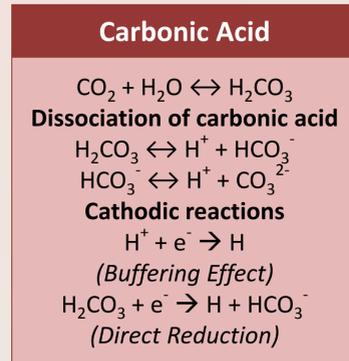


## Background

Sweet corrosion was recognized as a concern for the oil and gas industry in the early 1940's. The first model proposed by De Waard and Milliams [1] in 1975 assumed the direct reduction of carbonic acid in order to explain a higher corrosion rate than a completely dissociated acid (HCl) at the same pH. In 1996, Nescic [2] proposed an electrochemical model to predict the CO<sub>2</sub> corrosion of mild steel, taking into account the effect of pH, temperature and flow velocity. His model is also based on the direct reduction of carbonic acid.

However, in a recent study, Remita et al. [3] conducted a series of experiments by using the rotating disk electrode to investigate the cathodic behavior of steel in CO<sub>2</sub> environment. These authors suggest that the role of carbonic acid is similar to a buffer, by providing and replenishing the hydrogen ions when these are consumed at the surface by the corrosion reaction. Hence, this mechanism is called the "buffering effect".



## Approach

### Using acetic acid

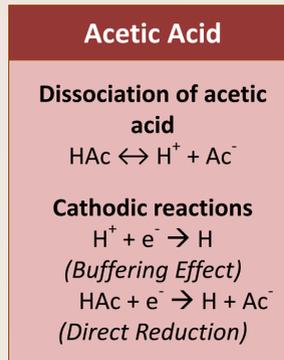
Since carbonic acid and acetic acid are both weak acids, it's assumed that they will have similar mechanisms. Hence, acetic acid, which is a relevant component found in many oil and gas upstream production lines, is a good candidate to investigate the corrosion mechanism. Another reason to study an acetic acid mechanism first and then relate it to the CO<sub>2</sub> corrosion mechanism is because higher concentration of acetic acid can be done easily in the glass cell at atmospheric pressure.

### Using stainless steel

Stainless steel (SS304) is used to investigate the effect of acetic acid on the cathodic reaction. By using stainless steel, the charge transfer current can be seen clearly without interference from the anodic reaction, as occurs on carbon steel. Carbon steel will be used in future experiments to confirm the mechanism defined by this research.

### Using 2 electrochemical techniques

- Steady-state technique: potentiodynamic sweeps
- Transient technique: electrochemical impedance spectroscopy (EIS)

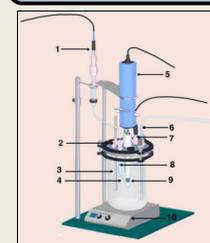


## Hypothesis

- If the buffering effect is correct, which means that acetic acid does not participate in the cathodic reaction, the charge transfer current should remain the same with increasing acetic acid concentration at the same pH. Indeed, in this case, acetic acid only dissociates to replace the hydrogen ions when the latter are consumed in the corrosion reaction at the metal surface.
- If the buffering effect is correct, since the only cathodic reaction is the reduction of hydrogen ions, the charge transfer current will be affected by pH.

## Experimental set-up and Test Matrix

A glass cell using 3 electrode set-up



- Reference electrode
- Gas outlet
- Temperature probe
- Platinum counter electrode
- Rotator
- Gas inlet
- pH-electrode
- Luggin capillary
- Working electrode
- Hot plate

(\*) RCE: Rotating Cylinder Electrode  
(\*\*) RDE: Rotating Disk Electrode

Parameters	Conditions	
Device	RCE (*)	RDE (**)
Material	SS304	SS304L
Temperature (°C)	25	
Gas	N <sub>2</sub>	
P <sub>total</sub> (bar)	1	
Undissociated HAc (ppm)	0, 100, 1000	
pH	2.0, 3.0, 4.0	
Electrolyte	3 wt.% NaCl	
Rotating Speed (rpm)	1000	

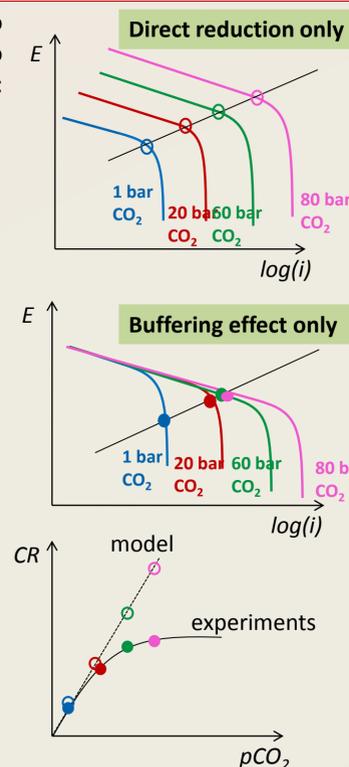
## Objective

The objective of this study is to investigate the corrosion mechanism to determine which pathway is dominant: direct reduction or buffering effect.

### Why is it important?

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<sub>2</sub> pressure keeps increasing. This observation can only be explained by the "buffering effect" mechanism.

Therefore, understanding the mechanism helps to improve the mechanistic model and make it more accurate taking into account more extreme conditions such as: high pH, high temperature, high acetic acid concentration, high pCO<sub>2</sub>, high H<sub>2</sub>S concentration.



