



Desktop review and corrosion modelling for integrity-based impacts of raising AS-4564 oxygen limits on Australian natural gas networks

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Abbreviations

Abbreviation	Units	Definition
<i>CR</i>	mm/yr	Corrosion rate
<i>F</i>	A.s/mol	Faraday Constant (96,485)
<i>i</i>	A/m ²	Current Density
<i>k_H</i>	mol/kg.bar	Henry's Law Constant
<i>k_m</i>	m/s	Mass Transfer coefficient
<i>p</i>	bar	Partial pressure
<i>pH</i>		log ₁₀ [H ⁺]
<i>T</i>	K	Temperature
<i>U</i>	m/s	Velocity
Subscripts:		
<i>α</i>		Reaction rate
<i>a</i>		anodic
<i>c</i>		cathodic
<i>corr</i>		corrosion
<i>lim</i>		Mass transfer limiting

Contents

Important Disclaimer	5
Acknowledgement	5
Project Information	4
1 SUMMARY OF REPORT	7
2 BACKGROUND	8
2.1 Corrosion Theory	8
2.1.1 Oxygen Reduction	9
2.1.2 Carbon dioxide Reduction	9
2.2 Corrosion Modelling	10
2.2.1 Freecorp Model	10
2.2.2 Empirical Model	11
3 RESULTS	12
3.1 Effect Of O₂	12
3.2 Effect of CO₂	13
3.3 Effect of Temperature	14
4 DISCUSSION	14
5 CONCLUSIONS AND RECOMMENDATION	16
6 REFERENCES	18

1 SUMMARY OF REPORT

This report aims to provide insight into the corrosion of natural gas pipelines after injecting biomethane with oxygen (O₂) concentrations greater than the AS 4564 allowable limit, i.e. 0.2 mol%. Corrosion rate calculations are performed by two approaches: a theoretical method simulated by FREECORP software, and an empirical model developed from experimental data. Key conclusions from the corrosion modelling are summarized as follows:

- The mechanism of corrosion in natural gas pipelines shows that O₂-induced corrosion requires liquid water to take place.
- If such free water is present, the increase in corrosion rate is approximately linearly proportional to the increase in oxygen partial pressure. This means doubling the oxygen concentration would likely double the internal corrosion rate in any existing asset.
- The corrosion rate increases with CO₂ partial pressure but the increase is less pronounced than that of O₂.
- The corrosion rate increases with the velocity of the aqueous phase, which may move more slowly than the bulk gas flow.
- The effect of temperature on the corrosion rate is also linear and stronger than CO₂ partial pressure.
- the most vulnerable assets are those operating under high total gas pressures and with a possibility of free water to be present.

Based on an analysis of international practice, it is recommended that Australian guidelines and/or regulations take a nuanced approach, as has been done in the UK and Europe. Specifically, it is recommended that a new NOTE be added to Table 4.1 in AS4564 as follows:

NOTE 6 Higher oxygen concentrations (up to 3%) may be permissible if appropriate validation of downstream assets and infrastructure permits. In such cases, additional risk mitigation actions may be required and should be discussed with the relevant regulatory authority. See Appendix A3.4.

With Appendix A3.4 expanded to read:

Internal corrosion of pipeline infrastructure is exacerbated by high partial pressures of oxygen. Such corrosion will occur if water is present as a free liquid, adsorbed to hygroscopic salt deposits or absorbed in liquid glycol carried over from dehydration units. Corrosion increases with temperature and in the presence of acidic gases (carbon dioxide and hydrogen sulfide).

2 BACKGROUND

A previous literature review on the feasibility of biomethane and natural gas mixing within pipelines showed that O₂ concentrations could exceed the current allowable oxygen limit in AS 4564, i.e. 0.2 mol% [1]. O₂ removal from biogas can be achieved by membranes or low-temperature pressure swing adsorption, but achieving O₂ concentrations compliant with AS 4564 is costly [2]. Therefore, it may be preferable to inject biomethane with O₂ concentrations greater than the AS 4564 limit. However, increased O₂ content in pipelines may present new corrosion issues. Previous workers have suggested that even 100 ppmv of oxygen in a wet pipeline can cause significant changes in pipeline integrity [3].

This report aims to predict internal corrosion rates of natural gas pipelines as a consequence of elevated O₂ levels from biomethane injection. The corrosion modelling considers O₂ concentrations of up to 1 mol% in natural gas pipelines.

2.1 CORROSION THEORY

Corrosion is an electrochemical process involving the movement of electrons within steel and ions within an electrolyte such as water. As such, it will not occur within a gas stream that is completely dry, as there is no mechanism for ions to flow.

