Corrosion Behavior of Hydrophobic Coatings in Aqueous CO_2 Environments

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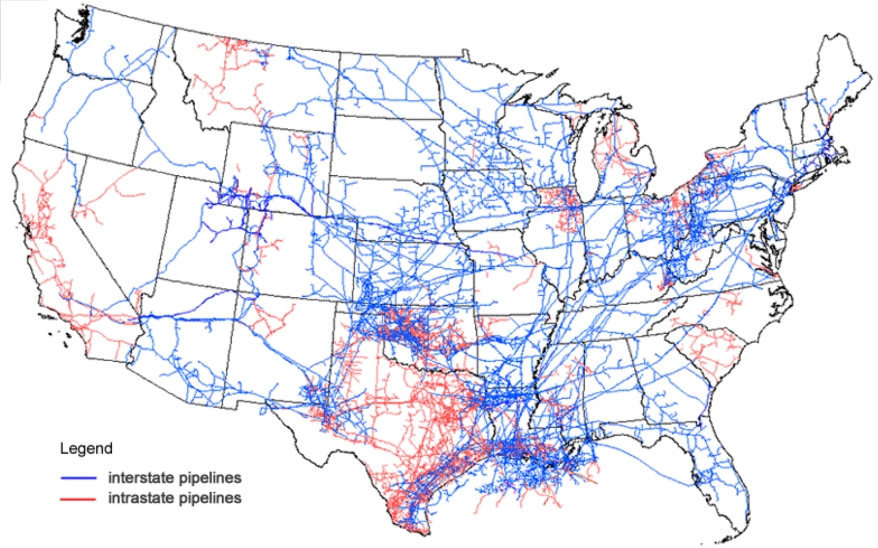
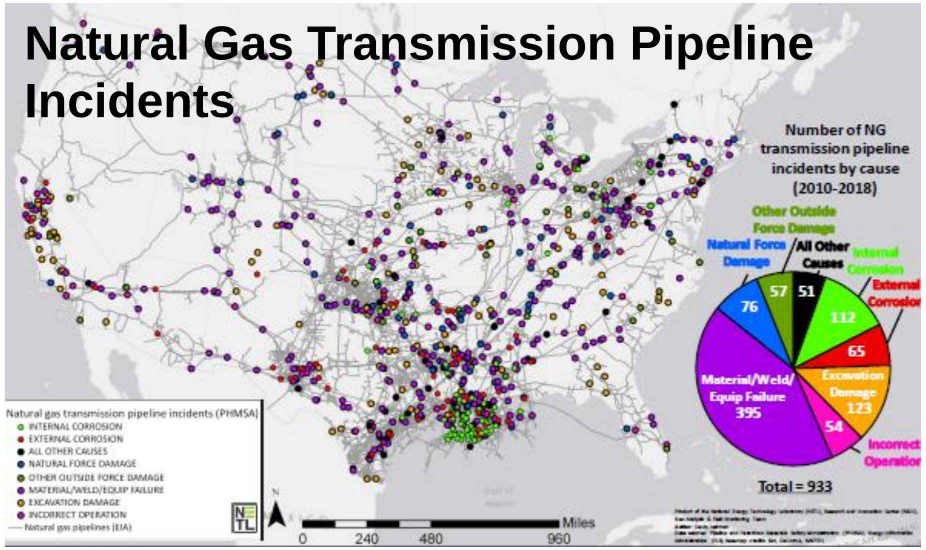
Introduction

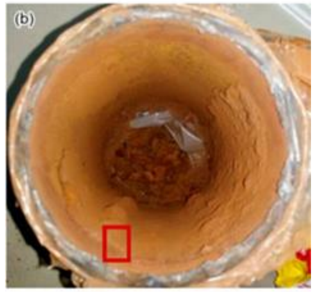
The U.S. natural gas transmission pipeline system is a ~$540 billion asset under corrosion.



Source: U.S. Energy Information Administration, *About U.S. Natural Gas Pipelines*



Internal corrosion

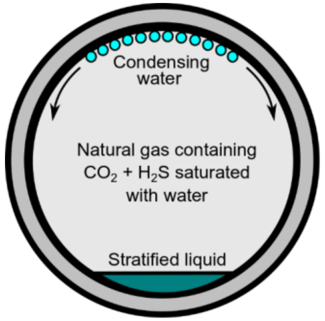


Justman, Rose & Bauer, NETL, 2017. Data analyzed from U.S. DOT PHMSA incident data

- Supplies 28 trillion cf of natural gas/year to 75 million customers.
- >$7 billion/year is spent on corrosion.
- Government legislation (49 CFR § 192.477) requires internal corrosion monitoring programs for pipelines.

Introduction

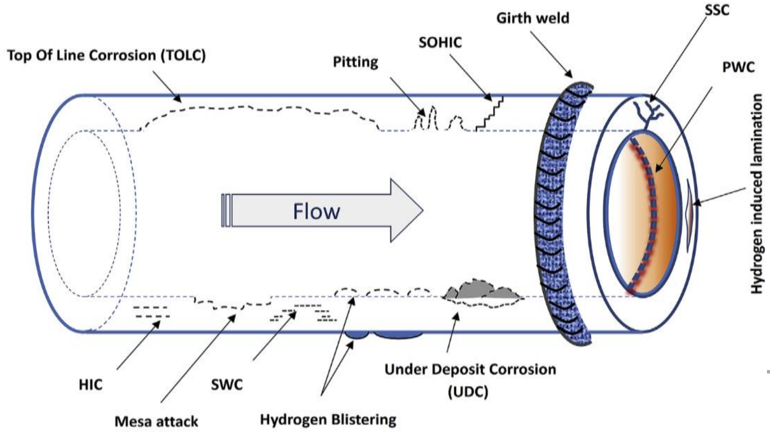
- Water is the primary factor causing corrosion inside gas pipelines.
- CO_2 is the second most important contributor to corrosion.
  - A natural gas transmission pipeline might be expected to have a partial pressure of 310 kPa (45 psig) of CO_2



NACE RP0775-2005

General Corrosion Classifications	
Low	<0.025 mm y^{-1}
Moderate	0.025-0.125 mm y^{-1}
High	0.125-0.25 mm y^{-1}
Severe	>0.25 mm y^{-1}

For example, a short-lived project can tolerate a higher corrosion rate than a long-term, high-investment project.



