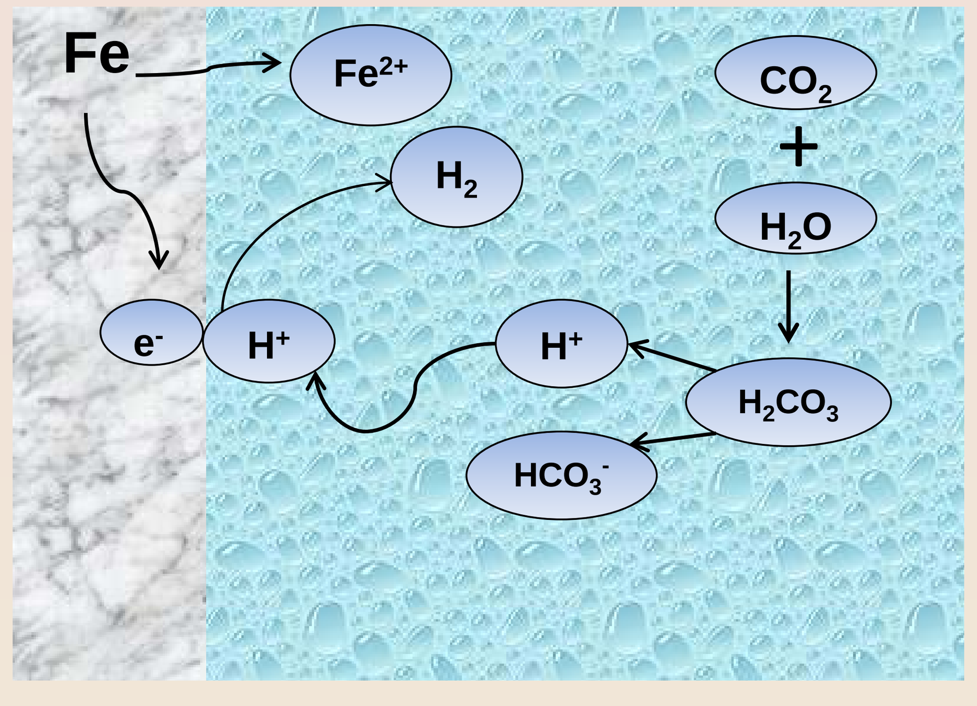
Thu Tran
Institute for Corrosion and Multiphase Technology, Ohio University

Corrosion Mechanisms of Mild Steel in Aqueous CO_2 Solutions

Background

Modeling the CO_2 corrosion mechanism has been a challenge to the oil and gas industry for several decades. A significant amount of research has been done to investigate the effect of CO_2 (as carbonic acid (H_2CO_3)) on the corrosion rate of mild steel. Two mechanisms have been proposed over the last 39 years[1-6], "buffering effect" or "direct reduction". However, there is still no compelling evidence to support whether or not carbonic acid is directly reduced at the metal surface.

Mechanism 1: **BUFFERING EFFECT** (BE)[1,2]



