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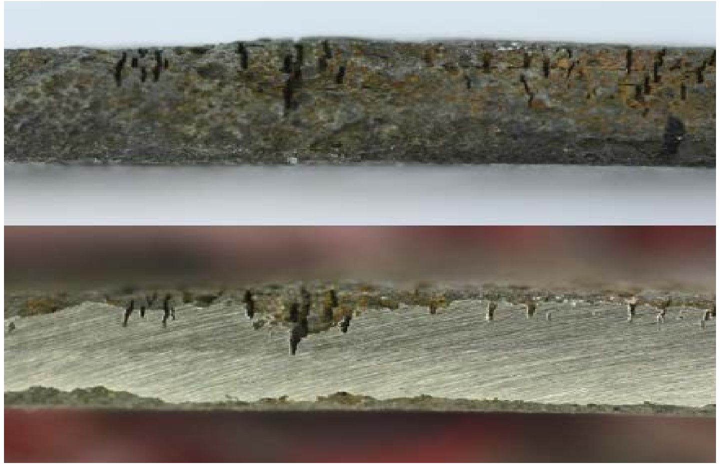
Flexible pipes-Corrosion of armour wires in Annulus

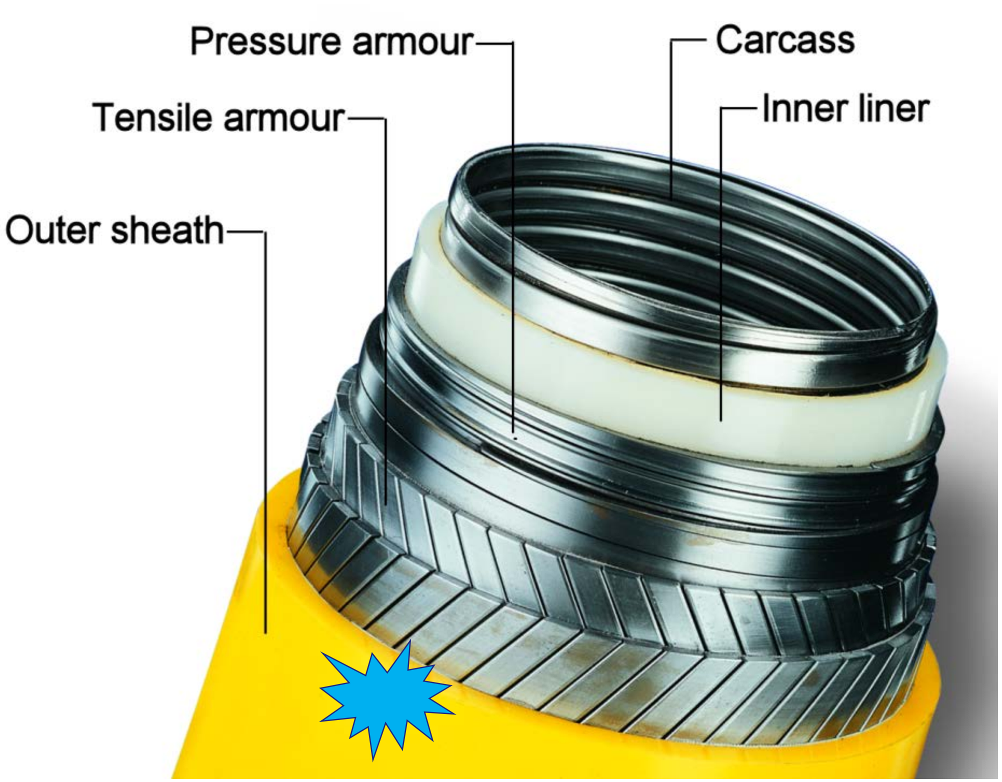
Flexible pipes – Management of Integrity, aging, sharing of experiences and continuous improvement, 4th December 2019

Presentation Outline

- Corrosion in confined environment
- Formation and break down of protective $FeCO_3$ films
- Air ingress through vent port and damaged outer sheath
- H_2S consumption



Corrosion modes



Diffusion:

- H_2O (high RH%- liquid)
- CO_2
- H_2S
- CH_4 +++

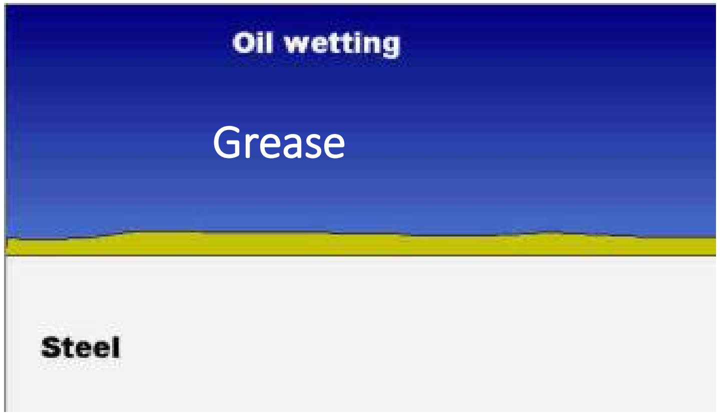
Damaged outer sheath:

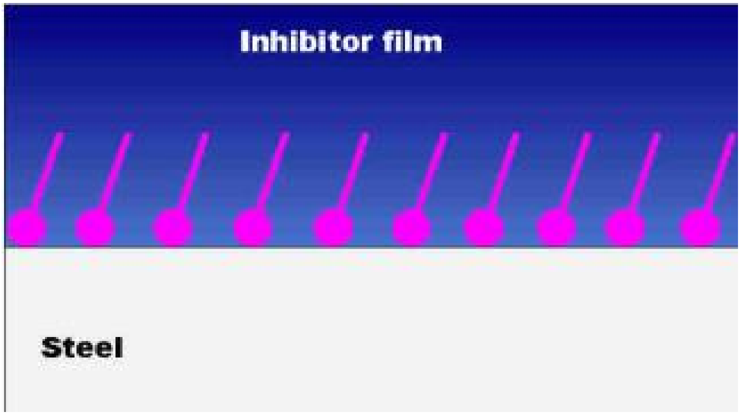
- air (O_2)
- sea water

Air through vent port

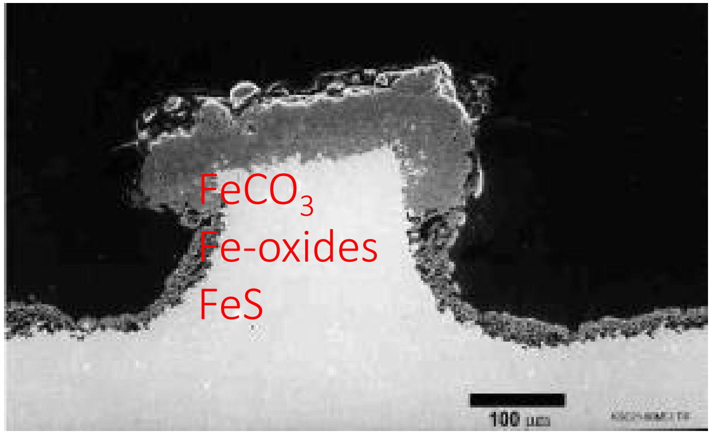
Confined environment:
Low ratio of free volume (V) to steel surface area (S), **V/S < 0.1 ml/cm²**

Carbon steel exposed to water + CO_2/H_2S/O_2 in the annulus corrodes too fast unless it achieves a protective layer on the surface





CP?



