Formation of Protective Iron Carbonate Films on Steel Pipeline

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Motivations

- CO_2 corrosion (sweet corrosion) is a significant problem for steel pipelines in the oil and gas production industry
- Sweet corrosion is caused by the dissolution of CO_2 in co-produced water
- Two opposing effects: dissolution accelerator (via the formation of a carbonic acid) and corrosion inhibitor (via the formation of a siderite film)
- Protective nature of the film depends on the conditions of its formation

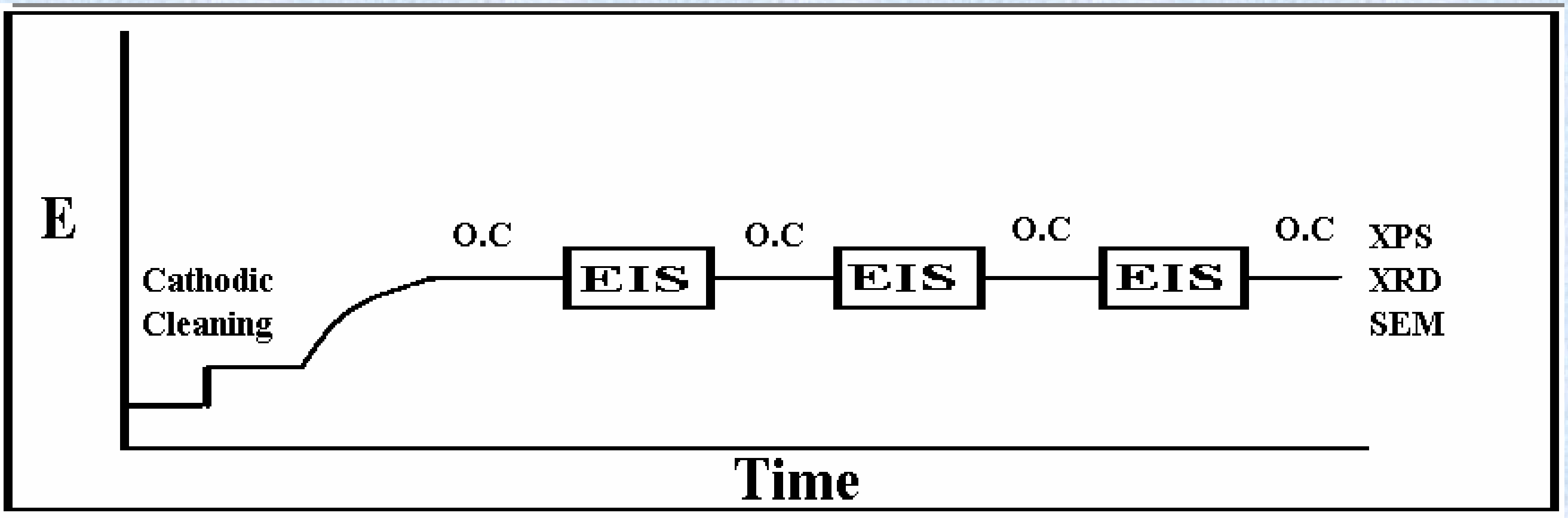
Experimental

Electrode: carbon steel cut from Edson mainline loop (from NRTC)

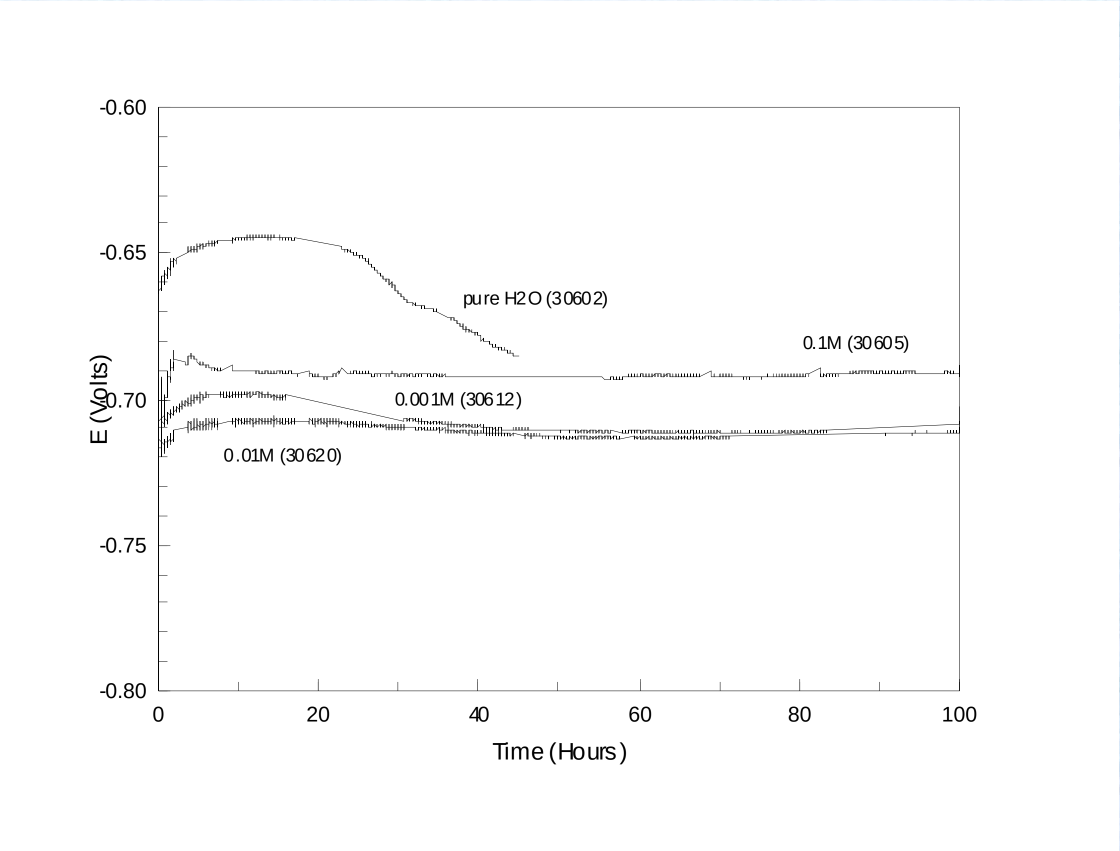
Solution: 0.1, 0.01, 0.001 mol/L $NaClO_4$ (+NaOH for pH adjustment)