Dissolution of iron

$Fe \rightleftharpoons Fe^{2+} + 2e^-$

Hydration of CO_2

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

Dissociation of H_2CO_3

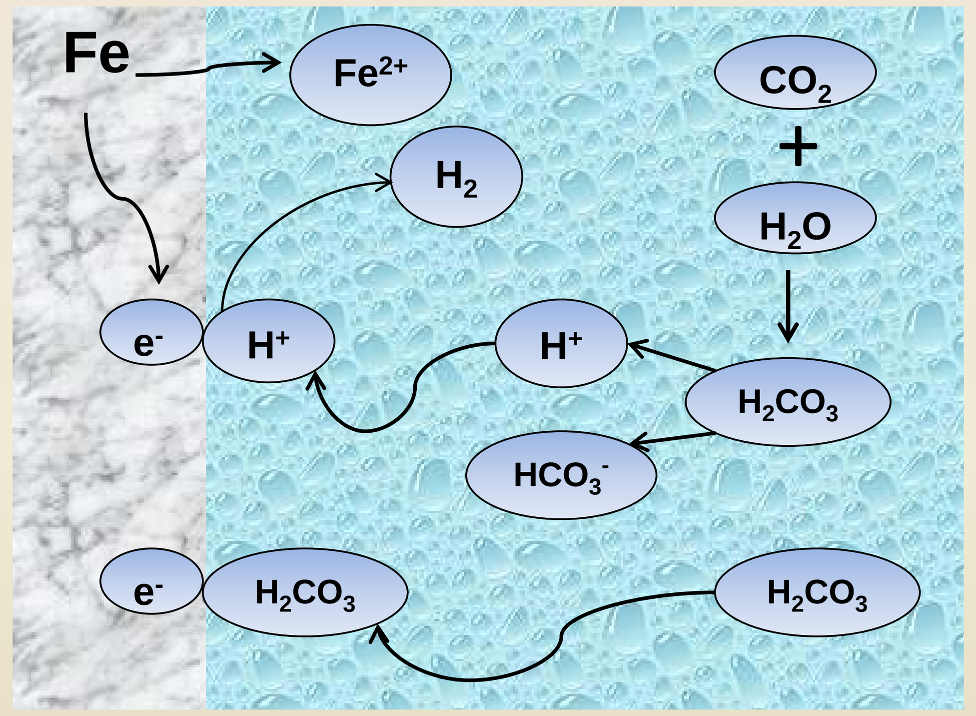
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

Reduction of H^+

$2H^+ + 2e^- \rightleftharpoons H_2$

In this mechanism, the role of carbonic acid is only as a reservoir of hydrogen ions.

Mechanism 2: **BUFFERING EFFECT + DIRECT REDUCTION** (BE + DR)[3-6]



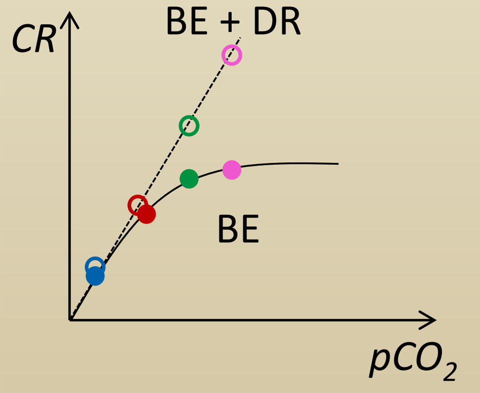
All reactions in mechanism 1 are still valid for mechanism 2. Additionally, there is another electrochemical reaction that needs to be taken into account:

Direct reduction of H_2CO_3

$2H_2CO_3 + 2e^- \rightleftharpoons H_2 + 2HCO_3^-$

In this mechanism, the role of carbonic acid is not only a reservoir of hydrogen ions, but also a cathodic species that participates in the reduction reaction.

Objectives – Significance of Research

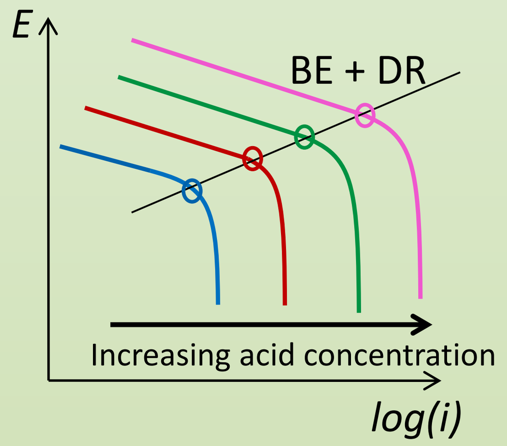


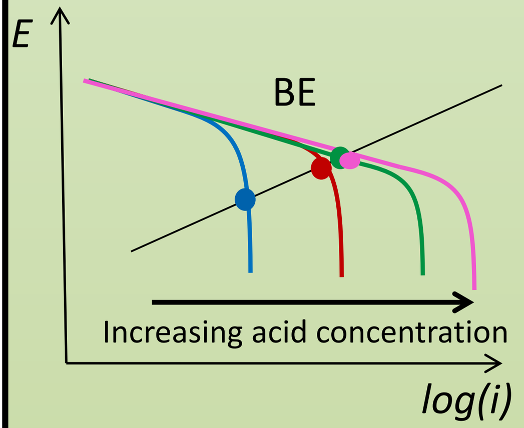
Corrosion rate prediction depends on the mechanism

Objective: to understand whether or not the direct reduction of carbonic acid needs to be taken into account in the development of a corrosion prediction model.

