Laboratório de Corrosão
COPPE|UFRJ
DMM ▪ PEMM ▪ Poli

Corrosion of Armor Wire Steel in the Annulus of Flexible Pipes at **Near Neutral pH**

The effect of environmental factors

Tatiane Seixas Campos

Advisor: Ponciano

Rio, nov/2019

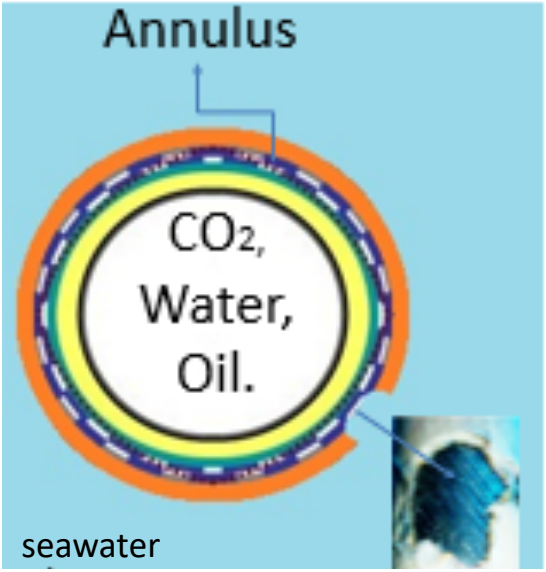
Co-workers

Emanuel Seixas
Jonas Sá

Marion Seiersten
Simona Palencsár
Arne Dugstad

Background

- Flexible pipes are being used as risers and flowlines at offshore oil fields.
- The armor is high strength carbon steel wires, designed to provide axial and tensile strength to the flexibles.
- The confined area with armor steel wires between the inner and the outer polymeric sheaths is referred to as annulus of flexible pipes.
- Corrosive environments may build up in the annulus as a result of the permeation of production gases through the inner sheath, i.e. CO_2, H_2S and H_2O, or seawater ingress due to damage to the outer sheath or improper sealing.



Background

- CO_2 that diffuses through the inner sheets maintains a low, but noticeable activity of dissolved CO_2 and carbonic acid in the water in the annulus.
- Although the CO_2 activity is lower than in the bore, it may cause noticeable corrosion of the armor wires.
- The cathodic and anodic reactions considered in this study are given in Eq. 1-5. The cathodic reactions consume acid or produce alkali.

$2H_2CO_{3(aq)} + 2e^- \rightleftarrows 2HCO^-_{3(aq)} + H_{2(g,\,aq)}$	**(1)**
$2HCO^-_{3(aq)} + 2e^- \rightleftarrows 2CO^{2-}_{3(aq)} + H_{2(g,\,aq)}$	(2)
$2H^+_{(aq)} + 2e^- \rightleftarrows H_{2(g,\,aq)}$	(3)
$2H_2O_{(l)} + 2e^- \rightleftarrows H_{2(g,\,aq)} + 2OH^-_{(aq)}$	(4)
$Fe_{(s)} \rightleftarrows Fe^{2+}_{(aq)} + 2e^-$	(5)

Cathodic reactions

Anodic reaction

Background

- If the alkaline corrosion products accumulate, the pH of the water in the annulus will increase and approach neutral pH.
- Due to the low ratio between the free volume (V) and the surface area of the wires (S) in annulus, even a low corrosion rate will result in rapidly increasing concentration of Fe^{2+} and CO_3^{2-}.

Siderite

$FeCO_3(s) \rightleftarrows Fe^{2+}(aq) + CO_3^{2-}(aq)$	(6)
$SR = \frac{{}^{a}Fe^{2+} \times {}^{a}CO_3^{2-}}{K_{sp}}$	(7)