Setup: two-side-arm cell deaerated with CO_2 at atmospheric pressure

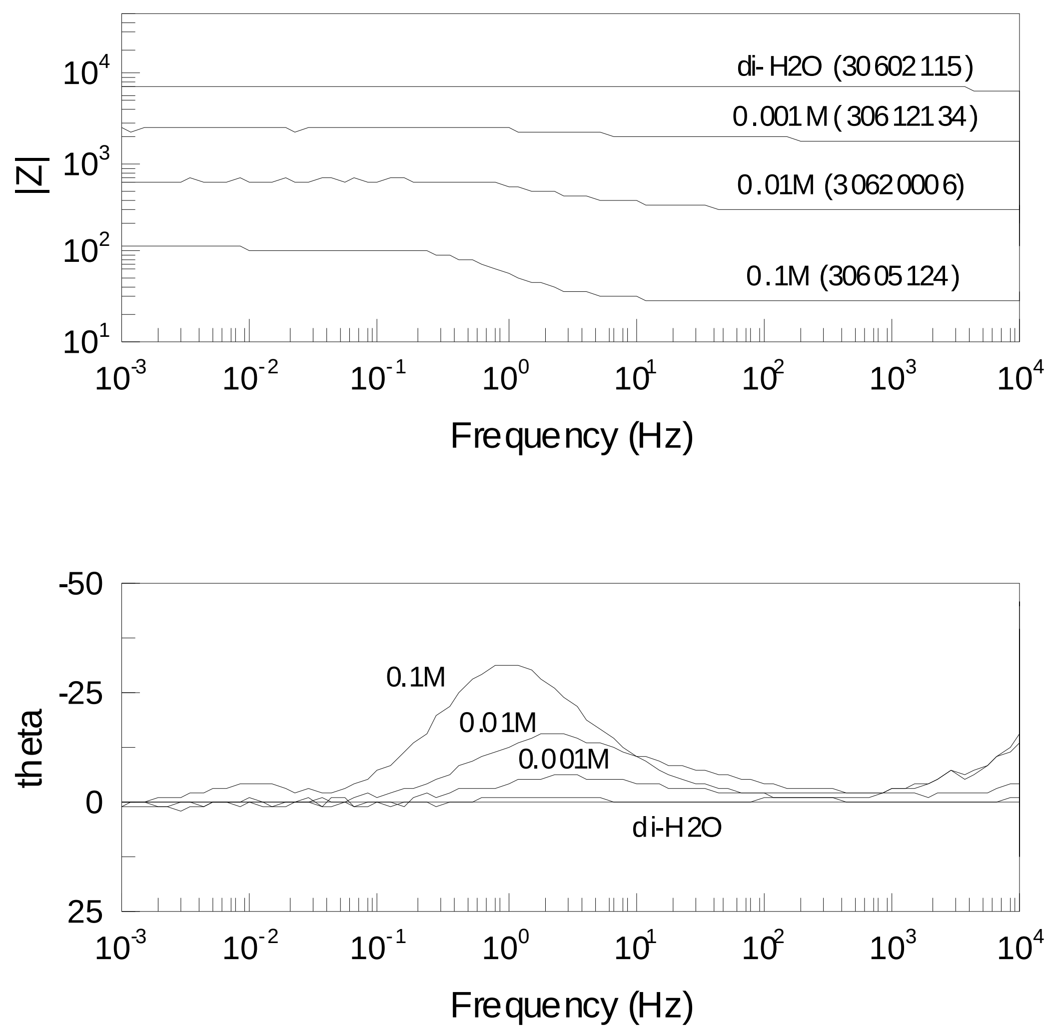
Procedures:



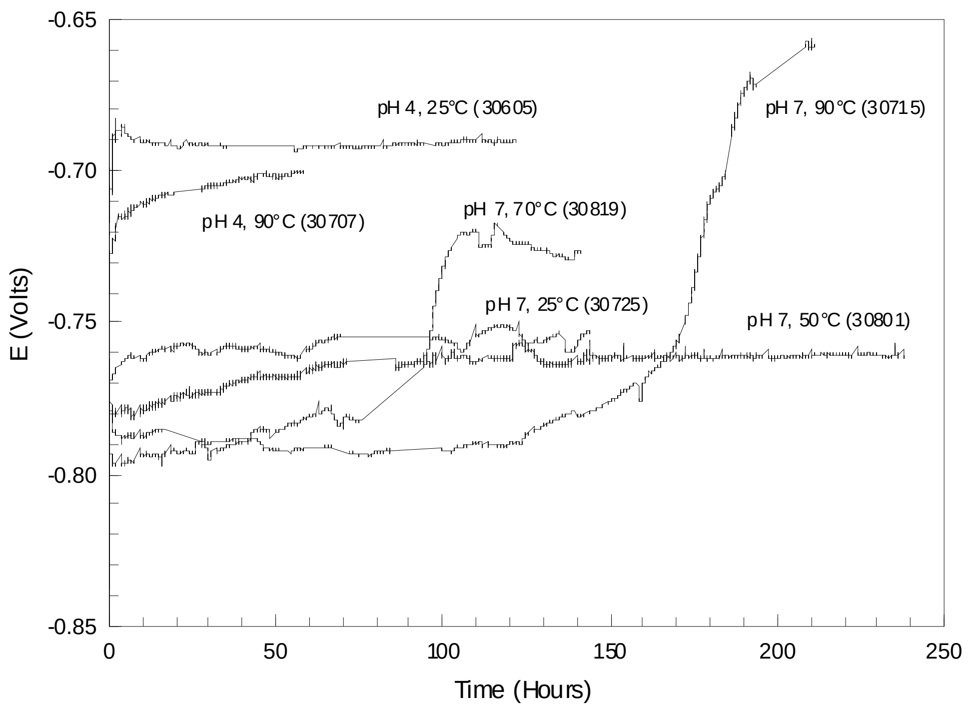
Is a supporting $NaClO_4$ electrolyte necessary?



Solution	0.1M $NaClO_4$	0.01M $NaClO_4$	0.001M $NaClO_4$	Deionized H_2O
Initial pH	3.755	3.756	3.840	3.796
Final pH	4.820	4.484	4.718	4.309
R_S (Ω)	28	290	1735	6192



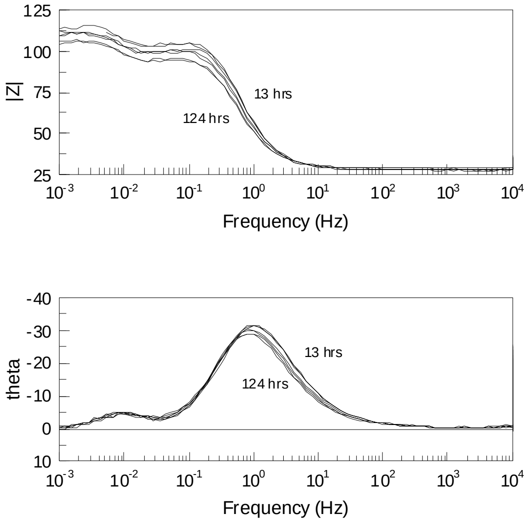
- The impedance magnitude increases and the maximum phase angle decreases with decreased concentrations
- EIS is dominated by R_s and little interfacial information is revealed in dilute solutions (< 0.01M)



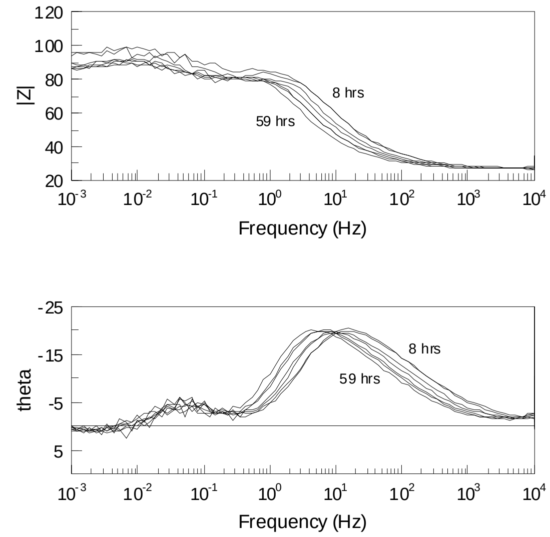
- pH ↑, E_{corr} ↓
  T ↑, E_{corr} ↓
- $E^e_C < E_{corr} < E^e_A$
- The sudden jump in E_{corr} in the neutral solutions at 70 and 90°C may indicate changes in the balance of corrosion kinetics

Conditions	$E^e_{H^+\|H}$	$E^e_{Fe\|Fe^{++}}$	E_{corr}
pH = 3.755 – 4.820, 25°C	-0.526	-0.740	-0.691 ± 0.003
pH = 3.555 – 5.209, 90°C	-0.616	-0.781	-0.706 ± 0.006
pH = 7.066 – 6.974, 25°C	-0.653	-0.867	-0.758 ± 0.003
pH = 6.991 – 7.017, 50°C	-0.690	-0.886	-0.765 ± 0.005
pH = 7.062 – 7.658, 70°C	-0.762	-0.942	-0.788 ± 0.005 (≤ 72h)
pH = 7.034 – 7.418, 90°C	-0.774	-0.940	-0.790 ± 0.003 (≤ 124h)

