **PURASPEC**<sub>JM</sub> Developing Technology

- Removal of Elemental Hg
- Gas & liquid duties
- Sulphur removal by reaction with metal oxide
   MO + H₂S → MS + H₂O
- Mercury removal by reaction with metal sulphide  $MS + Hg \rightarrow M_2S + HgS$
- PURASPEC chemically reacts with the sulphur &/or mercury therefore become bound in the structure of the absorbent pellet.
- Sulphur & Mercury cannot be liberated into the process





#### **PURASPEC**<sub>JM</sub> Developing Technology

- For over 15 years PURASPEC has provided the optimal solution to removal of Elemental Hg
- Hg can be present in other forms, and if there is an aqueous phase associated with the Hg containing stream, then the presence of Hg salts is potentially within it
- Development product currently being tested for Hg removal from water





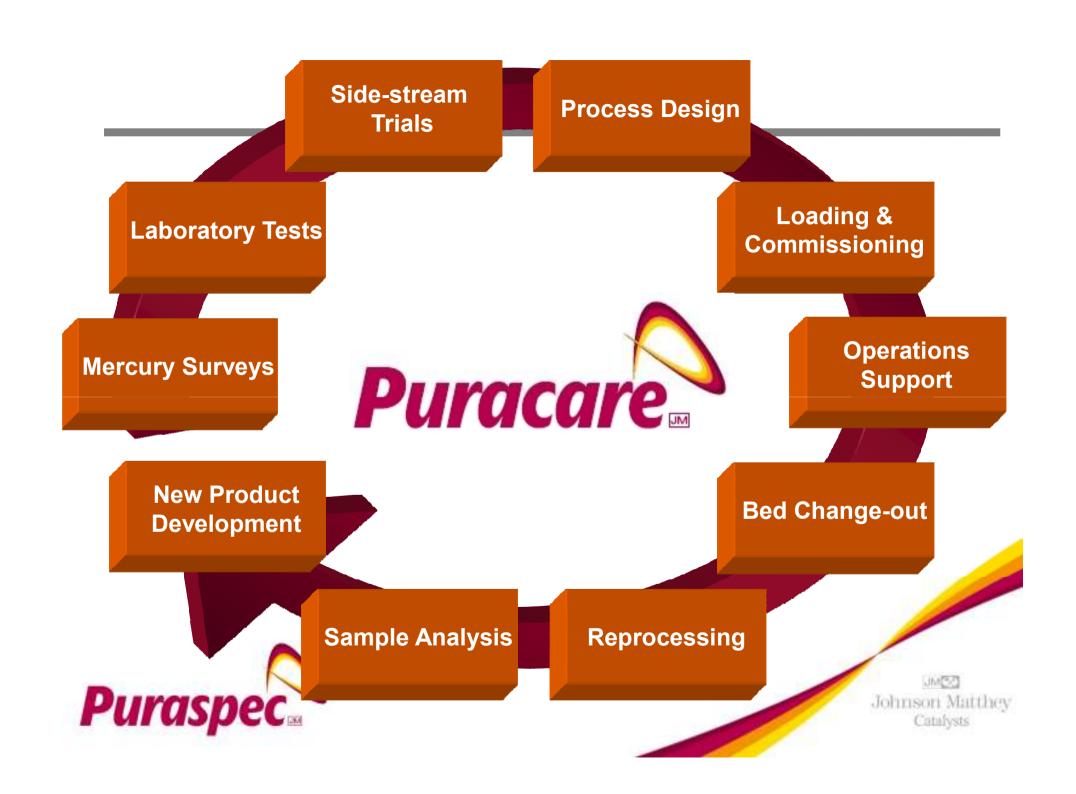
#### Advantages of PURASPEC Processes

- Simple fixed bed technology
- Selective precise removal
- Flexible & robust
- Can be used on liquids
- No utilities required
- No operator involvement
- No effluents or emissions
- Cradle to Grave Service











JM⊠ Johnson Matthey Catalysts

#### **Appendix 5**

Naphthenic acid corrosion: an analytical approach (E. Guerrini, S. Trasatti, Milan University)

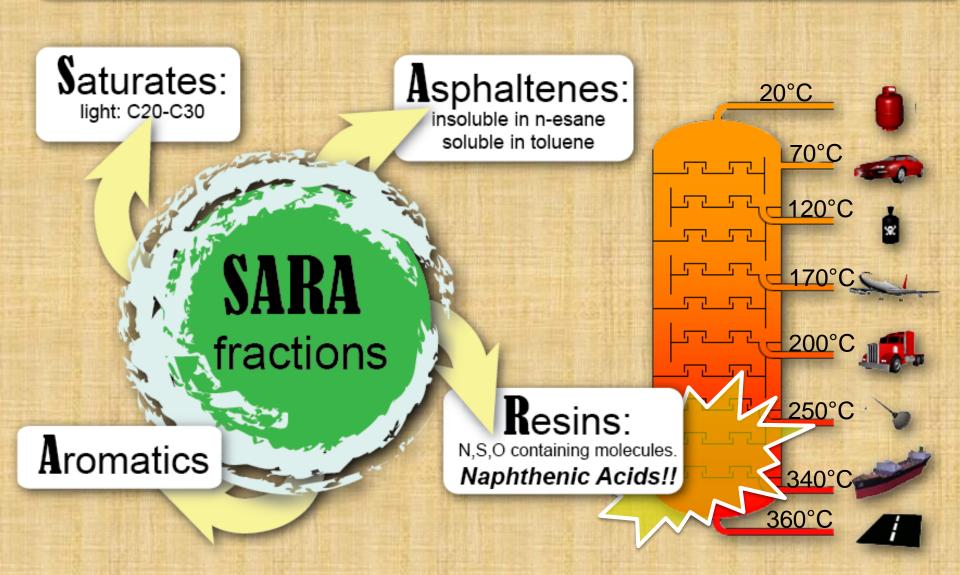
## Naphtenic Acids Corrosion: an analytical approach

Edoardo Guerrini<sup>1</sup>, Stefano Trasatti<sup>1</sup>, Cristina Flego<sup>2</sup>, Luciano Montanari<sup>2</sup>
Marino Tolomio<sup>3</sup>

<sup>1</sup> University of Milan, Milano, Italy
 <sup>2</sup> eni, r&m, Research Centre, San Donato Milanese, Italy
 <sup>3</sup> Venezia Tecnologie, Porto Marghera, Venice, Italy



## **Crudes composition**



Separation by polarity classes or by distillation

Total Acidity: Is there a correlation between Acidity and Corrosion?

#### **NO CORRELATION**

(almost not sure)





Corrosion





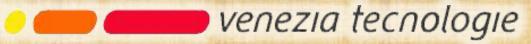


Corrosion

NOT only Acidity, but many more parameters

Analytical approach

The present work is part of a research project on Crudes Aggressiveness of



## Parameters: A starting point

- TAN: Total Acid Number ASTM D974 regulated implementation.
- 2 Conductance (G) G vs. T, D<sub>0</sub>
- **3** Naphthenic Acids fractions





## How to weight parameters?

P, T, TAN, G, S, CO<sub>2</sub>, ... Aggressiveness Life prediction **Neural Network Application Addressing Corrosion prevention** of adequate towers

## ... too many tasks?

**START:** Find parameters within a reproducible environment



MIX: build-up of a mixture of NA in a non corrosive matrix

Chemical	Type	TAN	
Diesel	matrix	0,019	
SynthOil	matrix	0,23	
CNA	NA	213,8	
FLUKA	NA	220,4	
DNA	NA	221,9	

## Synthetic Mix manipulation



#### re-Separation of NA

yield evaluationapplication to Crudes

#### **Fractionation**

- praticability
- Total and single yield

#### Synthetic vs. natural Crudes

-Separation of NA into fractions

## TAN: ASTM D974

Kind: colorimetric titration

**Solvent:** 50% toluene; 49,5%

isopropanol; 0,5% water

Titrant: KOH 0,1M in isopropanol

Chemicals	TAN
Isopropanol	0,064
Toluene	0,051
Solvent (blank)	0,055

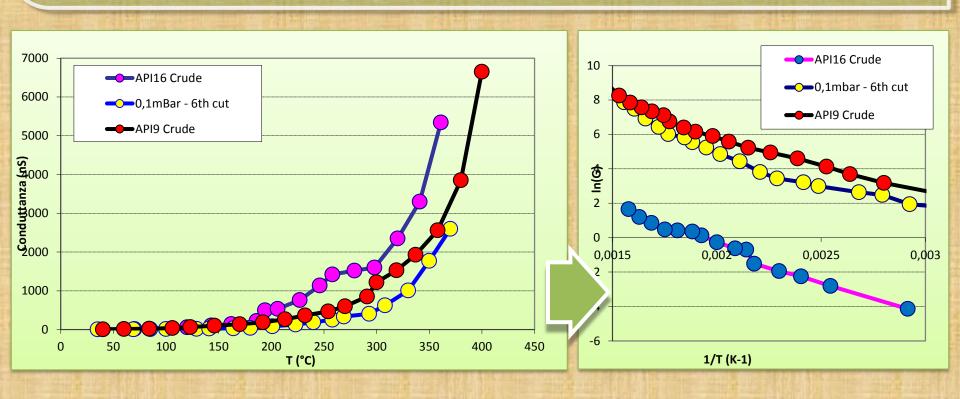
**Problems:** CO<sub>2</sub>, natural colour.

