Biomethane – Oxygen Content Assessment

17985-AI-RPT-001 Rev 5

Gas Networks Ireland

June 2018

Penspen
4th Floor
Central Square South
Orchard Street
Newcastle upon Tyne
NE1 3AZ
United Kingdom

This document is issued in accordance with an agreement between Penspen Limited and the Client, which sets out the entire rights, obligations and liabilities of the parties with respect to the content and use of this document.

Any other party relying in any way on any aspect of this document does so at its own risk. Penspen makes no warranty or representation, express or implied, to any party other than its client under the Agreement and only then as stated therein, with respect to the accuracy, completeness, or usefulness of any information contained in this document. Penspen assumes no liabilities with respect to any other party's use of, or damages suffered as a result of, any use of or reliance on, any information, conclusions or recommendations contained in or imputed from the document.

Penspen Limited, incorporated in England, registered office: 3 Water Lane, Richmond Upon Thames, Surrey, TW9 1TJ, reg. no. 0584446

Revision, change control and authorisation history.

Document owner:	*CDE for Materials and Corrosion*					
Rev	**Date**	**Description and/or change history**	**No of pages**	**Prepared** Name Job title	**Checked** Name Job title	**Authorised** Name Job title
A	21/11/17	Internal review	22	BGK CDE	MT Consultant	BGK CDE
0	22/11/17	Client issue/review	22	BGK CDE	MT Consultant	BGK CDE
1	24/01/18	Client comments incorporated	22	BGK CDE	MT Consultant	BGK CDE
2	12/04/18	Further client comments incorporated	24	BGK CDE	MT Consultant	BGK CDE
3	09/05/18	Final modifications	26	BGK CDE	MT Consultant	BGK CDE
4	05/06/18	Additional content incorporated	26	BGK CDE	MT Consultant	BGK CDE
5	25/06/18	References revised	26	MT Consultant	MT Consultant	BGK CDE

CONTENTS

ABBREVIATIONS

ALARP	As Low As Reasonably Practicable
CER	Commission for Energy Regulation (now Commission for Regulation of Utilities)
ECE	Electronic Corrosion Engineer
GNI	Gas Networks Ireland
HSE	Health and Safety Executive
LEL	Lower Explosive Limit
mm/yr	Millimetres per year
mpy	mils per year
PE	Polyethylene
ppmv	Parts per million (volume)
SGN	Scotia Gas Networks
UEL	Upper Explosive Limit
WWU	Wales and West Utilities

1 EXECUTIVE SUMMARY

1.1 Introduction

Gas Networks Ireland operate both transmission and distribution gas networks in Ireland. GNI has recognised biomethane as a renewable fuel which can significantly improve the sustainability of the natural gas network and reduce dependency on imported natural gas. Consequently the company is reviewing the injection of biomethane into its network. Currently the oxygen limit for injection into the networks is 0.2%, however, it is likely that some biomethane sources will not be able to meet this limit and GNI wish to assess the impact of increasing the oxygen limit up to 1%.

GNI have requested an assessment to be completed that shall consider the implications for both the Transmission and Distribution Networks and the report should recommend a safe oxygen limit for both the Distribution and Transmission networks. Consideration shall be given to demonstrating ALARP in line with regulator guidelines, CER/16/106 ALARP Guidance.

1.2 Conclusions and Recommendations

1.2.1 Conclusions

The following conclusions were drawn from the work:

- Increasing the oxygen content to 1% will have no effect on the PE distribution network.

- Increasing the oxygen content to 1% will have a negligible effect on the steel distribution and transmission networks, provided that the mitigation measures (monitoring and automatic diversion of off specification gas) that have already been recommended are implemented.

- Increasing the oxygen content to 1% will have no significant effect on the lower and upper explosive limits (LEL and UEL) of the gas.

- Increasing the oxygen content to 1% will have no effect on the calorific value of the gas with respect to maintaining the range specified in the gas quality specification.

- The use of the proposed mitigation measures will demonstrate that the introduction of 1% oxygen is ALARP.

- Increasing the oxygen content to 1% will have no significant effect on corrosion or operability of end user equipment.

- The key to maintaining acceptable corrosion rates within the pipeline systems is to control the water content rather than the corrosive species.

1.2.2 Recommendation

The following recommendation is made following the work:

- Due to the importance of water content for corrosion, it is recommended that no attempt is made to relax the water content specification at the same time as the oxygen content.

2 INTRODUCTION

2.1 Background

Gas Networks Ireland (GNI) operate both transmission and distribution gas networks in Ireland. GNI has recognised biomethane as a renewable fuel which can significantly improve the sustainability of the natural gas network and reduce dependency on imported natural gas. Consequently the company is reviewing the injection of biomethane into its network. Currently the oxygen limit for injection into the networks is 0.2%, however, it is likely that some biomethane sources will not be able to meet this limit and GNI wish to assess the impact of increasing the oxygen limit up to 1%.

GNI have requested[1] an assessment to be completed that shall consider the implications for both the Transmission and Distribution Networks and the report should recommend a safe oxygen limit for both the Distribution and Transmission networks. Consideration shall be given to demonstrating ALARP in line with regulator guidelines, CER/16/106 ALARP Guidance[2].

2.2 Objective

The objective of the work is to determine whether a proposal to increase the oxygen content of the natural gas supplied by GNI, from 0.2% to 1% would be acceptable. Acceptability would be based on the principle of ALARP, in line with regulator guidelines, CER/16/106 ALARP.

