Appendix 1

List of participants and excused persons

Participants EFC WP15 meeting 6th September 2005 Lisbon

Surname	Name	Company	Country
Martin	Richez	Total	FRANCE
Stuart	Bond	TWI	UK
Chris J	Claesen	Nalco	BELGIUM
Hennie	de Bruyn	Borealis AS	NORWAY
Paul	Eaton	Champion Technologies Inc	USA
Alec	Groysman	Oil Refineries Ltd	ISRAEL
Craig A.	Howard	GE Infrastructure	AUSTRALIA
Joanna	Hucinska	Gdansk Technical University	POLAND
Russell	Kane	Intercorr	USA
Maarten	Lorenz	Shell Global Solutions Inetrnational B.V.	NETHERLANDS
Ellina	Lunarska	Institute of Physical Chemistry	POLAND
David	Owen	GE Betz	UK
Andrew M	Pritchard	Corrosion & Fouling Consultancy	UK
John	Pugh	Innovene Grangemouth	UK
Roberto	Riva	Eni Tecnologie	ITALY
Francois	Ropital	Institut Français du Pétrole	FRANCE
Rob	Scanlan	Conoco	UK
Günter	Schmitt	Lab for Corrosion Protection	GERMANY
Laszlo	Simor	Danube Refinery	HUNGARY
Nick	Smart	Serco Assurance F	UK
Stefano	Trasatti	University of Milan	ITALY
Stefan	Winnik	Exxon Mobil Chemical	UK

Excuses received for the EFC WP15 meeting 6th September 2005 Lisbon

Surname	Name	Company	Country
Curt	Christensen	Force Institutes	DENMARK
André	Claus	GE Betz	BEGIUM
Michael	Davies	CARIAD Consultants	GREECE
Nicholas	Dowling	Shell Global Solutions International B.V.	NETHERLANDS
Charles	Droz	Exxon Mobil	FRANCE
Sebastien	Duval	Saipem	FRANCE
Carlo	Farina	Corrosion Consultant	ITALY
Tiina	Hakonen	FORTUM Oil & Gas Oy	FINLAND
Martin	Holmquist	AB Sandvik Steel	SWEDEN
Andrew	Kettle	Chevron Texaco Ltd	UK
Mario	Lanciotti	Polimeri Europa S.p.A	ITALY
Morten	Langøy	Bodycote Materials Testing AS	NORWAY
Istvan	Lukovits	Chemical Research Center	HUNGARY
Richard	Pargeter	TWI	UK
Kirsi	Rintamaki	FORTUM Oil & Gas Oy	FINLAND
Iris	Rommerskirchen	Butting Edelstahlwerke GmbH&Co KG	GERMANY
Liane	Smith	Intetech Ltd	UK
Betrand	Szymkowiak	IFP Technology Group - AXENS	FRANCE
John	Thirkettle	Thor Corrosion	UK
Alan	Turnbull	National Physical Laboratory	UK

Appendix 2

EFC WP15 Activities

Presentation of the activities of WP15

European Federation of Corrosion (EFC)

- Federation of 32 National Associations
- 19 Working Parties (WP) + 1 Task Force
- Annual Corrosion congress « Eurocorr »
- 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
- Task Force 2: Corrosion and Protection of steel structures

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

Publications

EFC Working Party 15 « Corrosion in Refinery » Activities

WP Meetings
·One WP 15 working party meeting in Spring,
(this year on 17-18 March 2005 in Trondheim)

·One meeting at Eurocorr in conjunction with the conference,
(this meeting during Eurocorr 2005 4-8 September in Lisbon)

Eurocorr Conference sessions (September)
Refinery Corrosion Session
+ Workshops or Joint Session with other EFC WP parties

WP15 page in EFC Web site
http://www.efcweb.org/WP_on_Corrosion_in_the_Refinery_Industry.html

EFC Working Party 15 « Corrosion in Refinery » Activities

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

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

[DECHEMA] [SITEMAP] [CONTACT] [RUSSIAN] [OUR WEBSITES]

Home
Structure
Member Societies
Working Parties
WP on Corrosion Education
WP on Corrosion by Hot Gases and Combustion Products
WP on Corrosion in Oil and Gas Production
WP on Corrosion in the Refinery Industry
WP on Automotive Corrosion
Board of Administrators
STAC
General Secretariat
Events and Highlights
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EFC Working Party 15: Corrosion in the Refinery Industry

Vision:

The Working Party meetings objectives are:

- Information Exchange
  - Sharing of refinery materials /corrosion/inspection experiences by operating company representatives.
- Forum for Technology
  - Sharing materials/ corrosion/ protection/ monitoring information by providers, users, R&D
- Scientific exchange
  - Sharing materials/ corrosion/ protection scientific works.
- Development of documents, guidelines, publications related to corrosion in the refinery industry.

Strategy Plan:

- Survey of corrosion problems in refinery industry

The group will collect information first on hydrotreatment and hydrocracking units, then processes as FCC, Catalytic reforming, Distillation, Sulfur plant, Alkylation, Sour water stripper will be considered. Guideline and publication will be issued

EFC Working Party 15 « Corrosion in Refinery » Activities

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

Excerpt of last meeting minutes

Minutes of the 15th September 2004 meeting and Appendices

Minutes of the 8-9th March 2004 meeting, Appendices 1-7, Appendices 8-11 and Appendix Literature

Minutes of the 30th September 2003 meeting and Appendix

Minutes of the 10th April 2003 meeting

Minutes of the 15th November 2002 meeting

Agenda of forthcoming meetings

WP 15 meeting on March 17-18th in Trondheim, Norway
The agenda is not completely finalised but one day will be dedicated to general topics and the other one will be dedicated to the guideline on Corrosion Under Insulation.

Publications

- EFC Publication No. 40 "Requirements for cooling water systems"
- EFC Publication No. 42 "Collection of Selected Papers"

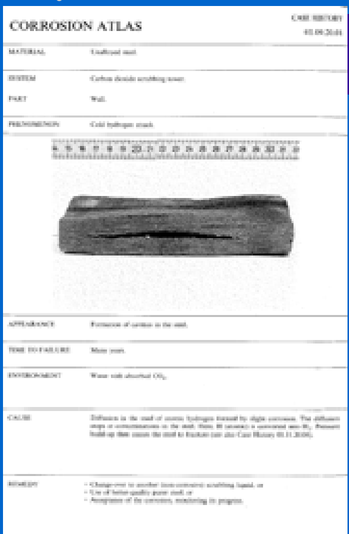
Publications are in preparation on the following subjects:

- Survey on amine unit corrosion
- Guideline on corrosion under insulation

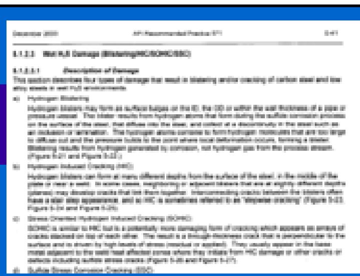
Appendix 3

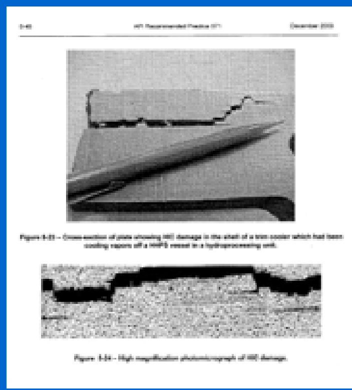
Proposal of a typical failure refinery corrosion cases atlas

Typical refinery failure cases atlas ?