The four elements that are common to all corrosion processes are (see Figure 1):

- An anode (the location where oxidation occurs)
- A cathode (the location where reduction occurs)
- A connection between the electrodes that allows electrons to flow from the anode to the cathode
- An electrolyte (allowing ions flow between the anode and the cathode)

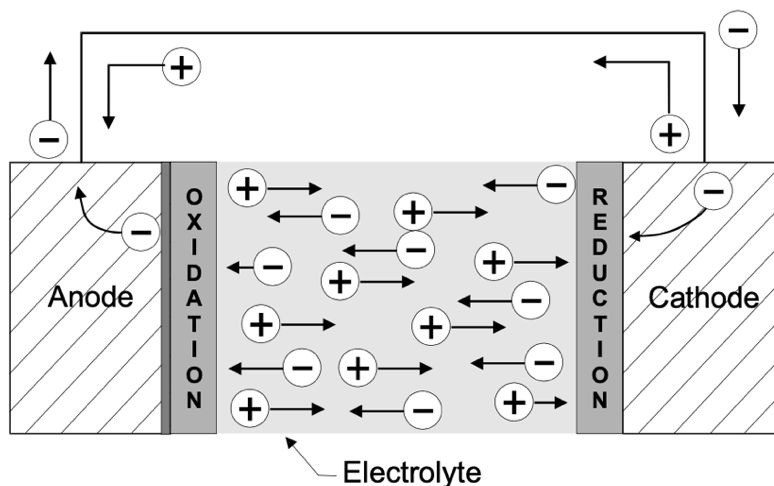


Figure 2-1 – Charge movement in a corrosion cell (copied from [4])

The electrochemical dissolution of iron (Fe) is the dominant anodic reaction, and this oxidation reaction results in a loss of iron through Equation 2-1.



The current density of this anodic reaction ($i_{a(Fe)}$) is known as the corrosion current density (i_{corr}) and must equal the sum of the current density of all the cathodic reactions.

$$i_{corr} = i_{a(Fe)} = i_{c(CO_2)} + i_{c(O_2)} + i_{c(H_2S)} + \dots \quad \text{Equation 2-2}$$

Dominant cathodic reactions include the reduction of carbon dioxide(CO₂), oxygen(O₂) and hydrogen sulphide (H₂S) as shown in Equation 2.2, but can also include the reduction of organic acids such as acetic acid.

The corrosion rate (in mm per year) may then simply be determined by relating the corrosion current density to the corresponding loss of iron. This gives Equation 2-3

$$CR = 1.1588 i_{corr} \quad \text{Equation 2-3}$$

2.1.1 Oxygen Reduction

Under the acidic conditions that are likely to predominate in natural gas liquids, the oxygen reduction reaction is given by Equation 2-4.



The rate of oxygen reduction is a function both of the rate of this reaction but also the rate of mass transfer of oxygen to the reaction zone. This can be expressed as a sum of resistances (Equation 2-5)

$$\frac{1}{i_{c(O_2)}} = \frac{1}{i_{\alpha(O_2)}} + \frac{1}{i_{lim(O_2)}} \quad \text{Equation 2-5}$$

Under most circumstances, mass transfer dominates[5]. Cox and Roethali[6] indicate that this is the case for oxygen concentrations below 5.5 cm³/L, which equates to 7ppm in the liquid phase or 18 kPa oxygen partial pressure in the gas phase. When this is the case, the cathodic current can be expressed in terms of the mass transfer coefficient ($k_{m(O_2)}$), the Faraday constant(F) and the concentration of oxygen within the aqueous phase ([O₂]) (Equation 2-6)

$$i_{c(O_2)} = 4k_{m(O_2)}F \cdot [O_2] \quad \text{Equation 2-6}$$

In turn, the mass transfer coefficient is a function of the velocity of the aqueous phase within the pipeline.

2.1.2 Carbon dioxide Reduction

Within the aqueous phase, CO₂ dissociates into carbonate and bicarbonate ions. The overall reduction reaction is given by Equation 2-7:



The most well known correlation relating Equation 2-7 to the corrosion rate (CR, mm/year) is that developed by De Waard and co-workers. This again considers both the reaction rate($CR_{\alpha(CO_2)}$) and mass transfer rate($CR_{lim(CO_2)}$), but these are determined directly as corrosion rates rather than current contributions (Equation 2-8)

$$\frac{1}{CR_{(CO_2)}} = \frac{1}{CR_{\alpha(CO_2)}} + \frac{1}{CR_{lim(CO_2)}} \quad \text{Equation 2-8}$$

$$\log_{10}(CR_{\alpha}) = 4.93 - \frac{1119}{T} + 0.58 \log_{10}(p_{CO_2}) - 0.34 (pH_{actual} - pH_{CO_2}) \quad \text{Equation 2-9}$$

$$CR_{lim} = \frac{2.45U^{0.8}}{d^{0.2}} p_{CO_2} \quad \text{Equation 2-10}$$

Where T is the temperature in Kelvin, p_{CO_2} is the CO₂ partial pressure in the gas phase in bar, U is the liquid velocity in m/s and d is the pipe diameter in m. The term pH_{CO_2} refers to the pH of a pure solution of water and CO₂ alone, so in the absence of H₂S or other acidic gases, this last term in Equation 2-9 can be ignored.

