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White Paper

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TITLE: Unintended Introduction of
Oxygen into Gas Export Systems

SUMMARY

Oxygen is not naturally occurring in natural gas, however, the introduction of relatively new technology designed to eliminate the need to flare gas routinely and hence reduce emissions has the unconsidered potential to introduce unacceptably high concentrations of oxygen into the gas which may (i) exceed agreed contractual specification limits and (ii) ultimately result in accelerated corrosion of pipelines and process infrastructure.

CONTENTS

	Page
1 General Background	3
2 Flare Gas Recovery Systems	4
3 Case Studies	5
3.1 Case Study 1	5
3.2 Case Study 2	7
4 Consequences of Oxygen Ingress.....	9
5 Sampling and Analysis to Determine Trace Oxygen	10
6 Summary.....	11
7 References	13

1 General Background

In the oil and gas industry, oxygen is not a naturally occurring constituent of the produced hydrocarbon and if once present originally in the formation, would have been consumed by oxidative reaction with the hydrocarbons during the millions of years of storage^[1]: however, it is well documented that reservoirs that undergo chemical treatments such as artificial water lifts and hydrate suppression are at risk of introducing oxygen into the process system as the chemicals (particularly methanol) involved often contain dissolved oxygen^[2]. The presence of oxygen is undesirable as it promotes several corrosion mechanisms in both sour and sweet wells. For this reason, specification limits on gas in transport pipelines are often set at single parts per million levels. In addition to the sources stated above, Qa³ has identified a new source of oxygen contamination which has resulted from new technology introduced by the industry's drive to reduce emissions. Whilst the presence of oxygen has major implications, it is not monitored by most gas exporters as it is not expected to be present.

There are a number of global initiatives aimed at reducing carbon dioxide (CO₂) and methane emissions, some of which specifically target reducing gas flaring which, for 2021, was estimated by the world bank^[3] as being 144 billion cubic meters of gas across the globe, resulting in approximately 400 million tons of CO₂ equivalent emissions, of which 361 MMtCO₂e was in the form of CO₂ and 39 MMtCO₂e was in the form of methane.

These global initiatives aimed at reducing gas flare emissions include but are not limited to the following examples:

- Launched in 2015 by the Global Gas Flaring Reduction Partnership (GGFRP), the Zero Routine Flaring (ZRF) initiative commits governments and oil companies to end routine flaring no later than 2030. The initiative aims to support cooperation between all relevant stakeholders so that solutions to gas flaring can be found through appropriate regulation, application of technologies and financial arrangements.
- The Oil and Gas Climate Initiative (OGCI) consists of 12 of the world's largest oil and gas companies that are committed to finding viable solutions to eliminate routine flaring in existing fields by 2030 at the latest^[4].
- The UK, as part of its commitment to reach net zero carbon emissions by 2050, includes a near term plan of reducing flaring emissions, improving and introducing the use of flare gas recovery systems (FGR)^[5]. This is a preliminary step to achieve no routine flaring by 2030^[6].

This will require most existing facilities to modify their process, for example, to incorporate gas reinjection back into the reservoir or, perhaps most commonly, to integrate Flare Gas Recovery systems into the existing infrastructure to prevent normal day to day flaring. ***By incorporating an FGR system, all gas that would routinely go to flare is diverted back into the gas production system; however, an unintentional consequence of this is the introduction of oxygen into the natural gas export.***

Whilst oil and gas companies welcome the challenge to reduce carbon emissions and re-engineer their process to incorporate FGR systems, the introduction of oxygen via the existing nitrogen generation system, which is required as an integral part of the FGR will not necessarily be taken into consideration. Since introducing nitrogen into the exported product gas was never intended, almost all nitrogen generation systems do not fully purify the nitrogen to eliminate all oxygen. It is expected that most of these systems will contain low % level oxygen (typically 0.5 – 5% v/v) which, if not considered or if

remedial actions are not put in place, could lead to extensive local corrosion in the FGR and low-pressure systems and unacceptable oxygen concentrations in the exported gas that exceed typical pipeline specification limits and ultimately accelerate corrosion of the pipeline / process infrastructure.

2 Flare Gas Recovery Systems

FGR systems are incorporated into a production process to eliminate the need for routine flaring and therefore reduce the carbon footprint of a producing asset. Modern flaring operation is moving towards being used solely for safety critical applications, which include system trips or over pressurisation events where the process system cannot handle the throughput of volumes / pressures exceeding the optimal working conditions.

In traditional routine flaring, gases that are sent to flare include some production gas from off gases such as water vessels or from low-pressure oil / condensate separators where the gas volume produced is considered negligible. Other gases include process gases such as nitrogen, which are used in maintenance, regeneration or as safety blanket gases in units such as flare headers.