SR >> 1

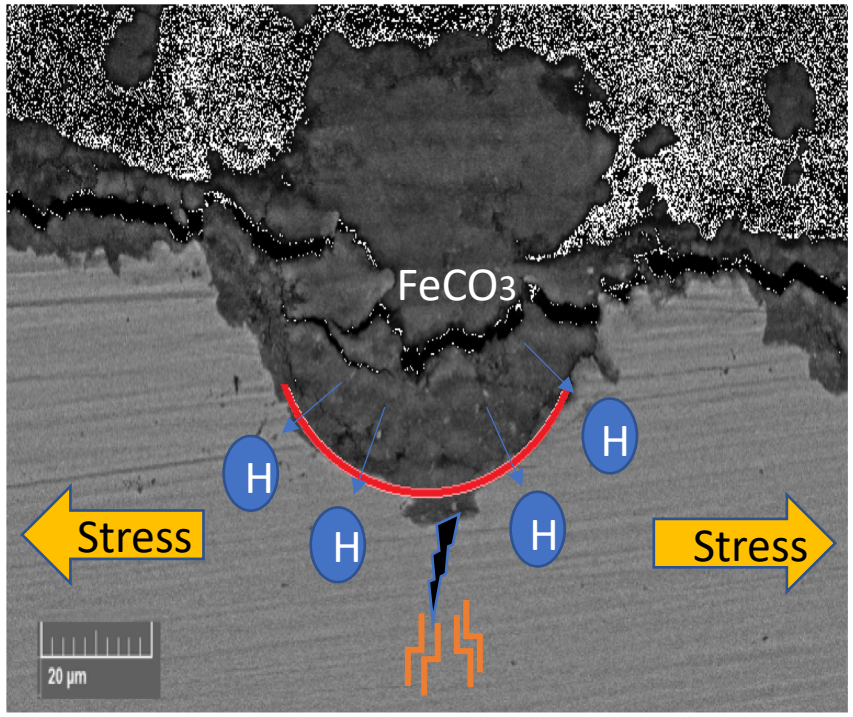
Armor wires

Fig.: Annulus configuration.

Background

- The composition of the trapped water in annulus has some of the same characteristics as the conditions that have induced SCC in carbon steel: that is a relatively high bicarbonate concentration and a low CO_2 partial pressure which result in a near neutral pH.
- Localized corrosion can be a great site to initiate SCC in near neutral pH.

According to the theory, SCC is…



Most common in colder climates.
Frequently reported in underground pipes (presence of bicarbonate in the soil).
Near neutral pH: 6-7.
Primarily transgranular cracking (from a pitting), being followed by a intergranular cracking and presence of secondary cracking.

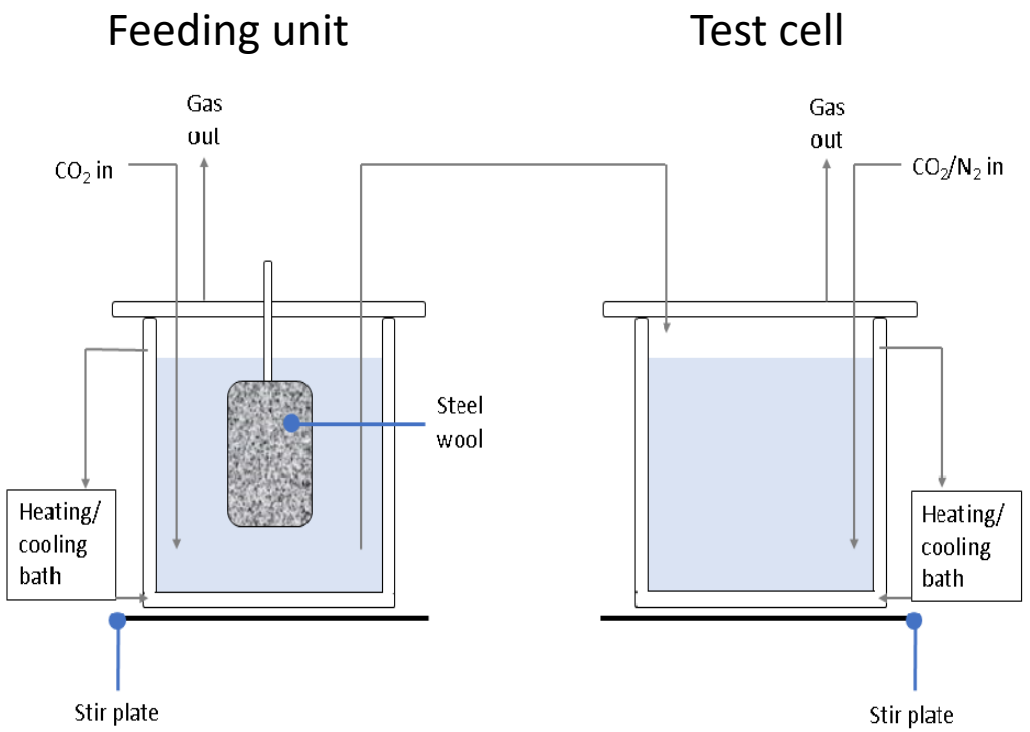
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$\downarrow \quad +$$
$$Fe \leftrightarrow Fe^{2+} + 2e^-$$
$$\downarrow \quad +$$
$$FeCO_3 + H^+$$
$$\downarrow$$
$$2H\ (adsorbed)$$

Questions to answer:

Can CO_2 corrosion of steel armor wires in the annulus of flexible pipes create an aqueous solution with high bicarbonate concentration that remains supersaturated with iron carbonate for a substantial length of time?
Can a protective siderite layer form on typical armor wire steels?
Is there an environmental condition that increases the possibility of SCC?

