Quantitative Investigation of the Role of Residual Cementite on the Performance of an Imidazolinium-type Corrosion Inhibitor with Carbon Steel

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Introduction

Motivation

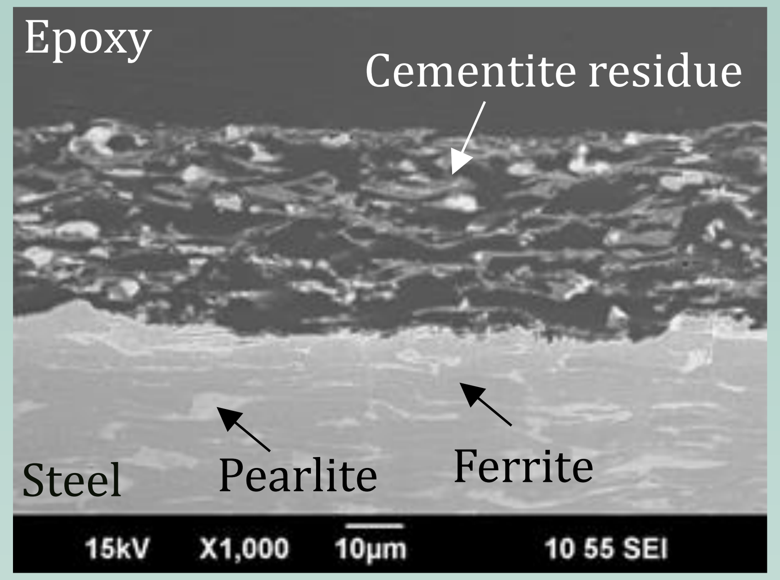
- Corrosion inhibitors (CIs) are widely used in the oil and gas industry to protect carbon steel tubulars against internal corrosion.[1-3]
- Various corrosion residues/products on internal wall of aged pipelines can affect the performance of corrosion inhibitors.[4-6]
- Residual cementite (Fe_3C) has a detrimental effect on inhibition efficiency (IE) *via* serving as an additional cathodic area [4-6], but the associated inhibition mechanism remains unclear.
- This effect varies with different types of corrosion inhibitor and steel [6] and has not been quantitatively evaluated.

Objectives

- Quantitatively evaluate the effect of cementite on corrosion inhibition.
- Understand how the inhibition mechanism is influenced by cementite.

Background

- During corrosion of carbon steel, ferrite dissolves and cementite remains on the surface.
- Cementite can accelerate corrosion rate (CR) *via* galvanic corrosion with ferrite owing to its electrical characteristics.



SEM images of cementite residue after pre-corrosion on C1018 steel with ferritic-pearlitic microstructure[5]

Experimental

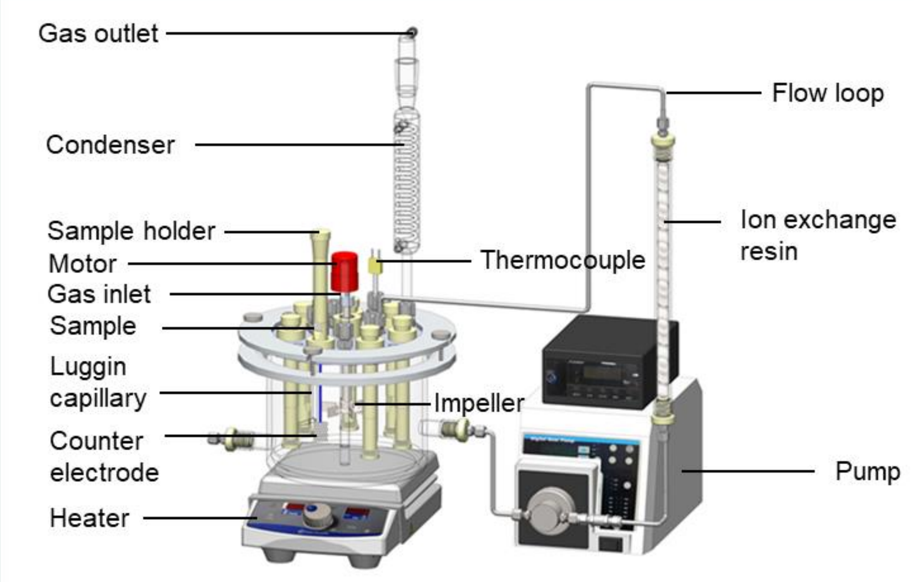
Material and Chemicals

Steel: UNS G10180 carbon steel (C1018) with a ferritic-pearlitic microstructure.

