4th ICEPIM & OMIC GAS 2018

Pipeline Corrosion – Issues, Causes, some failure case histories

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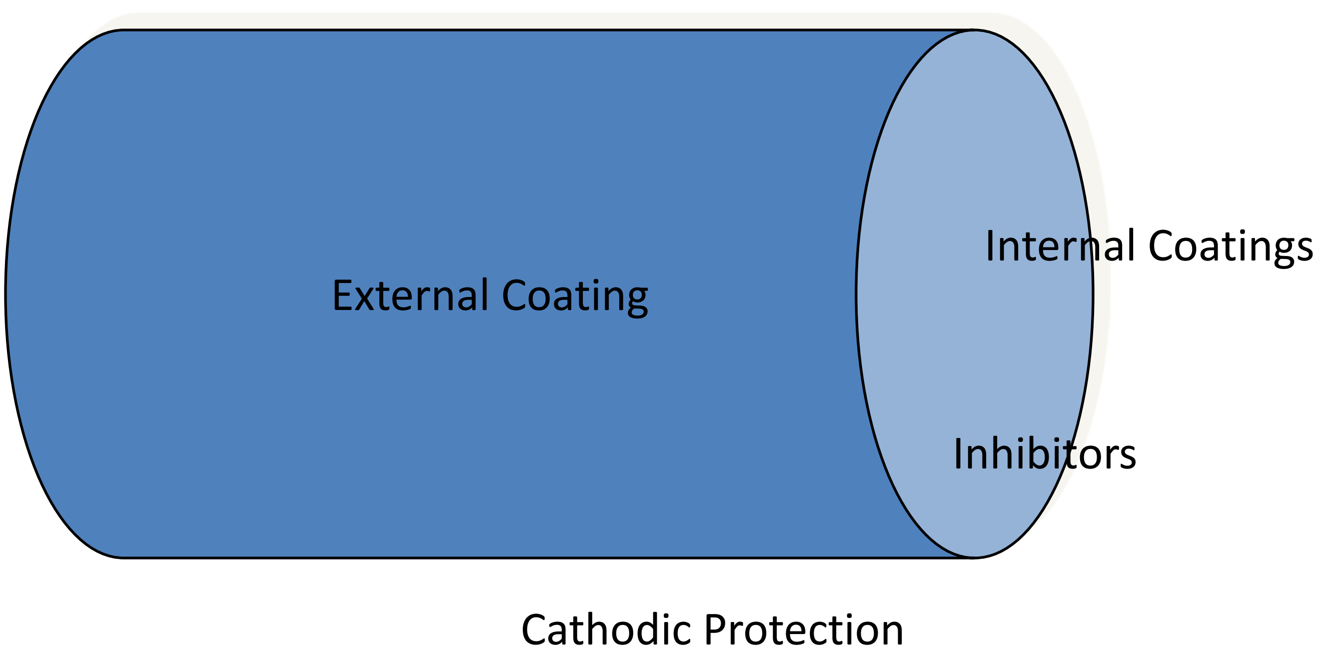
CORROSION CONTROL IN PIPELINES

COATINGS
CATHODIC PROTECTION
INHIBITORS



Pipeline Steel composition

Element /Grade	C	Mn	P	S	Cr	Cu	Ni	Mo	Al	Si	Nb/Ti	Yield Strength (MPa)	Ultimate Tensile Strength
X42	0.09	0.84	0.013	0.004	0.07	-	0.02	0.02	0.03	0.22	-	290	414
X46	0.09	1.28	0.014	0.009	0.02	-	0.03	0.03	0.02	0.25	-	317	434
X52	0.09	1.31	0.012	0.006	0.01	-	0.07	0.003	0.03	0.25	-	359	455
X56	0.12	1.27	0.017	0.004	0.07	-	0.14	0.19	0.02	0.26	-	386	490
X60	0.12	1.48	0.013	0.004	0.01	-	0.09	0.02	0.008	0.27	-	414	517
X70	0.13	1.71	0.012	0.001	0.07	-	0.07	0.02	0.05	0.30	1	483	565
X100	0.064	1.56	0.024	0.002	-	.38	0.54	0.28	0.03	0.13	0.089/ 0.011	690	760

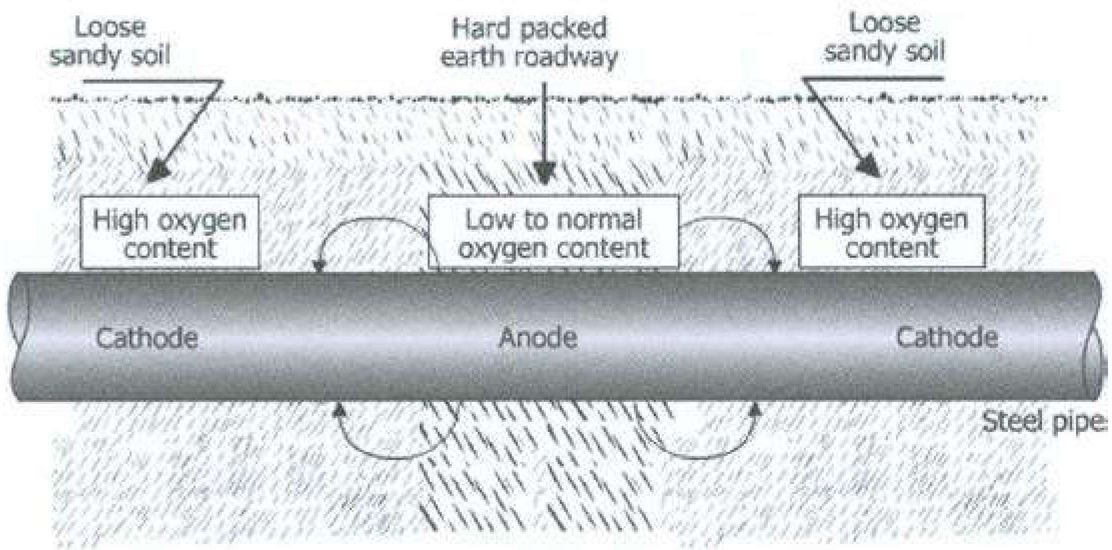
Organization	ID	Title
ASME	B31.4	Liquid Petroleum Transportation Piping Systems
ASME	B31.8	Gas Transmission and Distribution Piping System
ANSI/AGA	Z223.1	National Fuel Gas Code (same as NFPA 54)
AWWA	C 200	Steel Pipe
AWWA	C 600	Pipe Laying
AWWA	M9	Concrete Pressure Pipe
AWWA	M11	Steel Pipe-Guide for Design and Installation
NFPA		Multiple Fire Protection Systems

Issues in Basic Design of Pipeline

1. **Better pipeline material selection to avoid, pitting, SCC, sulphadic corrosion.**
2. **External Coatings – backed by Cathodic Protection**
3. **Internal Corrosion – by thin epoxy coatings or by inhibitor injection**