2.3 Scope

The assessment will cover both the transmission and distribution networks. The assessment will consist of three activities, namely:

1. Corrosion assessment. The effect of the proposed increased oxygen content will be studied. Principal activities will be to determine whether there would be increased corrosion if the oxygen content was increased and, if there was, would it be significant compared to other forms of corrosion. The likelihood of any corrosion at all occurring will be evaluated.

2. Explosion assessment. The likelihood of the natural gas having a greater tendency to explode will be evaluated.

3. The change in the calorific value of the gas will be assessed.

The likelihoods will then be assessed to determine whether their effect on pipeline integrity was within the ALARP region.

The methodology is given in more detail in section 4.

Downstream appliances have also been considered as discussed in section 7.

During the kick off meeting[3] it became evident that the first of these activities was the most important, and therefore the majority of the work is concentrated on this activity.

3 ASSET DETAILS

GNI operate both transmission and distribution networks. The transmission network consists of steel pipelines with maximum allowable operating pressures in the range 19 to 85 barg. The distribution network consists mostly of polyethylene pipelines and steel pipelines operating at maximum allowable operating pressures of 4 barg and 7 barg respectively.

The current quality specification of the natural gas was supplied[4]. The information contained within the specification that is relevant to the current work is given in Table 3-1.

Parameter	**Specification**
Total Sulphur (including Hydrogen Sulphide)	<50 mg/m^3
Oxygen	≤0.2 mol%
Carbon Dioxide	≤2.5 mol%
Hydrogen Sulphide	≤5 mg/m^3
Water Content	≤50 mg/m^3
Gross Calorific Value (Real Gross Dry)	36.9-42.3 MJ/m^3
Wobbe Index (Real Gross Dry)	47.2-51.41 MJ/m^3
Delivery Temperature	1°C to 38°C
Nitrogen	≤5 mol%

Table 3-1 Quality specification of natural gas at entry points (excerpts)

4 METHODOLOGY

The methodology for the corrosion assessment uses the following steps:

1. A literature review of standards and research reports covering oxygen contents and corrosion in natural gas.

2. Calculation of corrosion rates using current and proposed gas specifications.

3. An assessment of the impact of the corrosion rates resulting from the proposed gas specifications on the integrity of the pipeline networks.

4. A literature review is performed to establish the effect of raising the oxygen limit on the calorific value and explosive potential of the gas.

5 CALORIFIC VALUE AND EXPLOSIVE LIMIT CONCERNS

5.1 Calorific Value

Calorific value is usually incorporated within the Wobbe number which is a ratio of calorific value to the square root of the specific gravity. An increase to 1% for the oxygen could have a small effect on the Wobbe by reducing the proportion of flammable gas, if the increase in oxygen was at the expense of the methane component. In this case oxygen is considered an inert gas. The reduction would be expected to be around 1.5% in the Wobbe number[5]. This reduction could normally be accommodated by the permitted range in Wobbe number.

Alternatively, if the increased oxygen level was accompanied by a reduction in the concentration of one of the other inert gases then there would not necessarily be a change in the Wobbe number.

It should be noted that there have been no alterations to the quality specification of the gas for either the calorific value or the Wobbe number. These parameters are also continuously monitored at the injection point. Therefore the use of biomethane will have no effect on the calorific value of the gas.

5.2 Explosion and Flammability Assessment

Earlier work[22] has concluded that oxygen limits of up to 1% should not result in any significant risk of explosion. A minimum oxygen concentration of around 10% was regarded as the lower level at which the explosive risk could increase.

A flammability diagram for methane, oxygen and nitrogen was included in a similar reference[5]. This diagram indicated that there is a negligible change in the lower explosive limit (LEL) between an air/methane mixture containing no oxygen and one containing 1% oxygen. There was also no significant difference between these mixtures and one of pure oxygen and methane. The lower explosive limit in all these cases was approximately 4.4%[22].

In pure methane/oxygen mixtures, the upper explosive limit (UEL) increases to 60% methane but the flammability diagram also indicated that there was a negligible difference in the UEL between an air/methane mixture containing no oxygen and one containing 1% oxygen (approximately 16% methane). The above statement concerning oxygen limits of around 10% being the lower level at which the risk of explosion increase is based on gas mixtures containing this level of oxygen being capable of ignition without the presence of additional oxygen from air.

Consequently, for biomethane containing up to 1% oxygen, there is no requirement to alter the settings of gas detection equipment.

6 CORROSION REVIEW

6.1 Corrosion in Natural Gas Pipelines

Corrosion in natural gas pipelines can be caused by the following corrosive species:

- Carbon dioxide;
- Hydrogen sulphide;
- Oxygen.

It is important to note that in the absence of free water there will be no corrosion.

6.2 Oxygen Limits in Other Countries

Around Europe there are many different permitted oxygen levels in natural gas. Many appear arbitrary in nature and there appears to have been a change in the permitted levels in many countries in recent years.

6.2.1 UK

In the UK the HSE has permitted the introduction of natural gas containing up to 1% oxygen at pressures of up to 38 bar into the gas distribution network[6,7]. This permission covers both transmission and distribution networks however the 38 bar limit would exclude the National Transmission Network.