Corrosion Inhibitor: Imidazolinium-type commercial package

Experimental Equipment

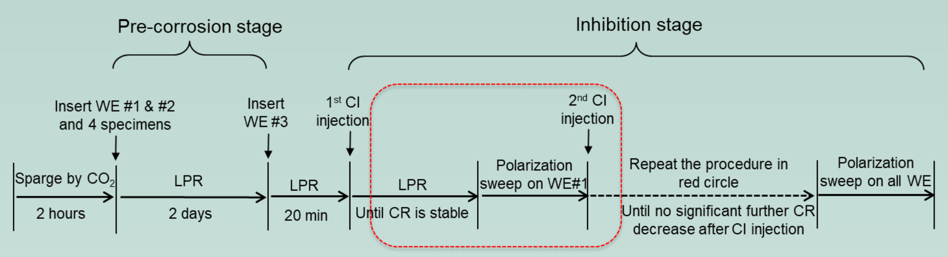
A glass cell with an impeller connected to a Fe^{2+} concentration controller *via* a flow loop and up to 7 specimens being exposed in the test environment (immersion specimens and working electrodes).



Test Matrix

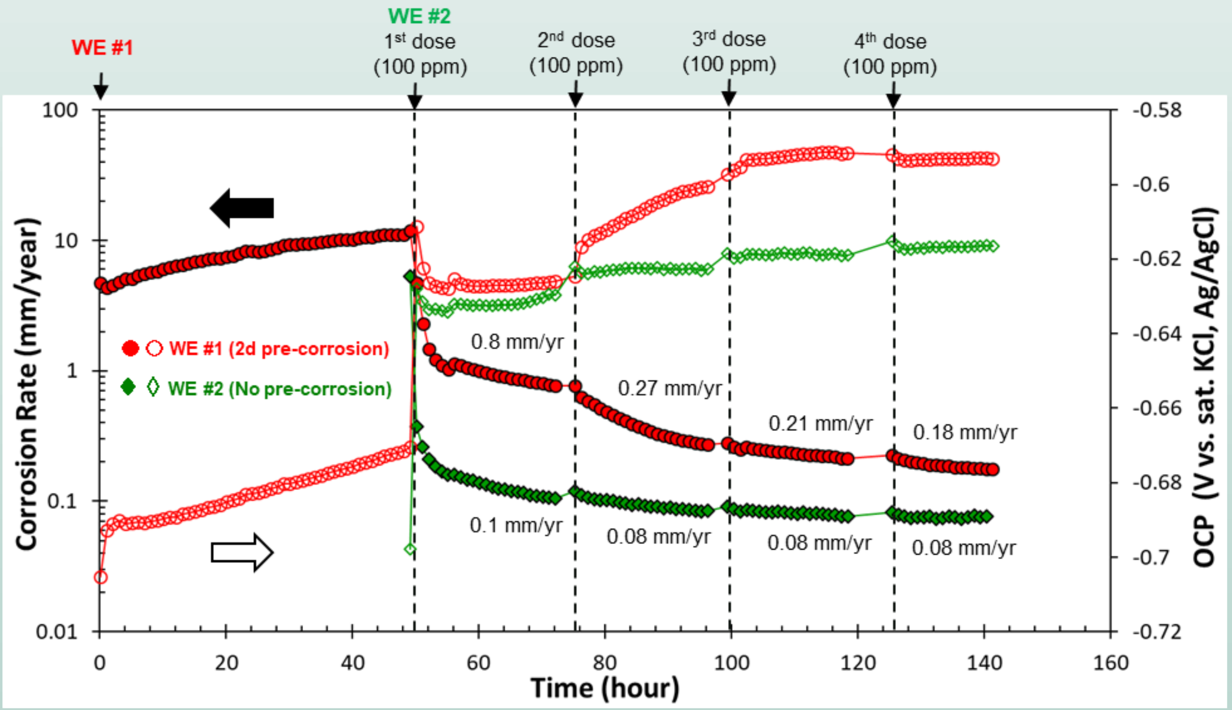
Parameters	Values
Electrolyte	5 wt.% NaCl
Working electrode	Flat square
Immersion specimen	Flat square
Temperature	55 ± 2 °C
Total pressure	1 bar
CO_2 pressure	0.86 bar (saturated)
pH	4.5 ± 0.1
Flow condition	Same mass transfer coefficient as flow of 1.61 m/s in a pipe with an ID of 0.1m (shear stress: 4.7 Pa)

