Appendix 1

List of participants and excused persons

Participants EFC WP15 meeting 13th September 2007 Freiburg

Name	Surname	Company	Country
Claesen	Chris J	Nalco	BELGIUM
de Bruyn	Hennie	Borealis AS	NORWAY
Gonzalez-Barba	Maria Luisa	Baker Petrolite	SPAIN
Groysman	Alec	Oil Refineries Ltd	ISRAEL
Hofmeister	Martin	Bayernoil Raffineriegesellschaft mbH	GERMANY
Hucinska	Joanna	Gdansk Technical University	POLAND
Invernizzi	Andrea	University of Milan	ITALY
Isaak	György	MOL Hungarian Oil & Gas Co	HUNGARY
Lorenz	Maarten	Shell Global Solutions International B.V.	NETHERLANDS
Loukachenko	Natalia	Industeel	FRANCE
Maffert	Joerg	Dillinger Huttenwerke	GERMANY
Michvocik	Miroslav	SLOVNAFT	SLOVAKIA
Munier	Michel	IFP Technology Group - AXENS	FRANCE
Ropital	Francois	IFP	FRANCE
Scanlan	Rob	Conoco	UK
Surbled	Antoine	Couronnaise de Raffinage	FRANCE
Trasatti	Stefano	University of Milan	ITALY
Turnbull	Alan	National Physical Laboratory	UK
Visgaard Nielsen	Anni	Statoil Refinery, Kalundborg,	DENMARK
Volden	Lars	Statoi ASA	NORWAY
Winnik	Stefan	Exxon Mobil Chemical	UK
Zetlmeisl	Mike	Baker Petrolite	SPAIN

Excuses received for the EFC WP15 meeting 13th September 2007 Freiburg

Name	Surname	Company	Country
Aiello	Carmelo	Eni	ITALY
Christensen	Curt	Force Institutes	DENMARK
Davies	Michael	CARIAD Consultants	GREECE
Holmquist	Martin	AB Sandvik Steel	SWEDEN
Lanfant	Mathieu	SOFRAP	FRANCE
MeLampy	Michael	Hi-Temp Coatings Technology	USA
Peultier	Jerome	Industeel	FRANCE
Richez	Martin	Total	FRANCE
Riva	Roberto	Eni R&M	ITALY
Rommerskirchen	Iris	Butting Edelstahlwerke GmbH&Co KG	GERMANY
Saarinen	Kari	Zerust Oy	FINLAND
Surbled	Antoine	Couronnaise de Raffinage	FRANCE
Urke	Hildegunn	Statoil ASA	NORWAY

Appendix 2

EFC WP15 Activities

Presentation of the activities of WP15

European Federation of Corrosion (EFC)

- Federation of 34 National Associations
- 19 Working Parties (WP)
- Annual Corrosion congress « Eurocorr » in September
- Thematic workshops and symposiums
- Working Party meetings (for WP15 twice a year)
- Publications
- EFC - NACE agreement
- for more information http://www.efcweb.org

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
- WP 16: Cathodic protection
- WP 17: Automotive
- WP 18: Tribocorrosion
- WP 19: Corrosion of polymer materials
- WP 20: Corrosion and corrosion protection of drinking water systems

WP 15 was created in sept. 96 with J. Harston as first chairman

EFC Working Party 15 « Corrosion in Refinery » Activities

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

Web site actually minutes of the last WP meetings
(developments to be proposed)

http://www.efcweb.org/WP_on_Corrosion_in_the_Refinery_Industry.html

EFC Working Party 15 plan work 2007-2009

. Appointment of a WP15 Deputy Chairman

· Task force an Corrosion Under Insulation lead by Stefan Winnik: Document EFC 55

· Failure cases atlas : living data base

· Cooling water treatment:
Creation of a task group of WP15 members to cooperate with EFC WP1 and NACE on publication of update or new documents

. Stress relaxation cracking: proposal of a guideline to prevent these failures

. Possible session with NACE at Eurocorr 2008 in Edinburgh "Detailed case study on RBI" contact with De Yuan Fan STG34 ?

. Session with WP1 (inhibitors) at Eurocorr 2008 in Edinburgh "Naphthenic acid corrosion" (proposal of WP1 group) partly dedicated to investigation and testing methods

EFC WP15 Annual Meeting 13 September 2007 Freiburg

Publications

• 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 documents by a task group from WP1 + WP15 + Nace
11106 "Monitoring and adjustment of cooling water treatment operating parameters" from Task Group 152 on cooling water systems and

24230 "Biocide monitoring and control in cooling towers" from Task Group 151 on biocide monitoring and control techniques

• 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

•Future publications
- compilation of papers from Workshops (naphtenic acid corrosion ?)
- other suggestions ?

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
Presentation of EFC WP15 activities by Rob S. during Nace STG meetings
New proposal: Presentation of STG activities during WP15 meetings

Appendix 3

External corrosion control program at the Humber Refinery

Rob Scanlan (Conoco Phillips)

External Corrosion Control Program

By

Rob Scanlan

EFC Conference - 13th September 2007

External Corrosion Control Program

- CUI & external corrosion is a major issue for the Humber Refinery.
- In recent years, the refinery has experienced several failures.
- External Corrosion Control Program instigated;
  - Thorough review of the equipment history.
  - Field survey of all areas in the refineries.
  - Consultation with experienced operational personnel.

External Corrosion Control Program

- The outcome of the assessment was a list of vessels and areas of piping most prone to CUI/External Corrosion.
- The areas of piping have included the following:
  - Priority list of vessels.
  - Whole piping units in critical areas.
  - Pipe-rack sections within a unit or across units.

External Corrosion Control Program

Refurbishment work included the following;

- 100% removal of the insulation on the priority vessels.
- 100% removal of insulation on piping to allow for CUI inspection and repair in critical areas.
- Inspection of painted lines in piperack, inspection includes lifting of lines to inspect for corrosion under the pipe supports.
- Sample inspection of less critical areas.

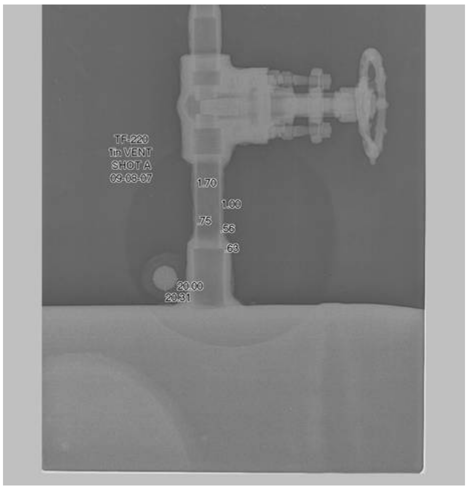
FCC Feed Drum

Sour Water Stripper

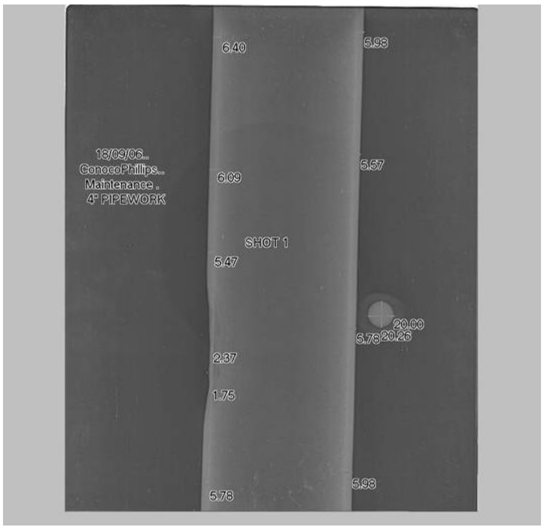
Aromatics Extraction Unit – Recovery Unit

3” Benzene Export Line


Naptha Vent Line



3” Hydrogen High Pressure Line



ECCP - Findings

Description	Grit Blast & Paint	Weld Repairs	Replaced	Total
Vessels	89	24	5	118
Piping	12	0	11	23
Total 2006	**74**	**20**	**9**	**103**
Total 2007	**27**	**4**	**7**	**38**

Appendix 4

How to use the

EFC WP15 Refinery Cases Web page

How to use http://project.ifp.fr/cui-efc-wp15

for collecting and consulting the corrosion failure cases atlas

Version 1 Revision 0 date 31 August 2007

Summary

1 Objectives of the web area

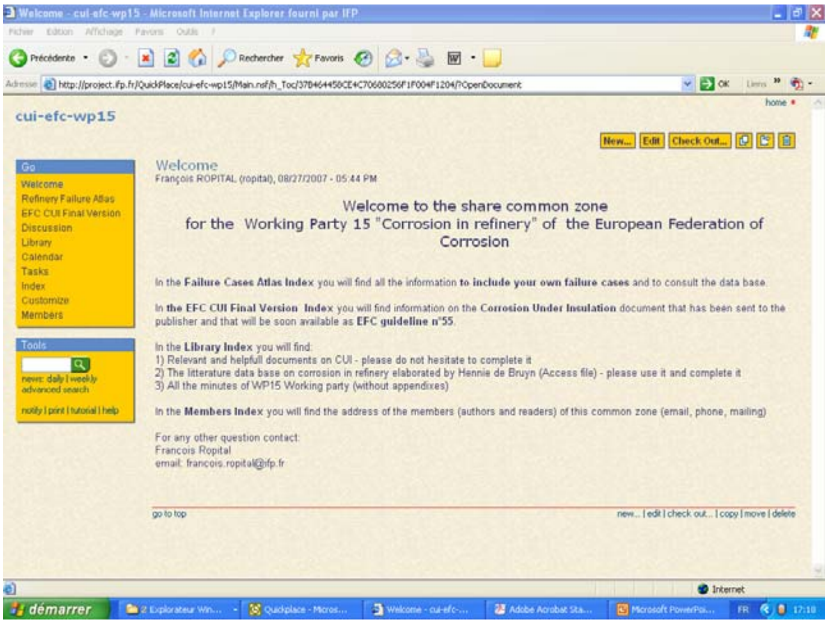
The aim of this web area is **to collect and consult typical corrosion failure cases of the refinery industry in order to share experiences** . If you want to be a member of the group you should send a email to Francois Ropital (francois.ropital@ifp) : a username and password will then be sent to you (see section 6).
The members can consult the database and add their own typical cases. Documents can be downloaded and incorporated