±5%

Chemical	TAN
Diesel	0,019
SynthOil	0,23
CNA	213,8
FLUKA	220,4
DNA	221,9

Use of ASTM D664?: potentiometric, more precise and accurate

## Conductance (G)

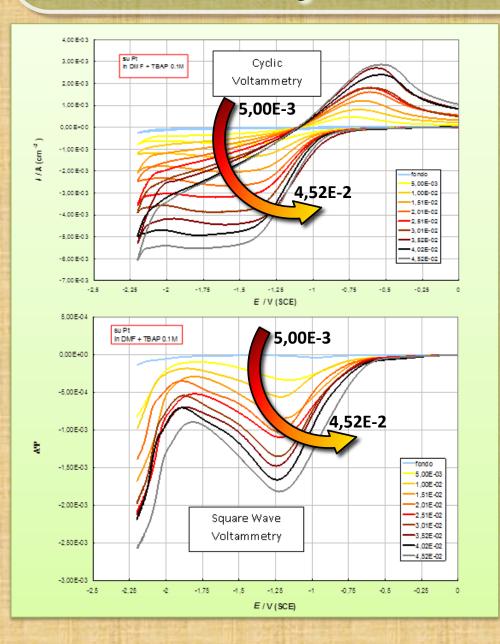


polar groups (NA) salts temperature

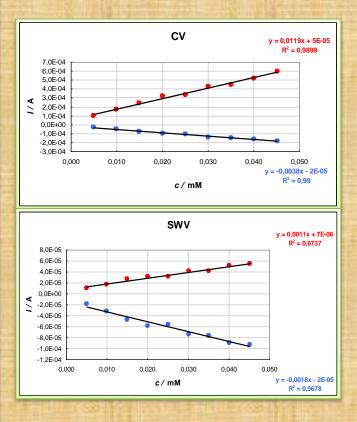
organic chains chelants

Overall evaluation of chemicals

## **Voltammetry**



#### ! Peak potentials change

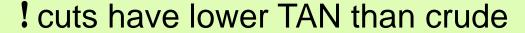


! NA are electro-active ! Straight calibration line

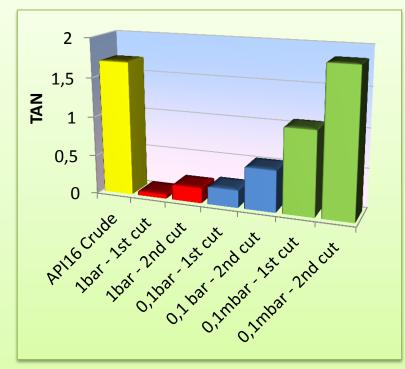
#### **NA fractions:**

How to obtain them



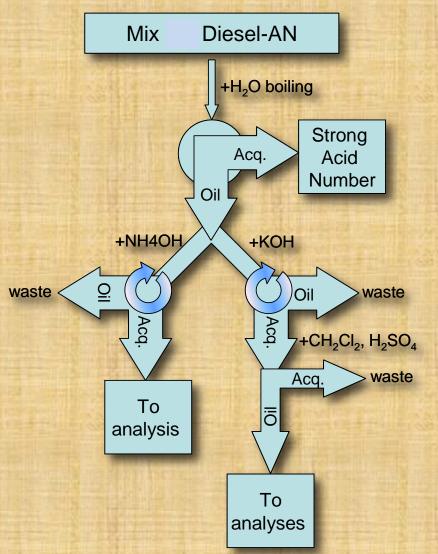


! NA are not separated by distillation



## **Extraction**

#### Upon 100% molar add of KOH



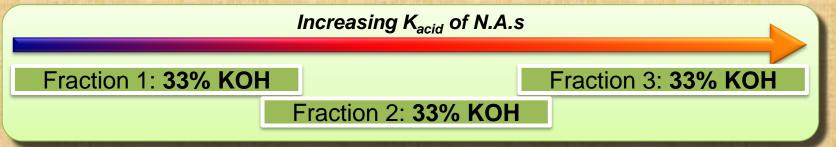
MIX:	Yield (%w)
Diesel + DNA	~ 96
Diesel <u>+ CNA (centrifuge</u> )	<u>~ 108%</u>
Diesel + CNA	73%
SynthOil+ DNA	84%
SynthOil+DNA (centrifuge)	87%
SynthOil+ CNA (centrifuge)	<u>101%</u>

- ! NA extractions are possible
- ! More complex mixtures give less NA extraction
- ! Centrifuge step needed
- ! Co-extraction of organics

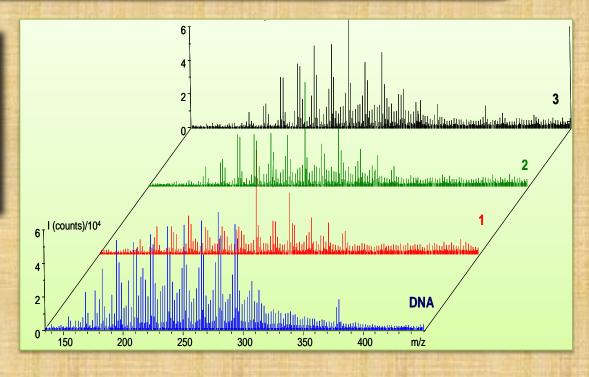
#### **NA fractions:**

#### PARTIAL extraction feasibility

#### Upon 3 consecutive 33mol% additions of KOH

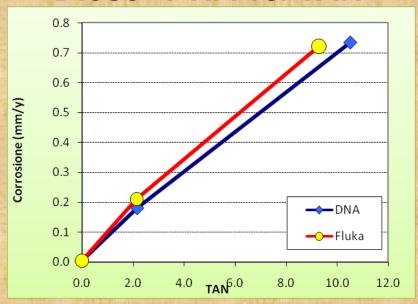


fraction	Yield %	TAN
1	20	226.9
2	52.5	200.1
3	25.1	176.7
Total:	97.6	



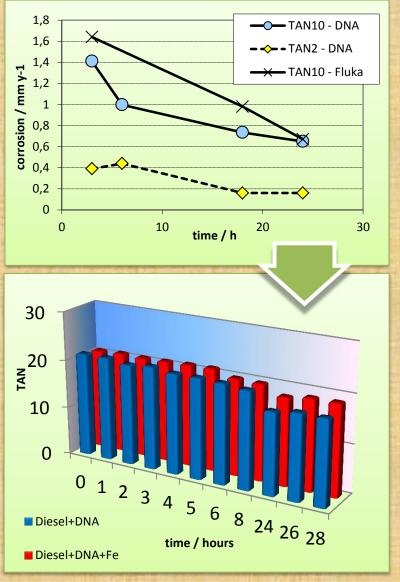
## **Corrosion tests**

#### Diesel + NA vs. TAN

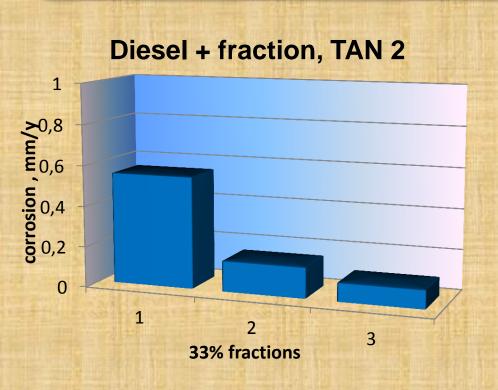


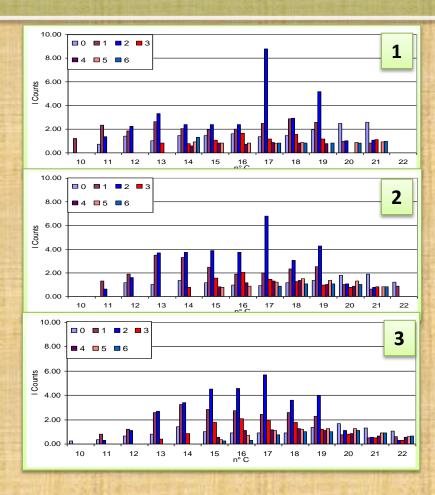
- ! NA differentiation
- ! Short-time differentiation
- ! TAN doesn't vary
- ! High T → SynthOil
- ! O<sub>2</sub> problems





