Appendix 1

List of participants
Participants EFC WP15 meeting 14\textsuperscript{th} April 2011 Paris (France)

<table>
<thead>
<tr>
<th>NAME</th>
<th>Company</th>
<th>Country</th>
</tr>
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<tbody>
<tr>
<td>Stein Brendryen</td>
<td>Statoil</td>
<td>Norway</td>
</tr>
<tr>
<td>Martin Richez</td>
<td>Total</td>
<td>France</td>
</tr>
<tr>
<td>Valerie Beucler</td>
<td>Nalco</td>
<td>France</td>
</tr>
<tr>
<td>Stefano Trasatti</td>
<td>University Milan</td>
<td>Italie</td>
</tr>
<tr>
<td>Edoardo Guerrini</td>
<td>University Milan</td>
<td>Italie</td>
</tr>
<tr>
<td>Alain Pothuaud</td>
<td>GE Betz</td>
<td>France</td>
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<tr>
<td>Claudia Laverte</td>
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<tr>
<td>Johan van Roij</td>
<td>Shell</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Fernando Bonilla</td>
<td>Vallourec</td>
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</tr>
<tr>
<td>Hennie de Bruyn</td>
<td>Johnson Mattey</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>Rachel Mansfield</td>
<td>Johnson Mattey</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>Carmelo Aiello</td>
<td>Consultant</td>
<td>Italie</td>
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<tr>
<td>Ridha Yahyaoui</td>
<td>Axens</td>
<td>France</td>
</tr>
<tr>
<td>Michel Munier</td>
<td>Axens</td>
<td>France</td>
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<tr>
<td>Francois Weisang-Hoinard</td>
<td>Outokumpu</td>
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<tr>
<td>Pascale Vangeli</td>
<td>Outokmupu</td>
<td>Sweden</td>
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<tr>
<td>Johan Sentjens</td>
<td>Temati</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Grzegorz Sielski</td>
<td>Sandvik</td>
<td>Poland</td>
</tr>
<tr>
<td>François Ropital</td>
<td>IFP Energies nouvelles</td>
<td>France</td>
</tr>
</tbody>
</table>
Appendix 2

EFC WP15 Activities

(Francois Ropital)
Welcome to the EFC Working Party Meeting

"Corrosion in Refinery" WP15

Paris 14 April 2011

**AGENDA EFC Working Party 15**

**Corrosion Refinery Industry Meeting**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
</table>
| 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)  
- failure case from the audience |
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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</thead>
<tbody>
<tr>
<td>13h30-14h15</td>
<td>Corrosion under insulation&lt;br&gt;Presentation &quot;CUI and coatings&quot; (Johan Sentjens - Temati)&lt;br&gt;Revision of the EFC CUI guideline n° 55</td>
</tr>
<tr>
<td>14h15-14h45</td>
<td>New stainless steels&lt;br&gt;Sandvik SAF 2707HD heat exchanger tubes for demanding application in crude oil refinery (Grzegorz Sielski)</td>
</tr>
<tr>
<td>14h45-15h15</td>
<td>Water treatment&lt;br&gt;3D Trasar for boiler technology (V. Beucler Nalco)</td>
</tr>
<tr>
<td>15h15-15h45</td>
<td>Monitoring&lt;br&gt;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)</td>
</tr>
<tr>
<td>15h45</td>
<td>Other topics of discussion from the audience</td>
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</tbody>
</table>

End of the meeting.

### 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: [http://www.efcweb.org](http://www.efcweb.org)
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 Working Parties

- 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
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 Working Party 15 « Corrosion in Refinery » Activities

Chairman: Francois 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,

Publications - Guidelines

Publications from WP15

  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  

- **EFC Guideline n° 42** Collection of selected papers  

- **EFC Guideline n° 55** Corrosion Under Insulation  

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

---

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

Increase the collaboration with NACE exchange of information on our activities - joint Eurocorr sessions
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 guideline
    - Amine acid gas treatment plants
  
  - New Publications: best practice guideline to avoid and characterize stress relaxation cracking?

- Education - qualification - certification

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

Tuesday 6 September: 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
<table>
<thead>
<tr>
<th>Time</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
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<tr>
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<td>Coffee break</td>
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<tr>
<td>11:30-12:30</td>
<td>Matching/Innovating</td>
<td>Matching/Innovating</td>
<td>Matching/Innovating</td>
<td>Matching/Innovating</td>
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<td>12:30-14:00</td>
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<td>15:00-16:00</td>
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<td>16:00-17:00</td>
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<td>17:00-18:00</td>
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</table>

**Notes:**
- Day 1: Paris, France
- Day 2: Location 1
- Day 3: Location 2
- Day 4: Location 3

**Additional Information:**
- All events are subject to change without notice.
- Please check the official website for the most up-to-date schedule.
- Transportation and accommodation details are available on the event website.
Information:
Future conferences related to refinery corrosion

- 5-8 September 2011
  EUROCORR 2011 Stockholm, Sweden
  Website: [www.efcweb.org/Events](http://www.efcweb.org/Events)

- 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](http://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: [www.efcweb.org/Events](http://www.efcweb.org/Events)
Appendix 3

Opportunity of duplex use in the amine units for CO$_2$ treatment

(F. Weisang-Hoinard, P. Vangeli Otokumpu)
Amine treatment: Gas treatment

- Use in refineries and CO₂ Capture
- CO₂ & H₂S Absorption/desorption
- Different types of Amines: MEA, DEA, MDEA & ….
- 2 wow in refineries:
  - Sour & sweet environments
  - H₂S from 30ppm to 50%
- CO₂ Capture/low H₂S content
A Typical Scheme of an Amine Unit

