Internal Corrosion of Pipelines: Mechanism, Modeling and Management

UNIVERSITY OF CALGARY

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Husky Energy

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St John's
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Thunder Bay
Fredericton
Halifax
NOVA SCOTIA
2,700 km
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The City of Calgary

- The fourth largest city in Canada, Calgary is the hub of oil/gas and pipeline industry in the world.




Banff National Park

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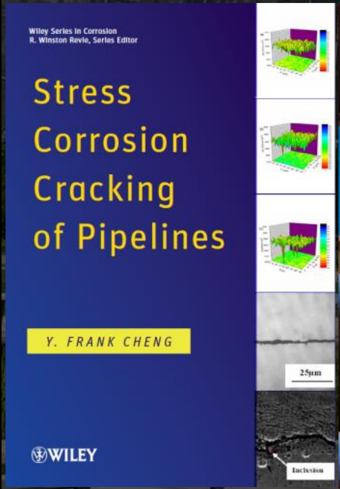
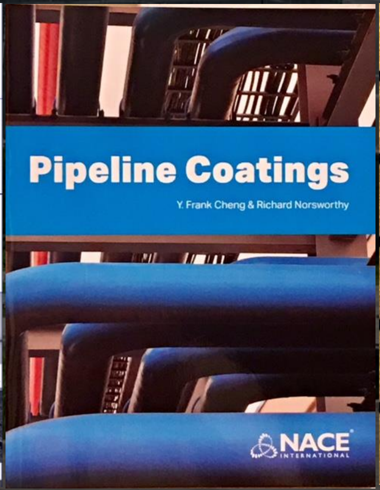
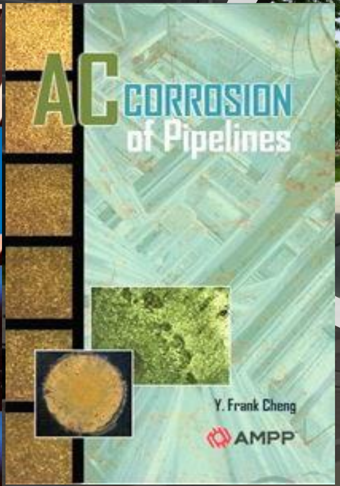
Cheng Laboratory for Research in Pipeline Corrosion, Integrity and New Energy Transmission Technology





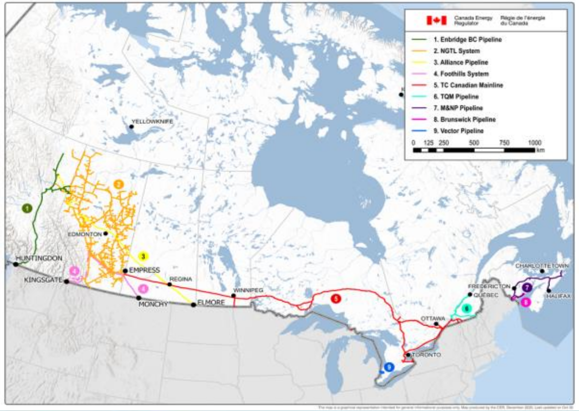


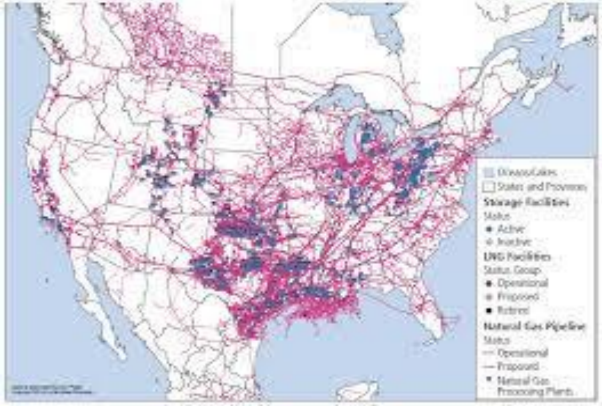
Pipelines for oil/gas transmission

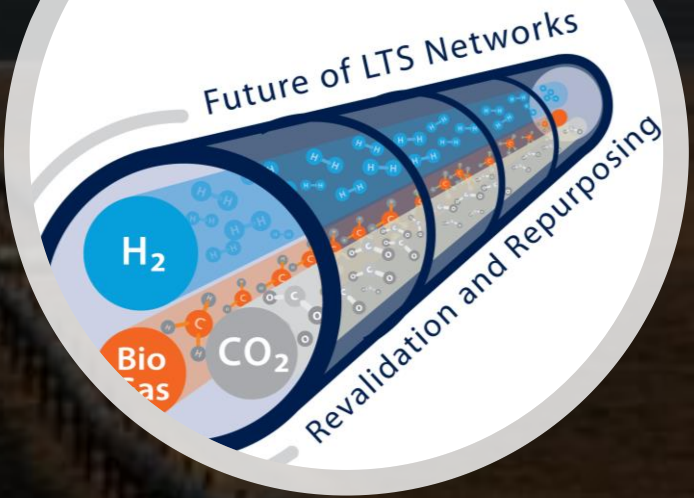
World primary energy supply by source

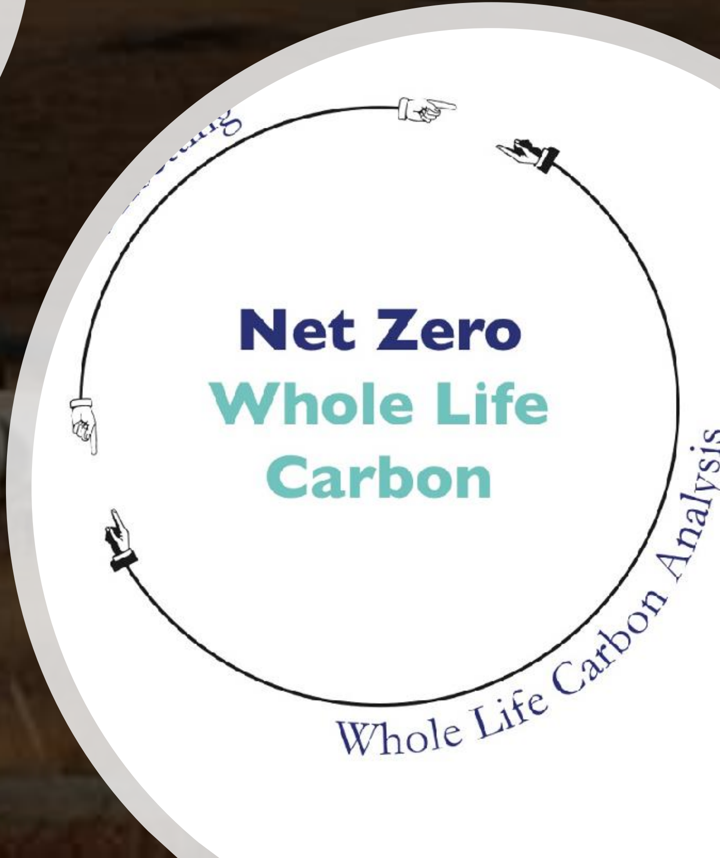
Units: EJ/yr

Source	2019	2030	2040	2050
Wind	5	20	42	81
Solar	4	25	54	85
Hydropower	15	22	25	26
Bioenergy	54	61	67	73
Geothermal	3	5	4	4
Nuclear	29	30	28	27
Natural gas	155	160	157	139
Oil	173	164	133	94
Coal	158	131	95	61
Total	**596**	**617**	**605**	**590**

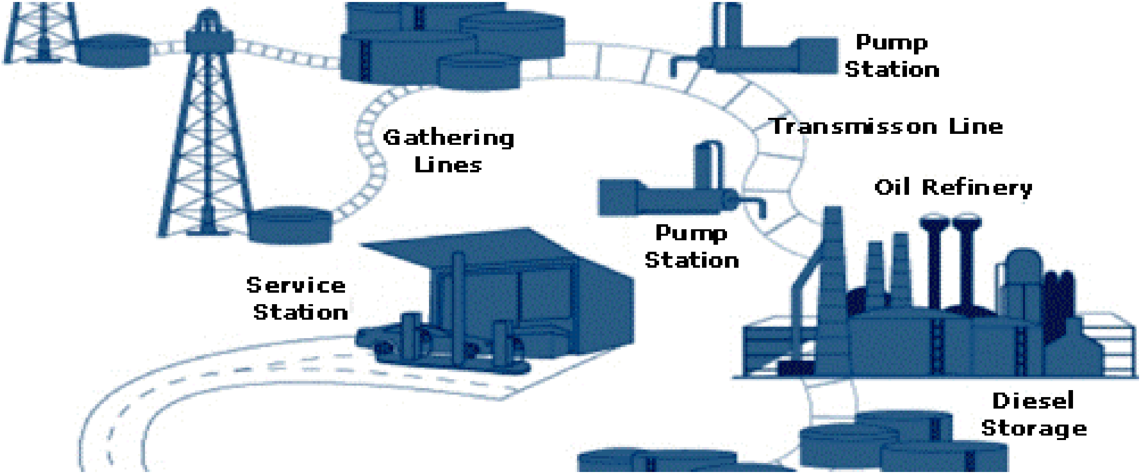








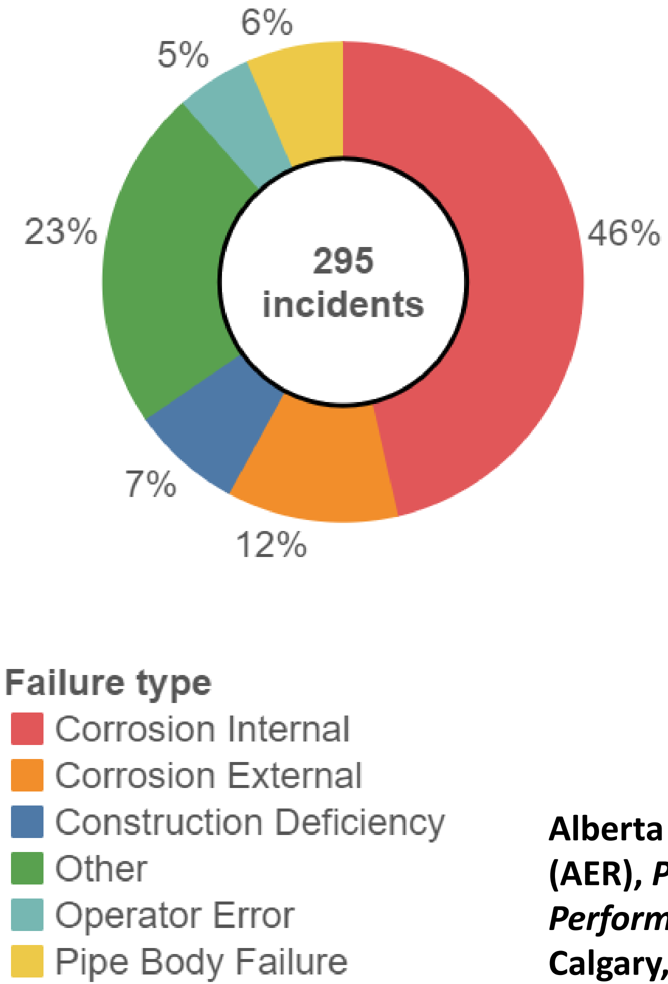
Pipelines for effective and economic transmission of new energies, contributing to the net-zero target



Types of pipelines

Today's talk focuses on upstream gathering pipelines

Internal corrosion is the most important mechanism causing failure of upstream pipelines



Alberta Energy Regulator (AER), *Pipeline Performance in 2019*, Calgary, Canada, Jul. 2020.