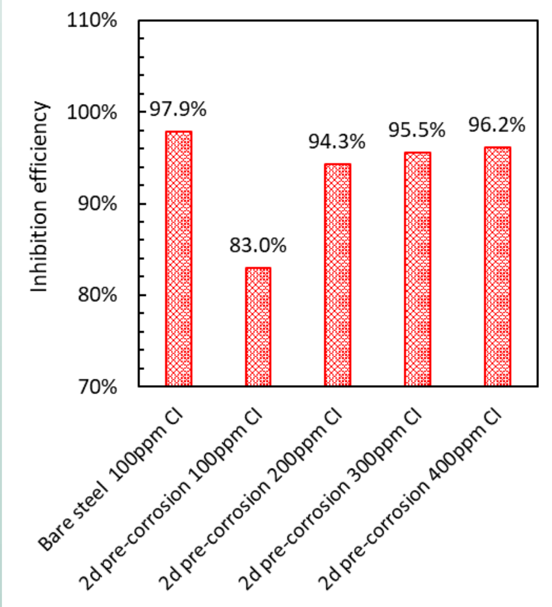
Procedure



Results

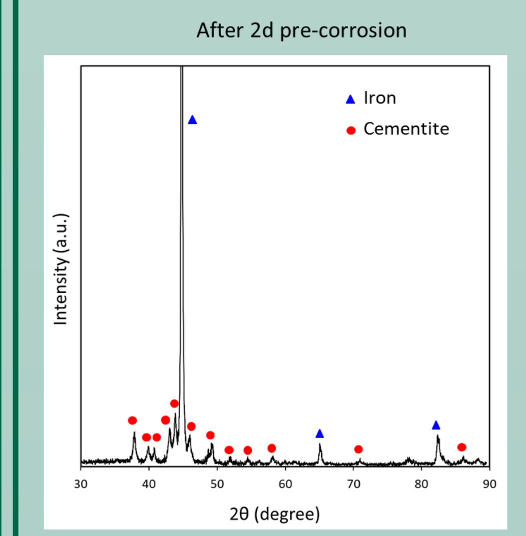
Corrosion Rate & Inhibition Efficiency

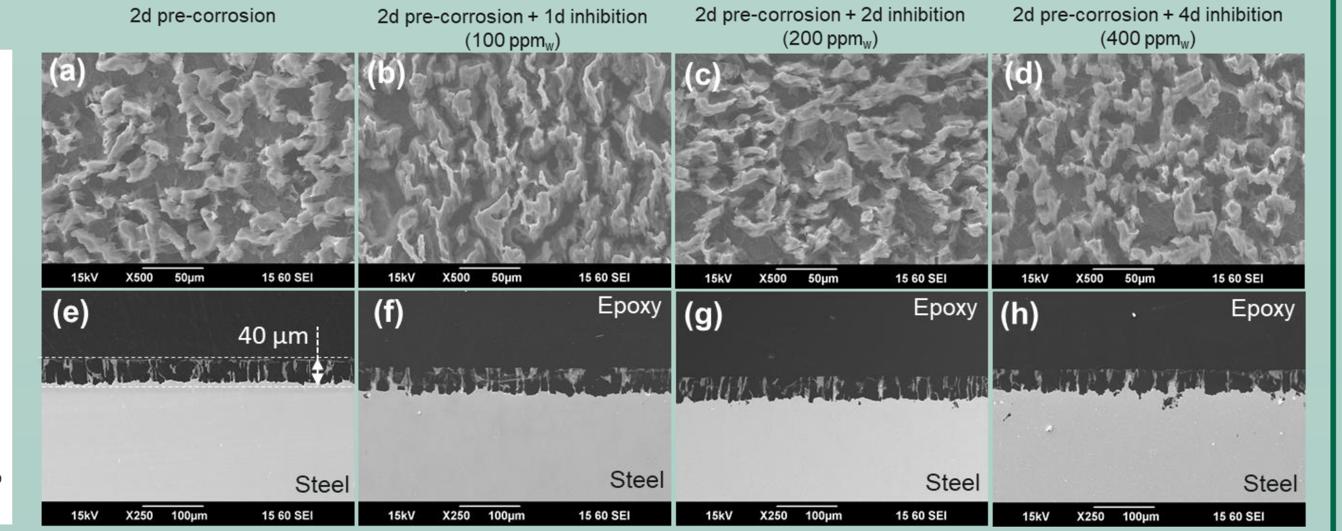




- IE was harmed after pre-corrosion and higher CI concentration helped to combat this detrimental effect.
- Minimum inhibited CR with pre-corrosion was higher than without pre-corrosion.

