Appendix 8

Case study

Assessing Operating limits for C-0.5Mo steel in high temperature H_2 service

Hennie de Bruyn   Statoil

Assessing operating limits for C-0,5Mo steel in high temperature H_2 service (case study)

Hennie de Bruyn
EFC WP15 – 9 March 2004

Case study:
C-0,5Mo in high temperature H_2

- *Coker distillate hydrotreating unit*
  - *Commissioned in 1975*
  - *C-0,5Mo steel piping*
    - *Reactor feed line*
    - *Reactor outlet line*
    - *Desulph. line (by-pass line)*
  - *Satisfactory performance*
    - *No history of cracking (HTHA)*
  - *Unit optimisation/debottlenecking*
    - *Increased operating temperature*
    - *Increased H_2 partial pressure*

Case study:

C-0,5Mo in high temperature H_2

STATOIL

Line	Current			Proposed		
	Pressure (bar)	Temp. (ºC)	pH2 (bar)	Pressure (bar)	Temp. (ºC)	pH2 (bar)
Reactor feed	*46*	*265*	*29*	*51*	*300*	*35*
Reactor outlet	*44*	*315*	*16*	*51*	*350*	*20*
By-pass (presulph)	*46 (20)*	*265 (35)*	*29 (20)*	*51 (20)*	*300 (35)*	*35 (20)*

Is this acceptable?

What about potential damage by high temperature hydrogen?

Case study:
C-0,5Mo in high temperature H_2

- ***High temperature hydrogen attack (HTHA)***
  - ***Dissociation of hydrogen***
    - $H_2 = 2H$
    - ***Thermally driven***
  - ***Carbide reaction***
    - $4H + MC = CH_4 + M$
  - ***Results in:***
    - ***Decarburization (high temperatures; lower*** pH_2***)***
      - ***Cr-Mo steels***
    - ***Internal fissuring/cracking (higher*** pH_2***)***
      - ***CS; C-0,5Mo; Cr-Mo steels***

Case study:
C-0,5Mo in high temperature H_2

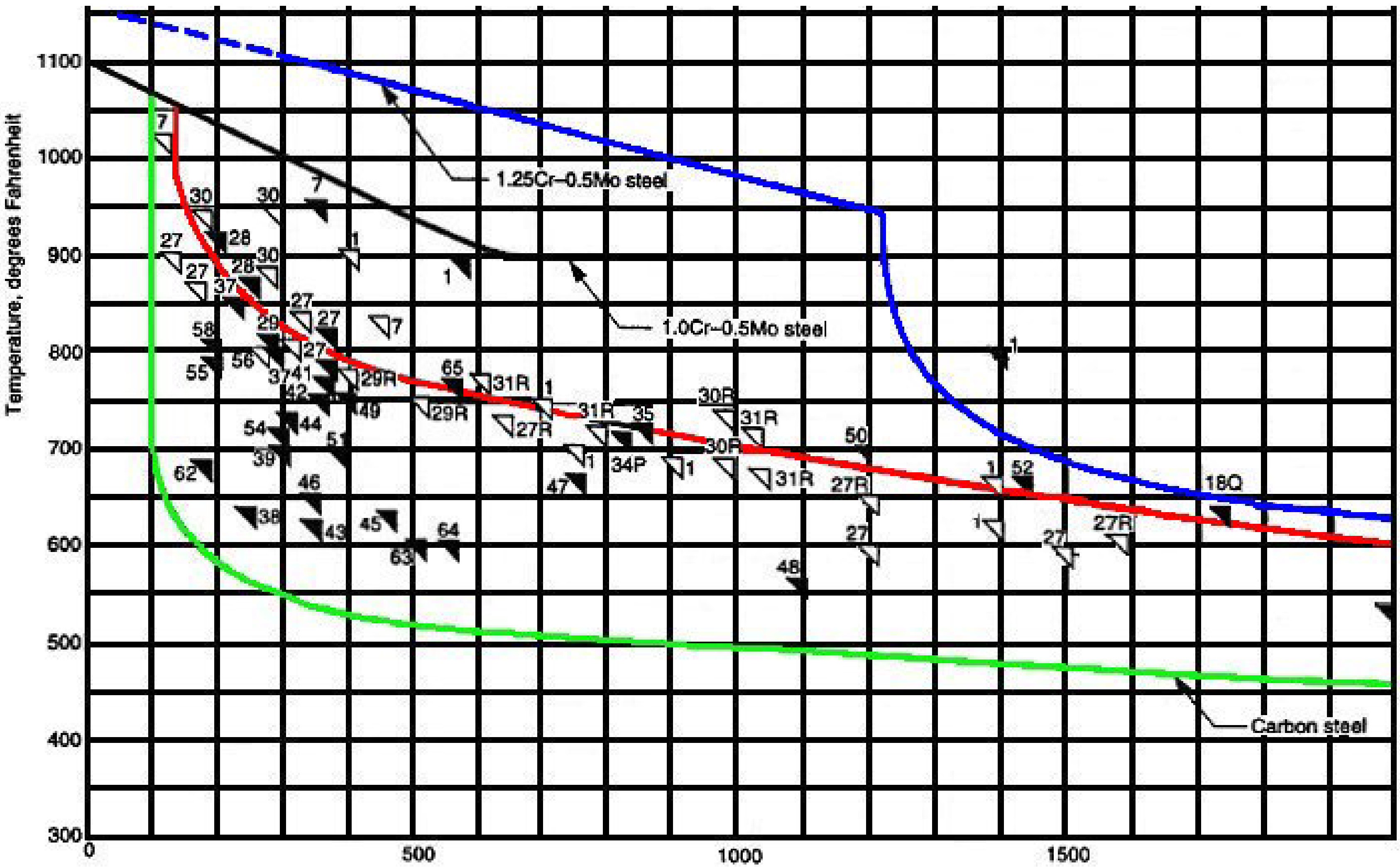
- *Nelson curves (G.A Nelson - Shell Development Co)*
  - *Collection of experience with high temperature hydrogen*
  - *Temperature-hydrogen partial pressure curves showing experience with different steels*
  - *Paper presented to API in 1949*
  - *Various updates 1950's & early 1960's.*
  - *Update in 1965*
    - *More curves*
    - *C-0,5Mo raised by 50ºF*

Case study:
C-0,5Mo in high temperature H_2

- *API 941 (<u>Steels for Hydrogen Services at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants</u>)*
  - *1st Edition: July 1970*
    - *Based on Nelson's 1965 curves + 2,25Cr-1Mo*
  - *2nd Edition: June 1977*
    - *Lowered curve for C-0,5Mo*
      - *Failures in conditions around the curve*
  - *3rd Edition: May 1983*
    - *More C-0,5Mo failures (catalytic reforming units)*
  - *4th Edition: April 1990*
    - *More industry failures of C-0,5Mo*
    - *1977 curve removed & presented separately*
    - *Caution on use of C-0,5Mo*