CORROSION ATLAS

Corrosion Atlas, Elsvier





API 571

CORROSION IN REFINERY INDUSTRY

CASE HISTORY n° 108 January 2002 FR-IFP-Materials Department

HYDROGENATION UNIT 217 – HOT SEPERATOR V23
SCREWS
CEDI – SOLAIZE - IFP

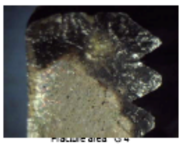
DATE OF INCIDENT AND/OR INFORMATION: 24/11/01 SA10

NATURE OF THE INCIDENT : temperature breakaway and breaks of screws

CONSEQUENCES : stop of the unit

MATERIAL: carbon steel

PHOTO AND SCHEME :



ASPECT : some parts of the fracture zone have a green colour and the others a dark brown one
The metallographic examination has revealed intergranular cracks.

MEDIA AND OPERATING CONDITIONS:
Air, normal operating temperature 380°C but increases up to 480°C

TIME TO DETERIORATION : A few months (design in august 2000)

CORROSION IN REFINERY INDUSTRY

CASE HISTORY n° 108 January 2002 FR-IFP-Materials Department ANSWER

TYPE OF CORROSION : MOLTEN METAL CORROSION

CAUSES :

X ray analysis have been performed with a Scanning Electron Microscope:

*on the fracture area Zinc, Cadmium, Sulphur, Oxygen were detected

*In the cracks Cadmium with Oxygen and locally Zinc, Chloride, Copper and Sulphur had been analysed.

As temperatures up to 480°C have been reached, Zinc and Cadmium were in the liquid state (the melting temperature of Cadmium is 320°C and the one of Zinc is 420°C) and they can provoke a molten metal type corrosion of the carbon steel screws. The blocking stresses have surely favoured the attack by the molten metals

REMEDY :

The origin of the zinc and the cadmium are looking for (paint, surface treatment of the screws, grease,… ?) in order to avoid them.

PUBLICATION - TECHNICAL REPORT: IFP technical note n°20/2002 RG30

BIBLIOGRAPHIC REFERENCES :

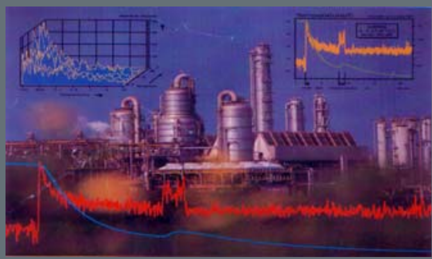
Typical refinery failure cases atlas ?

Appendix 4

Electrochemical noise in corrosion monitoring

A. Cafissi and S. Trasatti (University of Milan)

“Electrochemical Noise in corrosion monitoring”



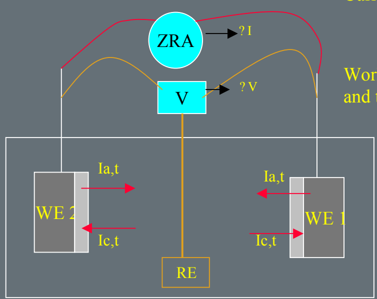
A.Cafissi and S.P.Trasatti
Departement of Physical Chemistry and Electrochemistry-
University of Milan- via Venezian, 21- 20133 MILAN (italy)

EUROCORR 2005 4-8 September 2005 , Lisboa (P)

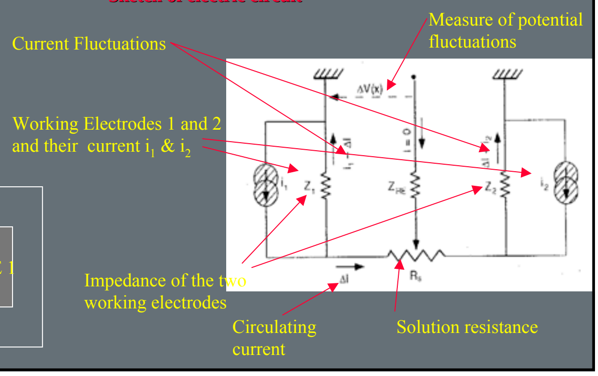
Electrochemical Noise

- **Electrochemical technique entails with registration and analysis of potential and current fluctations associated with electrochemical phenomena at the electrode/solution interface.**
- **Current fluctations between two working electrodes involve in the process are in the range of 10^{-11}-10^{-3} A**
- **Potential fluctuations between the working electrodes and the reference electrode are in the range 10^{-6}-10^{-1} V**

Experimental set-up



Sketch of electric circuit



Applications of Elettrochemical Noise

The EN has a wide range of appplications, i.e.:

- **Determination of active/passive transition**
- **Study of the passive film breakdown (pitting, crevice corrosion, etc.)**
- **Growth and detachment of hydrogen bubbles (acid corrosion)**
- **Determination of fluctuations due to diffusive phenomena**
- **Coating failure on metallic substrate**
- **Biological corrosion phenomena**
- **Electrocrystallization associated with diffusion processes**

Analysis of Electrochemical Noise data

It can be performed as follows:

First:

- **Direct analysis of raw data**

Second

- **Statistical analysis: d_V , d_I, variance, kurtosis, skewness, average values, etc.**
- **Determination of Rn (Noise resistance), a useful parameter for the corrosion rate:**

$$(Rn \approx Rp) \quad Rn = d_V / d_I$$

- **Determination of localization index**

$$L_I = d_I / I_{rms}$$

Third

- **Fourier Trasform analysis (power spectral density, PSD).**

Experimental scope

Evaluation of Electrochemical Noise tecnique for monitoring corrosion of industrial plants

- **Study of different corrosion morphologies**
- **Study of the influence of physical and mechanical parameters (flow rate, bacteria, temperature, tensile load,etc)**
- **Definition of statistical parameters (d_V, d_I, R_n, L_I, PSD)**
- **Development of a statistical metodology of the electrochemical signal by the use of neural networks**

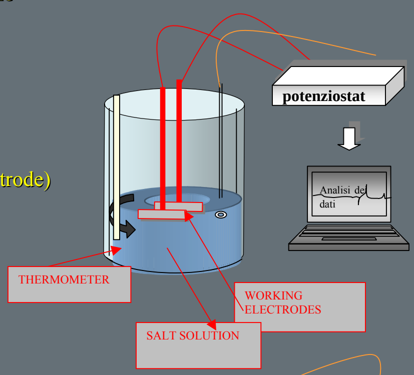
Acquisition set up for static experiment

-Potenziost/galvanostat in ZRA configuration

-A reactor for electrochemistry reaction

-A reference electrode (i.e. SCE saturated calomel electrode)