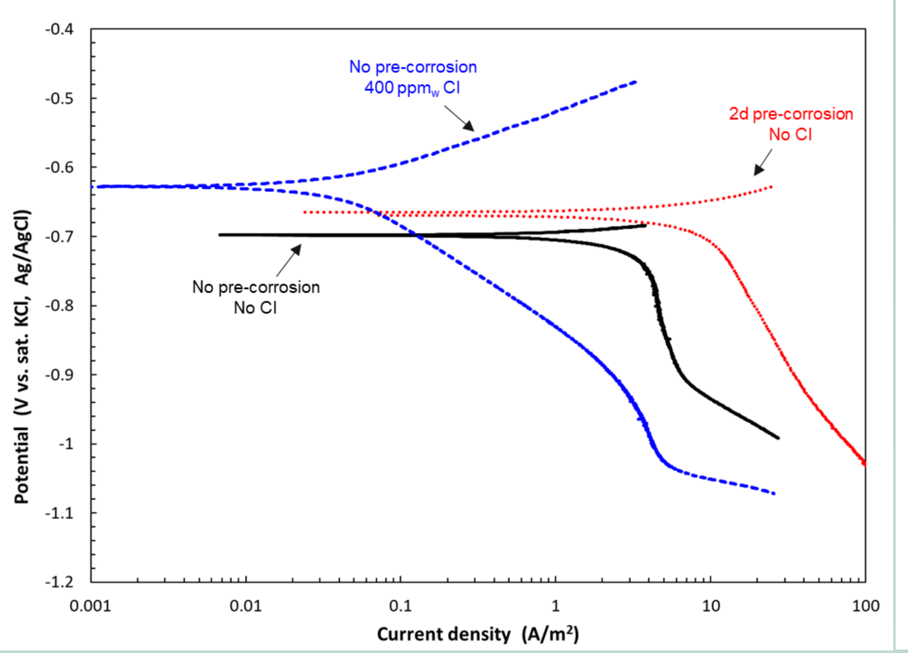
Surface Characterization

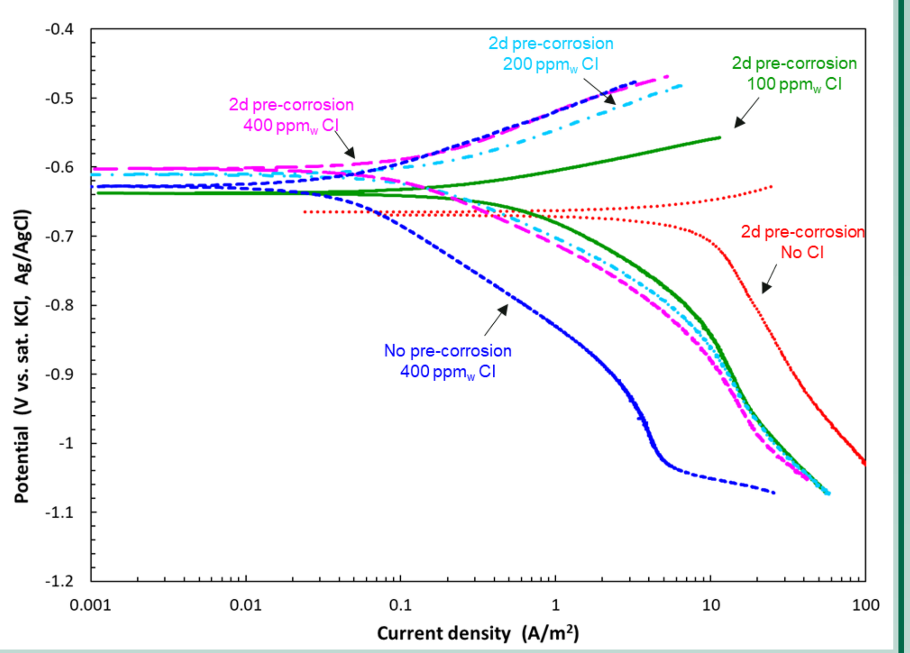




A cementite skeleton remained on the specimen surface after pre-corrosion and its thickness remained the same indicating the effectiveness of the inhibition.

Potentiodynamic Polarization





- After pre-corrosion, the cathodic limiting current was significantly accelerated.