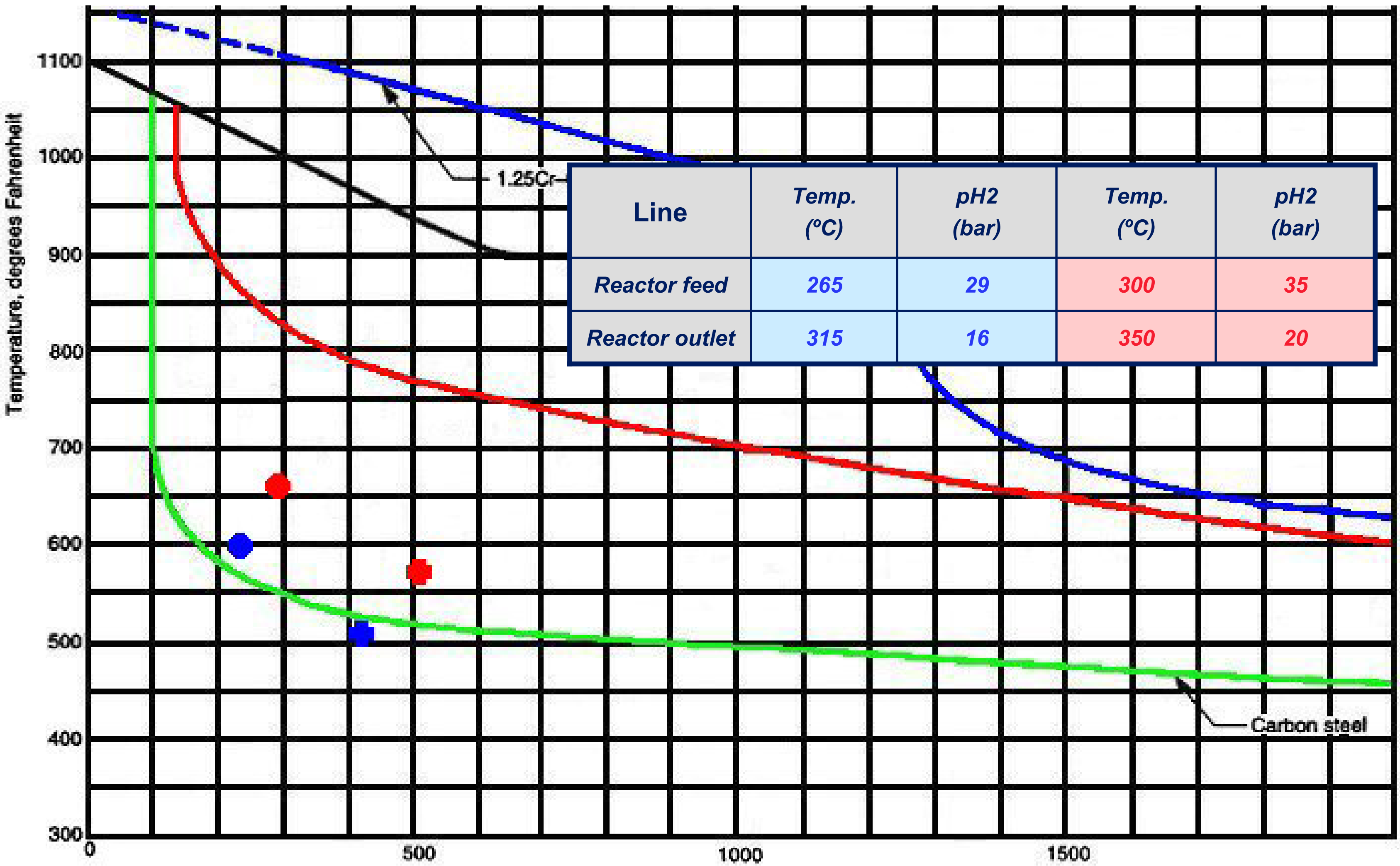
Case study:

C-0,5Mo in high temperature H_2



Case study:

C-0,5Mo in high temperature H_2



Line	Temp. (ºC)	pH2 (bar)	Temp. (ºC)	pH2 (bar)
Reactor feed	*265*	*29*	*300*	*35*
Reactor outlet	*315*	*16*	*350*	*20*

Case study:
C-0,5Mo in high temperature H_2

- *Disadvantage of curves in API 941*
  - *Does not indicate ageing effects*
  - *HTHA is also time dependent*

- *Single parameter P_V was developed relate time, pH_2, temperature*
  - *API 581 Appendix I: HTHA Technical Module*

  - $P_V = \log(pH_2) + 3{,}09 \times 10^{-4} (T) (\log(t) + 14)$

    - *pH_2 – hydrogen partial pressure in kgf/cm²*
      (1 kgf/cm² = 14,2 psia)
    - *T – temperature in K (K = C + 273)*
    - *t – time (age) in hours*

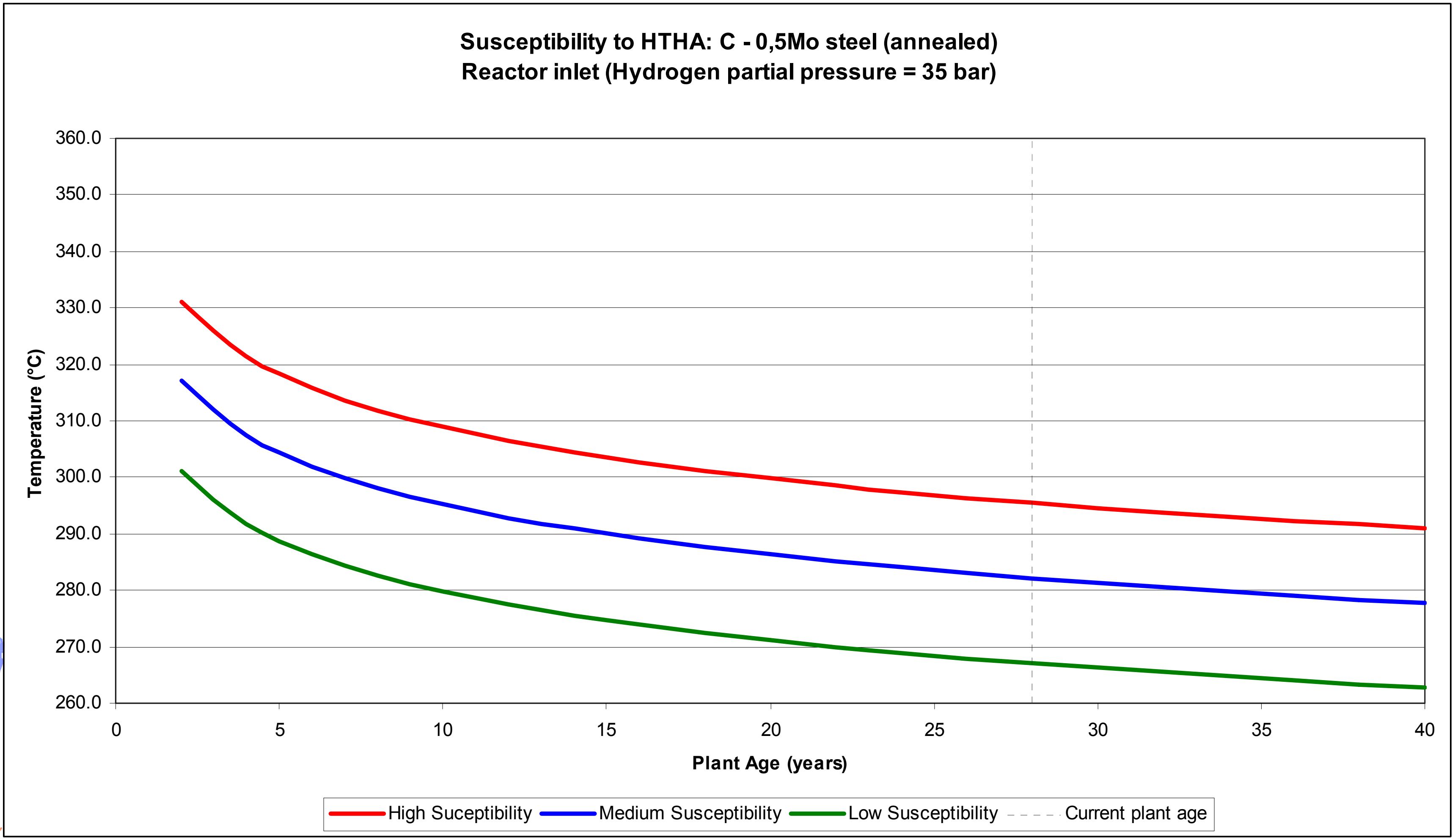
Case study:

C-0,5Mo in high temperature H_2

- *Carbon & low alloy steel susceptibility to HTHA (API 581)*

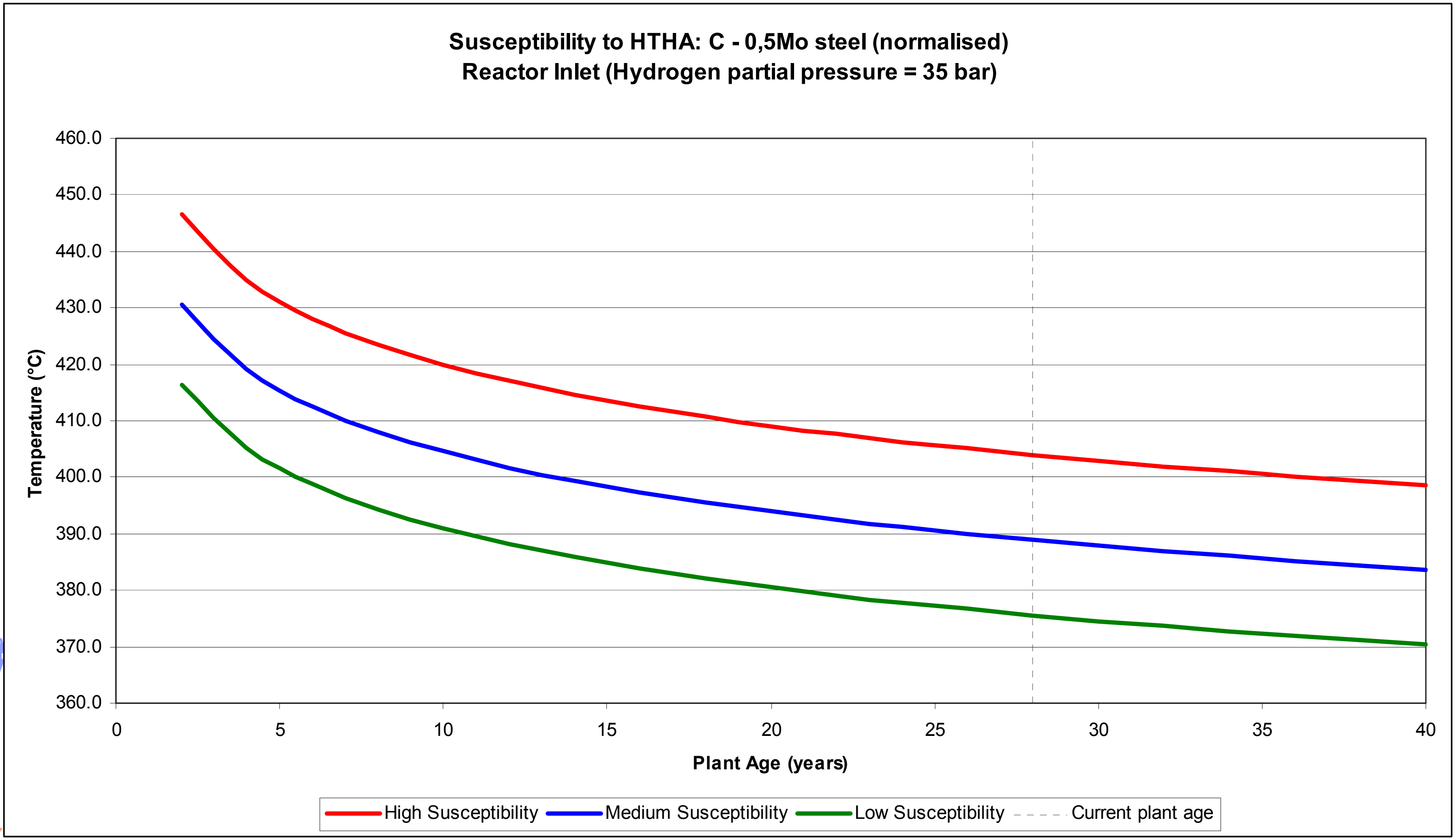
Material	*Critical PV factors*			
	High susceptibility	*Medium susceptibility*	*Low susceptibility*	*No susceptibility*
Carbon steel	$P_V \geq 4{,}70$	$4{,}61 < P_V \leq 4{,}70$	$4{,}53 < P_V \leq 4{,}61$	$P_V \leq 4{,}53$
C-0,5Mo (annealed)	$P_V \geq 4{,}95$	$4{,}87\ P_V \leq 4{,}95$	$4{,}78 < P_V \leq 4{,}87$	$P_V \leq 4{,}78$
C-0,5Mo (normalised)	$P_V \geq 5{,}60$	$5{,}51 < P_V \leq 5{,}60$	$5{,}43 < P_V \leq 5{,}51$	$P_V \leq 5{,}43$
1,25Cr–0,5Mo	$P_V \geq 6{,}00$	$5{,}92 < P_V \leq 6{,}00$	$5{,}83 < P_V \leq 5{,}92$	$P_V \leq 5{,}83$
2,25Cr-1Mo	$P_V \geq 6{,}53$	$6{,}45 < P_V \leq 6{,}53$	$6{,}36 < P_V \leq 6{,}53$	$P_V \leq 6{,}36$