-Two identical working electrodes

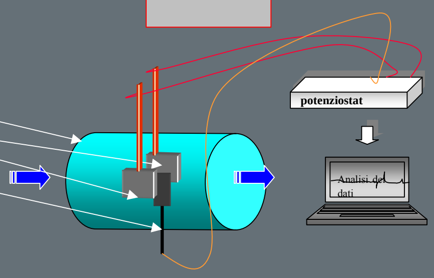


Acquisition set up for dynamic experiment

- A flowdynamic reactor

-Two working electrode of steel

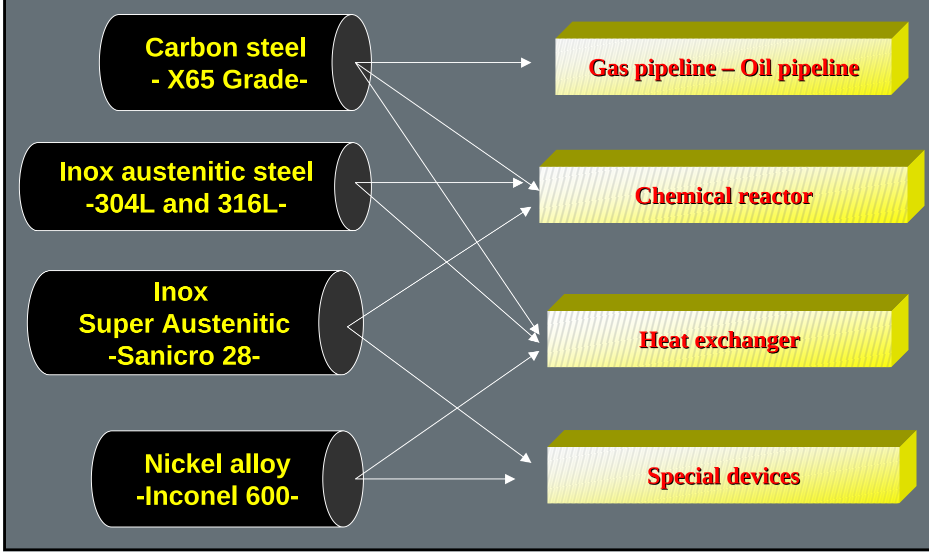
-A metallic (Pt,Ru) reference electrode



Informations available from different testing conditions

Testing	Experiment Purpose
Static test	Study of different corrosion morphology
Tensile test	Applicability of EN in stress corrosion cracking
SRB corrosion test	Monitoring the influence of SRB bacteria
Flow dynamic test	Monitoring the influence of dynamic conditions

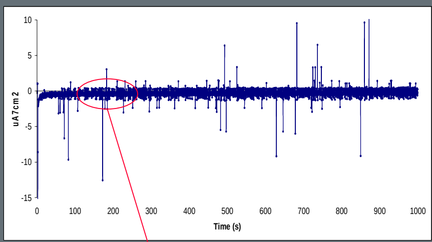
Materials



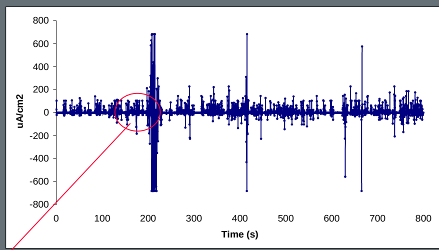
INFLENCE OF BACTERIA ACTIVITY ON STEEL CORROSION

Bacterial activity
- forms a biofilm on the metallic surface
- reduces the activity of inhibitors
- forms corrosive H_2S gas in solution
- prevents oxygen diffusion in the solution
- creates a differential areation on the substrate

Bacterial activity causes
- increase of corrosion current
- metal depassivation
- blistering in the steel
- decrease in pH solution



Current fluctations for a typical steel pipe in a 3,5% NaCl solution in the absence of SRB bacteria: current spike of 12 µA/cm²



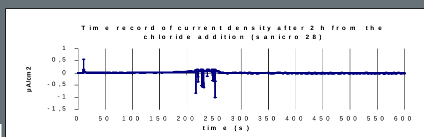
Current fluctations for steel pipe in a 3,5% NaCl solution in the presence of Bacteria SRB (temperature: 30 °C): current spike in the range of 600 µA/cm²

Immersion Time (h)	µA/cm² X65	µA/cm² X65 + SRB	mm/y X65	mm/y X65+SRB
8	5	200	31.4 x 10-3	2.51

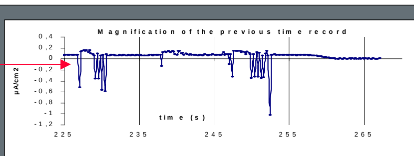
Surface appearance of carbon steel after SRB corrosion

Super austenitic stainless steel : Sanicro 28

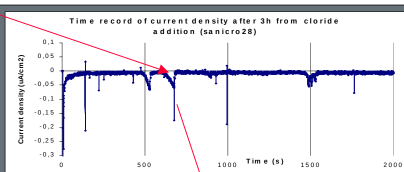
Typical Time record of current density for Sanicro 28 in a 3,5% NaCl solution at room temperature

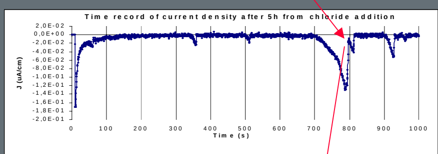


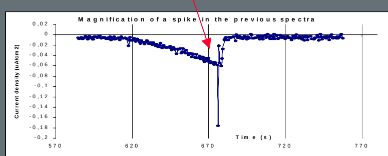
Immersion Time (h)	µA/cm² Background Noise	Spike Charge (µC/cm2)	CR:mm/y Background Noise
2	0,02	0,3	2,5 x 10-4
3	0,016	1,8	2,0 x 10-4
5	0,01	3,6	1,25 x10-4

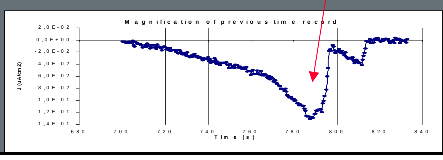


Note: very good material , so very few spikes & low corrosion







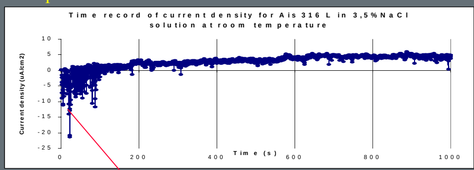


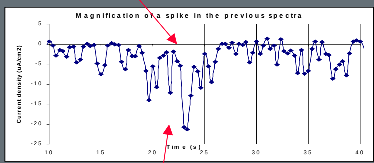
AISI 316 L

Time record of current density for AISI 316L Steel in a 3,5% NaCl solution at room temperature and relative magnification of transient spike

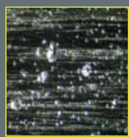
Immersion Time (h)	µA/cm² background	Spike Charge (µC/cm2)	Height of Spike µA/cm²	CR: mm/y Background-Noise
2	2,7	3	8	$33{,}8 \times 10^{-3}$
3	2	5,1	7	$25{,}1 \times 10^{-3}$
5	3	31,5	22	$37{,}6 \times 10^{-3}$

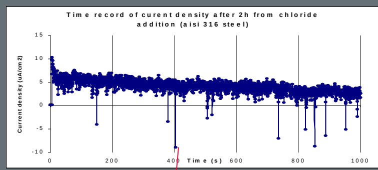
Note :Grow of current spikes and localized corrosion as the test proceed

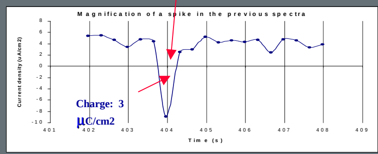


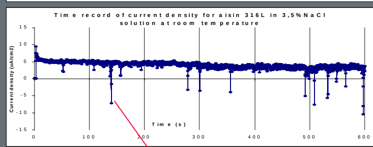


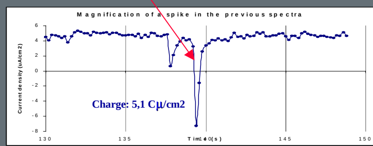
Charge: 31,5 µC/cm2









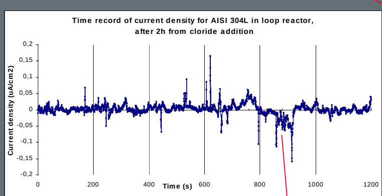


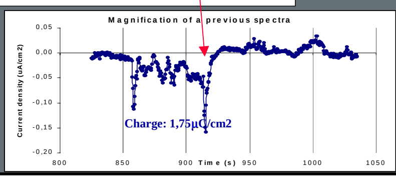
AISI 304 L in the loop

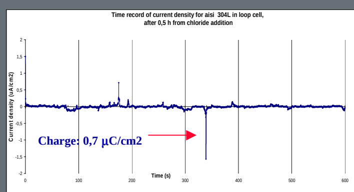
Time record of current density for Aisi 304L in loop reactor in a 3,5% NaCl solution at room temperature and relative magnification of transient spikes

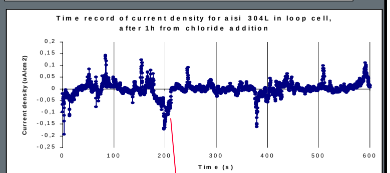
Note :Very low current density due to high oxygen concentration caused by turbolence conditions (flow rate 6 l/min).