Annulus environment

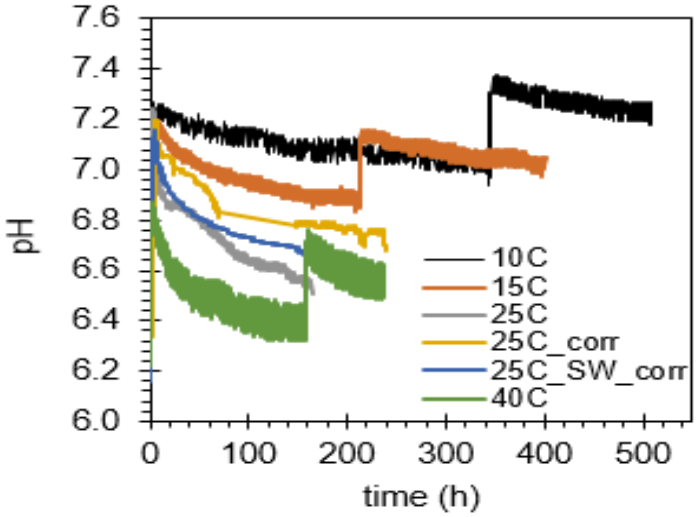
How is possible to mimic the annulus environment (↓V/S)?



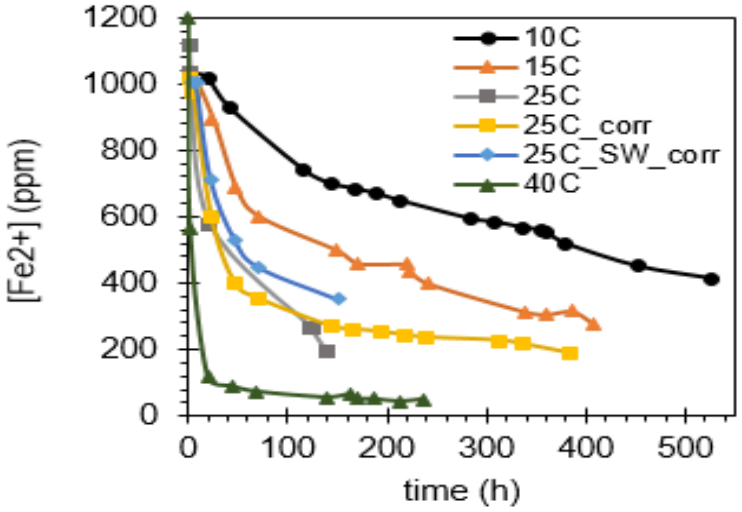
The setup

Test cell:
Temperature controlled: 10- 40 °C
Purged with CO_2 and N_2,
CO_2 partial pressure: 5, 10 kPa.
Continuous pH monitoring.
Sampling to analyse dissolved iron and alkalinity:
Initial $[Fe^{2+}]$: ~20 mmol/kg – ~1100 mg/kg,
stoichiometric alkalinity.
Electrochemical tests during 100-500 hours.

Annulus environment evolution

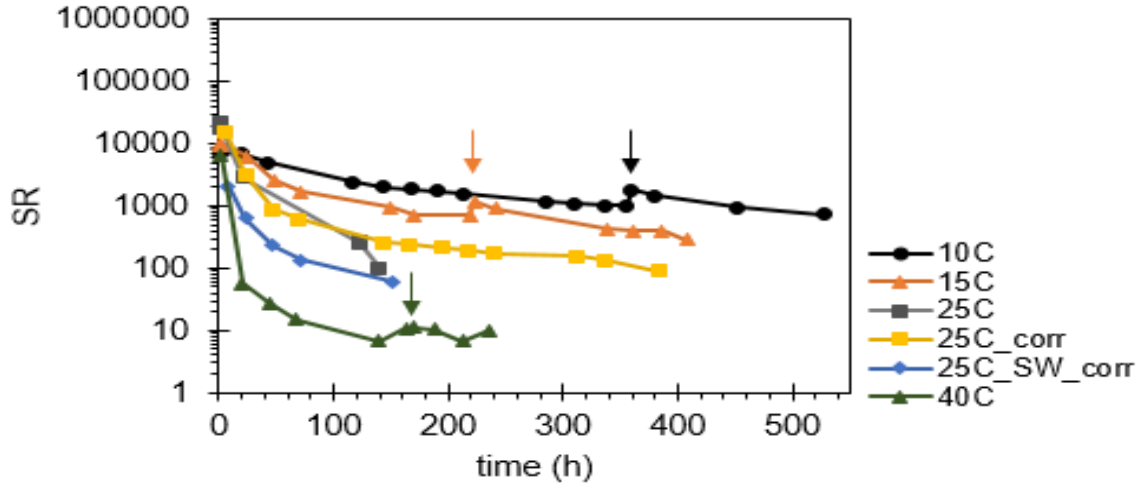


(a)



