

EFFECT OF TRACE DISSOLVED OXYGEN ON THE CATHODIC KINETICS OF CARBON DIOXIDE CORROSION OF CARBON STEEL

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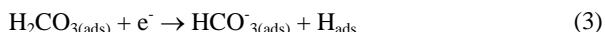
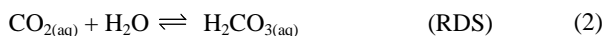
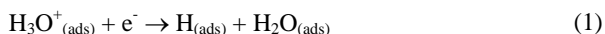
Summary: The corrosion of carbon steel in carbon dioxide saturated brine solutions is controlled by a mixed activation-mass transfer process in the cathodic reaction mechanism. Cathodic polarisation curves of carbon steel in carbonic acid solutions exhibit a limiting current behaviour that is dependent on the rate of mass transfer. In studies using the jet impingement technique, the magnitude of this limiting current behaviour has been found to be strongly affected by the presence of trace levels of dissolved oxygen. This paper presents a theoretical assessment of the mass transfer limited cathodic current to illustrate the pronounced effect of dissolved oxygen contamination <15 ppb. Discussion is presented regarding the implications of dissolved oxygen contamination on the interpretation of the mechanism of carbon dioxide corrosion.

Keywords: Carbon dioxide corrosion, dissolved oxygen, mass transfer, cathodic polarisation curves, jet impingement, limiting current, carbon steel, brine.

1 INTRODUCTION

The rate and mechanism of carbon dioxide corrosion is strongly affected by trace levels of dissolved oxygen (<15ppb). Research has shown that the corrosion rates can be three times greater in the presence of as little as 4 ppb dissolved oxygen in comparison to its relative absence (<0.5 ppb) [1-3]. Of particular note is that the presence of trace levels of dissolved oxygen significantly modifies the mass transfer dependency of the corrosion rate. In the absence of trace levels of dissolved oxygen at 30 °C, the rate of carbon dioxide corrosion is essentially independent of the mass transfer, whilst a strong dependence is observed in the presence of 4-15 ppb dissolved oxygen. A similar relationship is observed when the corrosion rate is inhibited using organic film forming corrosion inhibitors. In the presence of trace levels of dissolved oxygen, variations in the inhibited corrosion rate with flow velocity can be directly correlated with the rate of mass transfer of oxygen [2, 4-8].

In carbon dioxide saturated brine solutions, cathodic polarisation curves on carbon steel exhibit a limiting current behaviour that has been the subject of numerous detailed discussions relating to the mechanism of carbon dioxide corrosion [2, 9-12]. Fundamentally, it is recognised that the cathodic limiting current density is directly dependent on the rate of mass transfer and accordingly it has been used to estimate the mass transfer coefficient to electrodes in flowing solutions [13]. It should be noted however that at temperatures below 60 °C the corrosion rate is controlled by a mixed activation-mass transfer mechanism (concentration polarisation) and is significantly dissimilar to limiting current density. The conventional perception is that the cathodic limiting current is derived from the evolution of hydrogen from two concomitant reaction mechanisms involving free protons (I) and carbonic acid (III) [9, 10, 12, 14, 15]. There still remains an uncertainty as to whether the carbonic acid is directly reduced (III) or simply provides an additional source of protons through dissociation.



The magnitude of the cathodic limiting current density is significantly greater than that of the actual the corrosion current density. The difference in magnitude however, reduces with increasing temperature and the corrosion rate begins to exhibit a

relationship with the mass transfer. This behaviour is consistent with the mixed activation-mass transfer control reaction mechanism attributed to carbon dioxide corrosion [2, 9]. It is also consistent with a concentration polarisation affect whereby the increased temperature (greater rate of hydration) and mass transfer both contributed to increasing the surface concentration of carbonic acid. Despite the high solubility of carbon dioxide, the actual concentration of carbonic acid is several orders of magnitude less than the dissolved carbon dioxide [16]. This is due to the relatively slow reaction kinetics of the hydration reaction, which is conceived to be the rate determining step (RDS) in the corrosion reaction. Therefore, any process that increases the rate of hydration would conceivably increase the corrosion rate.