- CI retarded both anodic & cathodic reactions and limiting current was unaffected.
- 400 ppm_w CI retarded anodic reaction to the same extent as on bare surface, while cathodic curve showed a pronounced difference due to the cementite skeleton.

Quantitative Evaluation

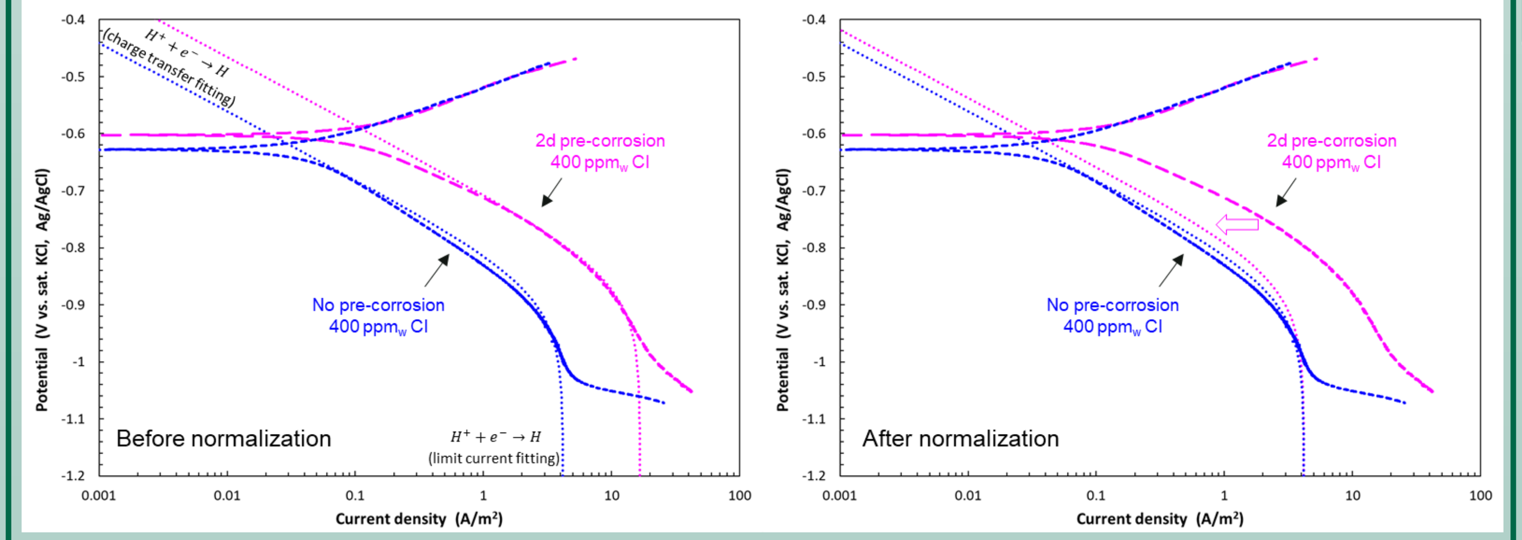
Cathodic Polarization Curve Normalization

Purpose: Compare cathodic curves with and without residual cementite based on same cathodic reaction area.