## Results

### Potentiodynamic Sweep Results

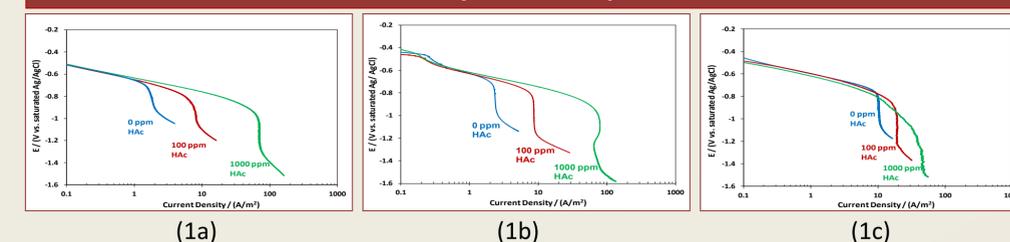


Figure 1: Effect of acetic acid on the charge transfer current  
(a) RCE, pH4 (b) RDE, pH4

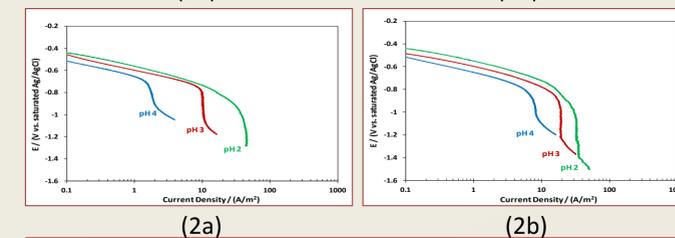


Figure 2: Effect of pH on the charge transfer current  
(a) RCE, 0 ppm HAc (b) RCE, 100 ppm HAc

### Test Reproducibility

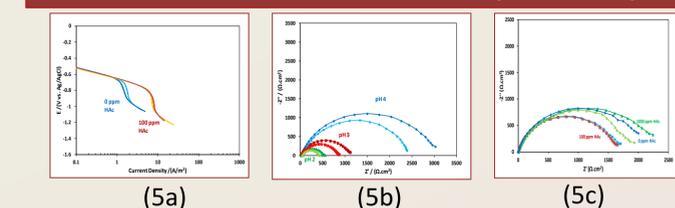


Figure 5: Replicated tests  
(a) RCE, pH4 (b) RCE, 100 ppm HAc, -0.6V (c) RDE, pH4, -0.6V

### Electrochemical Impedance Spectroscopy Results

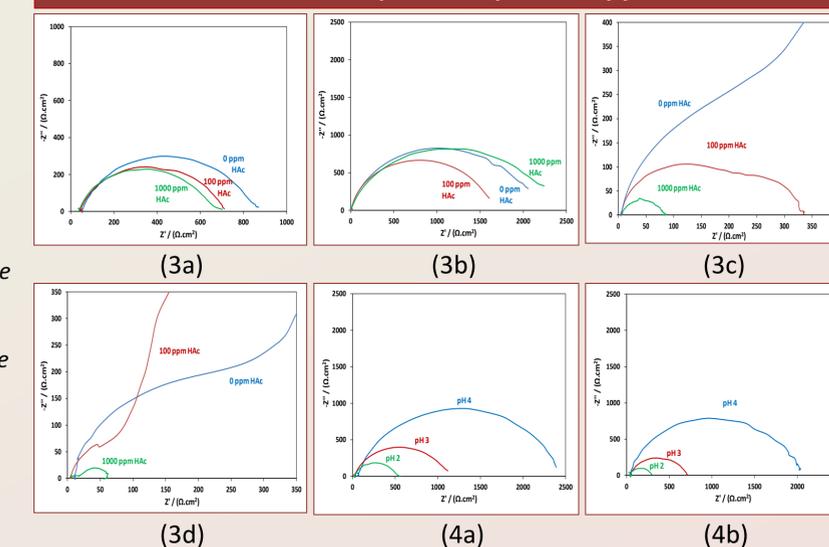


Figure 3: Effect of acetic acid on the charge transfer resistance  
(a) RCE, pH3, -0.6V (b) RDE, pH4, -0.6V (c) RDE, pH4, -0.8V (d) RDE, pH4, -1V

Figure 4: Effect of pH on the charge transfer resistance  
(a) RCE, 0 ppm HAc (b) RCE, 100 ppm HAc

## Discussion

- Figure 1 shows that the charge transfer current remains the same with change of acetic acid concentration at a given pH. This demonstrated that there is no reduction of acetic acid at the surface. The only cathodic reaction is the reduction of hydrogen ions, which explains a change of charge transfer current at different pH, as shown in Figure 2.
- EIS results confirm the findings from the steady-state technique. Indeed, the charge transfer resistance R<sub>ct</sub> (which is the diameter of the semi-circle) does not change significantly with increasing acetic acid concentration at a given pH (Figure 3a and 3b). The effect of acetic acid are only shown in the region affected by the mass transfer (Figure 3c and 3d). Figure 4 shows the effect of pH on the R<sub>ct</sub> since due to the reduction of hydrogen ions at the metal surface.
- Figure 5 shows good test reproducibility.

## Conclusion

A good agreement was observed between electrochemical steady-state and transient methods. Both techniques show that there is no effect of acetic acid on the cathodic reaction, which is only the reduction of hydrogen ions. In other words, the "buffering effect" mechanism is confirmed for acetic acid.

## Future work

Tests will be conducted at higher partial pressure of CO<sub>2</sub> on stainless steel and carbon steel to determine the CO<sub>2</sub> mechanism. The effect of acetic acid in the presence of iron carbonate will be investigated and related to H<sub>2</sub>S.

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- S. Nescic, J. Postlethwaite, and S. Olsen, "An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions," *Corrosion Science*, vol.52, 1996, pp. 280-294
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## Acknowledgements

**Advisor:** Prof. Srdjan Nescic

**Project leader:** Bruce Brown

**Special thanks to:** Bernard Tribollet, Université Pierre & Marie Curie, Paris, France