It is theorised that the presence of trace levels of dissolved oxygen affect the rate of hydration of dissolved carbon dioxide and thereby the corrosion rate. It has already been shown that mere presence of 4 ppb dissolved oxygen affects both the rate of carbon dioxide corrosion and more significantly the dependence on the mass transfer. This investigation will explore this affect in relation to the cathodic limiting current in the presence (12 ppb) and relative absence (<0.5 ppb) of the trace levels of dissolved oxygen.

2 EXPERIMENTAL

The effect of dissolved oxygen on the uninhibited rate of carbon dioxide corrosion was investigated using a jet impingement cell (JIC) over a range of flow velocities. A dissolved oxygen concentration of 12 ppb was achieved using a certified gas mixture of carbon dioxide tainted with 129 ppm oxygen (BOC Gases). A high purity carbon dioxide (BOC Gases), that contained approximately 5 ppm oxygen impurity was filtered through a high capacity oxygen scrubber (Trigon TTO-750) and a self-indicating oxygen trap (Trigon TTIO-150) to achieved <0.5 ppb., where <0.5 ppb represents a conservative detection limit. An Orbisphere dissolved oxygen meter (model 3655) was used to measure the dissolved oxygen *in situ*. The meter was calibrated in air according to the manufacturer's recommendations and cross checked against certified gas mixtures. At atmospheric pressures CHEMetrics® dissolved oxygen tubes (K-7511) with an analytical range of 0-20 ppb were also used as an additional verification.

The JIC incorporated a standard three electrode arrangement for electrochemical measurements, comprising a Hastelloy C-276 reference electrode, mild steel working electrode and a platinum mesh counter electrode. The working electrode was machined from a carbon steel rod (BHP Grade 1020) into 50 mm long hollow cylinder of 1 mm wall thickness with a 5.5 mm internal diameter. The electrode was embedded into an epoxy resin and consecutively ground using 600, 800 and 1000 grit SiC paper on the axial end to expose a ring with a surface area of 0.204 cm². A brine solution consisting of 30 g L⁻¹ NaCl and 0.1 g L⁻¹ NaHCO₃ was used as a common non-scaling electrolyte. All tests were performed at 30 °C with a carbon dioxide partial pressure of 1.88 bar, equivalent to a dissolved carbon dioxide concentration of 0.05 M. The cathodic limiting current behaviour was investigated using potentiodynamic polarisation measurements. The measurements were conducted by scanning the potential in the cathodic direction to -250 mV from the open circuit potential (OCP) using a scan rate of 1 mV s⁻¹. All tests were carried out following a 30 minute equilibration period to minimize recession of the active electrode from the inert epoxy surface, variations in the solution composition and the electrode surface.

3 RESULTS AND DISCUSSION

A series of cathodic polarisation curves were measured using a carbon steel electrode in a non-scaling synthetic brine solution saturated with carbon dioxide, over a range of jet velocities. Comparative cathodic polarisation curves in the presence (12 ppb) and relative absence (<0.5 ppb) of dissolved oxygen are illustrated in Figure I for a flow velocity expressed as the jet velocity of 14 m s⁻¹ (which in fluid mechanics terms corresponds to a Reynolds number (Re) of 32,000 for the jet geometry). It is clear from this comparison that the cathodic limiting current density is significantly greater in the presence of 12 ppb dissolved oxygen. Furthermore, the shapes of the curves show minor differences in the attainment of the limiting current. A true limiting behaviour is achieved in the presence 12 ppb dissolved oxygen, however in the absence of dissolved oxygen there still remains some minor influence of an activation control.