Different forms of internal corrosion in natural gas pipelines.**

*https://www.rosen-group.com/global/solutions/industry-case-studies/oil-gas/Case-Study-Black-is-Black.html
**M. Askari et al., Journal of Natural Gas Science and Engineering, 71, November 2019, 102971.

Approach to Mitigate Internal Corrosion & Methane Emission

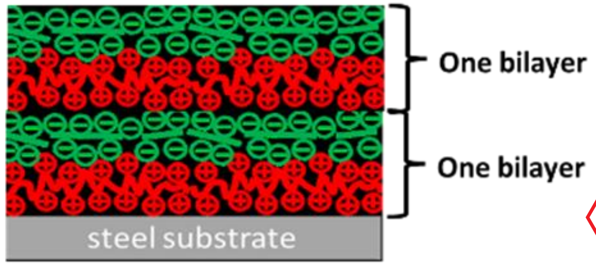
Several prevention methods have been suggested to mitigate internal corrosion, such as:

- Corrosion inhibitors
- Internal coatings

Challenges:
Corrosion underneath the coating (i.e., under film corrosion), eventually developing into surface blisters and localized pitting corrosion.

Superhydrophobic Anti-Corrosion Coatings

- To reduce the coating's permeability and the contact area with corrosive species.
- Superhydrophobic coatings are based on hydrophobic materials with microscopic surface roughness, which can trap air on the surface and thus increase the effective contact angle.



Two bilayers

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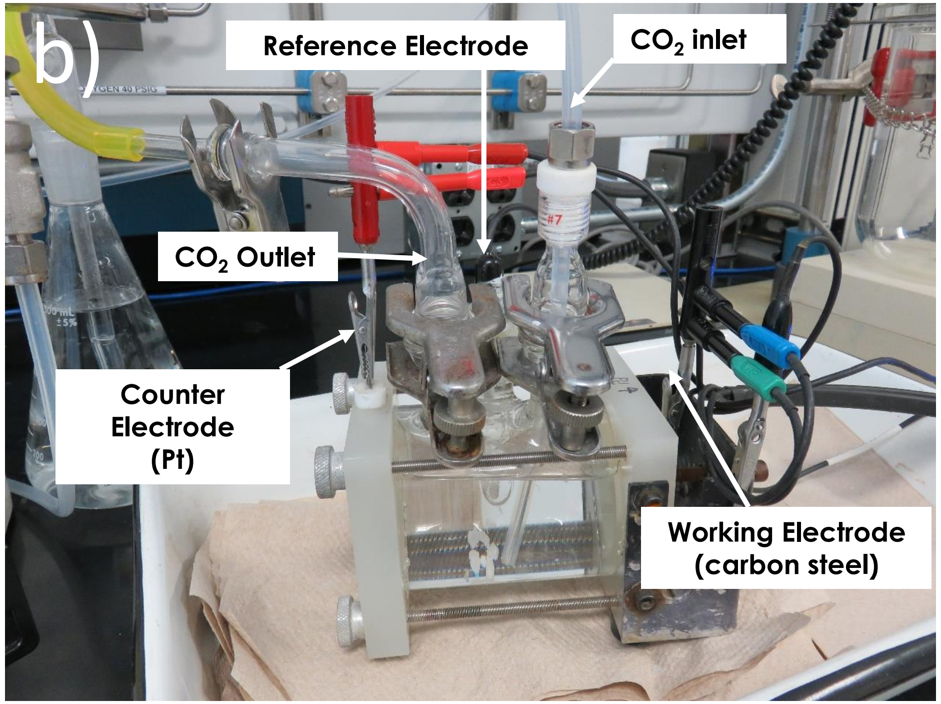
Experimental Setup & Test Matrix