Amine Unit Corrosion: Key Factors

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

MEA ≥ DEA ≥ MDEA

- pH
- Thermal activation
- HSS
- Velocity Turbulences

- Uniform weight loss corrosion
- Erosion – corrosion
- Amine stress corrosion cracking
**Wet Acid Gas Corrosion: Key Factors**

- Flue gas composition / Inadequate scrubbing
- Inadequate design
- Too low gas flow rates
- CO₂ content in treated gas

→ H₂S / CO₂ ratio/Condensation
→ Amine wall wetting/Condensation
→ Water accumulation
→ Condensation in the treated gas lines

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

**Main Corrosion Areas: Sweet Gas unit**

**Absorbeur:**
- Bottom
- Head
- Erosion/Corrosion
- Acid gas corrosion

**Rich Amine lines:**
- Degasing
- Erosion/corrosion
- Stress corrosion cracking

**Rich/lean amine HEX:**
- Erosion Corrosion
- Wet acid gas corrosion
- Uniform corrosion

**Regenerator:**
- Head
- Acid gas outlet/condensor
- Bottom
- Erosion/Corrosion

**Reboiler:**
- HSS
- Uniform corrosion

**Lean Amine lines:**
- HSS turbulence
- Erosion/Corrosion
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/Cl- corrosion
HSS corrosion resistance
Costs

Chemical Composition and Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>EN</th>
<th>ASTM</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>PRE*</th>
<th>Rp0.2**</th>
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<td>LDX 2101®</td>
<td>1.4162</td>
<td>S32101</td>
<td>21.5</td>
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<td>450***</td>
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<td>S32205</td>
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<td>S32750</td>
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<td>7</td>
<td>4</td>
<td>0.27</td>
<td>43</td>
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<td>0.27</td>
<td>43</td>
<td>530</td>
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<td>8.1</td>
<td>-</td>
<td>-</td>
<td>18</td>
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<td>-</td>
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<td>N08904</td>
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<td>-</td>
<td>34</td>
<td>220</td>
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<tr>
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<td>S13254</td>
<td>20</td>
<td>18</td>
<td>6.1</td>
<td>0.20</td>
<td>43</td>
<td>300</td>
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</table>

* PRE = %Cr + 3.3(%Mo + %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

Typical chemical composition weight %
Positioning of Duplex grades
An excellent combination of high strength and corrosion resistance

Mechanical Properties
Data according to EN 10088

Proof strength, Rp0.2
Tensile strength, Rm

P = hot rolled plate and bar
H = hot rolled strip
C = cold rolled coil and strip, cold drawn bar

* Mechanical properties according to ASTM A240
** Mechanical properties according to internal standard AM 641.
1) Refers to A90 = 20% for gauges less than 3.0 mm
CO2 Corrosion

CO2 corrosion resistance depending of Cr level

Ref: Sumitomo: SM-Serie Brochure 2010

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
Corrosion resistance

<table>
<thead>
<tr>
<th>Corrosion Resistance, CPT typical</th>
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<tr>
<td>4307</td>
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<tr>
<td>LDX 2101®</td>
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<td>4404</td>
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<td>2205</td>
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<td>LDX 2404®</td>
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<td>2507</td>
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<tr>
<td>254 SMO</td>
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<td>4565</td>
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PRE | 18 | 26 | 24 | 26 | 25 | 28 | 33 | 33 | 35 | 34 | 43 | 43 | 46 |

Use of Materials in Flowlines

Ref: Environmental cracking and embrittlement of duplex steel. R Francis TWI 1994
**Effect of H2S/CO2 ratio**

Temperature/H₂S effect for duplex steels

![Graph showing the effect of H₂S on temperature for duplex steels with different Cr content.](image)

**SSC tests**

![Graph showing the results of SSC tests.](image)

*Figure 3. Summary of SSC tests performed on LDX 2101 and 2304 [6,7,8]. SSC = sulphide stress cracking, SC = selective corrosion.*
Thermal expansion

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal expansion $\times 10^{-6}/^\circ C$</th>
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<td>Carbon steel</td>
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<td>304</td>
<td>1.4301</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4401</td>
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<td>317L</td>
<td>1.4438</td>
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<tr>
<td>904L</td>
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<td>254 SMO®</td>
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<td>LDX 2101®</td>
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<td>2005</td>
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</tr>
<tr>
<td>2507</td>
<td>1.4410</td>
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</table>

Temperature: -20°C to +50°C, 2 m panel

Carbon steel: +1.7 mm
Austenite: +2.2 mm
Duplex: +1.8 mm

Stress Corrosion Cracking (SCC)

Chloride induced stress corrosion cracking in standard austenitic stainless steels - 4301, 4404

SCC is caused by a combination of:
- Corrosive environment
- Tensile stresses

Environments that can cause SCC:
- Chloride containing solutions (+H₂S)
- Hot alkaline solutions

Austenitic stainless steels with high content of Ni and Mo
- 904L
- 254 SMO®
- 4565

Duplex stainless steels
- LDX 2101®
- 2304
- LDX 2404™
- 2205
- 2507
Alloying costs for the nickel content at different nickel price

Duplex grades can be an alternative in CO2 Amine treatment

- Equal or higher corrosion resistance
- Minimal maintenance, longer lifetime
  - life-cycle cost advantage!
- Lower nickel content
  - cost stability!

The Benefit is in the Cost!
More information

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 – A Refinery Issue?

