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WeARE Research Area

- Corrosion Engineering.
- Materials Science and Engineering.
- Applied Electrochemistry.

Motivation or Background

Like humans, engineering materials age and decay overtime. Corrosion is a form of materials degradation that results from the electrochemical reaction between a metal or alloy and its environment [1]. Economic costs associated with corrosion alone in the USA have been estimated \$126 billion per year [1], in addition to the significant toll in human life and environmental safety. With the advancement of science and technology, continuous efforts are being made to provide practical solutions to reduce material loss associated with corrosion and its detrimental effects on the mechanical performance of engineering materials; particularly in critical areas of the energy sector. For instance, the transportation of natural gas (NG) consists of a complex network of carbon steel (CS) pipelines designed to quickly and efficiently transport the gas from its source to areas of high demand. Naturally, produced NG contains a gas mixture consisting primarily of methane, but commonly including varying amounts of hydrogen sulfide (H₂S) and carbon dioxide (CO₂). During NG transportation, managing pipeline systems are generally achieved by adequate corrosion inhibition and H₂S scavenging strategies since dissolved H₂S contributes with H⁺ (acid) and HS⁻/S²⁻ (sulfur) species that accelerate corrosion and can result in stress corrosion cracking (SCC). However, SCC of steel pipes have been reported when using certain amine-based H₂S scavengers [2]. *In this work, the electrochemical behavior of carbon steel was evaluated using electrochemical techniques such as linear polarization resistance (LPR) and cyclic potentiodynamic polarization to measure corrosion rate prior and after scavenger addition in presence of H₂S/CO₂.*



Figure 1. SCC failure in presence of amine-based H₂S scavengers

Objectives

The main objective of this research project was to measure the corrosion rate of carbon steel prior and after scavenger addition in presence of H₂S/CO₂ utilizing electrochemical techniques to aid another project on the understanding of SCC. For this purpose two tasks were performed: 1) Determine the corrosion rate using LPR technique and the Stern-Geary Equation, and 2) Determine the corrosion rate from cyclic potentiodynamic curves via Tafel extrapolation technique.

Methodology

• Apparatus: A conventional three-electrode configuration was used for the electrochemical measurements. A platinum (Pt) mesh served as a counter electrode (CE), and a saturated Ag/AgCl reference electrode (RE). The reference electrode was placed within the cell via a Luggin capillary.[5] A Gamry Interface 1000E potentiostat was used. The working electrode (WE) was made out of carbon steel pipe used in sour service for natural gas transportation. In addition, the electrochemical cell contained inlet and outlet ports to allow flow of inert and test gas prior and during polarizations, as well as an injection port to add the H₂S scavenger. As result from the Hazardous nature of the project, M.S. Yncierte performed the experiments.

• LPR: This technique was chosen as a screening method to measure the corrosion rate prior and after H₂S scavenger addition because of its nondestructive nature and fast response compared to conventional weight loss measurements, which require several days. The method relies on determining the slope of the linear portion of the polarization curve, which is inversely proportional to the corrosion rate [4], as shown below. Polarization measurements were carried out within a narrow potential domain of +/- 15mV vs OCP at a scan rate of 0.1667mV/s.

$$\text{Stern-Geary Equation [3]:}$$

$$i_{\text{corr}} \left(\frac{\text{mA}}{\text{cm}^2} \right) = \frac{b_1 b_2}{b_1 + b_2} \times \frac{1}{R_p} \quad (1)$$

$$\text{Corrosion rate} \left(\frac{\mu\text{m}}{\text{y}} \right) = 11.7 \times i_{\text{corr}} \times 1000 \quad (2)$$

• Tafel extrapolation: This technique was chosen to compare/validate results obtained. The Tafel region of a polarization curve can be extrapolated back to the OCP to obtain corrosion rate (i_{corr}) [3]. Cathodic polarization data is preferred since it is generally more reliable than anodic polarization [1]. Ideally, at least one decade of linearity on the semilog plots is required to determine i_{corr} by Tafel extrapolation, measured from the OCP to E' (50mV past the OCP). Polarization measurements were carried out for a wide potential domain of at least - 500mV vs OCP in the cathodic direction, and by setting a limit in current density of 5mA/cm² to cause the reversal of the forward anodic scan, with the returning scan ending at OCP. The scan rate in both cases was 0.1667mV/s.

• Software: OriginPro 2020 from OriginLab Corporation was used for data analysis, while easy to use Excel spreadsheets were used to calculate the corrosion rate.

Figures 2 shows how to determine the slope (R_p) using the Origin software, which essentially is the LPR technique. The slopes were calculated at $i=0$.

Figure 3 shows how to determine the tafel slope and the i_{corr} by extrapolation of the cathodic tafel slope to OCP (Tafel extrapolation technique). As can be seen from the graph, the OCP is the starting point on the left where the i is equal to zero and the cathodic tafel slope (b_c) is determined at a cathodic overpotential of 50mV. From there the slope was calculate at least 1 decade of linearity, which is the b_c for this example.