2.2 CORROSION MODELLING

In this report, we compare two different approaches to calculating the rate of corrosion. In both cases, the input data shown in Table 1 is used, to be representative of Australian transmission pipeline conditions. A relatively high CO₂ concentration (2 mol%) is used, to be indicative of ‘worst case’ conditions.

Table 1. Corrosion modelling conditions

Modelling Parameter	Value
Temperature	14 °C
Pressure	50 bar
Diameter	0.2477 m (DN250)
Velocity*	3.7 m/s
Gas Composition	CO ₂ : 2 mol% O ₂ : 0.2 to 1 mol%

* The velocity is representative of 3000 scmh as the combined biomethane and natural gas flowrate in DN250 pipe.

2.2.1 Freecorp Model

The first model used was developed by the Ohio University and is available as an Excel ‘Add-in’ known as FREECORP. It is based on the corrosion theory described above and predicts uniform corrosion rates of carbon steel caused by these species[7]. Figure 1 shows the main window of the FREECORP software where pipeline parameters including temperature, total pressure, pipeline diameter, and velocity are required as inputs. Additionally, the model requires the partial pressure of CO₂ in the gas phase, dissolved Fe(II) and O₂ concentrations in the aqueous phase and pH. The FREECORP model has limitations, and the recommended ranges of inputs are:

- Temperature: 1-120 °C
- Pipe diameter: 0.01-1 m
- Velocity: 0.001-20 m/s
- Fe(II) concentration: 0-100 ppm
- pH: 3-7
- O₂ concentration dissolved in water: 0-10 ppm

Beyond the recommended ranges, the FREECORP software still operates, but the accuracy of predictions may be compromised. The model provides “uniform” corrosion rates only, and no localized corrosion has been considered.

In the present work, we assume the mixed gas is free of H₂S and organic acids. An analysis of Fe²⁺ concentration in condensates recovered during pipeline pigging showed a median value of 4 ppm[8], so this value is used directly. Henry's law was used to estimate the concentration of dissolved O₂ in water according to:

$$x_{O_2} = k_H p_{O_2} \quad \text{Equation 2-11}$$

where x_{O_2} is the dissolved concentration of O₂ in water (mol/kg) and p_{O_2} represents the partial pressure of O₂ in the gas (bar). The Henry's law constant, k_H at 14°C is 0.00158 mol/kg.bar [9].