- Where is mercury containing crude oil found?
- Why remove mercury?
- Mercury Distribution
- PURASPEC_{JM}
Including natural gas, crude oil, coal and other hydrocarbons.
Mercury belt and global hot spots for mercury in oil and gas reserves

Northern Europe
Hg (gas) = 180 µg/Nm³
Hg (cond.) = 26-40 ppb

North Africa
Hg (gas) = 50-80 µg/Nm³
Hg (cond.) = 26-40 ppb

South America
Hg (gas) = 50-120 µg/Nm³
Hg (cond.) = 26-40 ppb

SE Asia, Australia
Hg (gas) = 200-1500 µg/Nm³
Hg (cond.) = 10-800 ppb
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

- **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

![Bar chart showing frequency of appearance of catalyst contaminants]

- Frequency of Appearance, %
- Catalyst Contaminants: Hg, As, Na, Si, Fe, Cl, Ca, Pb, Mg, Ti, Zn, Cu, Ni, V, Br, K, Pb, N, Mn, Cr
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)
  – 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 Intertek
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, $\text{H}_2\text{O}$)
- 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 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(Al) + 6H_2O = Al_2O_3\cdot3H_2O + H_2 + Hg

• Presence of amalgams in refinery process equipment may render the materials susceptible to other corrosion mechanisms (organic acids, sour water, etc.)
Mercury distribution

Acid Gas Removal (Amine/Membrane) 
- Regen / Permeate: 65% Hg

Gas Dehydration (Glycol/Mol Sieve) 
- Dehydration Regen Gas: 5% Hg
- 25% Hg

AI Heat-Exchanger 
- 20% Hg

Separator 
- 19% Hg
- 15% Hg

Multiphase Flow 
- 100% Hg

Produced Water

Oil Export/Storage

Fuel Gas
- 4% Hg

Gas Export

NGL Export

Puraspec
Mercury Compounds in Refinery

• Elemental mercury (Hg\(^0\))
  – 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\(^0\))
Mercury Distribution in Crude Column
**PURASPEC\textsubscript{JM}** Developing Technology

- **Removal of Elemental Hg**
- Gas & liquid duties
- Sulphur removal by reaction with metal oxide
  \[ \text{MO} + \text{H}_2\text{S} \rightarrow \text{MS} + \text{H}_2\text{O} \]
- Mercury removal by reaction with metal sulphide
  \[ \text{MS} + \text{Hg} \rightarrow \text{M}_2\text{S} + \text{HgS} \]

- 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
PURASPECJM 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
Appendix 5

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

Edoardo Guerrini¹, Stefano Trasatti¹, Cristina Flego², Luciano Montanari², Marino Tolomio³

¹ University of Milan, Milano, Italy
² eni, r&m, Research Centre, San Donato Milanese, Italy
³ Venezia Tecnologie, Porto Marghera, Venice, Italy
Crudes composition

Saturates:
- light: C20-C30

Asphaltenes:
- insoluble in n-esane
- soluble in toluene

SARA fractions

Aromatics

Resins:
- N,S,O containing molecules
- Naphthenic Acids!!

Separation by polarity classes or by distillation
Total Acidity: Is there a correlation between Acidity and Corrosion?

NO CORRELATION
(almost not sure)

Crudes \( \times \) Corrosion

...but

Acidity \( \rightarrow \) 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

1. **TAN: Total Acid Number**
   ASTM D974 regulated implementation.

2. **Conductance (G)**
   \[ G \text{ vs. } T, D_0 \]

3. **Naphthenic Acids fractions**

Distillation

Salification
How to weight parameters?

- P, T, TAN, G, S, CO$_2$, ..

Neural Network Application

- Aggressiveness
- Life prediction
- Corrosion prevention
- Addressing 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

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<thead>
<tr>
<th>Chemical</th>
<th>Type</th>
<th>TAN</th>
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<tbody>
<tr>
<td>Diesel</td>
<td>matrix</td>
<td>0.019</td>
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<tr>
<td>SynthOil</td>
<td>matrix</td>
<td>0.23</td>
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<tr>
<td>CNA</td>
<td>NA</td>
<td>213.8</td>
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<td>NA</td>
<td>220.4</td>
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<tr>
<td>DNA</td>
<td>NA</td>
<td>221.9</td>
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Synthetic Mix manipulation

6 mixtures

MIX

re-Separation of NA
- yield evaluation
- application to Crudes

Fractionation
- practicability
- 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

**Problems:** CO₂, natural colour. ±5%

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<tr>
<th>Chemicals</th>
<th>TAN</th>
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<td>Isopropanol</td>
<td>0.064</td>
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<tr>
<td>Toluene</td>
<td>0.051</td>
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<tr>
<td>Solvent (blank)</td>
<td>0.055</td>
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</table>

**Use of ASTM D664?:** potentiometric, more precise and accurate
**Condutanza (G)**

- Polar groups (NA)
- Salts
- Temperature
- Organic chains
- Chelants

**Overall evaluation of chemicals**
Voltammetry

Cyclic Voltammetry

Peak potentials change

Straight calibration line

NA are electro-active
NA fractions: How to obtain them

Distillation

! cuts have lower TAN than crude
! NA are not separated by distillation

Extraction

\[ \text{AH}_{(\text{OIL})} + \text{KOH} \rightarrow \text{A}^-_{(\text{water})} + \text{H}^+ \]
Upon 100% molar add of KOH

<table>
<thead>
<tr>
<th>MIX:</th>
<th>Yield (% w)</th>
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<tr>
<td>Diesel + DNA</td>
<td>~ 96</td>
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<tr>
<td>Diesel + CNA (centrifuge)</td>
<td>~ 108%</td>
</tr>
<tr>
<td>Diesel + CNA</td>
<td>73%</td>
</tr>
<tr>
<td>SynthOil + DNA</td>
<td>84%</td>
</tr>
<tr>
<td>SynthOil + DNA (centrifuge)</td>
<td>87%</td>
</tr>
<tr>
<td>SynthOil + CNA (centrifuge)</td>
<td>101%</td>
</tr>
</tbody>
</table>