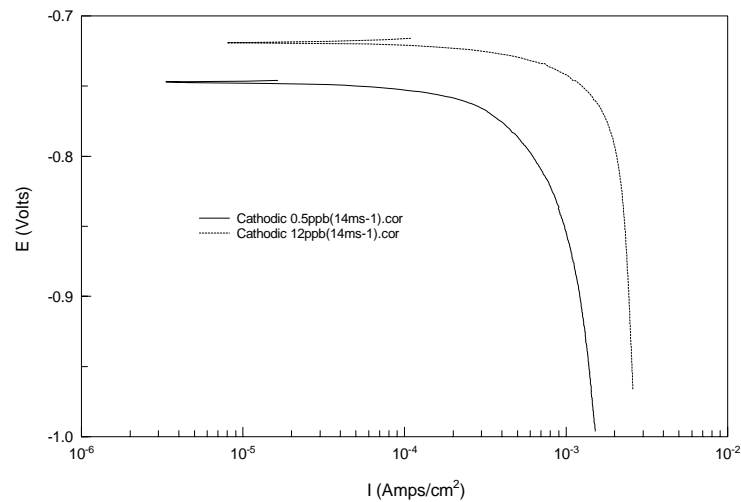


Figure 1: Cathodic polarisation plots of carbon steel (Grade 1020) in carbon dioxide saturated brine in the JIC with a DO <0.5 ppb and 12 ppb. 5.5 mm ID x 1 mm wall thickness ring electrode; 30 °C; 30 g L⁻¹ NaCl + 0.1 g L⁻¹ NaHCO₃; Jet Velocity 14 ms⁻¹ (Re~32500); [CO₂] = 0.05 M; pH 4.5.

The origin of the cathodic limiting current has been attributed to the superposition of the diffusion limited reduction of protons (H⁺) and carbonic acid (H₂CO₃) [10, 11]. Following this concept a theoretical diffusion limiting current can be estimated from the mass transfer to the ring electrode, where the mass transfer to the ring electrode was empirically characterised for this specific JIC using the diffusion limited reduction of ferricyanide on platinum electrodes [17]. Theoretical diffusion limited current densities are compared to the measured cathodic limiting current densities in Tables (I) and (II) for dissolved oxygen concentrations of <0.5 ppb and 12 ppb, respectively. In both tables the mass transfer relationship of the cathodic polarisation curves is clearly evident from the change in current density with flow velocity. This relationship is further emphasised by the consistency in the percentage contribution of the diffusion limited theoretical current density with respect to the measured limiting current density, across all flow velocities. Significantly, however, there is a stark difference in the average value of the percentage contribution in the relative absence (~107% (Table I)) and presence of dissolved oxygen (~67% (Table II)). In the relative absence of dissolved oxygen (<0.5 ppb) the entire cathodic limiting current can be accounted for by the available reactants in solution. The slight overestimation in the total percentage contribution (~7%) is considered to be within the combined experimental error for the mass transfer, pH and carbonic acid concentration used in the calculation. Conversely, in the presence of 12 ppb dissolved oxygen only ~67% of the measured limiting current can be attributed to the available cathodic reactants. This value includes the diffusion limited contribution from the dissolved oxygen which only accounts for less than 1% of the limiting current density.

Table 1: Comparison of theoretical diffusion limited current density with the measured corrosion and cathodic limiting current over a range of flow velocities with a dissolved oxygen concentration of <0.5 ppb. 5.5 mm ID x 1 mm wall thickness ring electrode; 30 °C; 30 g L⁻¹ NaCl + 0.1 g L⁻¹ NaHCO₃; [CO₂] = 0.05 M ([H₂CO₃] = 5.75 x 10⁻⁵ M); pH 4.5.