2 Connexion

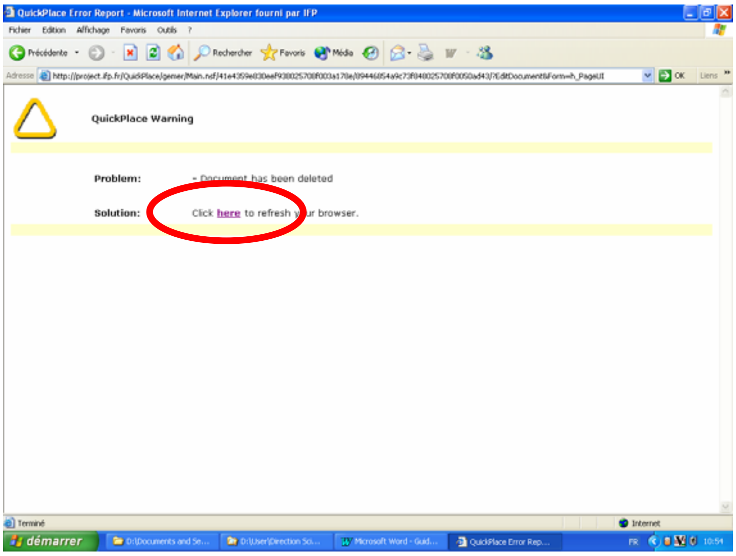
The address is: http://project.ifp.fr/cui-efc-wp15

The following window appears:

You have to enter the username that has been sent to you and your password. The following window appears that give you the content of the web pages:



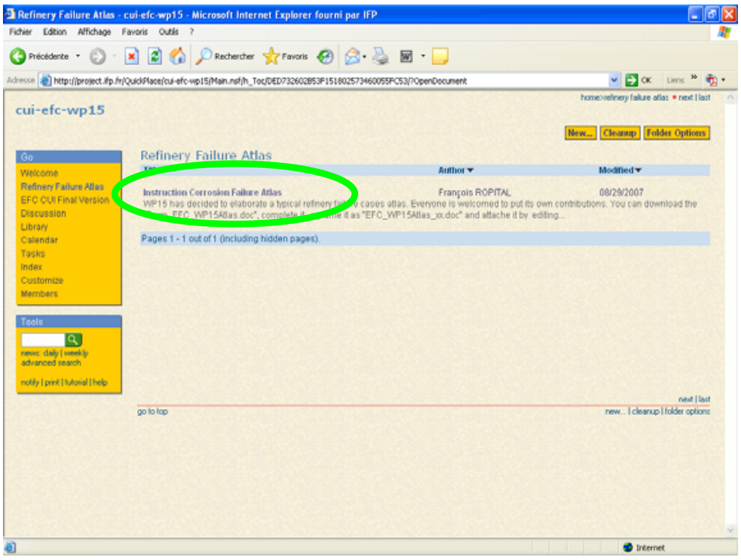
If you use a destroyed page link, the following window can appear after your connexion: :



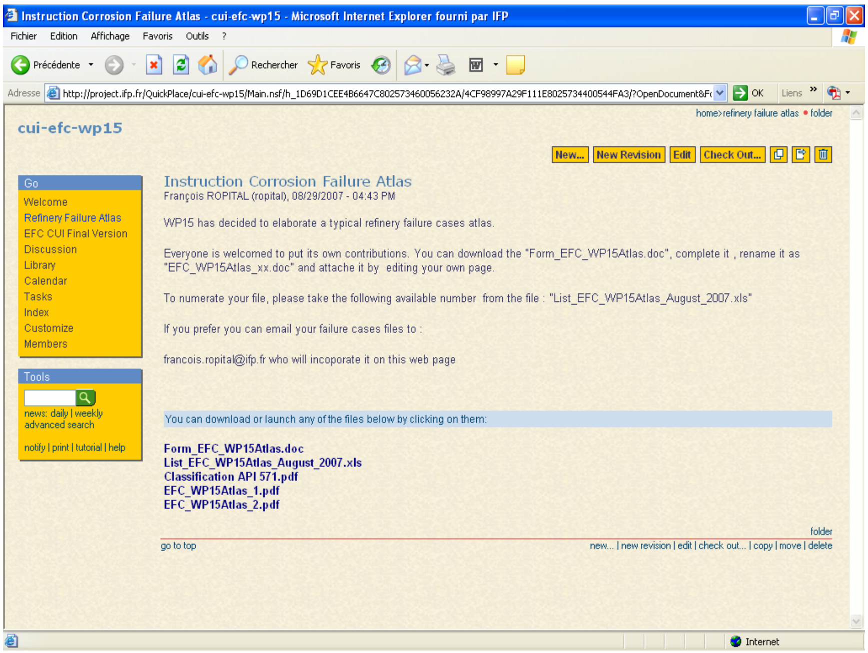
To access to the welcome page , clicks as indicated on this copy of the screen.

3 Access to the corrosion failure atlas folder:

When you click on "Refinery failure atlas" you access to the folder:



To consult the failure files and to download them (and also some reference documents) you click on "Instruction Corrosion Failure Atlas" line:



You can download the following document:
"Form_EFC_WP15Atlas.doc" that an empty form to be completed if you want to include another failure cases in the data base (1 failure case / file)

Form_EFC_WP15Atlas.doc

"List_EFC_WP15Atlaus date.xls" is an Excel file with the list of the failure cases. If you want to include another failure case, name it with the next free file number (the file will be regularly updated by Francois Ropital).

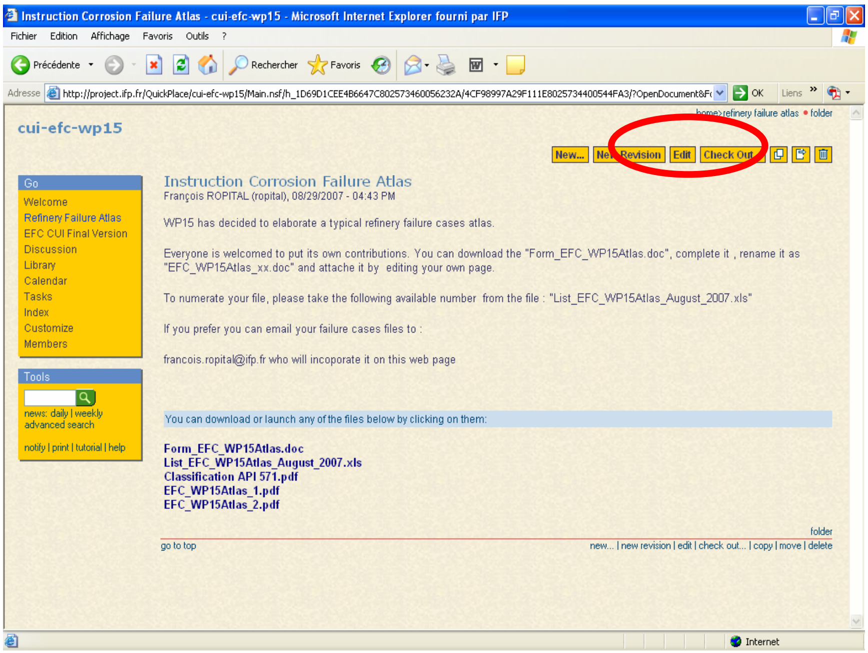
"Classification API 571.pdf" to help you to find the proper API classification number for your failure(s) case(s).

Classification API
571.pdf

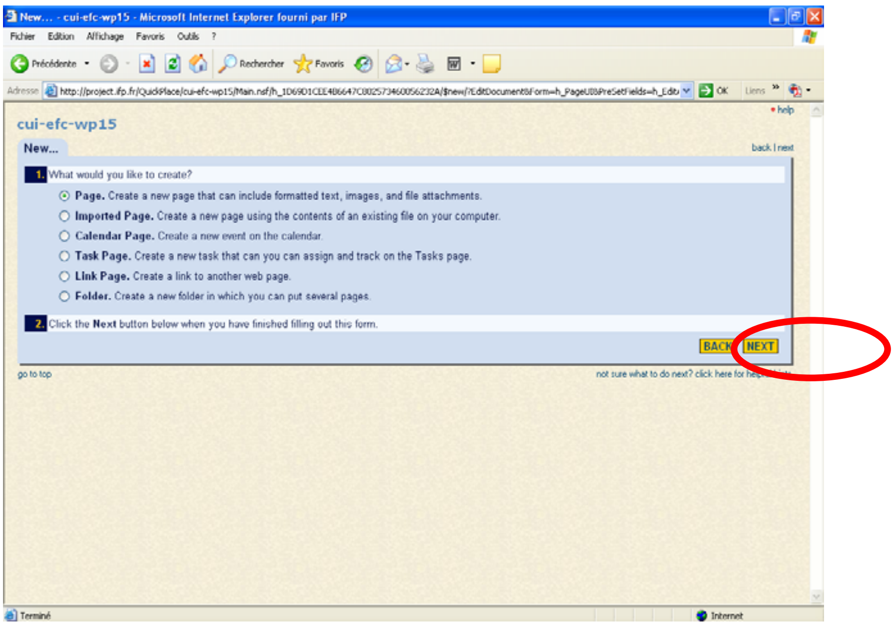
"EFC_WP15Atlas_x.pdf": the file for failure case n°x.