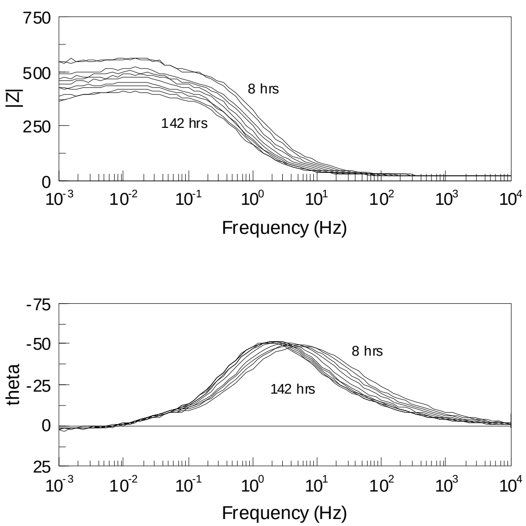
pH 4, 25°C (30605)



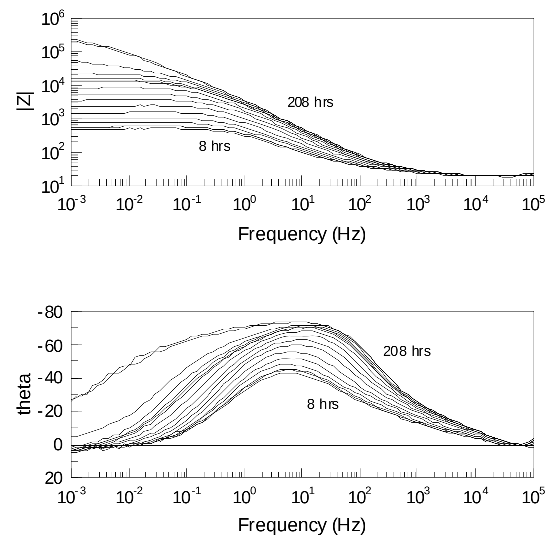
pH 4, 90°C (30707)



pH 7, 25°C (30725)



pH 7, 90°C (30715)



Methods to calculate polarization resistance R_p

Extrapolation

$$R_p = \lim_{\omega\to 0}|Z| - \lim_{\omega\to\infty}|Z|$$

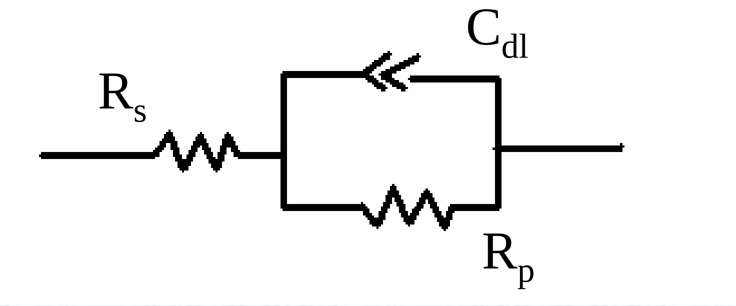
Tangential approximation

$$R_P \cong 2|Z_m|\tan\phi_{\max}$$

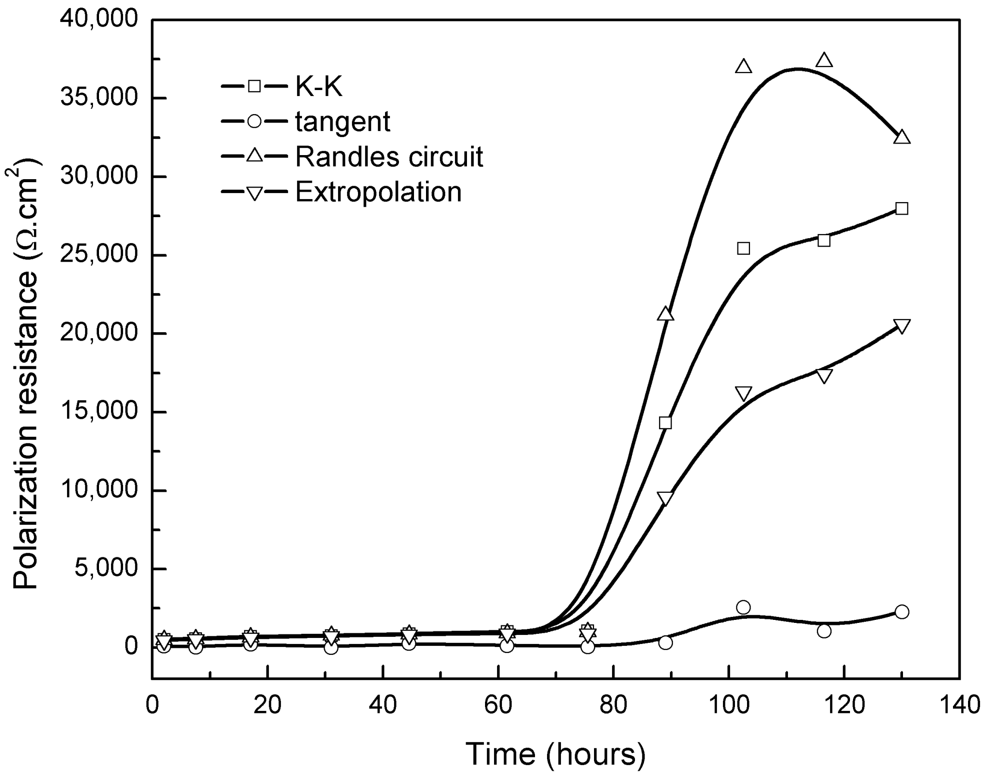
Kramers-Kronig transform

$$R_P \cong 2.932\left|\int_{\log\omega_m}^{\infty} \mathrm{Im}[Z(\omega)]\,d\log\omega\right|$$

