Appendix 1

List of participants and excused persons

Participants EFC WP15 meeting 9th September 2009 Nice (France)

Boillot	Pauline	Arcelor Mittal	FRANCE
Boinet	Mikael	EPA	FRANCE
Claesen	Chris J	Nalco	BELGIUM
Chambers	Brian	Honeywell	USA
Comerman	Claude	Heurtey Petrochem SA	FRANCE
de Bruyn	Hennie	Borealis AS	NORWAY
Deves	Jean Marie	AXENS - IFP Technology Group	FRANCE
Dupoiron	François	Total Petrochemical	FRANCE
Glaser	Andreas	OMV	AUSTRIA
Goldberg	Linda	Nace International	USA
Groysman	Alec	Oil Refineries Ltd	ISRAEL
Hofmeister	Martin	Bayernoil Raffineriegesellschaft mbH	GERMANY
Hucinska	Joanna	Gdansk University of Technology	POLAND
Keane	Tony	Nace International	USA
Kivisakk	Ulf	Sandvick	SWEEDEN
Loukachenko	Natalia	Arcelor Mittal	FRANCE
Lyublinski	Efim	NACE	USA
Owen	David	GE Betz	UK
Richez	Martin	Total	FRANCE
Ropital	François	IFP	FRANCE
Roy	Danny	Total Petrochemical	USA
Schultz	Marcele	Petrobras	BRAZIL
Tems	Robin D.	Saudi Aramco	SAUDI ARABIA
van Roij	Johan	Shell Global Solutions International B.V.	NETHERLANDS
Vanacore	Mario	Nalco	ITALY

Excuses received for the EFC WP15 meeting 9th September 2009 Nice

NAME	ADDRESS 1	ADDRESS 5
Mike Zetlmeisl	Baker Petrolite	SPAIN
Roberto Riva	Eni R&M	ITALY
Rob Scanlan	Conoco	UK
Larry Lambert	Nynas AB	UK
Joerg Maffert	Dillinger Huttenwerke	GERMANY
Iris Rommerskirchen	Butting Edelstahlwerke GmbH&Co KG	GERMANY
Maarten Lorenz	Shell Global Solutions International B.V.	NETHERLANDS
Carmelo Aiello	Eni	ITALY
André Claus	GE Betz	BEGIUM
Miroslav Michvocik	MOL Group, SLOVNAFT	SLOVAKIA
Andrew Kettle	Exxon Mobil	UK
Richard Carroll	BG Group	UK
Curt Christensen	Force Institutes	DENMARK
György Isaak	Env. & Corr. Manager	HUNGARY
Kari Saarinen	Zerust Oy	FINLAND
Stefano Trasatti	University of Milan	ITALY
Ksenija Babic	Baker Petrolite	USA
Dimphy Wilms	Applus RTD Benelux	NETHERLANDS
Dr Stefan Winnik	Exxon Mobil Chemical	UK
Melitza Lobaton	Couronnaise de Raffinage	FRANCE
François Dupoiron	Total Petrochemical	FRANCE

Appendix 2

EFC WP15 Activities

Welcome to the EFC Working Party Meeting

"Corrosion in Refinery" WP15

Nice 9 September 2009

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

AGENDA EFC Working Party 15

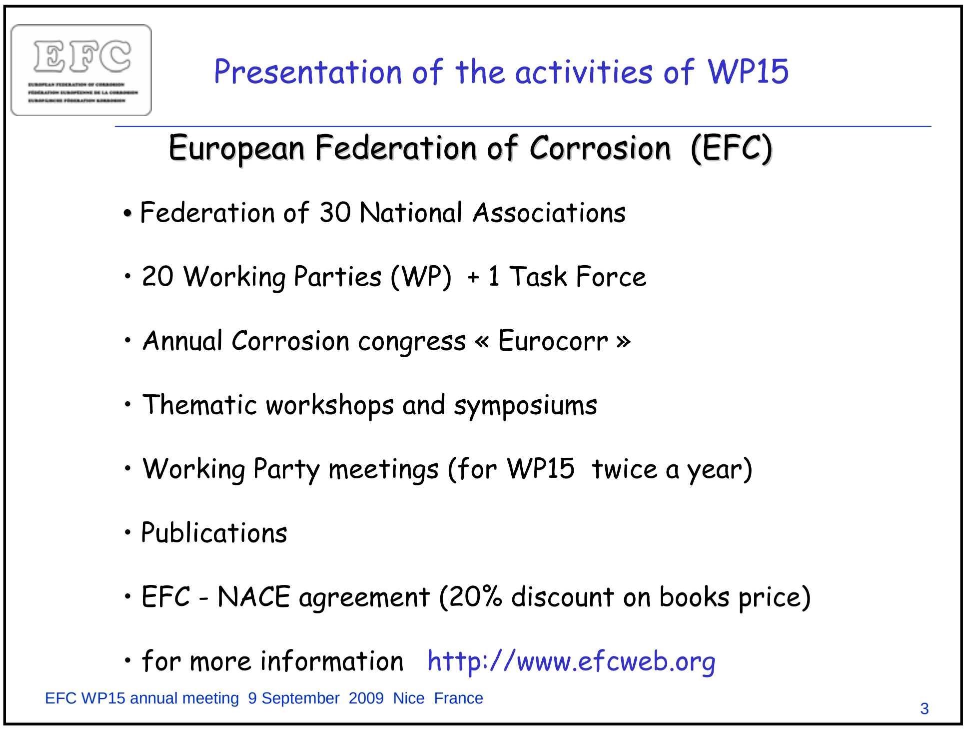
Corrosion Refinery Industry Meeting

10h50-12h30 Welcome - WP15 Activities (F. Ropital)
next Eurocorr 2010 (Moscow) and 2011 (Stockholm) sessions and workshops,
publications,
collaborations with NACE (publications, joint conferences)
information refinery failure cases
next meeting: spring 2010 ?
other points

Corrosion of storage tanks
corrosion failures in oil storage tank roofs and corrosion protection of product side tank bottoms (E. Lyublinski)

12h30-14h00 Lunch break

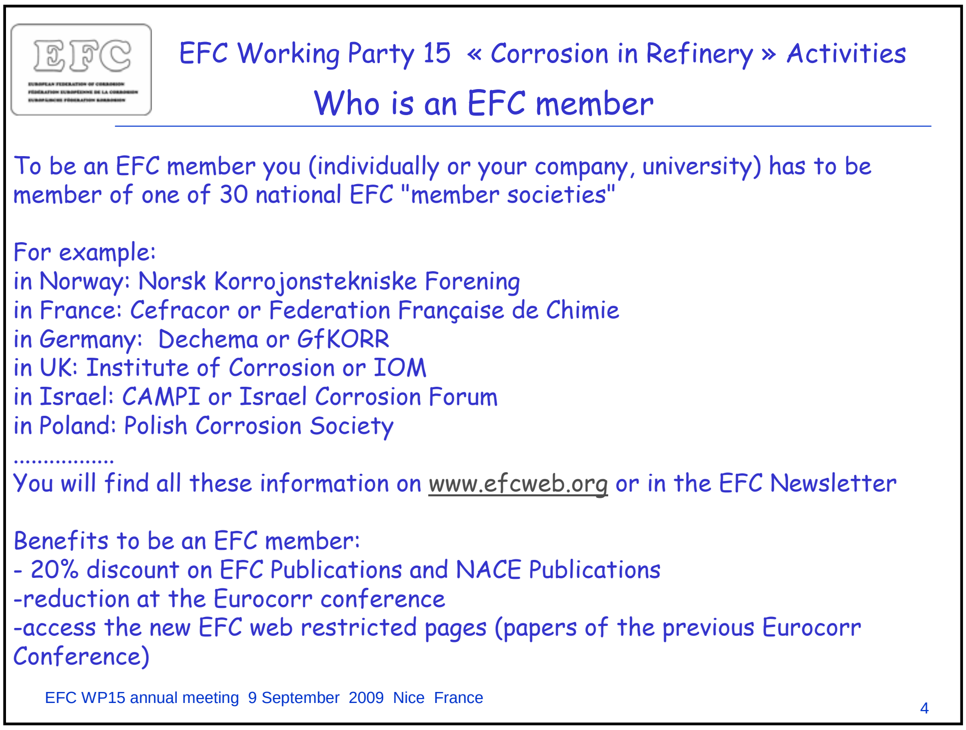
14h00 Workshop on Relaxation Cracking of Stainless steels
presentation prepared by F. Dupoiron: phenomena, survey,....
discussions on future recommendations and guideline
discussions and presentations from the audience



Presentation of the activities of WP15

European Federation of Corrosion (EFC)

- Federation of 30 National Associations
- 20 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 (20% discount on books price)
- for more information 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 30 national EFC "member societies"

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
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)

EFC Working Parties

http://www.efcweb.org

- WP 1: Corrosion inhibition
- WP 3: High temperature corrosion
- WP 4: Nuclear corrosion
- WP 5: Environmental sensitive fracture
- WP 6: Surface science and mechanisms of corrosion and protection
- WP 7: Education
- WP 8: Physico-chemical methods and corrosion 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 heritage artefacts

EFC Working Party 15 « Corrosion in Refinery » Activities

http://www.efcweb.org/Working+Parties-p-104085/WP%2B15-p-104111.html

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

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

Update in relation with Nace document 11106 "Monitoring and adjustment of cooling water treatment operating parameters" Task Group 152 on cooling water systems: the document is now available Nace item n° 24238

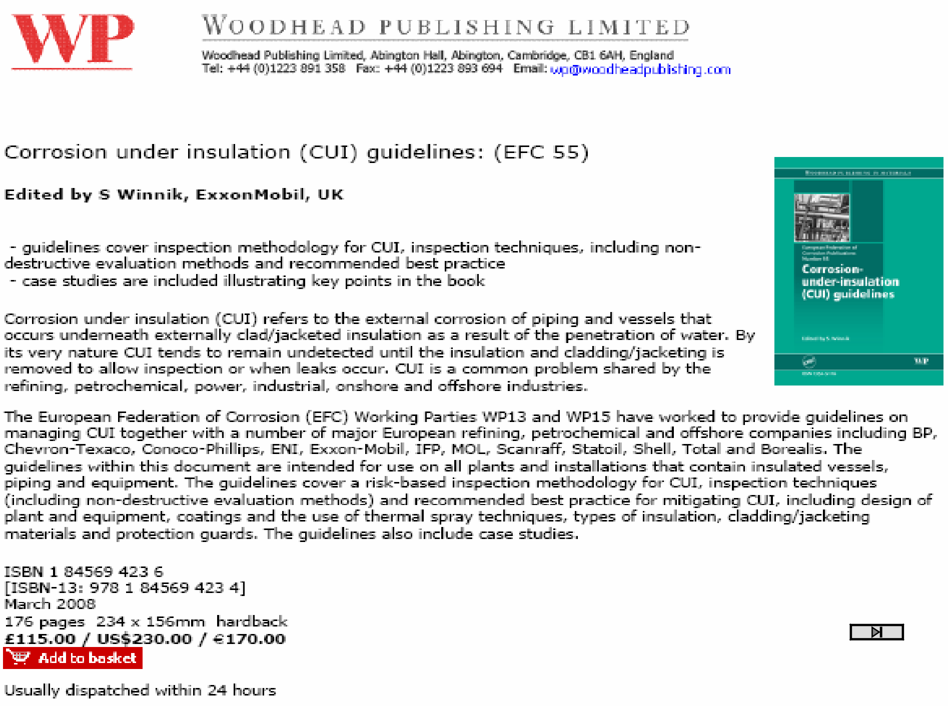
- EFC Guideline n° 46 on corrosion in amine units http://www.woodheadpublishing.com/en/book.aspx?bookID=1299

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

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

you can by these books at the Maney booth during this conference

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



WOODHEAD PUBLISHING LIMITED
Woodhead Publishing Limited, Abington Hall, Abington, Cambridge, CB1 6AH, England
Tel: +44 (0)1223 891 358 Fax: +44 (0)1223 893 694 Email: wp@woodheadpublishing.com

Corrosion under insulation (CUI) guidelines: (EFC 55)

Edited by S Winnik, ExxonMobil, UK

- guidelines cover inspection methodology for CUI, inspection techniques, including non-destructive evaluation methods and recommended best practice
- case studies are included illustrating key points in the book

Corrosion under insulation (CUI) refers to the external corrosion of piping and vessels that occurs underneath externally clad/jacketed insulation as a result of the penetration of water. By its very nature CUI tends to remain undetected until the insulation and cladding/jacketing is removed to allow inspection or when leaks occur. CUI is a common problem shared by the refining, petrochemical, power, industrial, onshore and offshore industries.