6.2.2 Germany

In Germany natural gas containing up to 3% oxygen is permitted in dry gas pipelines and 0.5% in wet gas pipelines[22].

6.2.3 Sweden

In Sweden natural gas from biomethane containing less than 1% oxygen is permitted in pipelines[8].

6.2.4 Switzerland and Austria

In Switzerland and Austria natural gas containing less than 0.5% oxygen is permitted in pipelines[22].

6.3 European Standards

A European Standard, EN16726[9], was developed to standardise gas quality specifications to permit the easy transportation of gas across national borders. The limit in this standard is 0.001% oxygen for instances where high oxygen levels could prove problematic. Underground storage installations, which are known for a tendency to be wet, were given as an example of such an instance. Where this is known not to be the case, the limit is 1%.

The standard was approved on September 2015 and had to be adopted as national standard by CEN members no later than June 2016. However, the standard is not legally binding for a number of reasons, principally failure to agree a Wobbe Number specification within the participating countries[10].

An additional Standard EN16723 was developed to specifically cover biomethane injection into the grid and its use as a fuel. It was quickly realised that the two uses had different requirements and the standard was split into two parts; Part 1[11] covering injection into the grid and Part 2[12] coving the use of biomethane as a fuel for vehicles. The requirements of the two standards differ slightly. On one hand Part 2 permits the presence of carbon monoxide as the fuel storage and combustion systems of a vehicle are regarded as a closed system. On the other, a number of impurities in biomethane are regarded as more problematic in vehicular fuels as they not diluted when used as fuels as they would be if injected into the grid. Regardless, the permitted oxygen content for vehicular fuels is 1%.

6.4 Comparison between Gas Networks in Ireland and the UK

A number of European countries permit significant levels of oxygen to be introduced with biomethane into, at least, parts of their gas networks and some of these countries are listed above. The UK system most closely mirrors the Irish system both in physical terms and in legislation. There are also strong similarities between end users in the two systems, e.g. for standards for appliances, hence it is reasonable to assume no major differences between the two. Consequently it is worthwhile to make a more detailed comparison between the gas networks of the two countries in order to determine the likely effects on the Irish system of increasing the oxygen limit, as set out in the following subsections:

6.4.1 Wobbe Index

The two countries have identical Wobbe Index requirements.

6.4.2 Transmission Systems

The UK gas transmission system consists of a National Transmission System of steel pipelines operating at pressures between 38 barg and 85 barg. There are also Local Transmission Systems that operate at pressures above 7 barg.

The Irish gas transmission system consists of steel pipelines operating at pressures between 19 barg and 85 barg.

There is little difference between the two systems except for the lower pressure limits.

6.4.3 Distribution Systems

The UK gas distribution system is divided into three pressure classes. These and the materials of construction are shown in Table 6-1:

Table 6-1 Distribution system pressure classes in the UK

Pressure	Materials of Construction
30 mbarg to 75 mbarg	Steel, PE and cast iron
75 mbarg to 2 barg	Steel, PE and cast iron
2 barg to 7 barg	Steel and PE

The gas distribution system in Ireland is divided into two pressure classes. These and the materials of construction are shown in Table 6-2. Small quantities of cast iron are still present in the distribution network.

Table 6-2 Distribution system pressure classes in Ireland

Pressure	Materials of Construction
30 mbar to 4 barg	PE
Up to 7 barg	Steel

Whilst the UK network uses PE pipelines at higher pressures, there is little practical difference between the two systems.

6.5 Corrosion Models

6.5.1 Carbon Dioxide Corrosion

Carbon dioxide corrosion is the most commonly studied form of internal corrosion, especially in the oil and gas industry. Over 15 models are known to exist. Some are internal company models and some are freely available in the public domain. The other main difference between the models is that some are purely empirical, being based on observation of pressure, temperature etc. on corrosion rates in laboratory and field experiments. Others attempt to be mechanistic, starting with the chemical equations thought to be occurring and the transfer of electrons and corrosive species and trying to build models from theory, rather than from experimentation, although using the latter for validation.

Probably the best known and accepted models are those of de Waard et al of Shell. The basic equation of the model developed in 1993 [13] is shown below;

$$\log(CR) = 5.8 - \frac{1710}{t + 273} + 0.67\log(p_{CO_2})$$

Where;

CR = Corrosion rate (mm/yr)

T = Temperature (°C)

P_{CO2} = Partial pressure of carbon dioxide (bara)

The basic equation can then be modified for fugacity, water cut, the actual pH of the liquid and the presence of glycol.

A weakness of the '93 model is that it does not consider the velocity of the fluid, and it is known that high velocity will increase the corrosion rate.

Further experiments were performed and the result was the De Waard et al '95 model[14]. This model took the general form;

$$\frac{1}{V_{corr}} = \frac{1}{V_r} + \frac{1}{V_m}$$

Where;

V_{corr} = Corrosion rate (mm/yr)

V_r = The highest possible reaction rate, i.e. mass transfer is infinitely fast. Its form is similar to the '93 model.

V_m = The highest possible mass transfer rate. The term includes the liquid velocity.

The '95 model therefore includes the effect of liquid velocity but at low velocities can under predict corrosion rates. For stagnant and low flow conditions, the '93 model can be more appropriate.

It is interesting to note that the NORSOK M506 corrosion model[15] was based on the same experimental data as the '95 model but has a very different form.