Understanding these mechanisms are of key importance for modeling and hence corrosion prediction. It provides a tool for the oil and gas industry to forecast the corrosion behavior of mild steel related to internal pipeline corrosion in the presence of CO_2.

Methodology



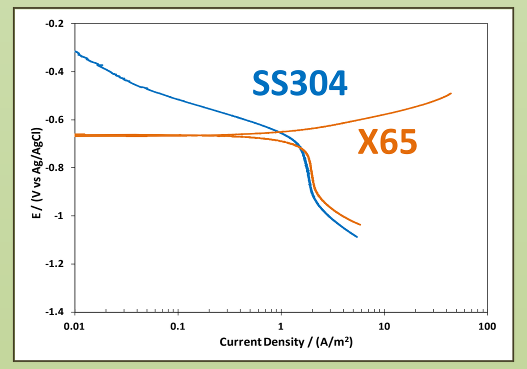


Method

If the direct reduction of carbonic acid is taken into account, it would affect the charge transfer current, due to the presence of another electrochemical reaction at the surface, in addition to the reduction of hydrogen ions. Therefore, by examining the charge transfer current, the mechanism can be revealed.

Technique

Polarization by potentiodynamic sweeps was used to investigate the effect of carbonic acid (or CO_2 partial pressure) on the charge transfer current. If the latter increases with increasing carbonic acid concentration, the direct reduction of carbonic acid needs to be considered. If the charge transfer current remains the same for different carbonic acid concentrations, the "buffering effect" mechanism is correct.



Comparison of potentiodynamic sweeps on SS304 and X65 at pH 4.0, N_2 saturated solution, 25 °C, RCE 1000rpm

Material

Stainless steel (SS304) was used to study the cathodic reaction. By using SS304, the charge transfer current can be seen clearly without interference from the anodic reaction, as occurs on mild steel. Mild steel was also used to confirm the mechanism defined by this research.