The European Federation of Corrosion (EFC) Working Parties WP13 and WP15 have worked to provide guidelines on managing CUI together with a number of major European refining, petrochemical and offshore companies including BP, Chevron-Texaco, Conoco-Phillips, ENI, Exxon-Mobil, IFP, MOL, Scanraff, Statoil, Shell, Total and Borealis. The guidelines within this document are intended for use on all plants and installations that contain insulated vessels, piping and equipment. The guidelines cover a risk-based inspection methodology for CUI, inspection techniques (including non-destructive evaluation methods) and recommended best practice for mitigating CUI, including design of plant and equipment, coatings and the use of thermal spray techniques, types of insulation, cladding/jacketing materials and protection guards. The guidelines also include case studies.

ISBN 1 84569 423 6
[ISBN-13: 978 1 84569 423 4]
March 2008
176 pages 234 x 156mm hardback
£115.00 / US$230.00 / €170.00

Usually dispatched within 24 hours

WP15 Meetings

One WP 15 working party meeting in Spring,

23 April 2009 in Vienna - Austria (hosted by Borealis)
15 April 2008 in Leiden -The Netherlands (hosted by Nalco)
26 April 2007 in Paris – France (hosted by Total)
31 March 2006 in Porto Marghera – Italy (hosted by Eni)
17-18 March 2005 in Trondeim – Norway (hosted by Statoil)
8-9 March 2004 in Milan – Italy (hosted by Eni) with Nace Italia
10 April 2003 in Pernis – The Netherlands (hosted by Shell)
in 2002 only one meeting on 15 November 2002 in Paris – France (hosted by Total)
6 April 2001 in Rueil-Malmaison – France (hosted by IFP)
25 March 1999 in UK (hosted by TWI)
23 April 1998 in Milan – Italy (hosted by Eni)

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

The minutes of the meetings are available on the EFC WP15 Web page
http://www.efcweb.org/Working+Parties-p-104085/WP%2B15-p-104111.html

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EFC WP15 Web page

http://www.efcweb.org/Working+Parties-p-104085/WP%2B15-p-104111.html

Now open page (as all the other WP pages)

In the future, an open page + restricted area to EFC members

EFC Web

http://www.efcweb.org

Now open page (as all the other WP pages)

In the future, open pages + restricted pages to EFC members

In the future acces for the EFC members to the proceedings of all the Eurocorr conference (with exclusion of the last one)

In project :Forum exchange pages ?

EFC Working Party 15 « Corrosion in Refinery » Activities

Education – Corrosion courses

EFC wants to list the corrosion courses hold in Europe by collection of the information in each Working Party

Concerning the corrosion in refineries, can every WP15 member send to WP15 Chairman (francois.ropital@ifp.fr) the ones you know:
-name of the course
-institution that run the course (may be Dechema, Manchester University, ...)
-web links to get information of the course (programme, etc...)

Qualification

Links, exchange of information between WP15 and National, European accreditation organisations

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EFC Working Party 15: Next Eurocorr's Refinery sessions

Eurocorr's web site: www.eurocorr.org

Eurocorr 2010
13-17 September 2010 in Moscow
"From the Earth's depths to the Space heights"
Sponsored by Gasprom and Gubkin Russian State University of Oil and Gas
✓ Refinery corrosion session
✓+ special workshop/roundtable on corrosion of high sulphur crude processing equipment
Deadline to submit an abstract: 15 January 2010

Eurocorr 2011
5-9 September 2011 in Stockholm
✓ Refinery corrosion session
✓+ Joint sessions with other EFC working parties ? (WP3 ?, 1 ?)

Eurocorr 2012
9-13 September 2012 in Istanbul

EFC Working Party 15 – Collaboration with Nace

The initial Proposal of Nace and EFC presidents was to co-organize a conference on "Corrosion in refineries – practical applications" around July 2010 that could have take place in Europe (Rotterdam)

The subject has been discuss within WP15 and within Nace STG34 (Carol Laughlin, Rob Scanlan, John Wodarcyk)

Due to budget travel restriction in our companies and not to overlap with the existing Nace annual and Eurocorr conferences, it has been suggested by Nace to organise in 2010 a video conference (Tony Keane)

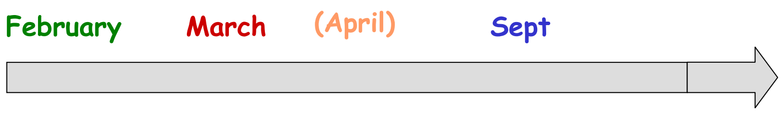
. Information on the last STG34 meetings

- Collaboration on standards
  - Revision of MR 01-03 ???

- Publications
  - EFC guideline 40 + RP 11106 on cooling water (item 24238 published in 2009)

EFC – NACE Joint Conference

Some corrosion in refineries annual events



Nace Annual Conf

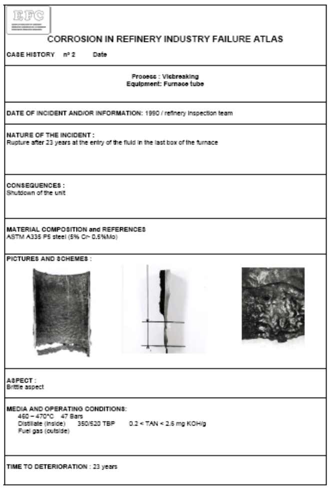
Eurocorr

Middle East Corrosion Conf
(2010-2012)

Nace Technical week

(WP15 spring meetinh)

Failure cases atlas


CORROSION IN REFINERY INDUSTRY FAILURE ATLAS

CASE HISTORY n° 2 Date

Process : Visbreaking
Equipment: Furnace tube

DATE OF INCIDENT AND/OR INFORMATION: 1990 / refinery inspection team

NATURE OF THE INCIDENT :
Rupture after 23 years at the entry of the fluid in the last box of the furnace

CONSEQUENCES :
Shutdown of the unit

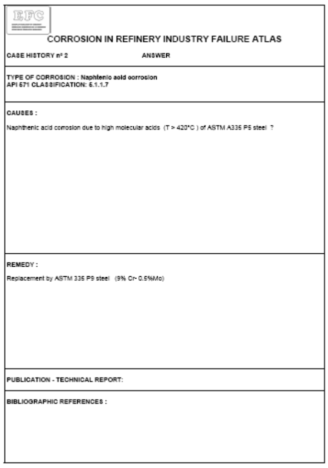
MATERIAL COMPOSITION and REFERENCES
ASTM A335 P5 steel (5% Cr- 0.5%Mo)

PICTURES AND SCHEMES :

ASPECT :
Brittle aspect

MEDIA AND OPERATING CONDITIONS:
460 – 470°C 47 Bars
Distillate (inside) 350/520 TBP 0.2 < TAN < 2.6 mg KOH/g
Fuel gas (outside)

TIME TO DETERIORATION : 23 years


CORROSION IN REFINERY INDUSTRY FAILURE ATLAS

CASE HISTORY n° 2 ANSWER

TYPE OF CORROSION : Naphtenic acid corrosion
API 571 CLASSIFICATION: 5.1.1.7

CAUSES :

Naphthenic acid corrosion due to high molecular acids (T > 420°C) of ASTM A335 P5 steel ?

REMEDY :

Replacement by ASTM 335 P9 steel (9% Cr- 0.5%Mo)

PUBLICATION - TECHNICAL REPORT:

BIBLIOGRAPHIC REFERENCES :

http://project.ifp.fr/cui-efc-wp15

Guide line : how to use the failure case web page available

Failure cases atlas

N° File	Writer	Date	Process	Equipment	Causes	API 571 Classification	Type of material
1	J. Hucinska	2006	Hydrocracking	Reactor	Sulfidation	5.1.1.5	347 SS
2	F. Ropital	29/06/1905	Visbreaking	Furnace	Naphthenic acid corrosion	5.1.1.7	5% Cr steel
3	A.Visgard Nielsen	13/09/2007	Hydrodesulfurizer	Heater	Creep	4.2.8	304 SS
4	F. Ropital	20/12/2007	Continuous Catalytic Reforming	Furnace	Metal dusting	4.4.5	2.25%Cr steel
5	J. Hucinska	30/03/2008	Continuous Catalytic Reforming	Furnace	Metal dusting	4.4.5	9%Cr steel

EFC Working Party 15 – Corrosion failures atlas

A few failure cases has been collected

F. Ropital will continue to fill the data base

If you have your own inputs, could you send them to F. Ropital

EFC Working Party 15 – 2010 Spring meeting

. Proposal of MOL to host the 2010 spring in the

Duna Refinery – Százhalombatta (Budapest)

.

MOL

Appendix 3

Eurocorr 20010 sessions

EUROCORR

The European Corrosion Congress

DECHEMA I SITEMAP I CONTACT I OUR WEBSITES I

- Home
- **EUROCORR 2010**
  - Committees
  - Scientific Programme
  - Authors' Information
  - Exhibition
  - Abstract Submission
  - General Information
- EUROCORR 2009
- EUROCORR 2008
- Imprint

EUROCORR 2010

From the Earth's Depths to Space Heights

13 to 17 September 2010 - Congress Center of World Trade

EUROCORR

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EUROCORR 2008
Imprint

Scientific Programme

Scientific and Technical Area:

Contributions are welcome in any of the EFC Working Party (WP) areas of interest:

WP 1: Corrosion and Scale Inhibition
WP 3: Corrosion by Hot Gases and Combustion Products
WP 4: Nuclear Corrosion
WP 5: Environment Sensitive Fracture
WP 6: Surface Science and Mechanisms of Corrosion and Protection
WP 7: Corrosion Education and Computer Applications
WP 8: Physico-chemical Methods of Corrosion Testing
WP 9: Marine Corrosion
WP 10: Microbial Corrosion
WP 11: Corrosion of Steel in Concrete
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 Corrosion
WP 18: Tribo-Corrosion
WP 19: Corrosion of Polymer Materials
WP 20: Corrosion and Corrosion Protection of Drinking Water Systems
WP 21: Corrosion of Archaeological Artefacts

Special workshops/Round Tables

In addition to these sessions, special workshops and roundtables will be organised, including:

A. Joint Session: Local Microprobes to Study Surface Treatments and Coatings Produced by Nanotechnologies (WP 6 & WP 8 & WP 14)
B. Workshop: Standards and Regulations in Corrosion Protection of Oil and Gas Production Equipment and Pipelines
C. Workshop: Diagnostics & Maintenance of Oil and Gas Transportation Facilities
D. Workshop: Corrosion and Corrosion Protection in Aerospace Industry
E. Workshop: Corrosion of High-Sulphur Crude Processing Equipment
F. Joint NACE / EFC - Workshop

To attract young participants to EUROCORR a contest of oral presentations of authors below 35 will be held.

Poster Exhbition / EFC Poster Award

The poster presentation of latest results is an important facet of the scientific programme. This role will be emphasised in Moscow by an **EFC Poster Award** which will be awarded during the closing session. Further information will be given as soon as possible.

We invite you to submit one page abstracts. Submission of abstracts will be possible from October 2010 on this website. Detailed information will be given.

EUROCORR

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- Imprint

Authors' Information

Dates to note

from October 2009: Submission of abstracts possible

15 January 2010: Deadline for submission of abstracts

March 2010 : Notification to authors

May 2010: Distribution of the programme

15 July 2010: Submission of full manuscripts for the CD-ROM

15 July 2010: Deadline for early registration

Proceedings

Full papers of all accepted lectures and posters will be available on a CD-ROM at the congress. For that reason please send us a full paper of your submission not later than 15 July 2010. Submission of full papers will be possible via internet. Please note: all contributions which will not be submitted until that deadline can not be included in the CD-ROM. The full paper should not exceed 1 MB.