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

*Increasing $K_{\text{acid}}$ of N.A.s*

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield</th>
<th>TAN</th>
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</thead>
<tbody>
<tr>
<td>Fraction 1</td>
<td>33% KOH</td>
<td>20</td>
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<tr>
<td>Fraction 2</td>
<td>33% KOH</td>
<td>52.5</td>
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<tr>
<td>Fraction 3</td>
<td>33% KOH</td>
<td>25.1</td>
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<tr>
<td>Total</td>
<td></td>
<td>97.6</td>
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</table>
Corrosion tests

Diesel + NA vs. TAN

Diesel + NA vs. time

- NA differentiation
- Short-time differentiation
- TAN doesn’t vary
- High T → SynthOil
- O₂ problems
Corrosion tests \textit{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

Neural Network scheme

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<th>Input</th>
<th>units</th>
<th>Min</th>
<th>Max</th>
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<td>Pressure</td>
<td>bar</td>
<td>1</td>
<td>69</td>
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<tr>
<td>Flow Rate</td>
<td>m/s</td>
<td>0.09</td>
<td>7</td>
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<tr>
<td>Time</td>
<td>h</td>
<td>6</td>
<td>60</td>
</tr>
<tr>
<td>TAN</td>
<td>mg KOH/g</td>
<td>0.5</td>
<td>47</td>
</tr>
<tr>
<td>S</td>
<td>% weight</td>
<td>0.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Cr</td>
<td>% weight</td>
<td>0.1</td>
<td>18</td>
</tr>
<tr>
<td>Mo</td>
<td>% weight</td>
<td>0.1</td>
<td>4.4</td>
</tr>
</tbody>
</table>
Appendix 6

Failure case of Dpcell Orifice flange for
Hydrotreater unit

(C. Aiello)
 Una "nuova" figura professionale: 
l'ispettore di impianto in un contesto di 
global inspection service

**Failure Case of Dpcell Orifice Flange**

**HYDROTREATER UNIT**

Carmelo Aiello  
Consulting Engineering

---

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

---

Una "nuova" figura professionale: 
l'ispettore di impianto in un contesto di 
global inspection service
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
Una "nuova" figura professionale:
l'ispettore di impianto in un contesto di
global inspection service
Una "nuova" figura professionale:
l'ispettore di impianto in un contesto di
global inspection service

Note the presence of recent oxidation (rust)

Note the old presence of iron oxide (Fe$_3$O$_4$ type (black))
Una "nuova" figura professionale:
l'ispettore di impianto in un contesto di
global inspection service

Hardness value
of weld : 350 HV

Hardness value
in HAZ : 370 HV

Hardness value
in BM : 185 HV

Average HV Hardness with Microdur MIC 10

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 N₂ 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 glass level, etc.

THANK YOU
Appendix 7

Unusual Corrosion Under Insulation

(M. Richez Total)
Unusual corrosion under insulation

Martin RICHEZ

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 gas line are hot wall made of 304H or 321H
Failure of the FCC regenerator top nozzle

- Leak under insulation on the regenerator's top nozzle
- Shut down of the FCC to investigate
- Operating temperature 750°C

FCC was built around 1981, nozzle is 22mm thick
T was entirely replaced in 2007 (creep damage). Nozzle wall thickness measured in 2007 15 mm
2010 minimum thickness measured 6mm
Failure of the FCC regenerator top nozzle

- Severe corrosion (wall loss of 8mm) led to cracking near the weld

The operating temperature being 700°C, an insulation acts as a barrier between the jacket sleeve (SS) and the carbon steel as shown in the picture.

- Yearly thermographies are done to monitor the wall temperatures and to alert for hot spots

Thermographies from 03/2010 and 09/2010 did not show a clear sign of a potential problem
Failure of the FCC regenerator top nozzle

What really changed in 2007

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

Two causes:

- The carbon steel was not cooled by the ambient temperature creating a high temperature oxidation under the insulation
- The insulation material (in the inside) put in place in 2007 was not sufficient (twice the normal quantity was advised on the drawings)
  - The carbon steel’s temperature got up to 600°C creating conditions for oxidation and creep
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 taken on cold wall equipment to keep the initial design or to evaluate the consequence of any change.
Appendix 8

CUI and coatings (J. Sentjens - Temati)
C.U.I.
EFC working party 15
Meeting April 14th 2011

Johan Sentjens

Statement
Insulation = Coating
Form of protection

Agenda
- CUI
  Don't only talk about the C but also about the I
- Life Cycle Engineering
- Inspection-detection
- Insulation Systems: "OPEN" versus "CLOSED"
- Questions / Discussion

Temati in a nutshell
- Technical Insulation
- Insulation System Supplier
- Knowledge & Solution Provider
Statement

CUI is not a Technical Issue but an Organisation Issue

Who's or where is the insulation expert/expertise?

No rocket science

If you can't explain it simply, you don't understand it well enough. — Albert Einstein

The reason for insulating

• Energy control
• CO₂ of NOₓ emission reduction
• Sound control
• Personal protection Past & Present
• Fire proofing
• Process conditions
Mission and Vision

We are committed to maintaining a safe work environment enriched by diversity and characterized by open communication, trust, and fair treatment.
Above all other objectives, we are dedicated to running safe and environmentally responsible operations.

Mission and Vision

Safety is always our top priority. We aim to have zero fatalities and no incidents that harm people, or put our neighbours or facilities at risk.