Freecorp[16] is a freely available piece of software produced by Ohio University. It uses a mechanistic model and is included here as it also includes the effect of oxygen on carbon dioxide corrosion and was used both in earlier work[5] and this work.

6.5.2 Oxygen Corrosion

Oxygen corrosion is often not considered when assessing hydrocarbon pipelines, principally due to the supposed absence of oxygen from these pipelines. However, oxygen ingress is possible, at compressors, pumps and in storage tanks where the inert atmosphere above the liquid hydrocarbon may contain significant amounts of oxygen. In the present case involving gas, the oxygen would be admitted to the pipeline network as a component of the biomethane.

A number of rate prediction models exist for oxygen corrosion. The two best known and accepted of these models are those of Oldfield et al [17] and Andijani and Turgoose[18]. These are both intended for flowing liquids.

The primary variables considered by these two models are oxygen concentration (in ppb), fluid velocity and temperature. Although the fluid velocity is used to determine fluid mechanics factors such as the Reynolds number.

It must be stated that these models are concerned with very low levels of oxygen, e.g. 10 to 100 ppb. They are commonly used in desalination plants, and also boilers and water injection where the oxygen has been removed by deaeration. Historically, it was quickly realised that carbon steel would be quickly corroded by flowing, oxygenated (sea) water. Therefore it was an unsuitable material and little research was performed into determining the corrosion rates.

For the present work, it is also worth mentioning that the models consider oxygen content in terms of concentration (i.e. ppm) rather than partial pressure. This is relevant due to the interest in the effect of oxygen partial pressure on corrosion expressed in other work[22].

6.5.3 Hydrogen Sulphide Corrosion

The significance of hydrogen sulphide corrosion is usually small unless it is present in large quantities relative to carbon dioxide, with the following relationships between the respective partial pressures applying:

- $pCO_2/pH_2S>500$ Hydrogen sulphide corrosion is ignored.
- $20>pCO_2/pH_2S>500$ Hydrogen sulphide corrosion will result in the formation of protective corrosion products which will generally reduce corrosion but may result in pitting of no greater than the carbon dioxide rate.
- $pCO_2/pH_2S<20$ Hydrogen sulphide corrosion will be dominant and will be difficult to predict. Carbon dioxide predictive models are not valid.

Hydrogen sulphide corrosion results in a thin tenacious film of iron sulphide scale which tends to stifle further corrosion unless the film is disrupted. If the film is disrupted, rapid pitting corrosion can occur due to galvanic effects, as the film is noble with respect to the underlying steel. Chlorides and oxygen can disrupt the film. The concentration of hydrogen sulphide in processed natural gas is usually extremely low. This is due to the processes designed to remove carbon dioxide, which could block the gas liquefaction plant, removing other acid gases too.

6.5.4 Mixed Corrosion

Little research has been performed to determine the effect of oxygen on corrosion in natural gas pipelines as, until recently, sources of natural gas were generally oxygen free.

Durr and Beavers[19] conducted experiments in which gas containing carbon dioxide and oxygen was flowed over stationary quantities of pure and salt water to determine the effect on the corrosion rate of steel samples. The maximum pressure used was 83 barg and the maximum oxygen concentration was 1,000 ppm (0.1%). Maximum corrosion rates were found at the vapour / liquid interface and at oxygen concentrations lower than the maximum concentration.

Lyle and Schutt[20] performed experiments over several years in which gas mixtures were flowed through test solutions that were all, except one set of experiments, stagnant. The concentrations of oxygen and partial pressures of carbon dioxide and hydrogen sulphide were varied. Oxygen concentrations of up to 10,000 ppm (1%) and pressures of 35 barg were used. A model was developed which took the form;

$$C = 8.6988 + 9.856\,x\,10^{-3}(O_2) - 1.48x10^{-7}(O_2)^2 - 1.30865(\text{�}H) + 4.934x10^{-2}(CO_2)(H_2\text{�}$$

$$-4.8231x10^{-5}(CO_2)(O_2) - 2.372x10^{-3}(H_2\text{�})(O_2) - 1.113x10^{-3}(O_2)(\text{�}H)$$

Where:

CR = General corrosion rate (mpy)

O2 = Oxygen concentration of gas (ppmv)

CO_2 = Carbon dioxide partial pressure (psi)

H_2S = Hydrogen sulphide partial pressure (psi)

pH = Initial pH of solution.

The use of imperial units should be noted.

Freecorp[16] is a mechanistic carbon dioxide corrosion rate models which also considers the effect of oxygen and hydrogen sulphide on corrosion, although it cannot evaluate the effect of both corrosive species at the same time. The use of the model for oxygen contents above 10,000 ppb (0.001%) is not recommended and the software will not work when an oxygen content of 10,000,000 ppb (1%) is entered.

An alternative approach used in some studies[21] is to consider oxygen and carbon dioxide corrosion separately and to consider the effects of the two corrosive species as additive.

6.6 Previous Studies

Health and Safety Executive research report RR882[22] prepared by GL Noble Denton in 2011 reviewed a number of possible consequences of permitting the introduction of biomethane into the distribution network. The report stated that increasing the oxygen content from 0.2 % to 1 % would double the carbon dioxide corrosion rate by disrupting the scales of corrosion product. It was further stated that these values were the result of using a model that was only validated to a partial pressure of oxygen of 0.345 bar. Consequently it was recommended that further research be performed. This work referred to the use of the model proposed by Lyle and Schutt[20].