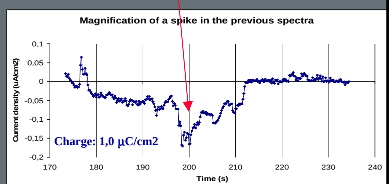
Immersion Time (h)	µA/cm² Background Noise	SpikeCharge (µC/cm2)	CR: mm/y
2	0,067	0,7	8,36 x 10-4
4	0,03	1	3,8 x 10-4
6	0,01	1,75	1,36 x10-4











SCC on AISI 304L

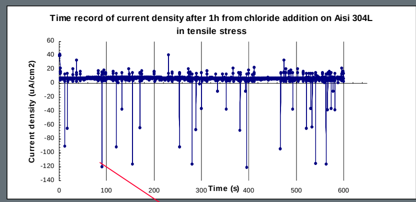
Time record of current density for AISI 304L in a 3,5% NaCl solution at different time and with constant tensile stress.

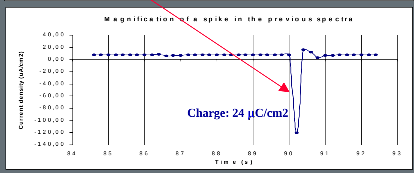
Relative magnification of transient spike

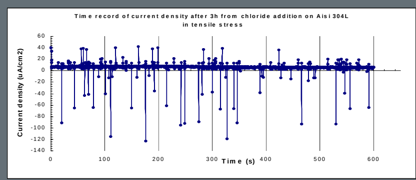
Immersion time Time (h)	Background Noise µA/cm²	Height spike µA/cm²	Spike Charge (µC/cm2)	CR:mm/y
1	7,7	110	24	9,7x10-2
3	8	120	27	0,1

Note :

- EN can be very helpful in monitoring the passive film break down (amplititede of the current spike), increased by the tensile stress applied that expose a new not passivated surface.



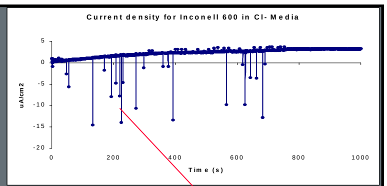


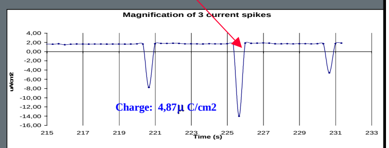


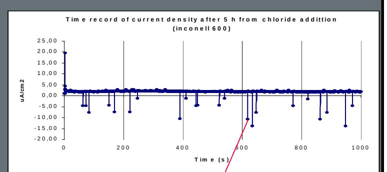
Inconel 600 alloy

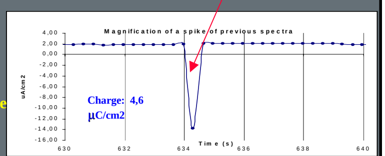
Time record of current density for Inconel 600 in a 3,5% NaCl solution ,pH=3, at room temperature and relative magnification of transient spike

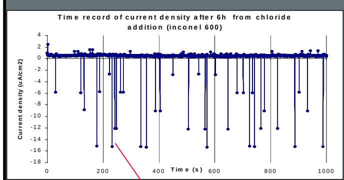
Immersion Time (h)	Background Noise µA/cm²	SpikeCharge (µC/cm2)	Heght of Spike µA/cm²	mm/y Backgroud Noise
3	6	4,9	15	7,5 x 10-2
5	1,4	4,6	14	1,8 x 10-2
6	0,5	5	15	0,63 x 10-2

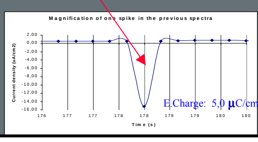


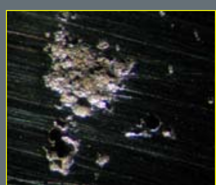












Photograf taken by optical microscope

Noise spectra transformation from the time domain to the frequency domain (FFT to obtain the PSD)

The aim of this transformation is:

↓

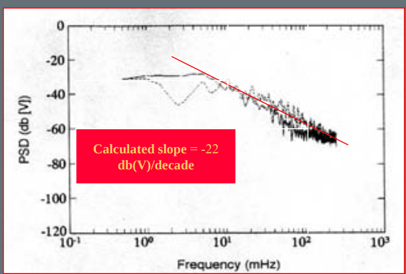
To filter the frequencies not associated to the electrochemical reactions (amplification noises, instrumentation interferences, power current).

↓

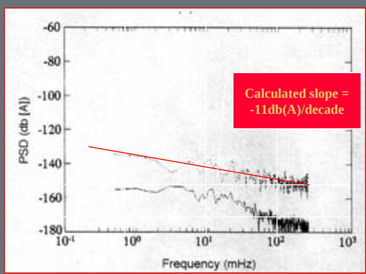
To determine the slope of the (PSD) spectra as an useful parameter to distinguish between uniform and localized corrosion.

Potential and current PSD

Localized corrosion



PSD (V) for localized corrosion



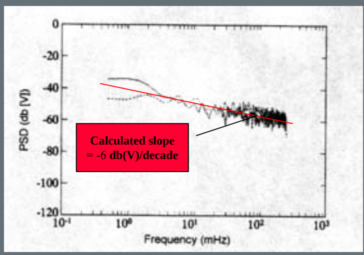
PSD (I) for localized corrosion

Type of Corrosion	Slope (db[V]/decade)		Slope (db[A]/decade)	
	Max.	Min.	Max.	Min.
Passivation	−15	−25	1	−1
Pitting	−20	−25	−7	−14
Uniform	0	−7	0	−7

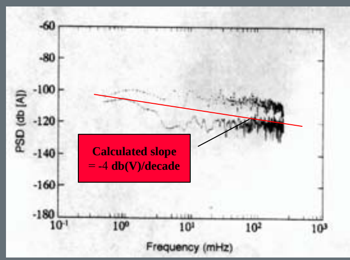
Slope values for different corrosion modes

Potential and current PSD

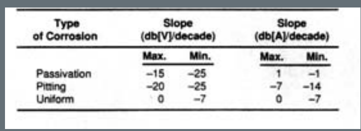
General corrosion



PSD (V) for uniform corrosion



PSD (I) for uniform corrosion



Type of Corrosion	Slope (db[V]/decade) Max.	Min.	Slope (db[A]/decade) Max.	Min.
Passivation	−15	−25	1	−1
Pitting	−20	−25	−7	−14
Uniform	0	−7	0	−7

Slope values for different corrosion modes

Theoretical calculation of metal mass loss during a current spike

Determination of hypothetic Pit volume

IF R_1 = radius maior of Pit in μm

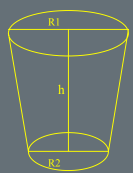
IF R_2 = radius minus of Pit in μm

If h = depth of the pit hole in μm

If $?_{Fe}$ = 7,3 $\mu g^3/\mu m^3$

We obtain :