Equivalent circuit



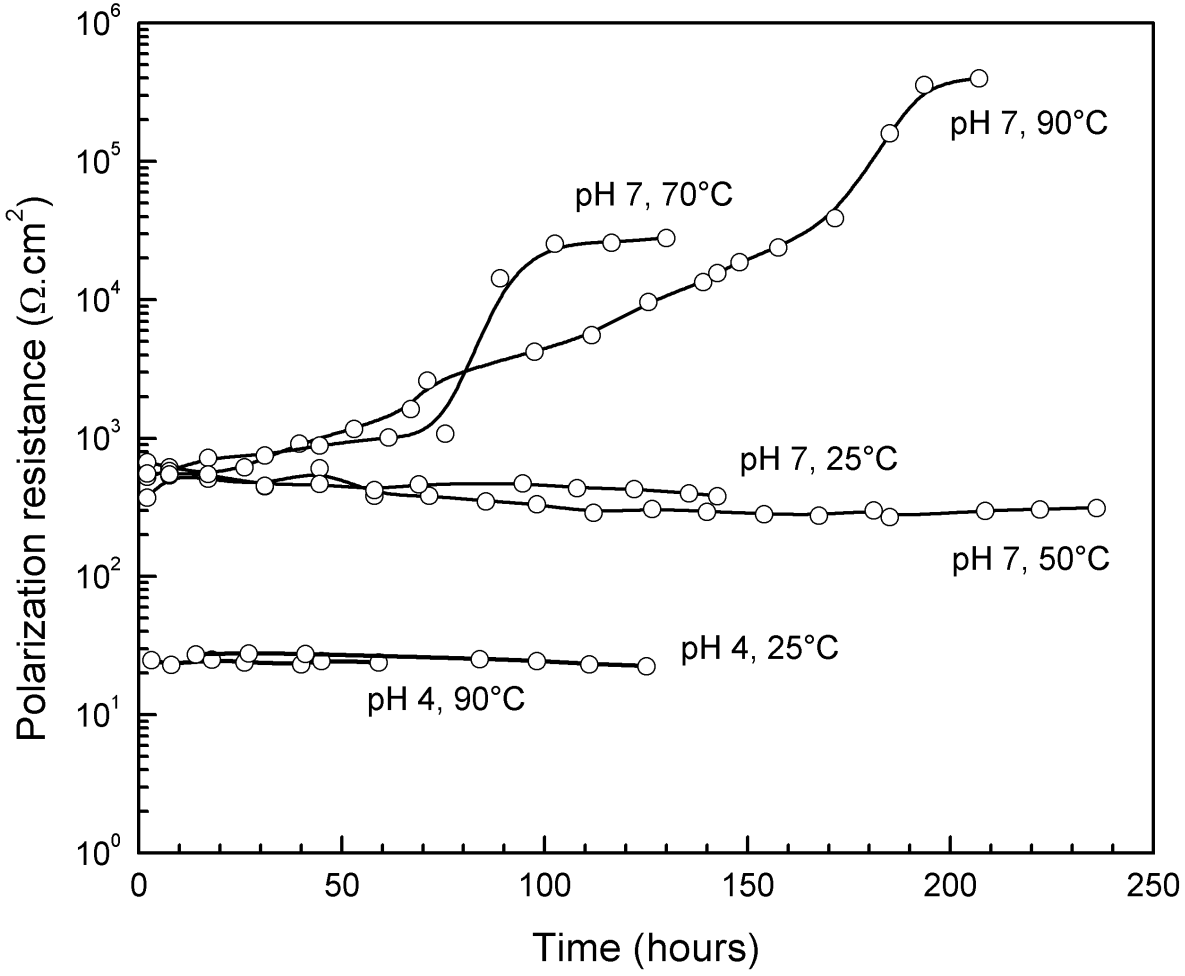
R_p calculated from the same set of EIS



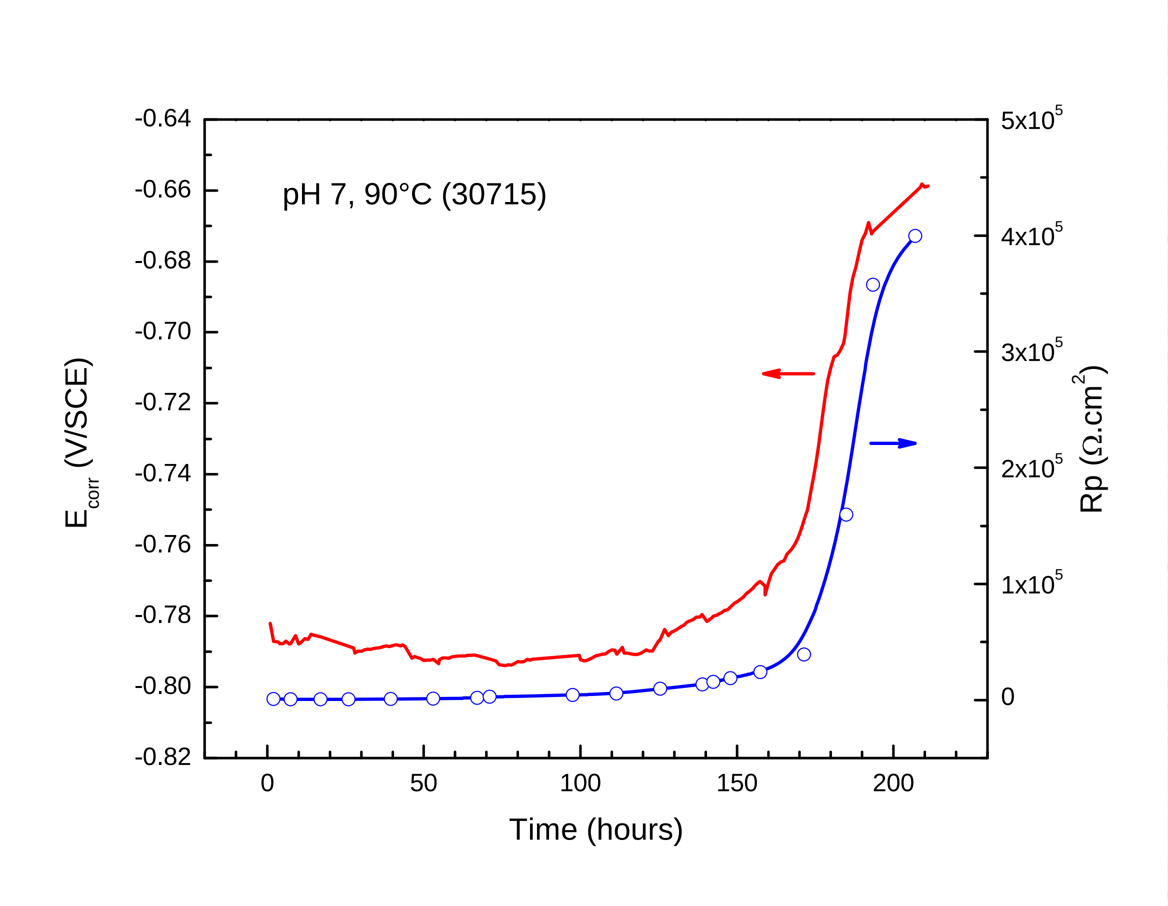
(b)

- ❖ Too low R_p values from Tangential approximation
- ❖ R_p given by K-K approximation in between those by the extrapolation and equivalent circuit

R_p calculated by K-K for various conditions