Mission and Vision

We act in a responsible manner and support the Responsible Care® initiatives. Economic considerations do not take priority over safety and health issues and environmental protection.

Mission and Vision

Values:
- Integrity
- Respect for People
- Protecting Our Planet

Strategic Themes:
- Financial Discipline
- Sustainability
- Performance Culture
- Profitable Growth

The reason for insulating

Coal-fired power plant: 1100 MW
300,000 m² insulated surfaces
Heat loss reduction: 25% when insulated sustainable.

This saves around 25,500 tons of coal every year, reducing annual CO₂ emissions by 27,000 tons. This is roughly equivalent to 12,890 cars with an annual mileage of 15,000 km. In financial terms, this would enable the plant operators to produce added power equivalent to € 4.8 million.
The reason for insulating

Return on investment?
Payback time 1 to 2 years

Food for Thought

- Moisture doesn’t only cause:
  1. Corrosion
  2. Decreases life cycle insulation material
  3. Decreases thermal conductivity

Maintenance organisation

Cost calculation

- Insulation
- Operating maintenance
- Planning
- Inspection
- Reliability eng.
- E&I
- Operating maintenance
- Planning

The need for insulation expertise?

<table>
<thead>
<tr>
<th>Insulation expertise</th>
<th>Maintenance manager</th>
<th>Reliability eng.</th>
<th>Production man.</th>
<th>Sr. inspector</th>
<th>Contractor/manufacturer</th>
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<tbody>
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<td>Design of cooling tower and equipment</td>
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<td>Construction of cooling towers</td>
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<td></td>
</tr>
</tbody>
</table>

The need for insulation expertise?

Maintenance man.
Sr. inspector
Reliability eng.
Production man.
Insulation expert
Contractor/manufacturer

Corrosion team
**Contractor manufacturer supplier**

- **C.U.I. projects**
  - Existing / older installations:
    - Little history
    - Full scale dismantling insulation
    - Fix / renew coating
    - Install new insulation

**C.U.I. projects**

**Same Insulation System ??**

Can we learn from the past?

**Life Cycle Engineering & C.U.I**

**L.C.E. & C.U.I ??**
L.C.E. & C.U.I

Integration of abstractions
Integration over the life cycle
IDE Domain

Function
Structure
Shape/Form
Design

Integration of disciplines

How to Prevent C.U.I.

Design "fit-for-purpose" insulation SYSTEM

How to Prevent C.U.I.

How to Prevent C.U.I.

CINI manual

CINI = Guideline

The need for insulation expertise?
**Smart engineering**

**K I S S !**

Pipe line distance

Steel structures

Pipesupports

**Finding C.U.I.**

Inspection/Detection
- Direct
- Indirect
Finding C.U.I.

- Indirect
  - Guide Wave
  - Eddy Current pulsed wave
  - Incotest®

Finding C.U.I.

- Indirect
  - Thermografic

Finding C.U.I.

- Direct
  - Visual inspection
  - Dismantling insulation
  - VIP (Vessel Inspection Plug)

Finding C.U.I.

- Direct / Indirect
  - Leak detection
  - (Semi)permanent moisture detection
  - (Semi)permanent film thickness measurement

Why only inspect coating?

Inspection Quality

Insulation System

<table>
<thead>
<tr>
<th>Condition</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>1</td>
</tr>
<tr>
<td>Very good</td>
<td>2</td>
</tr>
<tr>
<td>Good</td>
<td>3</td>
</tr>
<tr>
<td>Moderate</td>
<td>4</td>
</tr>
<tr>
<td>Poor</td>
<td>5</td>
</tr>
<tr>
<td>Very poor</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial deterioration</th>
<th>Limited deterioration</th>
<th>Visible deterioration, no function loss</th>
<th>Occasionally impaired function</th>
<th>Advanced deterioration, irreversible function loss</th>
<th>Complete function loss</th>
</tr>
</thead>
</table>
**Insulation solutions for C.U.I.**

Insulation Systems
- "CLOSED" system
- "OPEN" system
- Non-Contact insulation

**Insulation materials**

1. Permeable
   - Mineral wool
   - Aerogel type
2. Impermeable
   - Cellular Glass
   - PIR/PUR
   - Phenolic Foam

**“CLOSED” System**
- Most implemented and traditional system
- Permeable insulation materials
- Non hygroscopic / water absorbing insulation material
- Cladding with sealed watertight joints
- 100% flashing of protrusions

**The right Sealant for the right application**
- Foster 95-44
- Kiiltoflex
- Gasket Sealant
- Foster 60-44

**Glass Reinforced Plastic (G.R.P.)**
- Watertight joints
- High mechanical resistance
- Stepping on insulation

**“OPEN” System**
- Permeable insulation material
- Non hygroscopic / water absorbing insulation material
- Cladding with watertight joints
- 100% flashing of protrusions
- Aircavity
- Drainage
Solutions for C.U.I.

- Tematol

Non-Contact System

Aircavity Inside

Insulation Solutions for C.U.I.

- PMU Drain Plug
- Protectem® Flangebelt™
- Foster® 57-73 Coating

C.U.I. challenges

Knowhow & solutions are at hand

Insulation solutions for C.U.I.