A similar study was performed for Scotia Gas Networks (SGN)[5] by GL Industrial Services in 2009. This study used Freecorp software[16] to perform the corrosion calculations and concluded that, although the increase in oxygen from 0.2% to 1% resulted in an increase in the overall corrosion rate by five times, this did not significantly affect the integrity of the pipeline, even when considered over 100 years. The reason for this was that the majority of the time the line was assumed to be dry, and without free water there would be no corrosion.

A weakness in this study when used in relation to the present work is that it only considered a pressure of 2 barg. This is in part due to the perceived need for models valid for higher partial pressures of oxygen[22]. An additional reason to exercise caution in using these results is that at only 2 barg total pressure and with 1% oxygen present, there is proportionally much more oxygen present than when the pressure is much higher. It would be expected that at higher pressures, the effect of the carbon dioxide would be greater.

Following on from the work undertaken for the HSE a corrosion study was performed for Wales and West Utilities (WWU) by GL Nobel Denton[23]. The purpose of this work was to estimate the corrosion risk to steel pipelines from permitted oxygen concentrations of greater than 0.2%. The pressures considered by the work were between 75 mbar and 14 bar. The Lyle and Schutt[20] model was also used for this work.

A number of issues were found with this report. These include;

- The Lyle and Schutt model assumes no movement of the liquid which was causing the corrosion.

- The work was reported to calculate corrosion rates at 38°C, the maximum inlet temperature for the UK grid. The experiments on which the model was based were performed at 60F (15.6°C) and the model itself does not contain a variable for temperature. The pH variables were adjusted for temperature but this is small compared to the effect that varying the temperature would be expected to have on a chemical reaction.

- The use of 38°C is also questionable as at this temperature no free water would be expected to be present. This is because it is far above the specified dew point.

- The work attempted to determine the effect of varying the partial pressure of oxygen. However all the corrosion rate models included in this report use oxygen concentration (ppm or %) rather than partial pressure (bara). The latter being used for carbon dioxide. If the input of a model including both oxygen concentration and carbon dioxide partial pressure was modified by increasing the total pressure then an increase in the corrosion rate would be expected. However the most likely reason for this would be the well-known relationship between carbon dioxide partial pressure and corrosion rate, rather than the increase in oxygen partial pressure which in not used as an input to any of the established corrosion rate models described here.

However, the overall conclusion that the inclusion of 1% oxygen would not cause signification additional corrosion in a gas distribution system is reasonable. This is principally due to the short proportion of the time that the line is wet and therefore sees any corrosion at all. The low pressures present in the distribution network would also result in low corrosion rates during the periods when water was present.

6.7 Corrosion Rate Calculation

6.7.1 Corrosion Rate Selection

As discussed above in section 6.5, no corrosion rate model has been found that had been validated for both 80 barg and 1% oxygen in addition to carbon dioxide corrosion. Upon reviewing the above models, the Freecorp software has been selected as one of the cases is within its stated validity. Electronic Corrosion Engineer (ECE) software[24] a commercial development based on the de Waard ’95 model was used to calculate an oxygen free carbon dioxide corrosion rate for comparison, as was a manual calculation using the de Waard et al ’93 model.

The input data for the corrosion rate calculations are given in Table 6-3. The velocity was assumed. It is much less than the 5-10 m/s expected as a gas velocity as small amounts of water tend to travel along a pipeline at a slower rate than the gas.

Parameter	Value
Temperature	15°C
Pressure	80 barg
Velocity	0.5 m/s
Carbon dioxide	2.5 mol%
Oxygen (Case 1)	0.2 mol%
Oxygen (Case 2)	1 mol%

Table 6-3 Calculation inputs

6.7.2 Oxygen Concentration

The two oxygen concentrations used are the existing limit of 0.2% and the proposed new limit of 1%. These are the concentrations in the gas phase. To determine the concentration in the (assumed) water, Henry's law will be used.

$$K_H = \frac{p_{O_2}}{(O_2 a\ )}$$

Where K_H is the Henry's law constant which for this case is 769.23 atm/M.

For 0.2% oxygen

$$\frac{0.002 \times 80}{769.23} = 2.08 \times 10^{-4} M/l$$

The molar weight of oxygen is 32g therefore the concentration is

$$2.08 \times 10^{-4} \times 32 = 0.006656 g/l$$

Or 6.66 ppm.

For 1% oxygen

$$\frac{0.01 \times 80}{769.23} = 0.00104 M/l$$

The molar weight of oxygen is 32g therefore the concentration is

$$0.00104 \times 32 = 0.033 g/l$$

Or 33 ppm.

6.7.3 Corrosion Rate

Using the data from the two sections above the rates shown in Table 6-4 were calculated.

Model	Oxygen (ppm in water)	Oxygen (% in gas)	Corrosion Rate (mm/yr)
Freecorp	0	0	2.3
Freecorp	6.6	0.2	4.1
Freecorp	33	1.0	11.5
ECE	0	0	1.21
De Waard '93	0	0	0.96

Table 6-4 Corrosion rates

The results show that increasing the permitted oxygen content from 0.2% to 1% would increase the corrosion rate by 2.8 times. Even the current limit increases the corrosion rate compared with the oxygen free case.