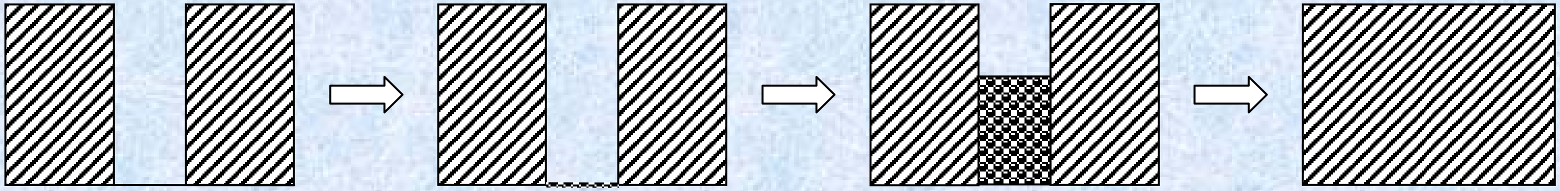


Formation of a protective film



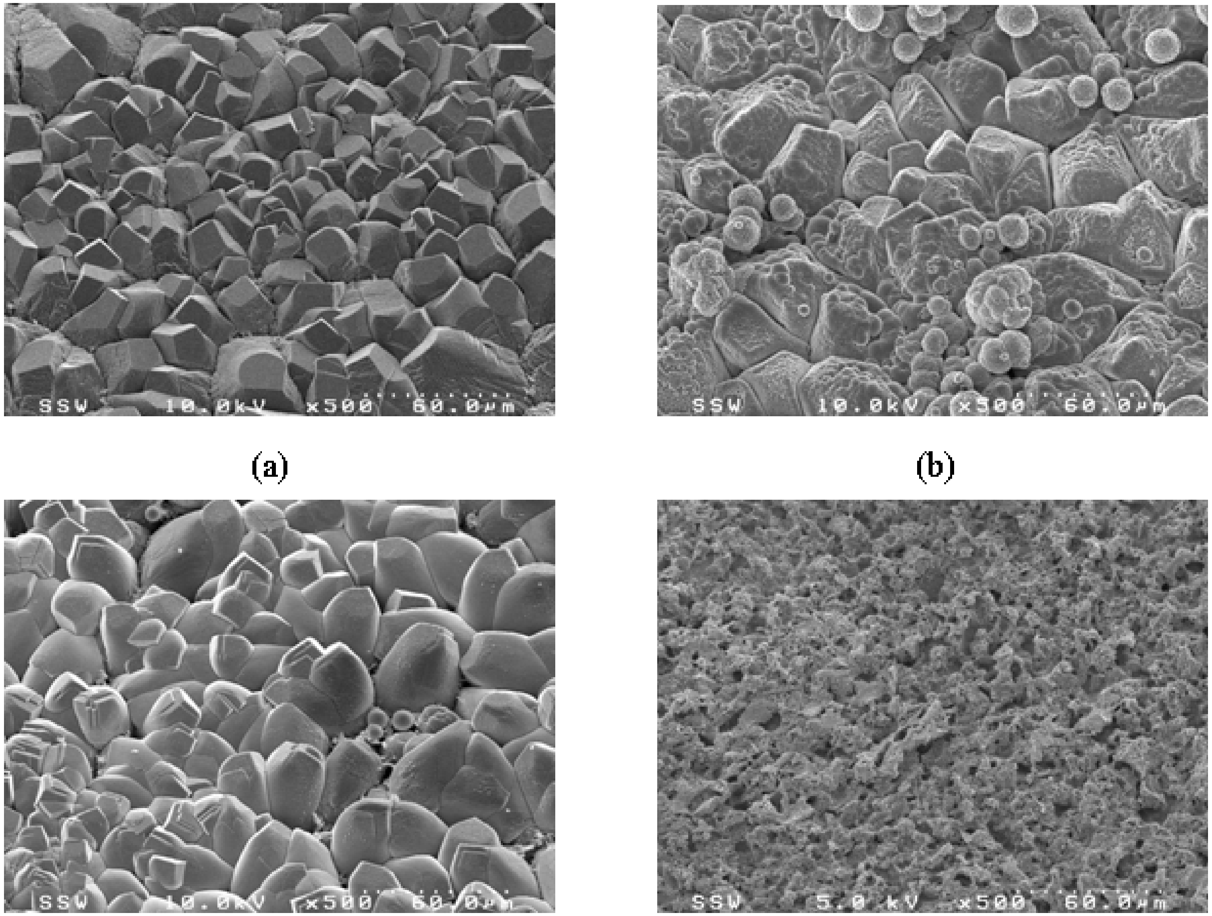
- The abrupt increase in R_p indicates the formation of a protective film that mitigates corrosion
- The increase in E_{corr} at the same time could attribute to switching the galvanic couplings