4 How to incorporate your failure cases.

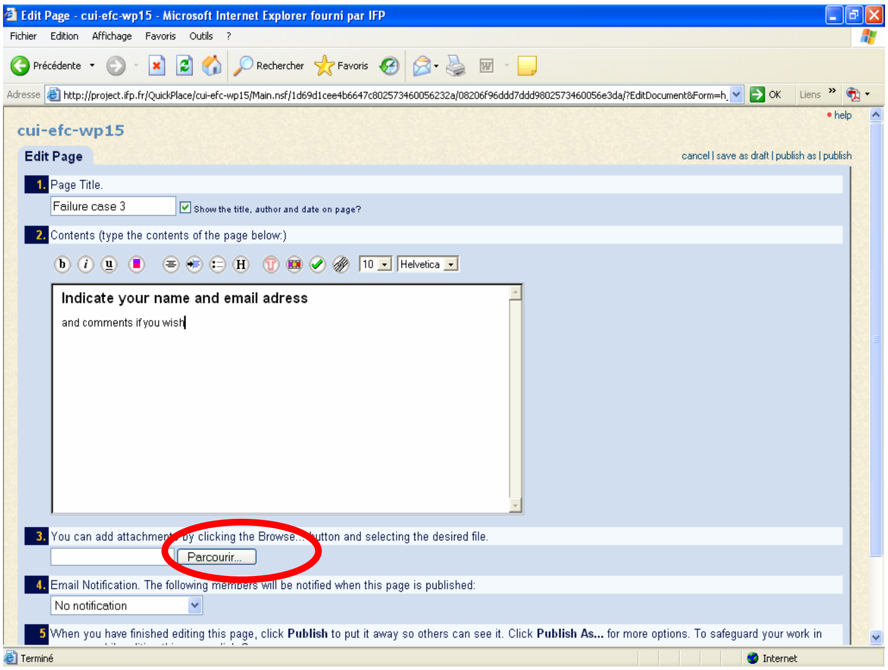
To incorporate your failure case file you have to edit a new page by clicking on "Edit"



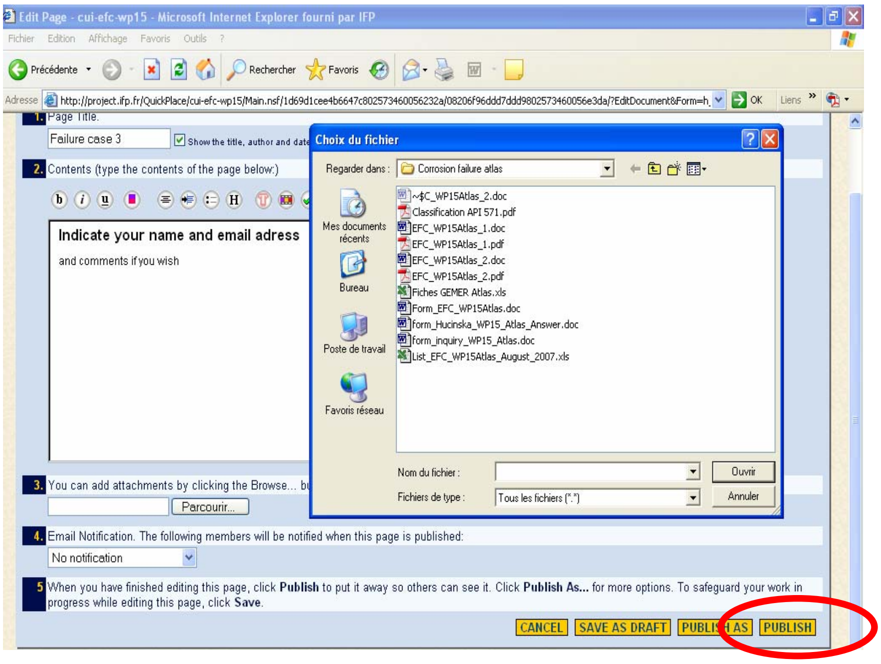
The following page will appear and file it as mentioned:



You have to create a **page.**

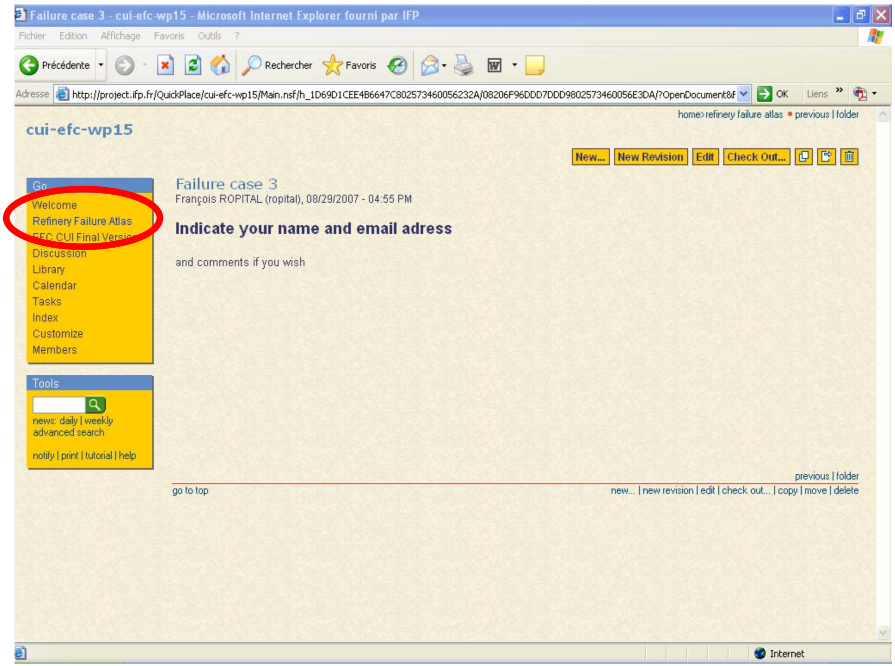


Then you have to complete your page:
1-Title: "Failure Case n°x"
2-Content: indicate your name, email address and any comment you like.
3-Attache your file "EFC_WP15Atlas_x.doc" (a Word file is preferred if further editing processing is required) by clicking on "Parcourir".

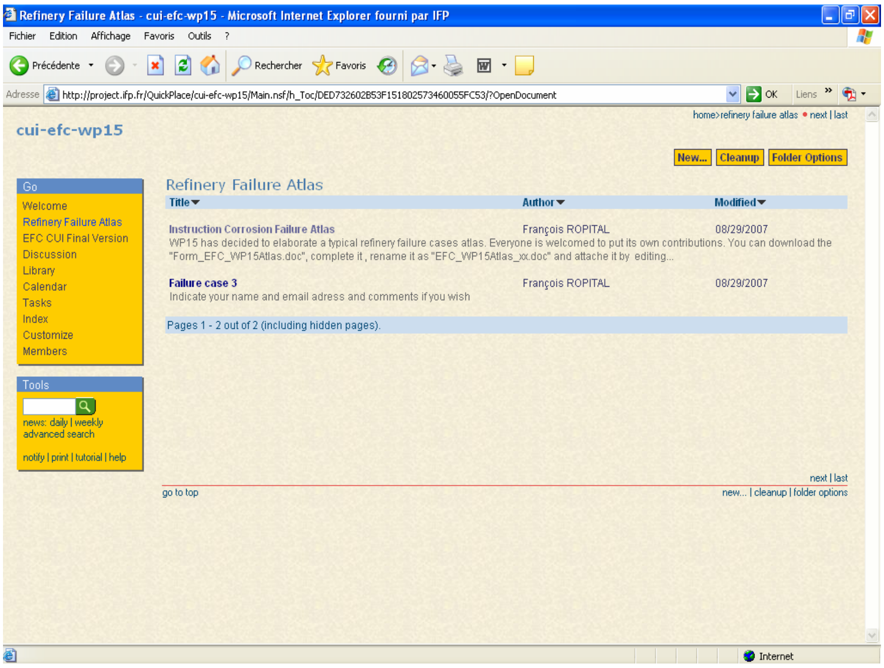


4- Email notification if you want to inform members of the group that you have include a new failure case.
5- Click on "Publish" to publish your page

Your new page appears then on the screen:



To go back to the "Refinery Failure Atlas" folder click on the indicated line in the yellow box. Your failure case is included in the data base

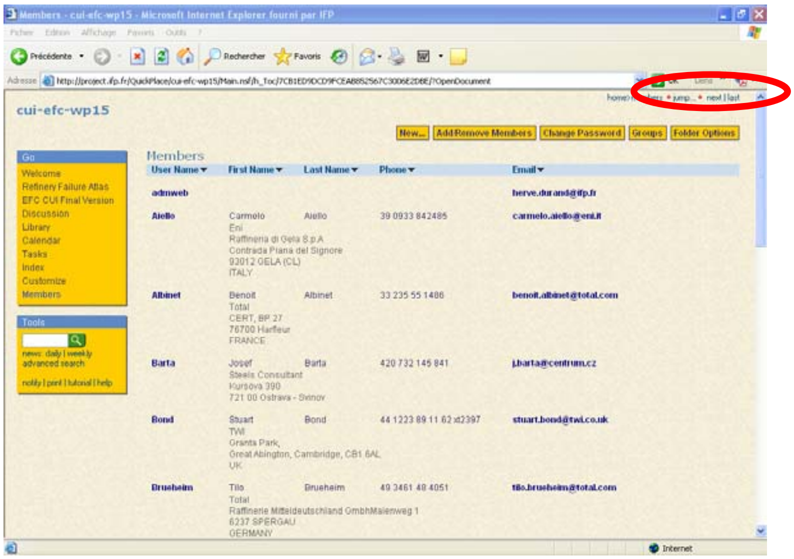


5 Change of your own password

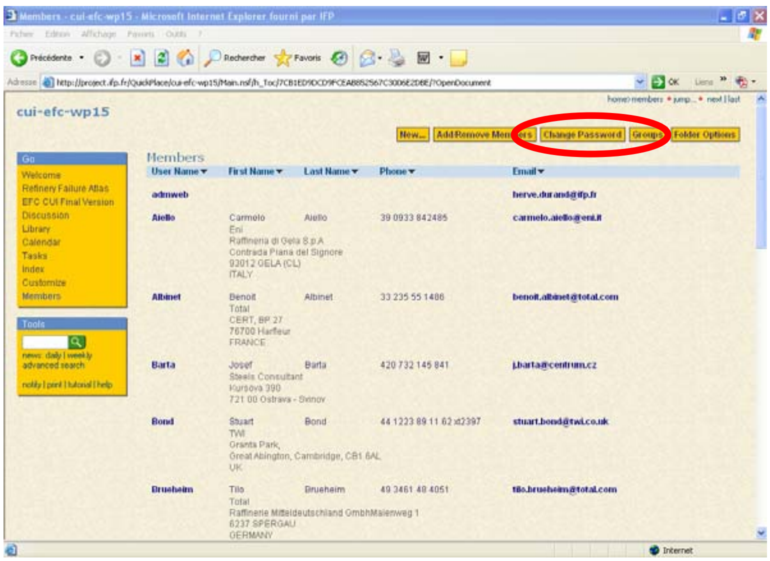
We advise you to change the password that has been attributed by the webmaster. For this you have to open the "members" page:

By clicking on Members
you have access to the Members page

The following screen appears:
Remark: the list of all the members is on several pages. To access to the other pages click on next or previous or last .