Appendix 4

Workshop on Relaxation Cracking of Stainless steels

CEFRACOR
French corrosion Society

Corrosion in Oil and Gas Industries
High temperature working group

Members :

CETIM , EPA, Haynes Intl , IFP , Industeel , Heurtey Petrochem, Technip, Total

---

Oil and gas High temperature group GT9 :

Specific CEFRACOR Comittee

Main goals :

- Return of experience exchanges
- « Forum « between users (Petrochemical, Refinery , Chemical industries) , Research center , producers , fabricatior, engineering .
- Works on specific topics : Stress relaxation cracking

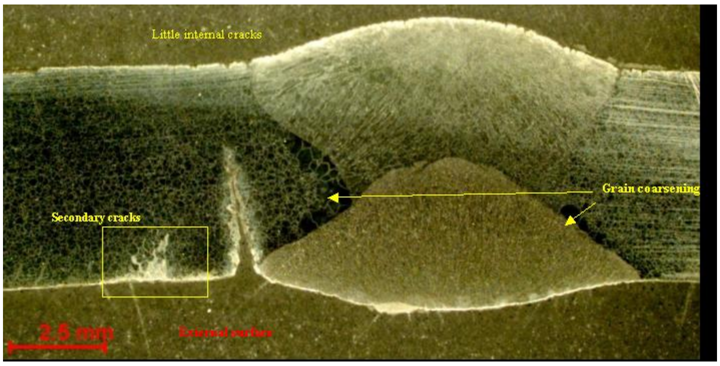
Stress Relaxation Cracking :

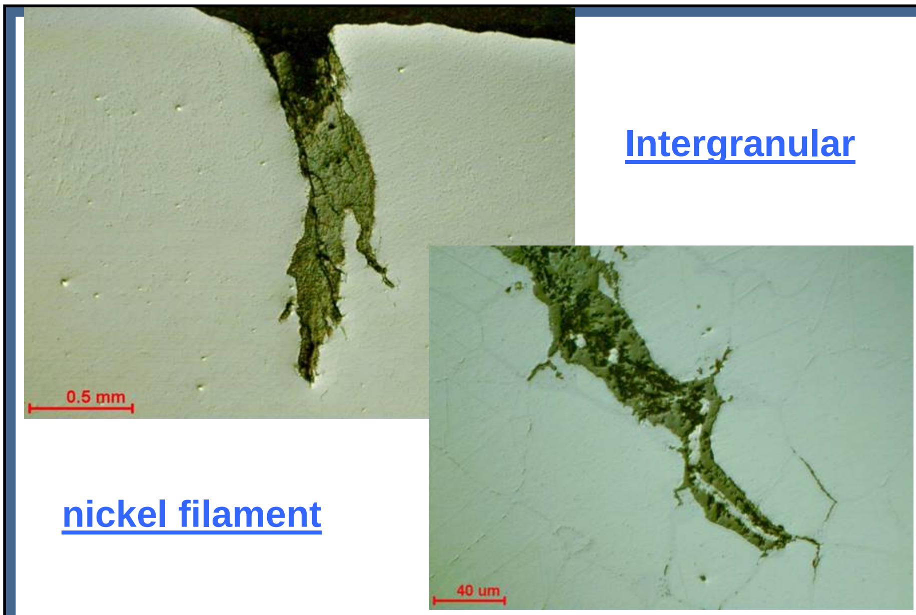
Location : primarily in heat affected zone but not only !

Stress Relaxation Cracking :

Cracking phenomenon of the austenitic grades working at high temperatures 450 à 800°C and particularly in case of high stress and strain.

Location : primarily in heat affected zone but not only !

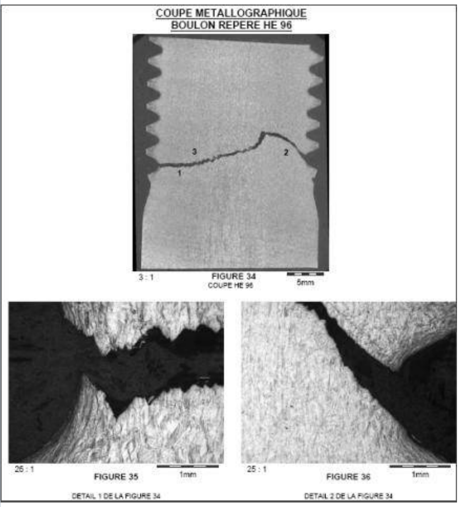


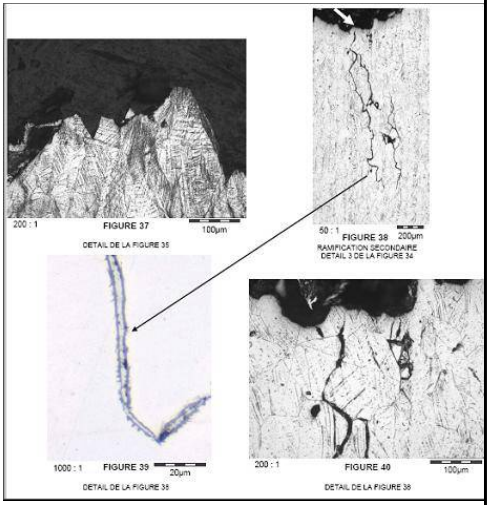


Intergranular

nickel filament

Location : primarily in heat affected zone but not only ! Cold work 304 Cu – 550°C





Grain size 2-3 , hardness 250-290Hv –Intergranular rupture – Metalic filament

Stress Relaxation Cracking 450-850°C

- **Thicker walls (>1”) more susceptible for cracking during fabrication; all thicknesses can crack in-service**
- **Location – primarily HAZ and highly stressed zone (stresses , cold worked)**
- **High sensitivity to grain size particularly coarser than 3**
- **Sensitivity to (?):**
  - Heat input and residual stresses
  - Cold work
  - Thermal expansion differences between filler material and base material
  - Filler metal contraction level

Stress Relaxation Cracking :

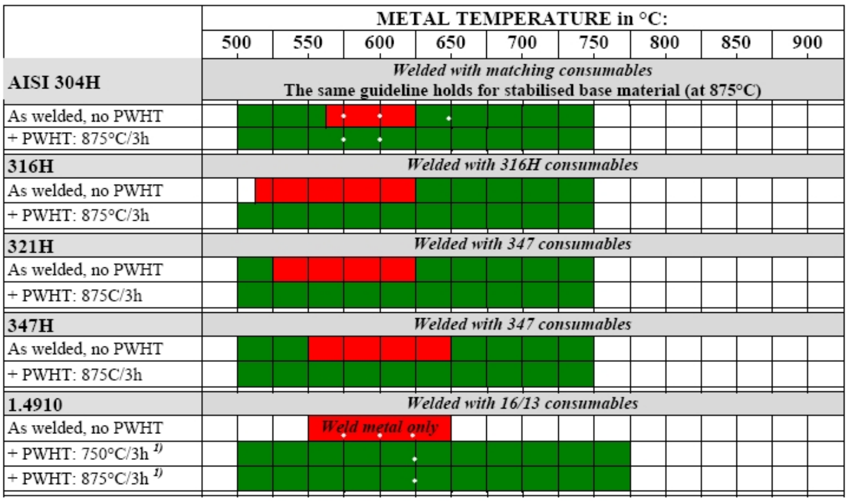
- **Caracterisation :**
  - Short term and high stresses:cracking can occur during heat treatment... => high heat rate in the sensitive zone and low cooling rate
  - Long term : cracks observed in the first 18 months
  - Expertise Intergranular:crack in the highly stressed zones, Ni filament

Stress Relaxation Cracking :

Caracterisation :

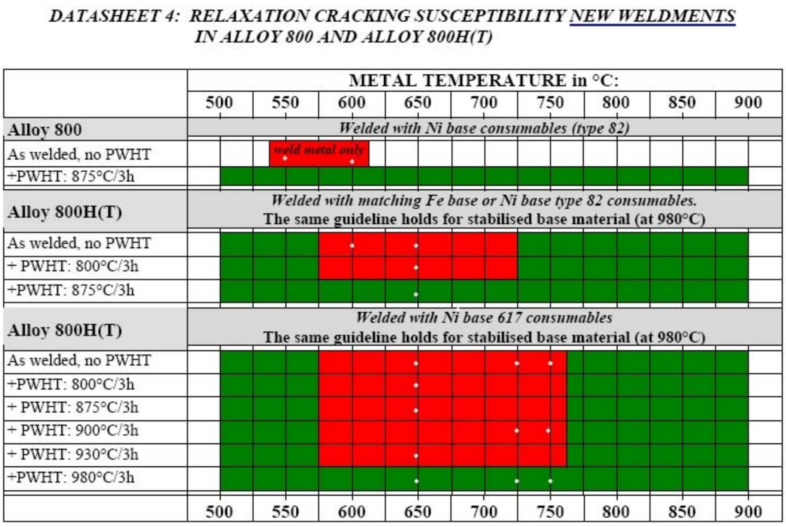
- Expertise Intergranular:crack in the highly stressed zones, Ni filament

DATASHEET 2: RELAXATION CRACKING SUSCEPTIBILITY NEW WELDMENTS IN AISI 304H, 316H, 321H, 347H and 1.4910



	METAL TEMPERATURE in °C:																	
	500		550		600		650		700		750		800		850		900	
AISI 304H	*Welded with matching consumables* The same guideline holds for stabilised base material (at 875°C)																	
As welded, no PWHT		🟩	🟩	🟩🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟩							
+ PWHT: 875°C/3h		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
316H	*Welded with 316H consumables*																	
As welded, no PWHT		🟥	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟩							
+ PWHT: 875°C/3h		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
321H	*Welded with 347 consumables*																	
As welded, no PWHT		🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟩							
+ PWHT: 875C/3h		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
347H	*Welded with 347 consumables*																	
As welded, no PWHT		🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟩							
+ PWHT: 875C/3h		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
1.4910	*Welded with 16/13 consumables*																	
As welded, no PWHT				🟥 *Weld metal only*	🟥	🟥	🟥											
+ PWHT: 750°C/3h [1]		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩						
+ PWHT: 875°C/3h [1]		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩						

1) A PWHT seems to be conservative

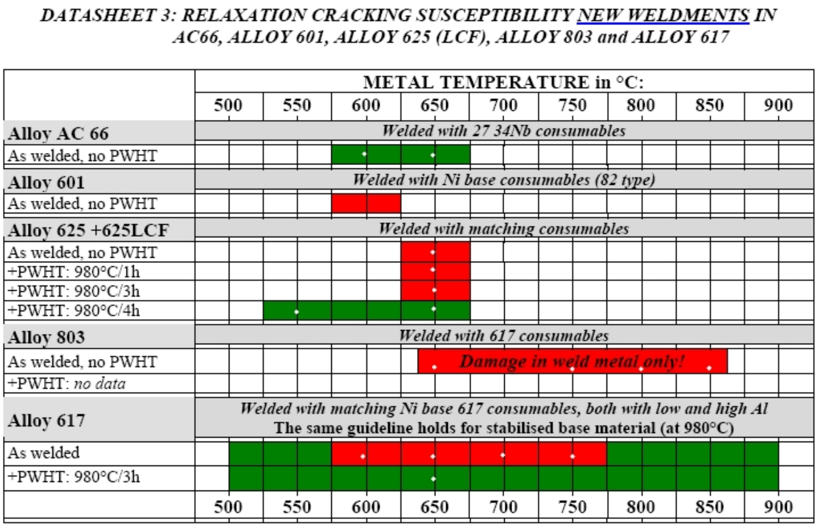


DATASHEET 4: RELAXATION CRACKING SUSCEPTIBILITY NEW WELDMENTS IN ALLOY 800 AND ALLOY 800H(T)

	METAL TEMPERATURE in °C:								
	500	550	600	650	700	750	800	850	900
Alloy 800	*Welded with Ni base consumables (type 82)*								
As welded, no PWHT		🟥 weld metal only	🟥						
+PWHT: 875°C/3h	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Alloy 800H(T)	*Welded with matching Fe base or Ni base type 82 consumables.* The same guideline holds for stabilised base material (at 980°C)								
As welded, no PWHT	🟩	🟩	🟥	🟥	🟥	🟩	🟩	🟩	🟩
+ PWHT: 800°C/3h	🟩	🟩	🟥	🟥	🟥	🟩	🟩	🟩	🟩
+PWHT: 875°C/3h	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Alloy 800H(T)	*Welded with Ni base 617 consumables* The same guideline holds for stabilised base material (at 980°C)								
As welded, no PWHT	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩
+PWHT: 800°C/3h	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩
+ PWHT: 875°C/3h	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩
+ PWHT: 900°C/3h	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩
+ PWHT: 930°C/3h	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩
+PWHT: 980°C/3h	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
	500	550	600	650	700	750	800	850	900

Stress Relaxation Cracking :

- **ASME Sect. VIII, UNF-56 (e) recently added a requirement to PWHT Alloy 800,H,HT at 885 min. for services >530°C**
  - Very difficult and costly to applied
- **No similar requirement in B31.3 or CODAP or other codes yet**



DATASHEET 3: RELAXATION CRACKING SUSCEPTIBILITY NEW WELDMENTS IN AC66, ALLOY 601, ALLOY 625 (LCF), ALLOY 803 and ALLOY 617

	METAL TEMPERATURE in °C:								
	500	550	600	650	700	750	800	850	900
Alloy AC 66	*Welded with 27 34Nb consumables*								
As welded, no PWHT			🟩	🟩					
Alloy 601	*Welded with Ni base consumables (82 type)*								
As welded, no PWHT			🟥						
Alloy 625 +625LCF	*Welded with matching consumables*								
As welded, no PWHT				🟥					
+PWHT: 980°C/1h				🟥					
+PWHT: 980°C/3h				🟥					
+PWHT: 980°C/4h		🟩	🟩	🟩					
Alloy 803	*Welded with 617 consumables*								
As welded, no PWHT				🟥	🟥	🟥 *Damage in weld metal only!*	🟥	🟥	
+PWHT: *no data*									
Alloy 617	*Welded with matching Ni base 617 consumables, both with low and high Al* **The same guideline holds for stabilised base material (at 980°C)**								
As welded	🟩	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟩
+PWHT: 980°C/3h	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
	500	550	600	650	700	750	800	850	900

Stress Relaxation Cracking :

- **Many works and publications :** see particularly H.Van Wortel , ENSMP publications

- **Sometime mentioned by steels and alloys producer (VDM)**

- **Often experimented by users : 316,347 , 321 , 304 , 310, 800H, 617 , HP , HK ....**

- **Sensitivity diagram application leads to .... high extracosts and/or impossibilities.**

- **Needs to precise the risk level depending on : grades , stress level , heat treatments, welding procedure => CIPG Working group**

Working group actions program (1) :

- **Return of experience in France**
  - Grades
  - Fabrications conditions
  - Service conditions

- **Propose a best pratice guide line in order to limit the risk :**
  - Grades sensitivity versus temperature;
  - Design recommandation
  - Fabrication recommended method (geometry , welding practices , filler material)

Working group actions program (2) :

- **Caracterisation test proposal** (based on the TNO methodology)

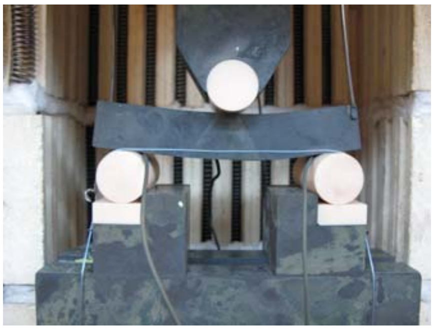
- **Discussion with producers**
  - to include the temperature range sensitvity in the grades brochures and documentations

- **Discussion with Codes authorities** to precise the codes requierments :
  - Avoid the complete heat treatment at 900°C (800H) when possible
  - Differenciate high stressed and low stressed welds

- **Open for international cooperations**

Working group actions program experimental part:

- Testing device :
  - Device design according TNO specification
  - Complementary instrumentation : acoustic emission to detect crack initiation.