(b)

$$SR = \frac{a_{Fe^{2+}} \times a_{CO_3^{2-}}}{K_{sp}}$$

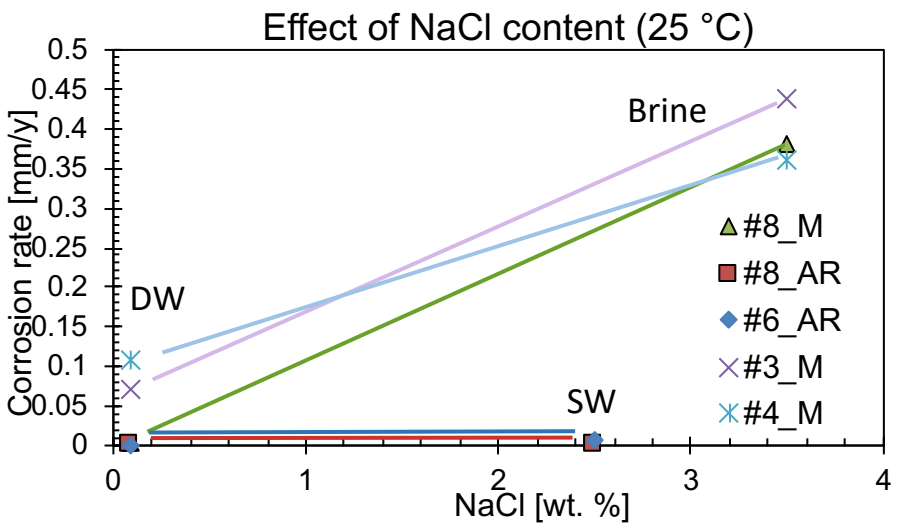


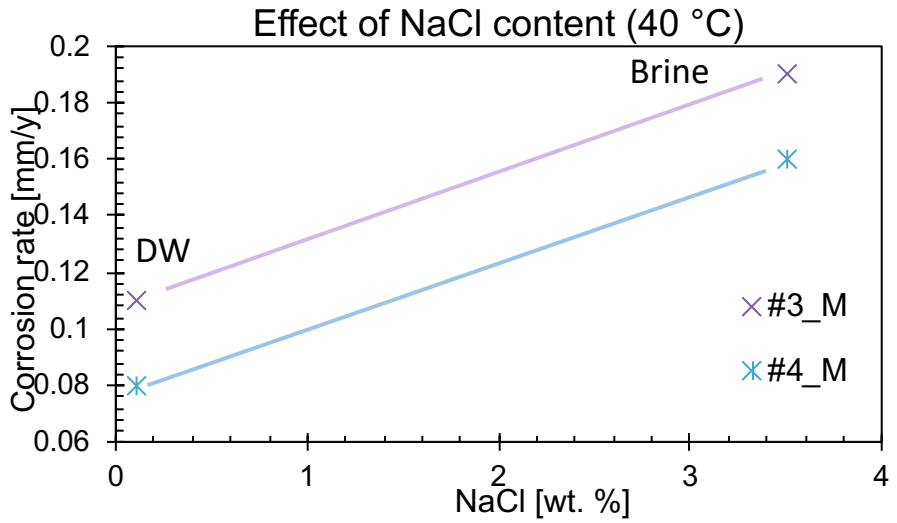
(c)

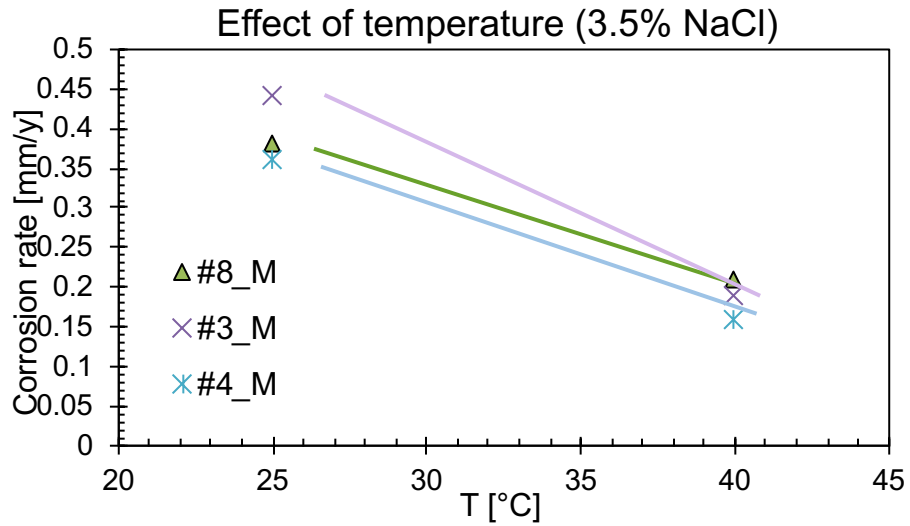
Bicarbonate cracking is raised as a possible degradation mechanism.