- Insulating coating
- Based on ceramic technology
- $\lambda > 0.03$ W/m.K
Change the mindset

Insulation Knowledge

Thank you for your attention

Johan Sentjens
Appendix 9

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

(G. Sielski - Sandvik)
Sandvik Materials Technology, EMEA
Grzegorz Sielski – Technical Marketing

EFC Working Party 15 Corrosion Refinery Industry Meeting
Paris, April 14th 2011

Sandvik – Global leader
Three business areas

Sandvik Tooling
Sandvik Mining and Construction
Sandvik Materials Technology

Sandvik Materials Technology
Global Presence

Market Areas
- Europe
- Africa
- Asia/Australia
- NAFTA
- South America
- Middle East

Sandvik Materials Technology

Sandvik Materials Technology

Outline
- Introduction to SAF 2707 HD®
- Mechanical properties
- Physical properties
- Corrosion properties
  - Localized corrosion
  - General corrosion
- Summary

Sandvik Materials Technology

High-technology special alloy materials and value-added products, developed in close co-operation with customers

Tube, strip, wire, resistance materials and process systems

Mechanical properties, physical metallurgy, and corrosion resistance of the Hyper Duplex Grade SAF 2707 HD®
Introduction

- Long experience with super duplex stainless steel in oil and gas, petrochemical and chemical processing
- Good properties:
  - High corrosion resistance
  - Good mechanical properties
  - Relative low cost
- Super Duplex does not corrode in seawater at low temperature, but there are limitations at higher temperatures
- Clear desire for a new duplex grade with increased corrosion resistance in chloride environments
  - Hot tropical seawater

Goals for the new grade

- PRE ≥ 50
- CPT ≥ 100°C in 6% FeCl₃ (Critical Pitting Temperature)
- CCT ≥ 60°C in 6% FeCl₃ (Critical Crevice Temperature)
- Good mechanical properties
- Weldable

Development of Duplex Stainless Steels

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

Nominal Chemical Composition

<table>
<thead>
<tr>
<th>Grade</th>
<th>UNS</th>
<th>%C max</th>
<th>%Cr</th>
<th>%Ni</th>
<th>%Mo</th>
<th>%N</th>
<th>PRE* Nominal</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF 2507</td>
<td>S32750</td>
<td>0.03</td>
<td>25</td>
<td>4</td>
<td>0.3</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>SAF 2707HD</td>
<td>S32707</td>
<td>0.03</td>
<td>27</td>
<td>6.5</td>
<td>5</td>
<td>0.4</td>
<td>49</td>
</tr>
<tr>
<td>254 SMO</td>
<td>S31254</td>
<td>0.02</td>
<td>20</td>
<td>18</td>
<td>6.1</td>
<td>0.2</td>
<td>43</td>
</tr>
</tbody>
</table>

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

Microstructure

- 50% ferrite
- Well-balanced composition
- Similar PRE number in the two phases
- Within 1 PRE unit in average

Mechanical properties
Proof strength

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Rp0.2 [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>150-200</td>
</tr>
<tr>
<td>100</td>
<td>250-300</td>
</tr>
<tr>
<td>200</td>
<td>350-450</td>
</tr>
<tr>
<td>300</td>
<td>550-650</td>
</tr>
</tbody>
</table>

Tensile strength

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Rm [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>500-600</td>
</tr>
<tr>
<td>50</td>
<td>700-800</td>
</tr>
<tr>
<td>100</td>
<td>900-1000</td>
</tr>
</tbody>
</table>

Elongation and hardness

<table>
<thead>
<tr>
<th>Elongation A [%]</th>
<th>A2</th>
<th>Hardness HRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical values</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Min values</td>
<td>25</td>
<td>32</td>
</tr>
</tbody>
</table>

Impact strength

Impact test of SAF 2707 HD in the temperature range -150°C to 100°C

High temperature

- At higher temperatures 250-300°C for longer period
- Heat-exchanger tubes can often be used at higher temperature
- Contact Sandvik for more information at specific cases

Physical properties
Physical properties
- Density: 7.8 g/cm³
- Resistivity: 0.75 µΩm at 22°C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Modulus of elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>178</td>
</tr>
<tr>
<td>300</td>
<td>166</td>
</tr>
</tbody>
</table>

Corrosion properties

Pitting corrosion

Potentiostatic test

"Green Death"
- 1% FeCl₃ + 1%CuCl₂ + 11%H₂SO₄ + 1.2% HCl
**Bending**

- Bended tube also has a CPT of 97.5°C

**Natural sea water at OCP pitting corrosion**

- No pitting corrosion were found visually
- No indication on pitting from the potential measurements

<table>
<thead>
<tr>
<th>50°C</th>
<th>65°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>OK</td>
<td>Not measured</td>
<td>OK</td>
</tr>
<tr>
<td>OK</td>
<td>OK</td>
<td>OK</td>
</tr>
</tbody>
</table>

**Natural sea water at OCP crevice corrosion**

- No corrosion were found visually
- No indication on corrosion from the potential measurements

<table>
<thead>
<tr>
<th>50°C</th>
<th>65°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>OK</td>
<td>Not measured</td>
<td>OK</td>
</tr>
<tr>
<td>OK</td>
<td>OK</td>
<td>OK</td>
</tr>
</tbody>
</table>

**Stress Corrosion Cracking**

- Autoclave
- 100 bar
- 8 ppm O₂
- Load = proof strength
- NaCl-solution
- 1000th (6 weeks)

**Acetic acid**

<table>
<thead>
<tr>
<th>Temperatures, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>

**Formic acid**

<table>
<thead>
<tr>
<th>Temperatures, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>
**Summary**

- Sandvik have developed a Hyper duplex stainless steel which is a new generation of duplex material
- **SAF 2707 HD**
  - PRE 49 – well balanced structure
  - CPT 97.5°C
  - CCT 70°C
- **Goals for the new grade**
  - PRE \(\geq 50\)
  - CPT \(\geq 100°C\)
  - CCT \(\geq 60°C\)
- **Good mechanical properties**
  - Proof strength 800 MPa (typical value at room temperature)
  - Tensile strength 1000 MPa (typical value at room temperature)
  - Elongation over 25% in quenched annealed condition
  - Good impact strength