Working group actions program experimental part:

- Planed program:
  - Generic program (all JIP members) :
    - Methodology and tests validation at TNO
    - Sensitivity factors study :
      - Heat input;
      - Grain size ;
      - Stress levels (primary and secondary);
      - Effect of filler material (composition , ferrite %);
  - Specific program (particular JIP members)
    - New grades : 803 , 4910 , MA ...
    - Specific welding procedures

Working group actions program experimental part:

- Program progress (done)
  - Device definition and realisation
  - Mechanical calibration in the temperature range (550-850°C)
  - Acoustic emission device and calibration
  - Material reference :
    - 800HT grade hight Temperature annealed
    - Welded (617 filler) and unwelded .
    - Austenitics stabilized grades (347 , 321)

Open for collaborations and exchanges

Thank you for your attention

Appendix 5

Stress relaxation cracking enquiry

EFC WP15 – CEFRACOR

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

CEFRACOR
CENTRE FRANÇAIS DE L'ANTICORROSION

Stress relaxation cracking enquiry
EFC WP15 Corrosion in Refinery – CEFRACOR Petroleum commission

Thank you for your time spent to fill this form.

Could you send it back before **2 November 2009** to: Francois Dupoiron

email: francois.dupoiron@total.com Fax: 33 4 37 23 70 91

Your name:
Company:
Address:
email:
phone number: fax number:

I have experience(s) with stress relaxation cracking: YES NO

If NO will you be interested by the results of this survey and receive a resume: YES NO

If YES can you give information on your experience(s) YES NO

If YES please fill one form for each experience (you can feel free no to answer some question)

NB: information on stress relaxation cracking
Stress relaxation cracking mainly occur for long term ageing between 450 to 700°C in welded area on stainless steels. It leads to a brittle intergranular rupture due to the relaxation of stresses.

Experience n°1:

Identification of the plant :

Identification of the unit or process :

Type of material that failed :

Welding procedure :

Application of an stress relieving heat treatment ?
Which one:

Temperature of the failed part:

Time to failure:

Thickness of the failed part:

Hardness of the failed part:

Microstructure, grain size of the failed part:

Information of the type and concentration of stress:

Remedy applied to prevent stress relaxation cracking

Information on the remedy behaviour:

Appendix 6

EFFECT OF TEMPER AND HYDROGEN EMBRITTLEMENT ON FRACTURE MECHANICS AND CVN PROPERTIES OF 2,25CR1MO STEEL GRADE – APPLICATION TO MINIMUM PRESSURISING TEMPERATURE (MPT) ISSUES

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Standard and Vanadium enhanced 2.25Cr1Mo plate steels (ASTM A387 gr. 22 and A542 type D) are commonly used in refining plants for the building of heavy reactors.

These reactors are made of heavy plates or forged shells (thicknesses up to 300-350mm) and are submitted to thermal cycles (stop and go) and to severe service conditions (high pressures, high hydrogen partial pressures, high temperatures). The main matter for end-user concerns the definition of Minimum Pressurizing Temperature (MPT). This temperature is the lowest temperature at which pressure can be put back in the vessel after shutdown. This minimum temperature insures no risk of brittle failure and is defined by fracture mechanics and/or CVN approaches and calculation.

This paper presents the methodology of MPT determination and the impact of ageing and hydrogen environment on material properties and then on MPT values. The method is explained in the case of a virtual pressure vessel but representative of refining cases.

INTRODUCTION

One of the leading risks in the petrochemical / refining industries is the risk of brittle (i.e. unstable) failure of pressure vessels. Heavy wall low-alloy pressure vessels are designed to operate at high temperatures, and at high pressures and hydrogen partial pressures leading to many problems.

During unit shutdowns, pressure and temperature are reduced to levels much lower than exposed to in operation. After conclusion of the maintenance procedures, the operation staff will restart the unit, raising the vessel pressure and temperature to the operational set points, thus starting a new production cycle. During the early stages of the start-up process, strict attention must be paid to metal temperature and internal pressure to insure sufficient toughness of the reactor material. This is done by controlling the heating and pressurization rate of the vessel, avoiding conditions that could cause brittle failure. This dramatic and unacceptable situation could occur if the low-alloy steel temperature is not high enough to achieve a level of fracture toughness that is sufficient to mitigate crack instability and catastrophic failure.

Ensuring sufficient toughness at every temperature deals with definition of Minimum Pressurizing Temperature (MPT) which then serves as a guideline for future operation of a given reactor. A vessel start-up program that is based on MPT concept includes a system of steps of temperature-pressure couples that must be abided by when the production cycle is restarting.

In the case of a newly fabricated reactor, the definition of MPT is quite easy because all needed material properties can be required at the delivery of the pressure vessel and then the reactor is designed to avoid the risk of brittle failure. Steelmakers, fabricators, engineers, and end-users are aware of the problems that can occur and safety margins are used. Evaluation of alloy embrittlement is also taken into consideration. Steel makers provide guarantees to their customers that the steels they produce have a satisfactory resistance to temper embrittlement. This guarantee stems from confidence gained in testing of the steels that comprise the pressure boundary. This testing is comprised of furnace heating of coupons and subsequent Charpy V-notch impact testing. In the furnace, the coupons are exposed to an accelerated aging simulation program, also called Step Cooling.

The situation becomes more complex when the low-alloy steels are exposed to hydrogen at elevated temperatures. The complexity arises because of the lack of data characterizing the affect of hydrogen on fracture toughness. The mechanical testing required to determine fracture toughness of low-alloy steels exposed to high hydrogen pressures at elevated temperatures is not very common, and is not easy to perform. This testing is important because of the strong embrittling effect of hydrogen on reactor steels. Another major problem concerns the definition of MPT in the case of vintage reactors that have been operating for years, for which historical operating data may not be fully available.

This paper will focus on the degradation mechanisms that promote embrittlement of low-alloy steels. The main actors are temper embrittlement and the embrittlement due to hydrogen. For pressure vessels operating in the creep range, creep embrittlement should also be taken into consideration. This paper will also present the findings of recent tests performed in hydrogen environments to assess mechanical properties.

1 – INITIAL PROPERTIES OF MATERIALS

The initial properties of low-alloy steels used for construction of pressure vessels for petroleum refining or petrochemical applications are assessed by many parameters. The first property is its chemical composition, and in particular the concentration of impurities in metal. Achieving the specified alloy chemical composition is the responsibility of the material supplier (steelmaker or filler material supplier). The mechanical properties of semi-finished products (e.g. plates, tubes, pipes, forged components), typically in the “as delivered” condition (and after thermal simulations) are provided by laboratory testing. Consideration on thermal simulation (Step-Cooling simulation) will be given in the next section.

Material properties of vessel components in the “as-delivered” condition are stipulated by customer specifications. These requirements then become the basis for all fabrication code calculations. The problem is that these initial mechanical properties are not those that exist in the finished pressure vessel.

The mechanical properties, as tabulated in the manufacturers material test reports generated by the steelmaker are affected by subsequent fabrication processes. All further thermo-mechanical operations performed by the vessel fabricator (e.g. shell rolling, head forming, welding of the shell courses, heads, and nozzles) will affect the initial mechanical properties, and modify the global behaviour of the structure. In general, customers ask steelmakers to assure given properties after minimum PWHT (corresponding to delivery state of the pressure vessel to final customer) and after maximum PWHT (corresponding to pressure vessel state after some weld repairs).

The tempering of a low-alloy steel can also modify mechanical properties. Special attention has to be paid to this influential parameter. Initial tempering by the steel maker, and further fabrication heat treatments (Dehydrogenation Heat Treatment (DHT), Intermediate Stress Relieving Treatments (ISR) and final Post Weld Heat Treatment (PWHT)) must be performed with great care. The final properties of the pressure vessel steels are not only a function of chemical composition, but is also a function of all the heat treatments performed during fabrication. A paper by CHAUVY et al. discussed on this point [0].

The following figures (1 and 2) give examples of evolution of conventional toughness properties (CVN properties and Drop Weight transition temperature) in the case of 2,25Cr1MoV steel. Similar evolution can be plotted for conventional 2,25Cr1Mo steel. More data can be found in reference [1] from PILLOT et al.

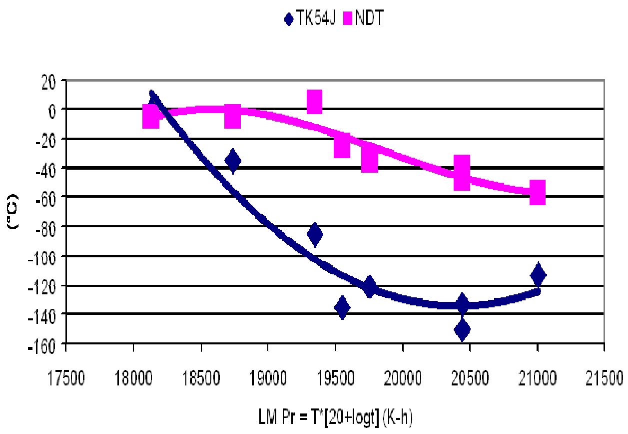

Figure 1 : Effect of tempering on CVN toughness and Drop Weight transition temperature for 2,25Cr1MoV grade (Base metal).

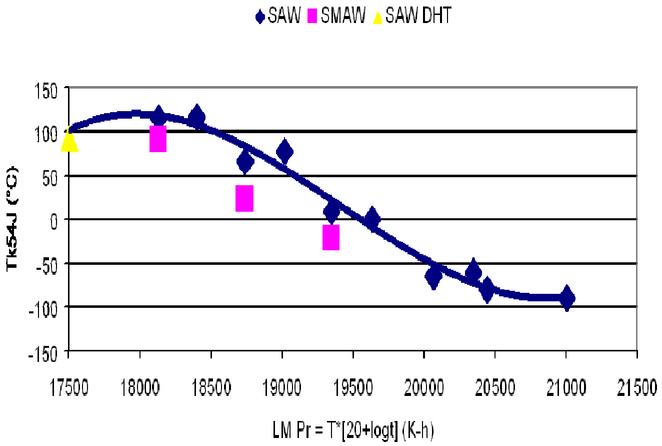

Figure 2 : Effect of tempering on CVN toughness 2,25Cr1MoV grade (SAW and SMAW weld metal).

Recommendations and guidelines concerning heat treatments have been published by API (American Petroleum Institute) [10] to control the whole pressure vessel fabrication process, and to assure sufficient properties to reactors. These properties can be considered as a basis for design, at the beginning of the life of the pressure vessels or reactors. However the properties will change with time and exposure to the operating environment.

2 – EFFECTS OF TEMPERATURE AND HYDROGEN ON MATERIAL PROPERTIES

Low-alloy pressure reactor vessels used in high-pressure refining processes are generally thick wall (typically 150-350mm), and built from forged rings or rolled and welded plates each forming shell courses. The inner diameters of these reactors typically range from 4 to 5 meters. The total weight of these very large components ranges from 500 to 800 metric tons. The reactor wall is a composite structure made from two different metallic materials. The primary pressure boundary is fabricated from low-alloy steel (e.g. Chromium-Molybdenum or Chromium-Molybdenum-Vanadium steel). The other component is a thin corrosion resistant layer of austenitic stainless steel. While small components can be fabricated from clad plates, the liner in large and thicker components is typically a weld overlay.