The Freecorp oxygen free case is significantly higher than the ECE result. Whilst the ECE is a well established and accepted piece of software, this is not totally unexpected. 0.5 m/s is the bottom of the velocity range for which the software claims its highest level of accuracy and, as the experimental results for a velocity of 1.5 m/s were disregarded in the original work due to their being a poor fit[14], even the 0.5 m/s claim might be regarded as optimistic. Often the '93 model will give a higher corrosion rate than the '95 model at low velocities, but this has not occurred on this occasion. This appeared to be due to the low temperature.

Only the lower (0.2% in gas or 6.6 ppm in water) oxygen was fully within the validity range of the Freecorp software. The higher oxygen concentration was within the range when the software would still operate but outside the recommended range (known as the soft limit by the software). This was still regarded as more valid than the use of other models or software.

The most important point to note is that no corrosion will occur without the presence of free water. This is discussed further in section 8.

6.8 Effect of Partial Pressure of Oxygen

Previous work has described the absence of experimental data on corrosion at high partial pressures of oxygen[23]. This is of moderate concern but is moderated by the following points.

The work for WWU[23] modelled corrosion at pressures up to 14 bar and oxygen contents of up to 5%. The modelling appeared to show a levelling off of corrosion rates at the highest pressures and oxygen concentration. See Figures 5 to 9 of the reference. Figures 10 and 11 of the reference, which apparently show an increase in corrosivity, do not separate the effects of oxygen and carbon dioxide. An increase in the partial pressure of carbon dioxide increasing the corrosion rate is well known[13].

The fugacity of a real gas will reduce at high pressures in comparison to an ideal gas. This means that it will be less chemically active.

Oxygen is thought to increase sweet corrosion rates by interfering with the formation of iron carbonate scales which can slow down corrosion. At ambient temperatures scale formation is not so noticeable so its protective effect will be less. Therefore damage to the scale should be less important.

7 IMPACT ON END USER EQUIPMENT

In principle, changing the oxygen content of natural gas or biomethane could affect the following:

- Theoretical air requirement;
- Caloric value;
- Flammability;
- Minimum ignition energy;
- Flame temperature;
- Burning velocity;
- Corrosion.

Calorific value and flammability have already been discussed in Section 5, and changes to these parameters were not considered to have significant effects. The other factors were evaluated in a previous work[5] and are described below. The likely effects on specific types of equipment are then considered.

7.1 Factors

7.1.1 Theoretical Air Requirement

The theoretical air requirement for stoichiometric combustion will vary by an insignificant amount between an air/methane mixture containing no oxygen and one containing 1% oxygen.

7.1.2 Minimum Ignition Energy

Changes in the minimum ignition energy would be expected to be small for oxygen levels of up to 3%. The 1% oxygen is well within this level. Therefore no significant effect would be expected.

7.1.3 Flame Temperature

For a stoichiometric methane/air mixture the flame temperature would be expected to increase from 2226 K to 2230 K which was not regarded as significant ((2230-2226)/2226=0.18%).

7.1.4 Burning Velocity

A stoichiometric methane/air flame has a burning velocity of 35.2 cm/s. An increase in the oxygen content from zero to 1% oxygen increases this to 35.6 cm/s. This was not considered to have a significant effect on flame stability or to increase the frequency of burner failures.

7.1.5 Corrosion

Increasing the oxygen content to 1% will not have an effect on the corrosion of end user equipment as the gas is dry and there is already an ample supply of oxygen once the gas is mixed with air. The referenced report[5] concluded that there would not be a significant effect on the operability of equipment, appliances and processes. This would be contingent on the dew point specification being maintained.

7.2 Equipment Types

The following equipment types were considered.

7.2.1 Domestic and Commercial Heating and Cooking Equipment

These may be grouped into two main kinds for the purpose of this review.

Equipment that uses partly pre-mixed burners, such as cookers, will see no impact as the oxygen in the fuel gas is inconsequential compared with the far greater amount of oxygen in the air that the fuel gas is mixed with for combustion.

For totally pre-mixed burners such as pilot lights and burners for ceramic kilns, even without modification no great impact would be expected for fuel gas oxygen levels not greater than 1%.

7.2.2 Industrial Boilers

These may be grouped into two main kinds for the purpose of this review.

Package burners would not be expected to see any impact from 1% oxygen in the fuel gas. As with domestic heating appliances the far greater amount of oxygen in the air blown into the flame results in tiny amounts of oxygen in the fuel gas inconsequential.

In recuperative and regenerative burners, the presence of up to 1% oxygen in the fuel gas would not affect performance significantly as such burners are usually designed to operate with a slight oxygen excess through the process. The presence of oxygen in the fuel could encourage cracking of hydrocarbons in the preheated fuel gas. This is intended to ensure complete combustion of the fuel.

7.2.3 Gas Turbines

These may be grouped into two main kinds for the purpose of this review.

Diffusion flame combustors: these have a robust design and no impact would be expected.

Premixed combustors: in principle, these could be impacted by changes in the auto-ignition properties of the fuel / air mixture. However, this would not be expected to be significant below 3% oxygen in the fuel, therefore 1% would not be considered to have an impact.

7.2.4 Natural Gas Vehicles

No impact is predicted to occur. An oxygen limit of 1% is the same as that permitted by EN 16723-2 for use in vehicles powered by biomethane. Additional reassurance may be gained from the successful use of gas containing up to 3% oxygen as a fuel for vehicles, for a number of years, in Germany.