Jet Velocity (m s ⁻¹)	Mass Transfer Coefficient (m s ⁻¹) x 10 ³		Theoretical Diffusion Limited Current Densities (mA cm ⁻²)		Total Diffusion Limited Current Density (mA cm ⁻²)	Measured Current Densities (mA cm ⁻²)	Percentage Contribution (% I _{Theory} /I _{Lim})
	H ⁺	H ₂ CO ₃	H ⁺	H ₂ CO ₃	I _{Theory}	I _{Lim}	
5	2.06	0.74	0.63	0.41	1.04	0.95	109
10	2.58	0.92	0.79	0.51	1.30	1.21	108
14	3.10	1.11	0.95	0.62	1.57	1.52	103
19	3.63	1.30	1.11	0.72	1.83	1.71	107
27	4.57	1.64	1.39	0.91	2.30	2.15	107

Table 2: Comparison of theoretical diffusion limited current density with the measured corrosion and cathodic limiting current over a range of flow velocities with a dissolved oxygen concentration of 12 ppb. 5.5 mm ID x 1 mm wall thickness ring electrode; 30 °C; 30 g L⁻¹ NaCl + 0.1 g L⁻¹ NaHCO₃; [CO₂] = 0.05 M ([H₂CO₃] = 5.75 x 10⁻⁵ M); pH 4.5.

Jet Velocity (m s ⁻¹)	Mass Transfer Coefficient (m s ⁻¹) x 10 ³			Theoretical Diffusion Limited Current Densities (mA cm ⁻²)			Total Diffusion Limited Current Density (mA cm ⁻²)	Measured Current Densities (mA cm ⁻²)	Percentage Contribution (% I _{Theory} /I _{Lim})
	O ₂	H ⁺	H ₂ CO ₃	O ₂	H ⁺	H ₂ CO ₃	I _{Theory}	I _{Lim}	
7	1.15	2.27	0.81	0.017	0.69	0.45	1.16	1.73	68
11	1.37	2.69	0.96	0.02	0.82	0.53	1.37	2.05	68
14	1.58	3.10	1.11	0.023	0.95	0.62	1.59	2.42	67
18	1.79	3.52	1.26	0.025	1.07	0.70	1.80	2.71	67
22	2.00	3.94	1.41	0.03	1.20	0.78	2.01	3.17	65

It is apparent from this theoretical analysis of the diffusion limited current densities that there has to be an additional reactant source or an increased supply of an existing reactant. The most plausible explanation for this apparent increase in cathodic reactant comes from the conventional reaction mechanism that considers the hydration of dissolved carbon dioxide as the rate limiting step. An increase in the rate of hydration would correlate with an increased supply of reactant and the observed increase in the cathodic limiting current. This perception implicates the involvement of trace levels of dissolved oxygen with the hydration process and more importantly an enhancement in the rate.

The hydration of dissolved carbon dioxide is a nucleophilic attack of the carbon atom by water molecules. In this instance water is a weak nucleophile and by definition the reaction is relatively slow in comparison to the rate of hydration from a strong nucleophile such as hydroxide [18-21]. It is therefore conceivable that a reaction product (OH⁻) or intermediate (H₂O₂) of oxygen reduction may provide the suitable catalyst to significantly enhance the rate of hydration and therefore the apparent concentration of carbonic acid at the surface. Alternatively, it is also possible that the reduction of oxygen and/or change in surface pH may promote the formation of surface oxides that are capable of catalyzing the hydration of dissolved carbon dioxide through a heterogeneous mechanism. The complex interplay between the interfacial pH and the rate of mass transfer would engender a variable rate constant for the hydration process that would be dependent on the flow velocity and the oxygen concentration [1].