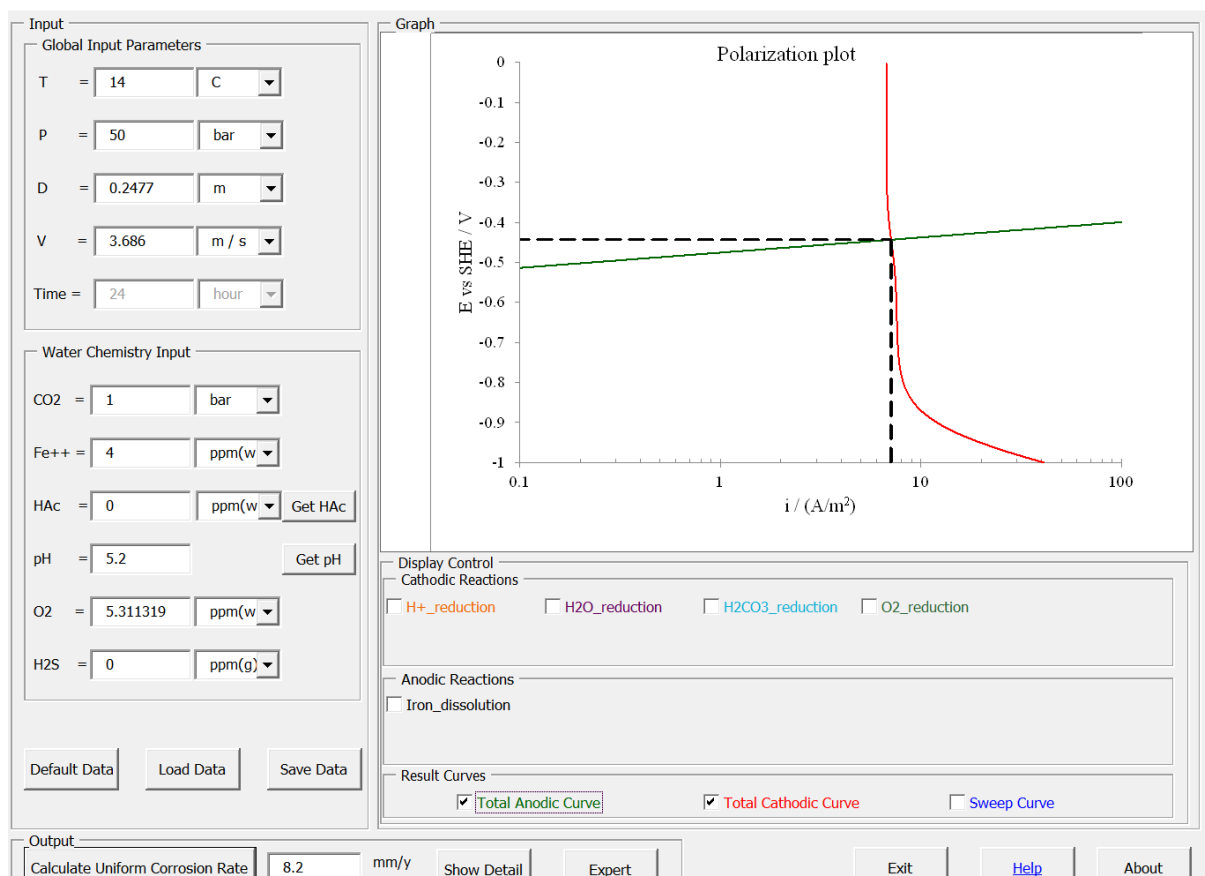


Figure 2-2. The main window of the FREECORP software including inputs and outputs

To estimate pH, a simple simulation of CO₂ dissolution in water was performed in Aspen Plus utilizing the ELECNRTL fluid package. This allowed the equilibrium concentration of the H⁺ ion to be calculated from which the pH was obtained.

2.2.2 Empirical Model

An empirical model has also been developed by Lyle and Schutt[3] based on experimental analysis of immersed corrosion coupons. The empirical model considers the effect of O₂, CO₂ and H₂S on steel corrosion under low flowrates and/or stagnant wet gas conditions:

$$CR = 8.7 + 9.86 \times 10^{-3}(C_{O_2}) - 1.48 \times 10^{-7}(C_{O_2}^2) - 1.31(pH) + 4.93 \times 10^{-2}(p_{CO_2})(p_{H_2S})$$

$$-4.82 \times 10^{-5}(p_{CO_2})(C_{O_2}) - 2.37 \times 10^{-3}(p_{H_2S})(C_{O_2}) - 1.1 \times 10^{-3}(C_{O_2})(pH)$$

Equation 2-12

in which the variables are defined as:

CR : corrosion rate in mils per year (1 mil is equivalent to 0.001 inches)

C_{O_2} : the O_2 concentration of the gas in ppmv

p_{CO_2} : the CO_2 partial pressure in the gas in psi

p_{H_2S} : the H_2S partial pressure in the gas in psi

pH : the initial pH

This empirical model was obtained from the analyses of test results at 60 °F (15.6 °C) and 500 psig (35.5 bar absolute) with a maximum O_2 concentration of 1 mol%. As the present analysis is conducted at 50 bar absolute pressure and it is well established that corrosion is proportional to the oxygen partial pressure, rather than the concentration in ppmv, the C_{O_2} value used in our analysis was taken as the value in ppmv, multiplied by a factor of 50/35.5.

3 RESULTS

In this corrosion modelling, liquid water is assumed to be present in natural gas pipelines for the entire duration of an operational year. This assumption is employed primarily because of the lack of information about how often liquid water is present in pipelines. As a result, calculated corrosion rates might not be reflective of actual corrosion values in transmission pipelines where liquid water does not normally exist but can be used to predict corrosion rates when this does occur.

3.1 Effect Of O_2

Corrosion rate calculations as a function of O_2 partial pressure in the gas phase is presented in Figure 2. The FREECORP software is limited to a dissolved O_2 concentration of 10 ppm, which is equivalent to 0.43 mol% O_2 at 50 bar. Similarly, the empirical model is valid up to O_2 partial pressures of 0.35 bar or 0.7 mol% O_2 at 50 bar. The models are both shown solid lines below, and as dashed lines beyond, these limits. The FREECORP model shows a linear relationship between the corrosion rate and O_2 partial pressure. The empirical model also indicates an approximately linear relationship at low O_2 partial pressures. This is in agreement with Cox and Roetheli[6] who observed a linear corrosion rate up to oxygen partial pressures equivalent here to 0.35 mol%. Above this concentration, the corrosion rate levels off. The most important implication of the linear relationship is that increasing the O_2 concentration in any pipeline would likely lead to a proportionate increase in corrosion rates. For example, doubling the O_2 concentration would likely double the corrosion rate, given the corrosion rate in the absence of O_2 is relatively small.