If you click on your name you can modify your address and change your password



6 Contact :

For any question contact

Francois Ropital email: francois.ropital@ifp.fr
Phone: 33 4 78 02 20 16
Fax: 33 4 78 02 21 41

Appendix 5

Cracking on the fireside of a gasoil heater

Anni Visgard Nielsen (Statoil)

CORROSION IN REFINERY INDUSTRY FAILURE ATLAS

CASE HISTORY n° 3 Date 17 September 2007

Hydrodesulfurizer Unit
Gas oil heater

DATE OF INCIDENT AND/OR INFORMATION:
from Anni Visgard Nielsen (Statoil) at EFC WP5 meeting 13/09/2007

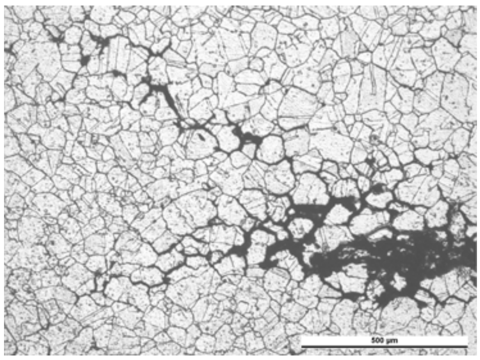
NATURE OF THE INCIDENT :
several longitudinal cracks on the fire side of heater tube some of them near HAZ. The ones near HAZ were penetrating the tube.

CONSEQUENCES : Retubing of both convection and radiant coil.

MATERIAL COMPOSITION and REFERENCES: AISI 304 Stainless Steel

PICTURES AND SCHEMES :



ASPECT : SS304 tubing is fully sensitized. Replica taken on several positions did show intergranular cracks. Some of them were not very deep. Green deposits containing high amount of sulfur and iron with some nickel and chromium have been observed.

MEDIA AND OPERATING CONDITIONS: The sulfur content in the fuel gas was 50 – 200 ppm
Poor combustion practices due to wrong measures for oxygen content forming a reducing atmosphere in the heater.

TIME TO DETERIORATION : near HAZ: during one TA. Others: doubt about if it is from one or two TA

CORROSION IN REFINERY INDUSTRY FAILURE ATLAS

CASE HISTORY n° 3 **ANSWER**

TYPE OF CORROSION : Polythionic acid corrosion

API 571 CLASSIFICATION: 5.1.2.1

CAUSES :

Polythionic acid corrosion is suspected due to the detection of a sulfur layer on the outside faces of the tubes and to the highly sensitisation of the 304 stainless steel. Probably because of poor combustion practices leading to a reducing atmosphere in the heater.

REMEDY :

Retubing to similar material (SS 304) and major repair of heater casing. Oxygen sensor moved from above convection zone to below convection zone.

PUBLICATION - TECHNICAL REPORT: -

BIBLIOGRAPHIC REFERENCES :

NACE Standard RP 0170-2004 Protection of austenitic stainless steels and other austenitic alloys from Polythionic Acid Stress Corrosion Cracking during shutdown of refinery equipment.

Appendix 6

Water wash injection point failure in a saturated gas plant

Rob Scanlan (Conoco Phillips)

ConocoPhillips

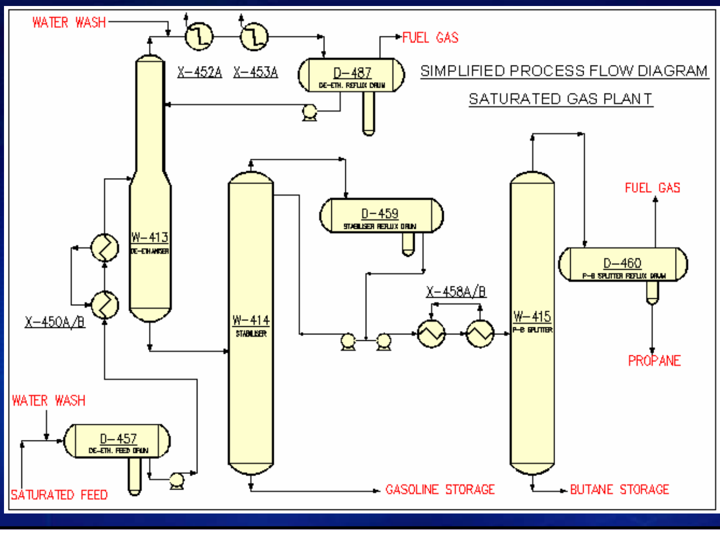
Determination Of The Corrosion Mechanism For A Water Wash Injection Point Failure In A Saturate Gas Plant

Rob Scanlan, Ricardo Valbuena & Dave Hughes
ConocoPhillips
&
Dannie Clarida
CorrMat International

Agenda

- The Saturate Gas Plant (SGP) Incident.
- The SGP Design/Operation/Inspection Requirements.
- Corrosion Mechanism Of Failure.
- Rebuilding The SGP.
- Corrosion Control Program Development.
- Conclusions.

The Saturate Gas Plant



The Saturate Gas Plant (SGP) Incident

- On 16th April 2001, an explosion and fire occurred at the ConocoPhillips Humber Refinery.
- A 6” pipe carrying flammable gases failed just after an intermittent water wash location on the De-Ethanizer Overhead system.

The Saturate Gas Plant (SGP) Incident

The SGP Design/Operational Basis

- The original design included a water wash for the feed stream.
- Soon after commissioning, an additional water wash was installed in the De-ethanizer overhead system.
- In 1984, a static mixer/quill was installed on the feed stream.
- Further modifications to the water wash were made in 1992 & 1994 increasing the water wash rate to 20 usgpm.
- The exact operation of the De-ethaniser overhead water wash could not be confirmed i.e. intermittent or continuous.

The Saturate Gas Plant Inspection History

- The De-ethaniser tower, & overhead equipment had received extensive inspection with some of the overhead equipment being replaced.
- The RBI analysis of the SGP piping was completed in Nov 2000.
- The system inspection was planned for July 2001. Unfortunately the pipe failed in April 2001.
- For reference, the point of failure had not been identified in the RBI analysis as an active injection point.

Corrosion Mechanism Of Failure

Physical Evidence

- The corrosion morphology indicated an aqueous phase running along the bottom of the pipe/outside of bend.
- No sulphide scale was evident at the thinned area of the pipe downstream of the water injection location.
- Black scale was evident further downstream of the failure indicating the presence of a protective iron sulphide film.

Corrosion Mechanism Of Failure

Corrosion Mechanism Of Failure

- The corrosion was caused by **ACIDIC SOUR WATER** due to presence of hydrogen sulphide (H_2S) in the aqueous phase.
- High system pressure (380psig) leading to high H_2S partial pressure.
- Low ammonia content in overhead system and sour water.
- H_2S content in sour water producing low pH.

Corrosion Mechanism Of Failure

- Initial considerations of Ammonium Bisulphide or Chloride attack were dismissed due to process conditions.
- The feed water wash system removed virtually all the ammonia and chloride.
- These findings were confirmed using specialised laboratory techniques & commercial software modelling.
- This phenomenon is believed to be unique in the refinery industry.

Industry Perspective

- Aqueous acidic hydrogen sulphide corrosion was not a documented issue in the refining industry prior to 2002.
- API 581 notes a concern with sour water at alkaline pH and below neutral pH and identifies acidic hydrogen chloride (not H_2S) as a corrosion concern.
- API RP571 now includes an acidic sour water corrosion mechanism.

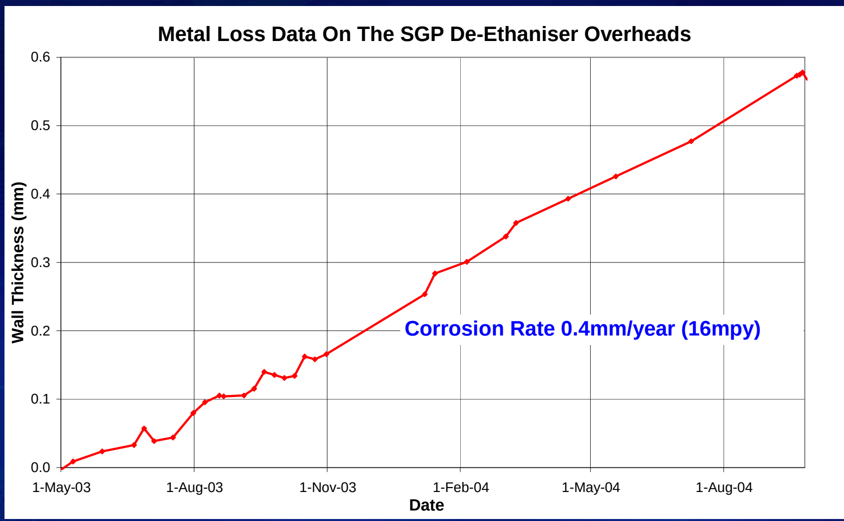
Rebuilding The Saturate Gas Plant

Several actions were implemented to reduce corrosion:

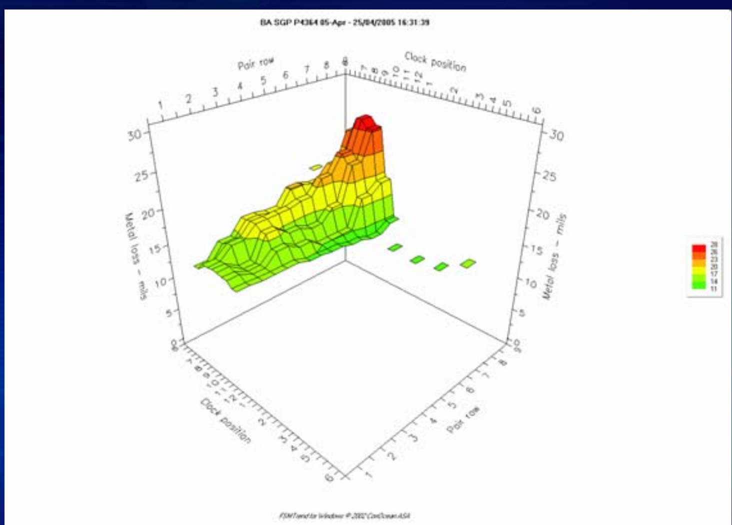
- Moving a correctly designed water wash injection location to the inlet of the OH condenser and making it continuous.
- Setting-up an Injection Point Management System.
- Installation of a non-intrusive corrosion monitoring system on the outlet piping of the OH condenser.
- Setting-up a Process Corrosion Variables program to monitor the corrosion performance on the SGP unit.