Tape

pH and SR dependent on the dissolved corrosion product concentration

$$Fe + 2H_2CO_3 \xrightarrow{(CO_2+H_2O)} Fe^{2+} + 2HCO_3^- + H_2$$

↑ pH, SR_{FeCO3}

$$SR_{FeCO3} = \frac{c_{Fe^{2+}} \cdot c_{CO_3^{2-}}}{K_{sp}} > 1$$

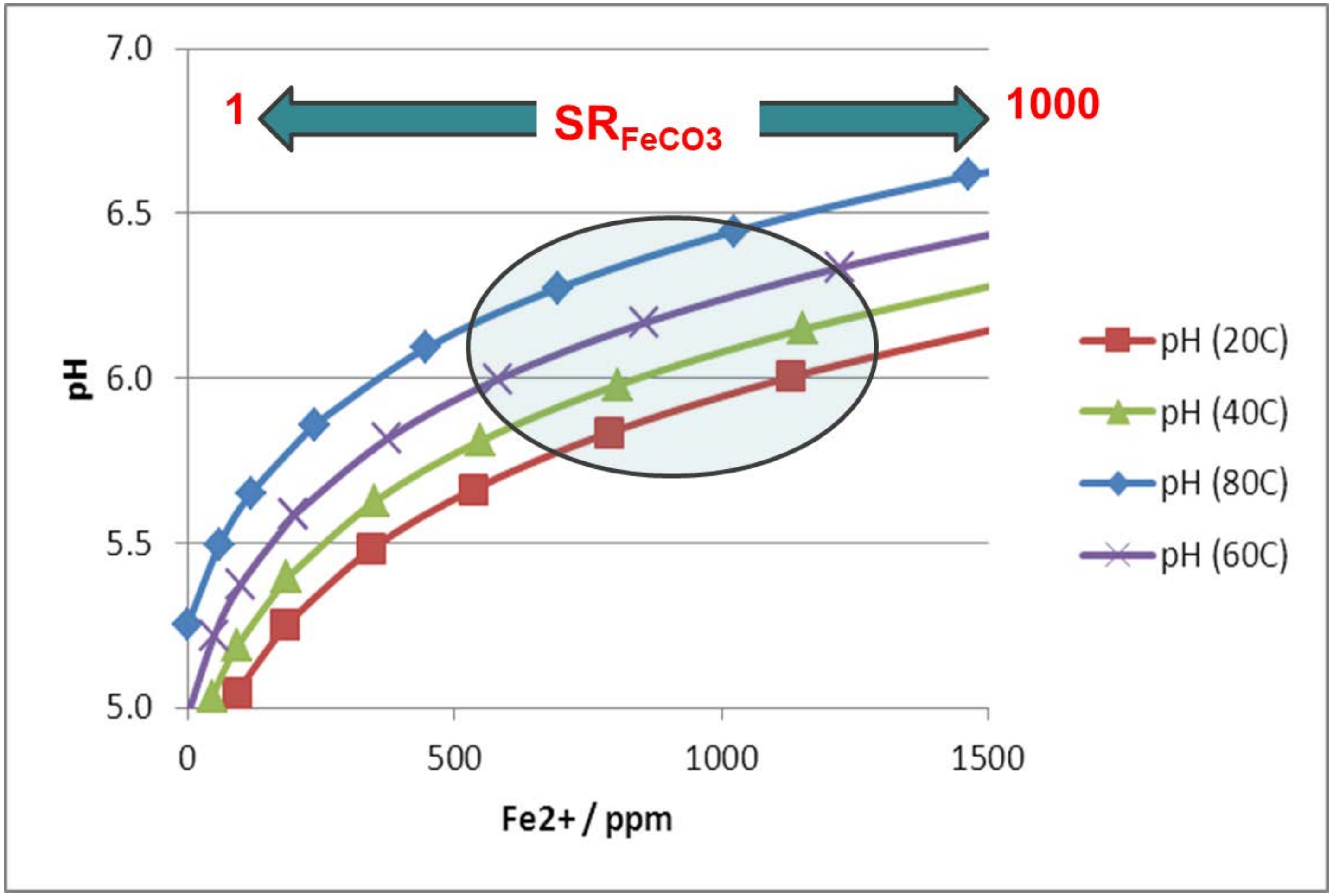
→ pH, SR_{FeCO3} =100-1000

$$Fe^{2+} + CO_3^{2-} = FeCO_3(s)$$

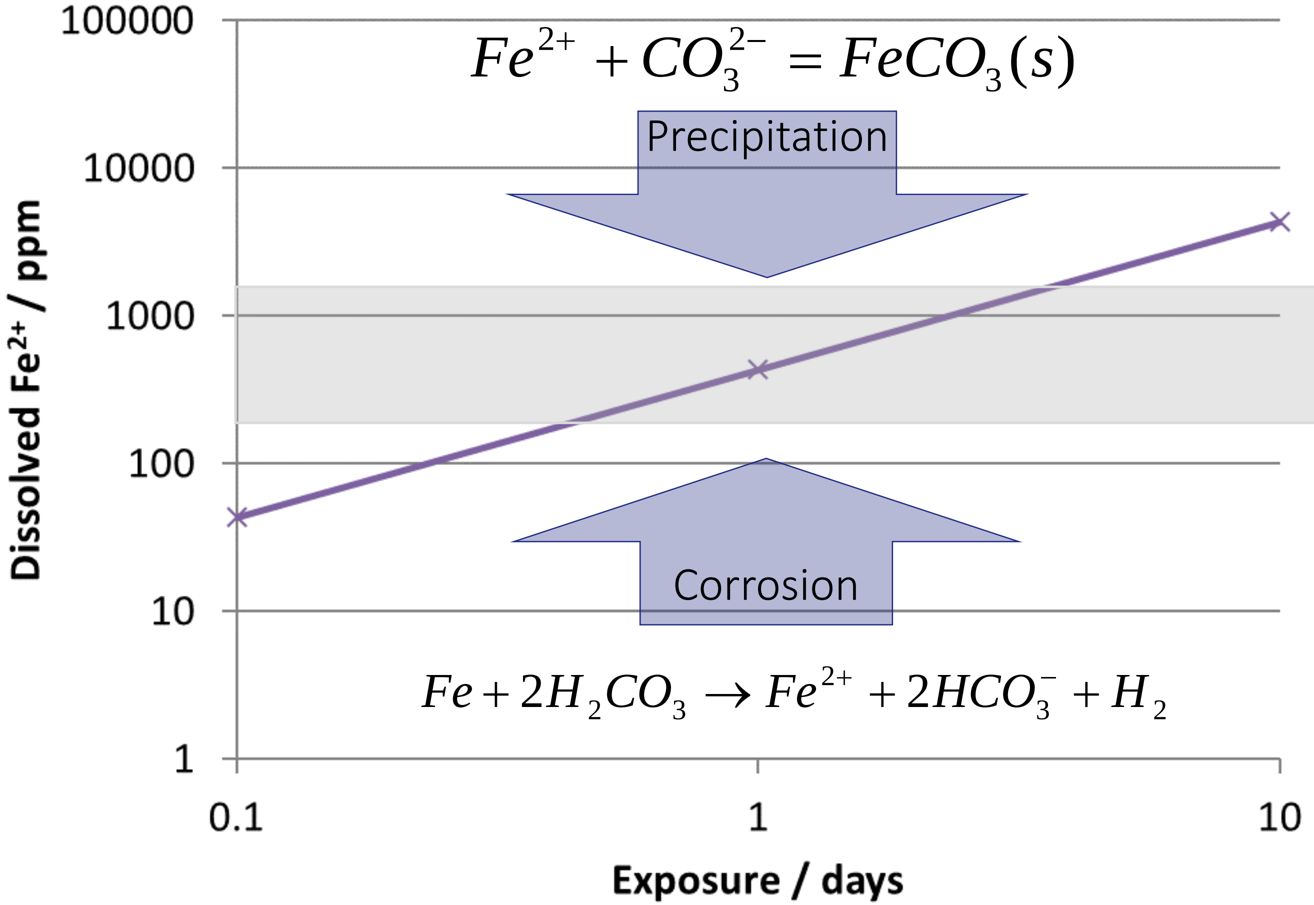
↓ pH, SR_{FeCO3}

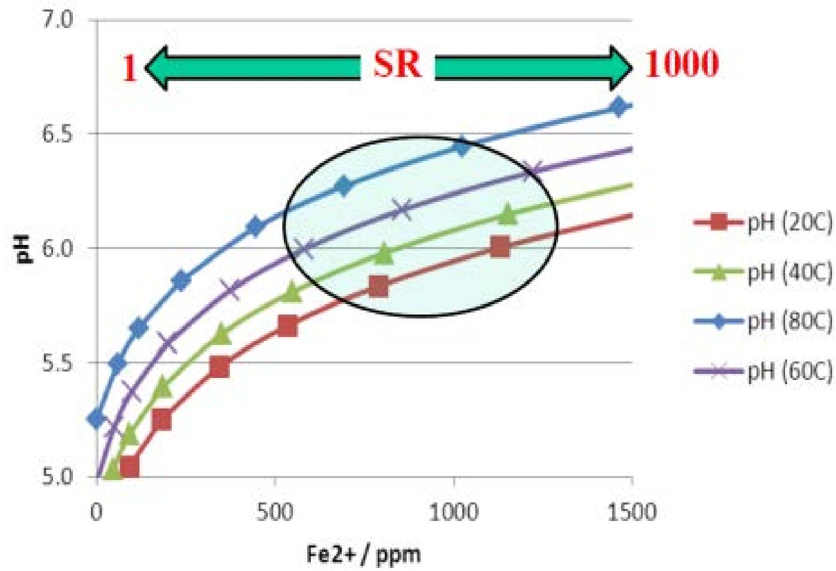
pH vs. Fe^{2+} in annulus

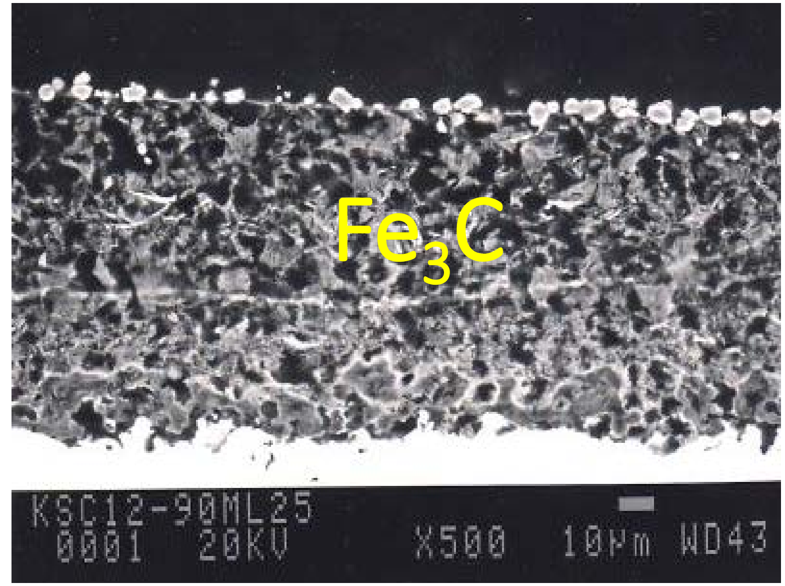
1 bar CO_2

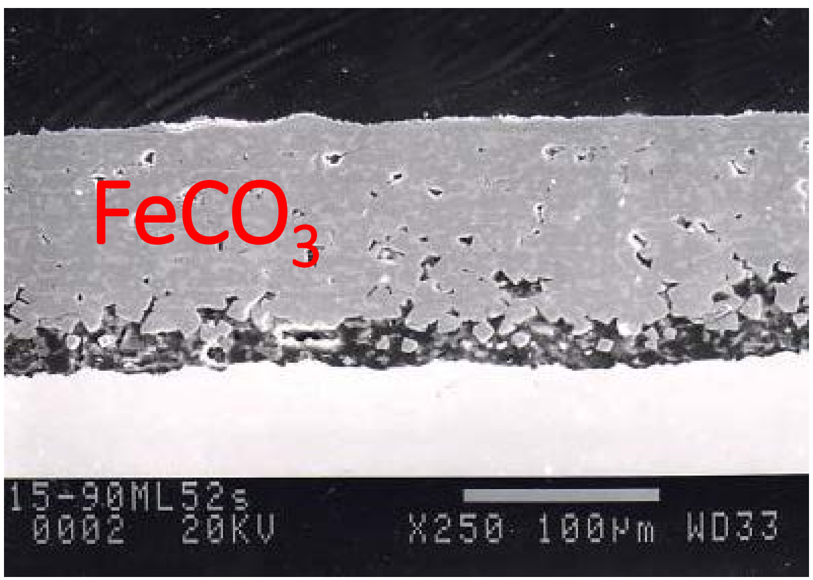


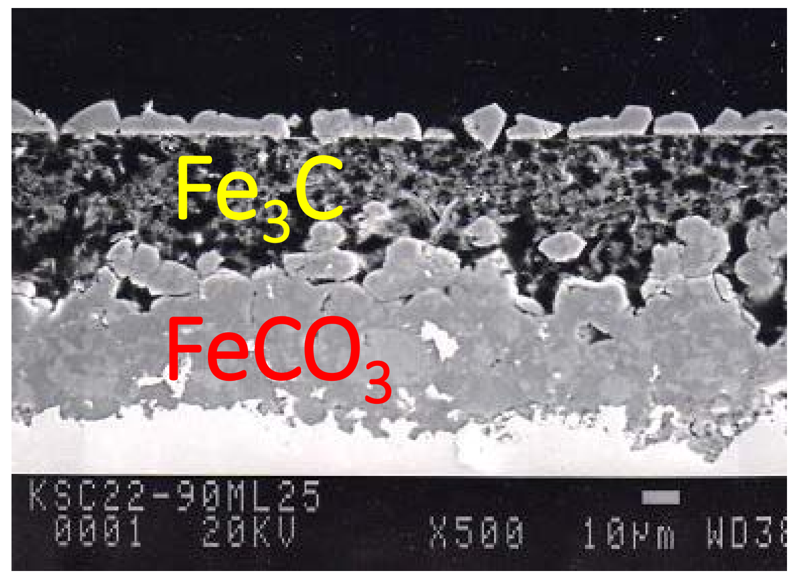
Accumulation of corrosion products V/S 0.1, CR=0.01 mm/y




1
SR
1000
7.0
6.5
6.0
5.5
5.0
pH
0
500
1000
1500
Fe2+ / ppm
pH (20C)
pH (40C)
pH (80C)
pH (60C)


Fe3C
KSC12-90ML25