Flat electrochemical cell

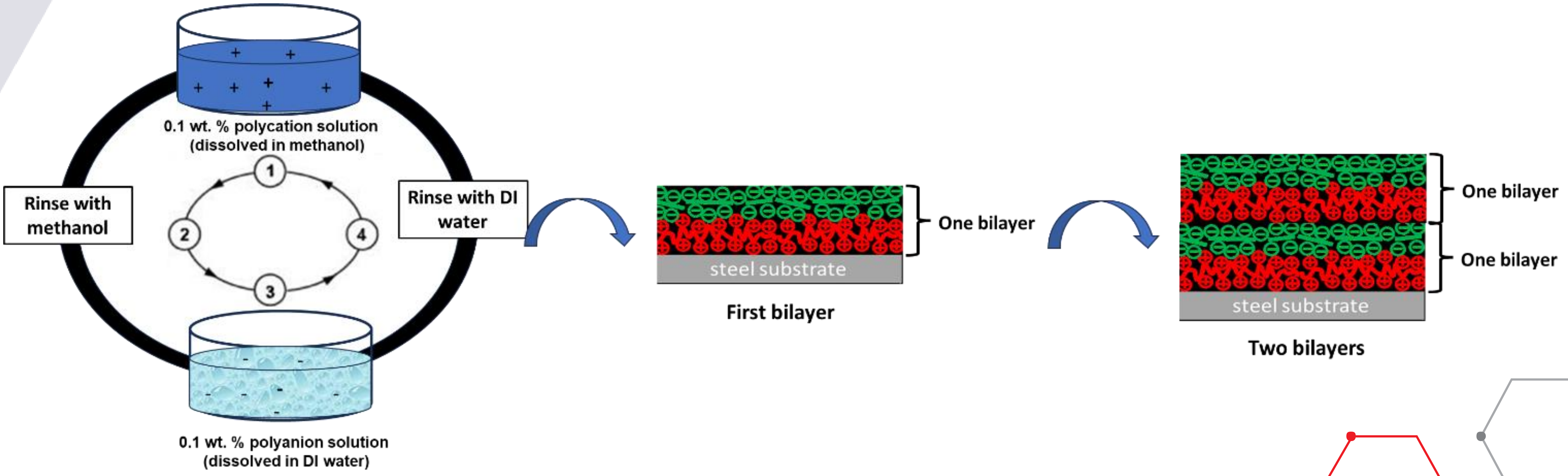


Experimental matrix

Parameters	
Total pressure (bar)	1
pCO_2 (bar)	0.97
Solution	0.25 L of 3.5 wt.% NaCl
Measured solution pH	3.88
Solution temperature (°C)	25
Duration (days)	8
Tested alloys	X65 carbon steel Coated X65 carbon steel

Experimental Setup & Test Matrix

Illustration of different steps for a layer-by-layer assembly technique.



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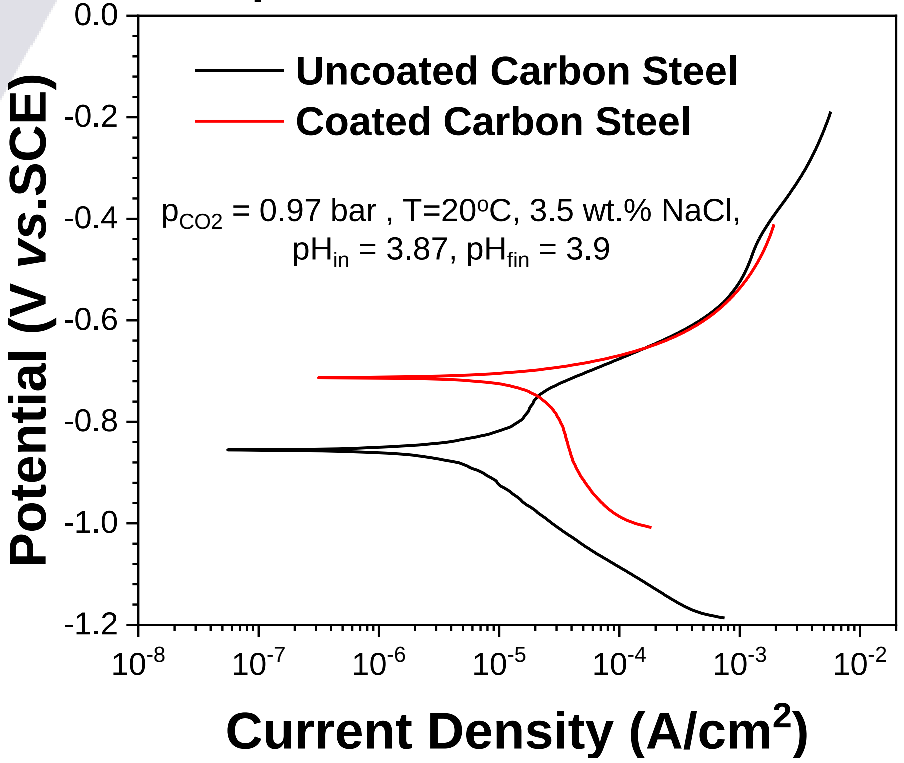
Electrochemical Results: Coated & Uncoated Carbon Steel Immersed in a CO_2 Saturated NaCl Solution

Potentiodynamic polarization curves



Chemical reactions

$$CO_2 + H_2O \overset{1}{\Leftrightarrow} H_2CO_3$$

$$H_2CO_3 \overset{1}{\Leftrightarrow} HCO_3^- + H^+$$

$$HCO_3^- \overset{1}{\Leftrightarrow} CO_3^{2-} + H^+$$

Electrochemical reactions

$$Fe \overset{1}{\Leftrightarrow} Fe^{2+} + 2\,e^-$$

$$H^+ + 2\,e^- \overset{1}{\Leftrightarrow} H_2$$

Chemical reactions

$$CO_3^{2-} + Fe^{2+} \overset{1}{\Leftrightarrow} FeCO_3$$

Corrosion Kinetic Parameters E_{corr}, i_{corr}, and CR for Uncoated and Coated Carbon Steel Immersed in a 3.5 wt.% NaCl Solution Saturated with CO_2 at 20 °C

Alloys	E_{corr} (V vs. SCE)	i_{corr} (A/cm²)	β_a (V/decade)	β_c (V/decade)	CR (mm/y)
Uncoated carbon steel	-0.85	5.35×10^{-5}	0.530	0.496	0.62
Coated carbon steel	-0.71	1.3×10^{-5}	0.462	0.975	0.15