EXTERNAL CORRORSION

Formation of Differential Oxygen Cells due to variation in soil type around the pipe



Formation of Differential Concentration Cells

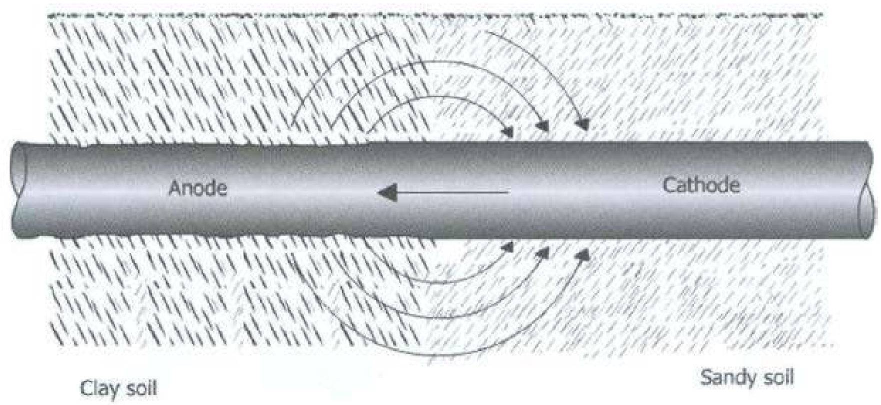
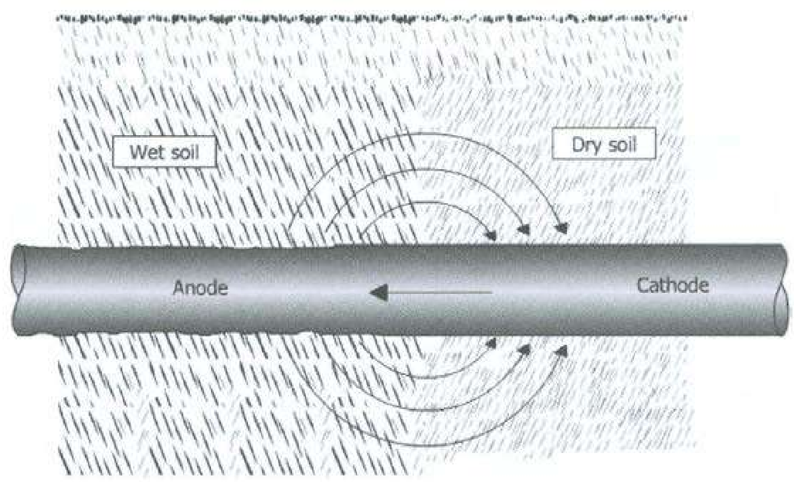
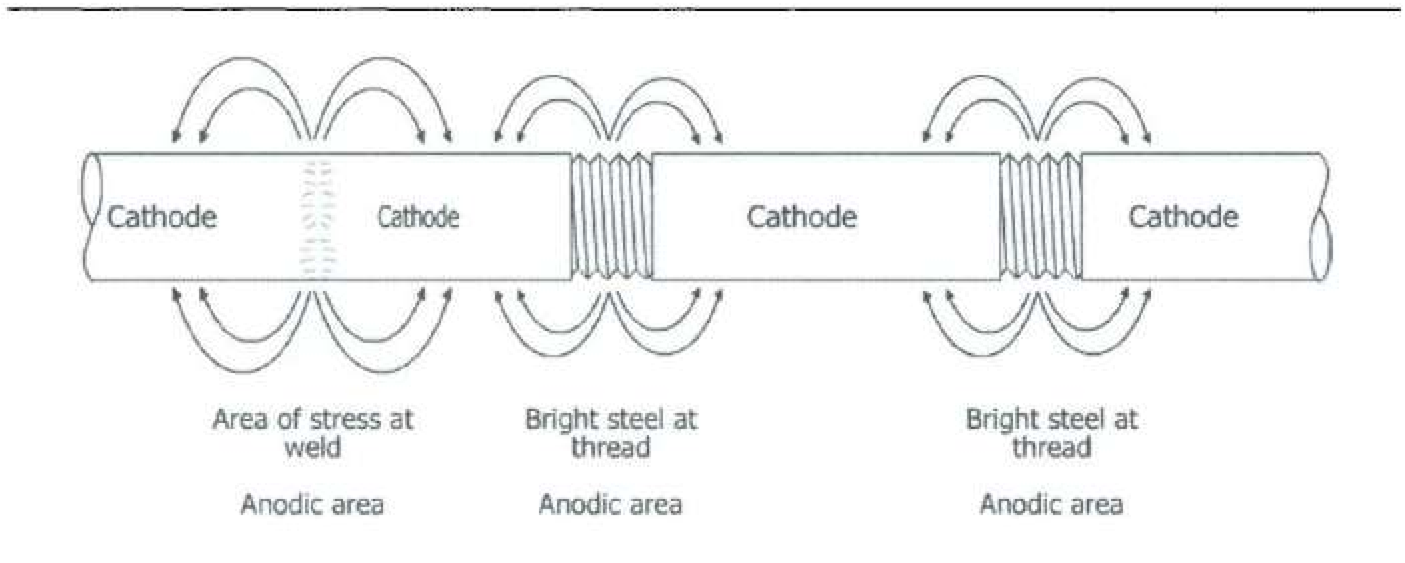