Corrosion Control Program Development

Corrosion Control Program Development



Corrosion Control Program Development



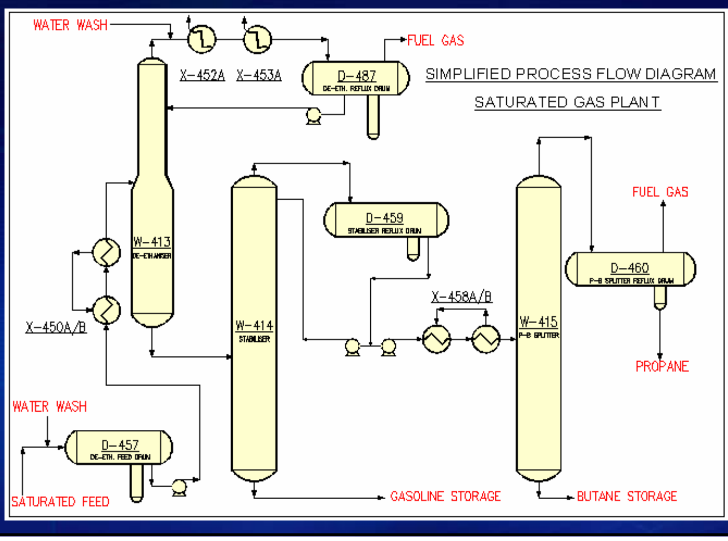
Corrosion Control Program Development

To increase the long term integrity of the plant a trial of switching off the front end water wash was initiated.

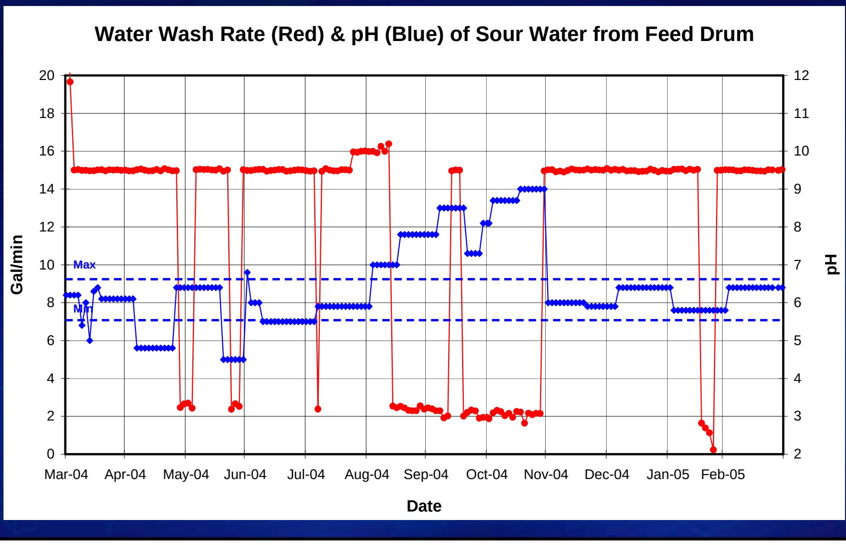
This had the effect of:

- Allowing the ammonia in the process stream to neutralize the hydrogen sulphide.
- This resulted in the pH and ammonia increasing in the Feed Drum.
- The Overhead Drum samples showed an increase in pH with a corresponding drop in Iron Count.
- The FSM data showed a reduction in the corrosion.
- However, excessive fouling was found throughout the overhead system, especially around the vessel bridles.

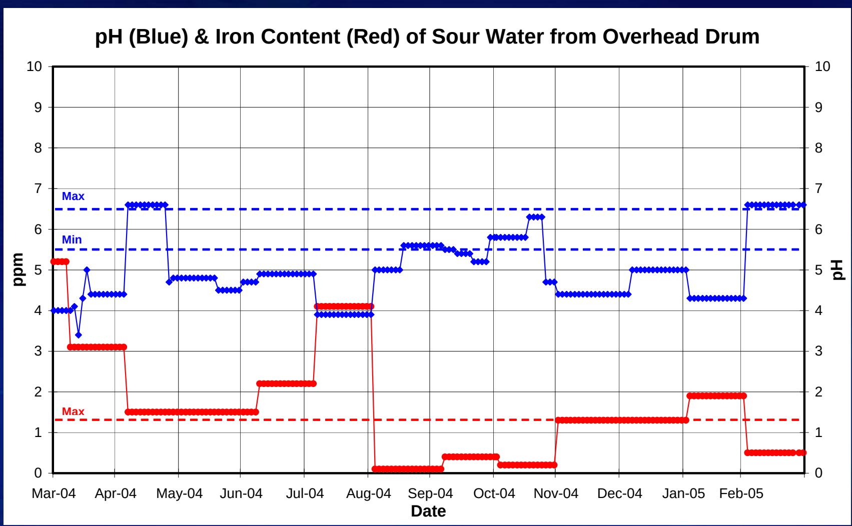
The Saturate Gas Plant



Corrosion Control Program Development



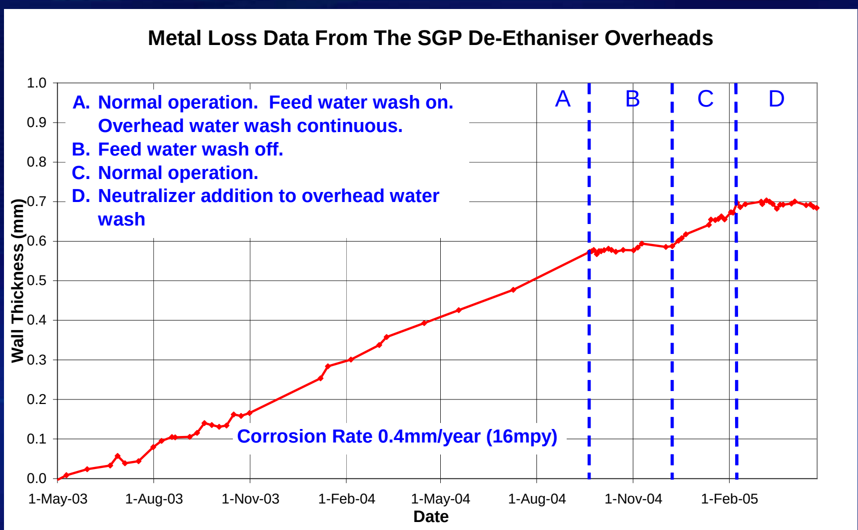
Corrosion Control Program Development



Corrosion Control Program Development

- Following the trial, the next step was to simulate this ammonia carry over without switching off the front-end water wash.
- This was achieved by the addition of a neutraliser to the overheads water wash.
- A neutralizing amine was installed in February 2005.

Corrosion Control Program Development



Conclusions

- We determined the corrosion mechanism, which wasn’t widely recognised within the refining industry.
- The mechanism was confirmed using software & laboratory work in collaboration with Corporate Technology.
- The on-going performance of the new SGP was monitored using a non-intrusive corrosion monitoring system.
- Technical solution was provided to reduce the corrosion without impacting operations.
- Installed an neutralizer injection system to reduce the corrosion to a manageable level.

Thank-You For Your Attention

Any Questions?

Appendix 7

Hydrogen embrittlement of austenitic stainless steel

Hennie de Bruyn (Borealis Group)

HYDROGEN EMBRITTLEMENT OF AUSTENITIC STAINLESS STEEL

Hennie de Bruyn
Chief Engineering – Materials Technology

BOREALIS
SHAPING the FUTURE with PLASTICS

HE of Austenitic Stainless Steel

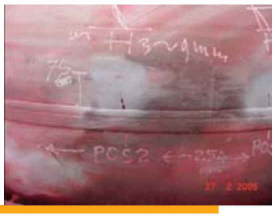
Incident & Background

- Cracker product separation
  - Methane Pre-Stripper Column
- Incident
  - February 2005
  - Hydrocarbon leaks detected
  - Icing detected
  - Fugitive emissions were earlier detected but believed to be leaking flanges
  - Delagging of the vessel top
  - 5 Penetrating cracks detected in the top ellipsoidal head

SHAPING the FUTURE with PLASTICS

HE of Austenitic Stainless Steel

Incident & Background



- Design Code
  - ASME Sec. VIII Div. I
- Material of construction
  - ASME SA-240 grade 304L
  - Thickness: 38mm
- Process
  - Design: 36.5bar(g) / -150ºC
  - Actual (top): pH_2 > 2bar(g) / -108ºC
- Column Dimensions
  - 29150mm (tangent-to-tangent line)
  - 2100mm ID

HE of Austenitic Stainless Steel

Repair

- Removal of top ellipsoidal head
- Crack removal – grinding
- Weld repair
- Heat treatment
  - Solution annealing
- Re-welding of head to vessel