Internal corrosion of pipelines is a complex phenomenon.

Multiple factors affecting the corrosion processes

- **Fluid chemistry**
  - CO_2/H_2S partial pressure, solution pH, salts, organic acids (acetic acid), oil phase, solid particles, etc.
- **Operating condition**
  - Temperature, pressure, flow velocity, fluid hydrodynamics, etc.
- **Pipe geometry**
  - Pipe size, inclination, elbow/bent, etc.

Multiple reactions occurring at the same time

Chemical reactions:

$CO_{2(g)} = CO_{2(aq)}$	$K_1 = \frac{a_{CO_2}}{f_{CO_2}} = \frac{C_{CO_2}}{\varphi \cdot p_{CO_2}}$	(1)
$CO_{2(aq)} + H_2O = H_2CO_3$	$K_2 = \frac{a_{H_2CO_3}}{a_{CO_2}} = \frac{C_{H_2CO_3}}{C_{CO_2}}$	(2)
$H_2CO_3 = H^+ + HCO_3^-$	$K_3 = \frac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}} = \frac{\gamma_{\pm 3}^2 \cdot C_{HCO_3^-} \cdot C_{H^+}}{C_{H_2CO_3}}$	(3)
$HCO_3^- = H^+ + CO_3^{2-}$	$K_4 = \frac{a_{CO_3^{2-}} \cdot a_{H^+}}{a_{HCO_3^-}} = \frac{\gamma_{\pm 4} \cdot C_{CO_3^{2-}} \cdot C_{H^+}}{C_{HCO_3^-}}$	(4)
$H_2O = H^+ + OH^-$	$K_5 = a_{H^+} \cdot a_{OH^-} = \gamma_{\pm 5}^2 \cdot C_{H^+} \cdot C_{OH^-}$	(5)
$HAc = H^+ + Ac^-$	$K_6 = \frac{a_{Ac^-} \cdot a_{H^+}}{a_{HAc}} = \frac{\gamma_{\pm 6}^2 \cdot C_{Ac^-} \cdot C_{H^+}}{C_{HAc}}$	

Electrochemical cathodic reactions:

$2H^+ + 2e = H_2$	$E_6 = E_6^0 + \frac{RT}{nF} \ln C_{H^+}^2$
$H_2CO_3 + e = HCO_3^- + H$	$E_7 = E_7^0 + \frac{RT}{nF} \ln \frac{C_{H_2CO_3}}{C_{HCO_3^-}}$
$HCO_3^- + e = CO_3^{2-} + H$	$E_8 = E_8^0 + \frac{RT}{nF} \ln \frac{C_{HCO_3^-}}{C_{CO_3^{2-}}}$
$H_2O + e = OH^- + H$	$E_9 = E_9^0 + \frac{RT}{nF} \ln \frac{1}{C_{OH^-}}$
$HAc + e = Ac^- + H$	$E_{10} = E_{10}^0 + \frac{RT}{nF} \ln \frac{C_{HAc}}{C_{Ac^-}}$

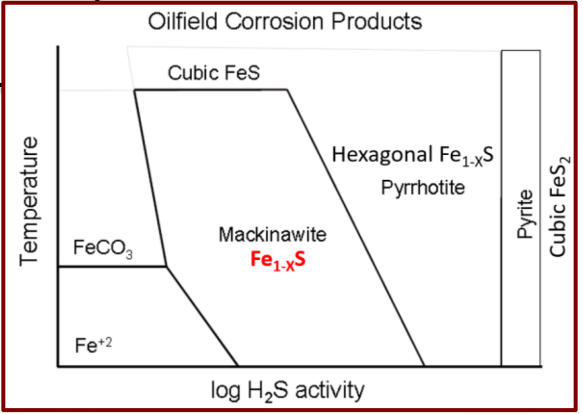
Electrochemical anodic reactions:

$Fe = Fe^{2+} + 2e$	$E_1 = E_1^0 + \frac{RT}{nF} \ln C_{Fe^{2+}}$
$Fe + HCO_3^- = FeCO_3 + H^+ + 2e$	$E_2 = E_2^0 + \frac{RT}{nF} \ln \frac{C_{H^+}^2}{C_{H_2CO_3}}$
$Fe + HCO_3^- = FeCO_3 + H^+ + 2e$	$E_3 = E_3^0 + \frac{RT}{nF} \ln \frac{C_{H^+}}{C_{HCO_3^-}}$
$Fe + CO_3^{2-} = FeCO_3 + 2e$	$E_4 = E_4^0 + \frac{RT}{nF} \ln \frac{1}{C_{CO_3^{2-}}}$
$Fe + H_2O = Fe(OH)_2 + 2H^+ + 2e$	$E_5 = E_5^0 + \frac{RT}{nF} \ln C_{H^+}^2$

Film formation:

$$\underset{1-\theta_1-\theta_2}{Fe} + HCO_3^- \xrightarrow{k_4} FeCO_3 + H^+ + 2e$$

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



Thermodynamics of pipeline internal corrosion

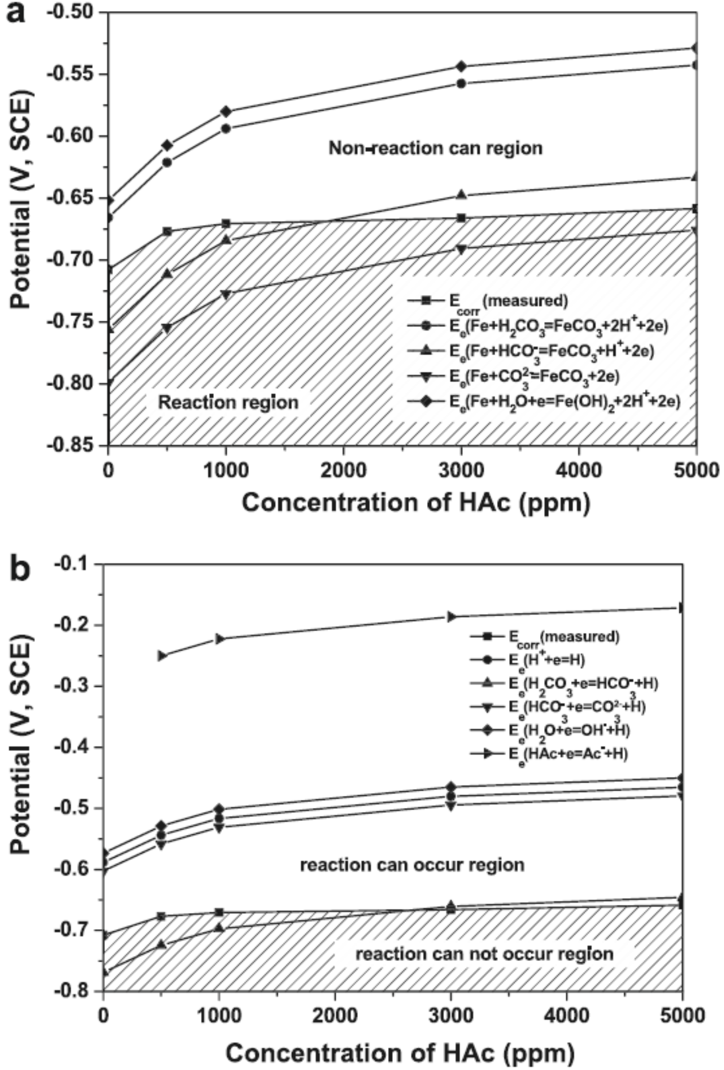
- Evaluate corrosion likelihood under given conditions and determine the dominant partial reactions.
- For chemical reactions, derive the **reaction equilibrium constants.**
- For electrochemical reactions,
  - calculate **standard electrode potentials** by Gibbs free energy.
  - determine **partial reaction potentials** by Nernst equation.

Constant
$K_1 = \frac{14.5}{1.00258} \times 10^{-(2.27+5.65\times10^{-3}\cdot T_f-8.06\times10^{-6}T_f^2+0.075I)}$
$K_2 = 0.00258$
$K_3 = 387.6 \times 10^{-(6.41-1.594\times10^{-3}T_f+8.52\times10^{-6}T_f^2-3.07\times10^{-5}P-0.4772I^{1/2}+0.1180I)}$
$K_4 = 10^{-(10.61-4.97\times10^{-3}T_f+1.331\times10^{-5}T_f^2-2.624\times10^{-5}P-1.166I^{1/2}+0.3466I)}$
$K_5 = 10^{-(29.3868-0.0737549T_K+7.47881\times10^{-5}T_K^2)}$
$K_6 = 10^{(18.67257-0.0076792T_K-6.50923\log T_K-\frac{1500.65}{T_K})}$

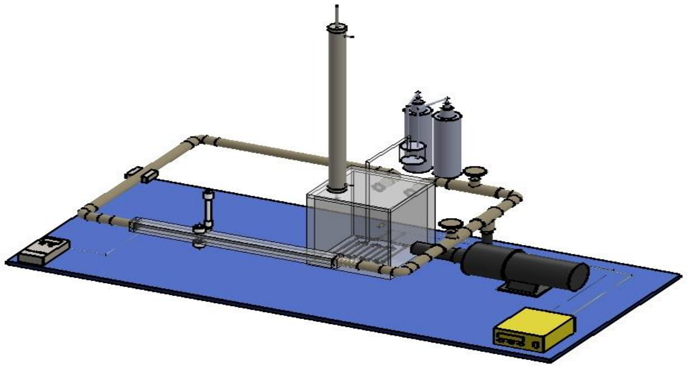
Species	ΔG_f^0 ($kJ \cdot mol^{-1}$)	Species	ΔG_f^0 ($kJ \cdot mol^{-1}$)
H^+	0	CO_3^{2-}	−527.9
H_2O	−273.14	Fe	0
H_2CO_3	−623.16	$FeCO_3$	−666.7
HCO_3^-	−586.85	$Fe(OH)_2$	−490.0
HAc	−390.2	Ac^-	−369.3

HAc concentration (ppm)	0	500
E_2	−0.6657	−0.6212
E_3	−0.7561	−0.7117
E_4	−0.7989	−0.7544
E_5	−0.6518	−0.6074
E_6	−0.5884	−0.5440
E_7	−0.7690	−0.7245
E_8	−0.6027	−0.5583
E_9	−0.5733	−0.5289
E_{10}	/	−0.2498