0001 20KV
X500 10μm WD43


FeCO3
15-90ML52s
0002 20KV
X250 100μm WD33


Fe3C
FeCO3
KSC22-90ML25
0001 20KV
X500 10μm

Will protective corrosion product films always form in confined environment?

- Natural inhibition (soft material, grease...), partial protection
- Non homogeneous distribution of corrosive gases and dissolved corrosion products
- Changes in operational conditions (temp., bore fluid, shut down)
- Consumption of CO_2 and H_2S
- Damaged outer sheath, sea water flooding
- Air/O_2 ingress, damaged outer sheath, venting ports
- Corrosion history - oxygen exposure prior to protective film formation

O_2 destabilizes protective $FeCO_3$ films

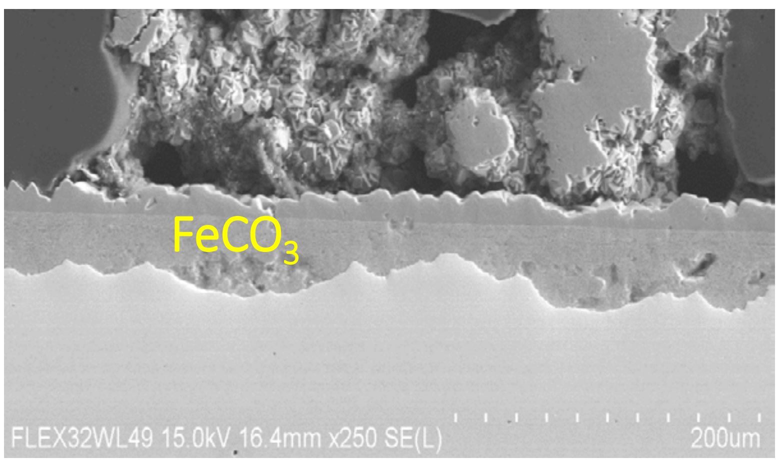
$$4\,Fe^{2+}(aq) + 4\,H^{+}(aq) + O_2(aq) \rightarrow 4\,Fe^{3+}(aq) + 2\,H_2O(l)$$