Case study:
C-0,5Mo in high temperature H_2



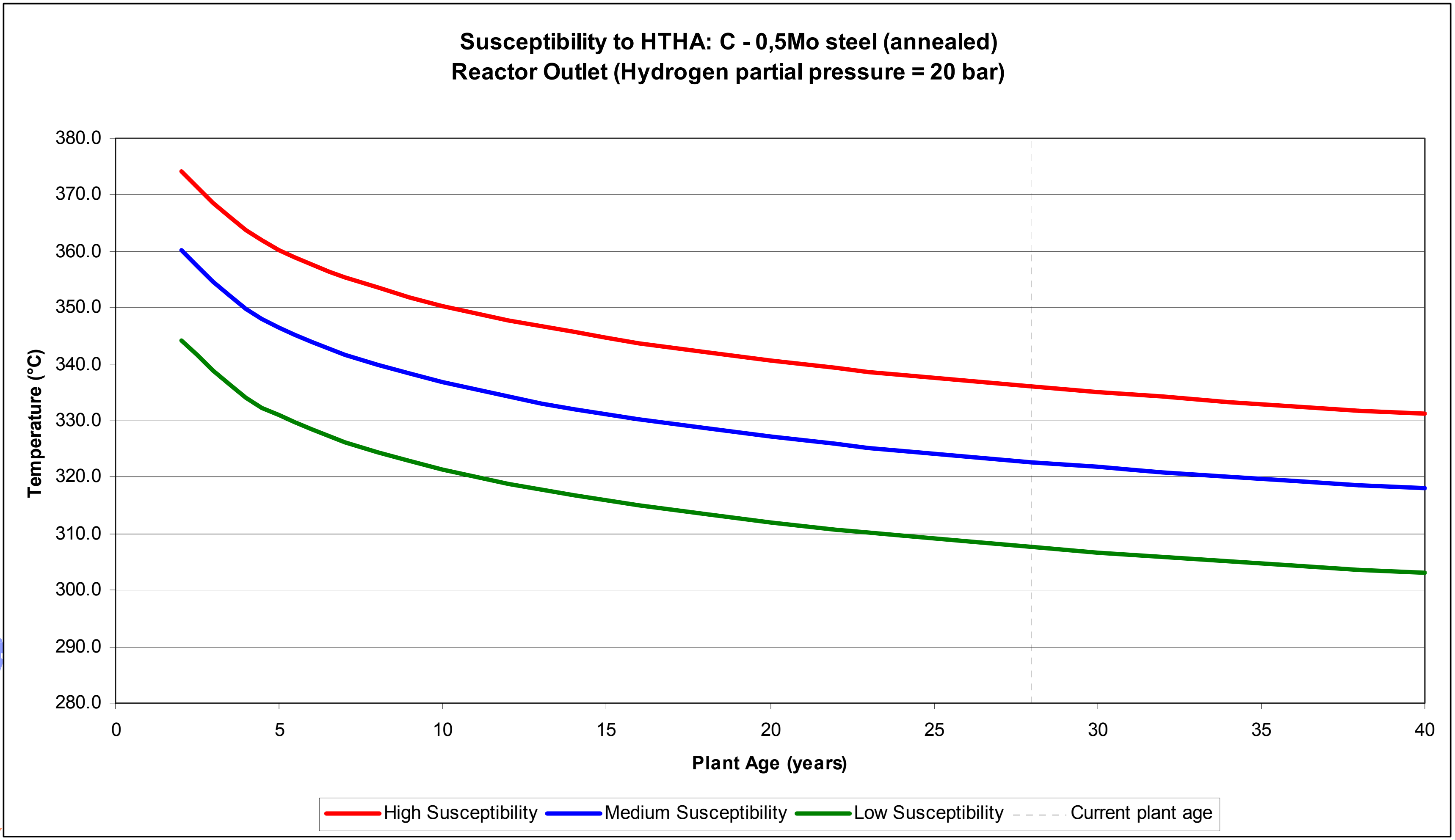
Case study:

C-0,5Mo in high temperature H_2

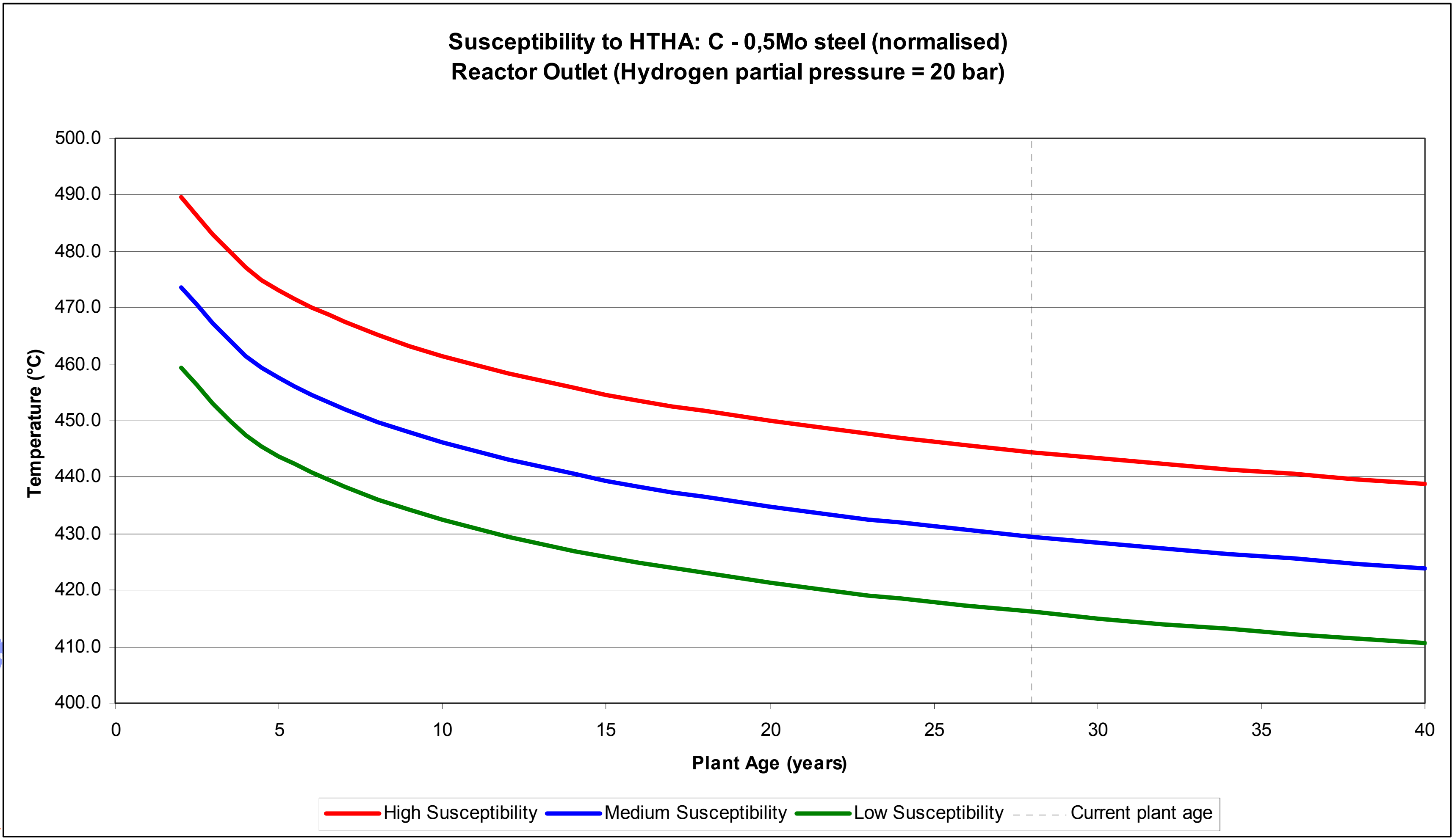


Case study:

C-0,5Mo in high temperature H_2



Case study:
C-0,5Mo in high temperature H_2



Case study:

C-0,5Mo in high temperature H_2

- *Conclusions*
  - *Uncertaincies about metallurgical condition*
    - *Annealed vs normalised*
    - *Piping systems: unlikely to be "normalised"*
  - *Reactor inlet*
    - *Restrict temperature to 275ºC @ pH_2 = 35 bar*
    - *Low susceptibility*
  - *Reactor outlet*
    - *Restrict temperature to 315ºC @ pH_2 = 20 bar*
    - *Low susceptibility*
  - *Change of materials (1,25Cr-0,5Mo) if higher temperatures are required*

Appendix 9

Naphtenic acid corrosion

Studies at Eni Technologie

Roberto Riva   Eni

Naphthenic acid corrosion of 9%Cr 1%Mo steel

Roberto Riva, Giovanna Gabetta, Marino Tolomio, Pietro Bruni

San Donato Milanese, 9 March 2004

Background

- Opportunity crude oils are cheap, but potentially corrosive because they may contain naphthenic acids and a high concentration of sulphur.
- Chemical analysis alone cannot predict their corrosivity; still, the total acid number (TAN) and the content of sulphur are key parameters.
- There is a subtle interaction between naphthenic acids and sulphur, which can be described by a simple model.