Figure 5.8 Corrosion caused by different types of soils

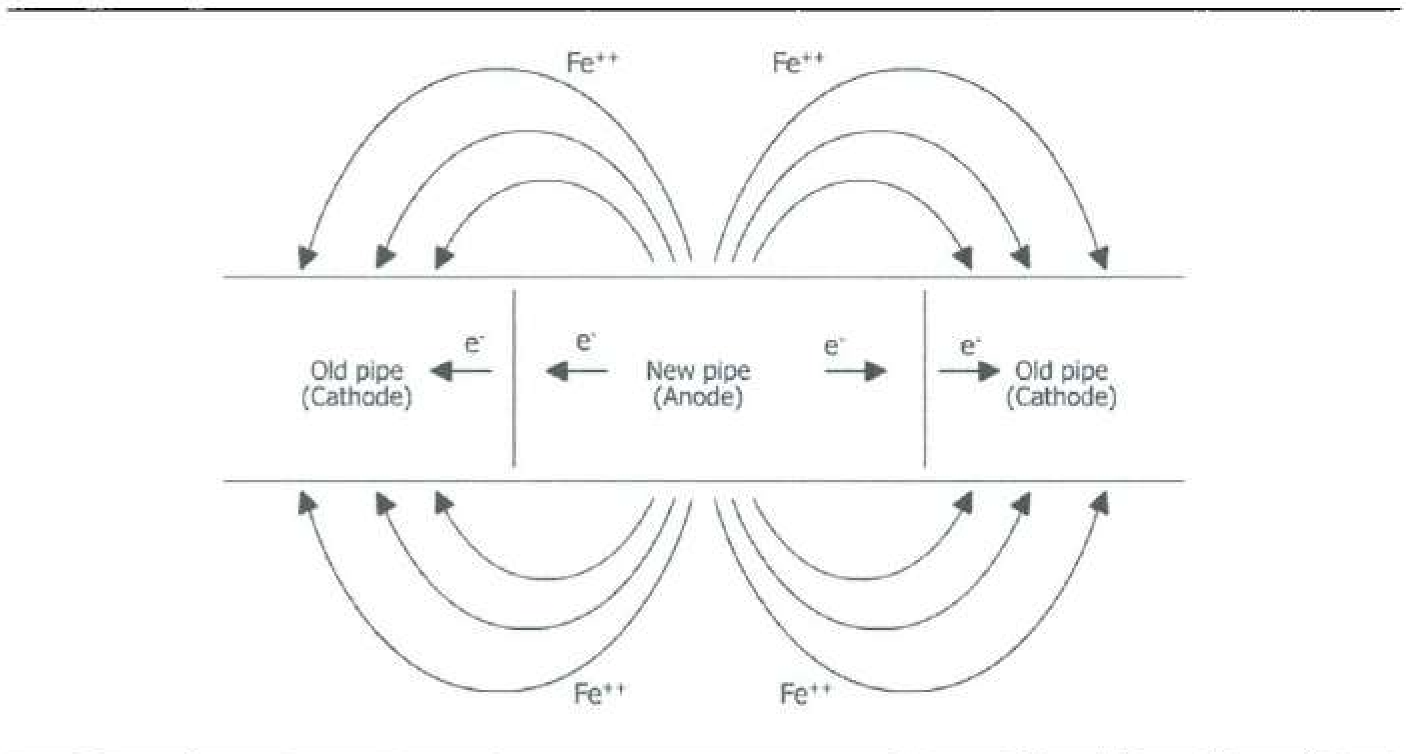


Mechanism of Corrosion of pipeline Caused in soil

Formation of Corrosion Cells with stressed and unstressed portion



Dissimilar anode cell formation by joining of an old Pipe with a new pipe



Microbiological induced Corrosion

- Sulphate reducing bacteria – Which if present in soil can cause severe pitting followed by loss in thickness of the pipe leading to catastrophic failure.
- Application of robust coatings help in reducing their attack

Internal Corrosion

Effect of various Environmental Factors

CO_2	Partial pressure of carbon-dioxide in the operating environment
pH	Hydrogen ion concentration of the operating environment
H_2S	Partial pressure of hydrogen sulfide in the operating environment
HCO_3	Amount of bicarbonates (HCO_3) present in solution
Cl^-	Dissolved chlorides in the operating environment
Temperature	Operating temperature for the environment
Dewpoint	Dew point of operating environment
Oxygen	Oxygen concentration in the environment
Fluid Velocity	Flowing Velocity of in the operating environment
Water/gas ratio	Ratio of water to gas in gas dominated systems (gas wells)

Dissolution of Carbon Dioxide:

Solubility is very important

$$CO_2 + 2H_2O \Rightarrow H_2CO_3$$
$$H_2CO_3 \Rightarrow H^+ + HCO_3^-$$
$$HCO^- + H_2O \Rightarrow CO_3^{-2} + H^+$$

The carbon dioxide - water system reaches equilibrium so that K_1 and K_2 for carbonic acid is satisfied.

$$K_1 = [H^+][HCO_3^-] / [H_2CO_3]$$
$$K_2 = [H^+][CO_3^{-2}] / [H_2CO_3^-]$$

Degree of Ionization

$$I = [H^+] \backslash [H_2CO_3]$$

MECHANISM OF CO_2 CORROSION OF STEEL

$$Fe \longrightarrow Fe^{++} + 2e^{-} \text{(Anodic reaction)}$$

$$H_2CO_3 + e^{-} \longrightarrow HCO_3^{-} + H \text{ (Cathodic reaction)}$$

The Overall Reaction

$$Fe + 2H_2CO_3 \longrightarrow Fe^{++} + 2\,HCO_3^{-} + H_2$$

Build up of bicarbonate ion can lead to an increase in the pH promoting precipitation of iron carbonate

$$Fe + 2HCO_3^{-} \longrightarrow FeCO_3 + H_2O + CO_2$$

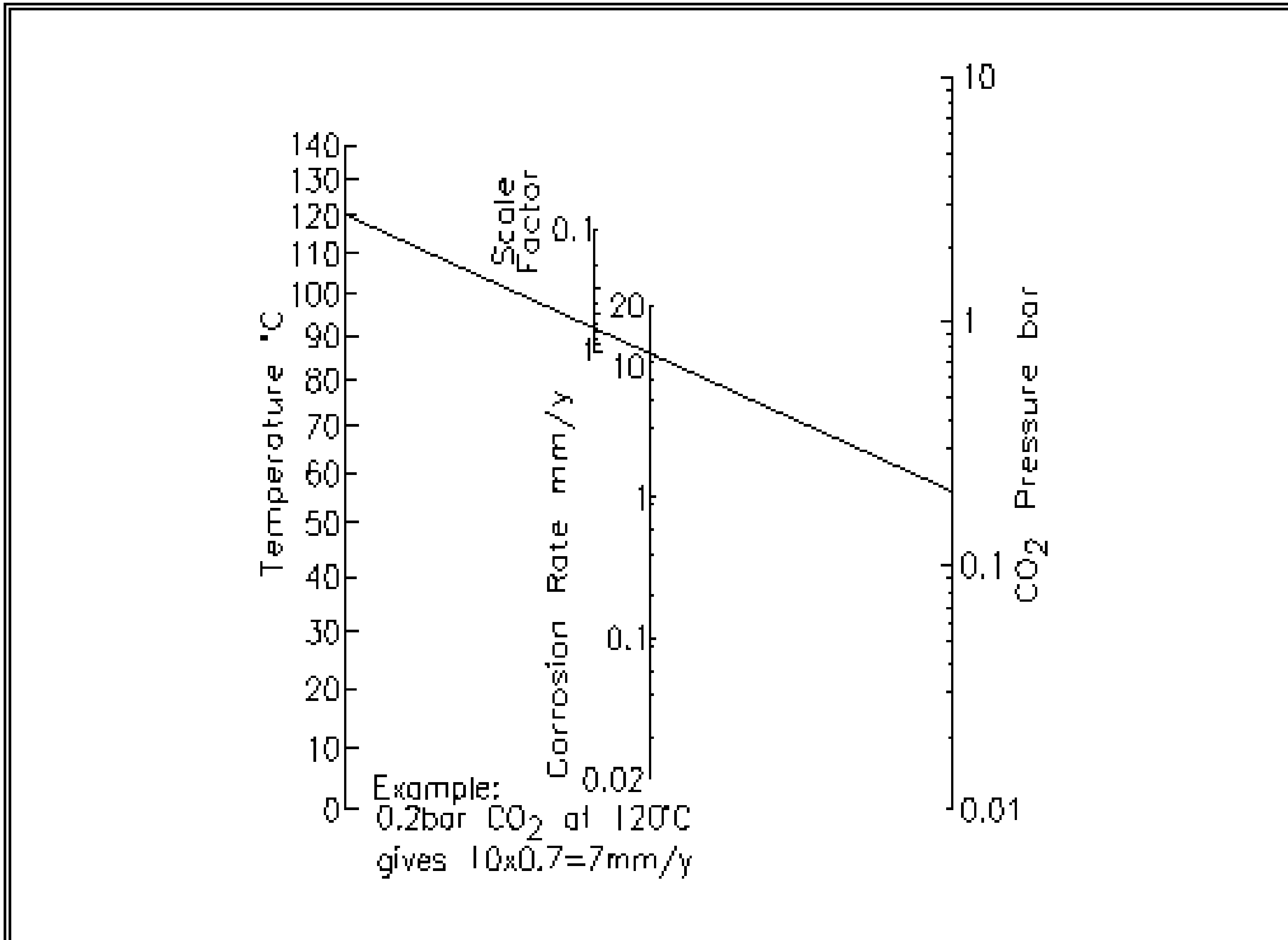
Iron carbonate solubility, decreases with increasing temperature,
Thus consequent precipitation of iron carbonate is a significant factor in assessing corrosivity. ,