7.2.5 Gas Engines

Gas engines are frequently designed to run on a variety of fuels including biomethane. Whilst concerns have been raised about the use of fuels gases containing oxygen these are generally for oxygen levels greater than 1%. Consequently, no issues would be expected for oxygen contents not greater than this amount. It is not possible to review all engine manufacturers here but, for example 1% oxygen is considered acceptable for Cummins gas engines[25].

7.2.6 Fuel Cells

For oxygen levels less than 2% or 3% fuel cells can operate without issue. Therefore a 1% limit is considered acceptable.

8 RISK ASSESSMENT

GNI operates under the Gas Safety Regulatory Framework and, as such, is required to ensure that the risks associated with its operations are either broadly acceptable or ALARP. Guidance on achieving risks that are ALARP are given in CER/16/106[2].

8.1 Unmitigated Corrosion Threat

The study used to justify the increase in oxygen to 1% in the UK[23] simply concluded that the risk was low if dehydration was effective. Whilst it would not be possible to perform a formal quantitative risk assessment without more data than was supplied to this work, which is limited to one hazard, a general argument may be proposed.

The corrosion rates calculated in section 6.7 for 1% oxygen are high and would not be considered acceptable. However, the rates for the existing oxygen limit and even zero oxygen are also high and would not be considered acceptable if they were to be experienced by the pipeline for the whole of its design life. With the absence of oxygen giving corrosion rates of 1 to 2 mm/yr, due to the carbon dioxide present, perforation of a 10 mm thick pipeline wall would be expected in 5 to 10 years.

As such the unmitigated risk of internal corrosion, even without the oxygen would be considered high.

8.2 Mitigated Corrosion Threat

The principal mitigation against corrosion within natural gas pipelines is the absence of water. The GNI pipeline network has a dewpoint specification of 50 mg/m^3. This is generally comparable with the UK specification of “Not more than -10 °C at 85 bar”. If the dew point is at least 10°C below the ambient temperature then there will be no free water available to permit corrosion.

The GNI dew point compliance figures were not available so general sources of water will be reviewed. However, it was reported that the expected water content of the biomethane would be 17.84 mg/m^3[26]. As no corrosion would be expected at any water content below 50 mg/m^3, if this is actually the case, then no corrosion issue would be expected.

The water in natural gas is usually removed at the site of production. Gas dehydration on offshore platforms is relatively effective and reliable with compliance to specification of over 99% being typical[27]. Gas supplied from LNG is even more unlikely to contain water. Water could enter the gas in underground storage facilities (e.g. salt caverns) but GNI do not use such facilities.

With corrosion only occurring during the 1% of the time that free water would be present, even with the high corrosion rate associated with 1% oxygen, it would be expected that perforation of the nominal 10 mm pipeline wall would not occur for around a 100 years. This would result in an extremely low probability of failure in the short, medium and long term.

An Impact and Risk Assessment for a biomethane development[28] supplied by GNI recommended the use of continuous monitoring or both dew point and oxygen content. These monitors would be both alarmed and connected to automatic valves which would divert off spec gas away from the grid. If these measures were included then the already extremely low risk could be considered negligible.

This argument is consistent with a number of the oxygen concentration limits reviewed in section 6.2. In these limits the permitted oxygen concentration depends on whether the presence of water is thought probable or possible. If water is not present then limits of 1% to 3% are permitted. Where the presence of water is considered likely, e.g. in underground storage facilities, then the limit is much lower. In one proposed limit it is 0.001%.

The possibility of water gathering in dead legs in the distribution network has been raised. The probability of this occurring in the first place would be extremely low, as it would require both a gross failure of the dehydration control of the gas source, and a similar failure of the network water content monitoring system and alarms. It would also require a flow in the line to permit the ingress of off-specification gas, and this flow would be expected to sweep any water that had gathered out of the piping. Even if water ingress did occur, the expected corrosion rate would be expected to be extremely low due to the low pressure involved. This report is primarily concerned with corrosion occurring in high pressure pipelines, but past studies have calculated the very low corrosion rates expected in distribution networks[5,23]. In true isolation, the corrosive species would be expected to be consumed but if there was contact with the bulk gas, once the dew point was restored to the specified level, the water would tend to evaporate. When the water had all evaporated, the corrosion would cease. The flow in the line which permitted the water ingress would also be expected to sweep the water out, unless the flow was an isolated occurrence. For this occurrence to happen at the same time as a dew point excursion would also be improbable.

A further possible scenario for water gathering in low points of a pipeline is following hydrostatic pressure testing. In principle, correct adherence to pre-commissioning procedures would ensure the removal of all water from a pipeline but it is not inconceivable that such procedures might not be followed exactly. Again, the passage of dewpointed gas would eventually remove the water, but there would be a period when corrosion could occur.

The PE distribution network is not subject to internal corrosion and increasing the oxygen level would have no effect on the degradation of the pipelines.

8.3 ALARP Demonstration

The proposed increase in oxygen content is predicted to increase the corrosion rate by two to three times. It follows that the risk of failure would be increased by an equivalent amount. However, the probabilities of failure associated with both the current and proposed oxygen specification are considered to be insignificant.