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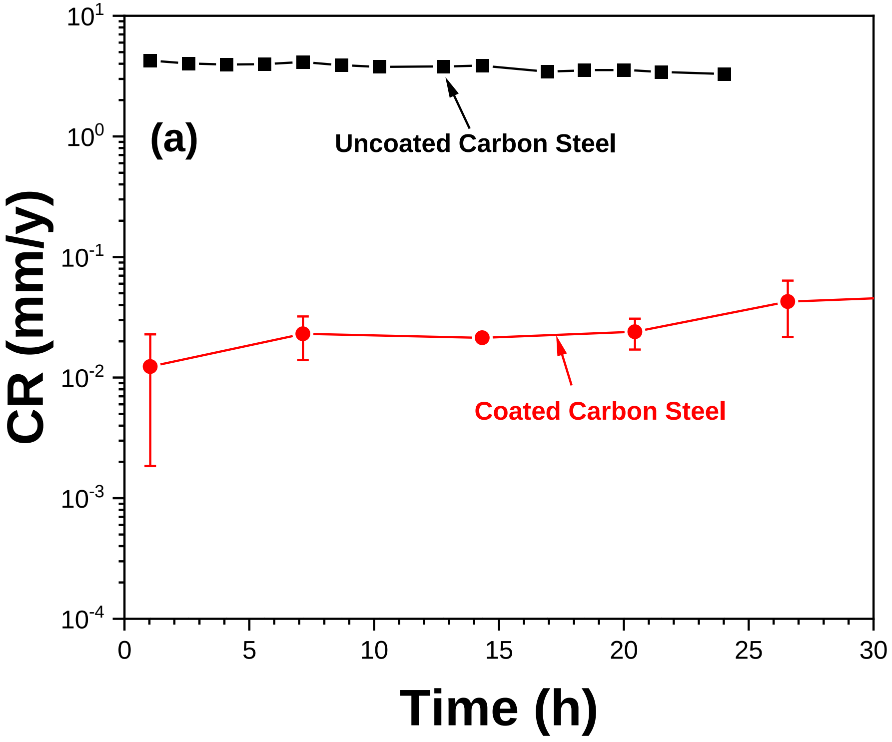
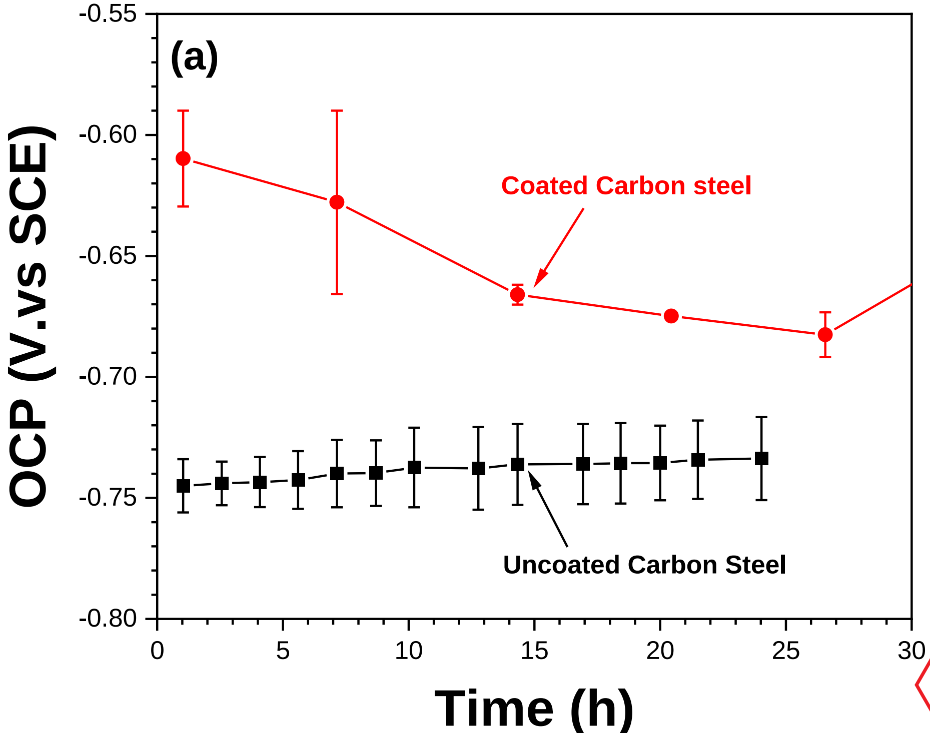
Electrochemical Results: Coated & Uncoated Carbon Steel Immersed in a CO_2 Saturated NaCl Solution

Corrosion rate

Open circuit potential

p_{CO2} = 0.97 bar , T = 20 °C, 3.5 wt.% NaCl, pH_{in} = 3.87, pH_{fin} = 3.9





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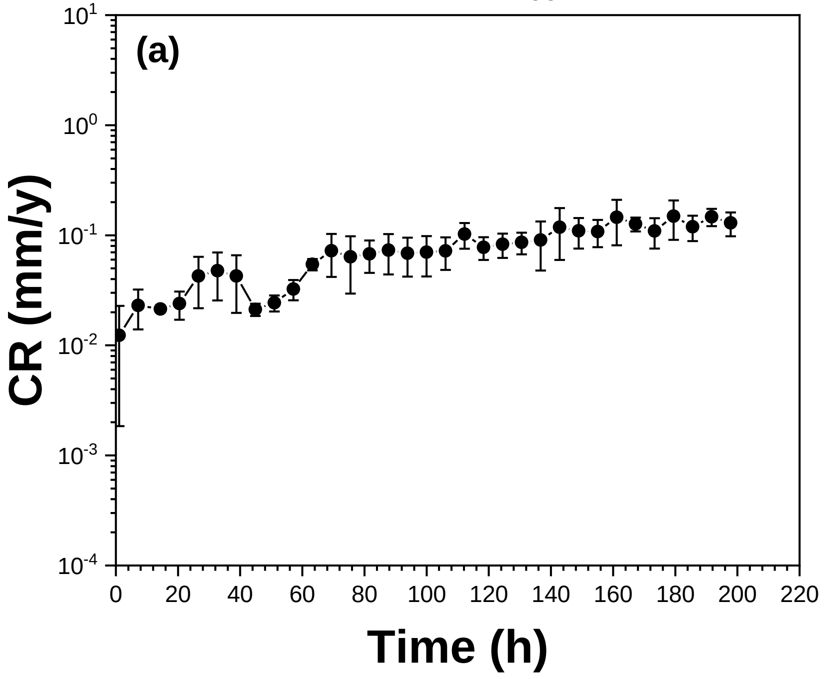