## Corrosion tests on extraction fractions



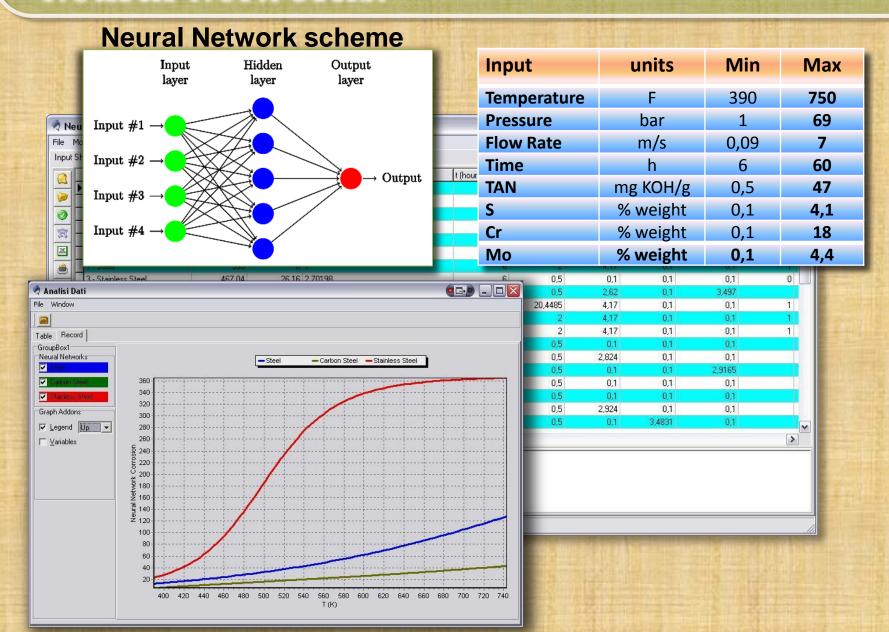


! The first extraction gives more aggressive acids (<C and <z)

! Second fraction has more acids with 1 or 2 rings

! Third fraction is less aggressive (>C and >z)

## Neural Networks: Development of an application



#### Appendix 6

#### Failure case of Dpcell Orifice flange for

**Hydrotreater unit** 

(C. Aiello)



Carmelo Aiello
Consulting Engineering

As you know the majority of accidents in petrochemical and refinery plants are due to failure of small components!!

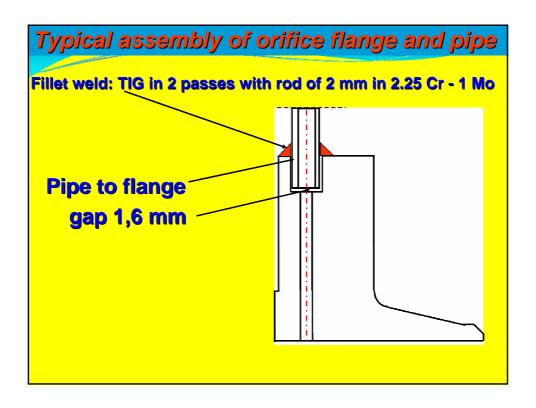
# However, very often, a failure is due to several concomitant causes.

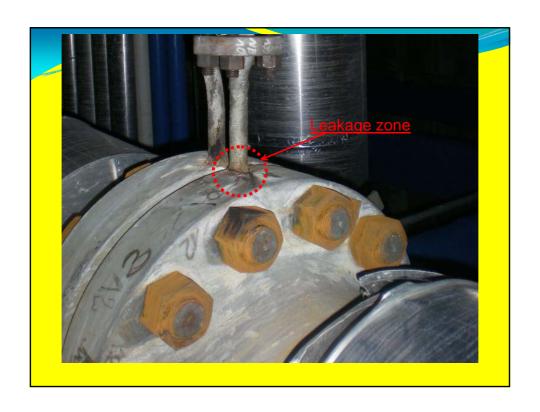
During start up operations after the commissioning of a Hydrotreater Unit there was a leakage of hydrocarbons, fortunately without consequences, by a fillet weld of a Dpcell pipe on the orifice flange.

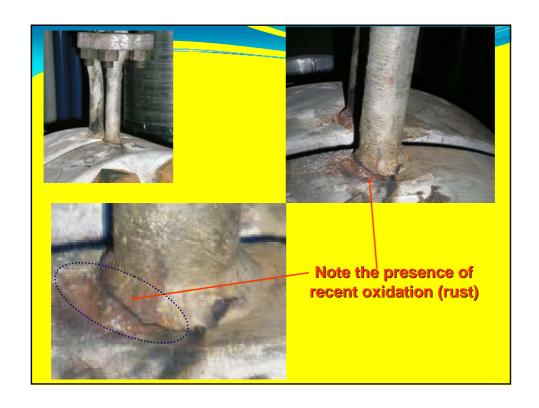
The stream had the following design conditions:

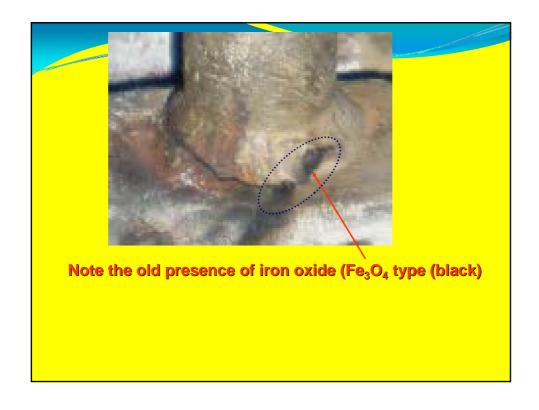
□Hydrocarbons + H₂S at 450°C and 90 bar

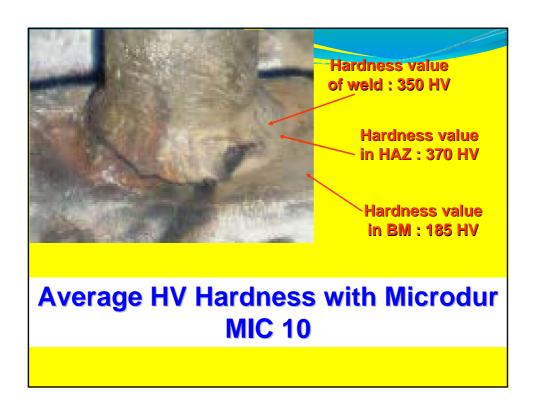
□Materials:
Flange 8" − 900#RF − ASTM A 182 F22
Pipe ¾" − Sch. 160 − ASTM A 335 P22











### **ANALYSIS**

Flanged tube on orifice flange had been assembled off-site, about 1 month before assembling the piping, by TIG welding with 2-1/4 Cr -1 Mo rod material in 2 passes.

Don't existed any certificate of NDT and PWHT

After construction and assembling of the sketch a pressure test with nitrogen, at 135 bar for 2h, was performed and certified.

However, during the start up of unit there was a leakage

How did this happen?

### NDT EXAMINATION AFTER THE LEAKAGE

### Visual inspection

Presence of old iron oxide (black) and recent oxidation (rust) close the crack

### Hardness test (average values):

Weld = 350 HV HAZ (flange side) = 370 HV BM flange = 185 HV

### **CONSIDERATIONS**

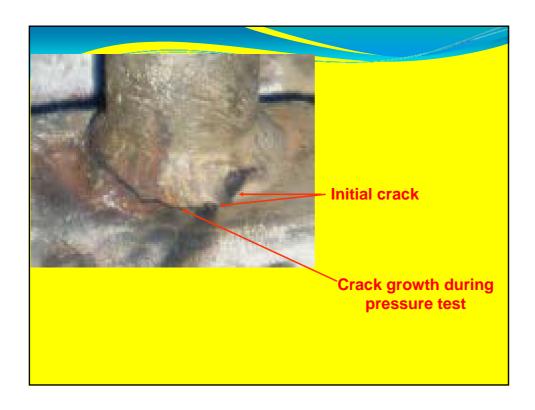
Hardness tests carried out lead to the following considerations:

- If was done preheating was not performed in a workmanlike manner
- -PWHT has not been carried out

Probably, given the rapid cooling caused by the thick flange and residual stress, has triggered a crack on the HAZ of the flange, already at first pass that has evolved on the surface at the end of welding after cooling.

So the crack was present before assembling made a few months later and had a greater oxidation. After the assembly was performed pressure test with N<sub>2</sub> that led to the crack growth. Did not detect any pressure drop during the pressure certified test.

Why??