The Safety Case for the Transmission System[29] assigns a risk of failure using a five by five Boston square in which Low or Very Low risk (i.e. risk ≤ 4) can be accepted without further mitigation measures, although if additional mitigation measures are reasonably practicable, they should be applied. Reviewing the Safety Case indicated that for internal corrosion, a risk of 3 (Low) was assigned. As the probability of failure has not been considered to have changed by a significant amount, and the consequences are unchanged, it is concluded that this risk level would not change.

To demonstrate ALARP it is necessary to show that all reasonably practicable risk reduction measures have been used. For the introduction of gas with an oxygen content of up to 1%, the proposed monitoring and off-spec gas diversion system described in section 8.2 would be such mitigation. Therefore ALARP will have been demonstrated.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The following conclusions were drawn from the work;

- Increasing the oxygen content to 1% will have no effect on the PE distribution network.
- Increasing the oxygen content to 1% will have a negligible effect on the steel distribution and transmission networks, provided that the mitigation measures (monitoring and automatic diversion of off specification gas) that have already been recommended are implemented.
- Increasing the oxygen content to 1% will have no significant effect on the lower and upper explosive limits (LEL and UEL) of the gas.
- Increasing the oxygen content to 1% will have no effect on the calorific value of the gas with respect to maintaining the range specified in the gas quality specification.
- The use of the proposed mitigation measures will demonstrate that the introduction of 1% oxygen is ALARP.
- Increasing the oxygen content to 1% will have no significant effect on corrosion or operability of end user equipment.
- The key to maintaining acceptable corrosion rates within the pipeline systems is to control the water content rather than the corrosive species.

9.2 Recommendation

The following recommendation is made following the work;

- Due to the importance of water content on corrosion, it is recommended that no attempt is made to relax the water content specification at the same time as the oxygen content.

10 REFERENCES

1 GNI, Request For Quotation, Biomethane – Oxygen Content Assessment, Reference Number: 14/008-55 Lot 2

2 Commission for Energy Regulation, CER/16/106, ALARP Guidance Part of the Petroleum Safety Framework and the Gas Safety Regulatory Framework, version 3.0, 29th March 2016

3 Kick off meeting by telephone between GNI and Penspen, 6th November 2017

4 GNI, Code of Operations, Quality Specification of Natural Gas at Entry Points

5 Brown, M. et al, GL Industrial Services UK Ltd, Review of Oxygen Specification for the below 7 bar Distribution Network, Report Number: 9434, October 2009, Prepared for CNG Services Ltd

6 Health and Safety Executive, Chief Executive's Report to the Board, Paper No: HSE/13/59, 26 June 2013

7 Ofgem, Future Billing Methodology, Project NGGDLGN04/1, April 2017

8 Bright A. et al, Advantage West Midlands and WRAP, An Introduction to the Production of Biomethane Gas and Injection to the National Grid, Project Code 280-11, Prepared by the Organic Research Agency, 5th July 2011

9 CEN, Gas infrastructure. Quality of gas. Group H,EN16726:2015, April 2016

10 Antonio Gómez Bruque, Joint workshop ENTSOG-Energy Community, INT NC amendment for Gas Quality, Vienna 19 October 2016

11 BS EN 16723-1:2016, Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network. Specifications for biomethane for injection in the natural gas network, November 2016

12 BS EN 16723-2:2017, Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network. Automotive fuels specification, August 2017

13 De Waard C. and Lotz U., Prediction of CO_2 Corrosion of Carbon Steel, paper 93069, NACE, Corrosion 93

14 De Waard C., Lotz U. and Dugstad A., Influence of Liquid Flow Velocity on CO_2 Corrosion: A Semi-empirical Approach, paper 95128, NACE, Corrosion 95

15 NORSOK, M506, CO_2 Corrosion Rate Model, Rev 2, June 2005

16 Freecorp Background and Software, Ohio University *from website*

17 Oldfield J., Swales G., and Todd S., Corrosion of metals in deaerated seawater. INCO Ltd

18 Andijani I. and Turgoose S., Prediction of oxygen induced corrosion in industrial waters, Water Science and Technology Vol 49 No 2 pp 115–120, 2004

19 Durr C. and Beavers J. Effect of Oxygen on the Internal Corrosion of Natural Gas Pipelines, paper 96612, NACE, Corrosion 96

20 Lyle F. and Schutt, CO_2/H_2S Corrosion under Wet Gas Pipeline Conditions in the presence of Bicarbonate, Chloride and Oxygen, paper 98011 NACE Corrosion 98

21 IEAGHG, Smith L. et al, Corrosion and Material Selection in CCS Systems, Report 2010/03, prepared by Intetech Consultancy Ltd and E-on Engineering, April 2010

22 Broomhall D., et al, Health and Safety Executive, Hazards arising from the conveyance and use of gas from Non-Conventional Sources (NCS), Research Report RR882 prepared by GL Noble Denton, 2011

23 Saithala J. and Illson T., Corrosion aspects of nonconventional gases in the natural gas pipeline Network, GL Noble Denton, Report number 12324, 30th April 2013

24 Wood Group Intetech, Electronic Corrosion Engineer, version 5.3

25 Cummins Westport Fuel quality Calculator, On-line

26 Email from GNI, 16th January 2018

27 Confidential figures from a North Sea operator

28 GNI, Impact and Risk Assessment Cush Biomethane-Issue 1, Spreadsheet dated 13th November 2017

29 GNI, Safety Case Transmission System, Manual No: HSQE/MN/012, Rev. 1, December 2016