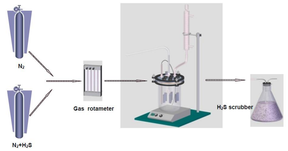
Exploration of the Mechanism for Localized H_2S Corrosion of Mild Steel

Jing Ning, Institute for Corrosion and Multiphase Technology, Ohio University, Athens, OH, USA

Research Gap

Corrosion caused by the presence of H_2S and CO_2 in produced fluids is frequently encountered in oil and gas production. Localized corrosion is considered to be the main cause of corrosion failures in facilities in the oil and gas industry, particularly in sour systems. However, compared to general corrosion, localized corrosion is much less understood and studied. It is notoriously difficult to predict and control different types of localized corrosion, therefore, prediction and mitigation are the key challenges for integrity management in the oil and gas industry. It is of key importance to understand the mechanisms of localized corrosion in order to mitigate the localized attack; however, the conditions leading to H_2S localized corrosion are currently unclear. Nevertheless, in the open literature, the mechanisms of H_2S localized corrosion have been usually associated with elemental sulfur, high salinity, high flow velocity, differences in local water chemistry at the metallic surface, and the microstructure of the mild steel. The focus of this research is the exploration of possible H_2S localized corrosion mechanism(s). Initiation of severe localized corrosion has been observed in experiments when there was an indication of the formation of greigite or pyrite. Based on these experimental results, a hypothesis for the localized H_2S corrosion has been proposed and tested with respect to possible galvanic effects (due to a difference in electrical conductance associated with polymorphous iron sulfides).

Experimental Setup



Hypothesis of a Mechanism for Localized H_2S Corrosion

❖ Electrochemical Half Reactions in H_2S Corrosion

Anodic half reaction

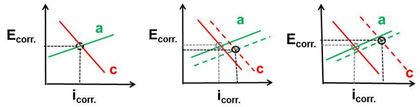
$$Fe(s.) \rightarrow Fe^{2+}(aq.) + 2e^-$$

Cathodic half reactions

$$2H^+(aq.) + 2e^- \rightarrow H_2(g.)$$

$$2H_2S(aq.) + 2e^- \rightarrow H_2(g.) + 2HS^-(aq.)$$

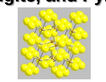
❖ Scenario of Half Reactions (Increase in Both OCP and CR)



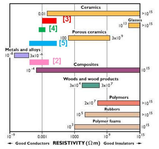
❖ Conductivity of Mackinawite, Greigite, and Pyrite

Mackinawite (FeS)
Electronic anisotropy, metallic conductor in the single sheet and an insulator between the sheets. [1]

Greigite (Fe_3S_4)
Semi-metallic [1]
Metallic [2]



Pyrite (FeS_2)
Experimentally measured
[2], [3], [4], [5] semiconductor



Resistivity of Pyrite [2], [3], [4], [5] compared to other materials.

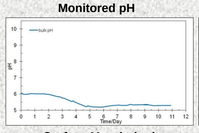
Experimental Results and Discussion

Test A: Spontaneously Occurring Localized Attack at 80ºC

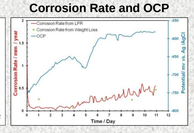
Test Matrix

Description	Parameter
Temperature	80ºC
Purged Gas	H_2S/N_2
pH_2S	0.053 bar (10%)
Stirring Speed	400 rpm
Solution	1 wt.% NaCl
Material	X65
Initial pH	6.0