The calculations of the corrosion rate were calculated analytically using the Stern-Geary Equation (LPR) & graphically by i_{corr} from the intersection of the OCP and b_c slope (tafel extrapolation).

The results of the calculated corrosion rates are shown in Table 1, 2, 3 & 4. Corrosion Rate was obtained using Equations 1 & 2

Results

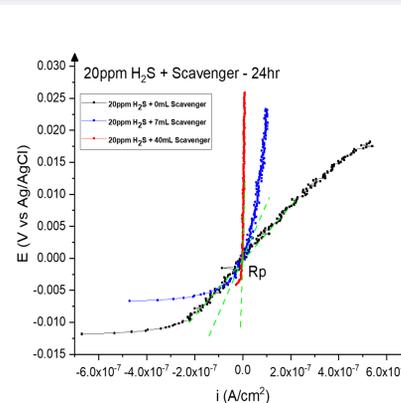


Figure 2. Example showing the slope calculation at $i=0$ for LPR technique.

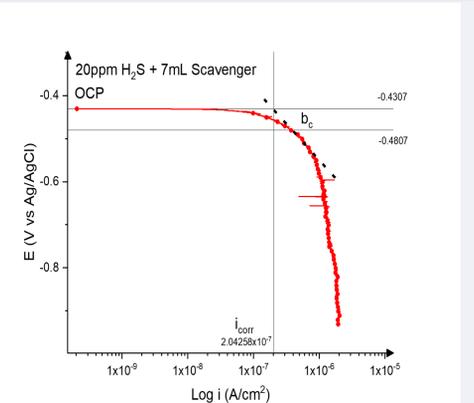


Figure 3. Example showing the Tafel Extrapolation technique.

Table 1. Corrosion Rate calculated through LPR technique (H₂S only):

	b_1 (mV/decade)	b_2 (mV/decade)	B_2 (mV)	R_p ($\Omega \cdot \text{cm}^2$)	i_{corr} (mA/cm ²)	Corrosion Rate ($\mu\text{m}/\text{y}$)
H ₂ S - 0hr	72.67	474.18	27.40	13253.20	2.07E-03	24.19
H ₂ S - 24hr	72.67	474.18	27.40	11813.58	2.32E-03	27.13
H ₂ S - 48hr	72.67	474.18	27.40	41186.24	6.65E-04	7.78
H ₂ S + 7mL - 0hr	143.43	168.99	33.73	56339.80	4.86E-04	5.69
H ₂ S + 7mL - 24hr	143.43	168.99	33.73	15220.37	1.80E-03	21.06
H ₂ S + 7mL - 48hr	143.43	168.99	33.73	21919.69	1.25E-03	14.62
H ₂ S + 40mL - 0hr	138.94	109.45	26.62	27154.00	1.24E-03	14.53
H ₂ S + 40mL - 24hr	138.94	109.45	26.62	36641.20	9.21E-04	10.77
H ₂ S + 40mL - 48hr	138.94	109.45	26.62	96449.66	3.50E-04	4.09
H ₂ S + 7mL + 40mL - 0hr	143.43	168.99	33.73	125014.52	2.70E-04	3.16
H ₂ S + 7mL + 40mL - 24hr	143.43	168.99	33.73	121895.20	2.77E-04	3.24
H ₂ S + 7mL + 40mL - 48hr	143.43	168.99	33.73	130322.01	2.59E-04	3.03
H ₂ S + 40mL + 7mL - 0hr	138.94	109.45	26.62	180149.78	1.48E-04	1.73
H ₂ S + 40mL + 7mL - 24hr	138.94	109.45	26.62	137649.02	1.93E-04	2.26
H ₂ S + 40mL + 7mL - 48hr	138.94	109.45	26.62	172426.58	1.54E-05	0.18
H ₂ S + 40mL + 40mL - 0hr	138.94	109.45	26.62	344116.00	7.74E-05	0.91
H ₂ S + 40mL + 40mL - 24hr	138.94	109.45	26.62	1973593.34	1.35E-05	0.16
H ₂ S + 40mL + 40mL - 48hr	138.94	109.45	26.62	411970.93	6.46E-05	0.76

Table 2. Corrosion Rate calculated through Tafel Extrapolation technique (H₂S only):

	i_{corr} (mA/cm ²)	Corrosion Rate ($\mu\text{m}/\text{y}$)
H ₂ S 0mL Cathodic	2.43E-03	28.39
H ₂ S 7mL Cathodic	2.04E-04	2.39
H ₂ S 40mL Cathodic	3.10E-05	0.36

Concluding Remarks:

- In the absence of the H₂S scavenger:
 - The corrosion rate reaches its maximum in both scenarios, as expected. However, dissolved CO₂ is more corrosive than H₂S.
 - In presence of H₂S, the corrosion rate significantly decreases after 24hr of exposure and then increases after 48hr. This could be attributed to the formation of an iron sulfide/magnetite (FeS/Fe₃O₄) layer that acts as a barrier limiting the diffusion of corrosive species to the metal surface. As the thickness of the corrosion product layer increases, internal stresses make it susceptible to cracking and delamination, thereby increasing the corrosion rate.
 - In presence of CO₂, the corrosion rate remains relatively constant. This could be attributed to the formation of a less dense and porous iron carbonate/magnetite (FeCO₃/Fe₃O₄).
- Adding the scavenger resulted in a significant decrease of the corrosion rate in both cases. As the scavenger concentration increases, changes in the slope of the LPR curves result in lower i_{corr} values.
- Results obtained via tafel extrapolation show a similar trend.