  At a fixed concentration of naphthenic acids the model predicts
  1) naphthenic acid corrosion at low S content
  2) inhibition of naphthenic acid corrosion at intermediate S content
  3) sulphidic corrosion at high S content.

Aims of the experimental work of Enitecnologie

- Testing the model that describes the interaction between naphthenic acids and sulphur.
- Developing a laboratory test capable of predicting the corrosivity of opportunity crudes, which could become a planning tool for refineries. We focus on furnace tubes.

Experimental procedure

- Rotating specimen (9% Cr, 1% Mo) in a sealed autoclave at 340°C.
- Two kinds of oil: 1) Ural crude oil (1.5% wt sulphur, TAN=0.2)
  2) lubricant base oil (3.8ppm wt sulphur, TAN=0.16).
- Acidity is increased through addition of a mixture of synthetic naphthenic acids (Fluka 70340, average molecular weight 230).
- Evaluation of the rate of corrosion through weight loss after cleaning.
- Evaluation of the weight of corrosion product deposited on the surface of the metal: difference between weight after test and after cleaning.

Equal concentration of naphthenic acids (TAN=4.9), but different sulphur content

High content of sulphur

Low content of sulphur

Reportedly, a different appearance corresponds to the attack of either corrosive agent:

- Sulphidic corrosion leads to the formation of sulphidic corrosion scales.
- No surface corrosion products after naphthenic acid corrosion.

Weight of corrosion products

High sulphur content

Average weight of corrosion products (9 tests with various TAN values)

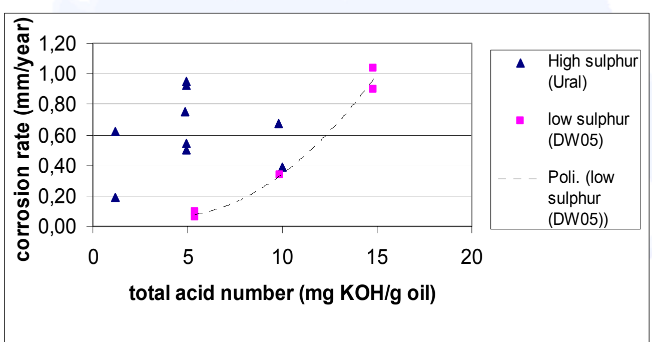
7.8 mg/cm²

Low sulphur content

Average weight of corrosion products (5 tests with various TAN values)

1.1 mg/cm²

Corrosion rate



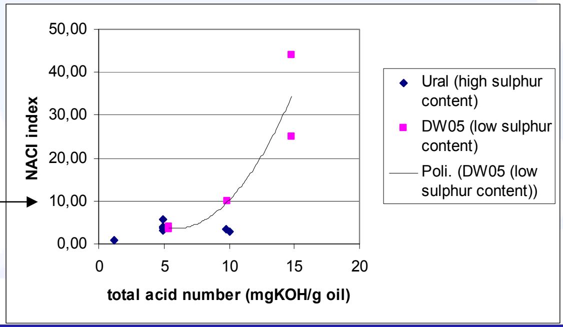
Naphthenic Acid Corrosion Index (NACI)
Craig H.L., 1995

NACI = [corrosion rate (mpy)]/[weight of corrosion product (mg/cm^2)]

NACI	***TYPE OF CORROSION***
< 10	sulphidation or, perhaps, oxidation
10 to 100	moderate naphthenic attack, perhaps inhibited by sulphidation
> 100	severe naphthenic attack

NACI index

Threshold of naphthenic acid corrosion



Discussion of the experimental results

The experimental results are roughly in agreement with the model given in the literature for the interaction between sulphur and naphthenic acids. For example:

- High sulphur content and TAN=10 lead to sulphidic corrosion
- Low sulphur content and TAN=10 lead to naphthenic acid corrosion.

BUT

A very high concentration of naphthenic acids (TAN□10) is necessary for the naphthenic acid corrosion to start. In contrast, far lower concentrations can give rise to naphthenic acid corrosion in refinery plants.

Pitfalls of sealed autoclave tests

The pressure reached in sealed autoclave tests is probably too high (20 to 30 bar). The compounds containing sulphur decompose gradually during the test, the concentration of dissolved H_2S rises consequently and appears to favour sulphidic corrosion.

Conclusions

- The experiments have confirmed the interaction between sulphur and naphthenic acids. The results are roughly in agreement with the model given in the literature.

- Very high concentrations of naphthenic acids (TAN□10) were required for the onset naphthenic acid corrosion. Such behaviour is surprising even for 9% Cr-1% Mo steel, which is quite resistant to naphthenic acids . Far lower concentrations (TAN□0.5) are potentially corrosive in refinery plants. The experimental set-up probably needs modifying, if plant conditions are to be reproduced.

Alternative autoclave tests

According to the literature, a closer agreement between laboratory tests and plant experience could be obtained with either of the following pieces of equipment:

- ***Pressure relief valve and condenser:*** at 3 to 7 bar and three days’ exposure corrosion rates are much closer to those experienced on refinery plants. (Kane & Cayard, 1998)
- ***Refreshed rotating cylinder apparatus:*** low fluid consumption (☐10 litres per 24 hours), high pressure (69 bar) (Pritchard A.M. et al., 2001).