**SAF 2707 HD welding**
Welding

- Filler material: Sandvik 27.9.5.L
  - Increased %Ni compared to base metal
- Gas shielded welding (TIG/GTAW)
  - Use 2-3% N₂ in the shielding gas
- Recommended welding parameters:
  
<table>
<thead>
<tr>
<th>Limit</th>
<th>Preheat</th>
<th>Interpass temperature</th>
<th>Heat Input</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not applicable</td>
<td>&lt; 100 C (212 F)</td>
<td>0.2 – 1.5 kJ/mm</td>
</tr>
</tbody>
</table>

All weld metal - Properties

- TIG welding with Ar + 2%N₂
- Tensile properties
  
  Typical values
  
<table>
<thead>
<tr>
<th>Sandvik 27.9.5.L TIG all weld metal</th>
<th>Rₚ₂, MPa</th>
<th>Rₚ₅, MPa</th>
<th>A, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>950</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

  - %Ferrite: 30 – 70 %
  - G48C CPT = 77.5°C

Refinery application

Oil Refining

Application Example: Oil Refinery

- Pump around heat exchanger - atmospheric distillation unit - USA
  - History:
    - C-steel: Service life of 9 months
    - Upgrade for SAF 2507. Successful in most heat exchangers, but operating close to limit. Pitting observed in the most severe locations, and one bundle experienced cracking (traced back to fabrication faults)
    - 2003: SAF 2707 HD installed in one complete bundle

Application Example: Oil Refinery

- Atmospheric crude distillation, overhead system aircoolers - Europe
  - History:
    - C-steel: Service life maximum 2 years
    - SAF 2707 HD tubes with external Al fins installed
    - Inspection after one year in service: Tubes in excellent condition
Application Example: Oil Refinery

- Overhead condensers in refinery CDU unit - Europe
- History
  - C-steel: Service life 5-7 months
  - SAF 2707 HD installed in Jan 2006

Application Example: Sea water

- Seawater cooled heat exchanger in the Middle East
- Shell side: Condensing HC => HCl dewpoints, deposits
- Tube side: Seawater, with temperature up to 70°C (158°F)

Conclusions

Sandvik SAF 2707 HD has:

- Excellent resistance to pitting and crevice corrosion in Cl-containing environments. Same is valid for SCC.
- Very high resistance to organic acids.
- High mechanical properties, allowing design and cost advantages.
- Good weldability.
- Excellent performance has been verified in a number of process plant heat exchanger installations.

Questions ?????

Thank you!
Appendix 10

3D Trasar for boiler technology

(V. Beucler - Nalco)
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.
Nalco’s 3D TRASAR Technology: System Protection through On-line Control

- **Detect** system variability
  - Nalco Corrosion Stress Monitor (NCSM)
  - TRASAR internal treatment control
  - Direct measurement assures appropriate response

- **Determine** appropriate response
  - Compares system condition to desired condition
  - Adjusts system control immediately before problems occur

- **Deliver** 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
What is 3D TRASAR Boiler Technology? ...

Cost Effective & Upgradeable Boiler Performance Automation
- Advanced monitoring & control
- Performance sensors
- Traced chemistry
- Communication of results

Phase 1 - Feedwater Automation Platform

Performance Management for Boiler Systems
What is 3D TRASAR Boiler Technology? …

Phase 2 – Upgradeable & Customizable

Until Recently, control of boiler chemistry looked like this … “test and adjust”

- Gather sample
- Test
- Adjust chemical feed
- “Repeat as necessary”
3D TRASAR Boiler Scale Control offers on-line, real-time control

Automatically responds

Directly measures and maintains optimum treatment levels

Keeps your boiler clean

Compare this to …
• Take test …
• Adjust pump …
• Take test next day…
• Adjust pump

24/7 TARGETED CONTROL

<table>
<thead>
<tr>
<th>MANUAL CONTROL</th>
</tr>
</thead>
<tbody>
<tr>
<td>TARGET</td>
</tr>
<tr>
<td>AVG</td>
</tr>
<tr>
<td>Std. Dev</td>
</tr>
<tr>
<td>3 SIGMA</td>
</tr>
<tr>
<td>OFFSET</td>
</tr>
<tr>
<td>TIME</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3D TRASAR CONTROL</th>
</tr>
</thead>
<tbody>
<tr>
<td>TARGET</td>
</tr>
<tr>
<td>AVG</td>
</tr>
<tr>
<td>Std. Dev</td>
</tr>
<tr>
<td>3 SIGMA</td>
</tr>
<tr>
<td>OFFSET</td>
</tr>
<tr>
<td>TIME</td>
</tr>
</tbody>
</table>
LARGE STEAM LOAD SWINGS

540% STEAM LOAD SWINGS

Taking a closer look ...

Pre-Boiler Corrosion Control

Controller

Nalco Corrosion Stress Monitor (NCSM)
Preboiler Corrosion Control Vision

Chemical | MOC
Indirect ► Direct
Residuals ► DA Inspections ► O₂ Monitoring ► Fe Testing ► NCSM (Nalco Corrosion Stress Monitor)
1940s ► Future

NALCO

Preboiler Corrosion Control
NCSM Technology

• **Measures** Corrosion stress
  – Oxidation-Reduction Potential (ORP) measures multiple simultaneous corrosion mechanisms
  – Measures all chemical factors in the feed water that could influence a corrosion reaction

• **Detects** variations from desired state

• **Responds** real-time
  – Varies oxygen scavenger feed
  – Maintains ideal reduced, low corrosion state

• **Communicates** via controller and web
Today we have fixed feed rates regardless of the boilers water’s potential to corrode.