4 CONCLUSION

Cathodic polarisation curves have been used to investigate the effect of trace levels of dissolved oxygen on the mechanism of carbon dioxide corrosion of carbon steel. An analysis of the cathodic behaviour illustrates a significant enhancement in the cathodic limiting current in the presence of 12 ppb dissolved oxygen in comparison to its relative absence (<0.5 ppb). The cathodic limiting current behaviour displays a mass transfer dependence in absence and presence of dissolved oxygen, though the relationship is notably more pronounced in its presence. A theoretical analysis of the cathodic limiting current accounted for the current density produced in the relative absence of dissolved oxygen (~107%), though it could not account for the limiting current density measured in the presence of trace levels of dissolved oxygen (~67%). This theoretical analysis was based on the conventional concept of a superposition of the diffusion limited current from protons and carbonic acid. It was conceived that the presence of trace dissolved oxygen must provide an additional source of cathodic current outside of its own contribution, which can only account for less than 1% of the measured cathodic limiting current. The most likely source, that is abundantly present at the reacting interface, is the dissolved carbon dioxide and its hydration to carbonic acid. It is plausible that the products from the reduction of oxygen on the electrode surface may promote the hydration of dissolved carbon dioxide and provide an enhanced supply of carbonic acid. Two possible mechanisms have been presented involving a homogeneous (solution reaction) and a heterogeneous (surface-solution reaction) catalytic hydration of excess dissolved carbon dioxide. The actual mechanism through which trace levels of dissolved oxygen engender this enhancement in the cathodic limiting current remains unclear and requires further research.

5 REFERENCES

1. D. John, S. Bailey, R. De Marco, and B. Kinsella, Corrosion 2007, Paper 07315, (2007).
2. D.A. John, Mechanism of Carbon Dioxide Corrosion and Inhibition Under High Flow: A Jet Impingement Study, PhD Thesis, Perth: Curtin University of Technology, (2006)
3. D. John, B. Kinsella, R. DeMarco, and S. Bailey, Corrosion and Prevention 2004, Paper No. 81, (2004).
4. E. Gulbrandsen, J. Kvarekvaal, and H. Miland, CORROSION 2001, (2001).

5. N.I. Podobaev and E.A. Larionov, *Prot. Met.*, 31, p. 457 (1995).
6. N.I. Podobaev and V.I. Kotov, *Uch. Zap., Mosk. Gos. Pedagog. Inst.*, p. 24 (1969).
7. E. Gulbrandsen, J. Kvarekvaal, and H. Miland, *Corrosion*, 61, p. 1086 (2005).
8. E. Gulbrandsen and A. Granå, *Corrosion*, 63, p. 1009 (2007).
9. E. Eriksrud and T. Sontvedt, *Advances in CO2 Corrosion*, ed. H.P. Godard and R. Hausler. Vol. 1, NACE, Texas, 1984.
10. S. Nestic, B.F.M. Pots, J. Postlethwaite, and N. Thevenot, *The Journal of Corrosion Science and Engineering*, 1 (Paper 3), p. 1 (1995).
11. G. Schmitt, *Corrosion* 83, Paper No. 43, (1983).
12. G. Schmitt and B. Rothmann, *Werkstoffe und Korrosion*, 28, p. 816 (1977).
13. G. Schmitt, C. Werner, and M.J. Schoning, *Corrosion 2002*, Paper No. 2280, (2002).
14. D. John, B. Kinsella, R. DeMarco, and S. Bailey, *Corrosion and Prevention 2004*, (2004).
15. C. de Waard and D.E. Milliams, *Corrosion*, 31, p. 177 (1975).
16. J.N. Butler, *Carbon Dioxide Equilibria and Their Applications*: Addison-Wesley Publishing Company. (1989)
17. T.J. Hanratty and J.A. Campbell, *Fluid Mechanics Measurements*, ed. R.J. Goldstein, Hemisphere Publishing Corporation, New York, 1983.
18. J.P. Guthrie, *Canadian Journal of Chemistry*, 77, p. 934 (1999).
19. M. Brauer, J.L. Perez-Lustres, J. Weston, and E. Anders, *Inorganic Chemistry*, 41, p. 1454 (2002).
20. A.L. Soli and R.H. Byrne, *Marine Chemistry*, 78, p. 65 (2002).
21. D.M. Kern, *Journal of Chemical Education*, 37, p. 14 (1960).