Saba Navabzadeh Esmaeely

Ohio University
Institute for Corrosion and Multiphase Technology

Effect of Calcium Ion on the Formation and Protectiveness of Iron Carbonate Layer in CO_2 Corrosion

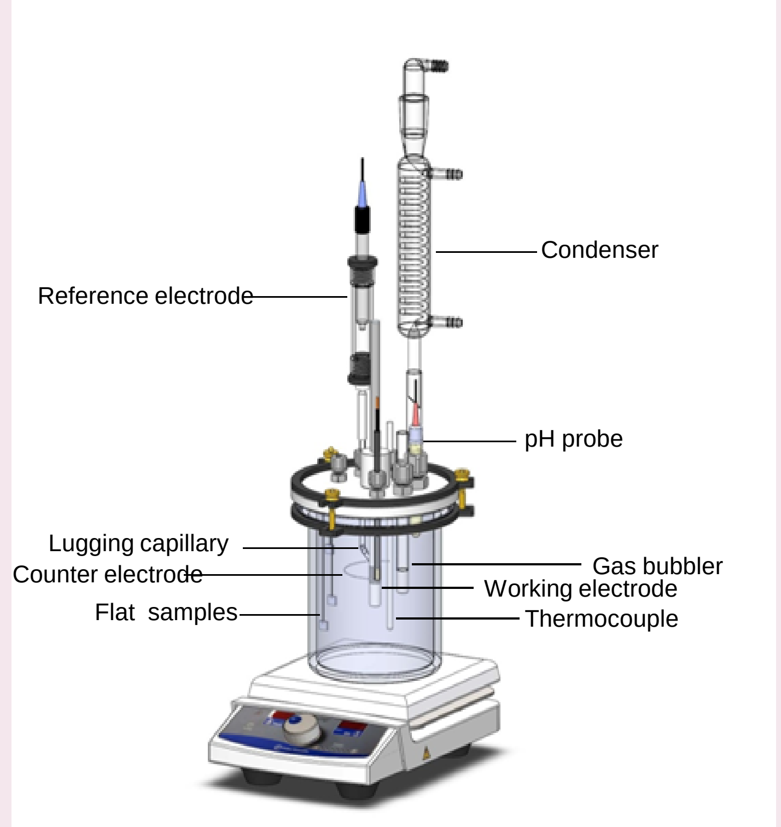
Introduction

In the oil and gas industry, CO_2 corrosion has been widely studied over several decades. However, simulated conditions in the laboratory have typically employed pure NaCl electrolytes. This overlooks the fact that brine chemistry of formation water is important due to the potential for cations dissolved therein to compete with Fe^{2+} in the formation of carbonate-type corrosion products and scale. In addition to changing the $FeCO_3$ morphology, compositional heterogeneity within the scale will be expected. Brines usually have a high concentration of Ca^{2+}. Therefore, the system will be saturated with respect to $CaCO_3$ precipitation and it will be deposited on a corroding steel surface. The presence of $CaCO_3$ or mixture with $FeCO_3$ would affect types of corrosion (uniform or localized). Results from this research will be applicable in CO_2 enhanced oil recovery (EOR) as well as injection of CO_2 into deep saline aquifers for CO_2 sequestration. The reported results are for a preliminary study relating to low pressure CO_2 corrosion.

Objective

Study the effect of Ca^{2+} on formation and protectiveness of $FeCO_3$ on casing steel as well as its potential to facilitate localized corrosion.

Experimental Setup/Details



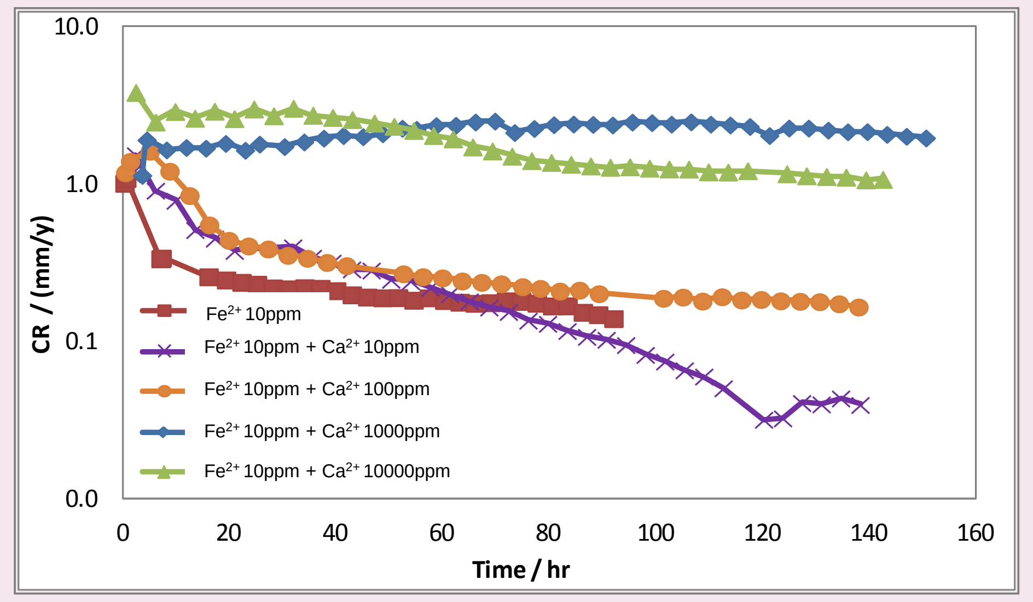
Parameters	Condition
Total / CO_2 Pressure	1 / 0.52 bar
Temperature	80 °C
Condition	Static
Electrolyte	1 wt.% NaCl
Initial [Fe^{2+}] / ppm	10 ppm
Initial [Ca^{2+}] / ppm	0,10,100,1000,10000
Initial pH*	6.6 (± 0.1)
Material	Carbon steel 1018
Duration	4 to 7 days