$$\log (V_{cor}) = 5.8 - 1710/T + 0.67 \log (pCO_2) \text{ ------ (1)}$$

where

V_{cor} = corrosion rate in mm/yr
T = operating temperature in K
pCO_2 = partial pressure of CO_2 in bar

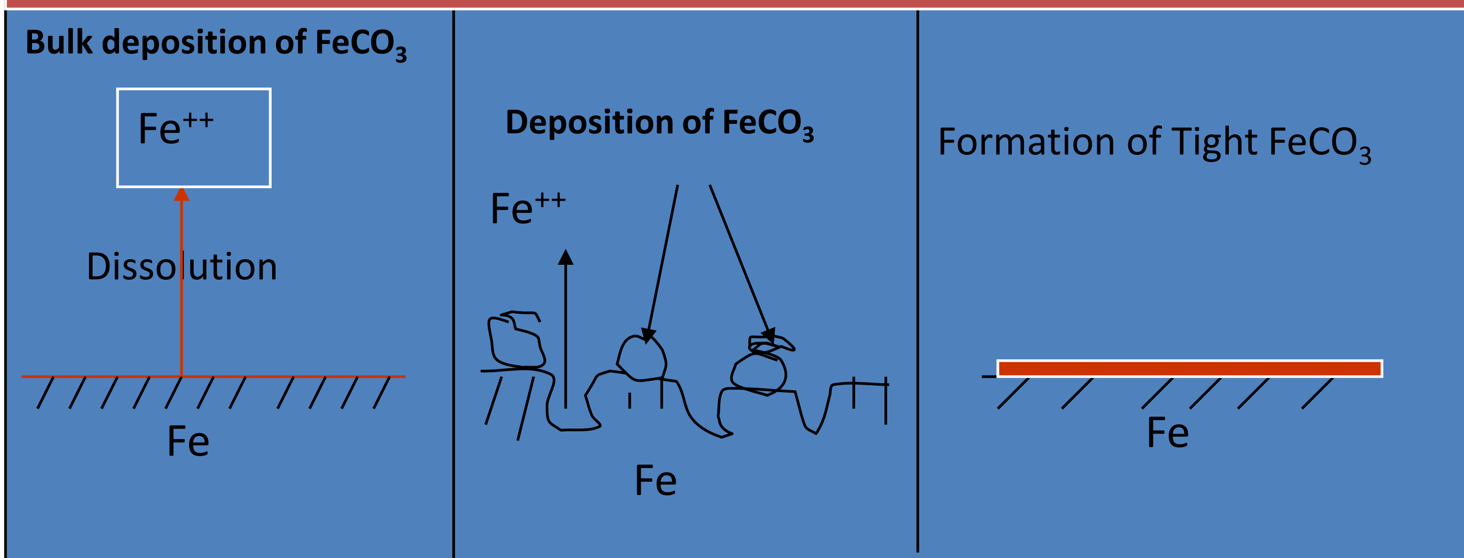
Effect of Temperature and partial Pressure of CO_2 on Corrosion of Steel



Ref: C. de Waard and U. Lotz, Prediction of CO2 corrosion of carbon steel, Corrosion/93, Paper 69, NewOrleans, 1993

Effect of temperature on the Corrosivity of Steel

Type 1	Type 2	Type 3
Low Temp. 40°C	Intermediate Temp 100°C	High Temperature 150°C.
Gen Corrosion	Pitting Corrosion	Protective Oxide



Temperature °C

150

100

60

30

Rate Determining Step : Solubility / permeability of the film

Solubility =F (PCO_2 T↑ C_{Ca} ↓ C_{Mg} ↑ T ↑ pH↓ C_{HCO3} ↓) ↓

Permeability : F(T, pH, Ccations (Hg, Al,, Cr , Si)

Corrosion rate : F (P_{CO2}, T, pH, Salts, flow, metallurgy)

Nature of Film – Protective property increases with Temperature

Rate Determining Step : H-evolution Controlled by Homogenous / Hetrogenous H_2CO_3 formation