→ $V_{pit} = 1/3\ \pi h(R_1^2+R_2^2+R_1+R_2)$



Example 1:

depth h = 0,5 mm = 500 μm

→ R_1 = 4 μm → R_2 = 1 μm

$V_{pit} \approx 11{,}5 \times 10^{+3}\ \mu m^3$

$\mu g_{Fe} = 84{,}1 \times 10^{+3}\ \mu g\ Fe = 84{,}1\ mg_{Fe}$

Example 2:

depth h = 0,05 mm = 50 μm

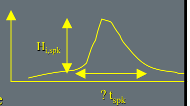
→ R_1 = 4 μm → R_2 = 1 μm

$V_{pit} \approx 11{,}5 \times 10^{+3}\ \mu m^3$

$\mu g_{Fe} = 8{,}41 \times 10^{+3}\ \mu g\ Fe = 8{,}41\ mg_{Fe}$

Metal Dissolution during a Current Spike

Theory:



IF $H_{i,spk}$ = Height of spike i in μA

If $?\ t_{spk}$ = duration time of a single spike i

if M_{eq} = equivalent weight of Fe : M_{eq} = 28 g/mole

If F = 96500 C (eletric charge of 1mole of electrons)

If f_{spike} : frequency of spike event : n°spike/sec

What's the amount of metal during a dissolution spike …m_{Fe} ?

$$m_{Fe} = (H_{i,spk} \cdot ?\ t_{spk} \cdot M_{eq}) / F$$

Example 1:

$H_{i,spk}$ = 10 μA; $?\ t_{spk}$ = 0,6 s

$m_{Fe} = 1{,}74 \cdot 10^{-9}$ g Fe

Example 2:

Hi,spk = 100 μA; Δt_{spk} = 0,6s

$m_{Fe} = 1{,}74 \cdot 10^{-8}$ g Fe

metal dissolution during a day ? $m_{Fe,Day.}$?

$m_{Fe} = 2{,}51 \cdot 10^{-6}$ g Fe

$m_{Fe} = 2{,}51 \cdot 10^{-5}$ g Fe

Mass of Iron dissolved in general corrosion: $m_{general}$

If Icorr : Background Current Noise : 2 $\mu A/cm^2$

$M_{general}$: $5 \cdot 10^{-5}\ g_{Fe}$/day cm^2 ⟶ 0,1μm/day cm^2

Practical examples

For:

- a mean height spike : Hi,spk =15, 30, 60 or 100 µA/cm^2
- a mean duration time of the spike ? t_{spk} = 3 seconds
- a mean number of spike in a day equal to 1440 or 4320 spikes
- and we assume a hypotetic pit , with this characteristics: Dept = 25 µm ,$V_{pit} \approx 5,76 \times 10^{+3}$ µm^3 , $4,2 \cdot 10^{-3}$ g Fe

We obtain the pit formation for 1440 spike /day in this time:

Mean Height Spike (µA/cm²)	Relative Mass of Iron dissolved (g)	Time to pit (Days)
15	$1,88 \times 10^{-5}$	223
30	$3,76 \times 10^{-5}$	112
60	$7,52 \times 10^{-5}$	56
100	$1,26 \times 10^{-4}$	33,4

And the pit formation for 4320 spike /day in this time:

Mean Height Spike (µA/cm²)	Relative Mass of Iron dissolved (g)	Time to pit (Days)
15	$5,64 \times 10^{-5}$	74,3
30	$11,28 \times 10^{-5}$	37,3
60	$22,56 \times 10^{-5}$	18,6
100	$3,78 \times 10^{-4}$	11,1

CONCLUSIONS

- Electrochemical Noise analysis can be successful applied to investigate corrosion processes and to estimate corrosion rate

- Testing in the presence of SRB activity has shown that the corrosion onset and propagation growth is strictly connected to the bacteria metabolism.

- EN can be conducted under both static and dynamic conditions as well as under tensile loading

- The PSD slope can be a useful parameter to distinguish among different corrosion modes

Appendix 5

New Technology for Prediction and Assessment of Corrosion in Refinery Operations

R.D. Kane (Honeywell)

New Technology for Prediction and Assessment of Corrosion in Refinery Operations

Russell D. Kane
InterCorr International, Inc.*

*Recently acquired by Honeywell

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Organization

- Topics of Discussion
  - Ammonium Bisulfide Corrosion
    - SourWater JIP Phase I and II
    - Predict®-SourWater Software; release 2.0
  - Amine Unit Corrosion
    - Amine JIP
    - Predict®-Amine
  - New JIP Activities starting in 2006
    - Sulfuric Acid Alkylation
    - High Temperature Crude Oil Corrosivity - II

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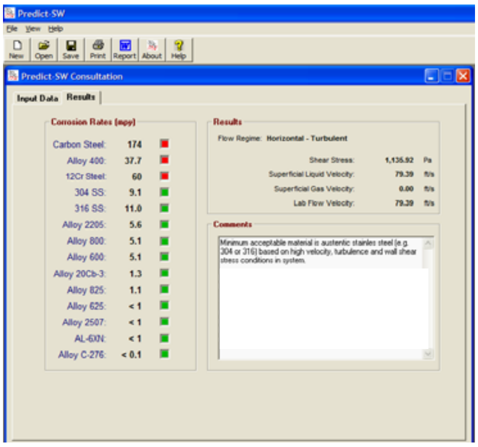
SourWater JIP Phase I & II

- Title: "Prediction & Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions" Phase I and II
- Jointly developed by InterCorr and Shell Global Solutions
- Phase I – H_2S-dominated sour water systems (REAC)
  - Two year effort completed in 2003
    - **Extensive engineering database** – parametric study of NH4HS concentration, H_2S partial pressure, temperature, inhibitors, flow (wall shear stress).
    - **17 sponsors / approx. $1 million US**
    - **Predict®-SW Software** – an integrated software tool for corrosion prediction and flow modeling for use in materials selection, risk assessment, inspection planning and enhanced unit operation.
    - **Predict-SW 2.0 Software** – is now available to both sponsors and non-sponsors; single-user and multi-user corporate licenses.

Predict®-SW 2.0

- Use of design or actual unit conditions to assess of corrosion severity. Includes **H_2S partial pressure effects** not found in current methods (e.g. K_p).
- Provides multiphase **flow modeling** to link unit conditions with JIP data.
- Queries **iso-corrosion and parametric relationships** over a broad range of system conditions.
- Output provides predicted corrosion rates for specific alloys based on
  - environmental conditions
  - flow regime, and
  - wall shear stress.
- Release 2.0 includes new features:
  - Updated Rules / Sensitivity Function
  - View Data
  - Units compatible with outputs from process models
  - Benchmarking, reporting & online Help

Output Screen



SourWater JIP – Phase II

Phase II – NH_3-dominated sour water systems

- Phase II currently in progress.
- Extensive engineering database – parametric study of NH4HS concentration, **H_2S & NH3 partial pressures**, temperature, **cyanides**, flow (wall shear stress).
- Involved 11 companies and approx. $700,000 in funding.
- New Information: **Conclusively shows a reversion to higher corrosion rates at high ammonia partial pressures.**
- Predict-SW software will be updated with this new information/rules.
- Program sponsors have two year confidentiality period.
- JIP will run through mid-2006.