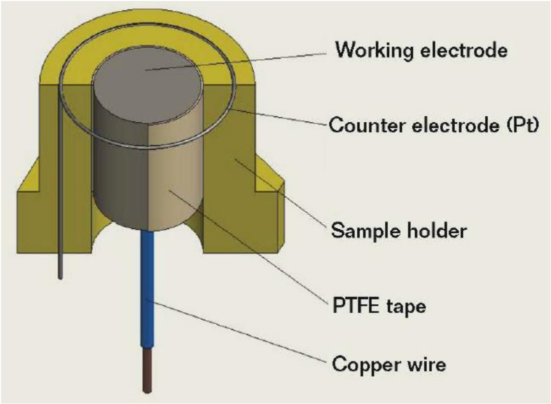
CO_2 corrosion thermodynamic model

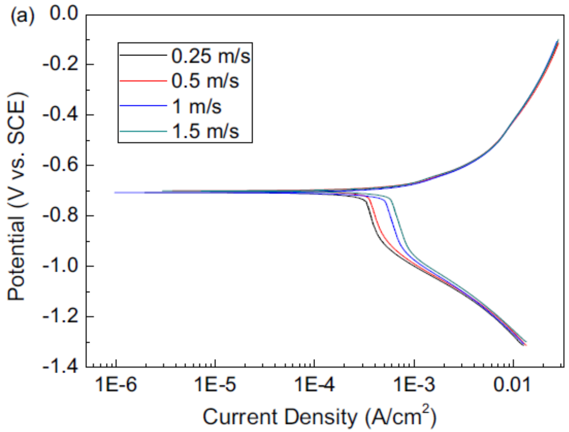


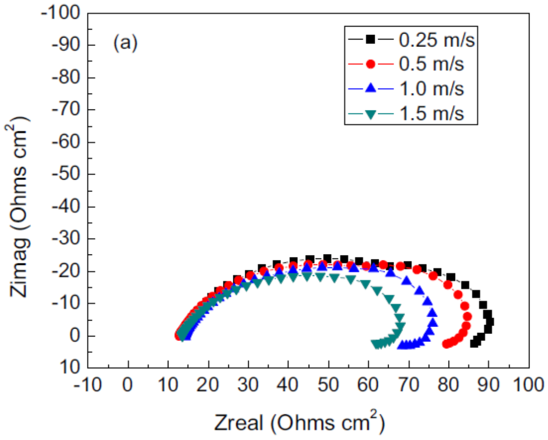
Critical role of fluid hydrodynamics (pipe flow)

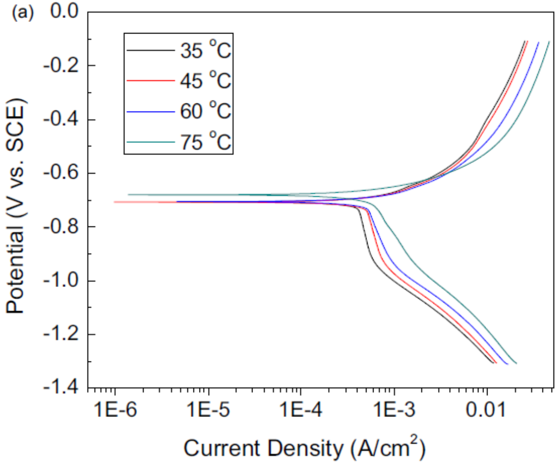


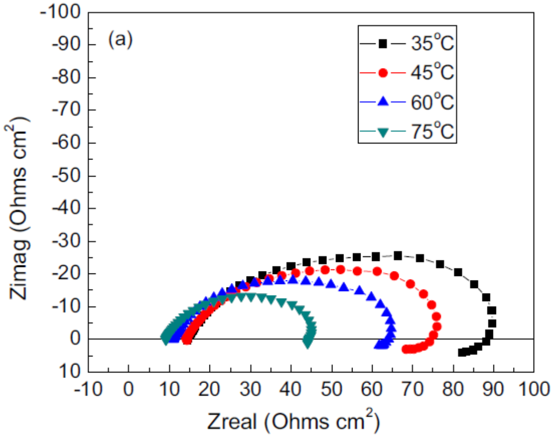
For corrosion of a straight pipe





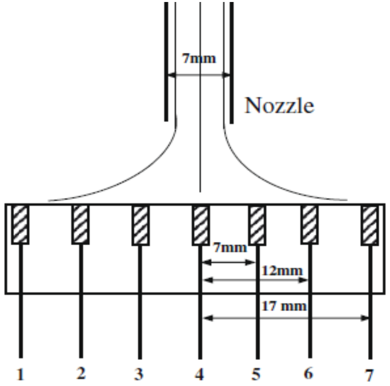


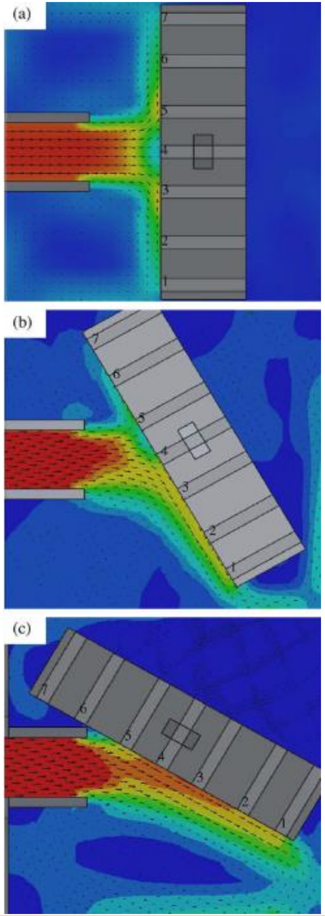


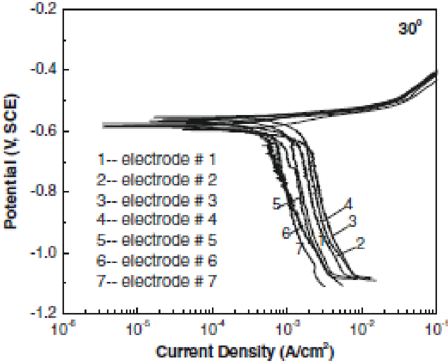


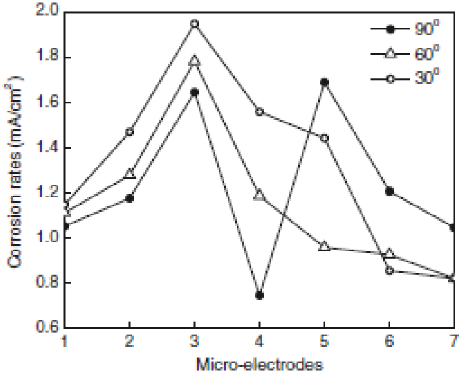
Critical role of fluid hydrodynamics (impingement)

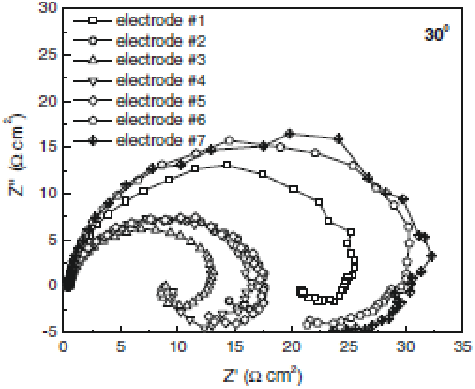
For corrosion at elbow

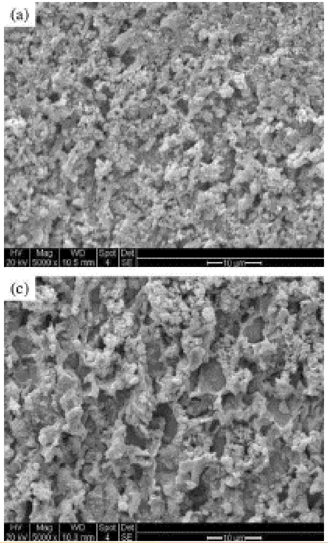




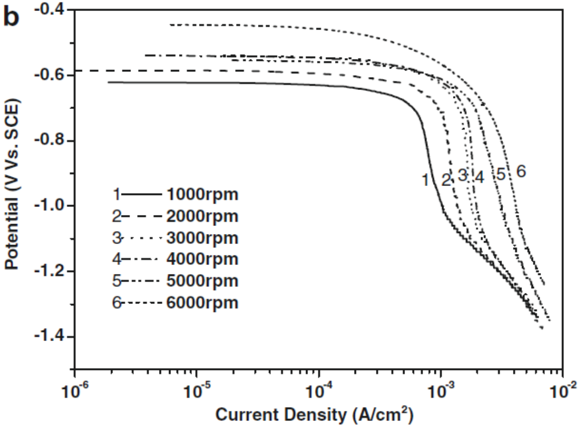




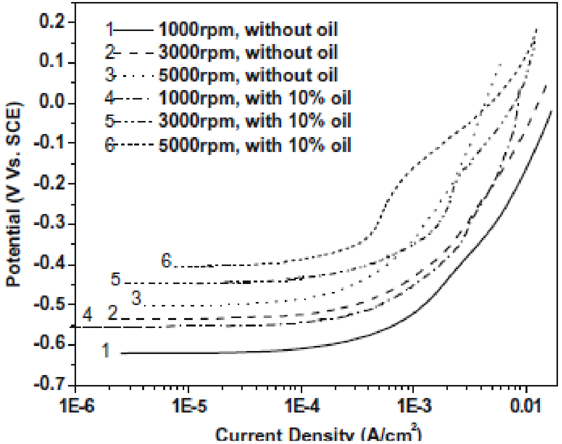


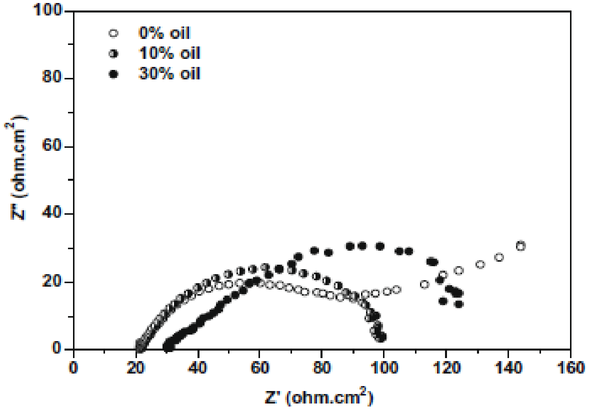


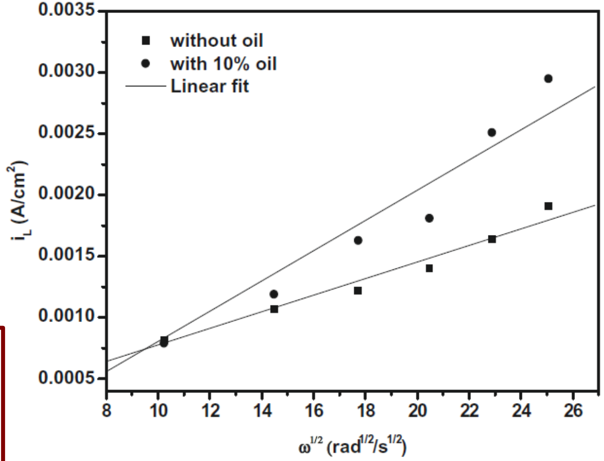
Inhibitive effect of oil phase

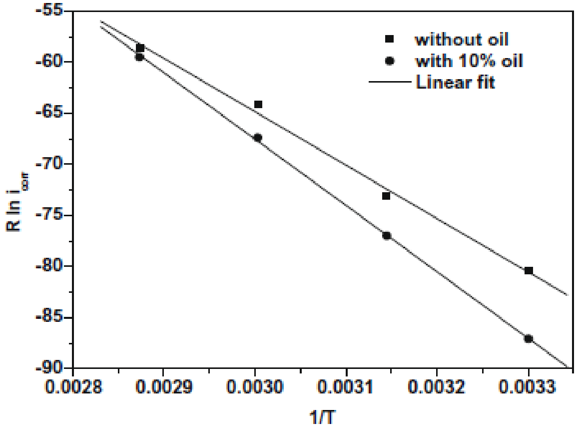


$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{nFAkC_O} + \frac{1}{nFAk_mC_O}$$
$$= \frac{1}{nFAC_O k_O \exp(-\alpha nF\eta/RT)} + \frac{1}{0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O}$$