Corrosion rates calculated by the FREECORP software at high flowrate conditions (velocity of 3.7 m/s) are considerably greater than the empirical model predictions. However, when the velocity is set to 0.001 m/s (the smallest possible velocity in the FREECORP software) to simulate the stagnant flow conditions of the empirical model, the corrosion rates computed by both models are of the same order of magnitude. Under such conditions, it is well known that a passivating film of corrosion products form on the steel surface restricting further corrosion.

As noted in Section 2.1.1, oxygen related corrosion is mass transfer limited, so highly dependent upon the velocity of the aqueous phase. Higher flowrates disrupt the passivating film.

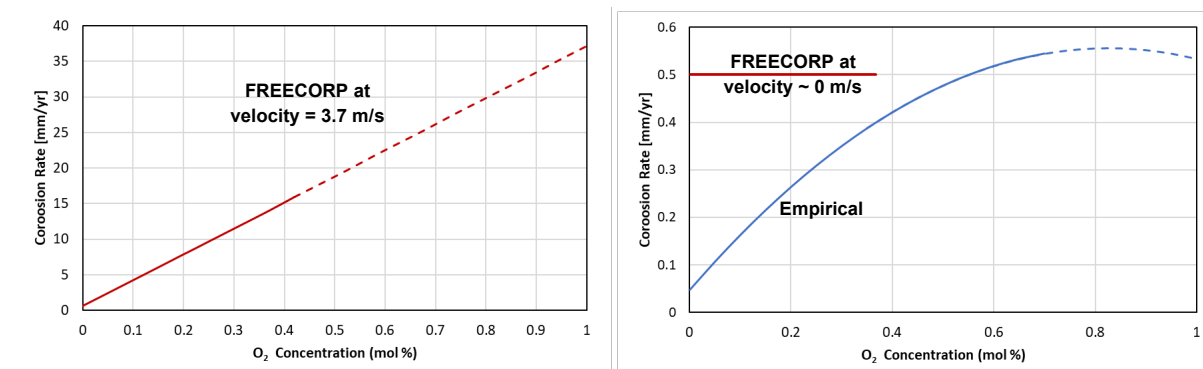


Figure 2-1. Effect of O₂ mol fraction in a gas of 50 bar total pressure on the corrosion rate. Modelling conditions are listed in Table 2. Both FREECORP and empirical models are restricted to the ranges shown by solid lines. Dashed lines indicate predictions beyond the recommended ranges of the model operation.

Water is expected to travel along a pipeline more slowly than the bulk gas. A related study has indicated that for this reason, a velocity of 0.5 m/s may be more realistic than the values of 5 – 10 m/s that are typical of gas flowrates[10]. To investigate this effect further, the influence of velocity was investigated using the Freecorp model at 0.2 mol% O₂ and 50 bar pressure (Figure 4). The corrosion rate linearly increases with the aqueous phase velocity, as might be expected given the mass transfer limitations of oxygen corrosion. When the velocity increases from 1 m/s to 4 m/s the corrosion rate increases by a factor of 2.3.

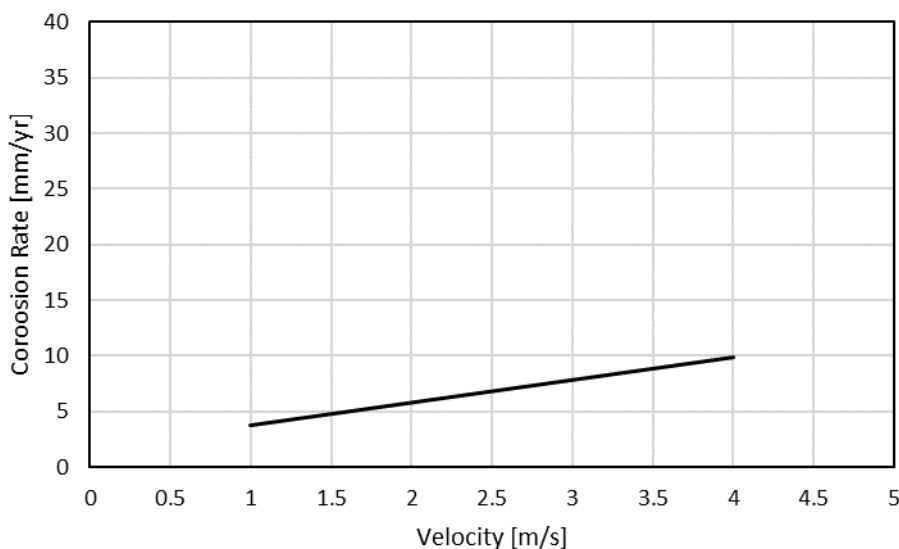


Figure 2-2. Effect of gas velocity on corrosion rate at 0.2 mol% O₂ in a total gas pressure of 50 bar. Other modelling conditions are listed in Table 2.