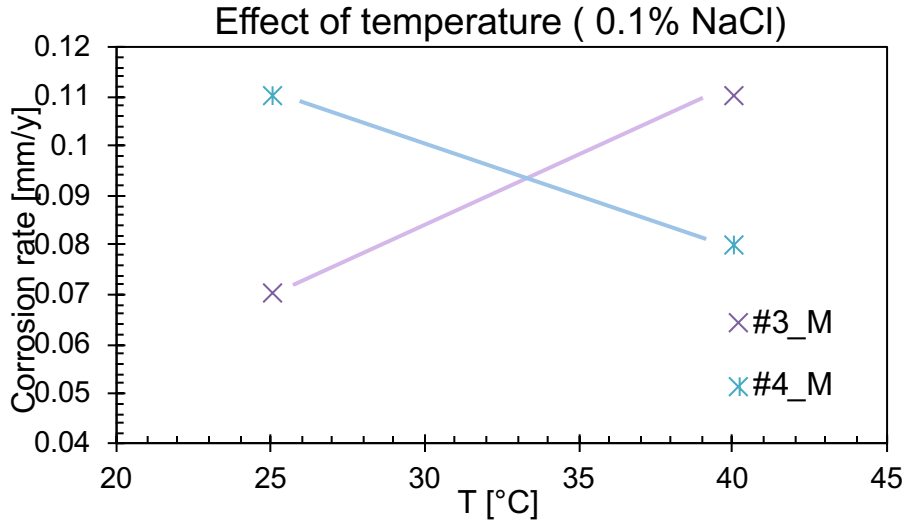
$$Fe + 2H_2CO_3 = Fe^{2+} + 2HCO_3^- + H_{2(g)}$$