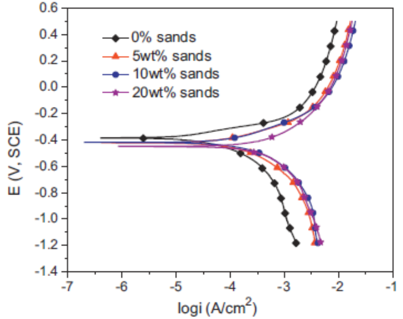


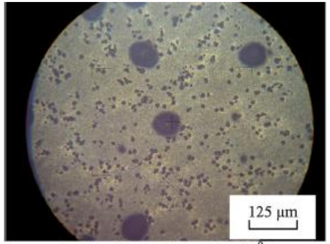
Erosive effect of solid sands

$T = C + E$

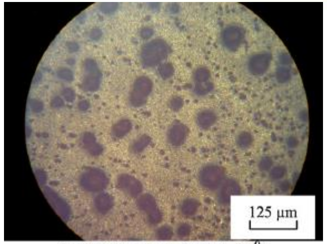
$T = C_0 + E_0 + C_e + E_c$

$E/C \le 0.1$	corrosion dominant
$0.1 < E/C \le 1$	corrosion–erosion
$1 < E/C \le 10$	erosion–corrosion
$E/C > 10$	erosion dominant

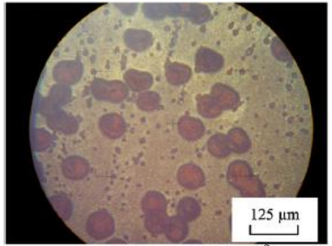




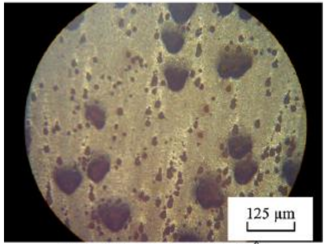
(a: 5wt% sands, 3 m/s, 90⁰)



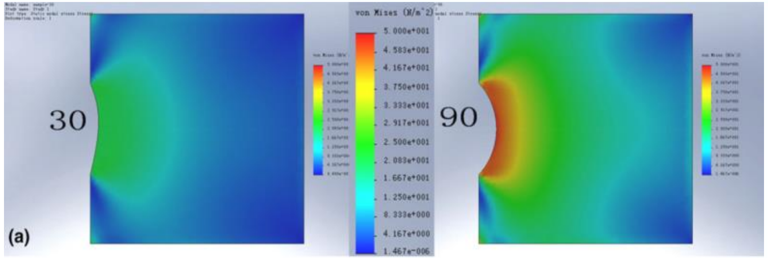
(c: 5wt% sands, 5 m/s, 90⁰)

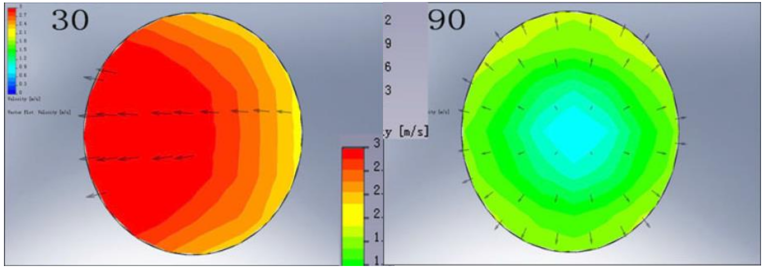


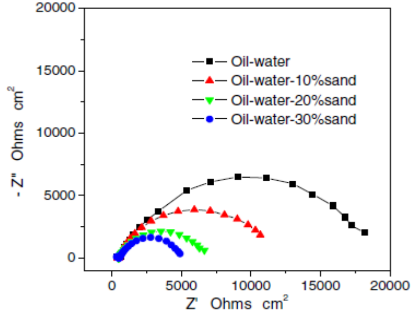
(b: 20wt% sands, 3 m/s, 90⁰)

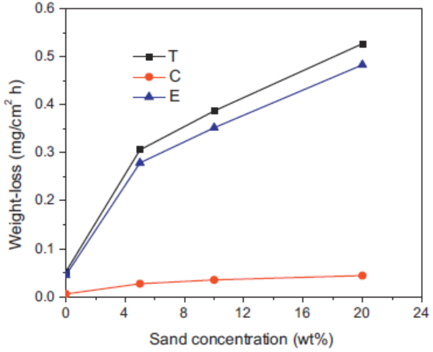


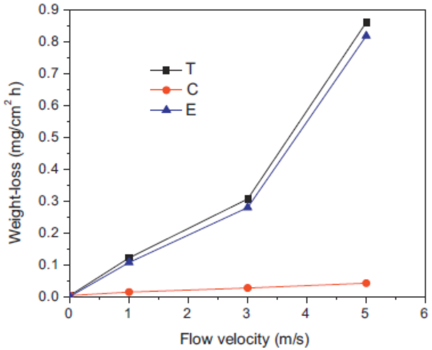
(d: 5wt% sands, 3 m/s, 30⁰)