The diagram below in *Figure 1* shows a traditional production process with routine flaring.

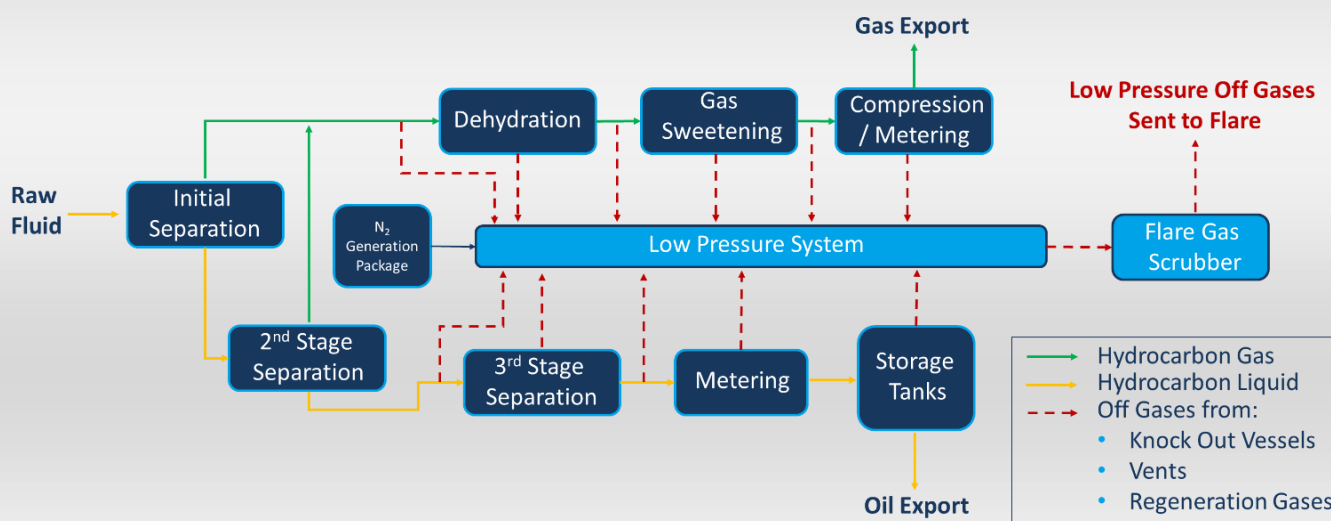


Figure 1 - Traditional production process with routine flaring

On offshore and onshore plants where FGR systems are installed, it can be expected that all routine gases normally sent to flare will be redirected, compressed and commingled into the production gas for export. One of the main areas of concern is that plant nitrogen will make up a significant proportion of this 'FGR gas', and as oxygen is a natural component of such nitrogen, will result in elevated oxygen concentrations in the export gas which, where the FGR gas is not sufficiently diluted by the production, may exceed the pipeline specification limit.

Figure 2 is a schematic of the same process with an FGR system incorporated into the design.