Corrosion of armor steel at near-neutral pH

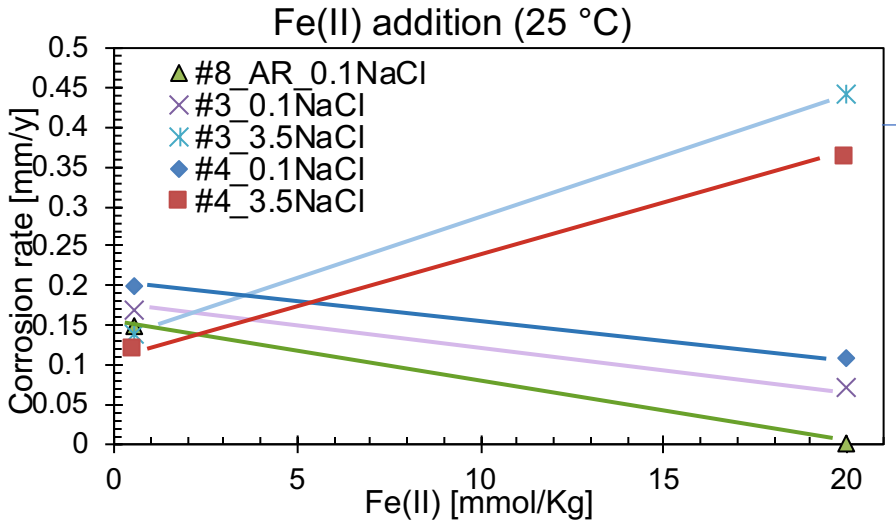


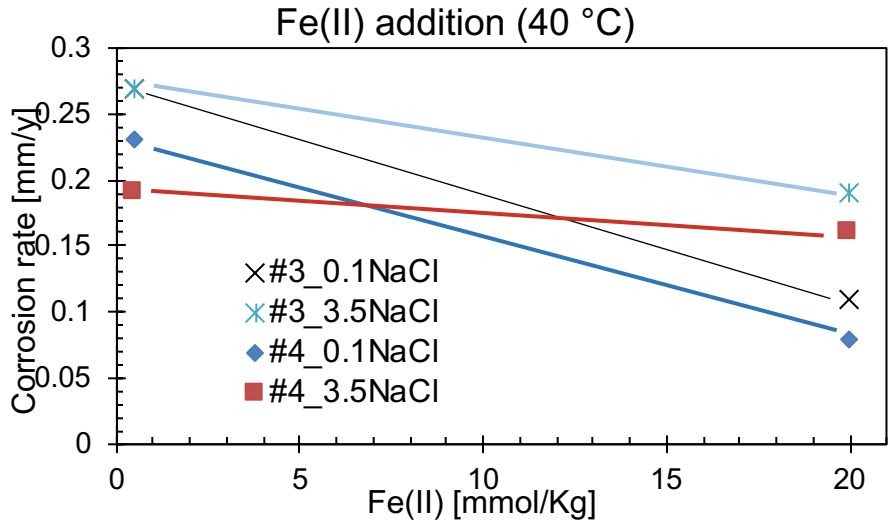






Corrosion of armor steel at near-neutral pH





Is that an indicative of localized corrosion?

Surface analysis

- #3M_3.5% NaCl_25 °C

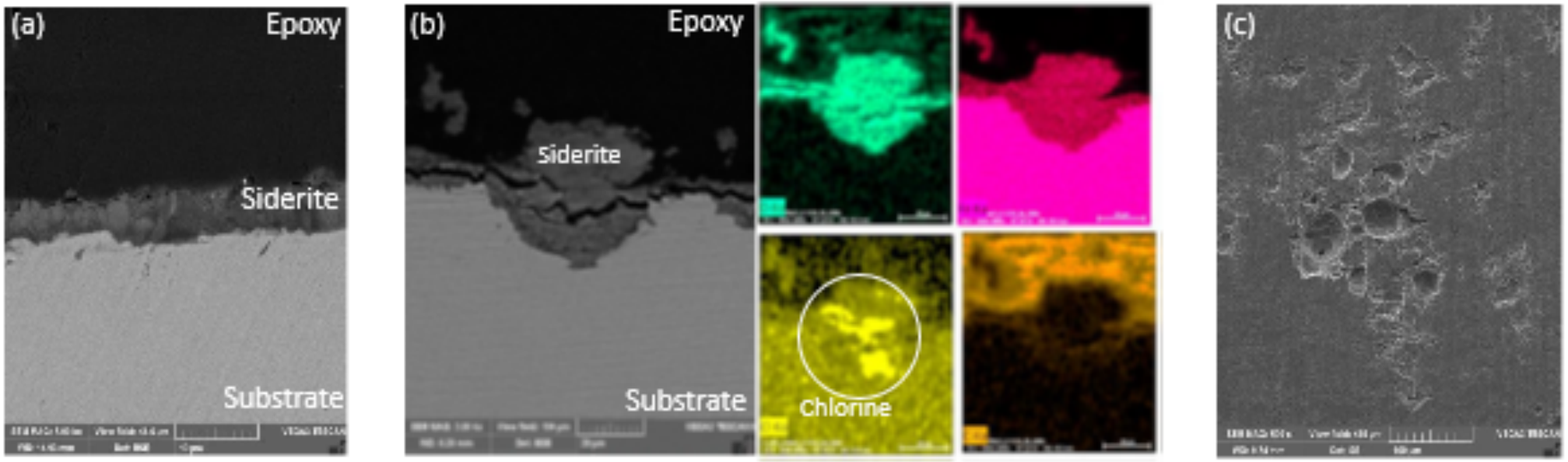
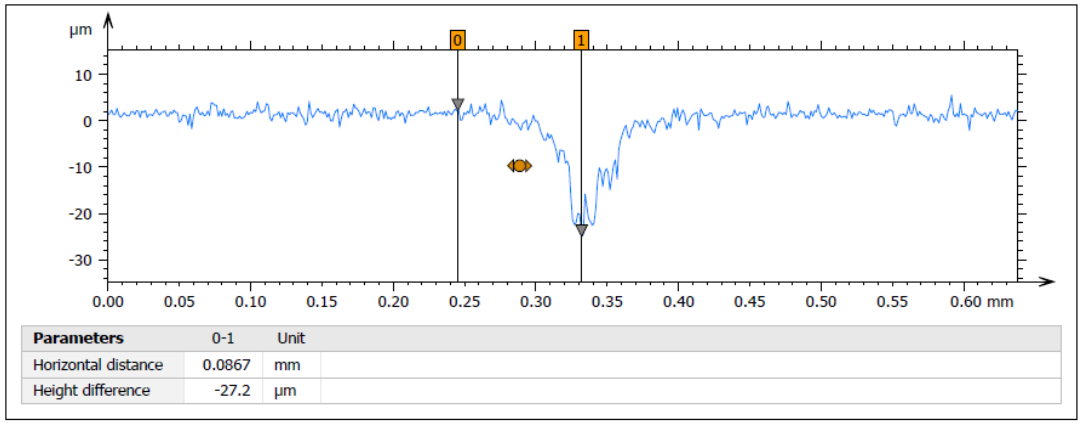