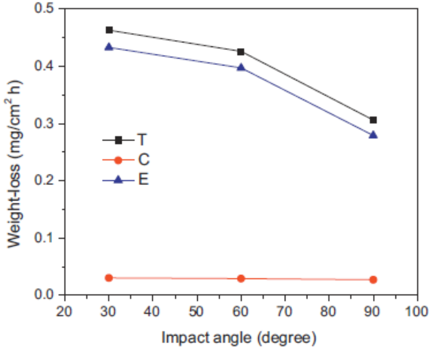






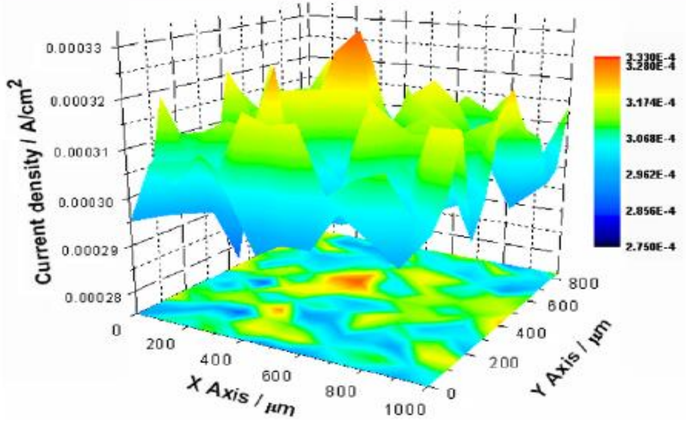


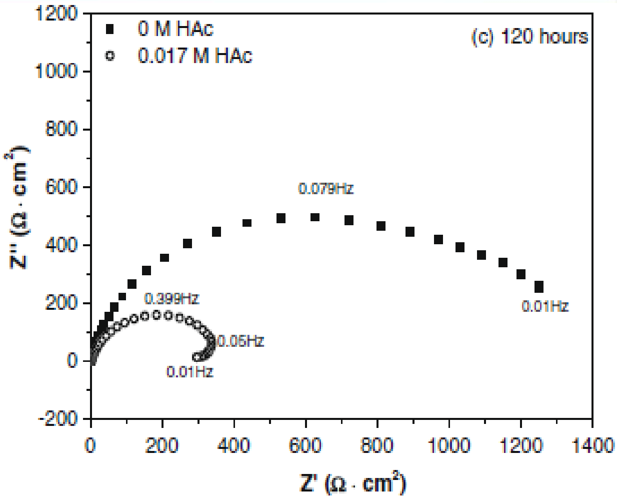


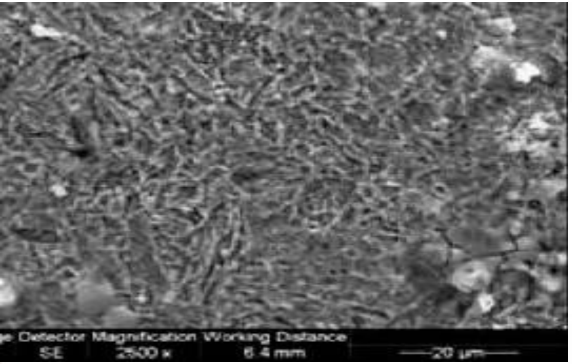


Effect of organic acid

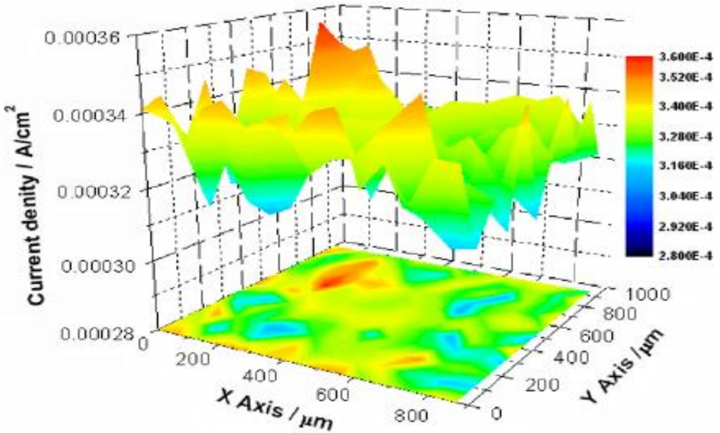
No acetic acid

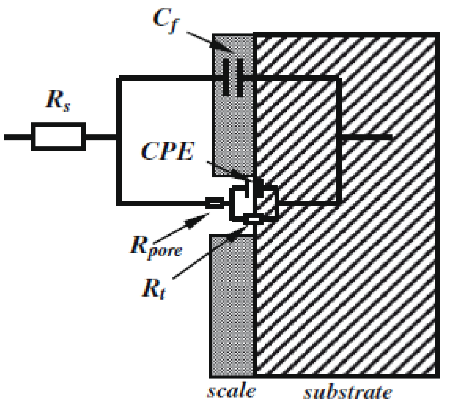




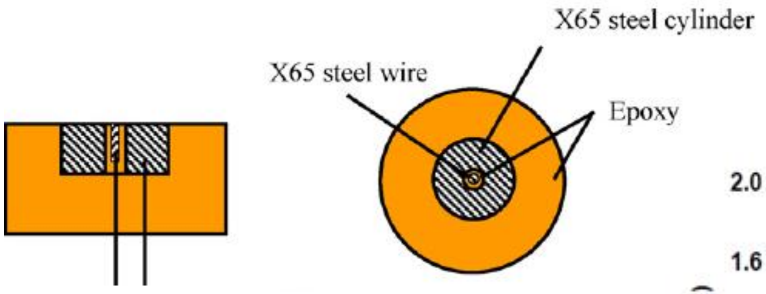


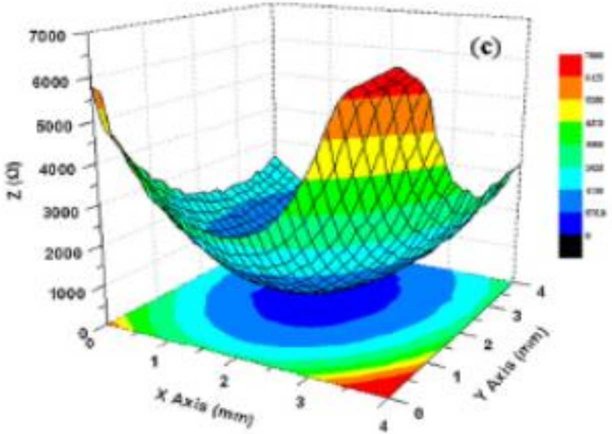
0.02 M acetic acid



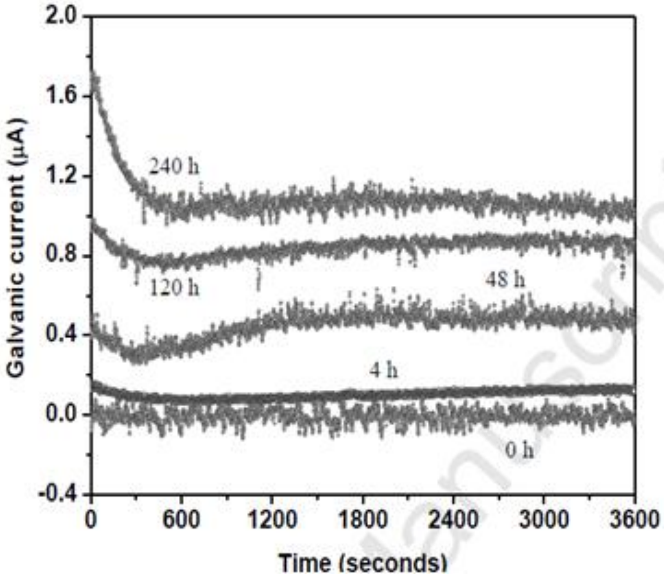


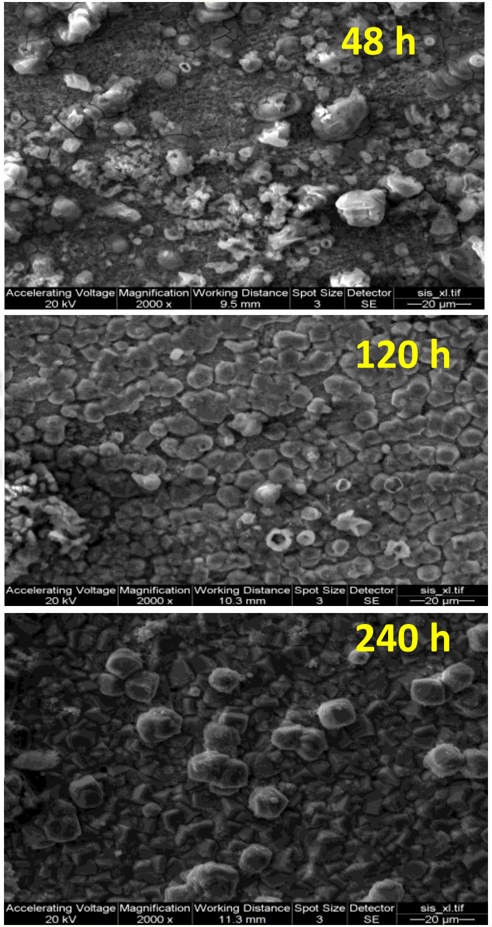
Pitting corrosion under $FeCO_3$ scale





In oilfeild formation water purged with 99.95% CO_2 at 60^0C





The galvanic coupling effect between the scale-covered steel and bare steel at pores results in pitting corrosion.

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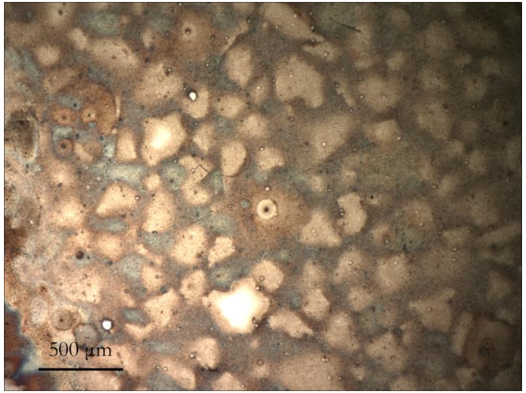
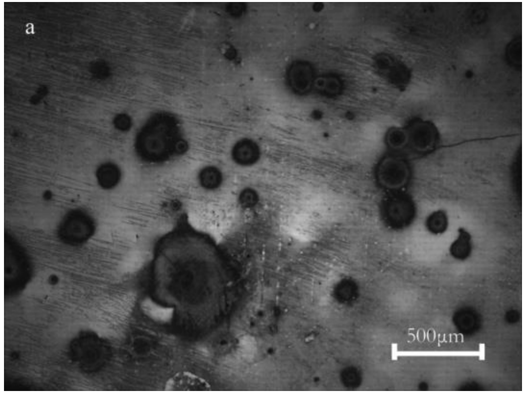
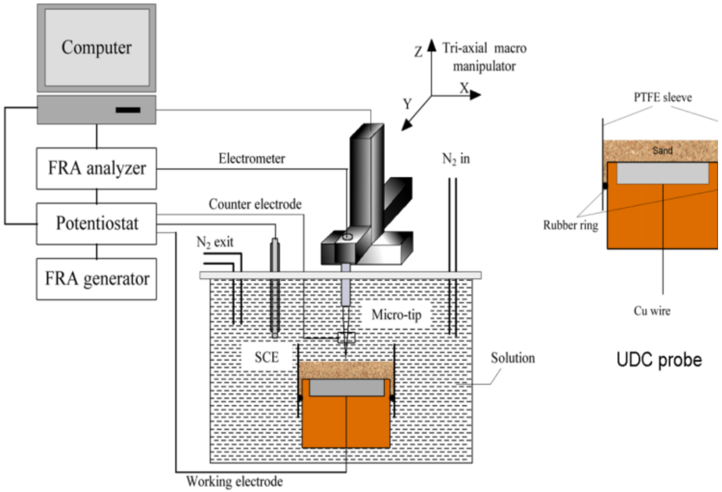
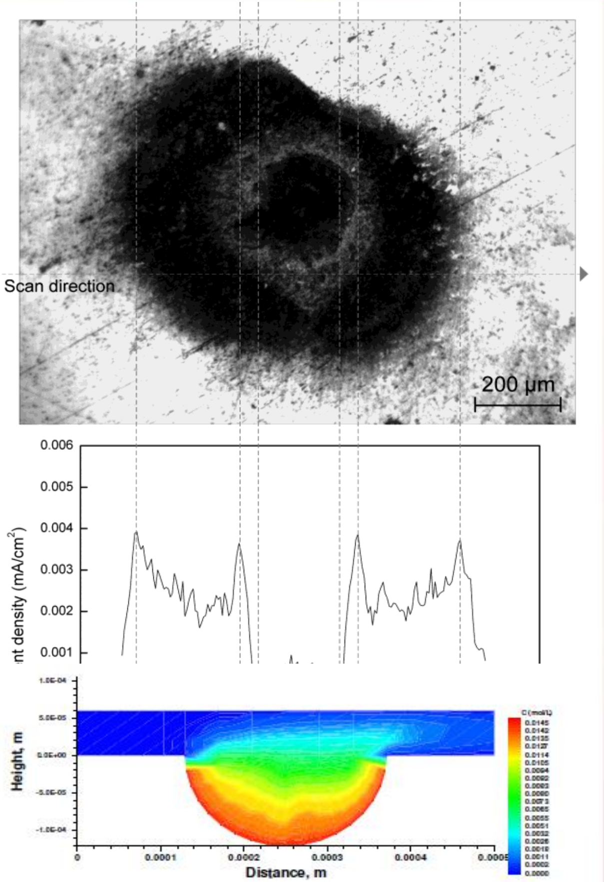
Internal pitting corrosion under sand bed





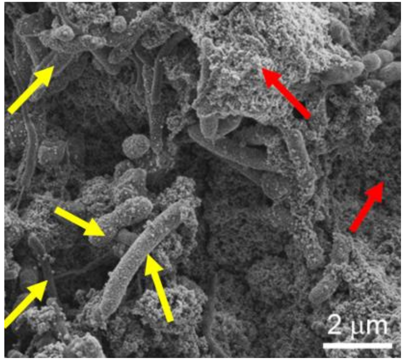


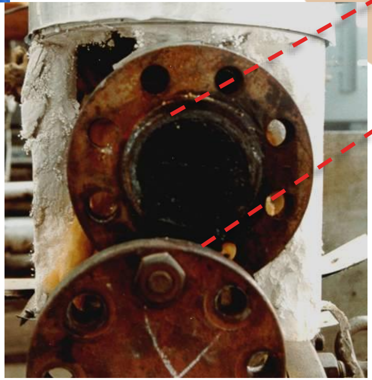


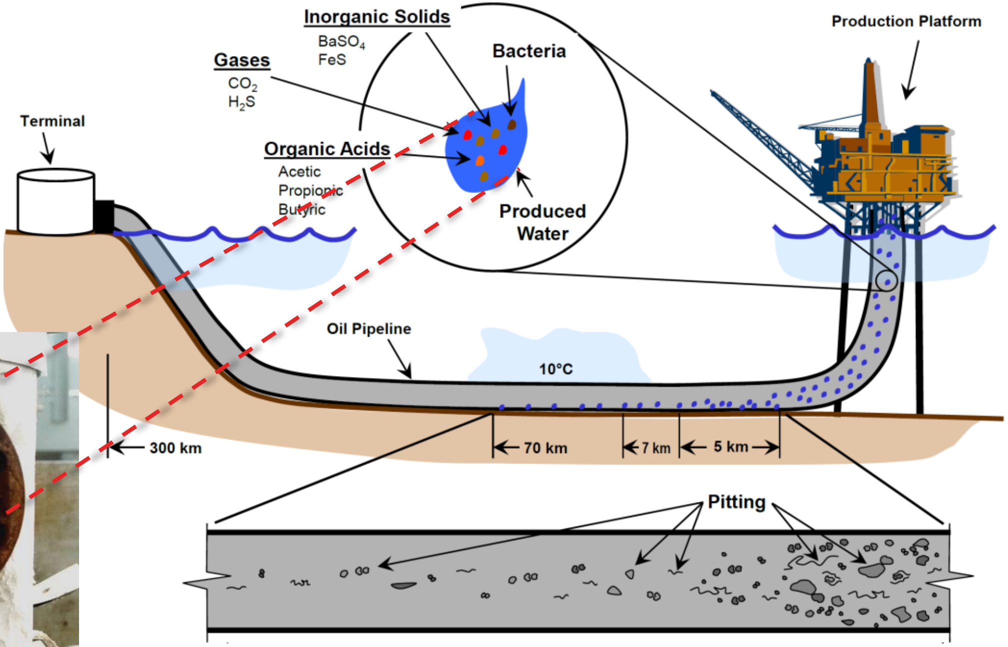
Pitting corrosion under sand bed and its modeling for prediction of pit growth

Internal microbial corrosion of pipelines

- In oil/gas industry, microbial corrosion has caused ~ 40% of all internal corrosion events in pipelines.