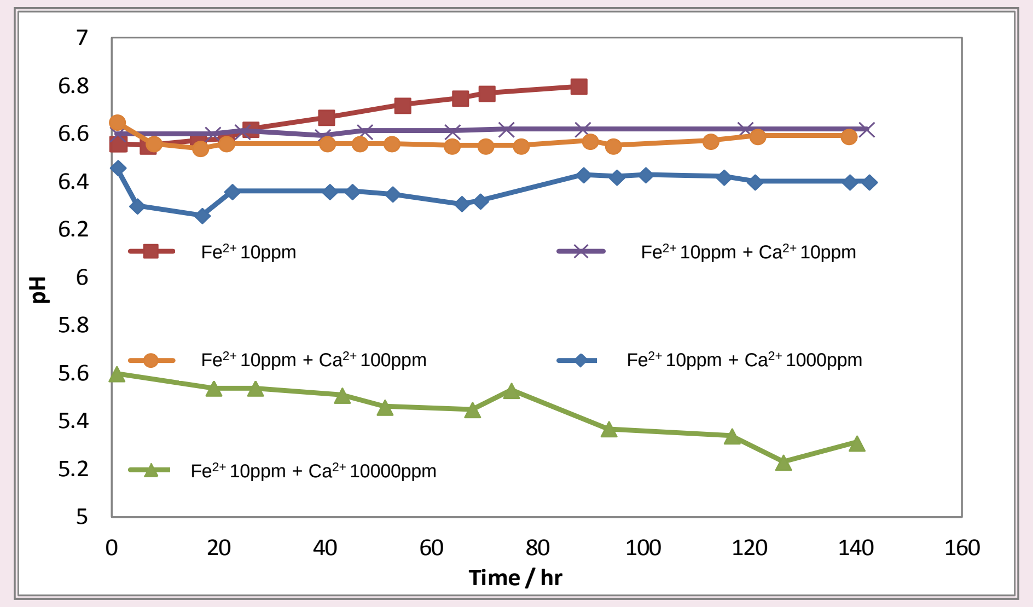
* Prior to $FeCl_2$ & $CaCl_2$ addition.