### **CONCLUSIONS**

As we have seen the failure is occurred for concomitant several causes:

- ➤ Incorrect execution of the welding without respect of WPS
- > Lack of non-destructive testing
- ➤ Incorrect pressure test even if certified

The description of this failure case wants to alert Companies as follows:

- ➤ Design a plant with adequate management of technical operations
- ➤ Carry out quality control in fabrication and construction of plant components with people reliable

All for to a targeted and appropriate control of WPS and tests of small parts such as vents, drains, nipples for DpCell, drains for class level etc.



## **Unusual Corrosion Under Insulation**

(M. Richez Total)

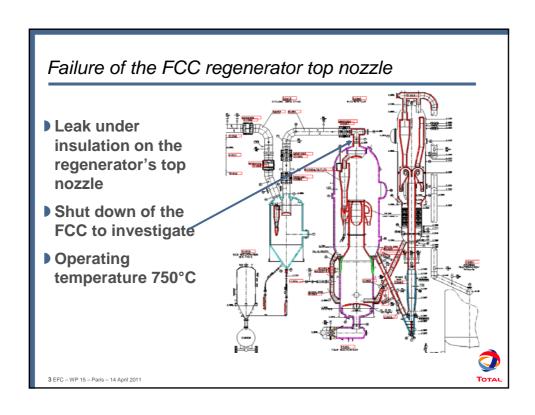
# Unusual corrosion under insulation

Martin RICHEZ

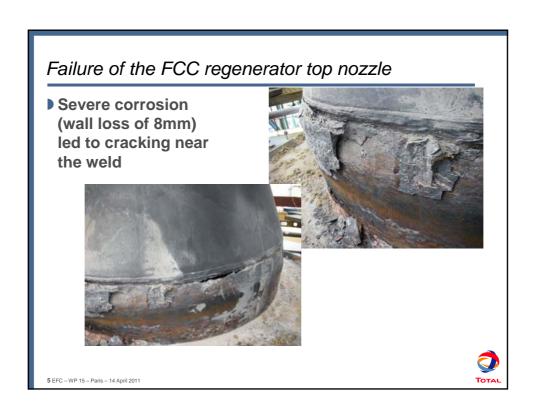


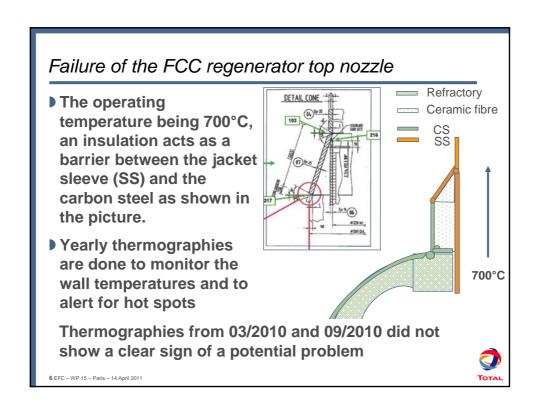
EFC - WP 15 - Paris - 14 April 2011

# FCC reaction zone FCC unit Equipment concerned: regenerator. Operating condition 2,4 bars ans 760°C Cold wall equipment, made of carbon steel with an internal insulating refractory. Flue gaz line are hot wall made of 304H or 321H



### Failure of the FCC regenerator top nozzle ▶ FCC was built around 1981, nozzle is 22mm thick T was enterely (RI) replaced in 2007 (creep damage). Nozzle wall thickness measured in 2007 15 mm 2010 minimum D 1002 thickness measured 6mm 4 EFC - WP 15 - Paris - 14 April 2011





### Failure of the FCC regenerator top nozzle

▶ What really changed in 2007

2007

2010





Insulation was extended up to the regenerator and covered the carbon steel area



7 EFC - WP 15 - Paris - 14 April 201

### Failure of the FCC regenerator top nozzle

### Two causes:

- ▶ The carbon steel was not cooled by the ambient temperature creating a high temperature oxydation under the insulation
- ▶ The insulation material (in the inside) put in place in 2007 was not sufficient (twice the normal quantity was adviced on the drawings)
  - ■The carbon steel's temperature got up to 600°C creating conditions for oxydation and creep

8 EFC - WP 15 - Paris - 14 April 201

### Failure of the FCC regenerator top nozzle

### Repairs:

▶ Replacement of the top nozzle

### Learnings:

▶ Modifications in the insulation can have a great impact. Great care shall be take on cold wall equipment to keep the initial design or to evaluate the consequence of any change.

9 FEC - WP 15 - Paris - 14 April 201

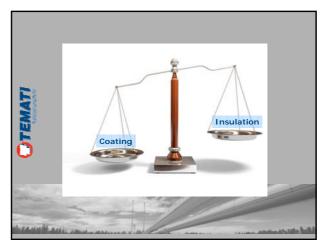


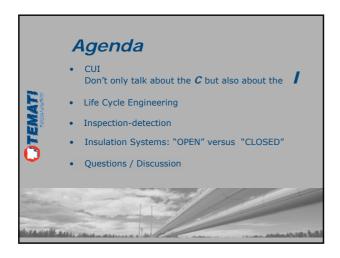
**CUI** and coatings (J. Sentjens - Temati)