3.2 EFFECT OF CO₂

Using the FREECORP software, corrosion rates at different CO₂ partial pressures are indicated in Figure 3. A very mild linear increase in the corrosion rate (approximately 16%) is seen as the CO₂ concentration in the gas increases from 2 mol% to 10 mol%, representing the stronger impact of O₂ on the overall corrosion of pipelines relative to

CO₂. Skaperdan and Uhlig[5] investigated the corrosion of steel pipes and reported that both dissolved carbon dioxide (CO₂) and O₂ resulted in an increase in the rate of corrosion, but the effect of O₂ on the corrosion rate was six to ten times greater than that of CO₂ in some circumstances.

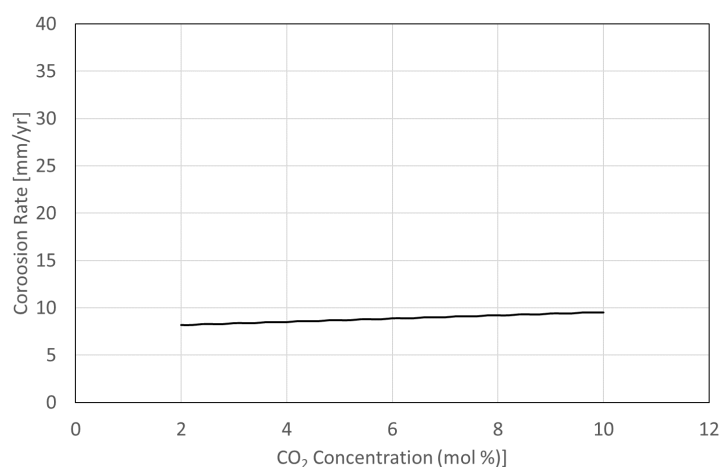


Figure 2-3. Effect of CO₂ on corrosion rate at 0.2 mol% O₂ in a total gas pressure of 50 Bar. Other modelling conditions are listed in Table 2.

3.3 EFFECT OF TEMPERATURE

The corrosion rate increases with temperature as shown in Figure 5. Although an increase in temperature lowers the dissolved concentration of O₂ in water, it causes more rapid diffusion of the oxygen to the metal surface. Changing the temperature from 14°C to 50°C resulted in a 76% increase in the corrosion rate.

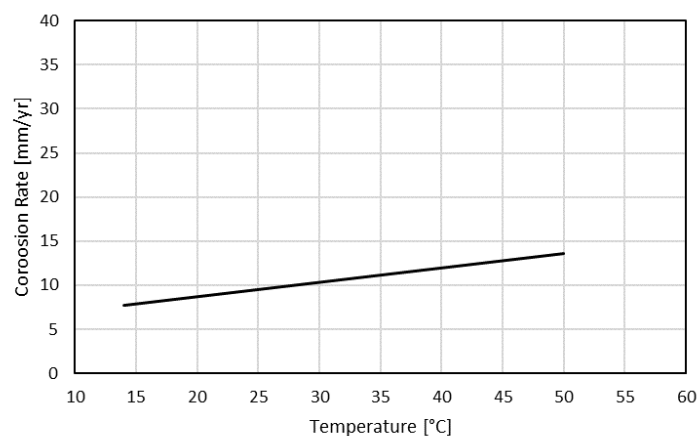


Figure 2-4. Effect of temperature on corrosion rate at 0.2 mol% O₂ in a total gas pressure of 50 bar. Other modelling conditions are listed in Table 2.

4 DISCUSSION

In our earlier literature review[1], two studies were found regarding the suitability of increasing the maximum oxygen limit from 0.2 to 1.0 mol % [10, 11] in natural gas networks, for the purposes of biomethane injection. The UK study[11] reported that steel corrosion rates in the presence of water were expected to increase five-fold for the corresponding five-fold increase in oxygen concentration; while the Irish study predicted a three-fold increase (see Table 2). We see a similar trend – a five-fold increase is predicted from the Freecorp software, while the empirical equation predicts a two-fold increase. This is because the increase in corrosion rate is directly related to the oxygen

partial pressure (see Equation 2-6). However, both studies concluded that concentrations up to 1 mol % oxygen were not expected to result in significant changes to the risks of using the gas, by concluding that the exposure to free water would be limited to only a small fraction of the total lifetime of the pipeline. The Irish study notes:

“the key to maintaining acceptable corrosion rates within the pipeline systems is to control the water content rather than the corrosive species”[10].