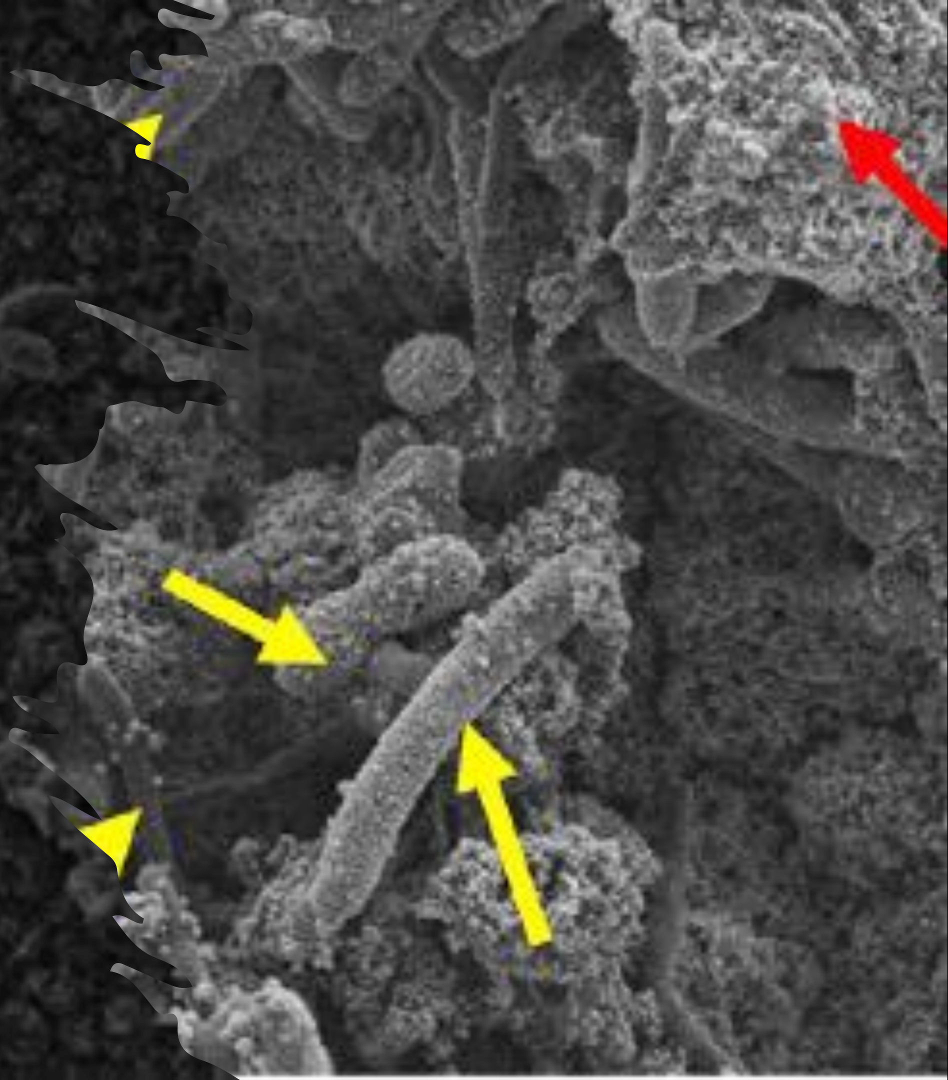


Internal microbial corrosion under deposit

- Unique corrosive environments: **<u>Deposit of a mixture of petroleum sludge, sands, water, microorganism, corrosion products, etc.</u>**

- A dual role of the deposit in limited supply of nutrients to bacteria and reduced disturbance to the biological environment

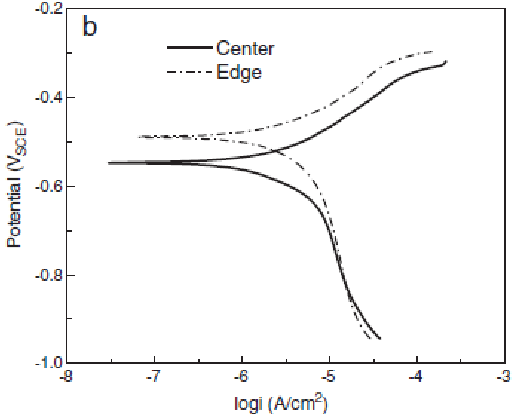
- Essential factors: Fluid flow, and porosity of the deposit

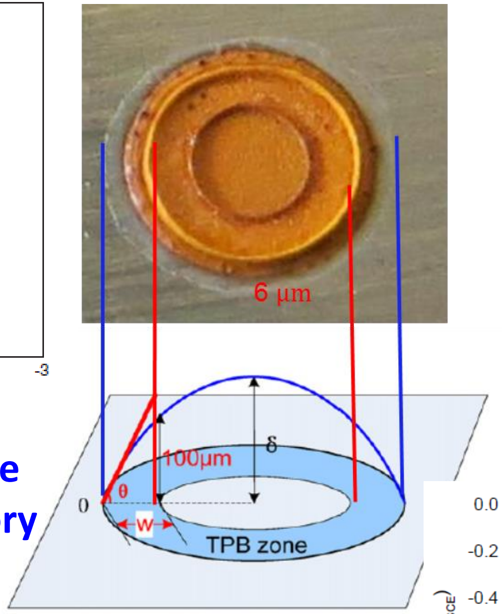


Gas pipelines: Internal microbial corrosion

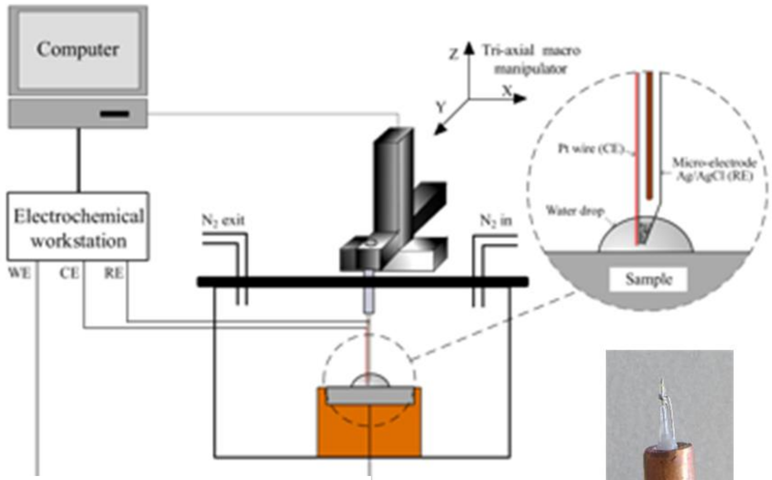
- Unique corrosive environments:
  - **A thin layer of electrolyte (or condensate water)**
    - Formation of a complete biofilm usually hard
    - Deposit of corrosion products
    - Essential factor: **Electrolyte layer thickness**
    - It will affect bacterial adhesion, corrosion reaction mechanisms, corrosion product film, corrosion rate
    - Difficulty in testing: Reproduce the thin electrolyte layer containing bacteria and the formed biofilm

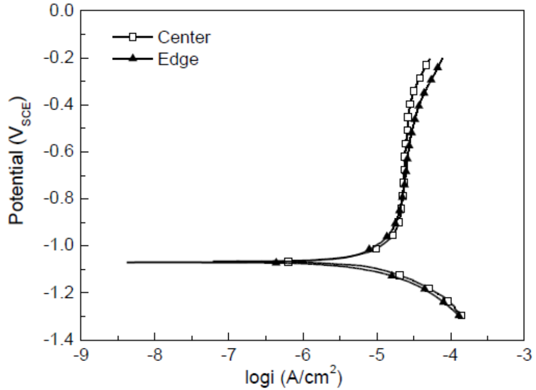
Internal corrosion in water condensate





Evans ring and three-phase boundary (TPB) zone theory





The home-made Ag/AgCl micro-reference electrode (RE), with Pt wire wrapped as CE

CFD modeling of oil-H_2O flow for pipeline corrosion prediction

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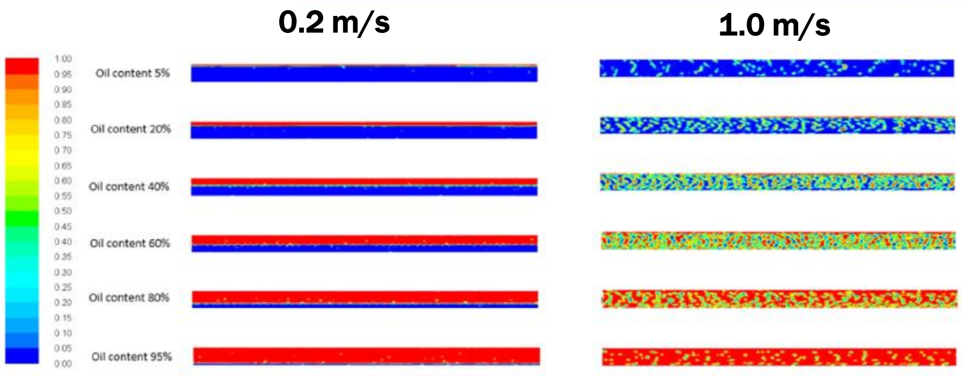
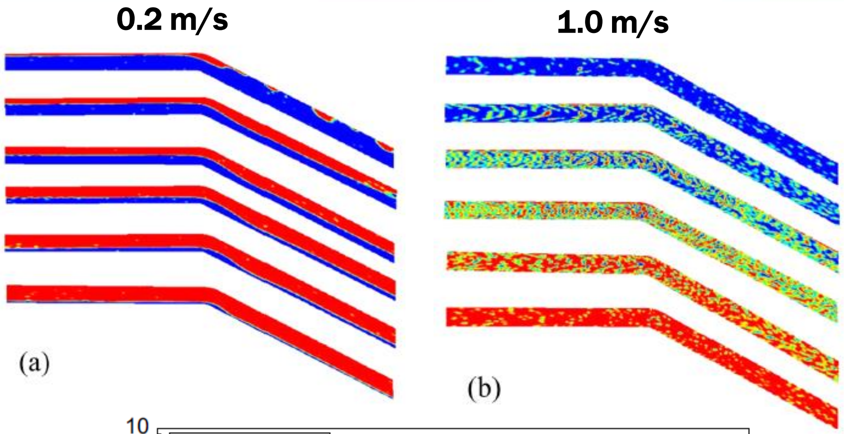
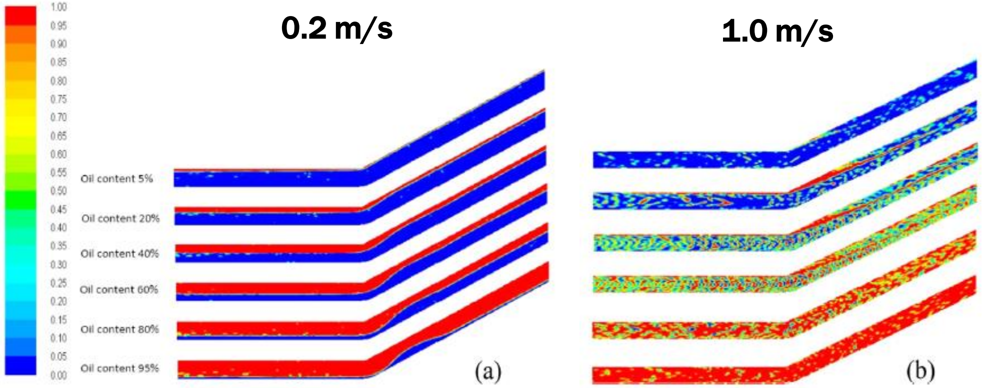
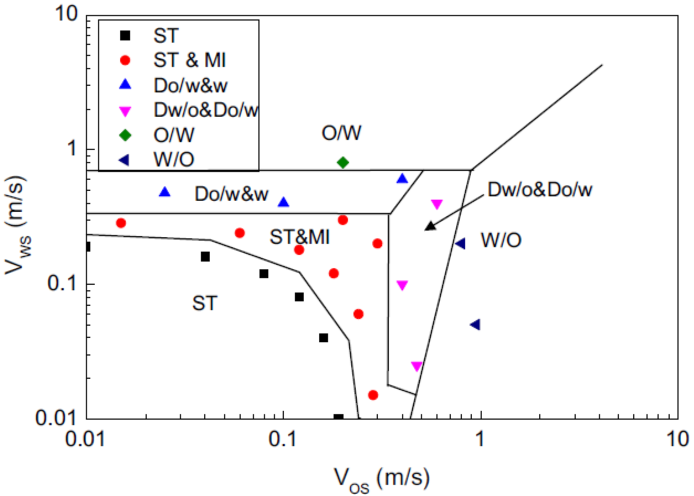