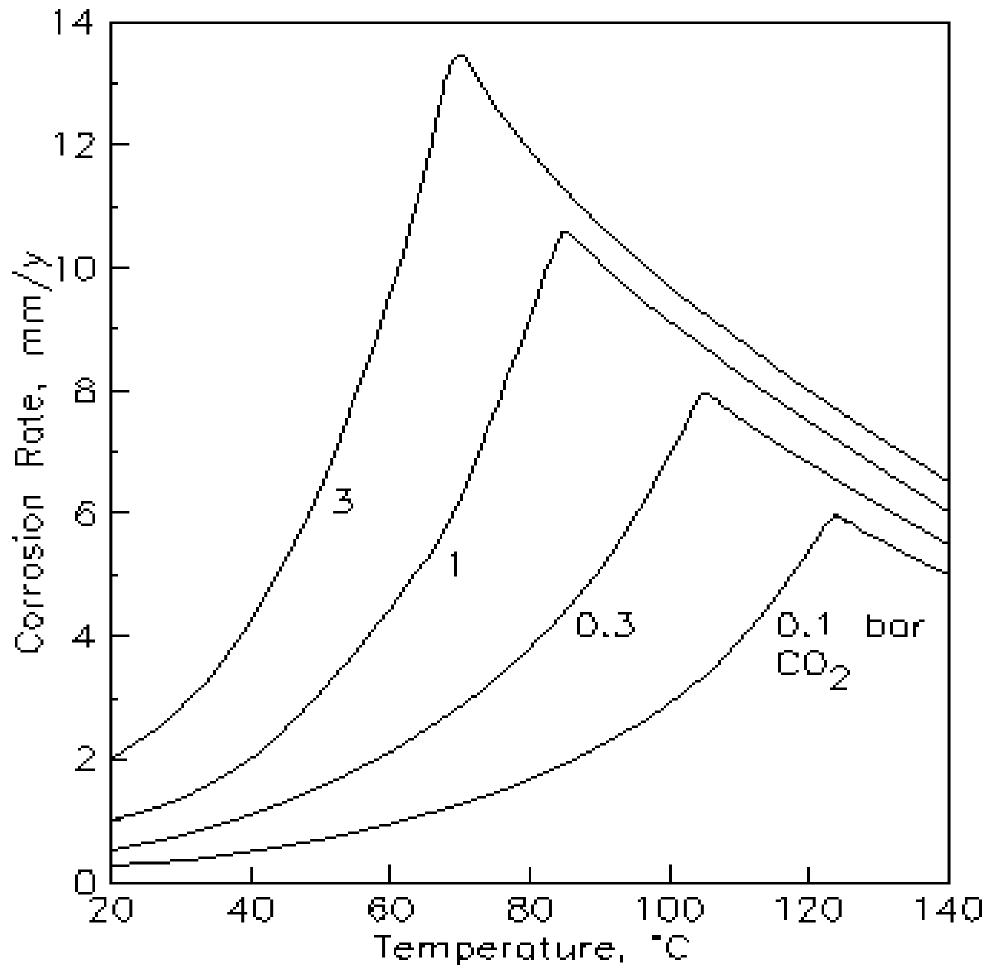
Corrosion rate : f(PCO_2 ↑ T ↑ pH, Metallurgy)

No Flow Control

Nature of Film : Non-protective,

$FeCO_3$, $Fe(Ca,Mg)CO_3$

Effect of temperature on the corrosion rate of steel in CO_2 atmosphere.



Ref: C. de Waard and U. Lotz, Prediction of CO2 corrosion of carbon steel Corrosion/93, Paper 69, NACE, Houston, TX 1993.

Effect of H_2S on the CO_2 Corrosion

H_2S level (< 0.01 psia), CO_2 is the dominant

- presence of H_2S has no realistic significance.

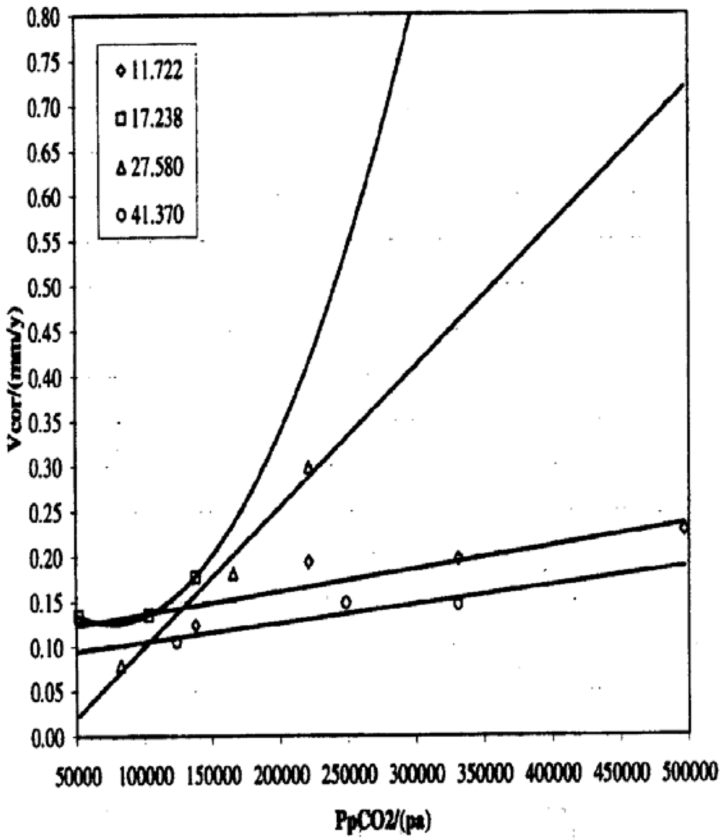
CO_2 dominated systems, with small amounts of H_2S (ratio of pCO_2/pH_2S > 200)

- Lead to the formation of an iron sulfide scale below 120°C.
- However, the FeS scale produced is directly function of Fe^{++} and S^{--} and is influenced by pH and temperature.
- This surface reaction can lead to the formation of a thin surface film that can mitigate corrosion.

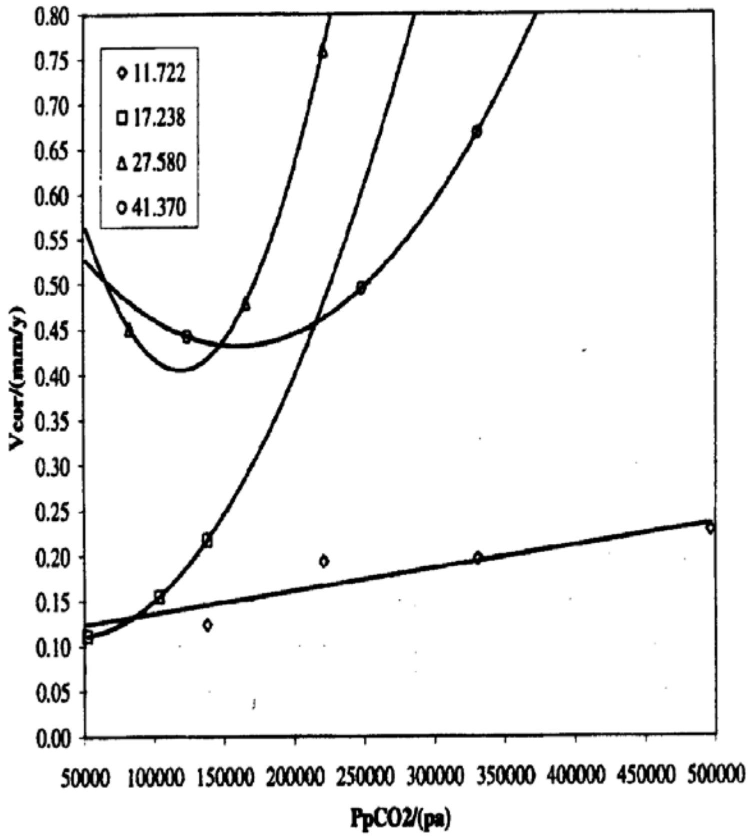
H_2S dominated systems (ratio of pCO_2/pH_2S < 200),

- Preferential formation of a meta-stable sulfide film in preference to the $FeCO_3$ scale; hence, there is protection available due to the presence of the sulfide film in the range of temperatures 60 to 240°C.
- At higher concentrations and temperatures, FeS becomes the more stable pyrhotite.
- However, at temperatures below 60°C or above 240°C, presence of H_2S enhances corrosion in steels since the presence of H_2S prevents the formation of a stable $FeCO_3$ scale.