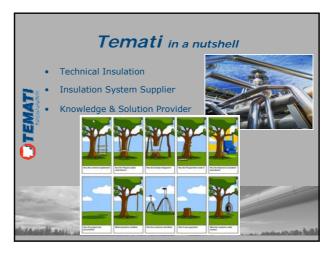








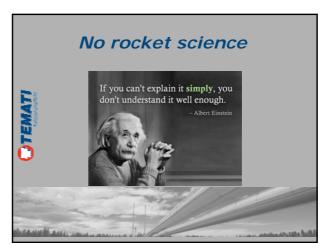


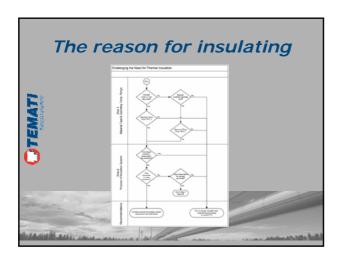
















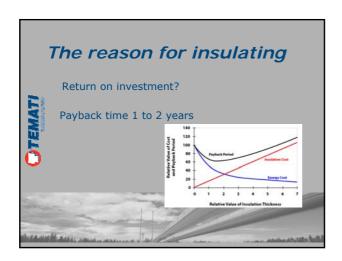


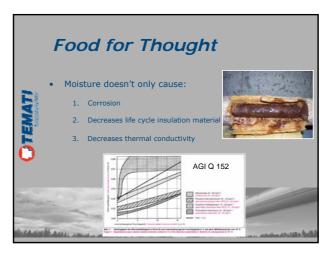


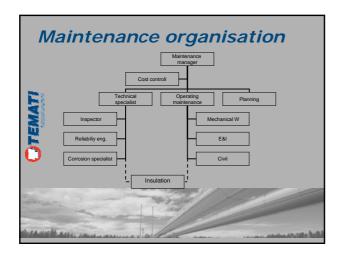












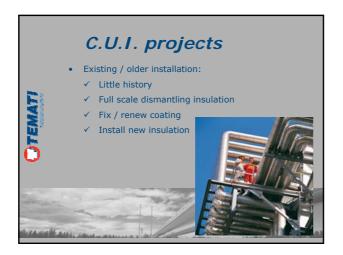


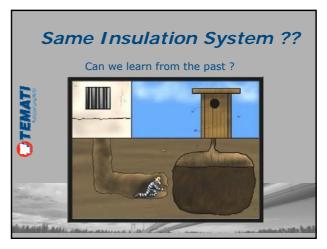


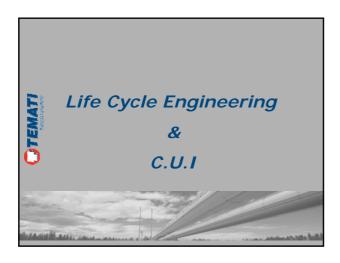


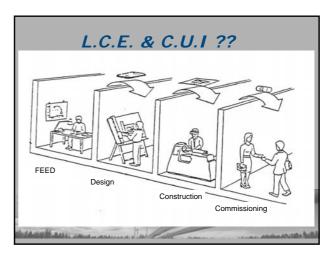


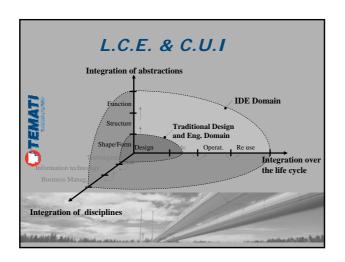






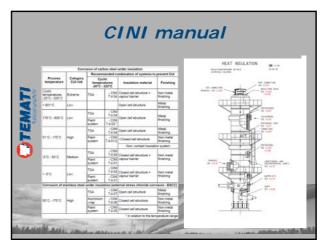


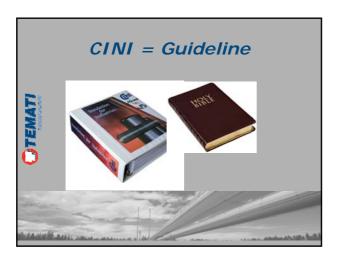




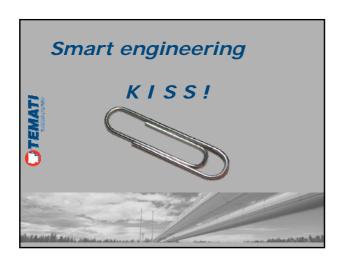


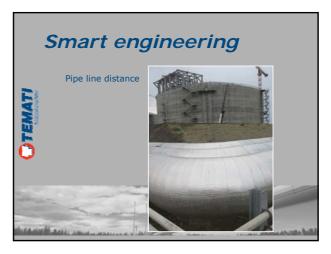




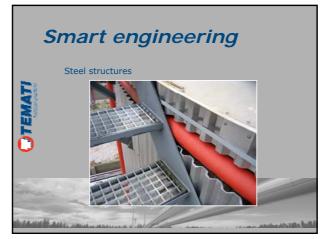




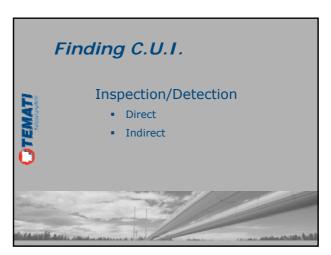


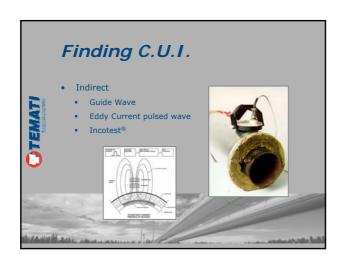


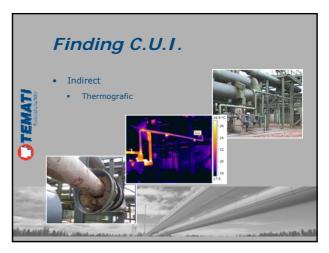


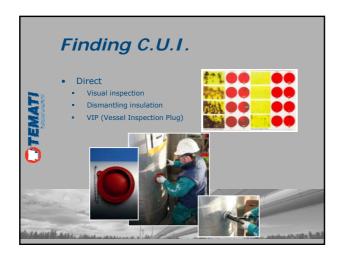


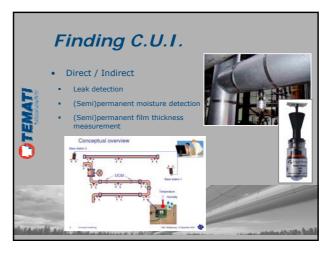




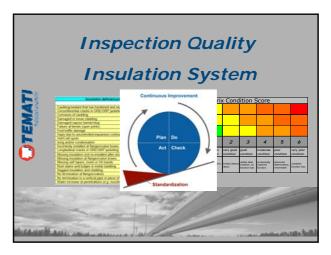














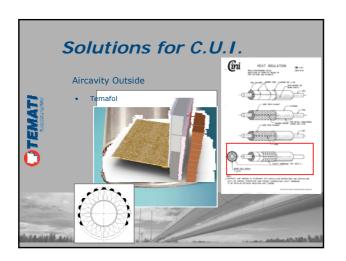




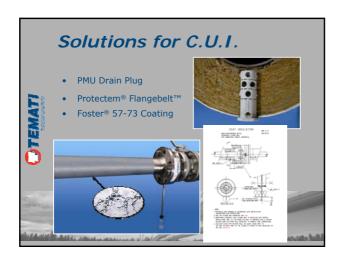








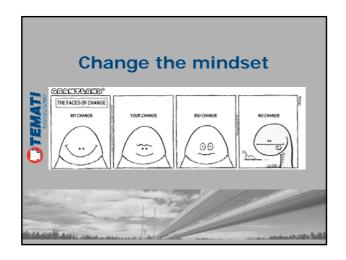


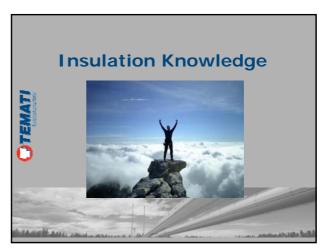










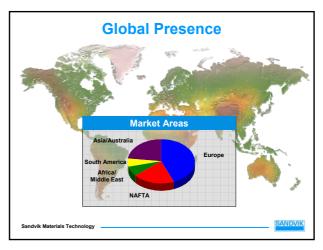




Sandvik SAF 2707HD heat exchanger tubes for demanding application in crude oil refinery

(G. Sielski - Sandvik)