Dissociation of acetic acid

$HAc \rightleftharpoons H^+ + Ac^-$

Cathodic reactions

$2H^+ + 2e^- \rightleftharpoons H_2$

$2HAc + 2e^- \rightleftharpoons H_2 + 2Ac^-$

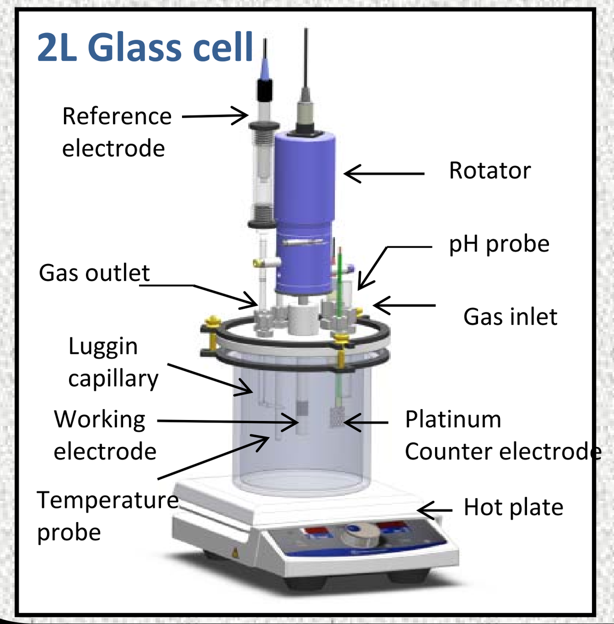
Anodic reaction

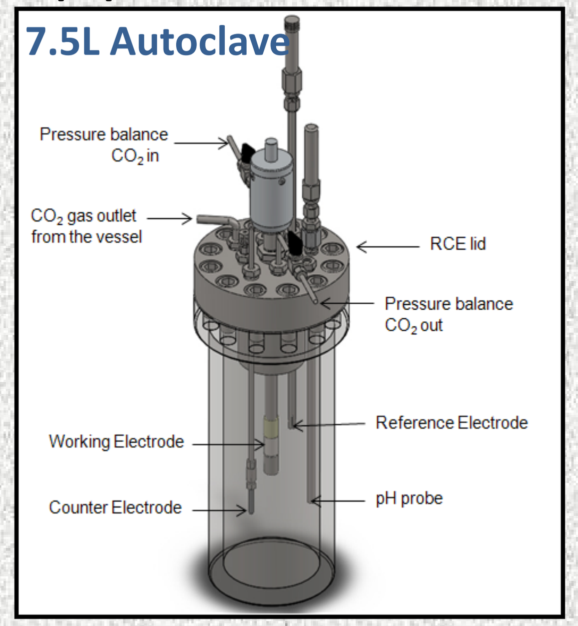
$Fe \rightleftharpoons Fe^{2+} + 2e^-$

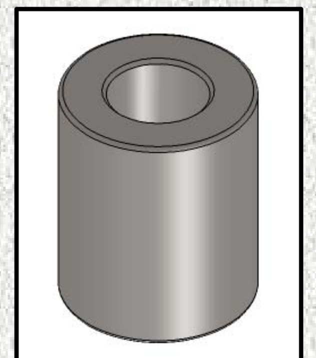
Using acetic acid for comparison

Since carbonic acid and acetic acid (CH_3COOH or HAc) are weak acids, it's assumed that they will have similar mechanisms. Hence, HAc, which is a relevant chemical found in many oil and gas upstream production lines, is a good candidate to investigate the corrosion mechanism. Another reason to study the acetic acid mechanism first, and then relate it to the CO_2 corrosion mechanism, is because higher concentrations of HAc can be achieved in the glass cell at atmospheric pressure.

Equipment







Cylindrical coupon

Results and Discussion

Test Matrix for Acetic Acid Work

Parameters	Conditions
Equipment	Glass cell
Device	RCE*
Material	SS304
Temperature (°C)	25
Gas	N_2
P_{total} (bar)	1
Acetic acid concentration (ppm)	0, 100, 1000
pH	2.0, 3.0, 4.0 (± 0.1)
Electrolyte	3 wt.% NaCl
Flow velocity (m/s)	0.5

Test Matrix for Carbonic Acid Work

Parameters	Conditions
Equipment	Glass cell, Autoclave
Device	RCE
Material	SS304, X65
Temperature (°C)	25
Gas	CO_2
P_{CO2} (bar)	0, 0.5, 1, 5, 10, 20
pH	3.4 ; 5.0 (± 0.2)
Electrolyte	3 wt.% NaCl
Flow velocity (m/s)	0.5

(*) Rotating cylinder electrode

❖ Figures 1 and 2 show the effect of acetic acid on the cathodic reaction occurring on stainless steel in a fixed pH solution at 25°C and 60°C, respectively. Acetic acid only affects the limiting current due to its ability to provide hydrogen ions via dissociation upon demand. However, the charge transfer current remains the same.

❖ Similarly, a change in partial pressure of CO_2 does not affect the charge transfer current in a fixed pH solution (Figures 4 and 5), which means that the direct reduction of carbonic acid can be neglected.

❖ The dominant cathodic reactant is hydrogen ions, resulting in a change of charge transfer current with pH, as expected (Figures 3 and 6).

❖ If the direct reduction of carbonic acid is assumed, the corrosion model predicts an increase of corrosion rate (CR) with increasing carbonic acid concentration. However, in reality, experiments show that the corrosion rate will stop increasing at some point even though CO_2 pressure keeps increasing (Figure 7). This observation can only be explained by the "buffering effect" mechanism.