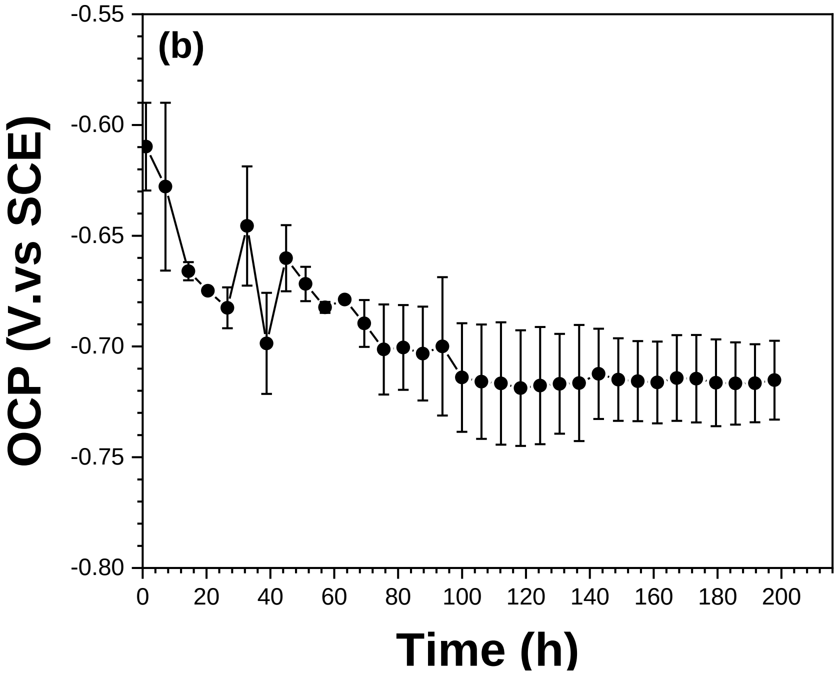

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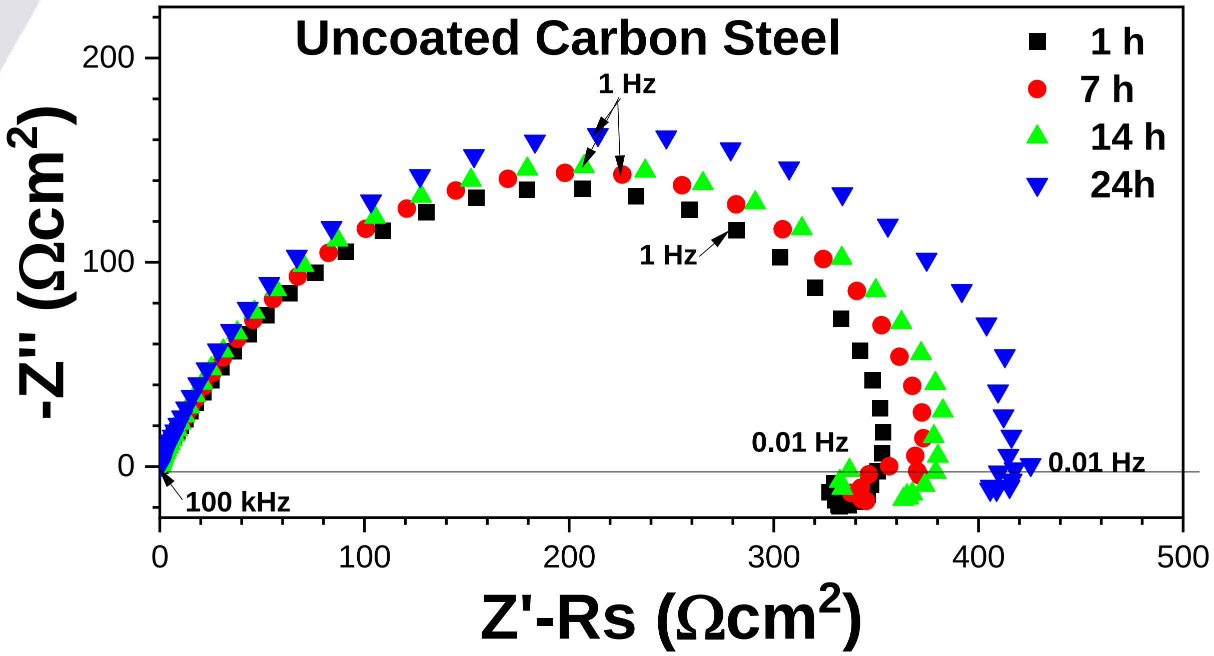
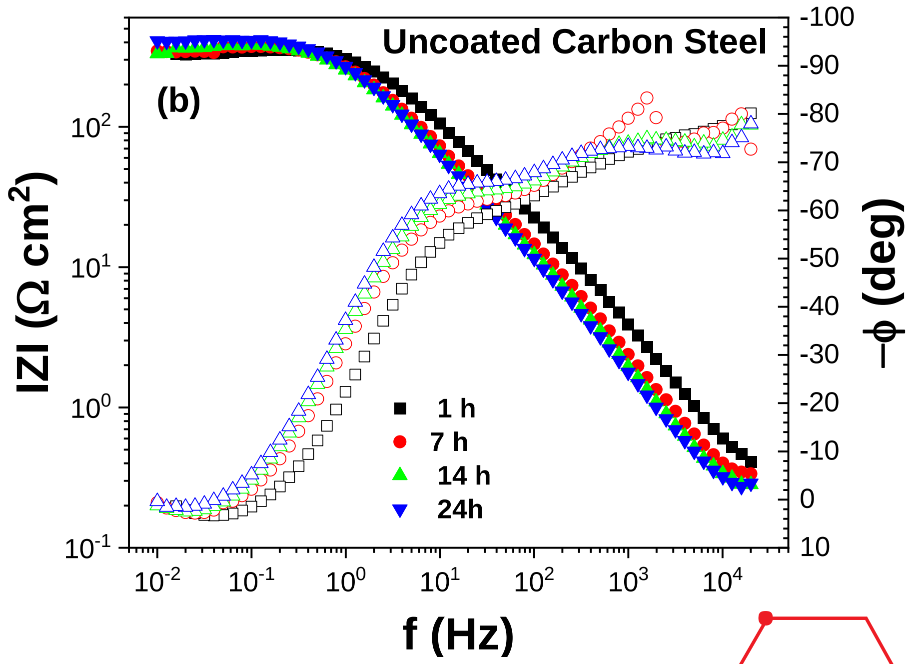
Electrochemical Results: Uncoated Carbon Steel Immersed in a CO_2 Saturated NaCl Solution