Appendix 10

Naphtenic acid corrosion

A neural network approach

S. Trasatti   University of Milan

Naphtenic acid corrosion: a neural network approach

Stefano P. Trasatti, Francesco Mazza
Dip.to di Chimica Fisica ed Elettrochimica, Università di Milano
Via C.Golgi 19 - 20133 Milano

EFC meeting 2004 - Enitecnologie 8/9 March 2004

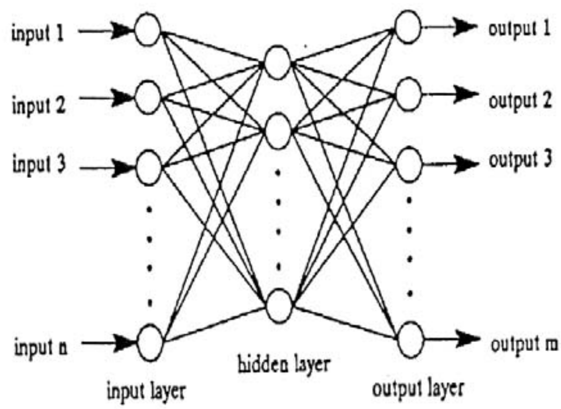
Neural Network

Mathematical model simulating neuronal activity of the human brain. It's an Artificial Intelligence System enables us to embed structured human knowledge into workable algorithms. NN learns the "weights" of the correlation between input and output data apparently not connected by any model (training step)

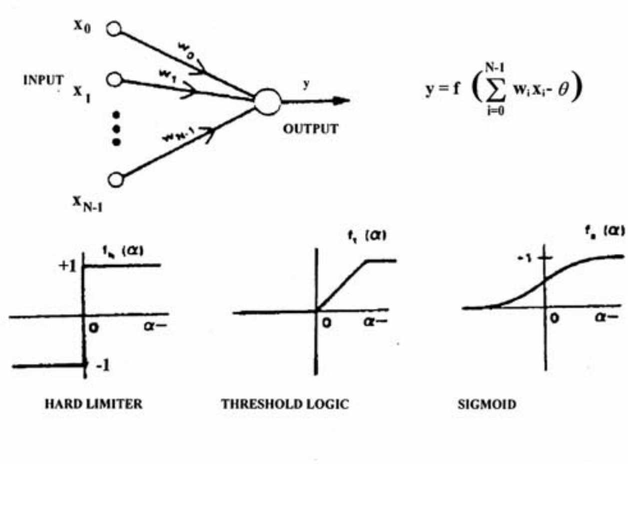
↓

Target: to predict output from input not used in the training step and to obtain information on the involved mechanism

Neural network structure:
Multilayer Perceptron



Transfer functions typically used by NN nodes and neurons



$$y = f\left(\sum_{i=0}^{N-1} w_i x_i - \theta\right)$$

Neural Network features

- Advantages
  - Adaptability to phenomena which are changing
  - High level og robustness (tolerance limit)
  - Non-linear calculation tool
- Limitations
  - Close box tool (no mechanistic understanding of the process being modelled)
  - High number of data for training step
  - Data filtering and codification

Neural Network applications

- Recognition of characters and images
- Analysis of spectra (Raman, NMR, IR, etc.)
- Petrochemical industry (rock properties, well productivity, seismic images)
- Noise filtering
- Chemical process optimization (recognition offailure cases)
- Loan calculation (banks)
- Medical diagnosis (electroencephalogram analysis)

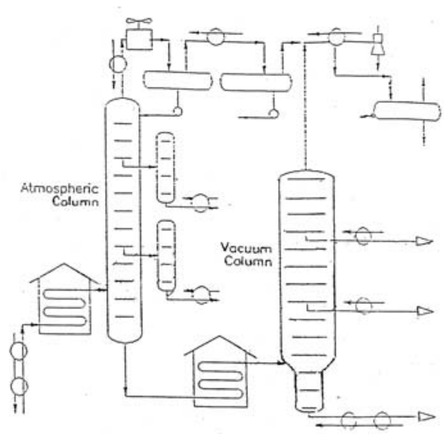
Applications of NNs to corrosion (1)

- H.Smets, W.F.L.Bogaerts – NNs to predict the SCC of 304ss in near-neutral solutions as a function of Cl-, O2 and T
- Urquidi-Macdonald et al. – NN for predicting the number and depth of pits in heat exchangers
- D.C.Silverman, E.M.Rosen – NN combined with an expert system to predict the type of corrosion from polarization curves
- S.P.Trasatti and F.Mazza – NN to study the initiation and propagation step in crevice corrosion of SS and related alloys in near neutral chloride containing media

Applications of NNs to corrosion (2)

- Ramamurthy et al. – NN to analyse impedance data for automobile paint finishes subjected to stone impacts
- S.Nesic, M.Vrhovac – NN to predict corrosion of steel in CO2-containing solutions
- A.Turnbull et al. – NNs to predict SSCC of Duplex ss
- T.F.Barton et al. – NN to identify pitting and revice spectra in electrochemical noise

Naphtenic acid corrosion



Fe + 2RCOOH = Fe(RCOO)2 + H2
Fe + H2S = FeS + H2
Fe(RCOO)2 + H2S = FeS + 2 RCOOH

TAN

Flow Rate

Temperature

%S

Crude oil type

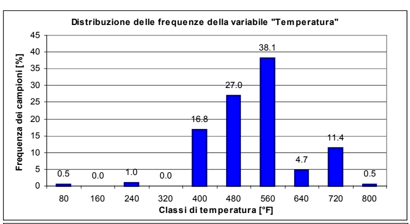
Two phase flow

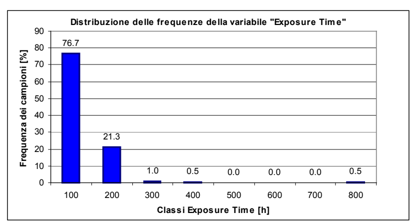
Metallurgy

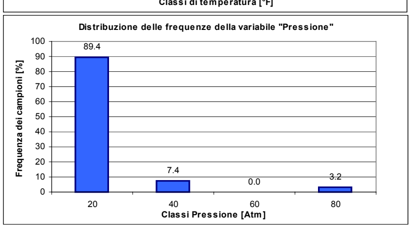
T (°F)	P (atm)	Flow rate (m/s)	Exposure Time (h)	TAN	%S	%Cr	%Mo	Corr.Rate (mpy)
70	1	0,9	210	1	0,3	12,43	0	0,7
330	40	0,9	152	1	0,3	12,43	0	2,6
70	1	0,9	210	1	0,3	0,03	0,01	0,6
600	40	0,9	66	1	0,1	0,03	0,01	9,4
400	1	0	120	18,1	0,1	7,09	0,58	15,4
455	1	0	82	9	0,1	7,09	0,58	24,4
455	1	0	82	17,7	0,1	7,09	0,58	42,2
375	1	0	164	46,1	0,1	9,03	1,08	9,2
400	1	0	120	8,85	0,1	9,03	1,08	19,4
560	6,9	0,8	82	13,2	0,1	9,03	1,08	35
560	20	0,8	65	23,1	0,1	9,03	1,08	159
560	5,5	0,8	93	8,2	0,1	17,46	2,02	0,3
450	1	0,9	74	29,2	0,1	18,59	0,18	1,2
500	1	0	48	0,74	0,1	0,03	0,01	3,3
500	1	0,1	6	4,5	0	0,03	0,01	46
560	1	0	48	20	0	0,03	0,01	320,6
500	1	0	48	20	0	17,4	2,06	1,8
662	69	6	24	2,9	0,4	0,25	0,2	13,4
550	1	7	24,5	7,2	0,4	0,03	0,01	425
550	1	7	28	7,2	0,4	0,03	0,01	262
698	1	3	72	2,35	1,1	1,5	0,45	27
698	1	3	72	2,35	1,1	18,7	3,13	2