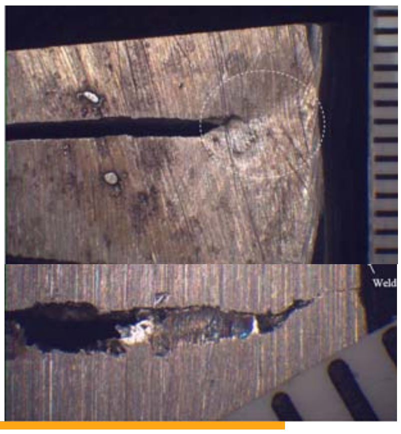
HE of Austenitic Stainless Steel

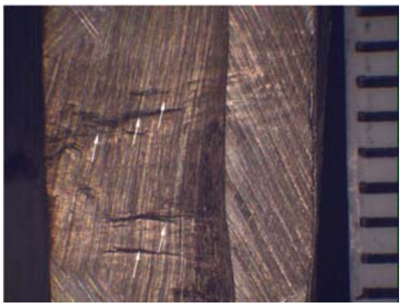
Investigation

- Removed crack for investigation
- Visual examination
- Hardness measurements
- δ-ferrite measurements
- Fractographic examination
- Metallographic examination
- Chemical analyses

HE of Austenitic Stainless Steel

Visual Examination



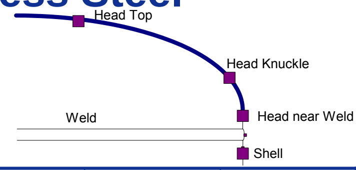


- Cracking penetrated the shell & weld
- Cracks & deformation bands detected

SHAPING the FUTURE with PLASTICS

HE of Austenitic Stainless Steel

Hardness Measurements



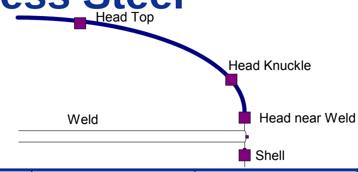
Brinell (HB) measure on internal surfaces

Average of 5 readings

Position	North	East	South	West	Average
Head Top	313	293	338	368	328
Head Knuckle	440	442	394	374	407
Near weld	345	347	362	339	348
Weld	293	341	273	313	305
Shell	316	240	272	323	287

HE of Austenitic Stainless Steel

Ferrite Measurements

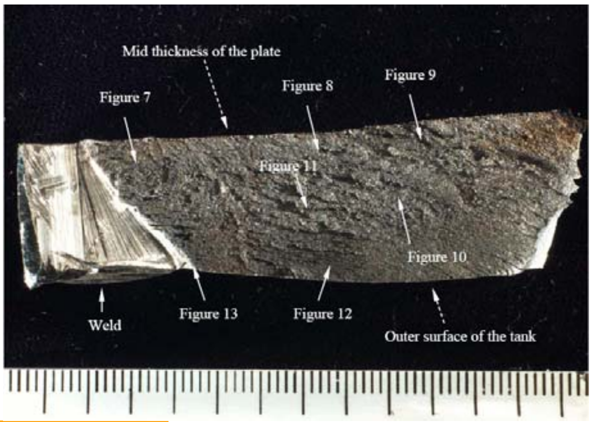


Measured on internal surfaces

Position	North	East	South	West
Head Top	8.5	11.8	9.3	11.3
Head Knuckle	18.5	23.0	18.4	16.6
Near weld	31.9	27.8	30.5	36.7
Weld	10.1	10.2	9.7	8.9
Shell	6.9	6.4	3.3	7.3

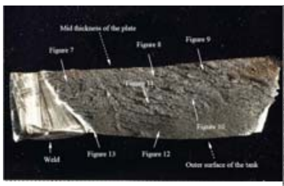
HE of Austenitic Stainless Steel

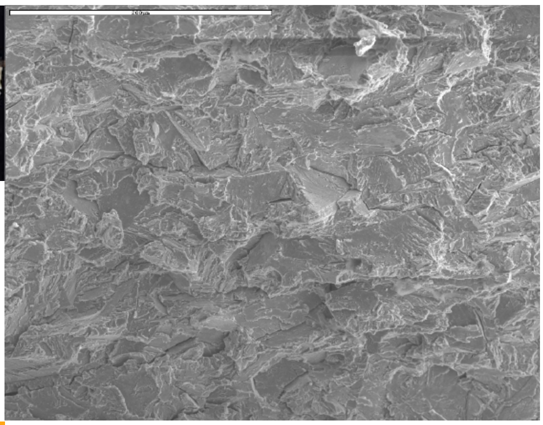
Fractographic Examination



HE of Austenitic Stainless Steel

Fractographic Examination

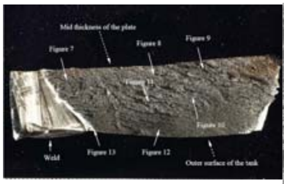




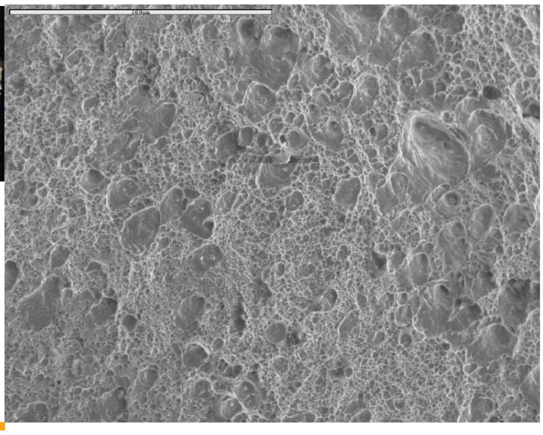
- Cracking in mixed-mode
- Intergranular & transgranular cleavage
- Positions 7, 8, 9,10,11,& 12

HE of Austenitic Stainless Steel

Fractographic Examination

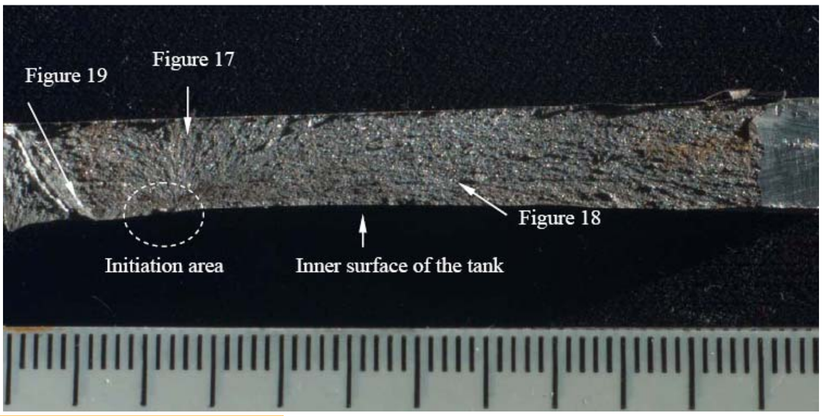


- Ductile fracture near the weld (position no. 13)



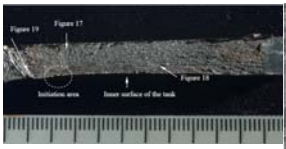
HE of Austenitic Stainless Steel

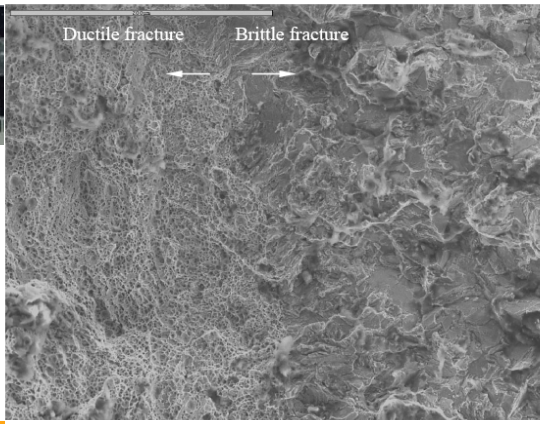
Fractographic Examination



HE of Austenitic Stainless Steel

Fractographic Examination

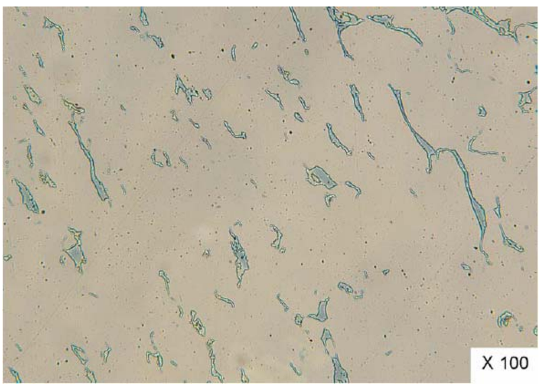




- Brittle to ductile transition at the heat affected zone

HE of Austenitic Stainless Steel

Metallographic Examination



- Microstructure of the base material, electrolytically etched in NaOH
- Appr. 10% δ-ferrite
- No intermetallic phases

HE of Austenitic Stainless Steel

Metallographic Examination

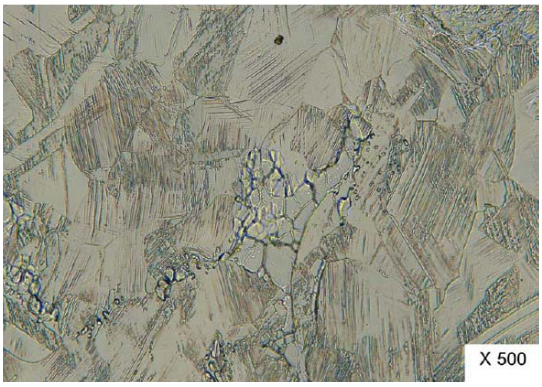
X 100

- Microstructure of the base material, electrolytically etched in 10% oxalic acid
- Note the presence of martensite in deformed austenite grains
- δ-ferrite noted

SHAPING the FUTURE with PLASTICS

HE of Austenitic Stainless Steel

Metallographic Examination



X 500

- Microstructure of the base material electrolytically etched in 10 % oxalic acid
- App. 50% martensite in deformed austenite grains.
- Presence of δ-ferrite

SHAPING the FUTURE with PLASTICS

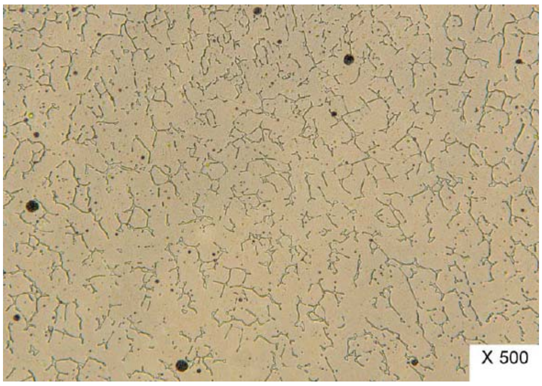
HE of Austenitic Stainless Steel

Metallographic Examination

- Bottom - weld metal
- Middle - heat affected zone
- Top -base material

HE of Austenitic Stainless Steel

Metallographic Examination



- Microstructure of the weld metal
- 5 – 10% δ-ferrite

HE of Austenitic Stainless Steel

Metallographic Examination

- Crack tip area etched electrolytically in 10% oxalic acid
- Note that the crack has propagated through the heat affected zone (HAZ) and into the weld.