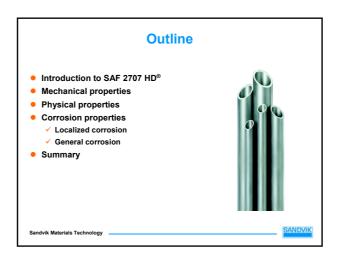


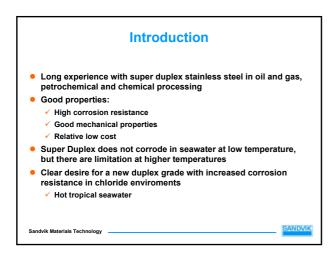


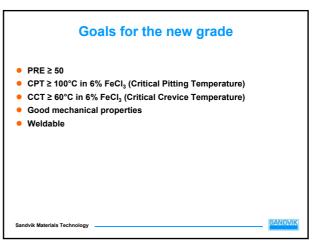


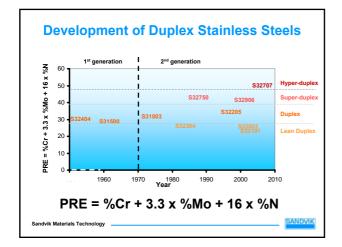


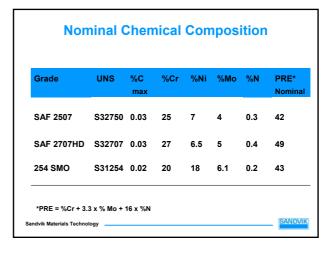


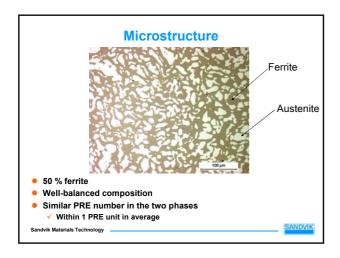


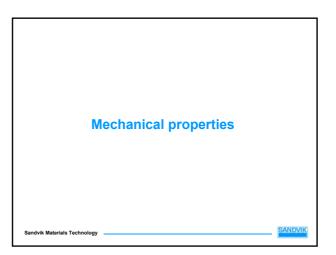


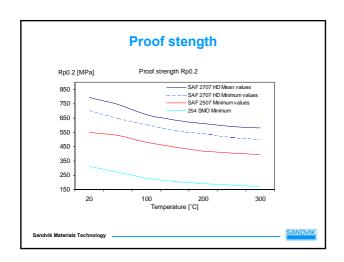


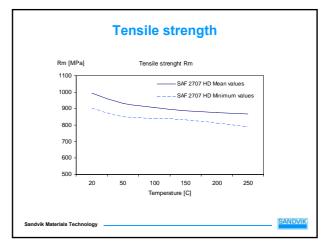


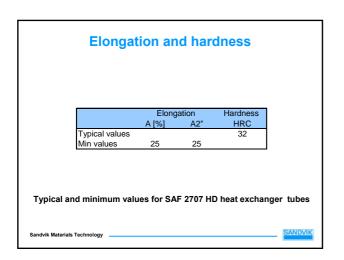


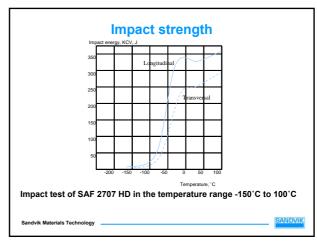


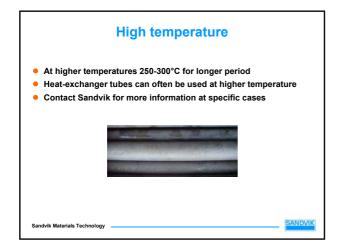


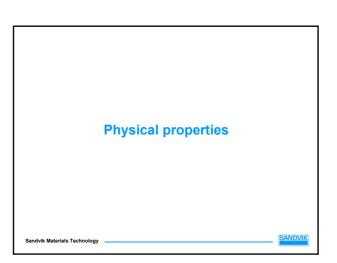


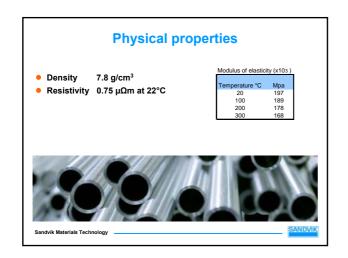


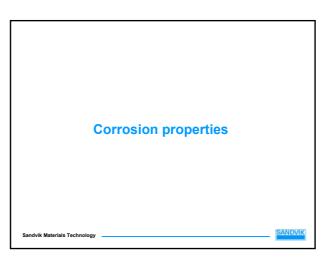


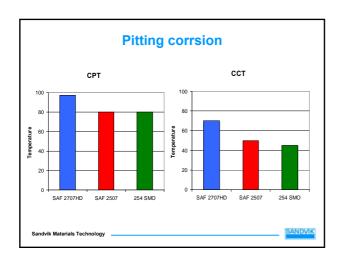


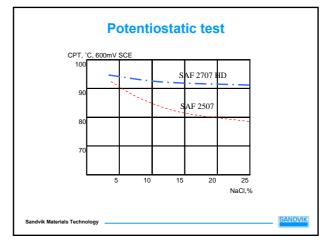


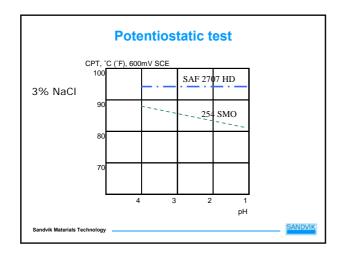


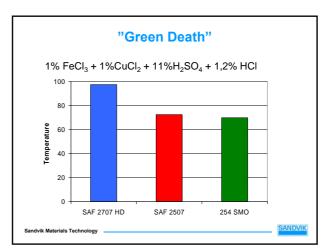


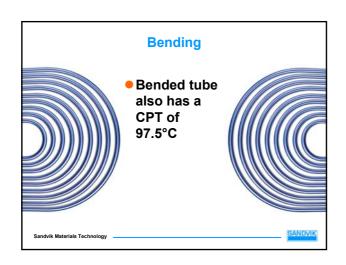


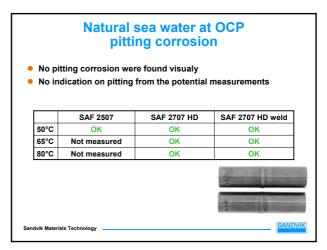


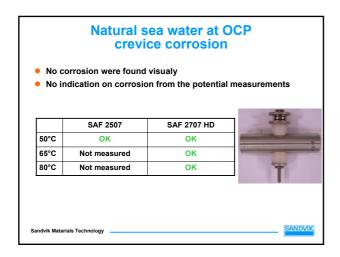


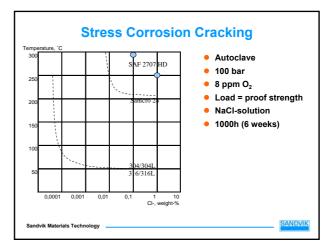


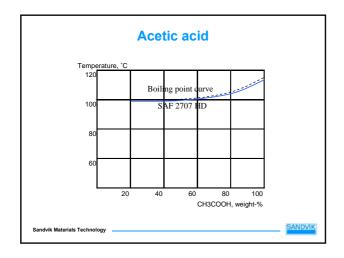


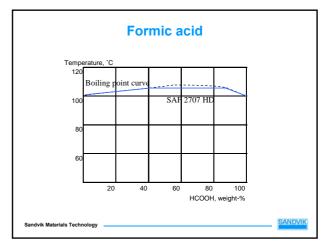


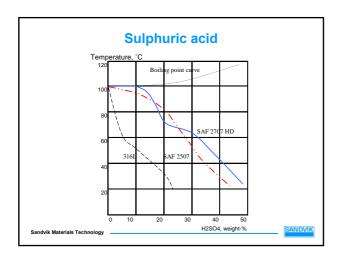


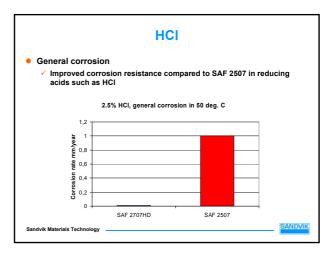


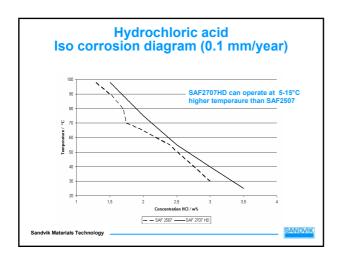


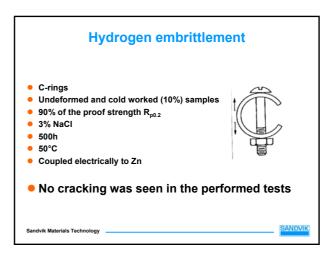


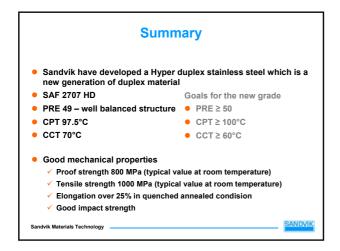




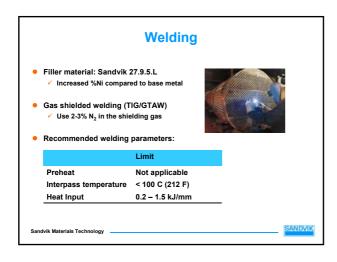


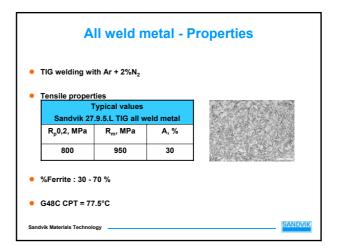


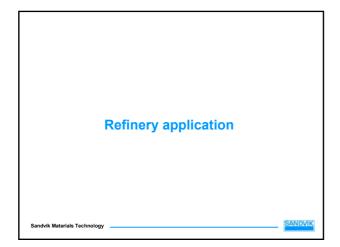


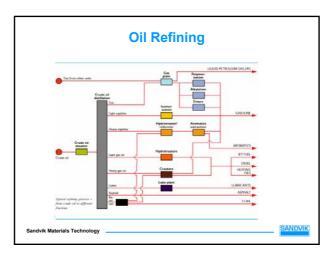


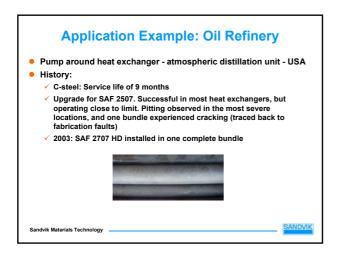


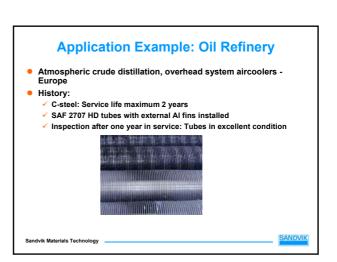


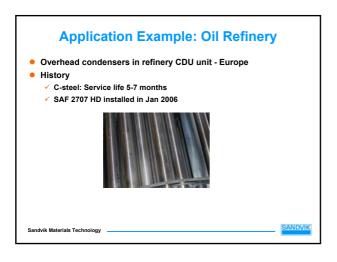


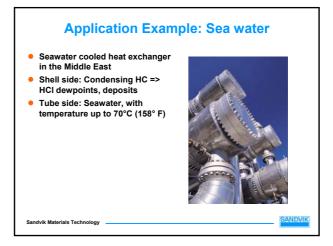


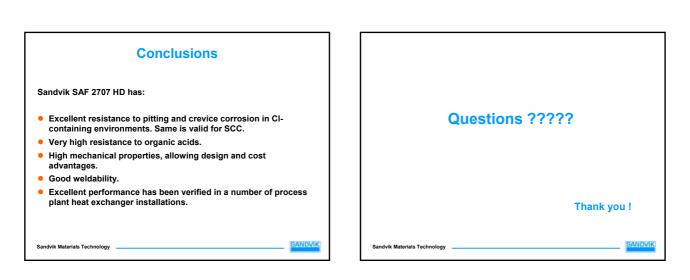












# 3D Trasar for boiler technology

(V. Beucler - Nalco)



### 3D TRASAR® Boiler Technology

**EFC Working Party 15** 2011 April 14th





How can we improve boiler water treatment control without more manpower?

We all agree that boiler water treatment is important, but we are "running lean," and we don't have additional labor available to dedicate to this area of the plant.