Corrosion rate as a function of CO_2 partial pressure at four different H_2S level at 38°C



API 5L grade B Steel

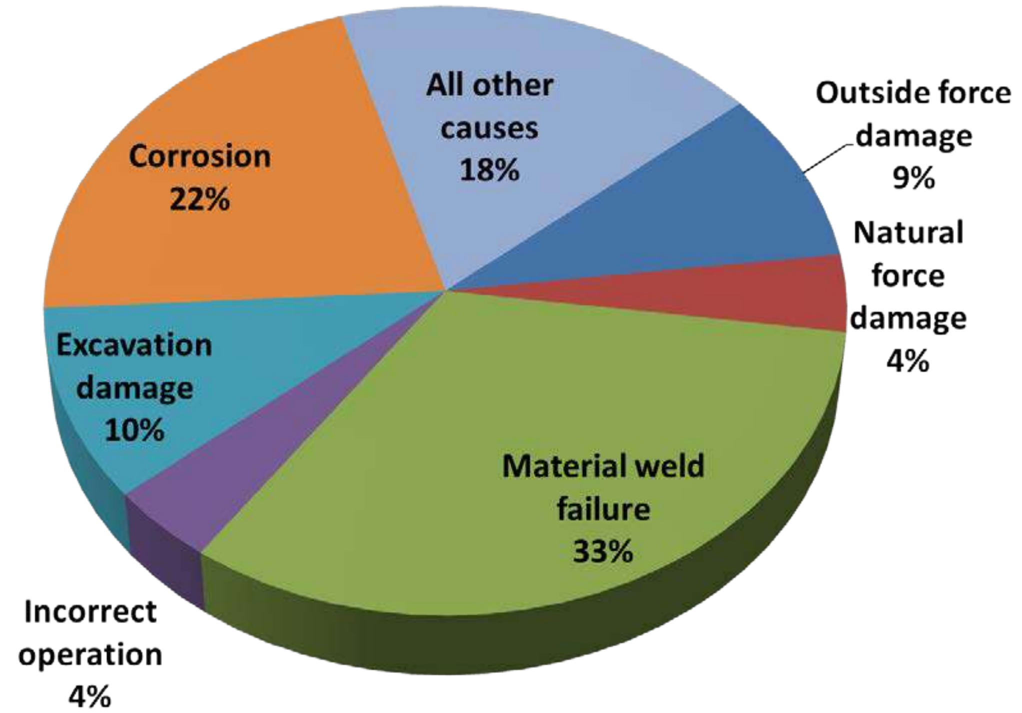


API 5L grade 52 Steel

Internal corrosion requirements

- Usually by adding inhibitors
- In case of sour pipelines, internal coatings is a must.
- In case of sea pipelines, internal metallic coating of Hastealloy is done

Causes of Pipeline Failure

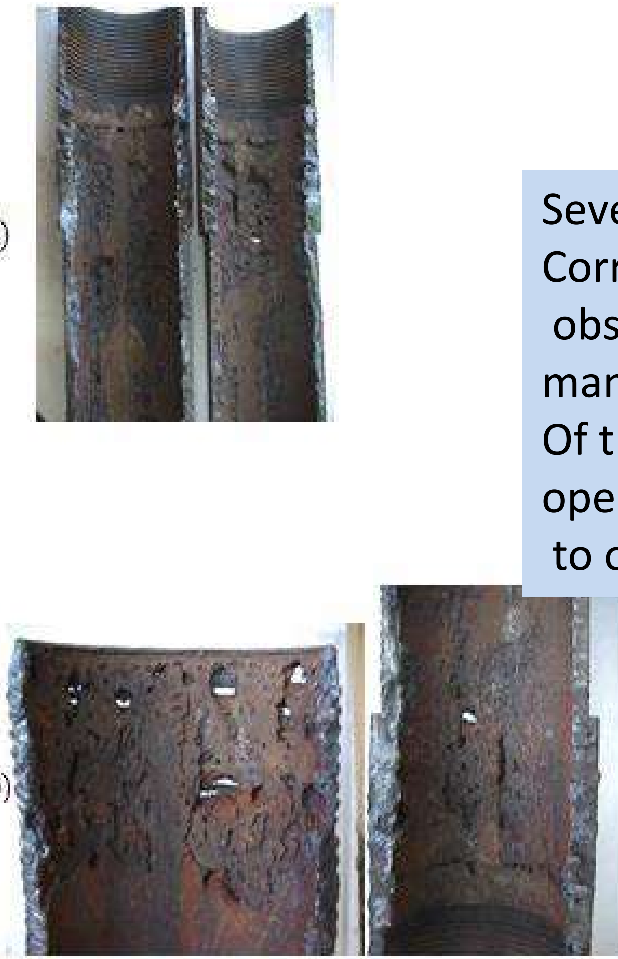


Case History of a Pipeline

Fluid composition	Gas/condensate/water
Pressure (psi)	4700 2150
CO_2 partial pressure (bar)	37 19
Water content (%) ~	45%
Oil Condensate content (%)	55%
Sand content	High
Temperature (^oC)	60 -65
H_2S partial pressure	None
pH Value	6.5
Pipe material	Carbon steel API grade L-80
Diameter	

(a)

(b)



Severe Pitting Corrosion was observed many Of them opened to outer side.

Conclusion of Analysis

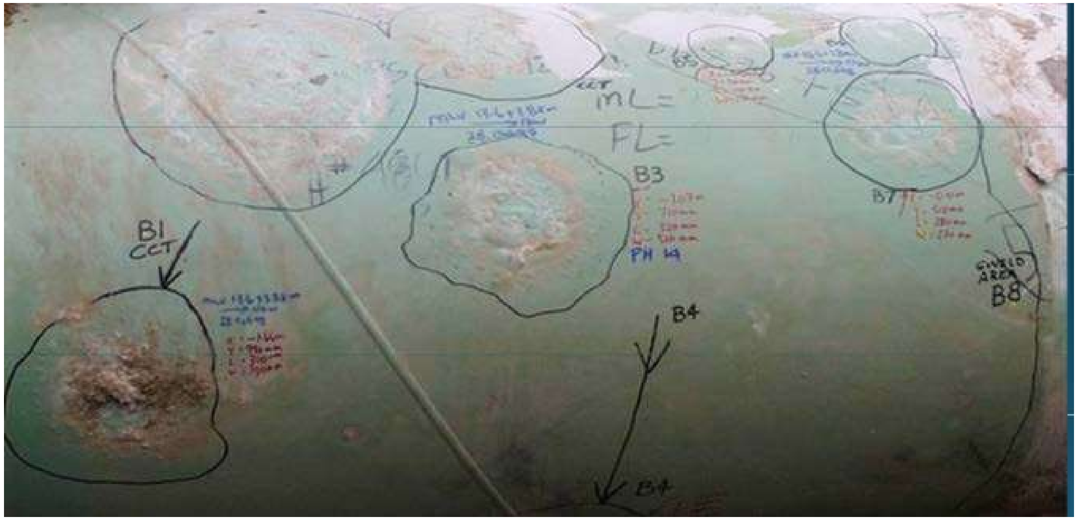
High CO_2 partial pressure, flow velocity, water content and sand in the fluid caused Corrosion