Table 2 Summary of Oxygen Corrosion Studies in Gas Pipelines

Parameter	Units	UK Study[11]	Ireland Study[10]	This Study
Pipe Material	-	Cast Iron	Steel	Steel
Temperature	°C	15	15	14
Pressure	kPa	200	8,000	5,000
Flow velocity (liquid)	m/s	0.5	0.5	3.7
CO ₂ Content	mol %	2.5	2.5	2.0
O ₂ Content	mol %	0.2, 1.0	0.2, 1.0	0.2 - 1.0
pH	-	6.3	Not specified	Calculated
Corrosion rate in wet gas at 1% O ₂ and maximum pressure	mm/yr	0.2	11.5	37
Methodology		Freecorp	Freecorp	Freecorp
Time water present	days per year	30	3.65	3.65
Average yearly corrosion rate		0.016	0.115	0.37

The UK study[11] assumes a total period of 30 days per year for exposure of the distribution network to water ingress, while the Irish study[10] assumes that free water would only be present in transmission pipelines for a maximum of 1% of time. This latter estimate assumes that monitoring and automatic diversion of off-specification gas is implemented (as is generally the case in Australia) and is also based on anecdotal evidence from a North Sea operator (i.e. offshore platform gas). The study notes that free water may accumulate in dead legs, particularly after hydrostatic testing. The passage of correctly dewpointed gas however, would lead to evaporation of any such residual water, so that corrosion would only persist for short periods[10]. On this basis, the corrosion rate reduces to 0.115 mm/year which is considered acceptable. In our case, based on a higher velocity, the rate of 0.37 mm/yr would be comparable to external corrosion rates (See Table 3), but still of concern.

Table 3 Corrosion rates of the external surface of piping exposed to soil, taken from ASME B31.8S-2010[12]

Corrosion Rate (mm/yr)	Soil Resistivity (Ohm cm)
0.075	> 15,000 and no active corrosion seen
0.15	1000 – 15,000 and/or active corrosion
0.3	< 1000 (worst case)

In general, corrosion is unlikely to be an issue in low pressure distribution systems, where water ingress is more common, due to the low gas pressures and thus low oxygen partial pressures. In the UK the Health Safety and Environment (HSE) Office has permitted the introduction of natural gas containing up to 1% oxygen at pressures of up to 38 bar[10]. The 38 bar limit would exclude their National Transmission Network which operates between 38 and 85 barg[10].

High pressure transmission pipelines are more vulnerable to high oxygen partial pressures. While free water is less likely to occur in these systems, it can arise from hydrostatic testing. Water vapor can also condense within hygroscopic salts deposited on pipeline internal surfaces[13] leading to highly corrosive deposits.

In related work[8], products from oxygen induced corrosion (e.g. magnetite) were noted as the dominant solids in pigging samples taken from 20 out of 28 locations within the Queensland gas network. Up to 8.6 wt% water was observed in the liquid fraction of these pigging samples, with an average value of 2.4 wt%. The majority of the liquid was glycol, which is known to reduce the rate of corrosion relative to an aqueous phase [14]. For example, Ekawati et al.[15] find that the corrosion rate in an oxygen-free solution reduces from 0.7 to 0.3 mm/yr when moving from a solution of 1 wt% NaCl in water to a 50 wt% mixture with monoethylene glycol. Smart and Roberts[16] suggest that at 90-99% triethylene glycol, the corrosion rate will be around 1% that in an equivalent aqueous solution. Sherik et al.[17] indicate that at a TEG content of 90 wt% and greater, the corrosion rates become virtually zero regardless of the gas composition, but these authors do not consider the concurrent presence of any salt. Oxygen can also exacerbate the thermal degradation of glycols. Smart and Roberts[16] indicate that this generates acids, with the glycol pH falling to as low as 3.5 and thus causing increased corrosion.

Given these findings, it may be prudent to consider the approach used in the UK (i.e. limit higher oxygen concentrations to low pressure pipelines) or that in Europe. The European Standard (EN 16726) stipulates an oxygen limit of 0.001 mol%[18]. Where it can be demonstrated however, that the installation is not sensitive to oxygen, this limit can be increased to 1 mol%. Underground storage chambers, which are known for a tendency to be wet[10], are listed as an example where the lower limit must apply. Similarly, in Germany the oxygen limit is set at 3% in dry gas grids, but 0.5% in wet grids (DVGW G260 and G262)[11].

5 CONCLUSIONS AND RECOMMENDATION

This report presents corrosion modelling of natural gas pipelines under elevated O₂ concentrations. Results showed that the corrosion rate would likely increase linearly proportional to O₂ partial pressure, whenever free water was present. This work also investigated the effects of CO₂ partial pressure, gas velocity and temperature on the corrosion rate. Results showed that changes to the velocity of the aqueous phase had the strongest impact on corrosion rate followed by the temperature and CO₂ partial pressure.