### DETECT DETERMINE DELIVER



- Automatically **Detects** system variability
  - Nalco Corrosion Stress Monitor (NCSM)
  - TRASAR internal treatment control
  - Direct measurement assures appropriate response
- Determines appropriate response
  - Compares system condition to desired condition
  - Adjusts system control immediately before problems occur
- Delivers results through improved control
  - Equipment protection / capital preservation
  - Energy efficiency
  - Prevention of unplanned outages
  - Labor efficiency





# 3D TRASAR Technology Multiple Application Platforms

- 3D TRASAR Technology Delivers Exceptional Economic and Operational Advantages...Across all Applications and Industries.
  - Boilers
  - Cooling
  - Reverse Osmosis
  - Process Applications

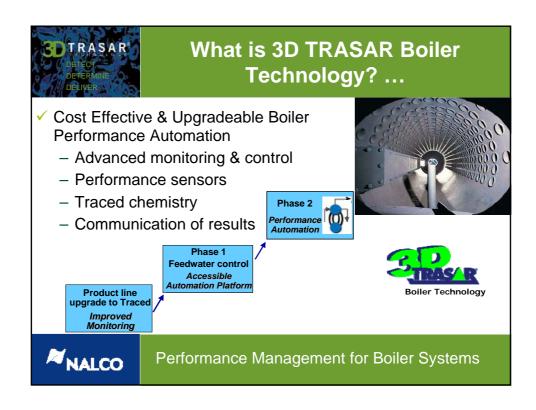


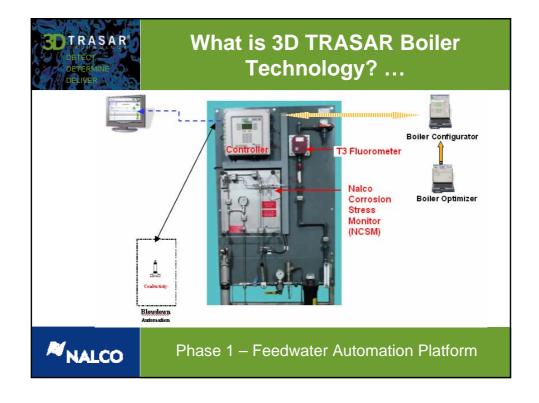


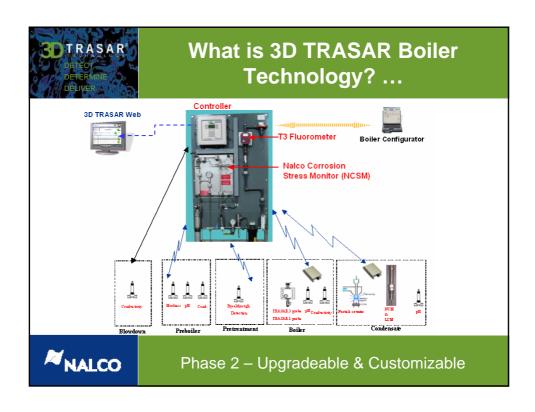
# 3D TRASAR Boiler Technology can meet many of CUSTOMER NAME water treatment needs ...

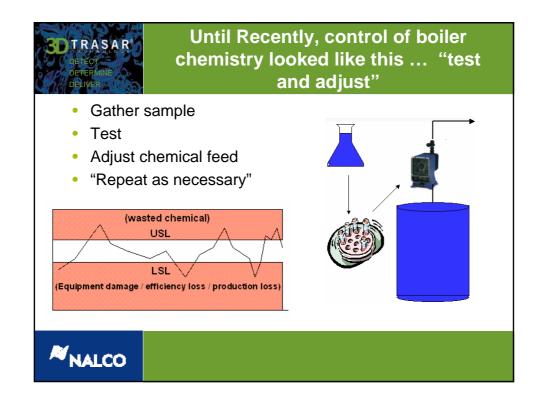
- Simplified, accurate program control w/ reduced need for operator intervention
- Assurance that no damage is done to boiler system
- Energy and water savings
- Continuous monitoring and automatic control
- Alarming capability to report when a potential problem exists
- Nalco rep freed up to provide more value-added services to the plant