The primary function of the low-alloy steel is to provide the strength and toughness necessary for a pressure boundary at high pressures and temperatures. In the following text, this part of the reactor wall will be referred to as the “Base Material”. The vessel’s mechanical behavior is defined by the base material. The function of the stainless steel weld overlay is to protect the low-alloy steel from corrosion.

Temper embrittlement of Cr-Mo steels

Temper embrittlement is a solid state reaction with very low kinetic reaction rates. Unlike hydrogen embrittlement, temper embrittlement takes a lot of time to appear, and then only old reactors that have been running for years are affected by it. On the contrary, hydrogen embrittlement can occur after only few days of service. At the very first cooling of the reactor after a production cycle, the risk of brittle failure due to hydrogen embrittlement is real.

The extent of temper embrittlement is measured by the shift of CVN transition to the higher temperatures and was first studied in Nickel-Chromium-Molybdenum-Vanadium steels used for forged rotors in low-pressure turbines in electrical power plants. It has been proven that temper embrittlement is linked to the co-segregation of impurities at prior austenitic grain boundaries. Impurities, such as Tin (Sn), Antimony (Sb), Arsenic (As), Phosphorus (P), co-segregate with alloying elements (primarily Silicon (Si) and Manganese (Mn), but also Chromium (Cr) and Nickel (Ni)). The result leads to grain boundary embrittlement, and subsequently to a risk of intergranular fracture. Temper embrittlement occurs at temperatures below 600°C, but mainly in the range 350-550°C (typical C-Curves of iso-embrittlement for a given temperature and time couple as shown in figure 5).

Some metallurgical parameters can influence the extent of CVN transition in low-alloy steels. Increasing grain size can be very detrimental. Additionally, microstructures that promote high hardness values are more sensitive than softer microstructures. This is why weld heat affected zones (HAZ), and in particular, coarse grain heat affected zone (CG-HAZ) are where problems are the most likely to occur. As previously stated, high Manganese and Silicon contents are known to promote temper embrittlement. The role of Molybdenum is more complex. Low concentrations of Molybdenum (about 0.5%wt, as in the case of P11) is much better than no addition, and better than higher concentrations (about 1%wt, for 2,25%Cr steels, such as P22). Some references on this subject are given in a paper by BOCQUET [2]. It is well known from end-users that the standard 2,25Cr1Mo is much more sensitive to temper embrittlement than the 1.25Cr and Vanadium modified 2.25Cr1Mo0.25V.

Different parameters based on chemical composition have been created to evaluate low-alloys (and in particular CrMo steels) sensitivity to temper embrittlement. These chemistry parameters have been developed using a statistical analysis approach, based on evaluation of CVN parameters and Ductile to Brittle Transition temperature (DBTT), also called Fracture Appearance Transition Temperature (FATT). This method involved the testing heats with minor differences in chemical composition after isothermal treatments, both laboratory samples and actual reactor steels.

The two most widely used parameters are Watanabe’s J-Factor for base materials, and the Bruscato X-bar Factor for weld metals. A third parameter, called the Equivalent Phosphorus content can be used for both base and weld metal but is not widely used. The definition of these parameters is given hereafter by equations 1 to 4.

- J-Factor is given by:

$$J = (Si + Mn) * (P + Sn) * 10000 \qquad \text{(eq. 1)}$$

computed with elemental concentrations expressed in weight percent.

A simplified factor is given by:

$$J' = (P + Sn) \qquad \text{(eq. 2)}$$

- Bruscato Factor is given by:

$$\overline{X} = (10 * P + 5 * Sb + 4 * Sn + As) / 100 \qquad \text{(eq. 3)}$$

computed with elemental concentrations expressed in ppm.

- Equivalent Phosphorus content is given by:

$$P_E = C + Mn + Mo + Cr/3 + Si/4 + 3{,}5*(10*P + 5*Sb + 4*Sn + As) \qquad \text{(eq. 4)}$$

computed with elemental concentrations expressed in weight percent.

Figure 3 shows FATT scattering as a function of J-Factor. It can be shown that FATT increases dramatically with increasing concentration of impurities. It suggests that a low level of impurities (low J factor) must be specified and obtained in order to get acceptable CVN toughness. Figure 4 shows the evolution of FATT at specific exposure times, at service temperatures for impurities concentrations (J-Factor). It can be seen that CVN properties of the 2,25Cr1Mo steels with low concentrations of impurities retain acceptable FATT below or just above room temperature. In the case of high J-Factor steels that have been exposed to elevated temperatures for very long time of service conditions, the CVN ductile-brittle transition temperature can approach 200°C. More results can be seen in papers by PRESCOTT [3 and 4].

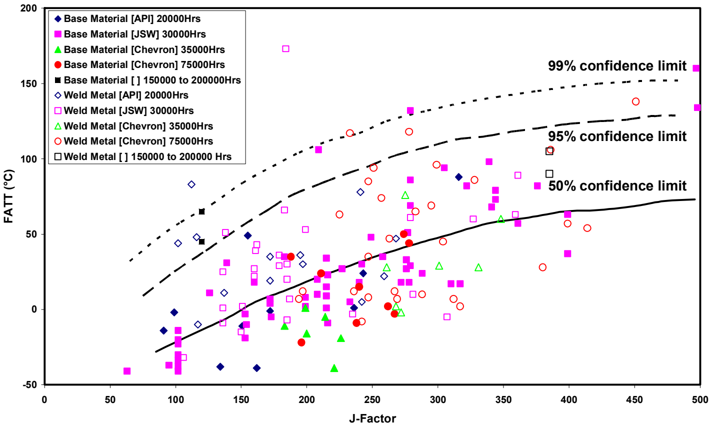

Figure 3 : Effect of impurities (J-Factor) on CVN properties (2,25Cr1Mo steel grades) – historical data

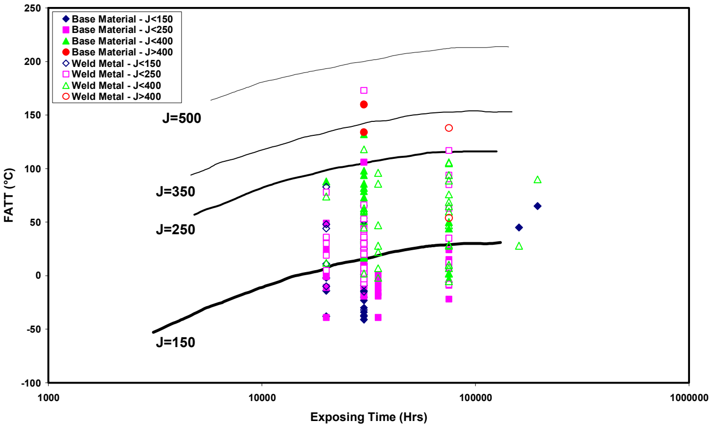

Figure 4 : Effect of impurities (J-Factor) on CVN properties after very long exposing time at service temperatures (2,25Cr1Mo steel grades) – historical data

To evaluate the sensitivity to temper embrittlement of the low-alloy steel grades used in refining plants, many users have opted to require a simulation heat treatment, test program called “Step Cooling” to be included as part of the purchase agreement. The purpose of this step cooling heat treatment program is to provide a relatively quick and cost-effective method to simulate the embrittlement behaviour that occurs after long-term isothermal exposure. It is based on the “iso-embrittlement” curves shown on the time-temperature diagram depicted in figure 5

While many different variations exist, a typical step cooling test program takes approximately two weeks of total time. In refining applications, the most traditional step-cooling program makes use of the following cycle: heat-up to 593°C, soaking for 1 hour, cooling at 5.6°C/hour with soaking steps at 538°C (15 hours), 524°C (24 hours), 496°C (60 hours) and 468°C (125 hours). Coupons exposed to this step cooling are then machined into Charpy V-notch samples, and then impact tested at various temperatures as required by API 934-A[10] (Materials and Fabrication of 2 1/4Cr-1Mo, 2 1/4Cr-1Mo-1/4V, 3Cr-1Mo, and 3Cr-1Mo-1/4V Steel Heavy Wall Pressure Vessels for High-temperature, High-pressure Hydrogen Service) to determinate an appropriate transition curve.

Historically it has been shown that step-cooling test programs do not simulate the full extent of embrittlement that has been observed in samples removed from retired reactors that have been in service for many years. Nevertheless, step-cooling testing does provide a relative measure of an alloy tendency to temper embrittle. In order to add a measure of conservatism to the design, the differences in temperature between the PWHT steel and the step cooled coupons at 54J fracture energy ("temperature shift") is multiplied by a factor of 2.5 or 3. Multiplying the test coupon shift temperature by 2.5 provides a useful correlation to reactors that have operated at 400-450C for periods up to 30 years.

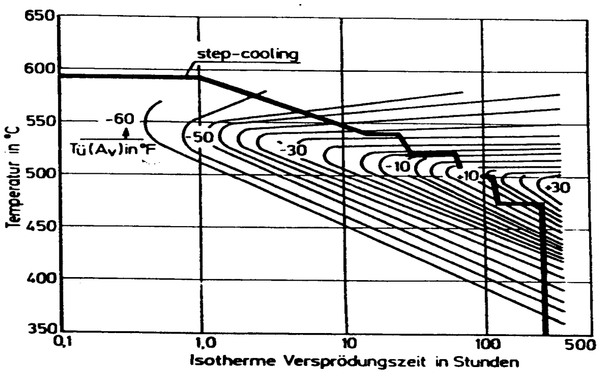

Figure 5 : Iso-embrittlement curves used to define Step Cooling Heat Treatments (taken from reference [2]).

For steelmakers, temper embrittlement mitigation considerations have led to further requirements. In general, steels devoted to high-temperature service are typically required to:

- have special chemistry requirements: the most common rules for base material are J<150 in the case of 1,25Cr0,5MoSi steel grade or J<100 for 2,25Cr1Mo(V) grades. Additional requirements for P+Sn<0,012%wt, can be added. For weld consumables, the most common criterion is Xbar <15 or 12.
- have coupons tested before and after Step Cooling heat treatment to evaluate the embrittlement of the given material.

Nevertheless, usefulness of Step Cooling must be balanced by noticing that 2,25Cr1Mo steels purity is now very good (J-factor always below 100 due, to strong improvements in steelworks) and then 54J impact energy is achieved in general close -100°C for base materials. For this very low J-factor steels, shift due to temper embrittlement is not significant anymore and then Step Cooling becomes not mandatory. Discussion between steelmakers and API are ongoing to remove this embrittlement test which is very detrimental to delivery schedules.

Hydrogen embrittlement of Cr-Mo steels

Hydrogen embrittlement of Cr-Mo reactor steels has not been studied as much as temper embrittlement judging by the lack of data available in the literature. Nevertheless, it is one of the most critical problems in

---

refining plants. Hydrogen comes from the dissociation of hydrogen molecules at high pressures and temperatures, and from cracking of hydrocarbon molecules in the reactor. Hydrogen is absorbed onto the surface, and then diffuses into the steel during the production cycle. At steady state conditions, equilibrium between hydrogen partial pressure inside the reactor and hydrogen concentration in the steel is reached. During shutdown, the equilibrium solubility of hydrogen is lower, and the hydrogen tries to equilibrate to room temperature conditions, diffusing through the low-alloy base and the austenitic overlay.

Figure 6 depicts the steady state concentration gradient of hydrogen through a reactor wall during operation and after cooling. Note that the concentration in the low-alloy steel is highest at the interface with the austenitic stainless steel overlay. One common problem associated with the diffusion of hydrogen is Hydrogen Induced Disbonding (HID) Phenomenon. This is discussed in detail in a paper from COUDREUSE et al.[5]. Also discussed in this paper is a method to compute hydrogen concentrations and the hydrogen gradient through the wall.

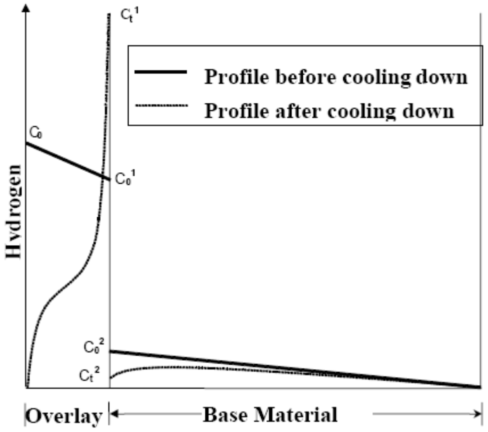

Figure 6 : Profiles of hydrogen concentration in Material and Overlay before and after cooling down of a reactor in refining plant.

Figure 7 shows the results of a calculation of hydrogen concentration in low-alloy steel reactor wall after cooling. This profile has been calculated using the REACT software [8].