HE of Austenitic Stainless Steel

Metallographic Examination

- Microstructure of the base material with a parallel crack to the main fracture

HE of Austenitic Stainless Steel

Metallographic Examination

- Base material with a crack parallel to the fracture
- Cracking through the austenitic grains, but following secondary grain
- Boundaries
- Cracking through the martensite phase, and deformation twins also observed

HE of Austenitic Stainless Steel

Conclusions from the investigation

- Presence of martensite
  - High level of deformation resulted in the formation of strain-induced martensite
- Heat treatment
  - Vessel top head was not heat treated (solution annealed) after forming
  - Type 304L is not a stable grade with regards to martensite formation at low temperatures
  - Solution annealing could have prevented the formation of martensite
- Cracking mechanism
  - Hydrogen is present in the process gas (pH_2 > 2 bar)
  - **Cracking was caused by hydrogen embrittlement**

HE of Austenitic Stainless Steel

Remaining questions

- By what mechanism does hydrogen charging occur at very low temperatures?
  - No significant corrosion mechanism to generate atomic hydrogen
  - No cathodic couple to charge the martensite bands with hydrogen
- Who should have been responsible to specify solution annealing of the ellipsoidal heads after forming?
  - No clear in ASME Sec. VIII Div. I
  - UHA-6 states: “Specific chemical compositions, heat treatment procedures, fabrication requirements, and supplementary tests may be required to assure that the vessel will be in its most favorable condition for the intended service”
  - Who should have know this? The process licensor, pressure vessel fabricator or user?

HE of Austenitic Stainless Steel

Literature References

- Han, G., et.al., “Effect of Strain-Induced Martensite on Hydrogen Environment Embrittlement of Sensitized Austenitic Stainless Steel at Low Temperatures,” Acta mater., 46 (13), pp. 4559 – 4570 (1998).
- Tsay, L.W., Yu, S.C. & Huang, R.-T., “Effect of Austenite Instability on the Hydrogen-Enhanced Crack Growth of Austenitic Stainless Steels,” Corrosion Science, 49, pp. 2973 – 2984 (2007).
- Hardie, D., et.al., “Hydrogen Embrittlement of Stainless Steel Overlay Materials for Hydrogenators,” Corrosion Science, 46, pp. 3089 – 3100 (2004).
- Pan, C., et.al., “Hydrogen Embrittlement Induced by Atomic Hydrogen and Hydrogen-Induced Martensites in Type 304L Stainless Steel,” Materials Science and Engineering, A351, pp. 293 – 298 (2003).
- Pan, C., etl.al., “Hydrogen Embrittlement of Weld Metal of Austenitic Stainless Steels,” Corrosion Science, 44, pp. 1983 – 1993 (2002).

HE of Austenitic Stainless Steel

Literature References

- El-kebir, O.A. & Szummer, A., "Comparison of Hydrogen Embrittlement of Stainless Steels and Nickel-Base Alloys," Int. J. of Hydrogen Energy, 27, pp. 793 – 800 (2002).
- Herms, E., Olive, J.M. & Puiggali, M., "Hydrogen Embrittlement of 316L Type Stainless Steel," Materials Science and Engineering, A272, pp. 279 – 283 (1999).
- Luppo, M.I., Hazarabedian, A. & Overjero-Garcia, J., "Effects of Delta Ferrite on Hydrogen Embrittlement of Austenitic Stainless Steel Welds," Corrosion Science, 41, pp. 87 – 103 (1999).
- Sun, D., et.al., "Tensile Behaviour of Type 304 Austenitic Stainless Steels in Hydrogen Atmosphere at Low Temperatures," Materials Science and Technology, 17 (3), pp. 303 – 308 (2001).
- MP Forum, "Corrosion of Types 316 and 304 SS Welded Pipe," Materials Performance, 44 (6), p. 13 (2005).

Appendix 8

Naphthenic acids corrosion

A. Invernizzi, S. Trasatti (University of Milan)

Naphthenic Acids Corrosion

A.J. Invernizzi and S.P.M. Trasatti
Dept. Of Physical Chemistry and Electrochemistry
University of Milan, Italy

EUROCORR

UNIVERSITÀ DEGLI STUDI DI MILANO

WP15 **Corrosion in the Refinery Industry**

Freiburg im Breisgau , 09-13 September 2007

OVERVIEW

1) Some words about Naphthenic Acids Corrosion (NAC)
   - A brief overview
   - What are these acids?

2) Our objectives

3) Experimental

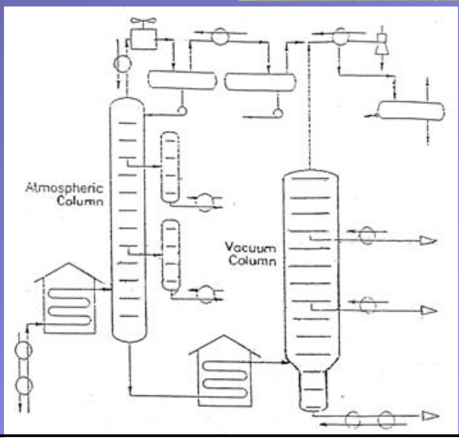
4) Some results

5) Conclusions and future work

NAC: an old unsolved problem

Mesa attack

$$Fe + 2RCOOH = Fe(RCOO)_2 + H_2$$
$$Fe + H_2S = FeS + H_2$$
$$Fe(RCOO)_2 + H_2S = FeS + 2\,RCOOH$$

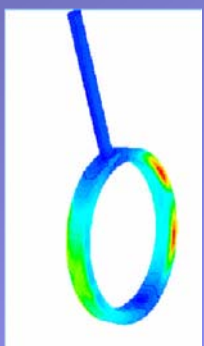


Main parameters:

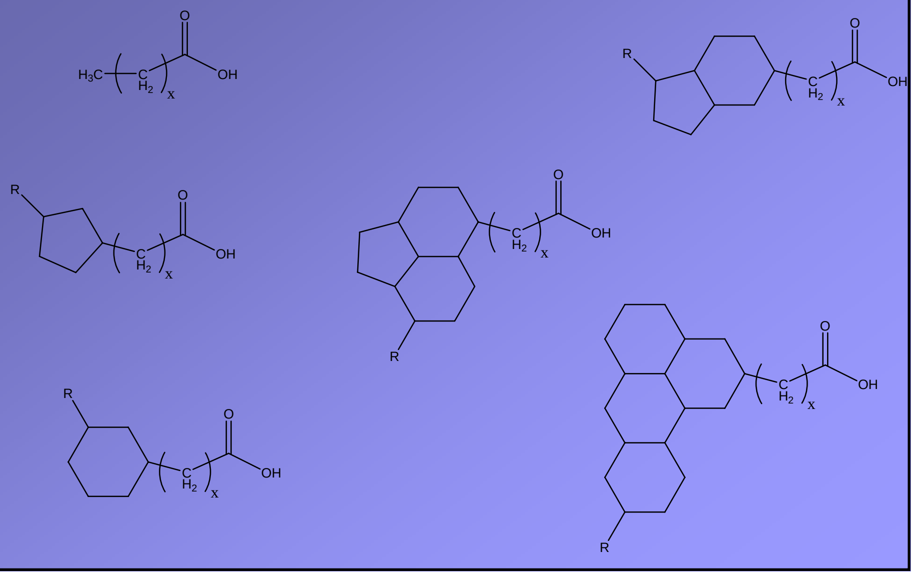
TAN	%S
Flow Rate	Crude oil type
Temperature	Two phase flow
	Metallurgy

NAC: an old unsolved problem

- Corrosion occurs only in the temperature range 200-400°C
- Corrosion rate is usually linearly related with TAN
- NAC could increase in the presence of sulfur corrosion
- Fluidodynamic conditions are crutical



Some examples of Naphthenic Acids: $R(CH_2)_xCOOH$



OBJECTIVES

- To bring an additional contribution to NAC
- Systematic study of corrosion behaviour starting from “simple” carboxylic acid
- To underline the importance of molecular structure on reachtivity
- To understand the reaction’s mechanism
- To study NAC as a function of acids concentration, temperature and sulfur content
- To investigate in more details the effect of sulfur

MATERIAL

Fe Armco – pure iron 99,5%

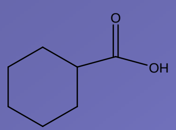
as a simple substrate

TESTING PROCEDURES

Weight loss tests

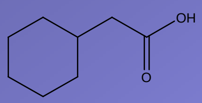
- 0.5 liter glass cell
- 30x20x1 mm flat coupons hung by means of a glass hook
- Test under N_2 or H_2S
- surface area/solution volume ratio was about 0.05 cm^{-1}
- H_2S 1.05% (mixed to N_2) bubbled inside the reactor
- DW05 synthetic oil (distilled between 388 and 475°C) containing < 3.8 ppm of $S^{=}$, density 845.9 g/l, TAN 0.16 mg KOH/g oil
- quasi-static hydrodynamic condition (magnetic stirring)

The carboxylic acids used:



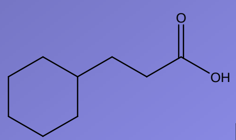
cyclohexanecarboxylic acid

pKa 4.8 (estimated value)



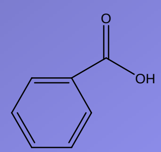
cyclohexylacetic acid

pKa 4.9 (estimated value)