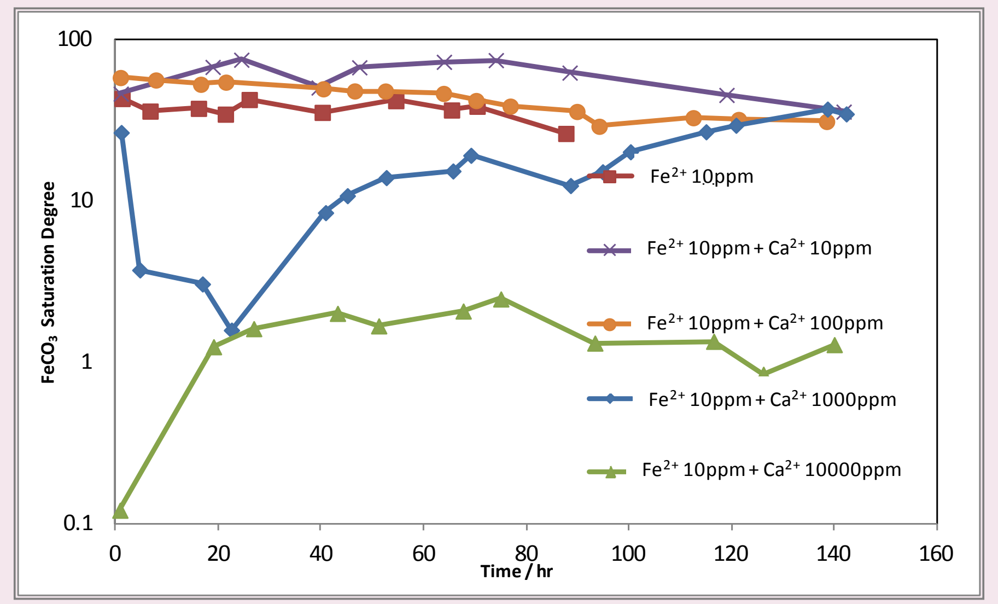
Hypotheses

- High concentration of Ca^{2+} results in compositional heterogeneity, this yields a less protective corrosion product scale.
- High concentration of Ca^{2+} in the presence of aqueous CO_2 will result in a casing surface covered by $CaCO_3$, which is ~2 orders of magnitude more soluble than $FeCO_3$. Due to the variable pH environments that will result when CO_2 is injected, this $CaCO_3$ layer won't be as persistent and protective as $FeCO_3$ and there will be the possibility of severe uniform or localized corrosion.