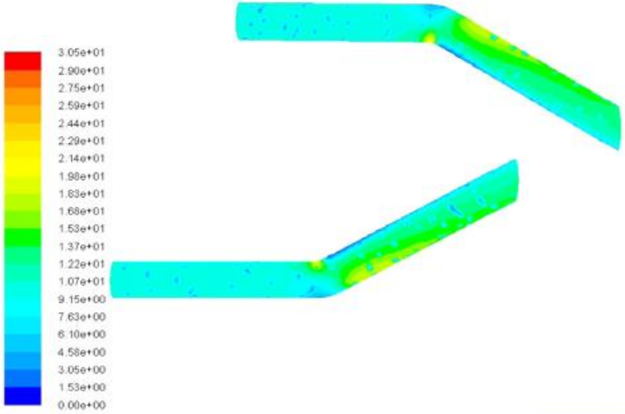
CFD modeling of oil-H_2O flow for pipeline corrosion prediction

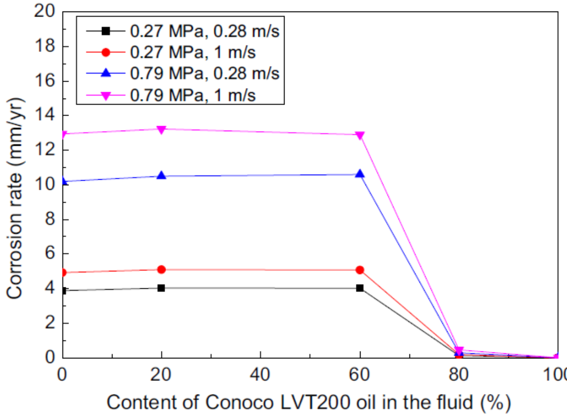
The oil content less than 60%:

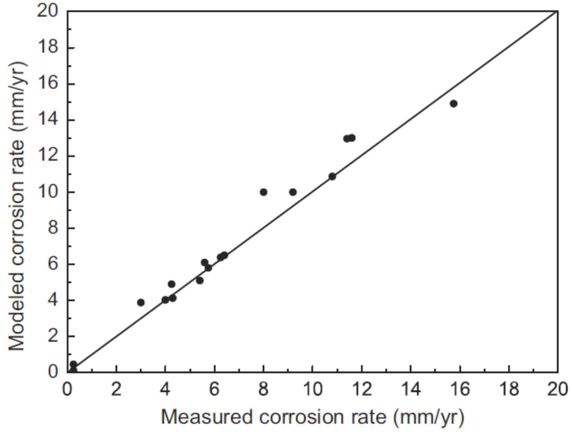
$$CR = k p_{CO_2}^{c} \tau^{b}$$

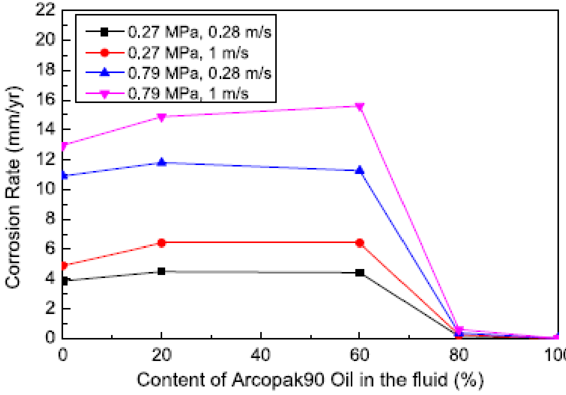
The oil content exceeds 70%:

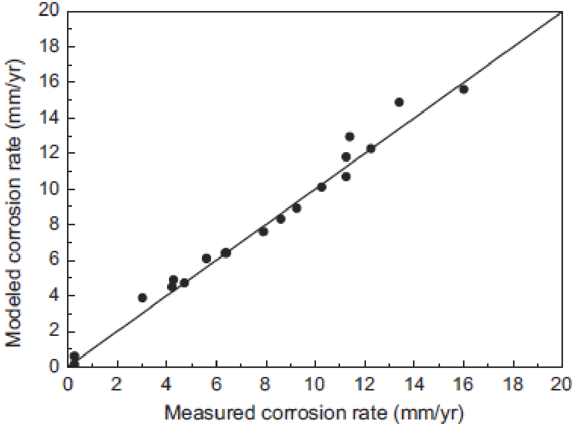
$$CR = 31.15\left(\frac{\Delta P}{L}\right)^{0.3} v^{1.6} p_{CO_2}^{0.8} e^{\left(-\frac{2671}{T}\right)}$$





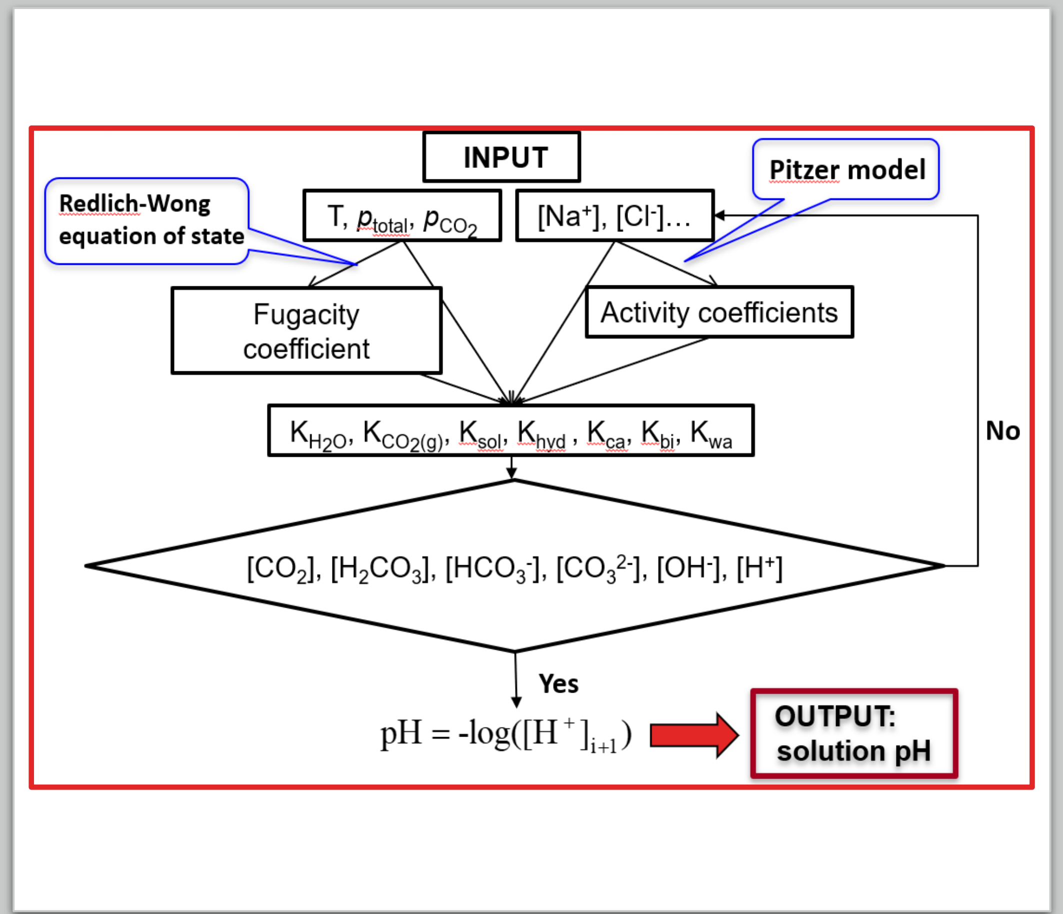


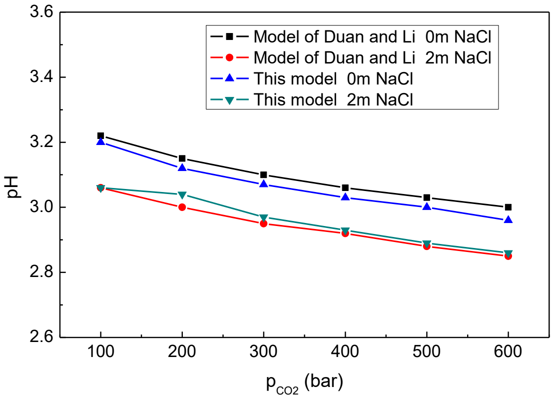


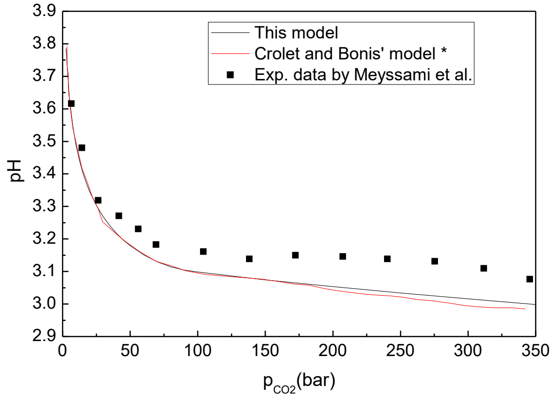


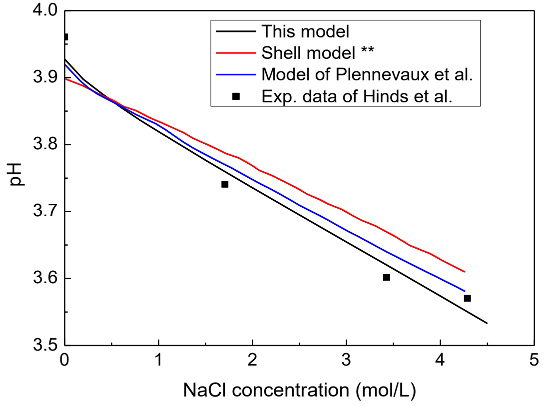
Water chemistry model for pipeline corrosion prediction

- Solution pH is critical for calculation of corrosion rate in CO_2 corrosion model.
  - Sampling of solution for pH measurements is usually difficult, and moreover, the measuring results deviate from the actual values.