$$Fe^{3+}(aq) + 3\,OH^{-}(aq) \rightarrow Fe(OH)_3(s)$$

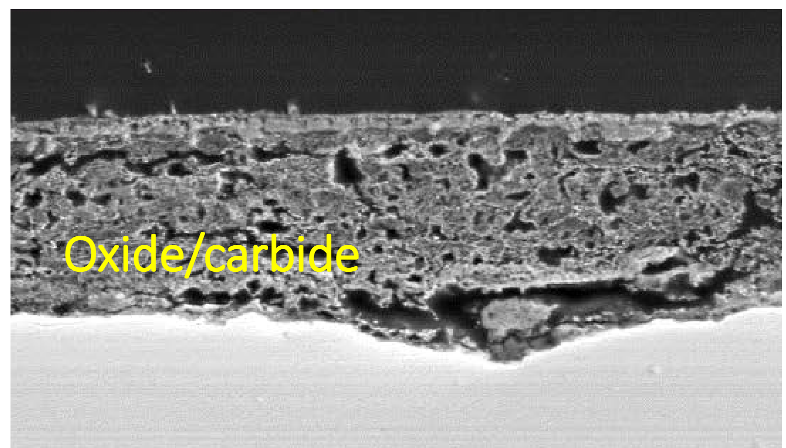
$$FeCO_3 \rightarrow Fe^{2+} + CO_3^{2-}$$

pH

Fe^{2+}



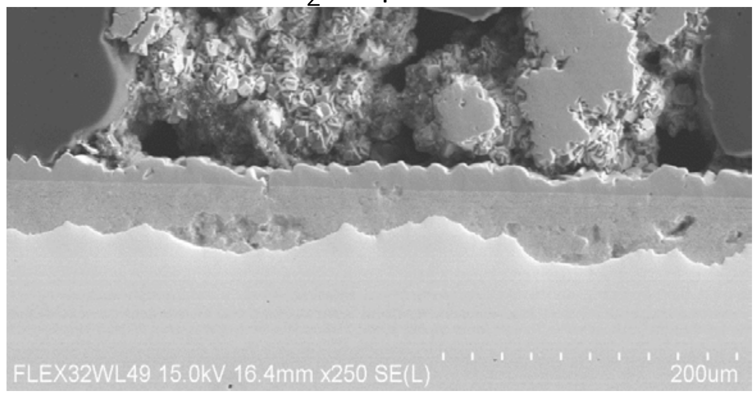
Low corrosion rate



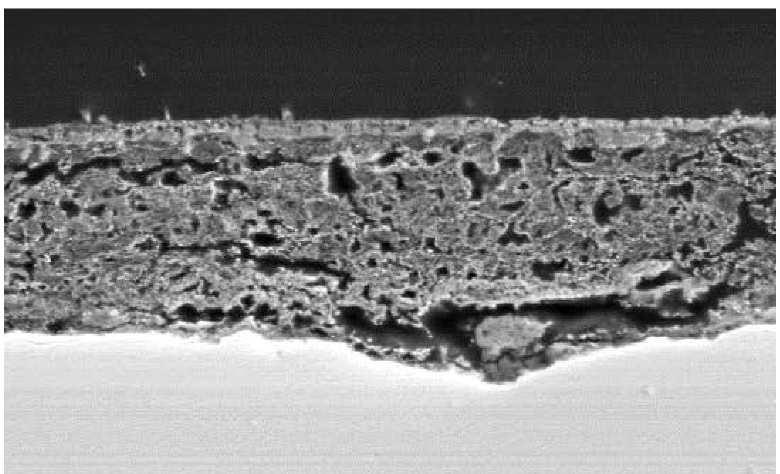
High corrosion rate

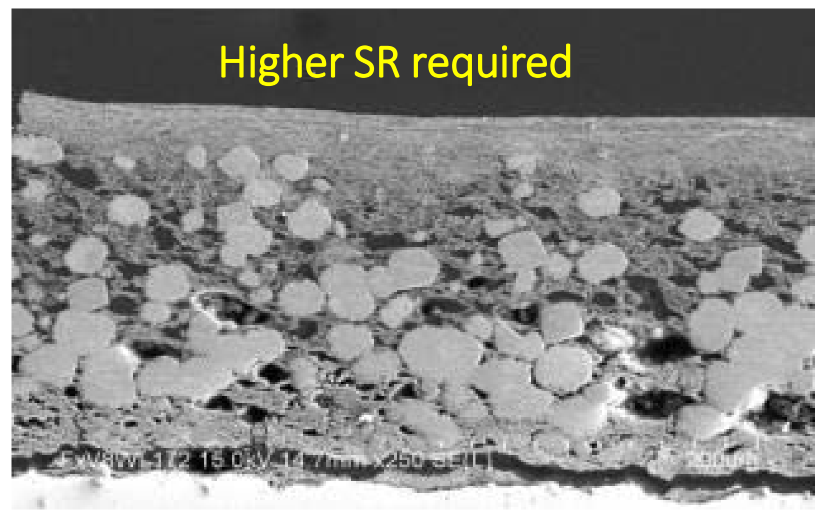
The required SR_{FeCO3} to achieve and maintain protection is «history» dependent