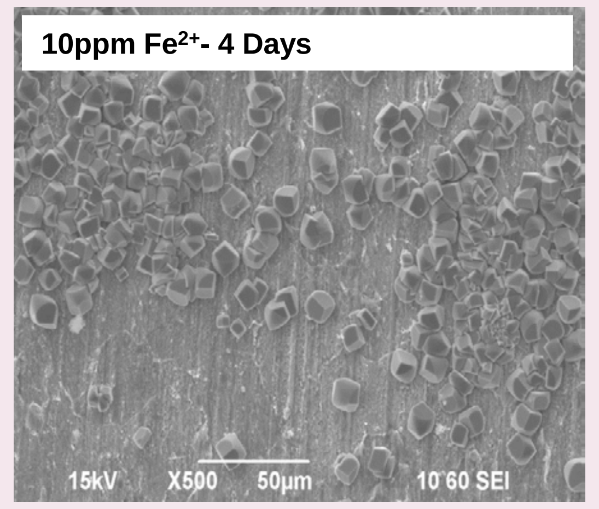
Experimental Results

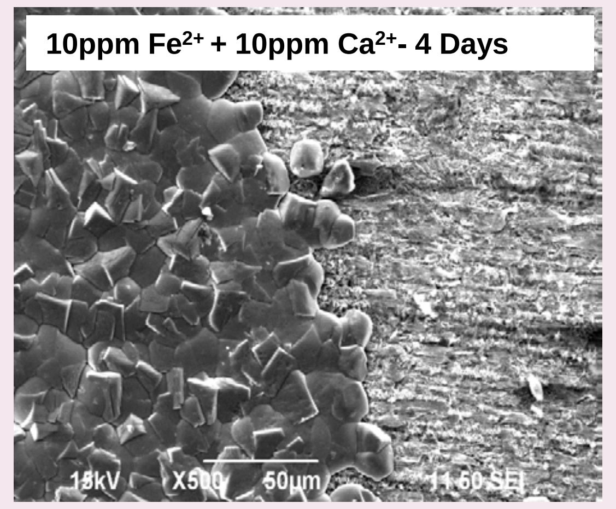


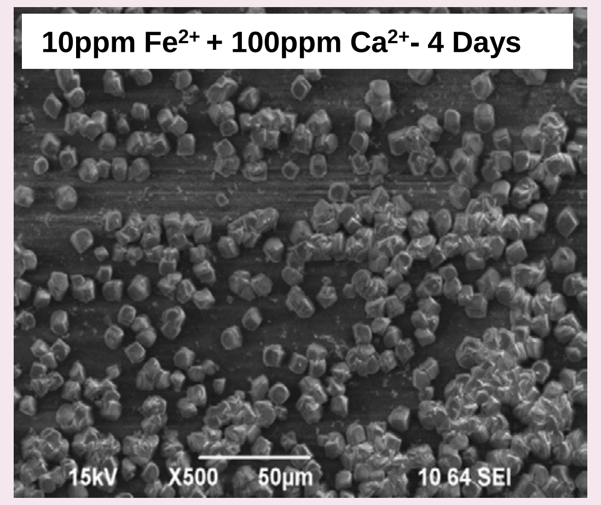


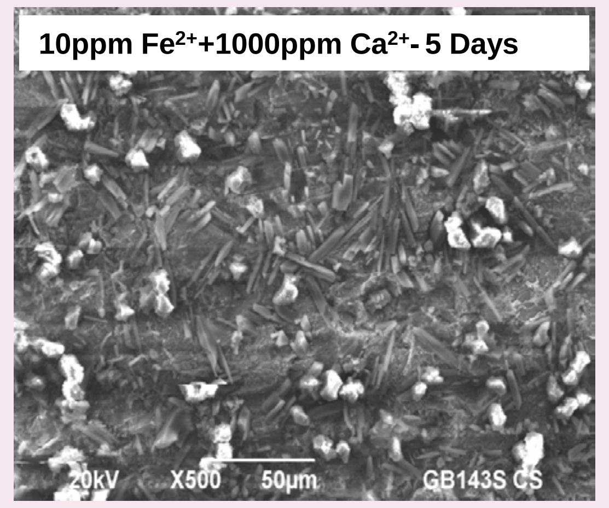


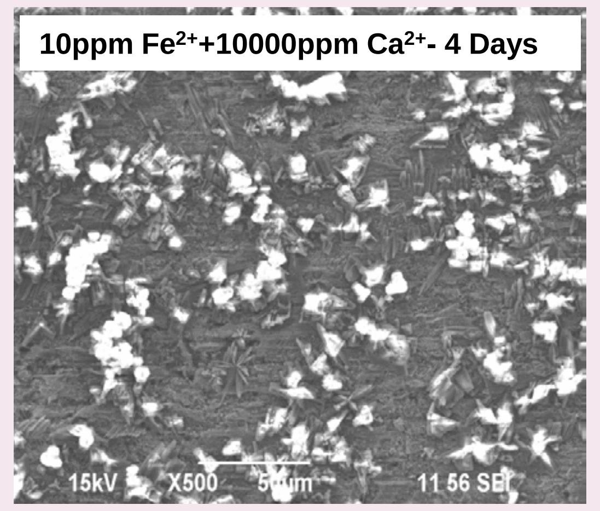
Corrosion Product Characterization with Increasing Ca^{2+} Concentration