Formation mechanism of protective films



- Precipitation of $FeCO_3$ would first form a porous film, and R_p is dominated by the low resistances in pores
- Precipitation then more likely occurs at the bottom of the pores
- The turning point in R_p could be the indication of virtually sealing film porosity. Then R_p becomes film resistance dominated
- The sealing layer might be very thin at first, but will grow until the whole length of pores are filled

SEM images after immersion



(a) (b) (c) (d)

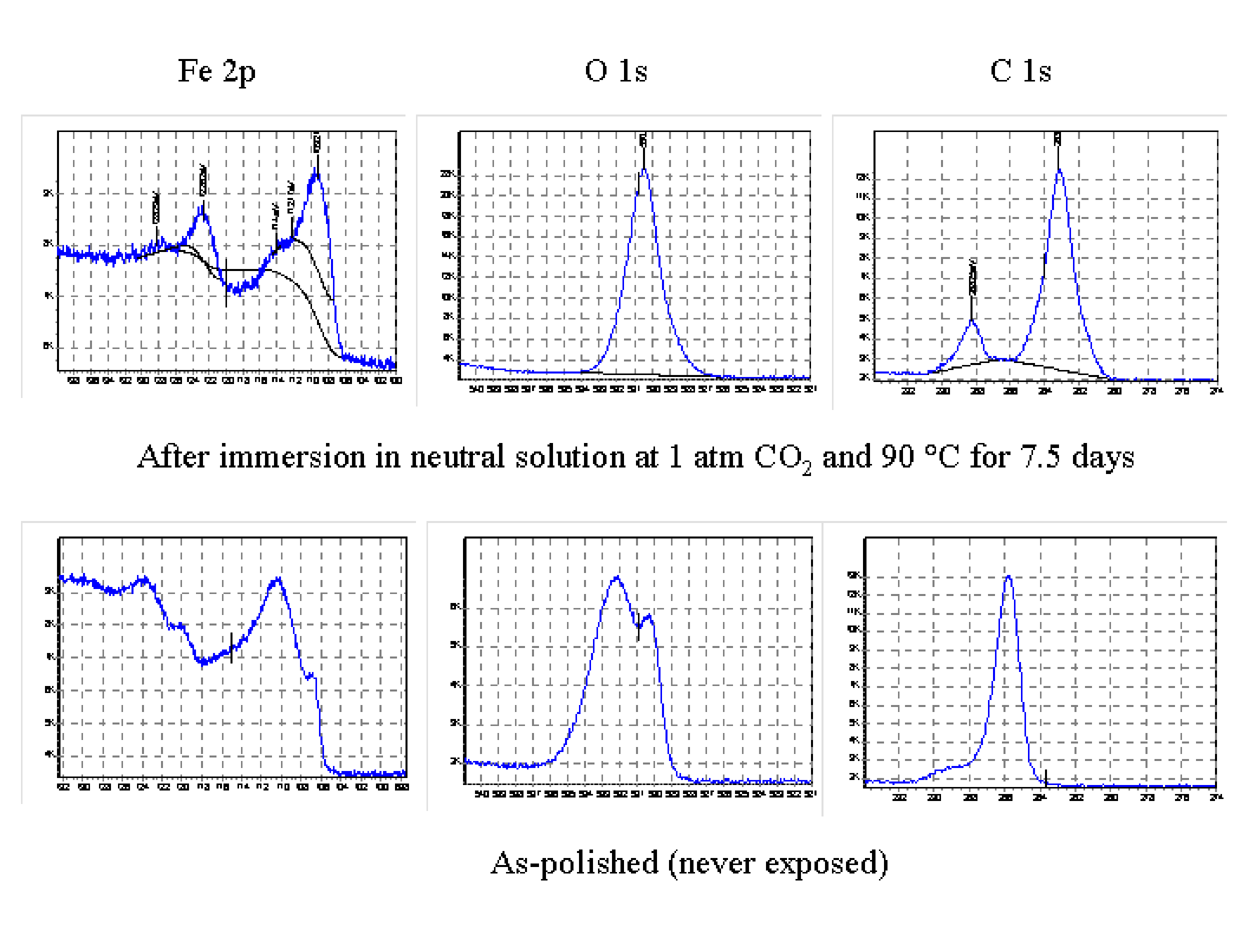
a. pH~7,90°C

b. pH~7,70°C

c. pH~7,50°C

d. pH~4,90°C

XPS confirmed siderite film on the surface of the immersed specimen

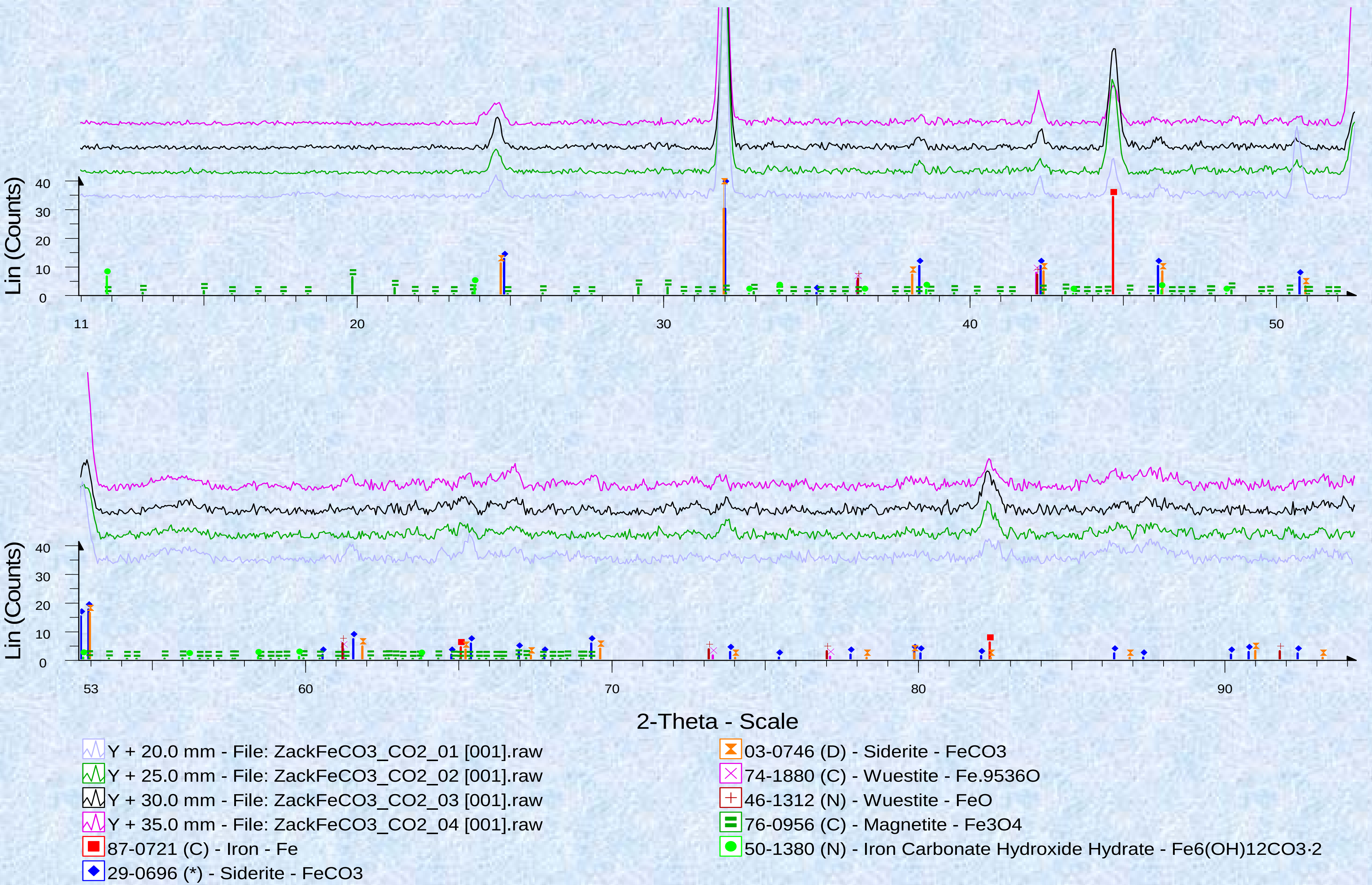


Peak	C1s	O1s	$Fe2p_{3/2}$	$Fe2p_{3/2}$ satellite	$Fe2p_{1/2}$
This study	289.5	531.9	710.7	715.4	724.0
Siderite*	289.4	531.9	710.2	714.9	723.7

* J. K. Heuer and J. F. Stubbins, Corrosion Science, 41 (1999), 1231-1243

LIST OF MATCHING PHASES

XRD Analysis



Conclusions

- A protective siderite film is formed in neutral solutions and temperatures higher than 70°C
- The transitions in R_p and E_{corr} indicate the formation of a protective film
- Precipitates of $FeCO_3$ would first form a porous film where corrosion continues at the base of pores. The film will become protective when the pores are sealed by thin $FeCO_3$ layers at the bases, since then corrosion has to proceed through the passive layer