CO_2-exposure

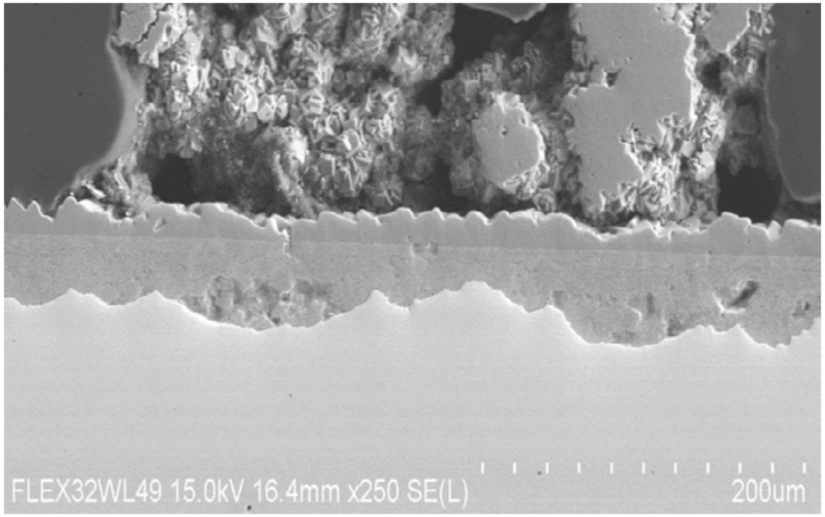


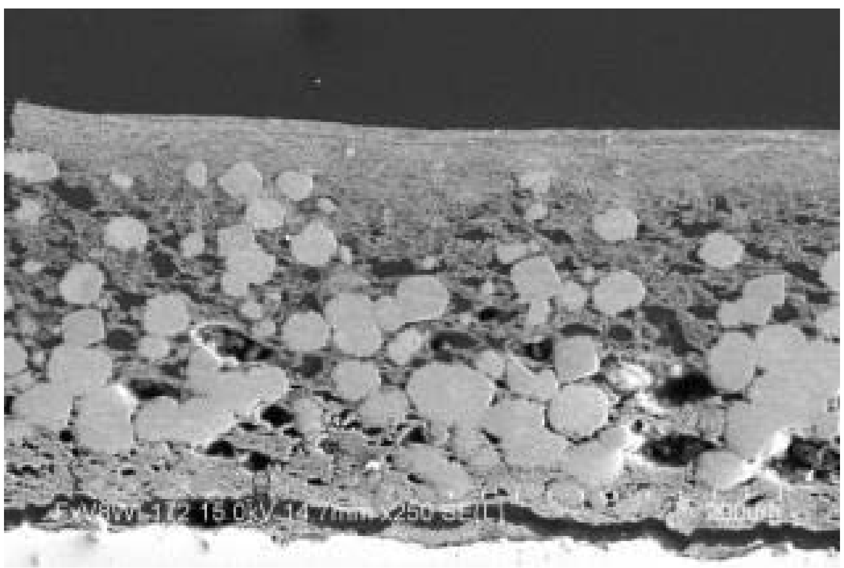
CO_2 exposure + failure/flooding–O_2 exposure + repair-CO_2 exposure



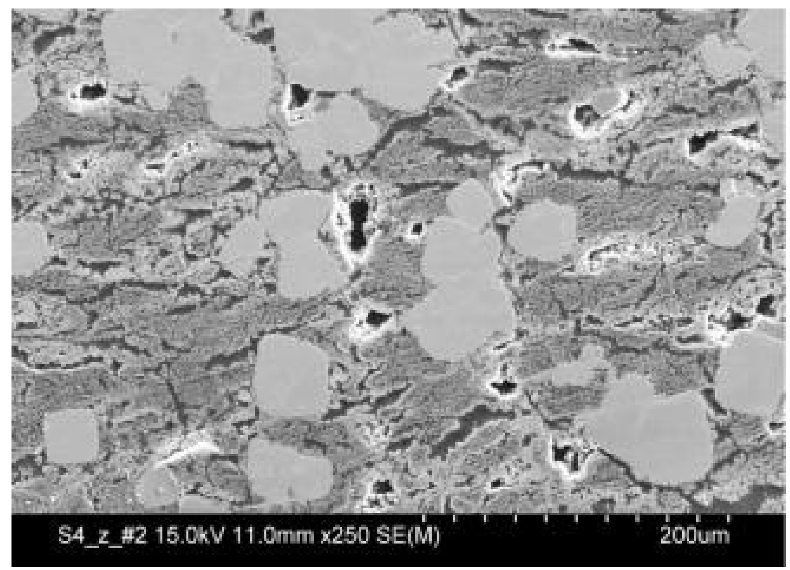


Experiments





Field case

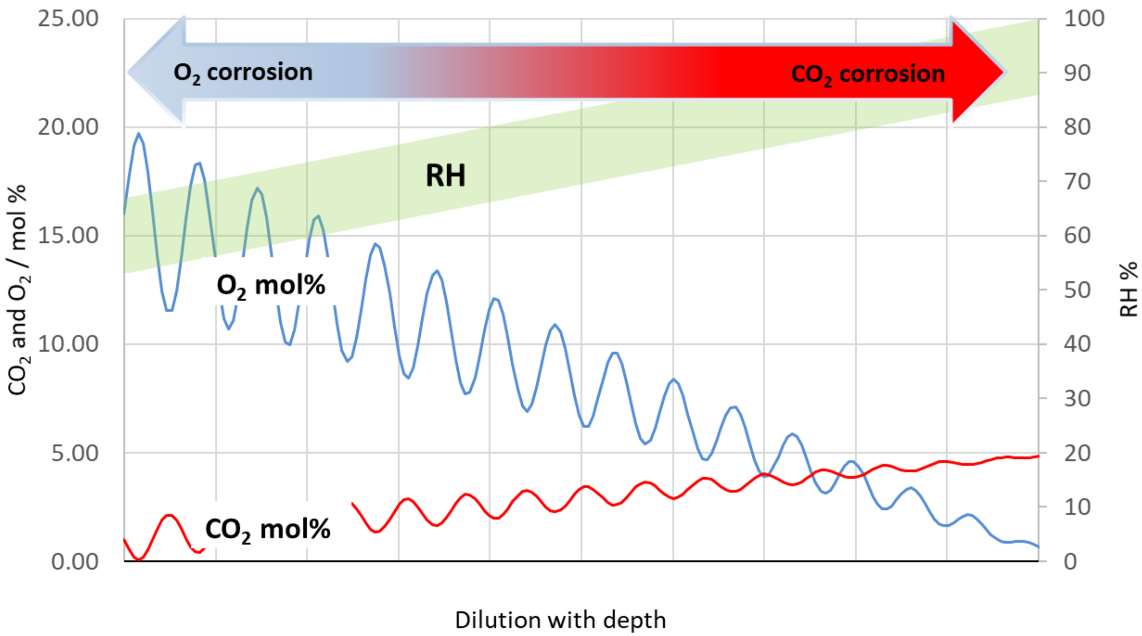


O_2 ingress

Air through vent port and damaged outer sheath

- Atmospheric pressure
- Temperature variation
  - Bore (shut down)
  - External temperature
- Venting rate of diffused gases
- Dead volume of venting tubes