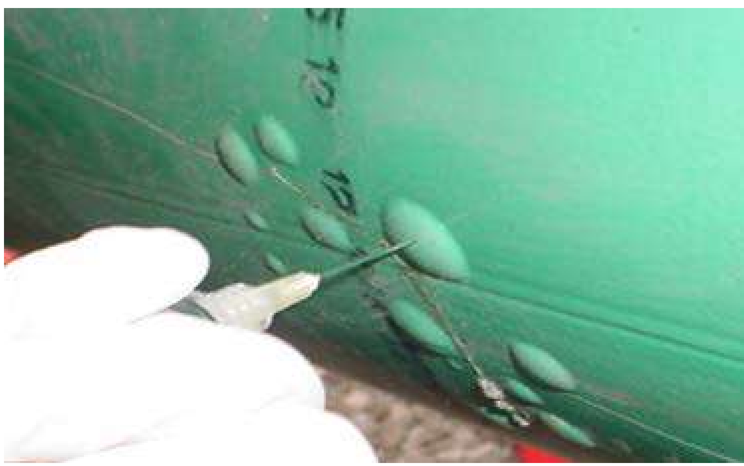
The failure of the core pipes is due to severe corrosion attack estimated to be **3 – 8 mm/yr**, which necessitates replacement of the pipelines.

Pipeline material is not suitable to combat the aggressive condition of the well fluid. It is only good for its mechanical properties to withstand the operating pressure.

It is recommended to use another grade of steel that contain Cr content higher than 3% (compared to 0.23% of the failed steel).

Failure Analysis of Fusion Bonded Epoxy Pipeline Coating





- Findings and Primary Cause

  1-Extensive disbondment after 15 years

  2-Corrosive soil

  3-Poor cathodic disbondment resistance

  4-Presence of high amounts of negativly charged ions, Cl^-, NO_3^-

  5-Surface contamination prior to coating

  6-Root Cause –Inadequate QC/QA prior and during coating process

Failure due to SCC

Though, there was no record of stress corrosion cracking (SCC) as a main cause of failures in Argentine pipelines, but as the pipeline system became old (beyond 15 years) this mechanism started to have an important impact on reliability.

From the three blowouts it was found that high pH, SCC in different oil and natural gas transmission pipelines, which occurred by the sudden propagation of longitudinal cracks at the outer surface of the pipes.

Failure analysis of SCC and SRB induced cracking of a transmission oil products pipeline

In April 2004, a transmission oil products API 5L X52 pipeline in Iran cracked, which led to oil leakage.

Causes of Corrosion was simultaneous effects of SCC and SRB induced cracking .

The investigation indicated that the applied polyethylene tape coating on the external surface of the pipeline became loose and overlapped, i.e., opened and disbanded in the corroded area, consequently, the surface of the buried pipeline was exposed to the surrounding wet soil environment.

As a result of the chemical interactions and the formation of carbonate–bicarbonate solution, and the existence of underweight arising bending stress, SCC induced cracking was introduced.

In addition to SCC, sulfate reducing bacteria (SRB) activities have intensified corrosion and related cracking process.

Failure of a subsea crude oil API 5L X52 steel pipeline

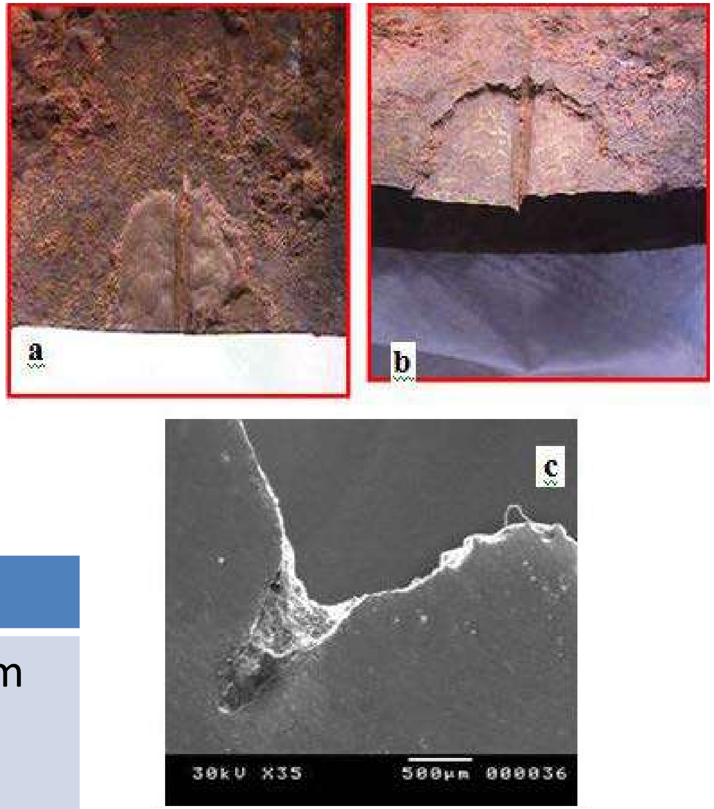
Oil leakage occurred after 27 years in service.

Some leaks were found to form at the bottom of the horizontal API 5L X52 steel pipeline near an elbow section which connected the pipeline to a riser.

Results of this investigation suggest that the cause of failure is electrochemical corrosion combined with mechanical process known as flow-induced corrosion.

The failure mechanism has been narrowed down to the fluid flow rate and chloride-containing water phase.

Failure Analysis of Crude Oil Shipping Pipeline



Pipe material	Grade API- X42 thickness 7.3 mm longitudinal seam longitudinal seam welded
Crude oil Characteristics:,	water content 5 %, Sulfur 4.5%, and pH value 6 -6.5
temperature	45^{o}C
Pressure	14 bar
	The plant was shut down 2, 9 and 6 months.

Cut piece showing
(a) severe pitting corrosion
(b) close-up of corrosion around seam welding groove.
(c) Electron micrograph of the V groove with oxide deposits at the root.

CONCLUSION – Failure Analysis

Failure occurred in one badly fabricated seam welded pipe. Internal pitting corrosion, due to sour oil, during 25 years of service was a trigger of cracking in the infused weld grooves which ended to complete rupture of the pipe.