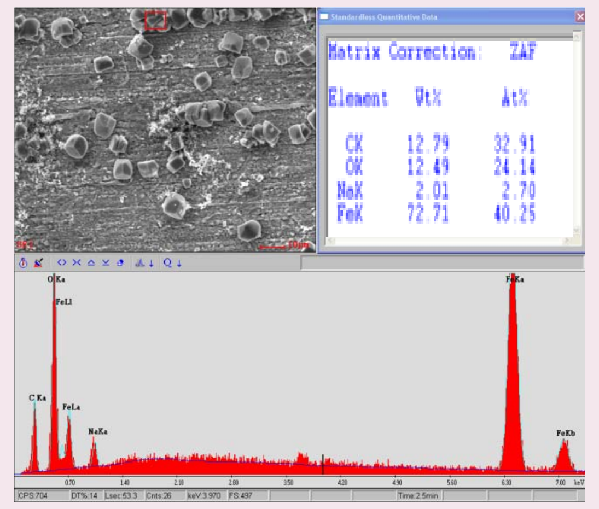

10ppm Fe^{2+}- 4 Days


10ppm Fe^{2+} + 10ppm Ca^{2+}- 4 Days

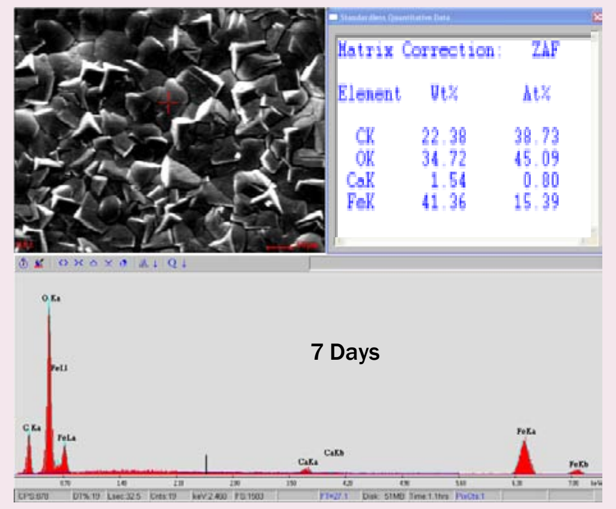

10ppm Fe^{2+} + 100ppm Ca^{2+}- 4 Days


10ppm Fe^{2+}+1000ppm Ca^{2+}- 5 Days

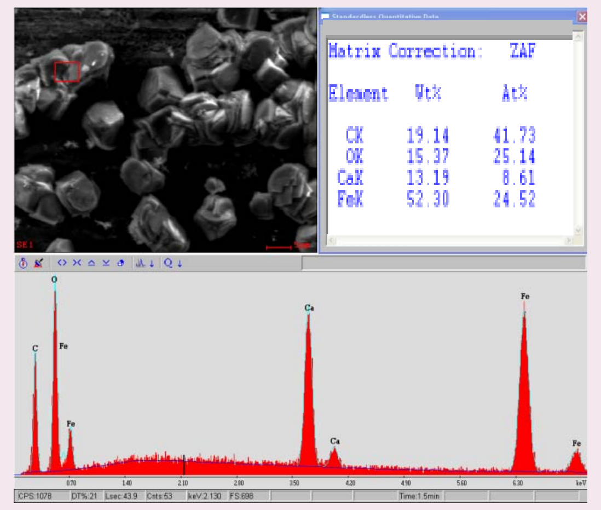

10ppm Fe^{2+}+10000ppm Ca^{2+}- 4 Days


Matrix Correction: ZAF

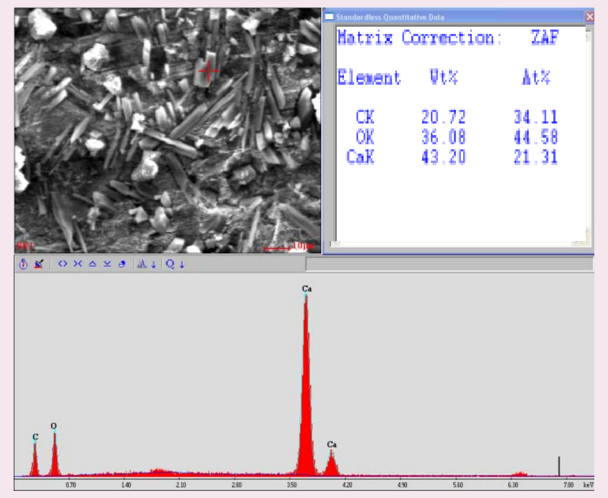
Element	Wt%	At%
CK	12.79	32.91
OK	12.49	24.14
NaK	2.01	2.70
FeK	72.71	40.25


Matrix Correction: ZAF

Element	Wt%	At%
CK	22.38	38.73
OK	34.72	45.09
CaK	1.54	0.80
FeK	41.36	15.39


Matrix Correction: ZAF

Element	Wt%	At%
CK	19.14	41.73
OK	15.37	25.14
CaK	13.19	8.61
FeK	52.30	24.52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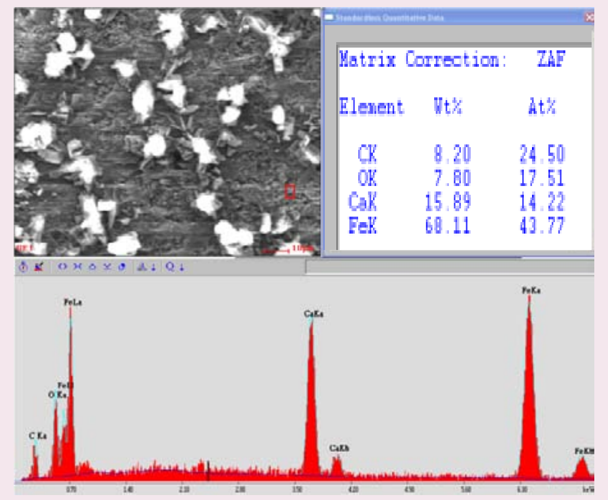
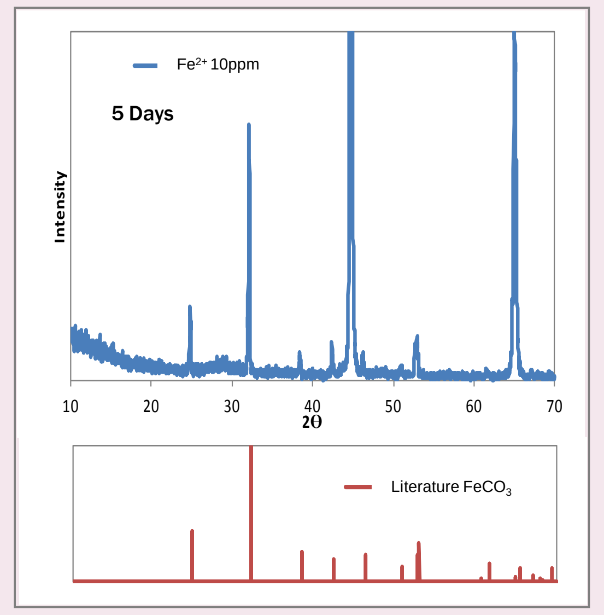
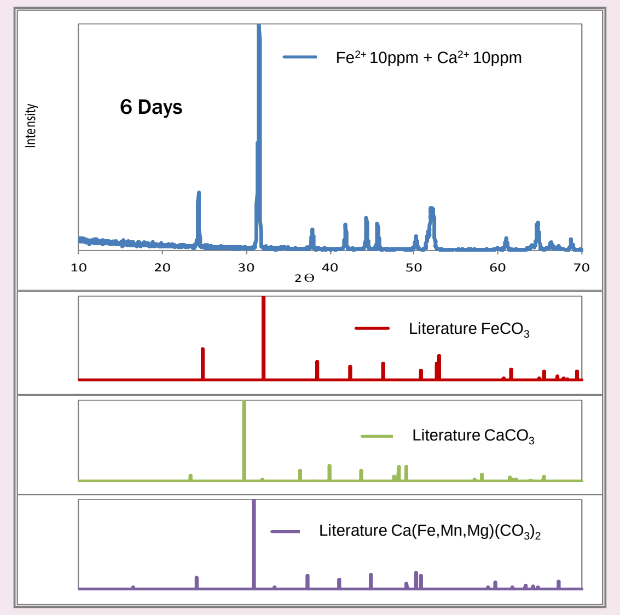
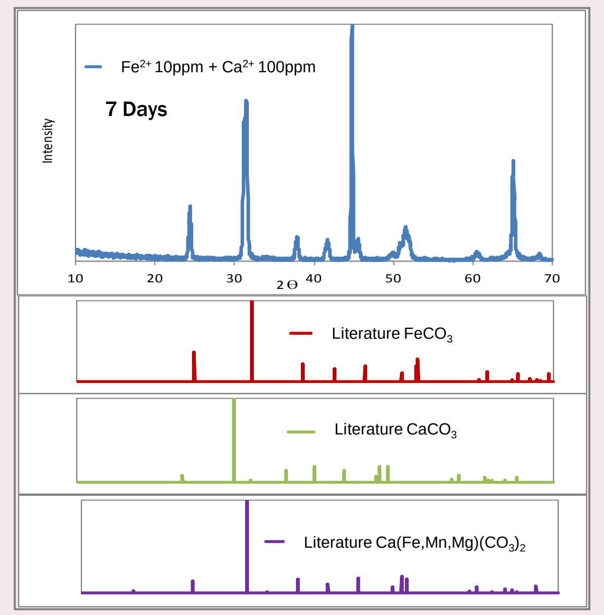
Element	Wt%	At%
CK	20.72	34.11
OK	36.08	44.58
CaK	43.20	21.31