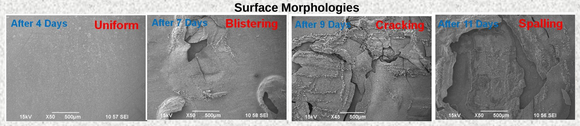
Monitored pH



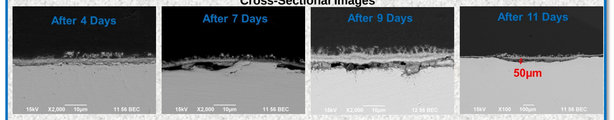
Corrosion Rate and OCP



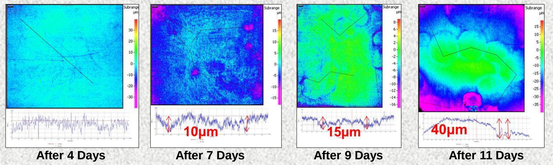
Surface Morphologies



Cross-Sectional Images



Surface Profilometry without Corrosion Product Layer



After 4 Days | After 7 Days | After 9 Days | After 11 Days

XRD Quantitative Analysis

Phases	4 days	7 days	9 days	11 days
Iron	55%	39%	45%	50%
Mackinawite	34%	30%	35%	33%
Pyrrhotite	2.6%	9%	1.2%	8.2%
Greigite	1%	2.1%	1.8%	0
Pyrite	2.1%	17%	10.2%	5.3%
Iron Carbide	4.8%	3%	7%	3.5%

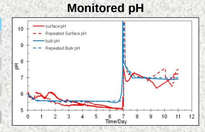
Mackinawite, pyrrhotite, greigite, and pyrite were detected as corrosion products of H_2S corrosion of mild steel at 80ºC. Increase in corrosion rate and initiation of localized corrosion were observed when there was an indication of the formation of greigite and pyrite.

Test B: Localized Attack with pH Adjustment After 7 Days at 25ºC

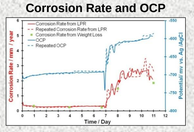
Test Matrix

Description	Parameter
Temperature	25ºC
Purged Gas	H_2S/N_2
pH_2S	0.1 bar (10%)
Stirring Speed	400 rpm
Solution	1 wt.% NaCl
Material	X65
Initial pH	6.0

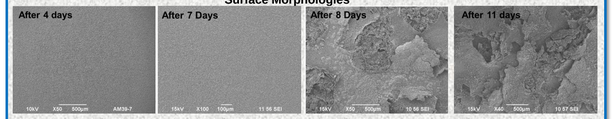
Monitored pH



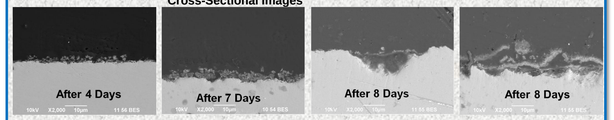
Corrosion Rate and OCP



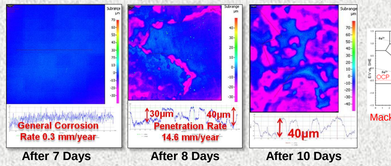
Surface Morphologies



Cross-Sectional Images

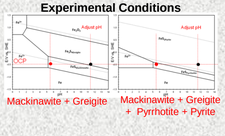


Surface Profilometry without Corrosion Product Layer



After 7 Days | After 8 Days | After 10 Days

Pourbaix Diagrams at Experimental Conditions



Mackinawite + Greigite | Mackinawite + Greigite + Pyrrhotite + Pyrite

XRD Quantitative Analysis

Phases	7 days	8 days
Iron	75%	37%
Mackinawite	22.6%	57%
Pyrrhotite	1.3%	0
Greigite	0	6%
Pyrite	0	0
Iron Carbide	1%	0

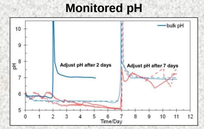
Usually only mackinawite and pyrrhotite can be observed as corrosion products of H_2S corrosion at 25ºC. Thus, the pH was adjusted after 7 days to facilitate the formation of greigite and pyrite according to the prediction made by Pourbaix diagram. Mackinawite was detected before and after adjusting pH, and greigite was detected after adjusting pH. Severe localized corrosion was observed after pH adjustment.

Test C: No Localized Attack with pH Adjustment After 2 Days at 25ºC

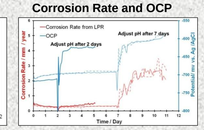
Test Matrix

Description	Parameter
Temperature	25ºC
Purged Gas	H_2S/N_2
pH_2S	0.1 bar (10%)
Stirring Speed	400 rpm
Solution	1 wt.% NaCl
Material	X65
Initial pH	6.0