Two other factors contributed to the failure

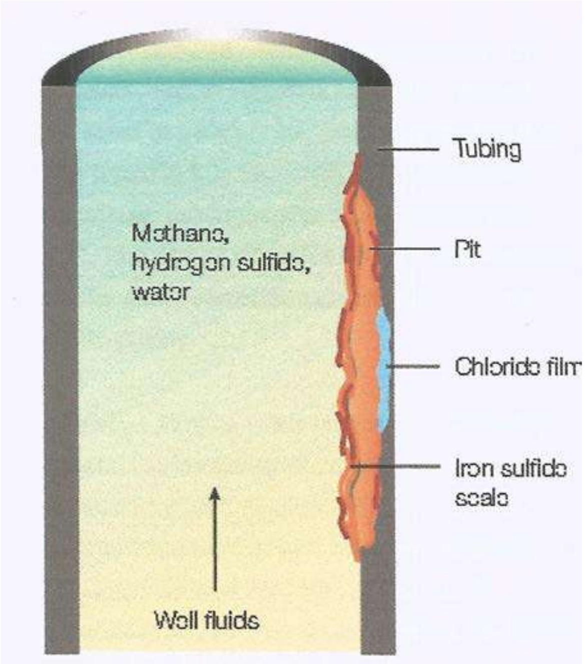
positioning of the weld (seam) line at the bottom (6 o’clock position where water accumulated, and stagnated during long shut down periods.

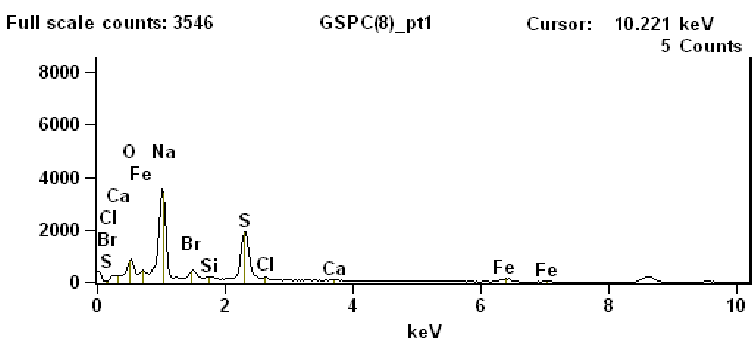
Remedial action: levelling of the pipes at the low lying areas should be carried out using concrete or sand bags as supports.

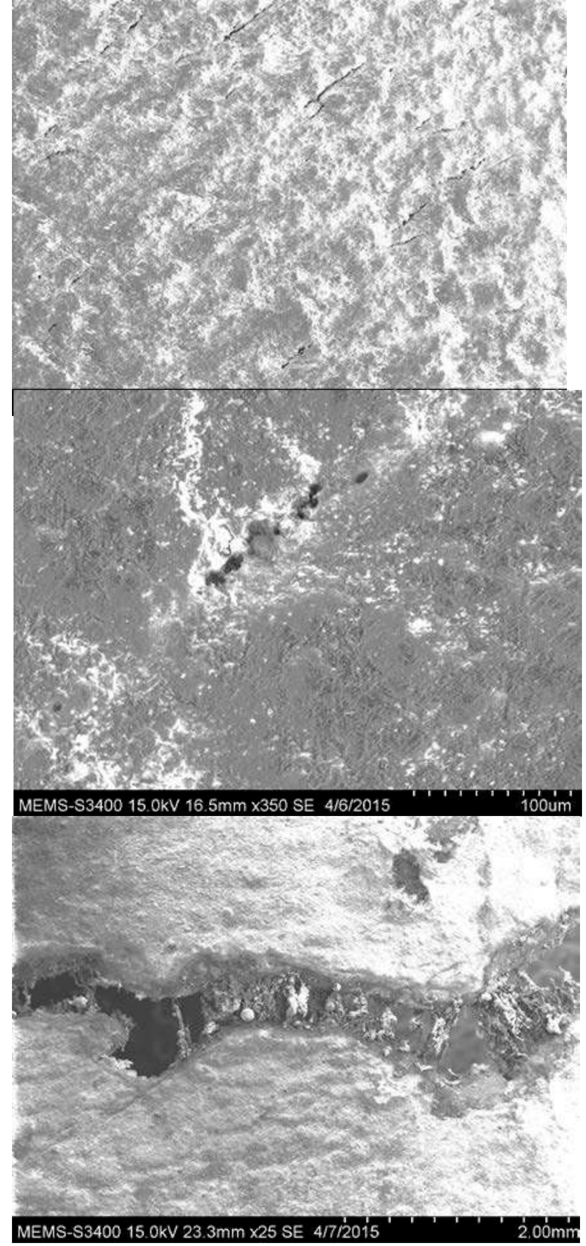
Any pipe having the seam weld line in the 6 O’ clock position should be accurately inspected for the remaining wall thickness.

Decision is up to the operators, to cut and remove the pipe if the thickness is critical or wait for complete rupture.

Failure Analysis of a Well Tube due to H_2S







- 13Cr
- Super 13Cr
- 22Cr duplex
- 25Cr duplex
- 28Cr stainless steel
- 825 nickel alloy
- 625 nickel alloy
- 2550 nickel alloy
- C276 nickel alloy

Fig. 5 SEM Micrographs of Failed area from outside showing a thick iron oxide scale, formed initially grows at localized area, leading to small crack, which finally leads to metal rupture.

Recommended inhibitors for oil and gas applications

Inhibitors	Oil and gas applications
3-phenyl-2-propyn-1-ol	API J55 oil field tubing in HCl solutions over a wide range of conditions [19]
Hydrazides and thiosemicarbazides of fatty acids with 11, 12, and 18 carbon atoms	Mild steel and oil well steel (N80) in boiling 15% HCl solution [20]
Mixtures of ketones, quinolium salts, and formic acid	Oil field tubular goods to temperatures as high as 204 ^{o}C in HCl [21]
2-Undecane-5-mercapto-1-oxa-3,4-diazole	Mild steel in 15% HCl at 105 + 2 ^{o}C and N80 steel in 15% HCl containg 5,000 ppm of 2-Undecane-5-mercapto-1-oxa-3,4-diazole [22]
2-Heptadecane-5-mercapto-1-oxa-3,4-diazole	
2-Decene-5-mercapto-1-oxa-3,4-diazole	
Dibenzylidene acetone	N80 steel and mild steel in HCl [23]
Di-N-dimethylaminobenzylidene acetone	
Methoxy phenol and nonyl phenol	N80 steel in 15% HCl at different exposure periods (6 to 24 h) and temperature (30 to 110 ^{o}C) [24]
N-(5,6-diphenyl-4,5-dihydro-[1,2,4]-triazin-3-yl)-guanidine	Mild steel in 1M HCl and 0.5M H_2SO_4 [25]
6-benzylaminopurine	Cold rolled steel in 1.0 to 7.0M H_2SO_4 at25 to 50 ^{o}C [26]
Mixture of synthetic magnetite and ferrous gluconate	Oil well steel (N80) in 50 mg/l sulphide concentration at various pH (5.5 to 11.5) and at high temperature pressure condition [27]
Rosin amide imidazoline	N80 and P110 carbon steels in CO_2 saturated simulated formation water [28]

Thanking You