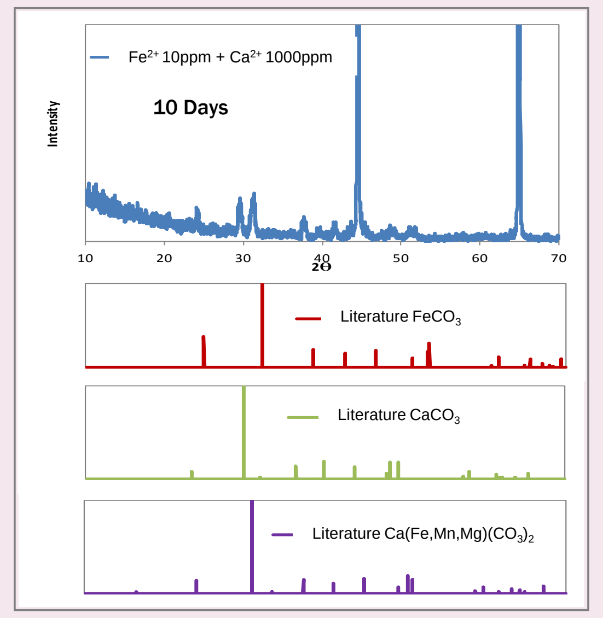

Matrix Correction: ZAF

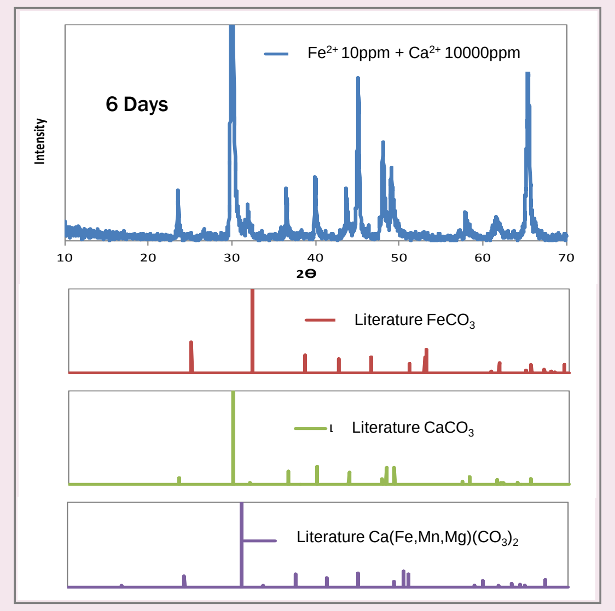
Element	Wt%	At%
CK	8.20	24.50
OK	7.80	17.51
CaK	15.89	14.22
FeK	68.11	43.77