Nyquist diagram



Bode diagram



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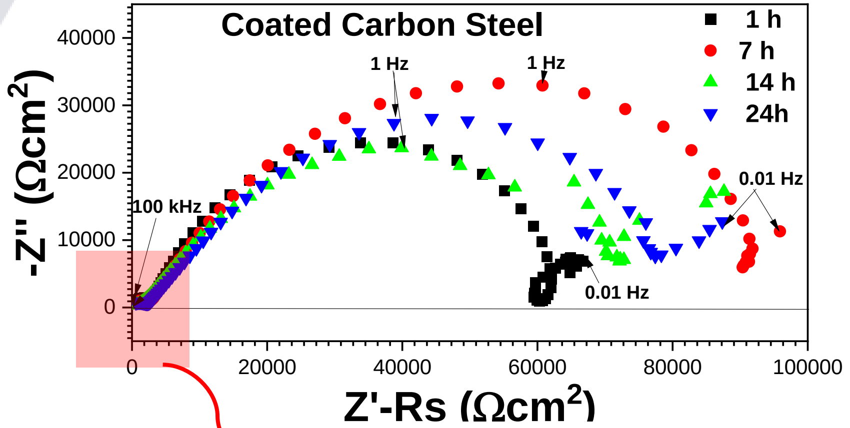
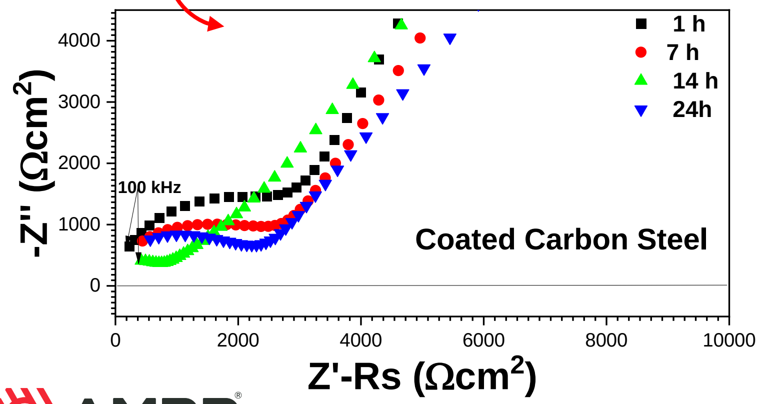
Electrochemical Results: Coated Carbon Steel Immersed in a CO_2 Saturated NaCl Solution

Nyquist diagram





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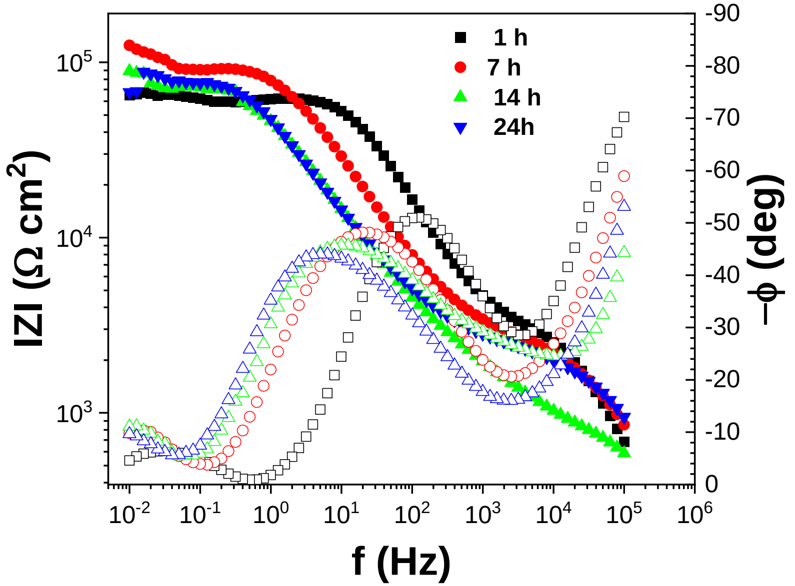