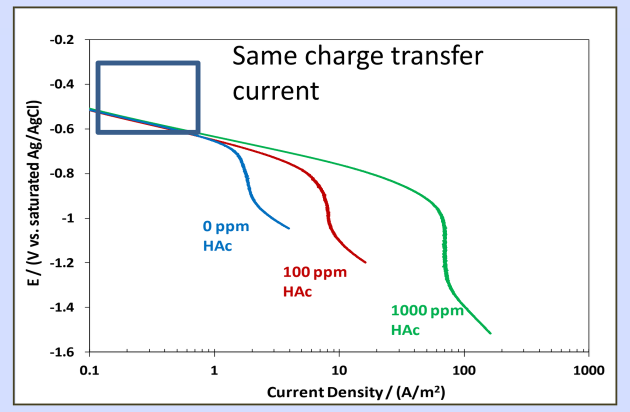


Figure 1: pH 4.0, 25°C

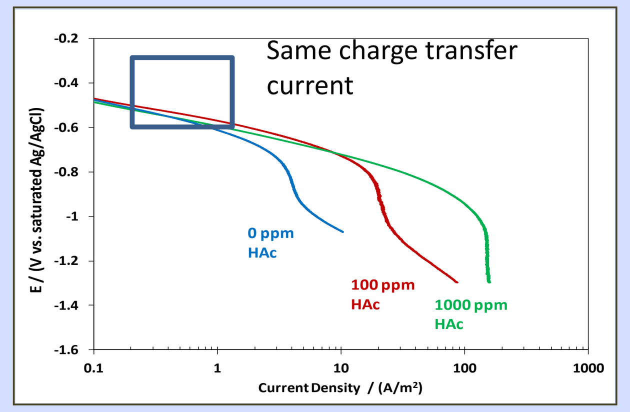


Figure 2: pH 4.0, 60°C

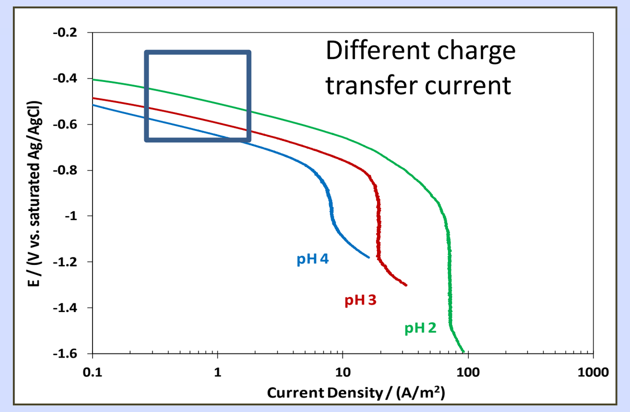


Figure 3: 100 ppm HAc, 25°C

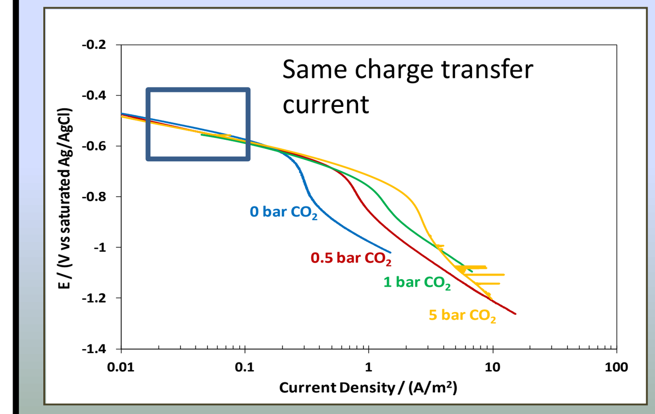


Figure 4: pH 5.0, 25°C

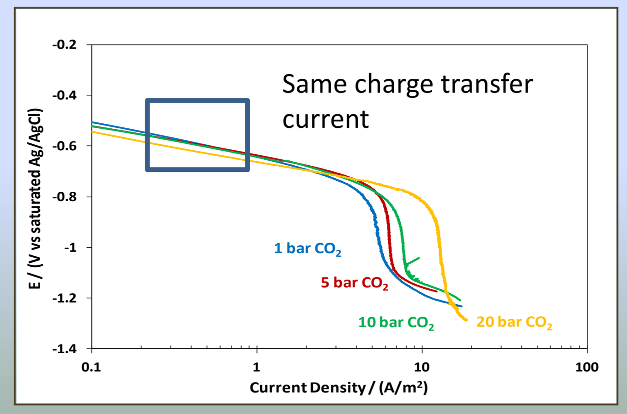


Figure 5: natural pH (3.4±0.2), 25°C

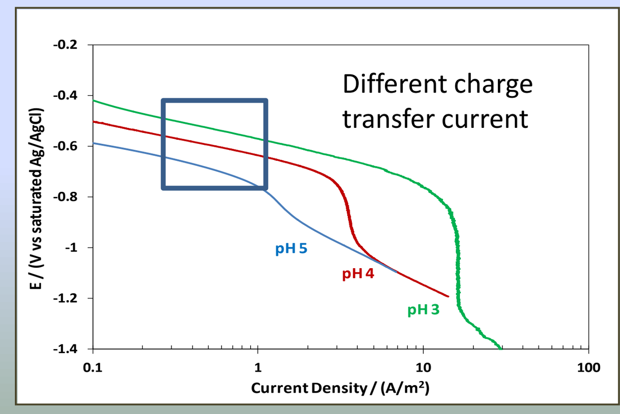


Figure 6: 1 bar CO_2, 25°C

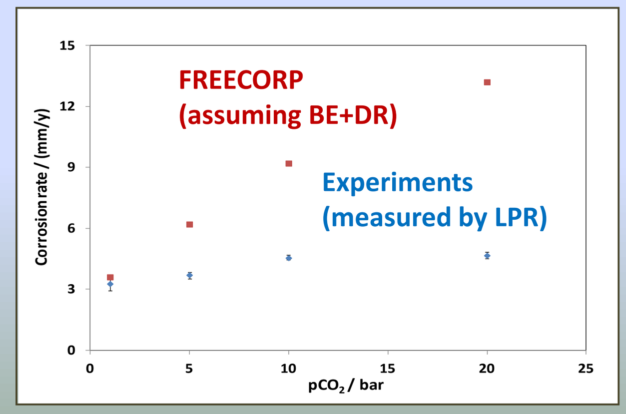


Figure 7: natural pH, 25°C

Conclusions and Future Work

❖ The charge transfer current is not affected by acetic acid and carbonic acid concentration. Therefore, the direct reduction of acetic acid and carbonic acid can be neglected in the studied condition range.

❖ Hydrogen ions are the dominant cathodic reactants reduced at the metal surface, resulting in a change of charge transfer current with pH.

❖ Future work: Propose a mechanistic model for the buffering effect mechanism.

Acknowledgements

Advisor: Prof. Srdjan Nesic

Project leader: Dr. Bruce Brown

References

[1] B. Linter and G. Burstein, "Reactions of Pipeline Steels in Carbon Dioxide Solutions," Corrosion Science 41, (1999): pp. 117-139.