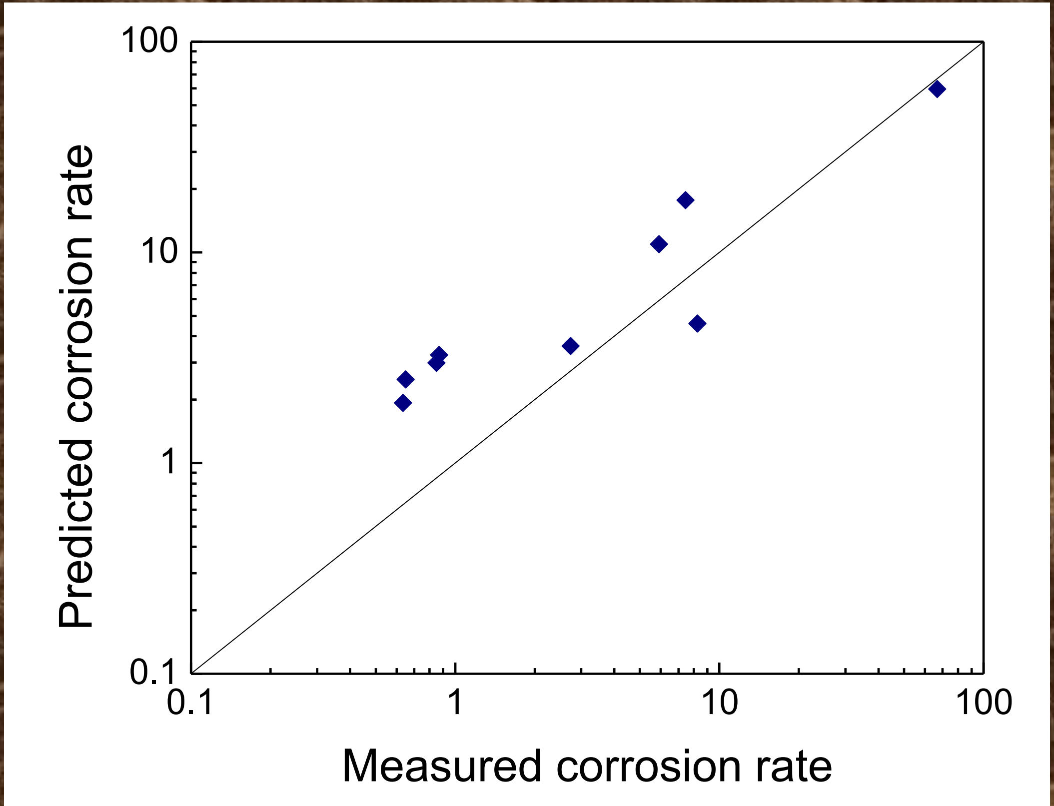






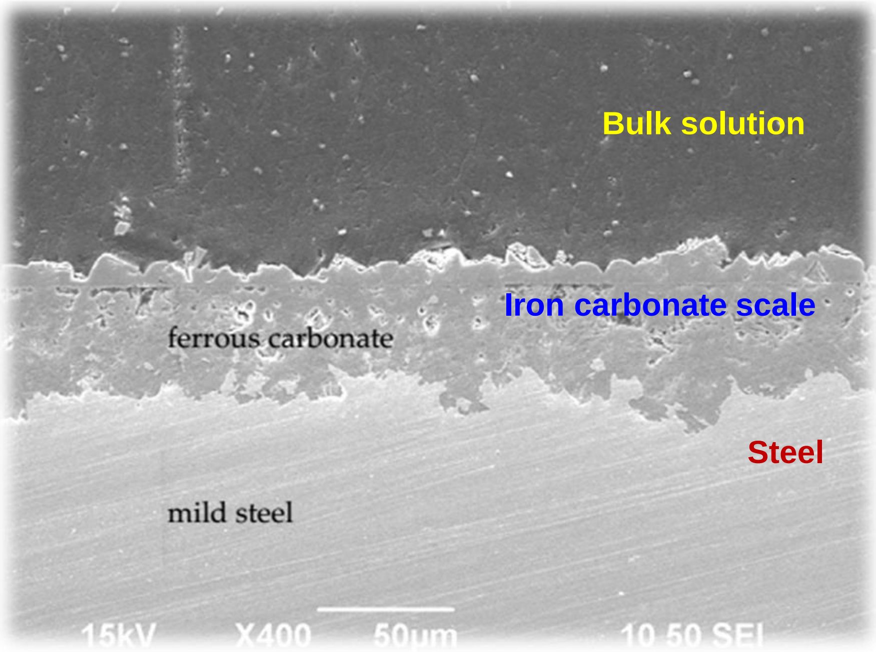
Validation of water chemistry modeling results

Water chemistry model for corrosion prediction



- Comparison of the corrosion rate of X65 steel determined by weight-loss testing with the predicted results by the developed model

A finite element-based multi-physics field coupling model



(1) Fluid hydrodynamic sub-model (Navier-Stokes equations)

$$\rho(\frac{\partial V}{\partial t} + V \cdot \nabla V) = -\nabla p + \mu \nabla^2 V + F$$

$$\nabla \cdot V = 0$$

(2) Mass-transfer sub-model (Nernst-Planck equation)

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c - \boldsymbol{V} c + \frac{Dze}{kT} c \nabla \phi \right]$$

(3) Electrochemical corrosion sub-model (Butler-Volmer equation)

Correction factors:

- Porosity of corrosion scale
- Erosive effect of sands
- Bacterial accelerating effect

$$Fe \rightarrow Fe^{2+} + 2e^-$$

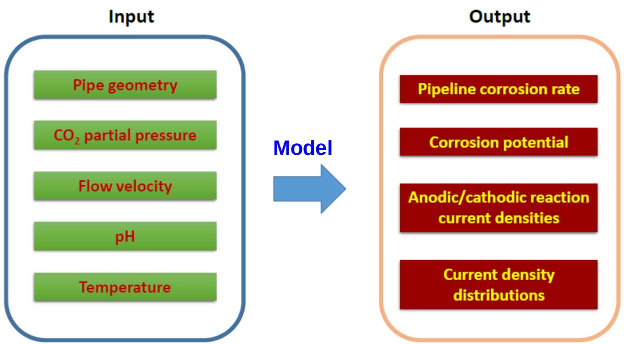
$$2H^+ + 2e^- \rightarrow H_2$$

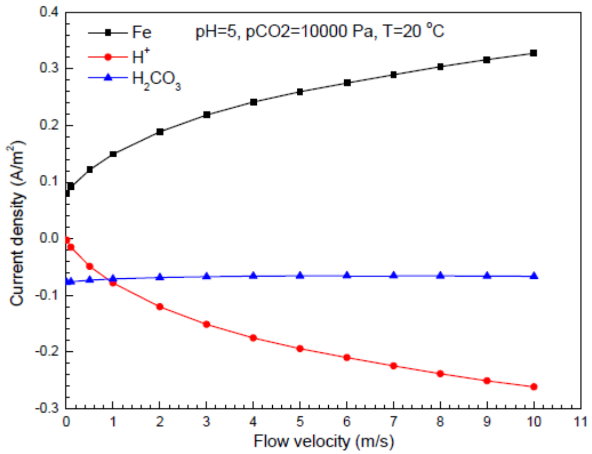
$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$$

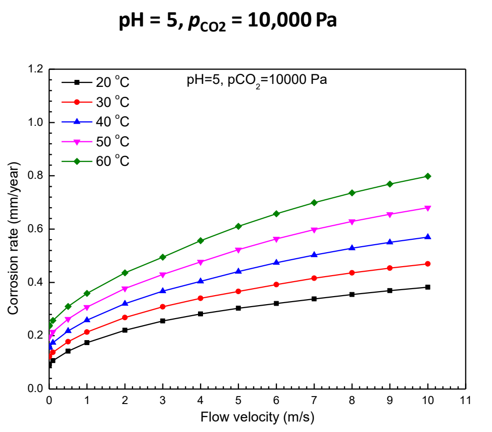
$$i_{a(Fe)} = i_{o(Fe)} 10^{\frac{E_{corr} - E_{rev(Fe)}}{b_{a(Fe)}}}$$

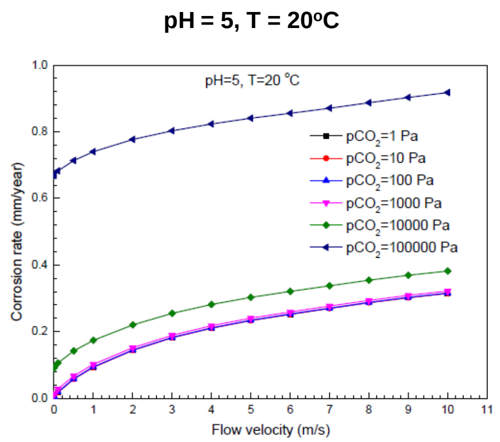
$$\frac{1}{i_{c(H^+)}} = \frac{1}{i_{\alpha(H^+)}} + \frac{1}{i^d_{\lim(H^+)}}$$

$$\frac{1}{i_{c(H_2CO_3)}} = \frac{1}{i_{\alpha(H_2CO_3)}} + \frac{1}{i^r_{\lim(H_2CO_3)}}$$









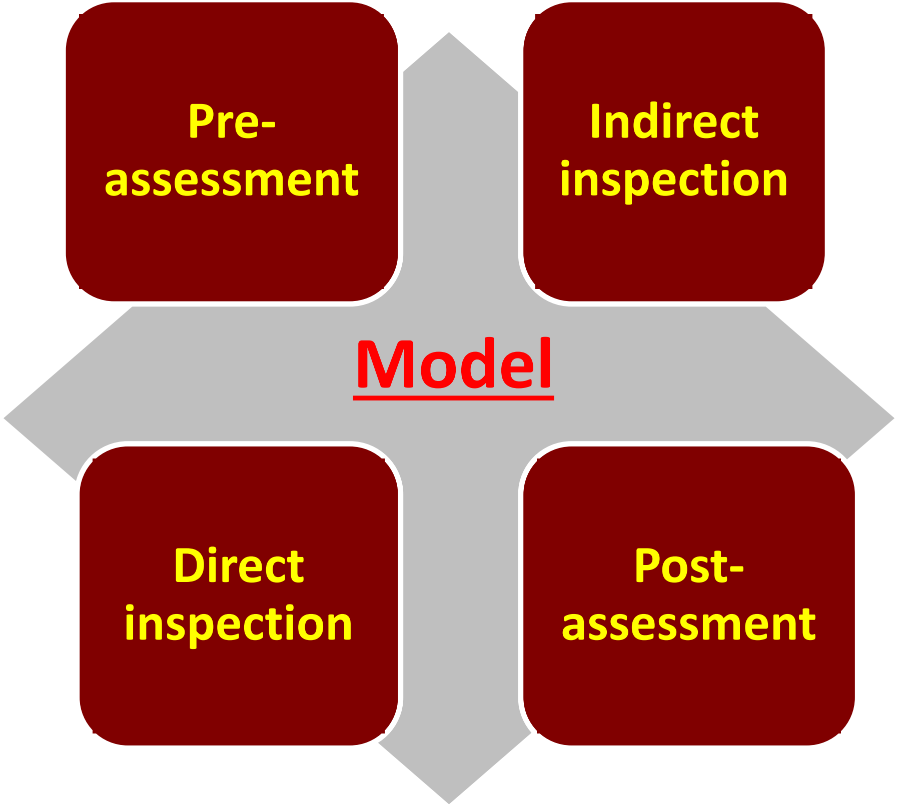
Modeling for pipeline CO_2 corrosion rate

Internal corrosion management

- **Internal corrosion models**
  - Locate corrosion occurrence, especially pitting and erosive corrosion
  - Predict corrosion rate
  - Predict pitting growth rate

- **Corrosion mitigation and control**
  - Periodic pigging to clean deposit/sludge
  - The performance of inhibitors/biocides is not satisfactory

Internal corrosion direct assessment (ICDA)



Pipeline internal corrosion: Mechanisms, modeling and management

Thank You!

Contact: Prof. Frank Cheng, +1 (403)220-3693, fcheng@ucalgary.ca