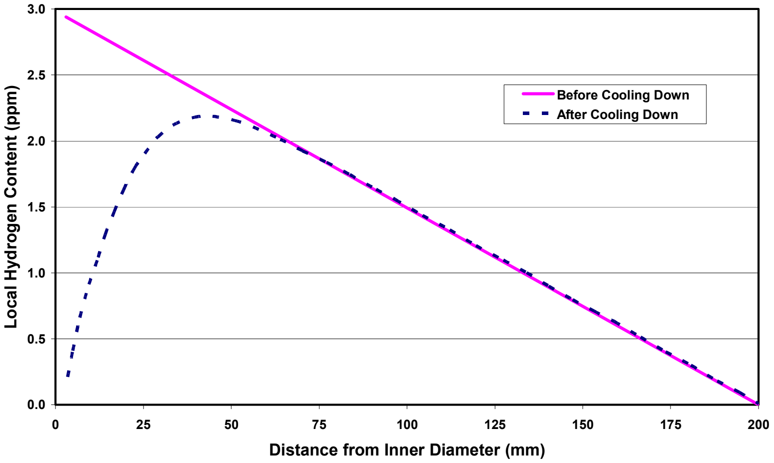

Figure 7 : Profiles of hydrogen concentration in Material and Overlay before and after cooling down of a reactor in refining plant.

The embrittling effect of hydrogen in the steel is very close to that attributed to temper embrittlement. Considering either CVN transition curves (with and without hydrogen) or fracture mechanics toughness transition curves, the effect of hydrogen results in an upward shift of transition temperature.

Recent CVN transition curves have been published by SAKAI et al [6] for 2,25Cr1Mo steel grade and PILLOT et Al [7] for 2,25Cr1Mo, 2,25Cr1MoV and C-Mn steels. Figures 8 and 9 show the shift in the TK54J (temperature for which impact energy equals 54J) value in the case of 2,25Cr1Mo and 2,25Cr1MoV steel, respectively. Values are shown for base metal, HAZ, and weld metal, in the "as-delivered" and after step-cooling conditions) as a function of hydrogen concentration in the steel.

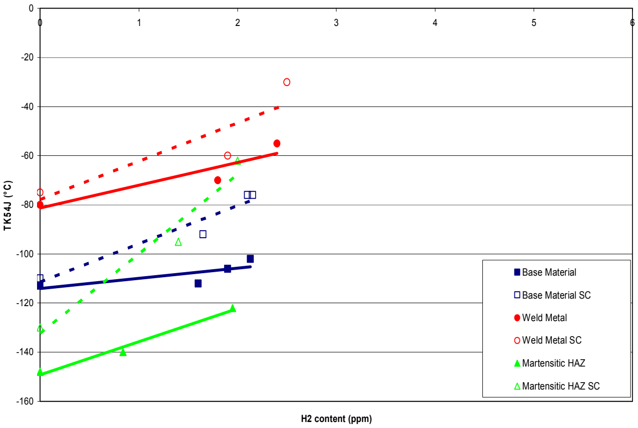

Figure 8: Evolution of TK54J as a function of H2 content (2,25Cr1Mo).

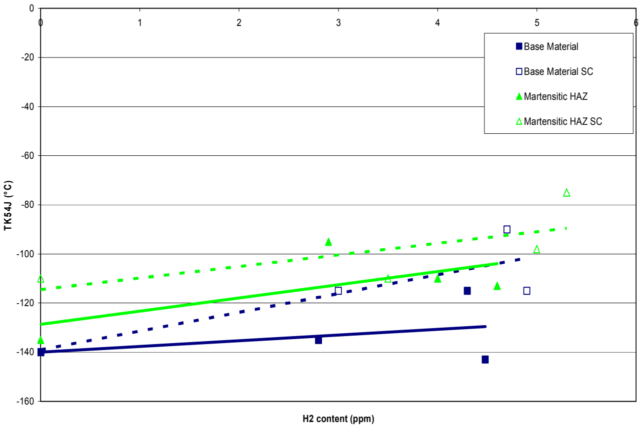

Figure 9: Evolution of TK54J as a function of H2 content (2,25Cr1MoV).

Figure 10 shows the shift in CVN transition temperature due to hydrogen concentration after various heat treatments. This corresponds to the slope of curves given in figure 8 and 9, that is to say, it indicates the loss of toughness as a function of ppm of hydrogen in the steel.

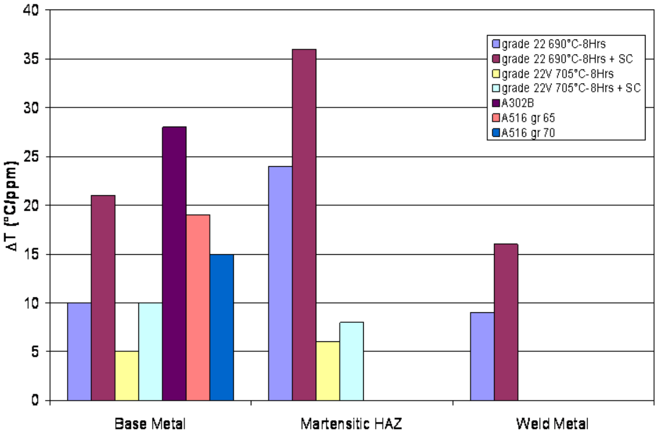

Figure 10: CVN transition curve shift as a function of hydrogen concentration (ppmw) in CrMo(V) and C-Mn steels

Figure 11 shows the decrease in fracture toughness with increasing hydrogen content. It can be seen that the higher the hydrogen content, the higher the transition temperature. Another way to evaluate the effects of hydrogen is to consider the toughness at a given temperature and then, the higher the hydrogen content, the lower the toughness.

The main database concerns K_{Ic} values of base materials in as delivered conditions. Some data relative to aged material and hydrogen charged material are also plotted in this figure. In this plot, KIC is represented as a function of T-T$_0$, where T$_0$ is the temperature for which static toughness is equal to 100 MPa.√m. In this case, T$_0$ is indexed on FATT temperature obtained with CVN specimens.

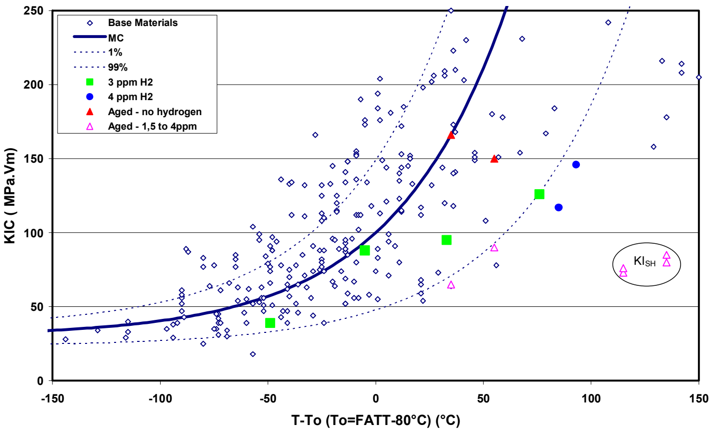

Figure 11: Review of K1C data for 2,25Cr1Mo steel (as delivered, aged, hydrogen charged and aged+hydrogen charged conditions).

3 – EVALUATION OF MATERIAL PROPERTIES TO ASSESS ACTUAL MPT

As previously said, MPT evaluation is not very difficult in the case of new pressure vessels, but it is a much more complex situation in the case of vintage reactors for which initial material data are not known and not well documented and/or in the case of embrittlement due to hydrogen.

On one hand, in the case of new pressure vessels, mandatory documentation supplied to end users is clearly sufficient to get the initial material properties and initial design is done to insure a safe MPT at a given temperature for given service conditions (operating temperature, operating pressure, environmental temperature). Final service conditions are defined at the very beginning of a project and then MPT is given as a basis. Engineers have to design the pressure vessels both to support service conditions and to insure the given MPT.

For example, in the case of refining plants located in cold climates where temperatures can be very low, toughness of material has to be much better than in the case of warmer regions to insure safe behavior and allow re-pressurization at or close to ambient temperature. Embrittlement is taken into consideration to maintain stable or quasistable MPT during the whole life of the reactor.

In this case, then, a method for calculating MPT can be summarized by the following formulae (5 and 6):

- $$Tk_{54J} + x \times \Delta_{Tk_{54J}\quad SC} + C_{H2} \times \Delta_{Tk_{54J}\quad H2} < TK_{CVN}(MPT) \qquad \text{(eq. 5)}$$

if we consider methodology based on CVN properties, or

- $$TK_{IC} + x \times \Delta_{Tk_{IC}\quad SC} + C_{H2} \times \Delta_{Tk_{IC}\quad H2} < TK_{KIC}(MPT) \qquad \text{(eq. 6)}$$

if we consider methodology based on fracture mechanics properties.

Where:

- TK$_{54J}$ is the temperature for which we get CVN impact energy equal to 54J just after building of the reactor
- ΔTK$_{54J\_SC}$ is the shift of temperature due to temper embrittlement in Step Cooling
- x is the correlation factor between Step Cooling embrittlement and actual embrittlement (in general taken equal to 2,5 or 3).

- ΔTK_{54J_H2} is the shift of temperature due to hydrogen embrittlement (per ppm of hydrogen)
- C_{H2} is the hydrogen concentration in the reactor wall
- TK_{CVN}(MPT) is the indexation temperature computed during design of the pressure vessel to link CVN properties required at the given MPT temperature (it takes into consideration safety margins).

Or:

- TK_{IC} is the temperature for which we get fracture toughness equal to 100MPa.√m just after building of the reactor
- ΔTK_{IC_SC} is the shift of temperature due to temper embrittlement in Step Cooling
- x is the correlation factor between Step Cooling embrittlement and actual embrittlement (in general taken equal to 2,5 or 3).
- ΔTK_{IC_H2} is the shift of temperature due to hydrogen embrittlement (per ppm of hydrogen)
- C_{H2} is the hydrogen concentration in the reactor wall
- TK_{KIC} (MPT) is the indexation temperature computed during design of the pressure vessel to link KIC properties required at the given MPT temperature (it takes into consideration safety margins).

The main considerations here are:

- Steelmakers and consumables manufacturers must provide base materials and filler materials that provide the required mechanical properties, and that will insure minimal degradation of these properties during the life of the pressure vessel.
- Fabricators have to insure that the required mechanical properties are maintained in the fabricated pressure vessel, especially as they pertain to the quality of welds and post weld heat treatments.

In the case of vintage reactor, the problem is clearly different. The pressure vessel is already operating, sometimes for years or decades, and end-users have to insure safe use of this pressure vessel. The material properties are not always known, and therefore a reverse the way of thinking, compared to previous case, is required.

The properties of the material cannot be changed and then the issue is to evaluate the safest temperature of re-pressurization, taking into account already accumulated degradation (temper embrittlement and hydrogen embrittlement).

Figure 12 explains how temper embrittlement and hydrogen embrittlement affects toughness properties of a given material. The black curve is the toughness mastercurve of the as delivered material at the very first start of the reactor. This initial state of material properties can be known or not. This point will be discussed later. The blue curve is the toughness mastercurve of the same material, taking into account temper embrittlement of the material. Some considerations on this curve will also be given hereafter. Pink to purple to red curves concern the effects of hydrogen on toughness. The cumulative effect of these two phenomenon applied on initial properties leads to a toughness transition curve that allow the calculation of MPT for a given reactor geometry, given flaw size and shape and then for given service conditions.

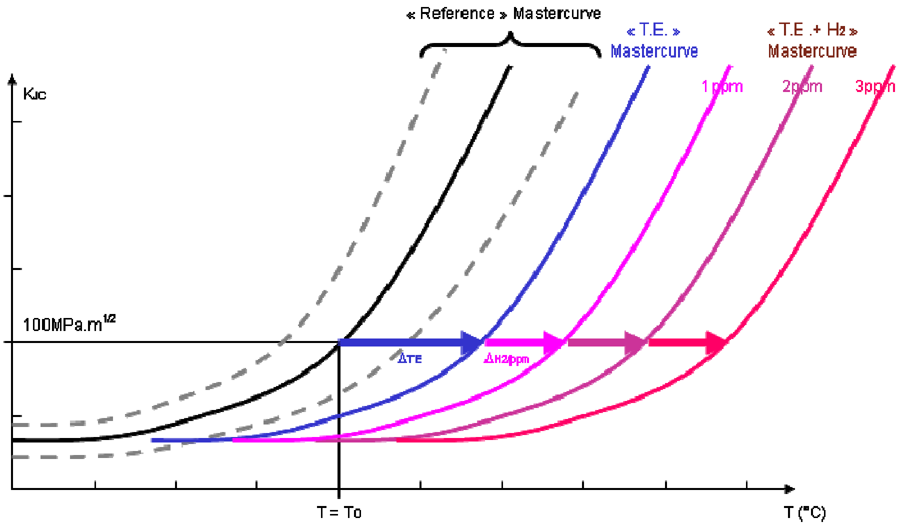

Figure 12: Cumulative effect of ageing and hydrogen embrittlement of quasi static fracture toughness.