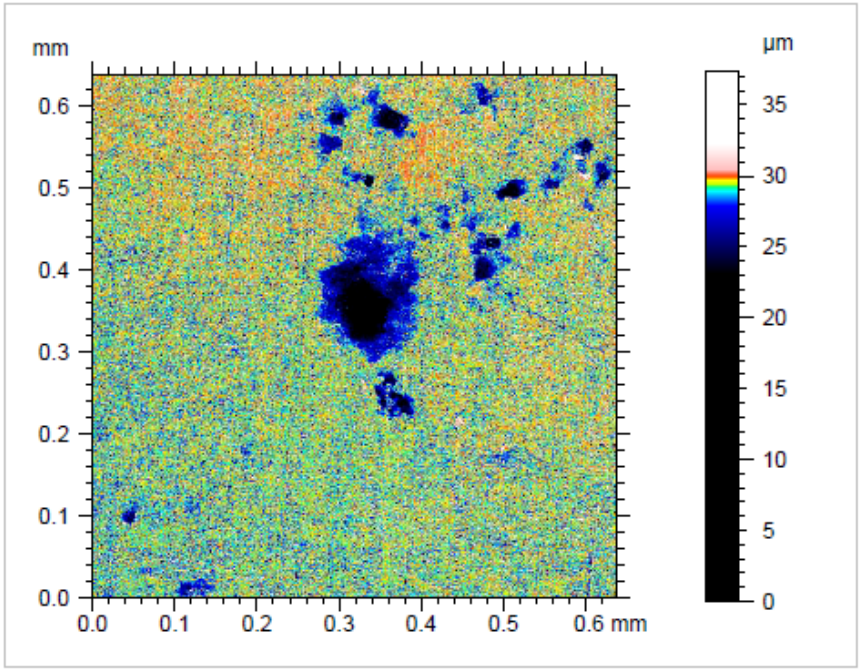
Fig.: *(a) Cross section image of corrosion film formed in 0.1 wt.% NaCl (b) cross section sample tested in 3.5 wt.% NaCl solution showing localized corrosion filled by siderite and the presence of chlorine element in corrosion tips and (c) stripped sample showing localized attack.*

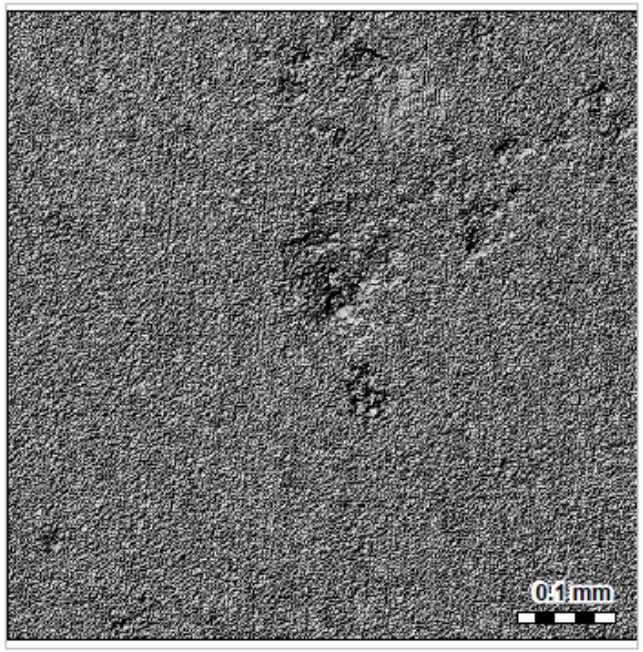
Surface analysis

- #3M_3.5% NaCl_25 °C



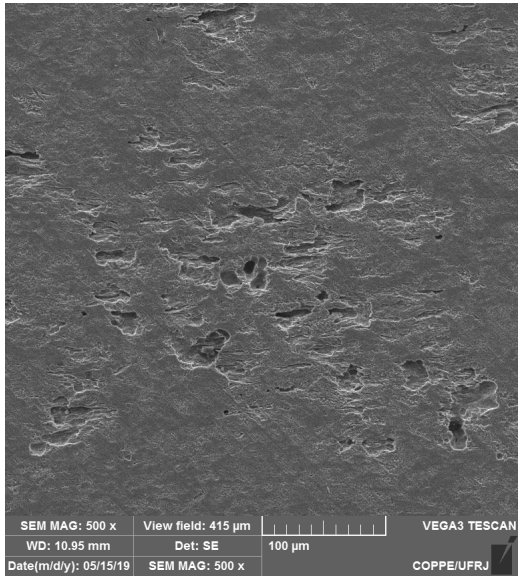
Parameters	0-1	Unit
Horizontal distance	0.0867	mm
Height difference	-27.2	µm