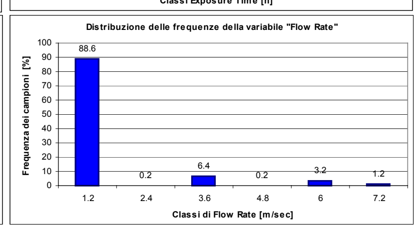
Variables

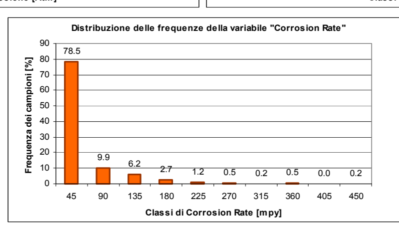
Parameter	Min.	Max.	Variable type	use
Temperature (°F)	70	725	Process	Input
Pressure (atm)	1	69	Process	Input
Flow Rate (m/s)	0	7	Process	Input
Exposure Time (hours)	6	768	Process	Input
TAN	0	46.1	Crude oil	Input
S_%	0	4.17	Crude oil	Input
Cr_%	0.01	20	Plant	Input
Mo_%	0	4.64	Plant	Input
Corrosion Rate (mpy)	0	425	Process	Output



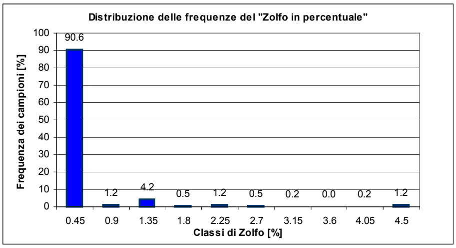


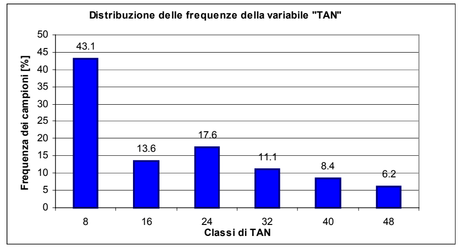


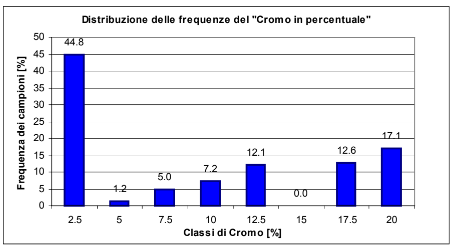


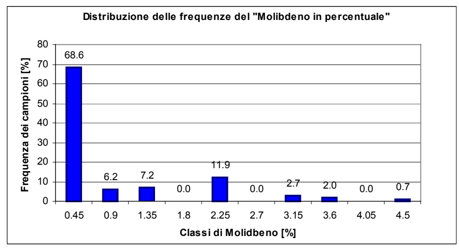


Data distribution (%)









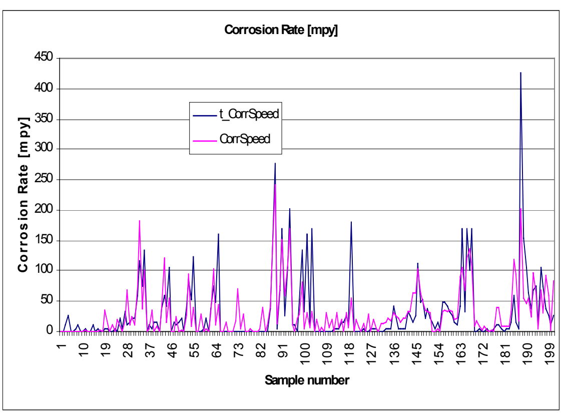
Normalizing range

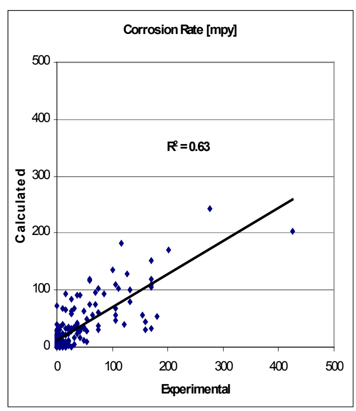
Parameter	Input min.	Input max.	Output min.	Output max.
Temperature (°F)	390	750	0.1	0.9
Pressure (atm)	1	69	0.1	0.9
FlowRate (m/s)	0.09	7	0.1	0.9
Exposure Time (hours)	6	150	0.1	0.9
TAN	0.5	47	0.1	0.9
%S	0.1	4.1	0.1	0.9
%Cr	0.1	18	0.1	0.9
%Mo	0.1	4.4	0.1	0.9
Corr.Rate (mpy)	0	425	0.1	0.9

Main component analysis

Variable	Ranking in input record	Value	%	Sum%
TAN	5	7.433	22.66	22.66
Press	2	5.168	15.76	38.42
Temp	1	4.471	13.63	52.06
ExpTime	4	4.421	13.48	65.54
FloRate	3	3.364	10.26	75.79
Mo_Perc	8	3.327	10.14	85.94
Cr_Perc	7	2.792	8.513	94.45
S_Perc	6	1.820	5.548	100