Concerning initial properties, it is only necessary to get them if end user wants to estimate the level of degradation due to temper embrittlement. If initial documentation of the pressure vessel does not contain this information, an estimation of the properties can be obtained by removing a test coupons from the reactor and then apply to it a de-embrittlement heat treatment (600°C for one hour followed by quick cooling to avoid re-embrittlement while crossing 350-550°C range).

This method avoids too much conservatism, but it is clearly not a perfect method and only an estimation of initial properties can be obtained. Scattering is very large and then special care must be taken to analyze the results. It is also based on the fact that tests coupons have been put inside the pressure vessel during construction of the plant. In some case it has been done, in some others, it hasn't and then this solution is not available.

The second method to assess properties of material, in the case where no coupons can be tested, is clearly conservative but is based on large return of experience. In a study performed by API in the early 80's [9], it has been shown that in the case of reactors built before 1975 not fully in accordance with API RP 934A [10] requirements concerning chemistry, embrittled materials can exhibit very poor CVN properties. In particular some reactors with electro-slag welds (ESW) have TK_{54J} values up to about 170°C (300°F). For pressure vessels containing such welds, this maximum value should be taken as a basis. In all other case, maximum transition temperature has been evaluated to about 120°C (250°F).

In the case of more recent pressure vessels with more restrictive chemistries and compliant with API RP 934A requirements, the highest transition temperature has been evaluated to be about 40°C (100°F).

For very new reactors, CVN or fracture toughness data available in the initial documentation (as delivered properties and embrittled by Step Cooling heat treatment) are sufficient to calculate material toughness.

Concerning hydrogen embrittlement, two philosophies are spread. The first one consists in thinking that hydrogen has a real effect on the material only if its content is above a threshold estimated to 3ppm. For lower contents, it is considered that fracture mechanics properties and especially fast "brittle" properties are similar to the case with no hydrogen. Figures 13 and 14, taken from PRESCOTT's literature review [4] and KOBE STEEL's work on 2,25Cr1Mo [15], show that hydrogen levels below 2ppm and up to 5ppm actually do affect fracture toughness. It has already been proved by PILLOT et al. [7] and SAKAI et al. [6] that low to medium contents of hydrogen also present a detrimental effect on CVN toughness (see Figure 8).

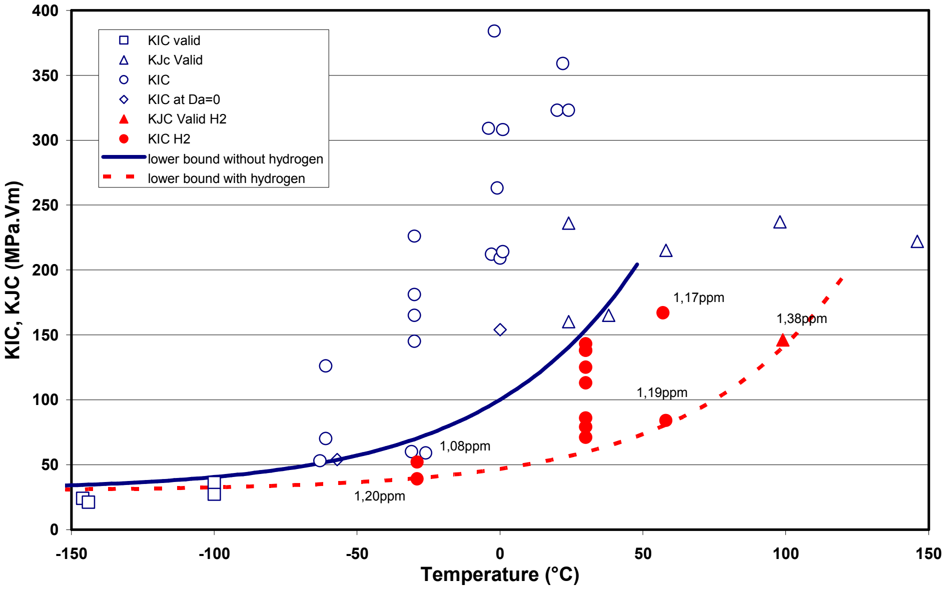

Figure 13: Effect of low hydrogen content on quasistatic fracture toughness (2,25Cr1Mo).

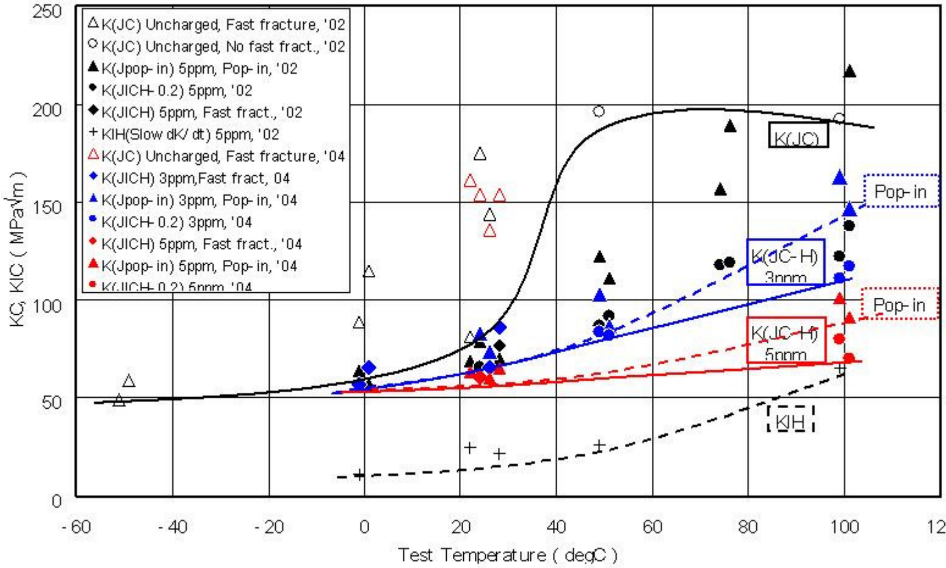

Figure 14: Effect of high hydrogen content on quasistatic fracture toughness (2,25Cr1Mo).

Figure 15 attempts to correlate CVN transition shift due to temper embrittlement and to hydrogen embrittlement with data coming from fracture mechanics tests. Shift measurements have been obtained using Figure 10 values and WALLIN correlation between K_{JC} and TK_{28J} as described in ASTM E1921 [11] test procedure or in ASTM Publication on Mastercurve Method [12]. For one inch thick specimen, this relationship is given by equations 7 and 8:

Equation 7 hereafter is devoted to the estimation of T_0 knowing TK_{28J}.

$$T_0 = T_{K28J} - 18°C \qquad \text{(eq. 7)}$$

with scattering estimated at ±15°C.

Equation 8 gives the fracture mechanics mastercurve with a given probability of failure P_f :

$$TK_{JC}(T) = 20 + (11 + 77.\exp(0{,}019(T - T_0))).\left(\ln \frac{1}{1 - Pf}\right)^{1/4} \qquad \text{(eq. 8).}$$

One other typical problem is the evaluation of TK_{28J}. In general, only TK_{54J} or FATT is known by end user. Some relations exist to extrapolate this value, but it includes further scattering in the data. Equations 9 and 10 are devoted to extrapolation of TK_{28J} knowing TK_{54J} and tensile properties (or other CVN values at one given temperature TKV) while equations 11 to 13 allow the extrapolation of TK_{28J} knowing FATT (only valid for 2,25Cr1Mo). These formulae come from the European Research Project QUALYTOUGH [13]. A security of 10°C can be added to be sure to be conservative in every situation. Figure 16 taken from [13] shows the error of TK28J estimation regarding initial CVN value considered (TK_{41J}, TK_{68J} or FATT).

$$\mathrm{TK}_{28J} = \mathrm{TKV} - \left(\frac{\mathrm{C}}{4}\right).\ln\left(\frac{\mathrm{CVN.(US - 28)}}{\mathrm{28.(US - CVN)}}\right) \qquad \text{(eq. 9)}$$

The constant C is given by $\mathrm{C} = 34 + \mathrm{YS}/35{,}1 - \mathrm{US}/14{,}3$ (eq. 10)

with:

- US the Upper Shelf CVN toughness (can be estimated typically to 250J for 2,25Cr1Mo steel)
- TKV the temperature for which CVN impact energy is known
- CVN the impact energy at temperature TKV
- YS the yield strength at room temperature

$$\mathrm{T} = \mathrm{F}ATT + \left(\frac{C}{2}\right).\ln\left(\frac{\mathrm{CVN - 2}}{\mathrm{US - CVN}}\right) \qquad \text{(eq. 11)}$$

with C given by equation 10.

Or

$$\mathrm{TK}_{28J} = (\mathrm{FATT} - 7) - \left(\frac{\mathrm{C}}{4}\right).\ln\left(\frac{\mathrm{54.(US - 28)}}{\mathrm{28.(US - 54)}}\right) \qquad \text{(eq. 12)}$$

with C given by equation 10.

Assuming that $TK_{54J} = FATT - 7°C$ (eq. 13)

in the case of 2,25Cr1Mo steel (taken from [4]).

These conventional relationships used in a pressure vessel are applied here in the case of hydrogen charged material. Figure 15 shows a good correlation between test data and the models, but very few data are available. A more accurate study should be done to further validate these relationships in the case of hydrogen charged materials.

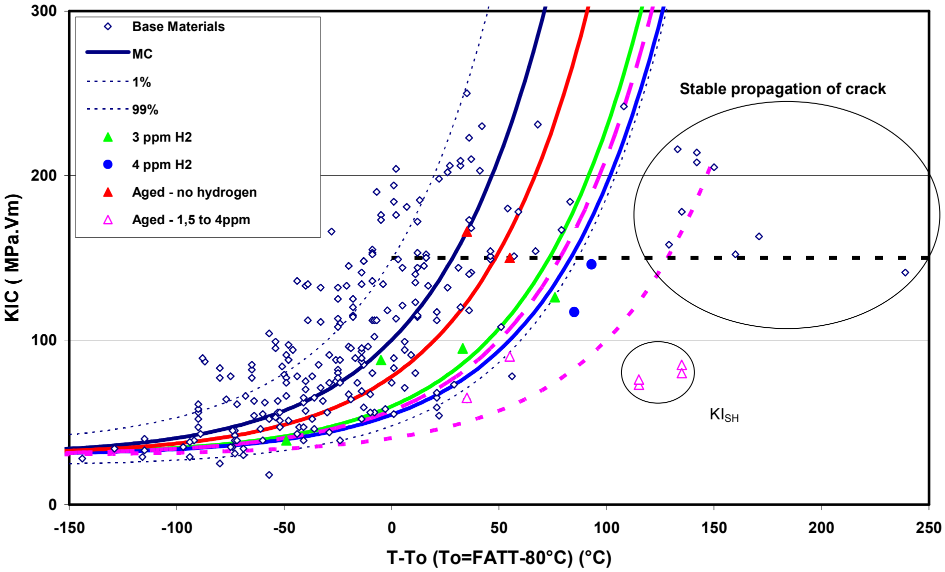

Figure 15: effect of temper and hydrogen cumulative embrittlement on fracture mechanics data (2,25Cr1Mo).

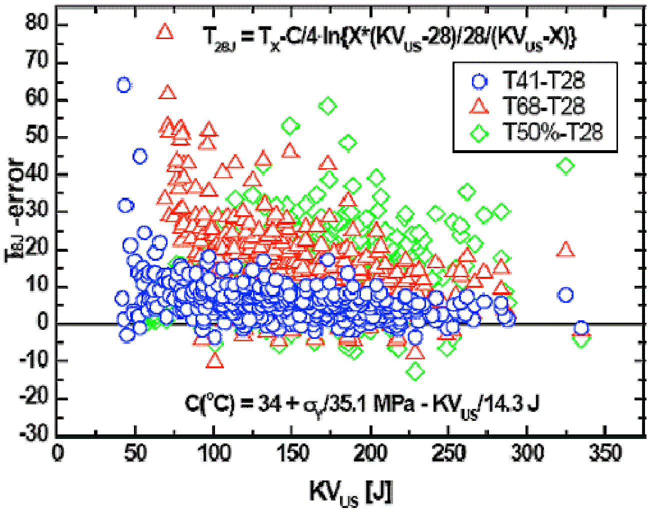

Figure 16: scattering in evaluation of TK28J.

In the next section, an application of these rules to a virtual pressure vessel will be developed as an example.

4 – APPLICATION OF PREVIOUS CONSIDERATIONS TO AN EXAMPLE

This section assesses a virtual pressure vessel to define its MPT regarding material properties and in service conditions. This virtual pressure vessel is representative of what can be found in reality to be as close as possible to actual field conditions. It considers a pressure vessel built in the early 70's with no special requirements concerning chemistry and then not in compliance with API Recommended Practice 934-A. Nevertheless, coupons have been put inside this pressure vessel and then actual data are available for determination of today's MPT.