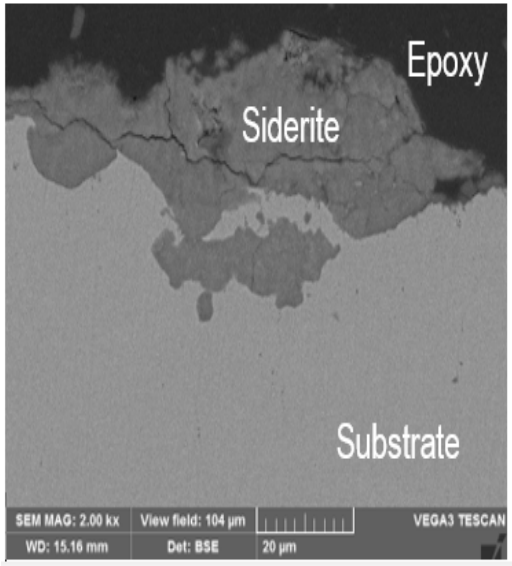




Surface analysis

- #4M_3.5% NaCl_25 °C





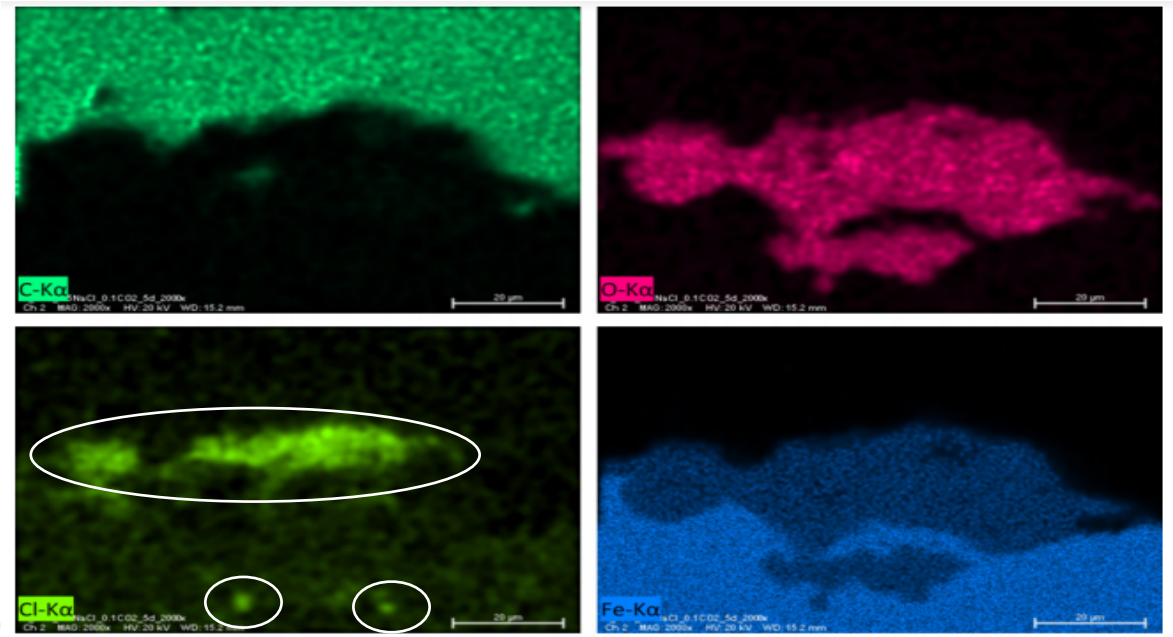


Fig.: SEM images of cross section sample showing localized attack filled by siderite and the presence of chlorine element on the top and in corrosion tips.

Backing to the questions

Can CO_2 corrosion of steel armor wires in the annulus of flexible pipes create an aqueous solution with high bicarbonate concentration that remains supersaturated with iron carbonate for a substantial length of time?	The saturation ratios (SR) of siderite can stay much higher than 1 and keep a near-neutral pH for long time, which can result in conditions for SCC occurrence.
Can a protective iron carbonate layer form on typical armor wire steels?	Protective corrosion product films formed fast even at room temperature in supersaturated environments, as encountered in annular space of flexible pipes. Fully protective films reducing the corrosion rate
Is there an environmental condition that increases the possibility of SCC?	According to the results, low temperatures and brine conditions gave elements that indicate increased risk of SCC.

Thank you.