- Tide water
- Waves

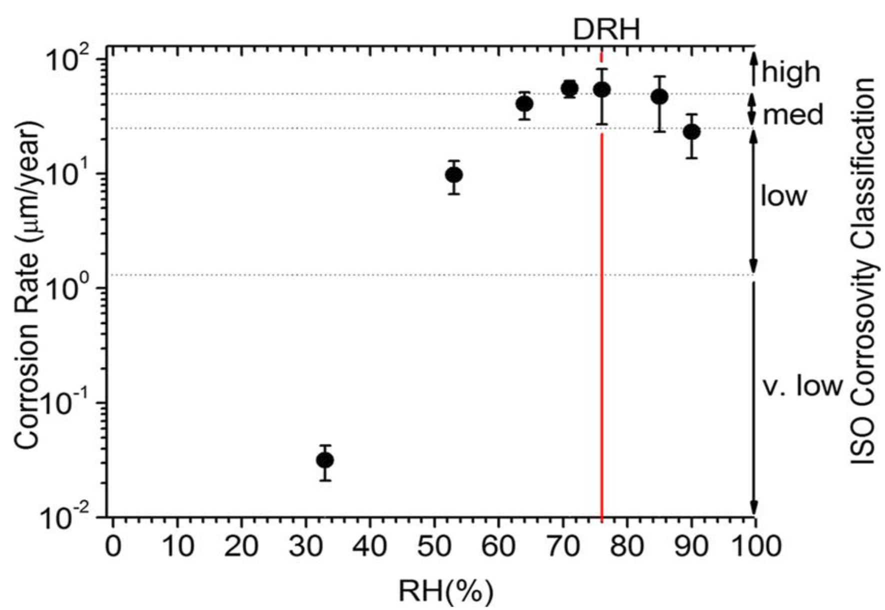


Corrosion RH > 60%

- CO_2 corrosion
- O_2 corrosion and/or
- O_2 reaction with $FeCO_3$

25 C	O_2, mg/l
Sea water	8
Air	260

32 times more O_2 in air



H_2S consumption

- FeS precipitates much faster than $FeCO_3$ for a given supersaturation.
  - Essentially instantaneous reaction: SR_{FeS} about 1 (?)

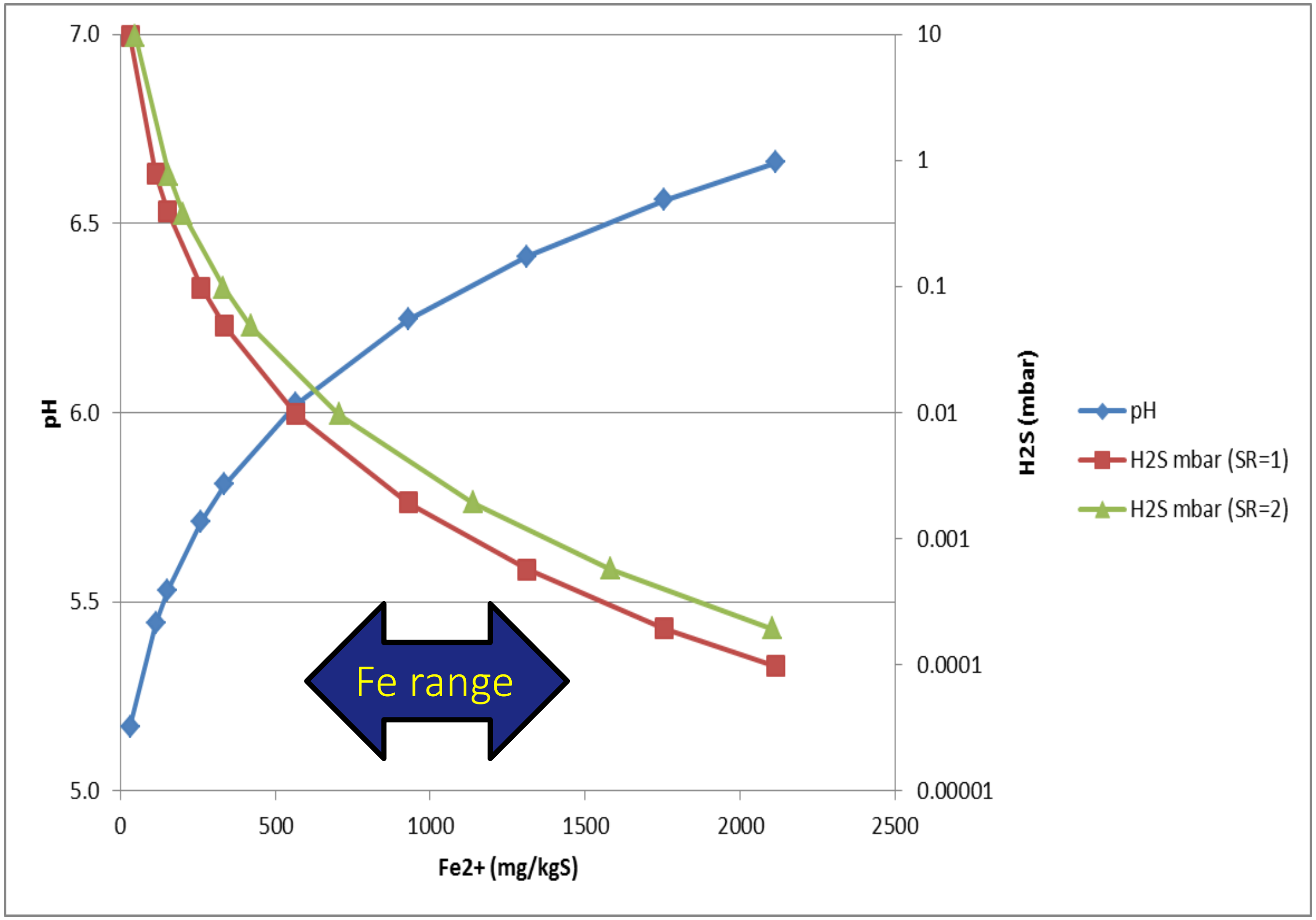
Consequences:

- Precipitation of FeS consumes the added H_2S
- Direct relationship between Fe^{2+} and H_2S concentration

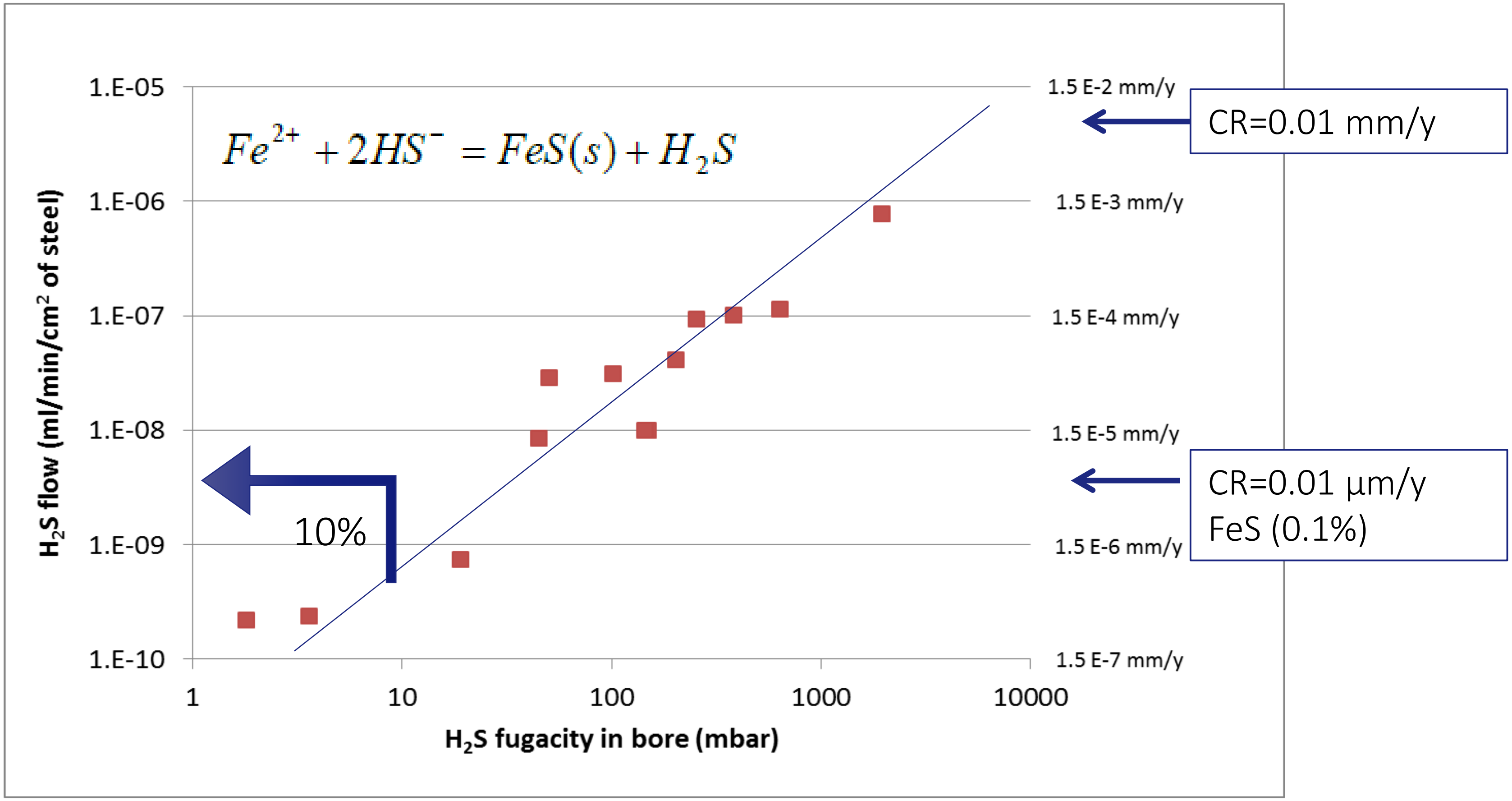
$$Fe^{2+} + 2HS^{-} = FeS(s) + H_2S \qquad SR = \frac{C_{Fe^{2+}} \cdot (C_{HS^-})^2}{K_{sp}}$$

Not possible to have high general corrosion rate and high H_2S content at the same time!

Estimation of pH_2S
25C, 1 bar CO_2, ASTM sea water



Estimated H_2S flow rate from bore to annulus for various projects and full scale experiments, Technip



N. Désamais, C. Taravel-Condat “On the Beneficial Influence of a Very Low Supply of H2S on the Hydrogen Embrittlement Resistance of Carbon Steel Wires in Flexible Pipe Annulus” OTC 19950, Houston, Texas, 4-7 May 2009

H_2S consumption in annulus
Issues to be addressed in more detail

- Will H_2S be consumed in the gas phase, RH% dependent!
- Is the concentration of dissolved corrosion products always high in a wet confined environment (i.e. does the steel corrode?)
  - Effect of grease, inhibition
- Can we assume that SR_{FeS} = 1 (close to 1) under all conditions?
- Benchmarking software for estimating pH_2S: Multiscale, OLI,...

Summary

- Most flexibles perform as expected, i.e. corrosion rates < 0.01 mm/y, no cracking
- The confined environment in the annulus does not always give corrosion product films with sufficient protectiveness
- Air ingress, damaged outer sheath and sea water flooding are challenging
  - Oxygen ingress destabilize protective $FeCO_3$ film and gives higher corrosion rates and pitting
- The annulus chemistry is complex, like a clockwork depending a large number of time dependent parameters

Sea water ingress

O_2 ingress

Pressure

Temp

O_2