Sour Water Participants (I & II)

- ChevronTexaco Energy Research & Technology Co.
- Flint Hills Resources, L.P
- Shell Global Solutions (US) Inc.
- ConocoPhillips, Inc.
- Petrobras - CENPES
- ExxonMobil Research & Engineering
- Sunoco
- Fluor Daniel Inc.
- UOP
- Saudi Aramco
- Syncrude Canada Ltd.
- Phillips Petroleum Co.
- Valero
- TOTAL
- BP
- Kuwait National Petroleum Co.
- Idemitsu Kosan Co., Ltd
- Lyondell-Citgo Refining LP
- Marathon-Ashland Petroleum

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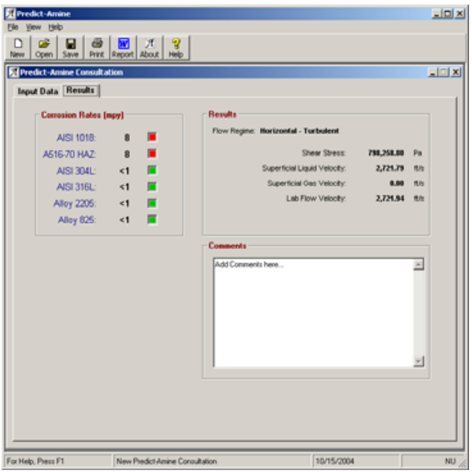
Amine JIP

Minimizing Amine Unit Corrosion

- Data development combining chemical and flow simulation (similar to Sour Water program)
- Program initiated with assistance of Flint Hill Resources.
- The program involves five tasks:
  - Task 1 – Baseline Data for Sour MEA, DGA, DEA Systems
  - Task 2 – Temperature
  - Task 3 – CO2/H2S Ratio
  - Task 4 – Heat Stable Salts
  - Task 5 – Development of a Software Corrosion Prediction Tool (Predict-Amine)
- Recently, tests included to evaluate MDEA.
- Program to be complete by mid-2006.
- Single user software license and 2 yr confidentiality period.
- New Lean Amine JIP being formulated.

Output Screen



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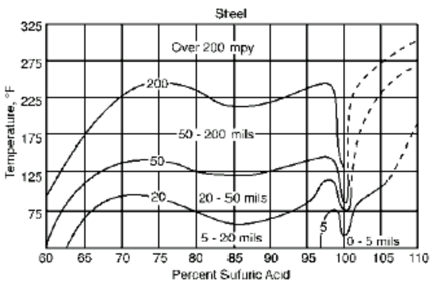
2006 JIP Activities

- The previous JIP's indicated that much work is needed to quantify the effects of process chemistry and flow conditions on corrosion of commonly used alloys.
- This approach has proven successful in studying:
  - Nap acid, sour water and amine corrosion.
- Based on end-user input, a similar parametric approach is being applied to:
  - Sulfuric acid alkylation unit corrosion
  - Current Nap Acid issues related to present limits for carbon steel, 5Cr, 9Cr, 12Cr and 316/317
- Programs are scheduled to begin in 2006:
  - Sulfuric acid alkylation: Q1 2006
  - Nap acid: Q3 2006

Sulfuric Acid Alkylation JIP - 1

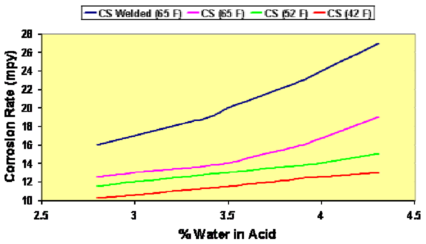
Prediction of Corrosion in Sulfuric Acid Alkylation Units

- A highly profitability refining operation.
- There is pressure on to maximize productivity (thru-put & availability) of alkylate processing units.
- Program was based on a gaps analysis conducted in early 2005:
  - Corrosion rates for steel at low temperatures
  - Influence of ASO
  - Role of contaminants
  - Limits for 316 and Alloy 20 at high temperatures
  - Influence of welding
  - Influence of flow & regime



Limited base data in API 581 for reagent grade H_2SO_4 corrosion from 1950's

Sulfuric Acid Alkylation JIP - 2



Limited data developed more recently indicates an effect of welding, temperature and velocity, but does not take into account wall shear stress.

- **JIP Technical Program:**
- **Task 1** – Chemical & Flow Modeling
- **Task 2** – Sensitivity studies on spent acid concentration, ASO and oxygenates
- **Task 3** – Parametric Study
  - Acid concentration
  - Temperature
  - Wall shear stress
- **Task 4** – Corrosion modeling and development of Predict®-SA software.
- Sponsors will have a 2 year confidentiality period
  - Includes single user version of software and use of data

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Minimizing Refinery Crude Corrosivity II

- Phase I was a pioneering JIP
  - Included support from over 20 companies
  - the most comprehensive experimental study.
- It identified critical parameters needed to better characterize the corrosivity of crude oil systems.
- Mechanisms of Nap Acid corrosion.
- Quantification of both chemical and flow-related mechanical factors.
- Limits for impingement attack of 5Cr, 9Cr & 12Cr.
- Influence of Nap Acid ring structures and sulfur speciation on corrosivity.
- Crude Corrosivity JIP-II starts in mid-2006
- Sponsors will have a 2 year confidentiality period
  - Includes single user version of software and use of data

- New program focuses on:
  - Major limitations of currently utilized risk matrix in API 581
  - Combined effects of TAN and sulfur
  - Liquid filled lines in turbulent flow for carbons steel, 5Cr, 9Cr and higher alloys
  - Needs for quick screening test for corrosivity assessment
  - Corrosivity software model (Predict®-Crude) to work with in-house proprietary assessment tools.

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Summary

- New Technology for Prediction and Assessment of Corrosion in Refinery Operations:
  - Ammonium Bisulfide Corrosion
    - SourWater JIP Phase I and II
    - Predict®-SourWater Software; release 2.0
  - Amine Unit Corrosion
    - Amine JIP
    - Predict®-Amine
  - New JIP Activities starting in 2006
    - Sulfuric Acid Alkylation
    - High Temperature Crude Oil Corrosivity – II

For more information contact R.D. Kane at: russ.kane@honeywell.com

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Appendix 6

Nickel alloys in hydroprocessing units

J. Hucinska (Gdansk University)

Nickel alloys in hydroprocessing units

JOANNA HUCIŃSKA

Gdańsk University of Technology, Gdańsk, Poland

EUROCORR 2005, EFC WP15

September 6, 2005 • Institutos Superior Tecnico • Lisbon, Portugal

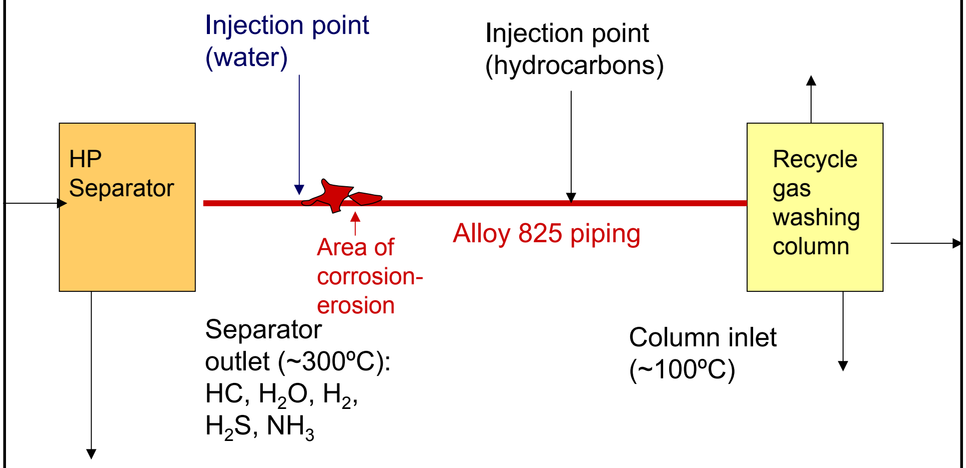
Lay-out

- Corrosion-erosion of reactor effluent air coolers (REACs) and piping
- Corrosion-erosion of Alloy 825
- Questions