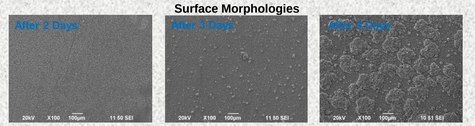
Monitored pH



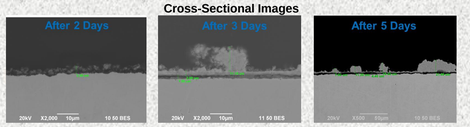
Corrosion Rate and OCP



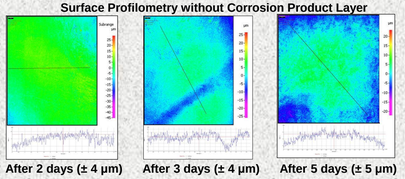
Surface Morphologies



Cross-Sectional Images



Surface Profilometry without Corrosion Product Layer



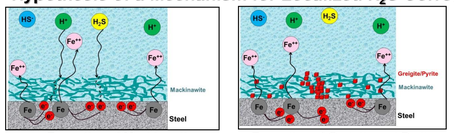
After 2 days (± 4 μm) | After 3 days (± 4 μm) | After 5 days (± 5 μm)

XRD Quantitative Analysis

Phases	2 days	3 days	5 days
Iron	84%	52%	45%
Mackinawite	16%	44%	49%
Pyrrhotite	0	1%	4%
Greigite	0	0	0
Pyrite	0	0	0
Iron Carbide	0	2%	2%

A short term test was conducted by adjusting pH after 2 days instead of the previous 7 days used to validate the hypothesis. The monitored pH and OCP showed good repeatability. Mackinawite was detected before and after adjusting pH, while neither greigite nor pyrite was detected. The test time was considered to be insufficient for conversion of mackinawite into greigite then pyrite. Consequently, there was no localized corrosion observed after adjusting pH.

❖ Hypothesis of a Mechanism for Localized H_2S Corrosion



Formation of Mackinawite | Formation of Greigite and Pyrite

Initiation of Localized Attack | Propagation of Localized Attack

Conclusions

- Initiation of severe localized corrosion was observed in experiments when there was an indication of the formation of greigite or pyrite. Based on the experimental results, a hypothesis for the localized H_2S corrosion has been proposed with respect to the galvanic effects due to a difference in electrical conductance associated with polymorphous iron sulfides.
- A test was conducted by adjusting pH after 2 days instead of the 7 days used to validate the hypothesis. Mackinawite was detected before and after adjusting pH, while neither greigite nor pyrite was detected, which was considered to be insufficient time for conversion of mackinawite into greigite then pyrite. Consequently, there was no localized corrosion observed after adjusting pH.

References and Acknowledgements

References

[1] A. J. Devey, "Computer Modeling Studies of Mackinawite, Greigite and Cubic FeS," Ph. D. Dissertation, University College London, 2009.
[2] D. J. Vaughan, Sulfide Mineralogy and Geochemistry, Reviews in Mineralogy and Geochemistry, vol. 61, 2006.
[3] R. Schieck, A. Hartmann, S. Fiechter, R. Konenkamp and H. Wetzel, "Electrical Properties of Natural and Synthetic Pyrite (FeS_2) Crystals," *J. Mater. Res.*, vol. 5, no. 7, 1990.
[4] M. Caban-Acevedo, M. S. Faber, Y. Tan, R. J. Hamers, and S. Jin, "Synthesis and Properties of Semiconducting Iron Pyrite (FeS_2) Nanowires, " *Nano Letters,* vol.12, 2012.
[5] P. K. Abraitis, R. A. D. Pattrick, D. J. Vaughan, "Variations in the compositional, textural and electrical properties of natural pyrite: a review," *Int. J. Miner Process,* vol. 74, pp. 41–59, 2004.

Acknowledgements

The author would like to thank her advisor Dr. Srdjan Nesic, project leader Bruce Brown, and the direction and financial support from the 25 industry sponsors listed below.

Sponsors: Anadarko, Baker Hughes, BP, Chevron, Clariant Oil Services, CNPC Tubular Goods, ConocoPhillips, DNV USA, ENI S.p.A., GRC, Hess, Inpex Corporation, M. I. Swaco, MultiChem, Nalco Champion, OXY, Petrobras, PETRONAS, Petroleum Development Oman, PTT, Saudi Aramco, SINOPEC, TOTAL, TransCanada, WGIM