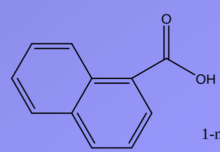
cyclohexylpropionic acid

pKa 4.8 (estimated value)



benzoic acid

pKa 6.3 (estimated value)

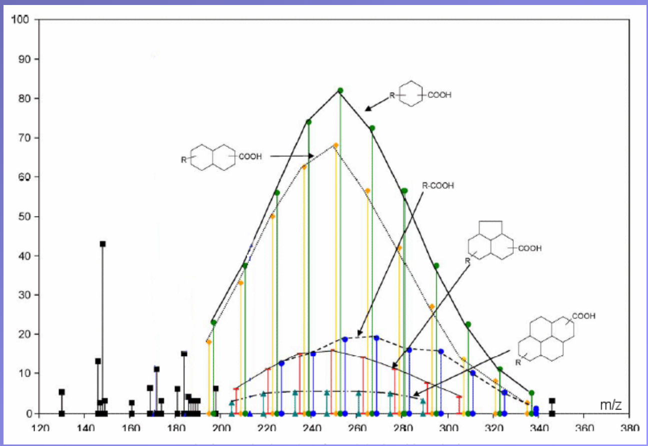


1-naphthoic acid

pKa 5.9 (estimated value)

Naphthenic Acids mixture used

Supplied by Van Loocke N.V
Two solution: a crude mixture and a distelled mixture (TAN 210)
Mainly C16 –C24 molecule

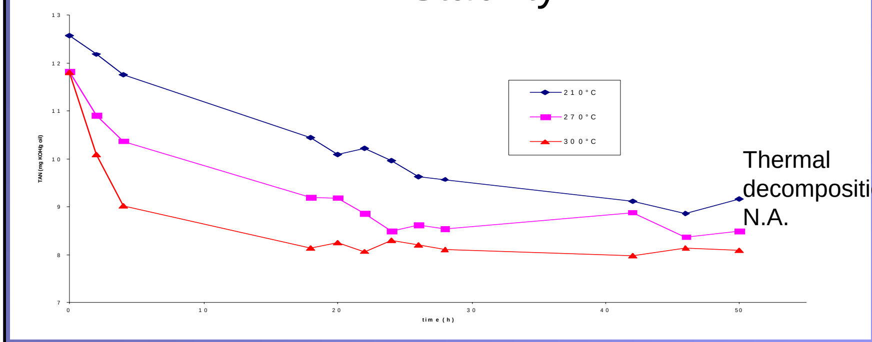


PRELIMINARY OBSERVATIONS

1) The presence of oxygen O_2 causes the degradetion of oil at temperature higher than about 200 °C.

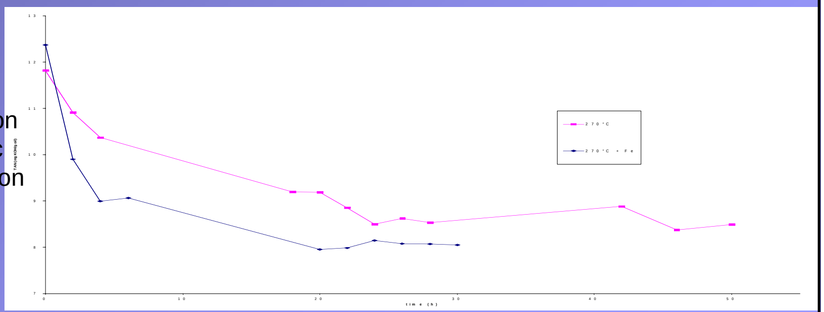
2) Working under nitrogen N_2 prevents this phenomenon.

Stability

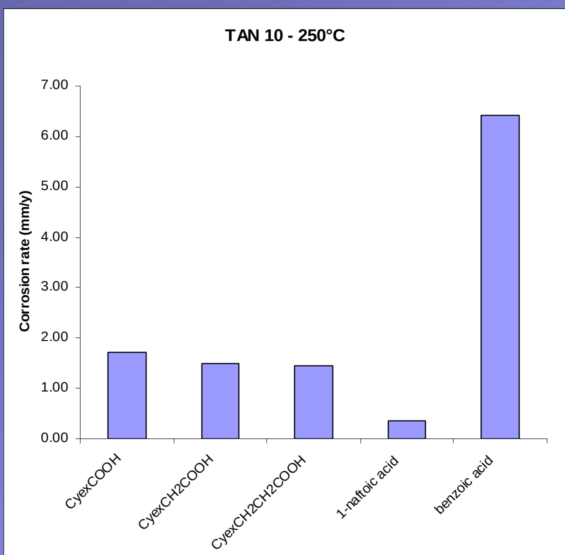


Thermal decomposition of N.A.

Comsumption and catalytic decomposition



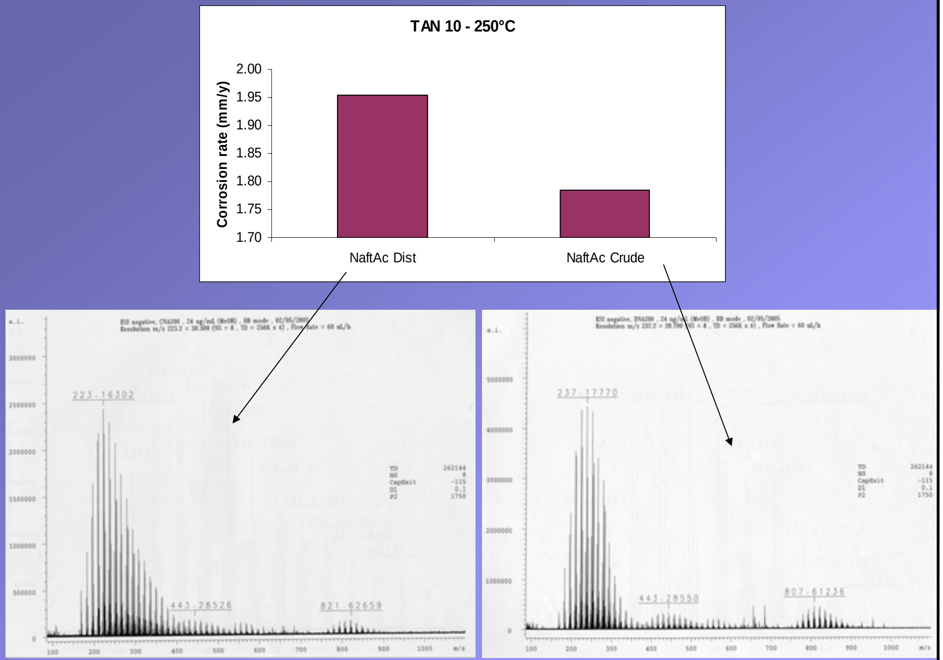
Stereochemistry



Acidity constants are nearly the same, except for benzioc acid.

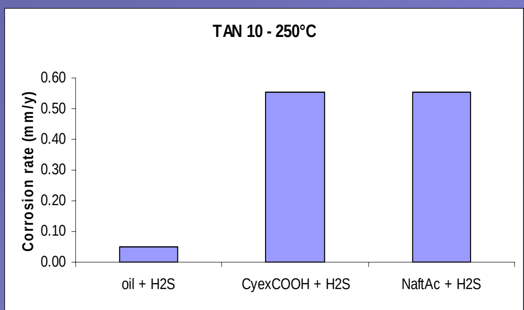
- Incresing chain lenght and steric effect causes a decrese in corrosin rate.

- Aromatics can adsorb easily.



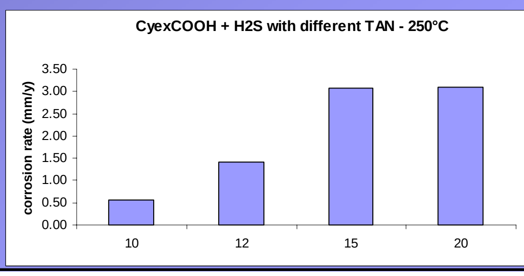
MASS Spectra

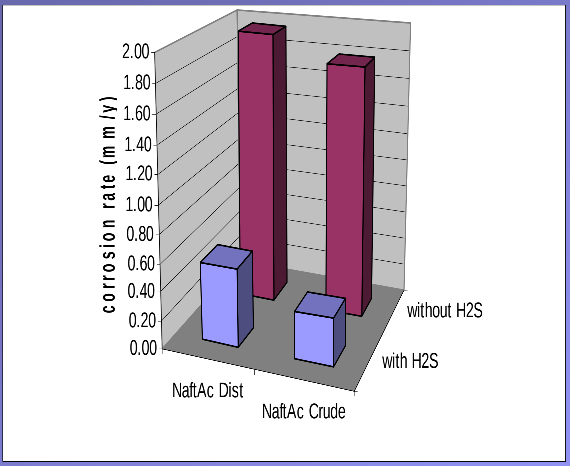
Sulfur



In presence of H_2S corrosion rate is one order of magnitude lower

Sulfur appears to be protective up to TAN 12



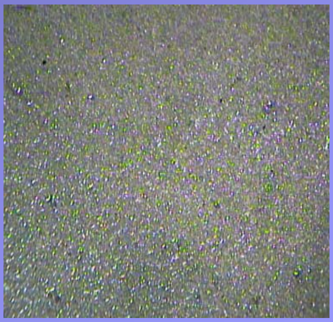


Sulfur reduces the corrosion rate also with NA mixtures.

- We never observed the *mesa attack* morfology (as expected)

- Corrosion morfology was generalized.

- Sulfur produces a black, compact and protective film on the surface



Without H2S

With H2S

CONCLUSIONS AND

- Oxygen causes degradetion of synthetic oil used
- Purging the solution with N_2 prevent this occurrence
- Acidity depends on the temperature due to the thermal decomposition of ZCOOH molecule
- Short chain lenght acids and/or with prominent steric effect are less aggressive
- Distilled (light fraction) naphthenic acids mixtures are more detrimental
- Aromatic carboxylic acids can adsorb easly and cause higher corrosion rate
- Sulfur can protect iron even if has no effect for high TAN
- An electrochemical study of N.A. is required (and we are realizing it) to better understand the dependence of corrosive phenomenon on molecular structure of acids

- ….suggestions?

Thank You for Your attention