Table 3. Corrosion Rate calculated through LPR technique (CO₂ only):

	b_1 (mV/decade)	b_2 (mV/decade)	B_2 (mV)	R_p ($\Omega \cdot \text{cm}^2$)	i_{corr} (mA/cm ²)	Corrosion Rate ($\mu\text{m}/\text{y}$)
CO ₂ - 0hr	92.93	600.79	34.99	6676.68	5.24E-03	61.32
CO ₂ - 24hr	92.93	600.79	34.99	7812.81	4.48E-03	52.40
CO ₂ - 48hr	92.93	600.79	34.99	6848.48	5.11E-03	59.78
CO ₂ + 8mL - 0hr	130.92	312.49	40.12	7804.29	4.48E-03	52.46
CO ₂ + 8mL - 24hr	130.92	312.49	40.12	6922.13	5.23E-03	61.18
CO ₂ + 8mL - 48hr	130.92	312.49	40.12	7542.88	4.64E-03	54.28
CO ₂ + 40mL - 0hr	26.84	353.31	10.85	68646.09	5.84E-04	6.84
CO ₂ + 40mL - 24hr	26.84	353.31	10.85	66136.46	6.07E-04	7.10
CO ₂ + 40mL - 48hr	26.84	353.31	10.85	25263.80	1.59E-03	18.58
CO ₂ + 8mL + 40mL - 0hr	26.84	353.31	10.85	30897.78	1.30E-03	15.19
CO ₂ + 8mL + 40mL - 24hr	26.84	353.31	10.85	11812.99	3.40E-03	39.73
CO ₂ + 8mL + 40mL - 48hr	26.84	353.31	10.85	11978.21	3.35E-03	39.18
CO ₂ + 40mL + 8mL - 0hr	26.84	353.31	10.85	122484.38	8.85E-05	1.04
CO ₂ + 40mL + 8mL - 24hr	26.84	353.31	10.85	148021.65	7.33E-05	0.86
CO ₂ + 40mL + 8mL - 48hr	26.84	353.31	10.85	276935.27	3.92E-05	0.46
CO ₂ + 40mL + 40mL - 0hr	26.84	353.31	10.85	572862.49	1.89E-05	0.22
CO ₂ + 40mL + 40mL - 24hr	26.84	353.31	10.85	40797.97	2.66E-04	3.11
CO ₂ + 40mL + 40mL - 48hr	26.84	353.31	10.85	405754.55	2.67E-05	0.31

Table 4. Corrosion Rate calculated through Tafel Extrapolation technique (CO₂ only):

	i_{corr} (mA/cm ²)	Corrosion Rate ($\mu\text{m}/\text{y}$)
CO ₂ 0mL Cathodic	4.44E-03	51.96
CO ₂ 8mL Cathodic	3.62E-04	4.23
CO ₂ 40mL Cathodic	1.73E-04	2.03

Skills and Experience

- Trained on the application of the LPR and Tafel Extrapolation techniques to Corrosion data.
- Basics of the program OriginPro
- Excel.

Future Plans

This research opportunity has taught me many things and within the experiences I had successes and failures. The research opportunity gave me a chance to step foot into a work environment that I would experience prior to a job when I graduate. I learned many new things along the trip, and I have to say corrosion is an interesting topic and would love to learn more about it. It is something that I will keep in mind for future terms to come.

What I Learned

- Basics of corrosion kinetics.
- Calculation of corrosion rates.
- Perform curve fitting and extrapolation on real experimental data.
- How H₂S and CO₂ can affect the corrosion rate of CS over time.
- How the addition of an H₂S scavenger modifies the chemistry of the environment, thus reducing the corrosion rate.

Acknowledgments

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References

- [1] Jones, D. (1992). *Principles and Prevention of Corrosion* [Ebook] (2nd ed., pp. 1-8,24,40-42,46-49,152-161). Prentice Hall. Retrieved 25 May 2020, from. H. Kaesche, *Metallic Corrosion*, NACE, Houston, pp. 216-19, 1985
- [2] Heaver, E. (2020, May 4). Internal Stress Corrosion Cracking of Shale Gas Flowlines.
- [3] Fontana, M. (1985). *Corrosion Engineering* [Ebook] (3rd ed., pp. 1-19,153,171,191-192,499). McGraw-Hill.
- [4] ASTM G59-97(2014), Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements, ASTM International, West Conshohocken, PA, 2014.
- [5] ASTM G5-14e1, Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements, ASTM International, West Conshohocken, PA, 2014.