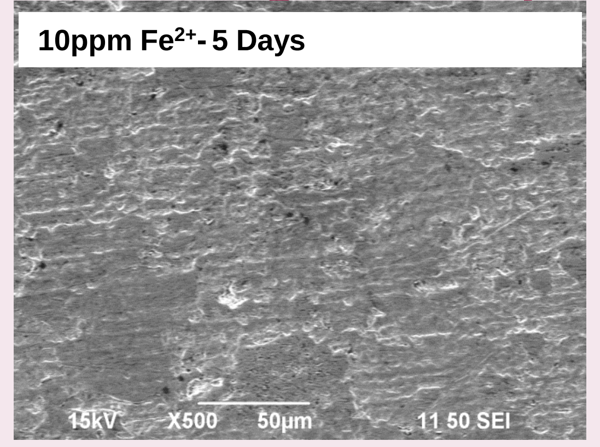


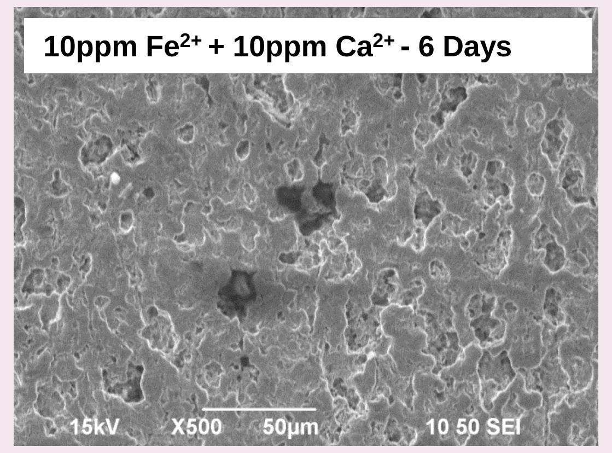


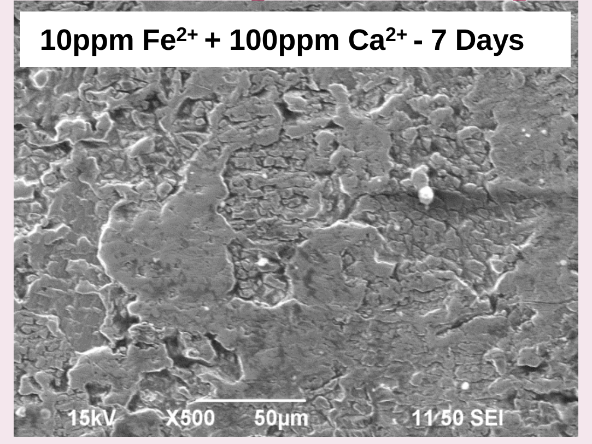


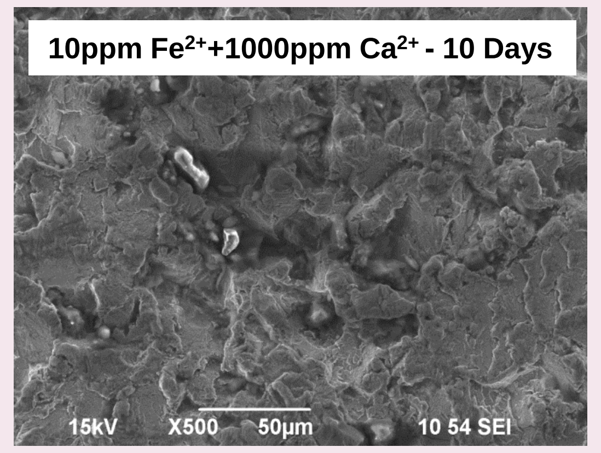


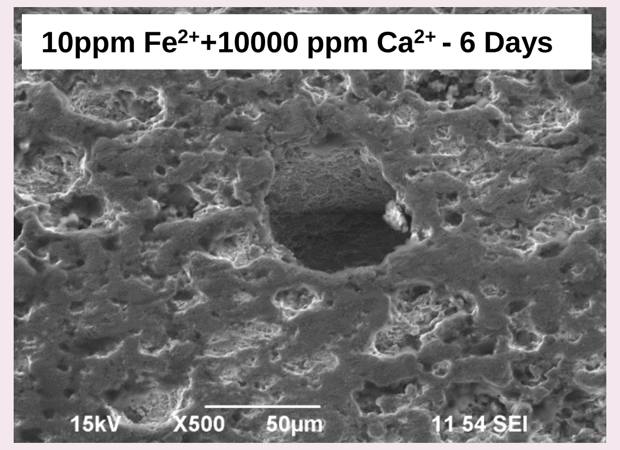
SEM image of samples after Clarke solution treatment [ASTM G1]