Method: Cathodic curve with cementite will be normalized based on the cathodic area for the bare surface.

Assumption: The ratio of cathodic area with and without cementite was equal to the ratio of corresponding cathodic limiting currents.

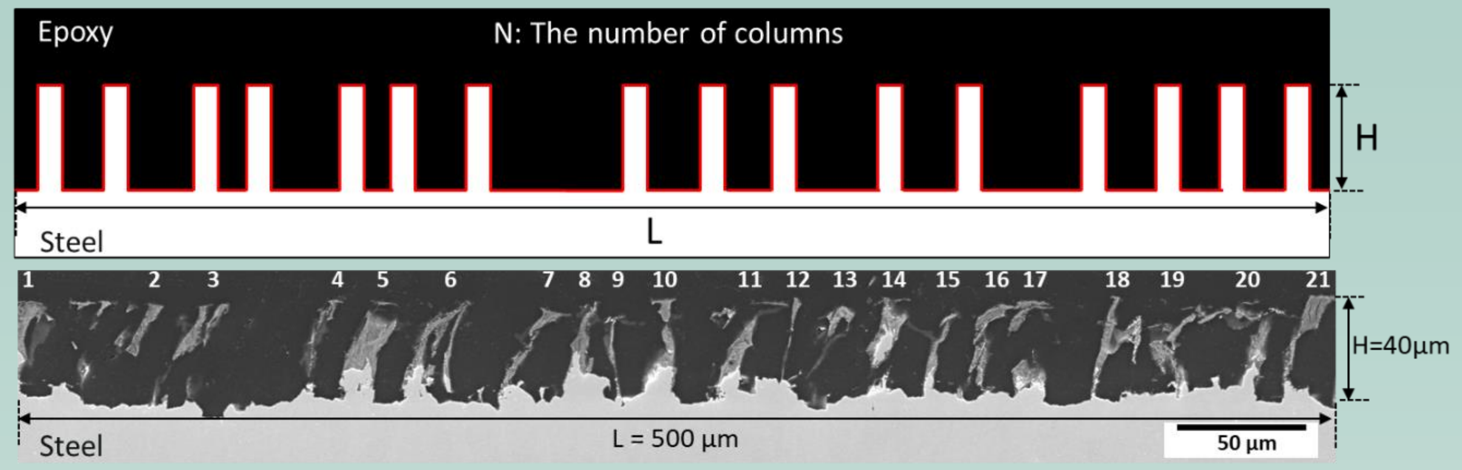
$$R = \frac{Cathodic\ area_{\ with\ Fe3C}}{Cathodic\ area_{\ without\ Fe3C}} = \frac{i_{lim,\ with\ Fe3C}}{i_{lim,\ without\ Fe3C}} \approx 4.0$$



- After normalization, cathodic reaction was retarded to the same extent as that on bare surface as well.
- The lesser retardation of the cathodic reaction reflected in the polarization curve was only due to the additional cathodic area by residual cementite.

Cathodic Area Ratio Verification

Method: The ratio of cathodic reaction area with and without residual cementite was estimated from cross-sectional SEM images.



$$R = \frac{Cathodic\ area_{\ with\ Fe3C}}{Cathodic\ area_{\ without\ Fe3C}} \approx \frac{Perimeter\ of\ the\ red\ line}{L} = \frac{2*N*H+L}{L} \approx 3.85 \pm 0.52$$

Conclusions

- Residual cementite harmed inhibition efficiency due to galvanic coupling effects *via* serving as an additional cathodic area.
- Both anodic and cathodic reactions can be inhibited equally as on bare steel.
- The lesser retardation of the cathodic reaction reflected in the polarization curve was only due to the additional cathodic area.
- The minimum inhibited corrosion rate with residual cementite was always larger than that on bare steel.

Limitation & Future Work

Limitation: Bulk concentration of CI decreased in this close system due to adsorption at different interfaces.

Future work:

- Continuously inject CI for long-term exposure to simulate CI injection in pipelines.
- Study this effect using different types of CIs and steels (different carbon contents and microstructures).

References

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