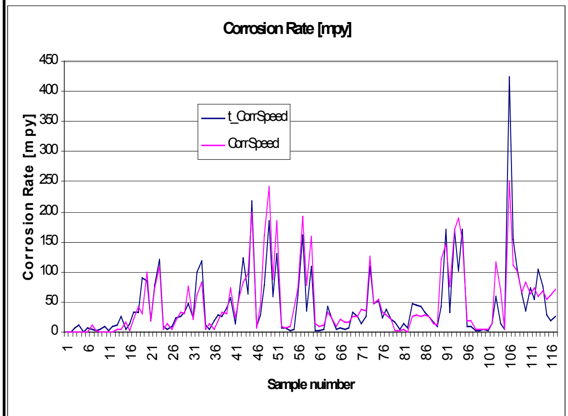
NN for all materials

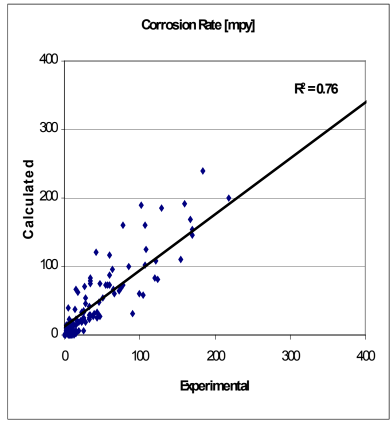




Input layer	8
Hidden layer 1	9
Hidden layer 2	3
Output layer	1

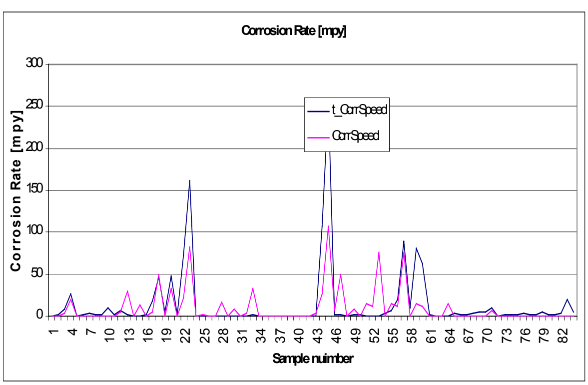
NN for Carbon Steel

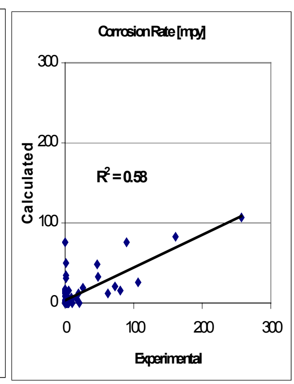




Input layer	8
Hidden layer 1	9
Hidden layer 2	5
Output layer	1

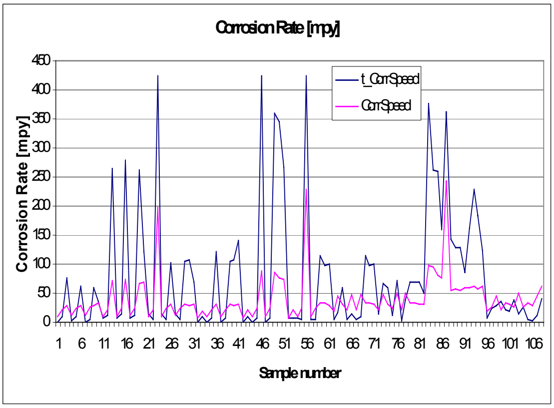
NN for Stainless Steel

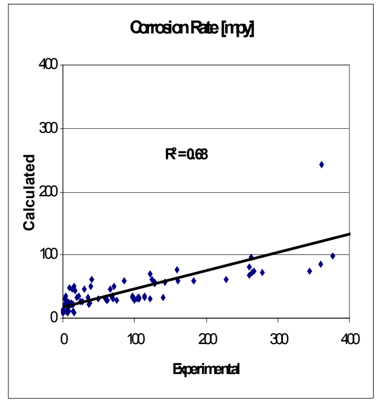




Input layer	8
Hidden layer 1	7
Hidden layer 2	3
Output layer	1

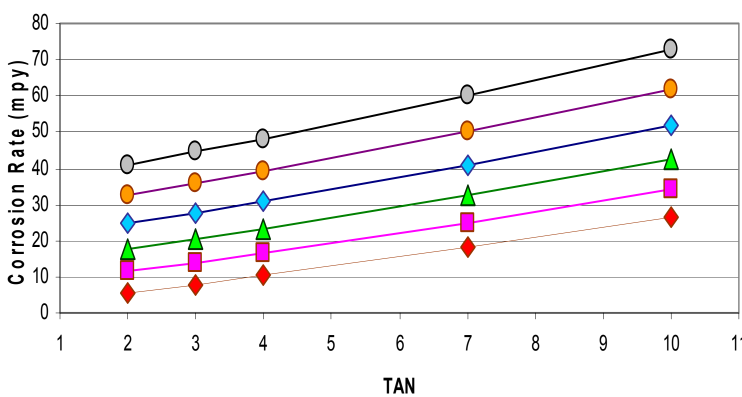
Validation step





Input layer	8
Hidden layer 1	9
Hidden layer 2	5
Output layer	1

Validation step



Temp. (°F)	Press. (atm)	FlowRate (m/s)	ExpTime (hours)	TAN	%S	%Cr	%Mo
400-650	1,00	0,00	48,00	da 2,00 a 10,00	0,10	0,03	0,01

Validation Step

Temp. (°F)	Press. (at m)	FlowRate (m/s)	Exp.Time (ore)	TAN	%S	%Cr	%Mo	Corr.Rate (mpy)	Corr.Rate predetta
644.0	19.0	3.2	228.0	1.2	0.1	8	1	7.5	20.13
644.0	22.0	3.2	72.0	1.2	0.1	8	1	24.4	26.07
644.0	20.0	3.2	84.0	4.9	0.1	8	1	29.5	45.84
644.0	28.0	1.9	108.0	4.9	0.1	8	1	36.6	21.73
644.0	18.0	1.9	96.0	4.9	0.1	8	1	21.6	33.93
644.0	18.0	1.9	108.0	4.9	0.1	8	1	19.7	31.86
644.0	25.0	1.9	104.0	4.9	0.1	8	1	37.4	25.08
644.0	16.0	1.9	180.0	10	0.1	8	1	15.3	50.33
644.0	37.0	1.9	163.0	9.8	0.1	8	1	26.4	26.45
644.0	18.0	1.9	108.0	5.4	0.1	8	1	3.9	34.05
644.0	16.0	1.9	168.0	5.4	0.1	8	1	2.4	29.73
644.0	19.0	1.9	168.0	9.9	0.1	8	1	13	46.13
644.0	25.0	1.9	168.0	14.8	0.1	8	1	40.5	61.55
644.0	20.0	1.9	168.0	14.8	0.1	8	1	35.4	57.4

Appendix 11

Nace Italia 2004 Conference

The NACE Italy , section of NACE INTERNATIONAL, organizes on the occasion of the recognition in Genoa what capital European of the culture 2004, his 2 ^ annual conference.
How custom, such conference is established to introduce, to discuss, to divulge, the connected problems to the technology of the corrosion.
The involvement of peoples that work with prevention and control of the corrosion is combined to the exhibition of products and services from the working Societies in the sector.
The papers interest all the sectors of the technology of the corrosion involving her thematic to it correlated (**Research, Corrosion, Corrosion Control, Coating, Cathodic Protection, NDE, Metallurgy, Materials and Services**).
Continuous evolution of technology calls us to give an exhaustive contribution : scientific, university, production and commercial, without forgetting the normative and institutional aspects.
The partecipation to the Conference becomes essential factor knowledge for deepened of this technology and remains the principal way to update the technicians that operated, to varied levels, in the different areas of the industry.
The Firms that present products and/or services have the possibility to intend and to introduce theirs last novelties in technological terms, doing grow the market and contributing so to an effectiveness cultural popularization.

Italia Section

NACE INTERNATIONAL
THE CORROSION SOCIETY

presents

CORROSION 2004 - ITALIA

Genoa

Jolly Hotel Marina - Porto Antico
November 25 – 26, 2004

CALL FOR PAPER

AND

with sponsorship of
"ISTITUTO ITALIANO della SALDATURA"

Final papers can be even as "extended abstract"

- Abstracts deadline : May 31, 2004
- Papers deadline : September 30, 2004

The language is italian but the oral presentation can be in english.
The "abstracts", "extended abstracts" and complete papers must be in .doc format and sent it at under following addresses so like the Firms that want presented them products or services.

- Istituto Italiano della Saldatura
  Lungobisagno Istria 15 – 16141 Genova
  - Alberto Lauro
    Tel. 010 / 8341354
    Fax 010 / 8341353
    e-mail : alberto.lauro@iis.it
  - Franco Lezzi
    Tel. 010 / 8341372
    Fax 010 / 8367780
    e-mail : franco.lezzi@iis.it

Organizing Committee

Chairman Nace Italia
Carmelo Aiello
Eni Group – Raffineria di Gela
Gela (CL)
Tel: 0933 842485
Email: carmelo.aiello@eni.it

Treasurer
Mario Celant
Pipeteam
Via Resistenza 2
20070 - Vizzolo Predabissi (MI)
Tel: +39 (0)2 98232820
Email: mario.celant@pipeteam.com

Vice-Chairman
Alberto Lauro
Istituto Italiano della Saldatura
Lungobisagno Istria, 15
16141 Genova
Tel: 010 8341354
E-mail: alberto.lauro@iis.it

Secretary
Massimo Cornago
ENI E & P
Via Emilia, 1
20097 S. Donato Milanese (MI)
Tel: 02 52063405
E-mail: massimo.cornago@agip.it

ndustry