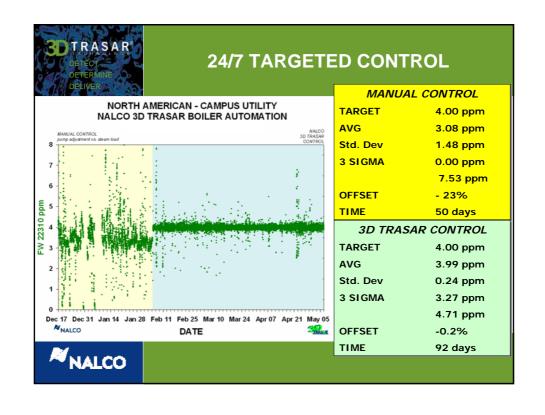


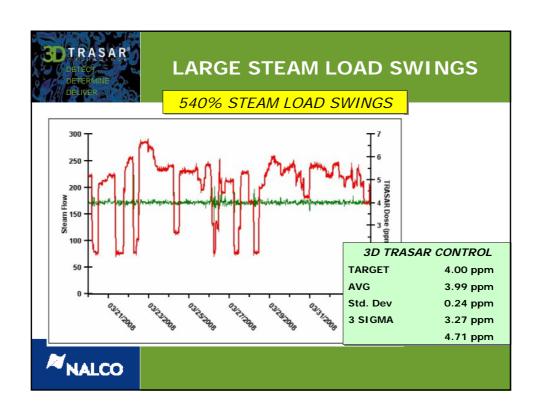


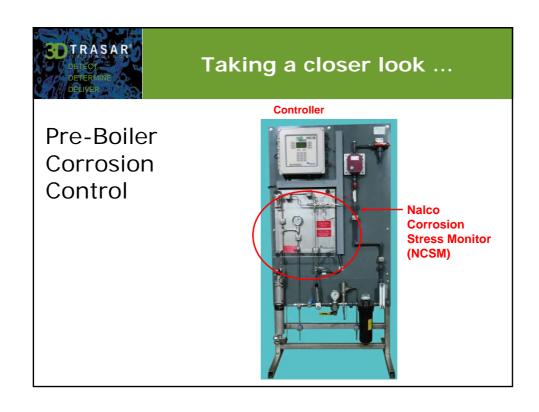


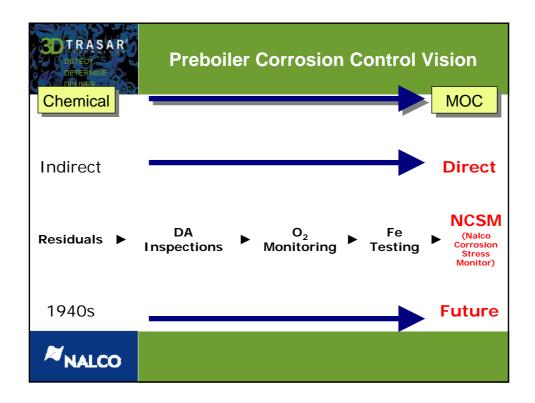


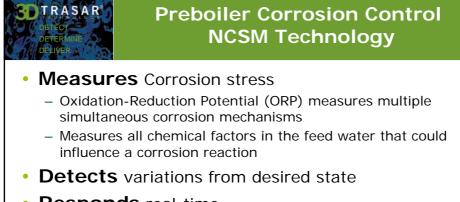






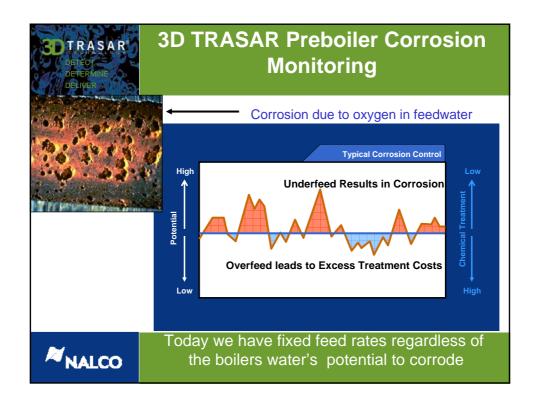


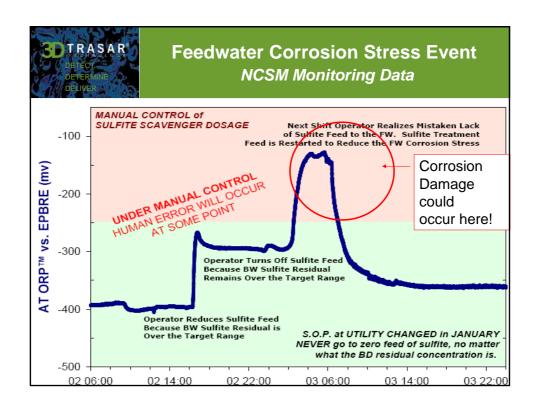


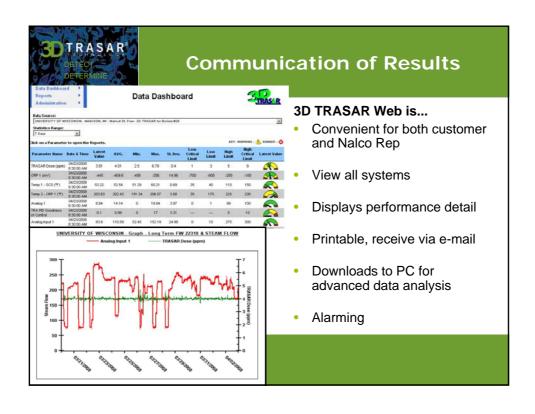


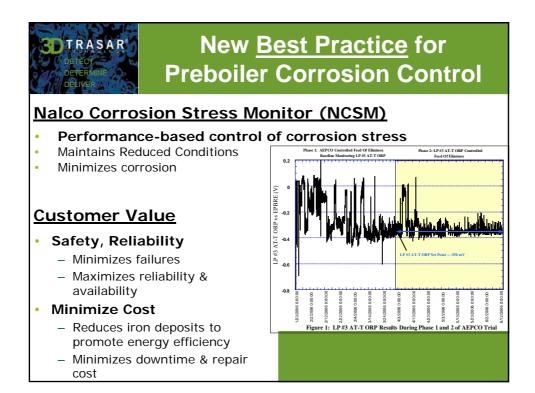
- Responds real-time
  - Varies oxygen scavenger feed
  - Maintains ideal reduced, low corrosion state
- Communicates via controller and web







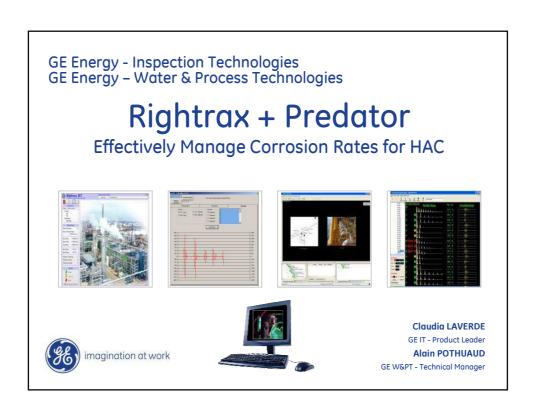


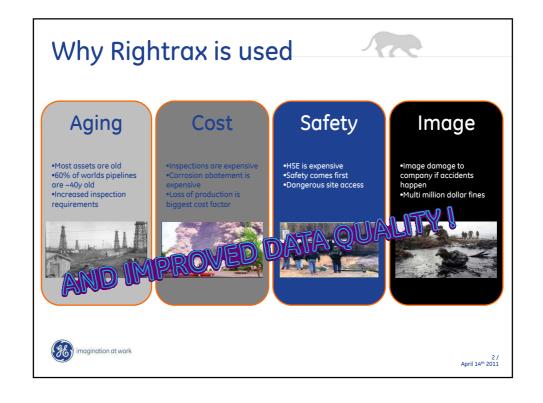


## **Appendix 11**

Corrosion Monitoring system can help refinery
plant to process opportunity crude by
monitoring the corrosion rate to control
inhibitor, to improve both plant versatility and
profitability

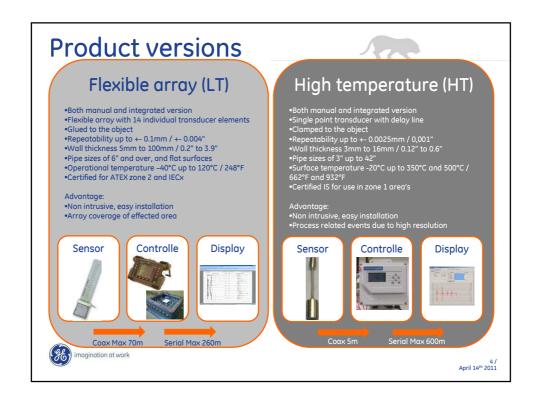
(Claudia Lavarde -A. Pothuaud - GE)



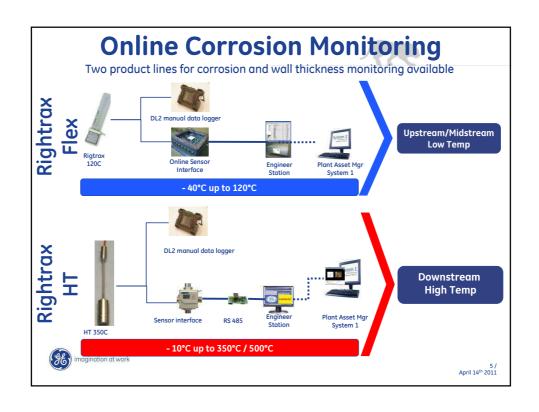


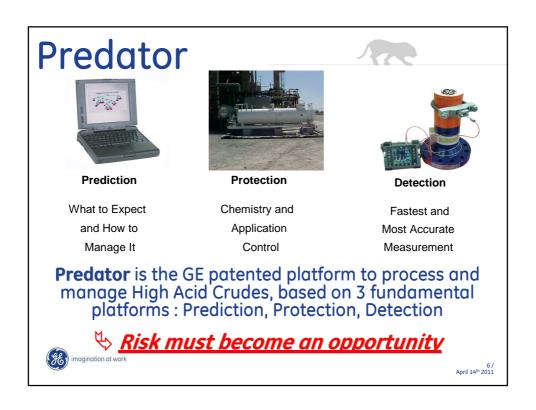






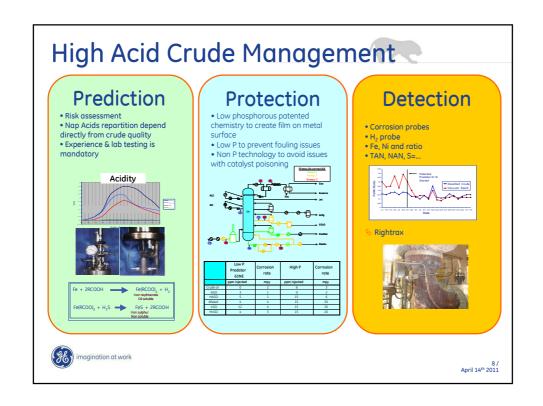


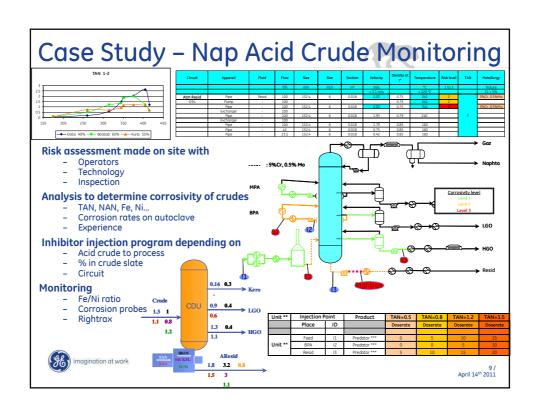


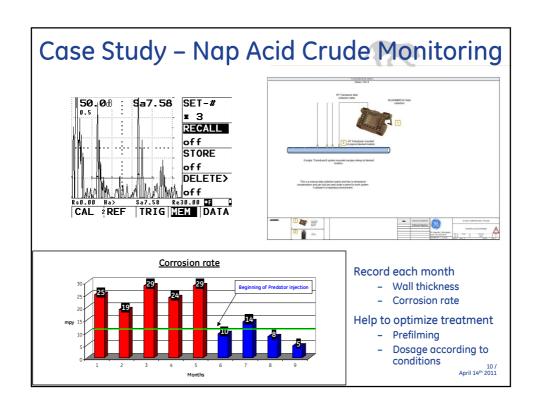




## HAC Discount to WTI Why Predator? WTI (\$5.00) (\$10.00) (\$15.00) Example of profitability \$\$ (\$20.00) Refinery capacity: 100.000 bbl/day 10 days per month with acid crude TAN=1.2 with 34% Baobab Crude cost differential: 5 \$/bbl ♦ Treatment cost # 500 k\$ Acid crude: 11% of total crude slate ➡Benefits on crude: 15 MM\$ GE imagination at work







## Other Applications FCCU overhead - High pH corrosion in wet environment - Filming inhibitor injected in water wash Wet Sour Gas Treater - Filming inhibitor efficiency control