First of all, the geometry of the pressure vessel can be assimilated to a cylinder shell with the following dimensions:

- Outer diameter is 4 meters (R_o), inner diameter is 3,4 meters (R_i)
- Total wall thickness is 0,3 meter
- Length (for information only) is 20 meters.

The service conditions are:

- Nominal temperature: 420°C
- Hydrogen partial pressure (P) : 150 bara (equals to total pressure to simplify)

Material is 2,25Cr1Mo with no stainless steel cladding.

Flaw geometry is assumed to be at the surface of the inner side of the reactor with semi-elliptical shape in longitudinal orientation. The dimensions of the defect are:

- The shortest axis (a) is very small regarding thickness of the pressure vessel.
- The longest axis (c) is longer than shortest axis.
- Shortest axis is radial and longest axis is longitudinal.

After cooling of the reactor, estimated maximal content of hydrogen in base and weld metal is about 3ppm, in accordance with Figure 7.

Material properties, measured on the coupon removed from the reactor follow (specimen thickness is 25mm):

- Quasistatic toughness of base material: K_{IC} at 20°C is 150 MPa.√m (aged material, no hydrogen).
- Quasistatic toughness of base material: K_{ISH} at 20°C is 50 MPa.√m and K_{ISH} at 100°C is 75 MPa.√m (aged material, about 3ppm hydrogen).
- Quasistatic toughness of weld metal: K_{IC} at 20°C is 50 MPa.√m (aged material, no hydrogen).
- Quasistatic toughness of weld metal: K_{ISH} at 20°C is 45 MPa.√m and K_{ISH} at 100°C is 70 MPa.√m (aged material, about 3ppm hydrogen).

All calculation are done using API 579:2007 Fitness-For-Service standard (FFS) [14]. Calculation of K_I value following level I of FFS can be made using Annex C and in particular paragraph C.5.10 (Cylinder – Surface Crack, Longitudinal Direction – Semi-Elliptical Shape, Internal Pressure). K_I is given by formulae 14 to 18:

$$K_I = \frac{P.R_o^{\,2}}{R_o^{\,2} - R_i^{\,2}} \left(2G_0 - 2G_1\left(\frac{a}{R_i}\right) + 3G_2\left(\frac{a}{R_i}\right)^2 - 4G_3\left(\frac{a}{R_i}\right)^3 + 5G_4\left(\frac{a}{R_i}\right)^4 \right) \sqrt{\frac{\pi a}{Q}} \qquad \text{(eq. 14)}$$

With:

$$Q = 1{,}0 + 1{,}464\left(\frac{a}{c}\right)^{1{,}65} \qquad \text{(eq. 15)}$$

$$G_0 = A_{0,0} + A_{1,0}\beta + A_{2,0}\beta^2 + A_{3,0}\beta^3 + A_{4,0}\beta^4 + A_{5,0}\beta^5 + A_{6,0}\beta^6 \qquad \text{(eq. 16)}$$

$$G_1 = A_{0,1} + A_{1,1}\beta + A_{2,1}\beta^2 + A_{3,1}\beta^3 + A_{4,1}\beta^4 + A_{5,1}\beta^5 + A_{6,1}\beta^6 \qquad \text{(eq. 17)}$$

Where

$$\beta = \frac{2\varphi}{\pi} = 1 \qquad \text{(eq. 18)}$$

If we consider the outer side of the flaw, inside the wall. ϕ is the angle of deepest point of the crack regarding the surface of the wall (equals to $\pi/2$).

Calculation of coefficients G_2 to G_4 is useless if we consider that the ratio a/R_i is small.

Coefficients Ai,j are taken from FFS in tables C.12 or C.10 for elongated defects.

Two cases are taken into consideration and lead to equations 19 and 20:

- Ratio a/c is close to 0 (e.g. the defect is a scratch or similar), and then G_0=1,12 and G_1=0,682 and $$K_I \approx \frac{2{,}24.P.R_o^{\,2}}{R_o^{\,2} - R_i^{\,2}}\sqrt{\pi a} \approx 8.07P\sqrt{\pi a}$$ (eq. 19).
- Ratio a/c is close to 1 (semi-circular defect), and then G_0=1,044 and G_1=0,741 and $$K_I \approx \frac{2{,}088.P.R_o^{\,2}}{R_o^{\,2} - R_i^{\,2}}\sqrt{\frac{\pi a}{2.464}} \approx 4.79P\sqrt{\pi a}$$ (eq. 20).

The worst case is clearly an elongated defect and then only this case will be considered in further calculation to be conservative.

Figure 17 and 18 give the evolution of toughness of the wall material as a function of temperature. Upper shelf toughness is limited to 220 MPa.√m in the case of base material and to 125 MPa.√m in the case of weld metal to take into account the risk of lowering of this plateau for very strong temper and hydrogen embrittlement.

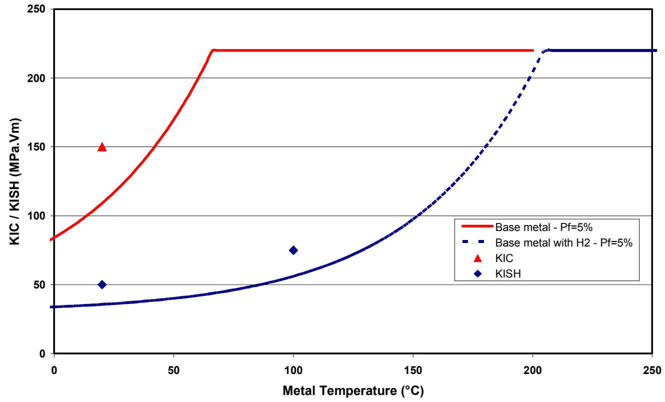

Figure 17: Evolution of material toughness (with and without hydrogen) regarding metal temperature (Base material) (25mm thickness specimens).

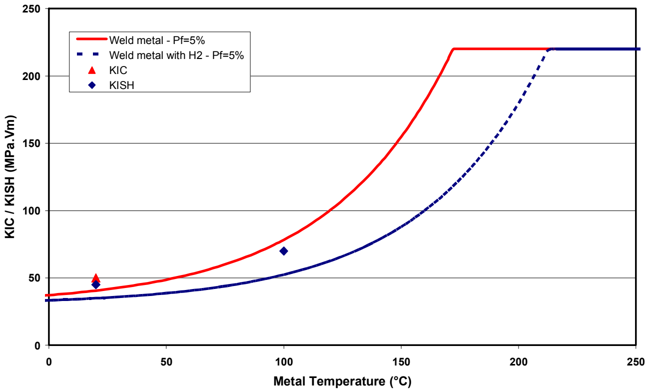

Figure 18: Evolution of material toughness (with and without hydrogen) regarding metal temperature (Weld metal) (25mm thickness specimens).

Thickness correction is made using Weibull's law described by Wallin et Al. in [12]. This leads to equation 21:

$$K_{Jc}(B) = 20 + (K_{Jc} - 20)(25/B)^{1/4}$$ (eq. 21)

B is the thickness of the reactor (300mm in our case).

Weld metal is the location where toughness is the lowest and then the assessment of MPT must be done in this region to be safe.

Figure 19 shows the evolution of toughness in the case of the full thickness wall (300mm). A shift to higher temperature (about 40°C) is then applied.

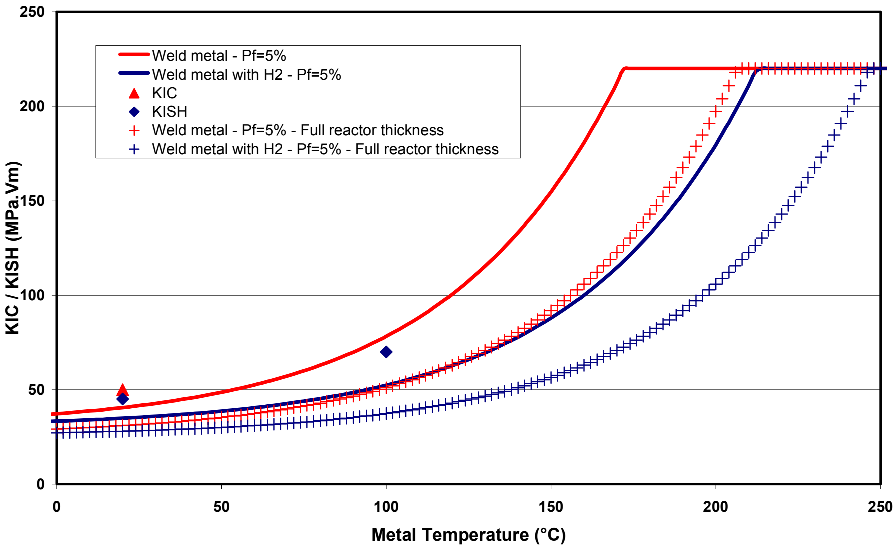

Figure 19: Evolution of material toughness (with and without hydrogen) regarding metal temperature (Weld metal) (Full thickness wall – 300mm).

Figure 20 represents the calculation of maximal admissible pressure regarding metal temperature. Different sizes of flaw are taken into consideration, from 2 to 10mm.

Considering equation 19, maximal admissible pressure is calculated by equation 22:

$$P_{\max}(T) = \frac{K_{ISH}(T)}{8{,}07\sqrt{\pi a_{\max}}} \quad \text{(eq. 22)}$$

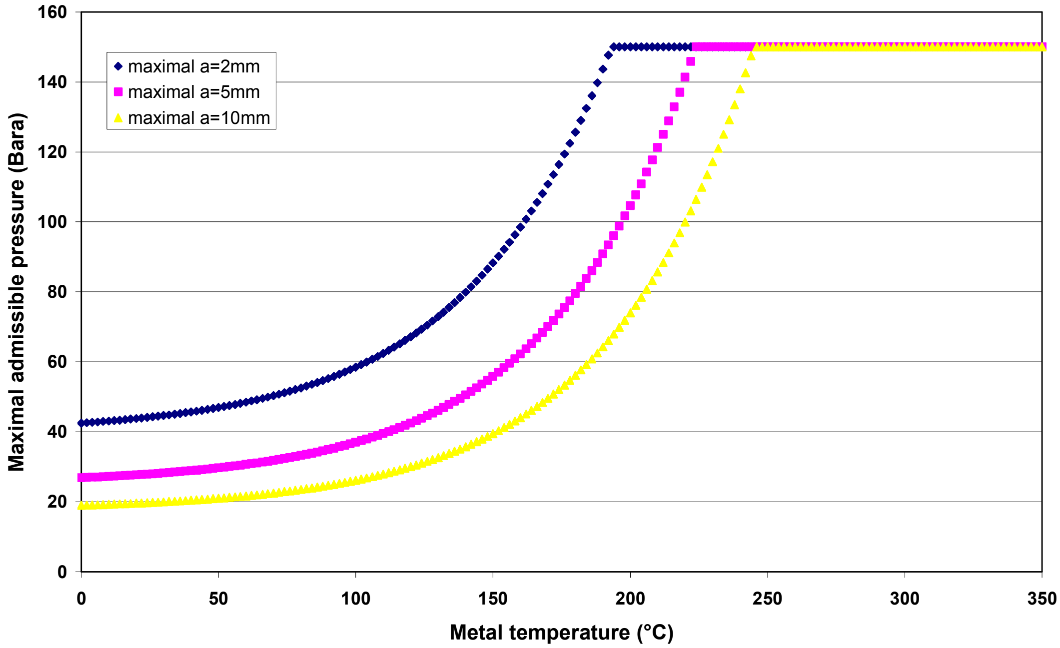

Figure 20: Evolution of maximal admissible pressure regarding metal temperature (Weld metal) (Full thickness wall – 300mm).

This last figure represents the MPT diagram, which corresponds to the maximal admissible pressure in the reactor at a given temperature for a given flaw size.

Some optimisation can be done to improve efficiency. More sophisticated calculations, taking into account plasticity can also be done to improve the accuracy of this diagram and then reduce maintenance cycle.

5 – CONCLUSIONS

The synergistic effect of in-service ageing and embrittlement of steel material under high temperature and hydrogen atmosphere conditions have been presented in this paper, emphasizing the importance of taking into account the effect of hydrogen even in low quantities in the metal. A method has been described to assess the present-day service and maintenance conditions to assure safe shutdown and startup cycles. It has also been demonstrated that a knowledgeable steel supplier is able to deliver a material that will be much more resistant to embrittling effects thanks to rigid control of the delivered metallurgy.

Some assumptions on the effects of hydrogen on fracture or CVN toughness have also to be taken into considerations and well validated, in particular the effect of high content of hydrogen on fast fracture mechanics. Hydrogen embrittlement is a very complex phenomenon and very few data are available. Then, particular attention must be paid to this matter.

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