Corrosion-erosion of reactor effluent air coolers (REACs) and piping

- Problem in hydrocracking and high severity hydrotreating units
- Reasons of damage: presence of aqueous amonium bisulphide (NH_4HS) and multiphase flow conditions
- Materials of construction: carbon steel, 321 steel, Alloy 800, Alloy 825

Corrosion-erosion of Alloy 825 in Used Oil Hydrotreatment Plant

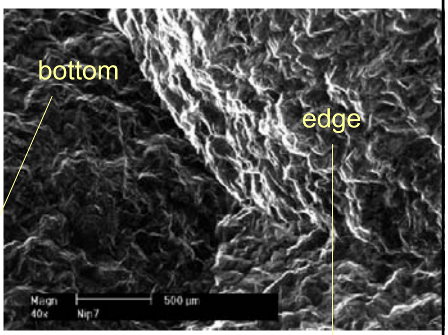


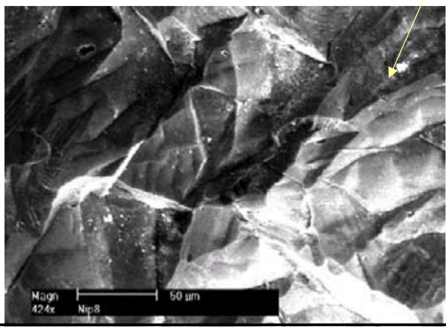
IS

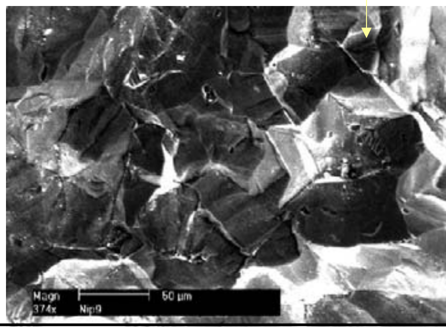
Macroscopic characteristics of corrosion-erosion after 5 months of service

Nominal: φ 219,1x12,7 mm, Alloy 825 gr. UNS N08825, ASTM/ASME B/SB705

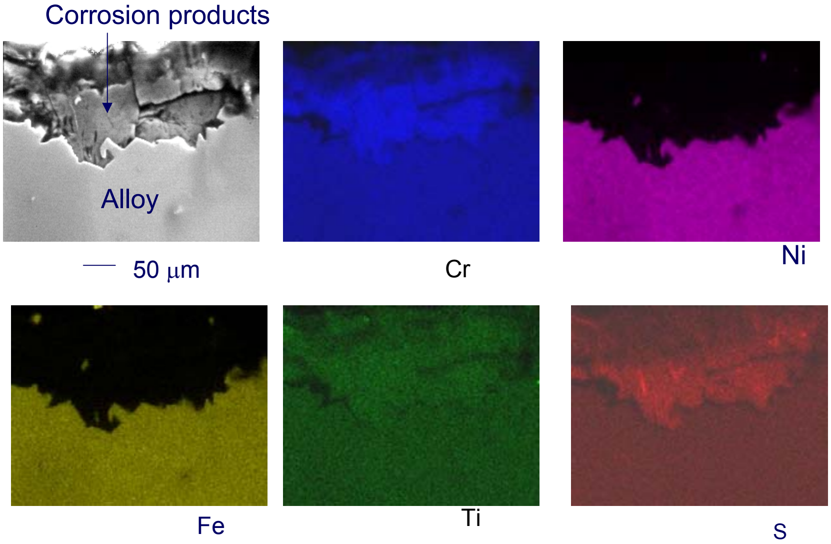
SEM micrograph of a cavity on the IS (free of corrosion products)







Microscopic characteristics of corrosion-erosion



Corrosion products on the IS, cross-section. SEM, EDS

Reasons of Alloy 825 brittle fracture

- (NH_4HS) + cavitation/droplet impingement
- Hydrogen?
- ?

Appendix 7

Metal dusting in plafforming CCR furnaces

J. Hucinska (Gdansk University)

Metal dusting in Platforming CCR furnaces

JOANNA HUCIŃSKA
Gdańsk University of Technology, Gdańsk, Poland

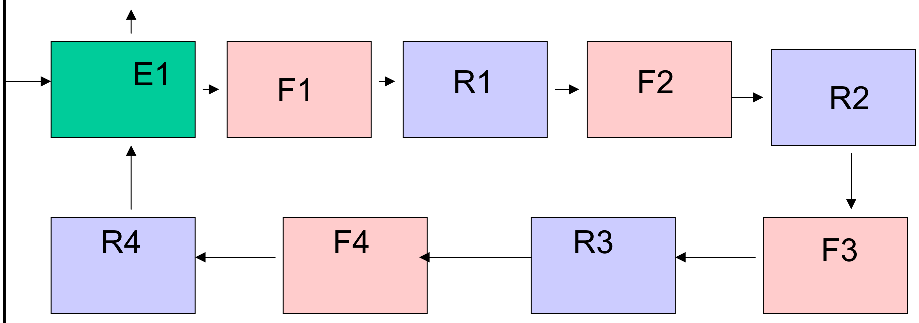
EUROCORR 2005, EFC WP15

September 6, 2005 • Institutos Superior Tecnico • Lisbon, Portugal

Lay-out

- Characteristics of furnaces, tubes, service conditions
- Non-destructive testing
- Destructive testing
- Questions

Unit: Platforming CCR (continuous catalytic reforming)



Characteristics of tubes and service conditions

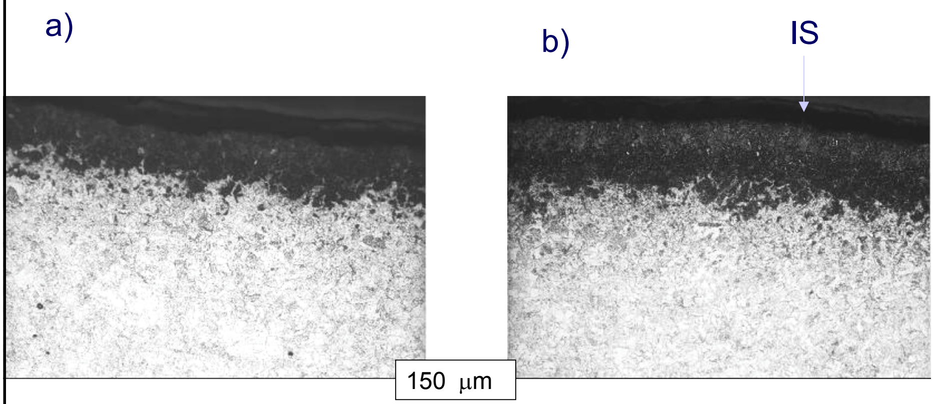
Characteristics	Description
Material of tubes	Steel 9Cr-1Mo, gr P9 ASTM SA-335
Nominal dimensions	114,3 x 6,0 mm
Environment	Heavy naphtha after desulphurisation and hydrogen gas: 440-520°C (F1), 400-520°C (F2), 450-520°C (F3), 470-520°C (F4), S~0.2 ppm (naphtha), S<0.5 ppm (hydrogen), ppH_2~0.65-0.8 MPa
Metal temperature	635ºC (design), ~600 ºC (service)
Time of service	10 years