If the oxygen concentration permitted in pipelines was allowed to increase from 0.2 mol%, the most vulnerable assets would be those operating under high total gas pressures and with a possibility of free water to be present. For this reason, it is recommended that Australian guidelines and/or regulations take a nuanced approach, as has been done in the UK and Europe.

Discussion with our industry advisory team has led to the following recommended changes to AS4564.

1. Add a new note to Table 4.1:

Table 4.1 — Limitations of gas properties

Characteristics and components		Limit
Wobbe Index	Minimum	46.0 MJ/m ³
	Maximum	52.0 MJ/m ³
Higher heating value	Maximum	42.3 MJ/m ³
Oxygen	Maximum	0.2 mol %
Hydrogen sulfide	Maximum	5.7 mg/m ³
Odour intensity	Minimum	Where required, detectable at a level not exceeding 20 % LEL
Total sulfur	Maximum	50 mg/m ³
Water content	Maximum	Dewpoint 0 °C at the highest MAOP in the relevant transmission system (in any case, no more than 112.0 mg/m ³)
Hydrocarbon dewpoint	Maximum	2.0 °C at 3500 kPa gauge
Total inert gases	Maximum	7.0 mol %
Oil	Maximum	20 mL/TJ
<p>The sulfur level upstream of the point(s) of addition of odorant shall be such as to allow for any increase due to the odorant.</p> <p>NOTE 1 m³ means 1 m³ of dry gas at the standard conditions (see 3.13).</p> <p>NOTE 2 mol % means the mole fraction of gas expressed as a percentage.</p> <p>NOTE 3 Where odorization is required, the odorant content required to satisfy the detectability at 20 % LEL needs to account for variations in the odorant used and residence time and may be subject to specific jurisdictional requirements.</p> <p>NOTE 4 Figure A.1 shows the dewpoint at zero degrees Celsius with water content plotted against pressure.</p> <p>NOTE 5 See Appendix A for further information on characteristics and components of natural gas.</p>		

NOTE 6 Higher oxygen concentrations (up to 3%) may be permissible if appropriate validation of downstream assets and infrastructure permits. In such cases, additional risk mitigation actions may be required and should be discussed with the relevant regulatory authority. See Appendix A3.4.

2. Modify Appendix 3.4 as follows:

Original Wording:

A.3.4 Oxygen

Corrosion products from oxidation in steel pipelines have the effect of stripping the injected odorant from gas.

Proposed Wording:

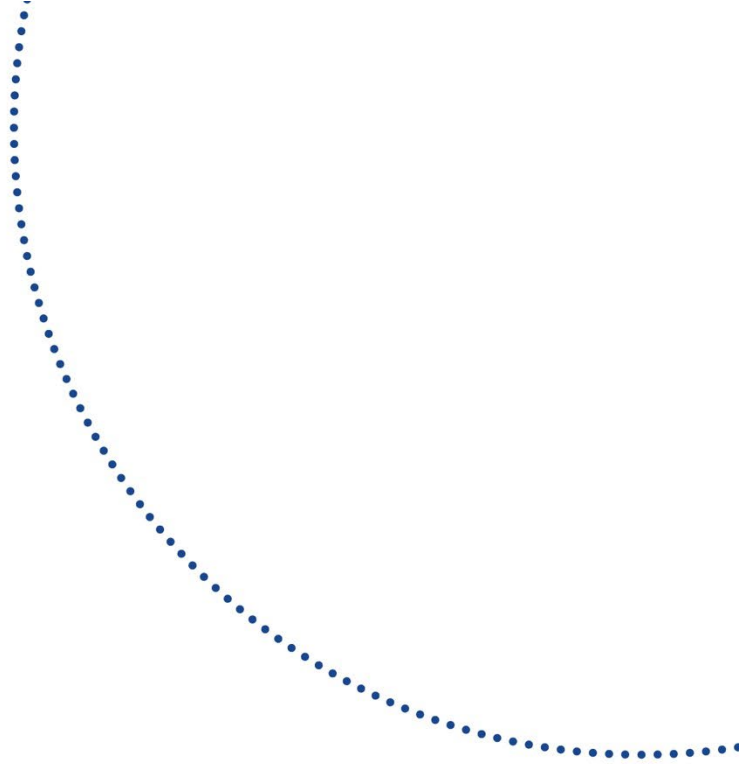
A.3.4 Oxygen

Internal corrosion of pipeline infrastructure is exacerbated by high partial pressures of oxygen. Such corrosion will occur if water is present as a free liquid, adsorbed to hygroscopic salt deposits or absorbed in liquid glycol carried over from dehydration units. Corrosion increases with temperature and in the presence of acidic gases (carbon dioxide and hydrogen sulfide). Corrosion products from oxidation in steel pipelines have the effect of stripping the injected odorant from gas.

6 REFERENCES

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