**3D TRASAR Preboiler Corrosion Monitoring**

- Corrosion due to oxygen in feedwater
- Typical Corrosion Control
  - High Potential
  - Low Chemical Treatment
- Underfeed Results in Corrosion
- Overfeed leads to Excess Treatment Costs

**Feedwater Corrosion Stress Event**

*NCSM Monitoring Data*

- MANUAL CONTROL of SULFITE SCAVENGER DOSAGE
- Next Shift Operator realizes mistaken lack of sulfite feed to the FW. Sulfite treatment feed is restarted to reduce the FW corrosion stress.
- UNDER MANUAL CONTROL: HUMAN ERROR WILL OCCUR AT SOME POINT
- Operator turns off sulfite feed because BW sulfite residual remains over the target range.
- Operator reduces sulfite feed because BW sulfite residual is over the target range.
- S.O.P. at utility changed in January. NEVER go to zero feed of sulfite, no matter what the BD residual concentration is.

Corrosion damage could occur here!
Communication of Results

3D TRASAR Web is...
- Convenient for both customer and Nalco Rep
- View all systems
- Displays performance detail
- Printable, receive via e-mail
- Downloads to PC for advanced data analysis
- Alarming

New Best Practice for Preboiler Corrosion Control

Nalco Corrosion Stress Monitor (NCSM)
- Performance-based control of corrosion stress
- Maintains Reduced Conditions
- Minimizes corrosion

Customer Value
- Safety, Reliability
  - Minimizes failures
  - Maximizes reliability & availability
- Minimize Cost
  - Reduces iron deposits to promote energy efficiency
  - Minimizes downtime & repair cost
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)
GE Energy - Inspection Technologies
GE Energy – Water & Process Technologies

**Rightrax + Predator**
Effectively Manage Corrosion Rates for HAC

Claudia LAVERDE
GE IT - Product Leader
Alain POTHUAUD
GE W&P - Technical Manager

---

**Why Rightrax is used**

**Aging**
- Most assets are old
- Corrosion rates are ~40y old
- Increased inspection requirements

**Cost**
- Inspections are expensive
- Corrosion abatement is expensive
- Loss of production is biggest cost factor

**Safety**
- HSE is expensive
- Safety comes first
- Dangerous site access

**Image**
- Image damage to company if accidents happen
- Multi million dollar fines

---

"And improved data quality!"
Where Rightrax is used

Access
- Building scaffolding
- Removing insulation
- Buried pipelines

Hazard
- Chemical areas
- Heat
- Radiation
- Height
- Explosion

Remote
- Offshore facilities
- Deserts facilities
- Jungle facilities
- Arctic facilities

Process
- Corrosion
- Erosion

Product versions

Flexible array (LT)
- Both manual and integrated version
- Flexible array with 24 individual transducer elements
- Glued to the object
- Repeatability up to ±0.3mm / ±0.004"
- Wall thickness 5mm to 100mm / 0.2" to 3.9"
- Pipe sizes 6" and over, and flat surfaces
- Operational temperature -40°C up to 120°C / 248°F
- Certified for ATEX zone 2 and IECx

Advantage:
- Non intrusive, easy installation
- Array coverage of effected area

High temperature (HT)
- Both manual and integrated version
- Single point transducer with delay line
- Clamped to the object
- Repeatability up to ±0.0025mm / 0.001"
- Wall thickness 3mm to 16mm / 0.12" to 0.6"
- Pipe sizes 3" up to 42"
- Surface temperature -20°C up to 350°C and 500°C / 662°F and 932°F
- Certified IS for use in zone 1 area’s

Advantage:
- Non intrusive, easy installation
- Process related events due to high resolution
Online Corrosion Monitoring
Two product lines for corrosion and wall thickness monitoring available

Rightrax Flex
-40°C up to 120°C
Upstream/Midstream Low Temp

Rightrax HT
-10°C up to 350°C / 500°C
Downstream High Temp

Predator

Prediction
What to Expect and How to Manage It

Protection
Chemistry and Application Control

Detection
Fastest and Most Accurate Measurement

Predator is the GE patented platform to process and manage High Acid Crudes, based on 3 fundamental platforms: Prediction, Protection, Detection

Risk must become an opportunity
**Why Predator?**

**Example of profitability $**

- 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$

---

**High Acid Crude Management**

**Prediction**
- Risk assessment
- Nap Acids repartition depend directly from crude quality
- Experience & lab testing is mandatory

**Protection**
- Low phosphorus patented chemistry to create film on metal surface
- Low P to prevent fouling issues
- Iron P technology to avoid issues with catalyst poisoning

**Detection**
- Corrosion probes
- Fe, Ni and ratio
- TAN, NAR, Sol...
Case Study – Nap Acid Crude Monitoring

Risk assessment made on site with
- Operators
- Technology
- Inspection

Analysis to determine corrosivity of crudes
- TAN, NAN, Fe, Ni...
- Corrosion rates on autoclave
- Experience

Inhibitor injection program depending on
- Acid crude to process
- % in crude slate
- Circuit

Monitoring
- Fe/Ni ratio
- Corrosion probes
- Rightrax

Record each month
- Wall thickness
- Corrosion rate

Help to optimize treatment
- Prefilming
- Dosage according to conditions
Other Applications

FCCU overhead
- High pH corrosion in wet environment
- Filming inhibitor injected in water wash

Wet Sour Gas Treater
- Filming inhibitor efficiency control