[2] E. Remita, B. Tribollet, E. Sutter, V. Vivier, F. Ropital and J. Kittel, "Hydrogen evolution in aqueous solutions containing dissolved CO_2: Quantitative contribution of the buffering effect," Corrosion Science 50, (2008): pp. 1433-1440.

[3] C. DeWaard and D. Milliams, "Carbonic acid corrosion of steel," Corrosion 31, 5 (1975): pp. 177-181.

[4] G. Schmitt and B. Rothmann, "Studies on the Corrosion Mechanism of Unalloyed Steel in Oxygen-Free Carbon Dioxide Solutions," Werkst. Korrosion 28, (1977): pp. 816-822.

[5] S. Nesic, J. Postlethwaite and S. Olsen, "An electrochemical model for prediction of corrosion of mild steel in aqueous carbon dioxide solutions," Corrosion, 52, 4 (1996), pp. 280-294.

[6] B. Pots, "Mechanistic Models for the Prediction of CO_2 Corrosion Rates under Multi-phase Flow Conditions," CORROSION/95, paper no. 137 (Houston, TX: NACE, 1995)

Sponsors: BP, Clariant, ConocoPhillips, WGIM, Eni, TOTAL, Saudi Aramco, PETROBAS, INPEX, PETRONAS, OXY, TransCanada, SINOPEC, GRC, PTTEP, Baker Huges, DNV USA Inc., Chevron, M.I. Swaco, Hess, MultiChem, CNPC Tubular Goods, Anadarko, Petroleum Development Oman, Nalco Champion