Non-destructive testing

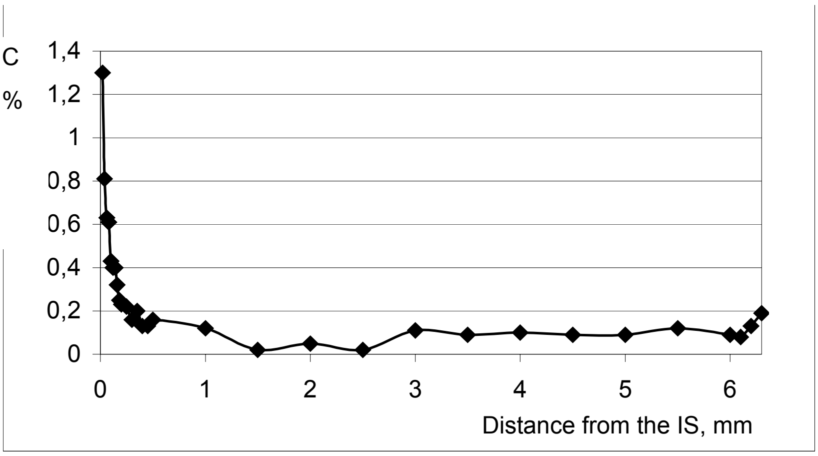
- Visual – no scale on the outside surface (OS) of the tubes
- Wall thickness – no losses
- Ultrasonic wave attenuation measurements – decrease in attenuation

Destructive testing

- Visual – thin, loose deposits of carbon on the inside surface (IS) of the tubes
- Metallographic: optical microscope (OM), transmission electron microscope (TEM)
- Electron probe microanalyser (EPMA)
- Tensile tests, Charpy-V impact tests



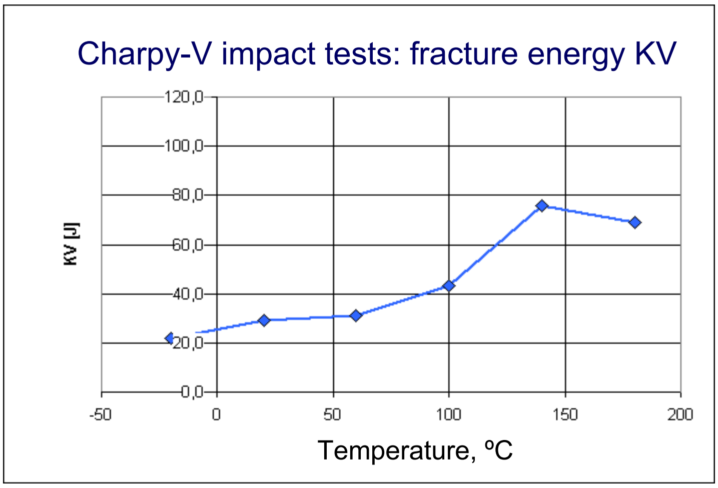
Cross-section of the tube wall, microstructure beneath the IS:
a) fire side, b) refractory side. OM

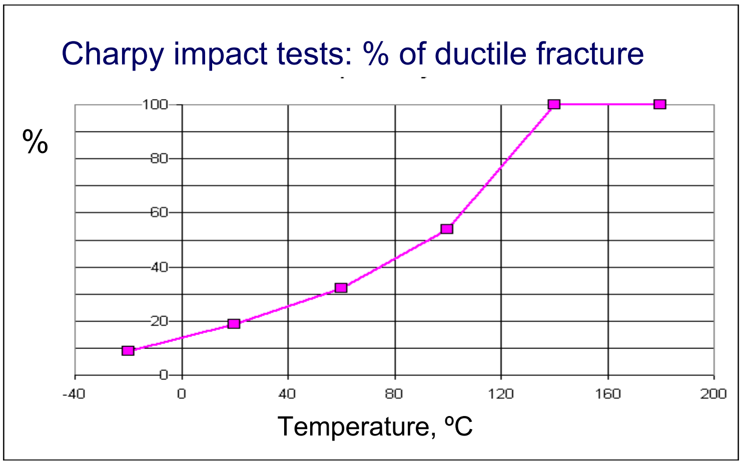


Cross-section of the tube wall, carbon profile. EPMA

Tensile tests

Material	Yield Stress MPa	Tensile strength MPa	Elongation %
Before service	337-400	556-588	32
After service	269-281	541-558	20
ASTM SA-335	205 min	415 min	27



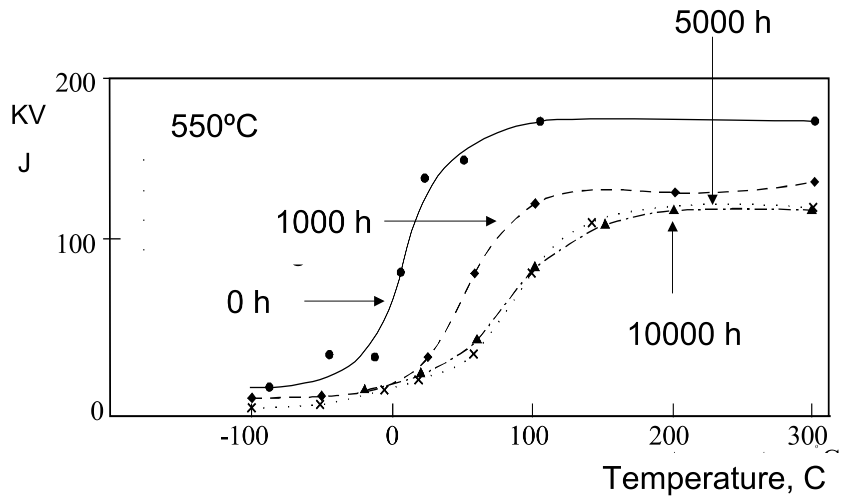


FATT 50=93ºC

FATT – fracture appearance transition temperature

Reasons of brittleness?

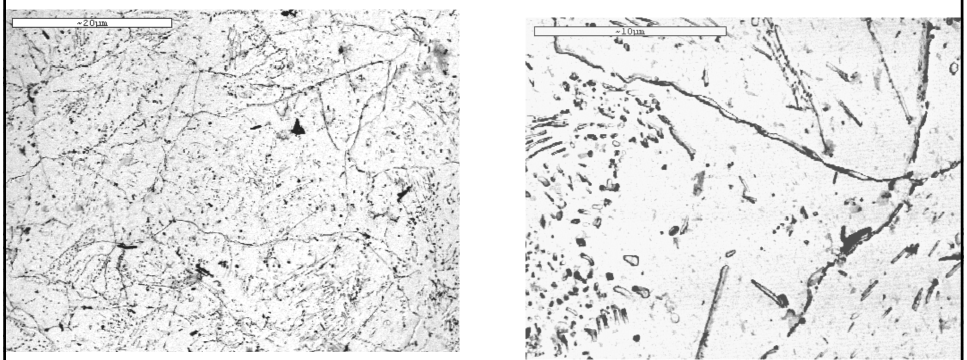
Literature data



Reason of brittleness: Laves phase Mo_2Fe at grain boundaries

(J.A. Hudson, S.G. Druce, G. Gage, M. Wall: Theoreticaland Applied Fracture Mechanics 1988, 10, p. 123)

Examinations



Mid-wall, carbon extraction replica. TEM

Chemical composition of precipitates, wt. %

No	Si	P	S	Cr	Mn	Fe	Mo
1	14.05	0.77	0.49	7.78	2.21	33.08	41.61
2	57.41	0.75	-	7.35	-	17.32	17.17
3	6.20	-	-	56.39	1.00	28.26	8.15
4	20.93	-	-	16.59	-	56.01	6.47
5	3.80	0.29	0.37	56.93	-	28.38	10.23
6	23.38	-	-	29.72	-	27.73	19.17
7	16.15	-	-	43.07	-	30.59	10.19

Questions

- Metal temperature 600ºC: too high for 9Cr-1Mo steel?
- Sulphur compounds added to the feed in platforming CCR unit are harmfull or advantageous ?