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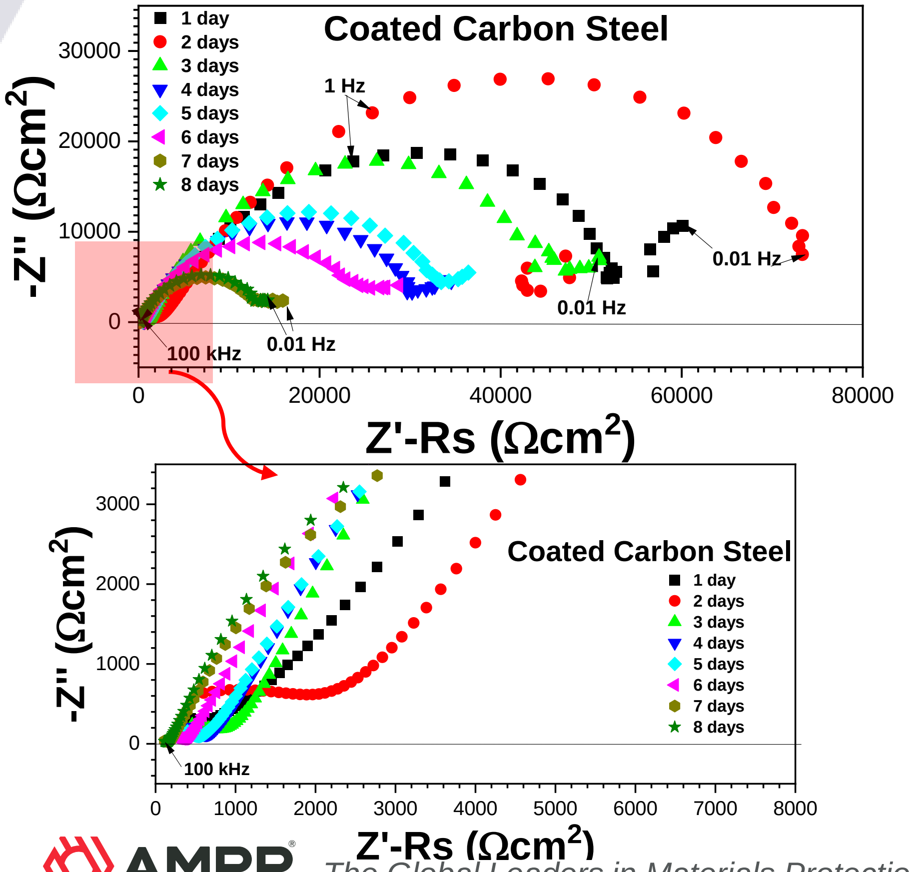
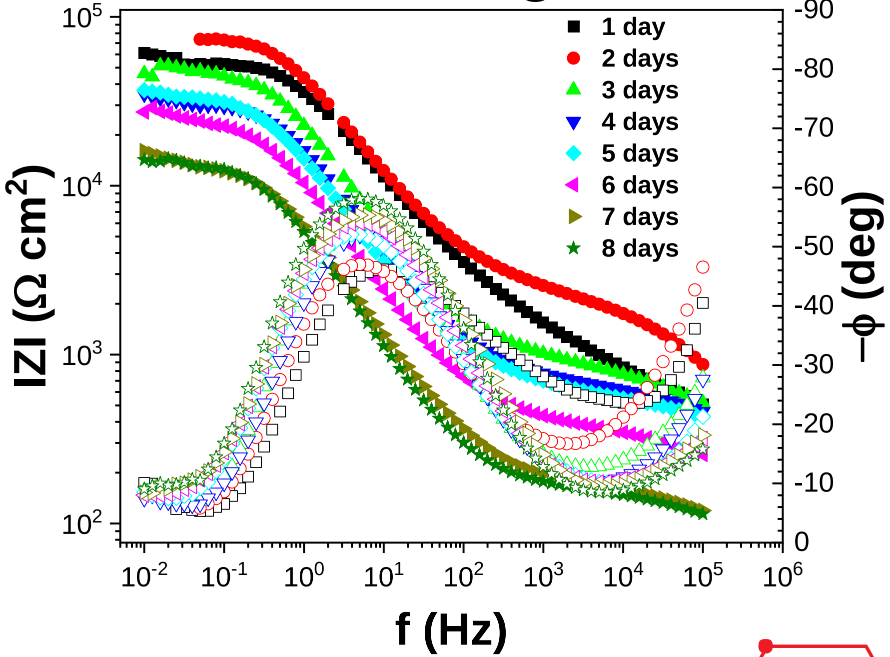


Bode diagram



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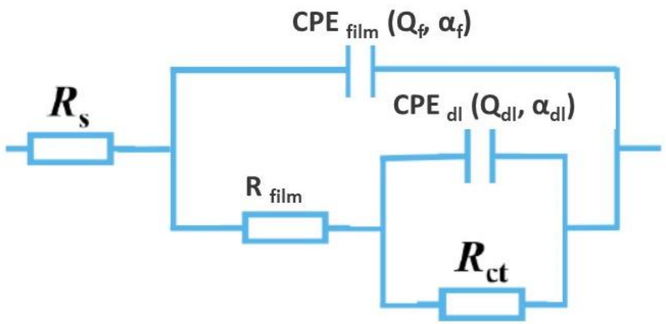
Estimation of Water Uptake of an Organic Coating by Electrochemical Impedance Spectroscopy

Equivalent circuit to model EIS data



Brug's formula to calculate C_{dl}

$$C_{dl} = Q_{dl}^{\frac{1}{\alpha}} * \left(\frac{R_s * R_t}{R_s + R_t}\right)^{\frac{(1-\alpha)}{\alpha}}$$

Hu and Mansfeld formula to calculate C_{film}

$$C_{film} = Q_{film}^{\frac{1}{\alpha f}} * \left(R_{film}^{\frac{(1-\alpha f)}{\alpha f}}\right)$$

The amount of water/solution in the organic coating (film) is a very important property, contributing to the assessment of the anticorrosive protection of organic coatings (the Brasher–Kingsbury (BK) equation).