10ppm Fe^{2+}- 5 Days

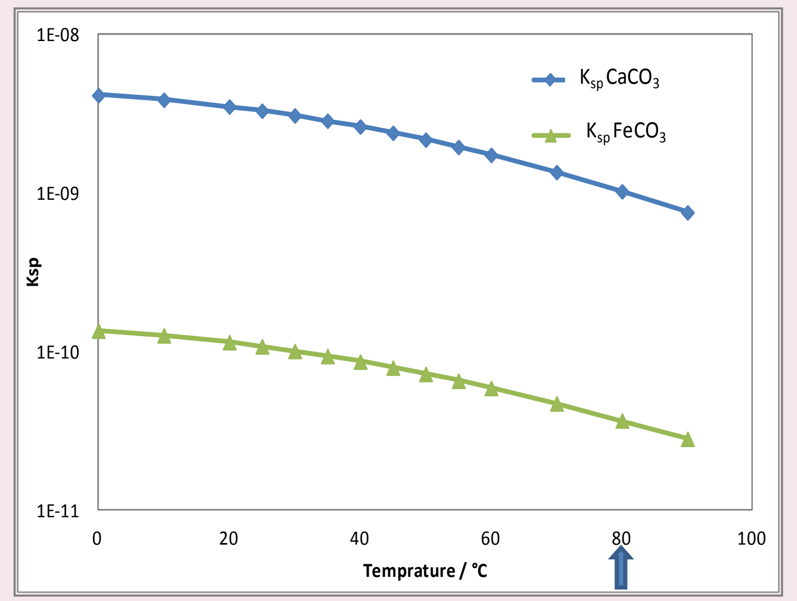

10ppm Fe^{2+} + 10ppm Ca^{2+} - 6 Days

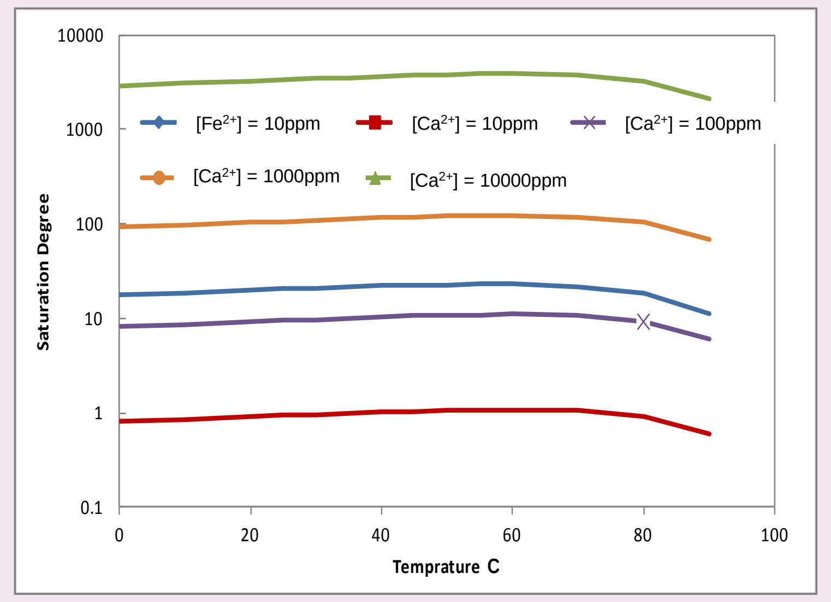

10ppm Fe^{2+} + 100ppm Ca^{2+} - 7 Days


10ppm Fe^{2+}+1000ppm Ca^{2+} - 10 Days


10ppm Fe^{2+}+10000 ppm Ca^{2+} - 6 Days

Thermodynamic Data at pH 6.6





Conclusions

- ✓ At low concentration (≤ 100ppm), Ca^{2+} didn't have a significant effect on corrosion.
- ✓ At high concentration (1000 & 10000ppm), Ca^{2+} increased the general corrosion.
- ✓ At the highest tested concentration (10000ppm), Ca^{2+} caused localized corrosion.

Future Work

- Low pressure experiments will be conducted to challenge formed $FeCO_3$ by Ca^{2+} addition.
- Experiments will be continued with high pressure CO_2 (up to 100 bar).

References

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- G. Zhao, J. Li, S.Hao , X.Lu, H.Li ,"Effect of Ca^{2+} and Mg^{2+} on CO_2 Corrosion Behavior of Tube Steel." J. Iron. Steel Res. Int., 2005, Vol. 12, pp. 38-42.
- C. Ding, K.Gao, and C. Chen ,"Effect of Ca^{2+} on CO_2 Corrosion Properties of X65 Pipeline Steel"Int. J. Miner. Metall. Mater., 2009, Vol. 16, pp. 661-666.

Acknowledgements

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Saba Navabzadeh Esmaeely
Department of Chemical and Biomolecular Engineering
Institute of Corrosion and Multiphase Technology
sn294410@ohio.edu