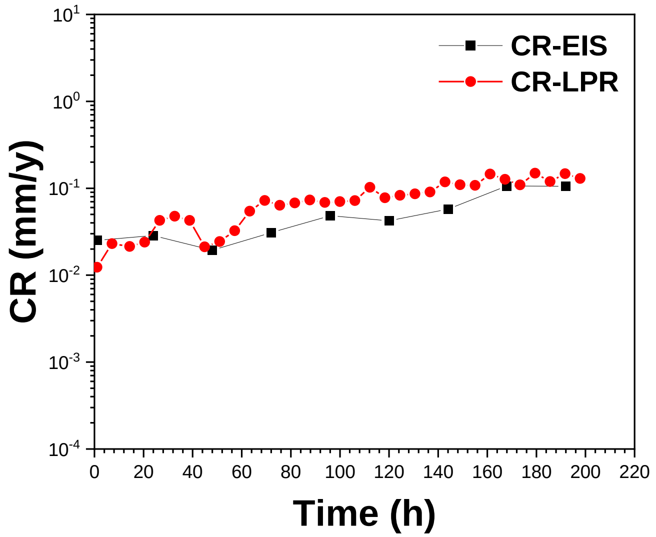
$$\phi_{water} = \frac{\log\left(C_{film}/C_0\right)}{\log \varepsilon_{water})}$$

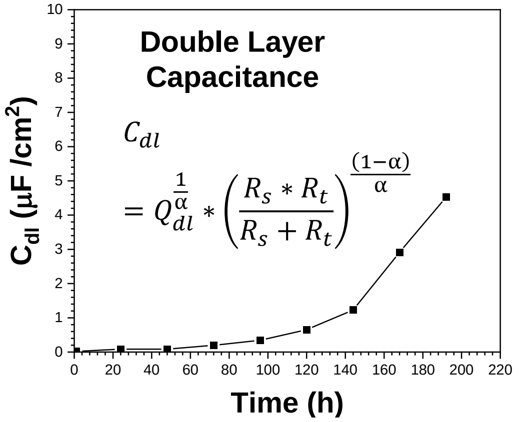
C_{film}: Capacitance of the film with time
C_0: Capacitance of the film coating at t = 0
ε_{water}: Dielectric constant of water = 80
Φ_{water}: Water content: A volume fraction of water at the time t

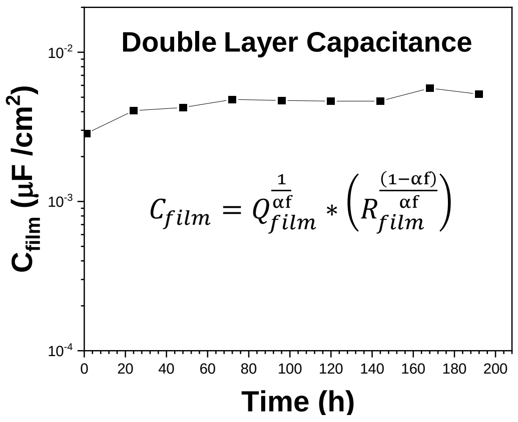
G.J. Brug, A.L.G. van den Eeden, M. Sluyters-Rehbach, and J. H. Sluyters, J. Electroanal. Chem. 176(1984) 275.
C. H. Hsu; F. Mansfeld, "Technical Note: Concerning the Conversion of the Constant Phase Element Parameter Y0 into a Capacitance", Corrosion 57, 9 (2001) p: 747.

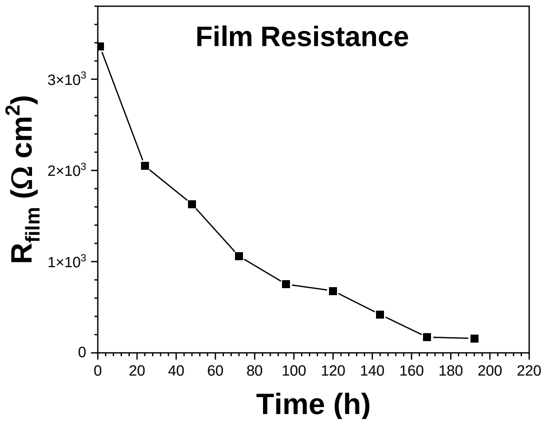
Estimation of Water Uptake of an Organic Coating by Electrochemical Impedance Spectroscopy

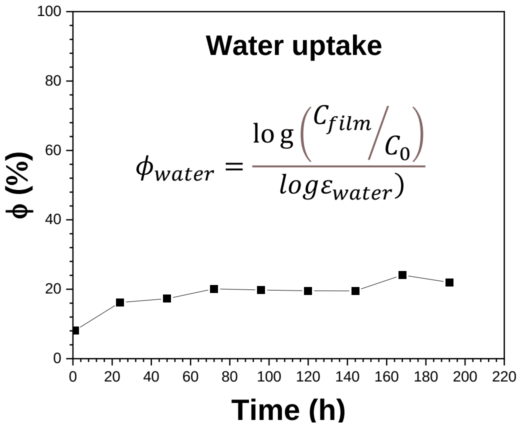
Corrosion rate











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Conclusion

- The corrosion performance of the hydrophobic coating was investigated in 3.5 wt.% NaCl saturated with CO_2 at 20 °C.
- The water uptake was estimated using the Brasher and Kingsbury relation.
- The corrosion of the base metal without coating (3.8 mm/y) was compared to coated carbon steel (0.02 mm/y). The superhydrophobic coating exhibited good behavior against CO_2 corrosion.
- The low water uptake of the superhydrophobic coating correlates to its corrosion resistance.
- The results showed that the superhydrophobic coating with innovative nano-based materials effectively protects the surface of metallic parts against mechanical aggressors, corrosion, and fouling agents. These coatings have proven to be ideal candidates to protect steel pipelines.

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