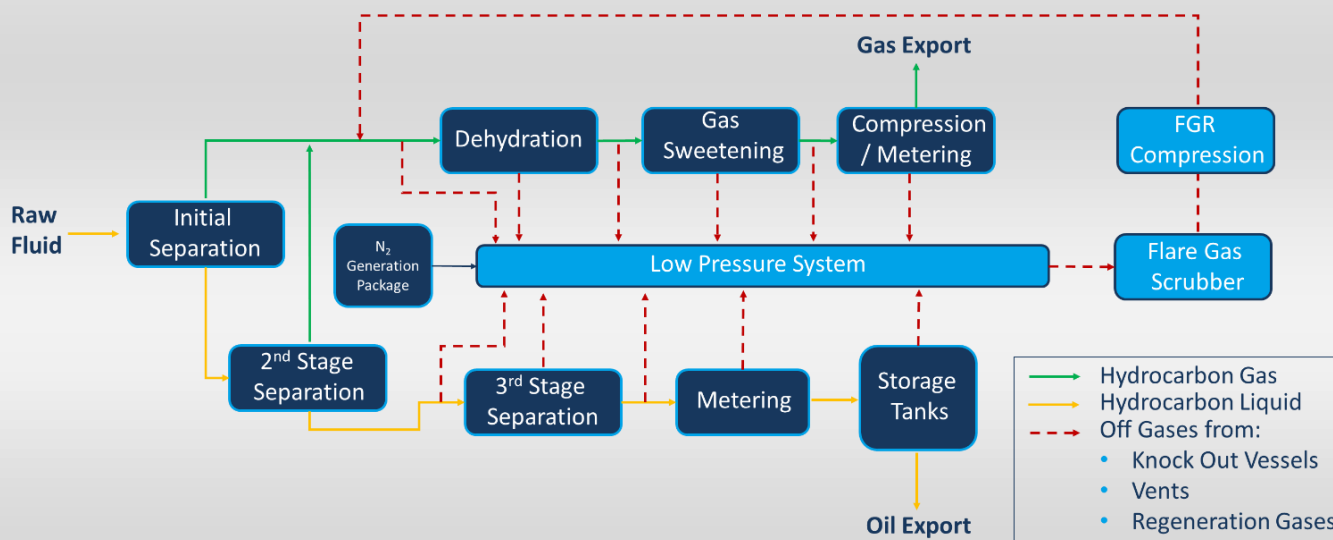


Figure 2 - Production process with FGR system incorporated

3 Case Studies

3.1 Case Study 1

A gas processing terminal in Europe receives gas from various offshore facilities and during a surveillance visit in 2020, the commingled entrants' gas was found to contain no oxygen and was compliant with pipeline specification limits; however, 18 months later the entrants' gas was found to contain an oxygen concentration of ~50 ppm v/v, exceeding the pipeline specification limit of 9 ppm v/v. A detailed investigation was completed at the terminal to ensure the oxygen readings were correct and that there was no plant integrity issues where air ingress could occur. The oxygen concentrations were validated and confirmed to be correct.

The oxygen concentrations recorded raised a serious safety concern as such levels greatly increase the potential for corrosion both at the gas plant and upstream offshore. This led to an immediate investigation to determine the source(s) of oxygen ingress that involved visiting each gas entrant facility to identify whether or not oxygen was present in the export gas and if present, identifying the point(s) of entry across the facility.

A visit to the first offshore platform entrant identified the exported gas to be free of oxygen and on discussion with the operations team, it was established that there had been no production issues or any recent changes to the existing system.

The export gas from the second entrant was also found to contain no oxygen; however, it was established that an FGR system had recently been installed and was in operation. The oxygen concentration in the FGR gas was found to be 100's of ppm v/v, however, the volume of FGR gas was diluted by the production gas such that the levels in the export gas fell below the reporting limit (< 1 ppm v/v) for oxygen. The FGR system on board this facility diverted only hydrocarbon offgas from storage tanks and did not include any nitrogen plant gas. As no nitrogen was sent to the FGR system, an immediate safety investigation was launched to identify the source of oxygen, which was thought to be due to the introduction of air into one of the many tanks on board the FPSO. In addition, it was highlighted that the plant nitrogen could contain up to 5% v/v oxygen and if this was diverted to the FGR

system in the future as part of the net zero incentive to reduce routine flaring emissions, then it could be expected that significant oxygen concentrations in the hydrocarbon gas would be observed. This would increase the overall oxygen concentration of the commingled gas received at the onshore plant and potentially increase the rate of corrosion in both the pipeline system and localised steel infrastructure on board the offshore installation.

The export gas from the third offshore installation was found to contain no oxygen. This facility had an FGR system installed but it was not commissioned for use, although future use to reduce routine flaring operations was planned. It was not possible to sample the low-pressure flare gas, which would constitute the FGR gas, however, the plant nitrogen, of which a significant volume is sent to flare, was found to contain 2.5% v/v oxygen. Thus, after commissioning of the FGR system, based on predicted metered flow rates of nitrogen to flare and the dilution exerted by the (average) production gas volume if the FGR gas is commingled, the minimum concentration of oxygen that may end up in the export gas from this facility was estimated to be 15 ppm v/v, which doesn't take into consideration any additional sources of nitrogen ingress.

The export gas from the fourth offshore facility a Floating Production Storage and Offloading system (FPSO), was found to contain oxygen in the concentration range 50 – 90 ppm v/v, far in excess of the pipeline specification limit and thus exposing both the infrastructure of the offshore facility and the subsequent pipeline to the onshore receiving terminal to elevated risk of oxidative corrosion. This facility had introduced the routine use of an FGR system, which redirects all gases originally destined for low-pressure (LP) flare back into production. This includes plant nitrogen that is used as a blanket for storage tanks and vessels across the process. The plant nitrogen contained up to 2% v/v oxygen that was diluted to 0.25% v/v oxygen when mixed with other LP gases before further diluting when mixed into the production gas.

The oxygen concentration measured in the commingled gas arriving at the onshore receiving terminal was in good agreement with that expected based on the respective flow rates of all the entrants and the oxygen concentration in the export gas from this FPSO.

A review of historical flow data showed that the FPSO was offline at the time of the first surveillance visit in 2020 which explains why no oxygen was found in the gas arriving at the onshore terminal.

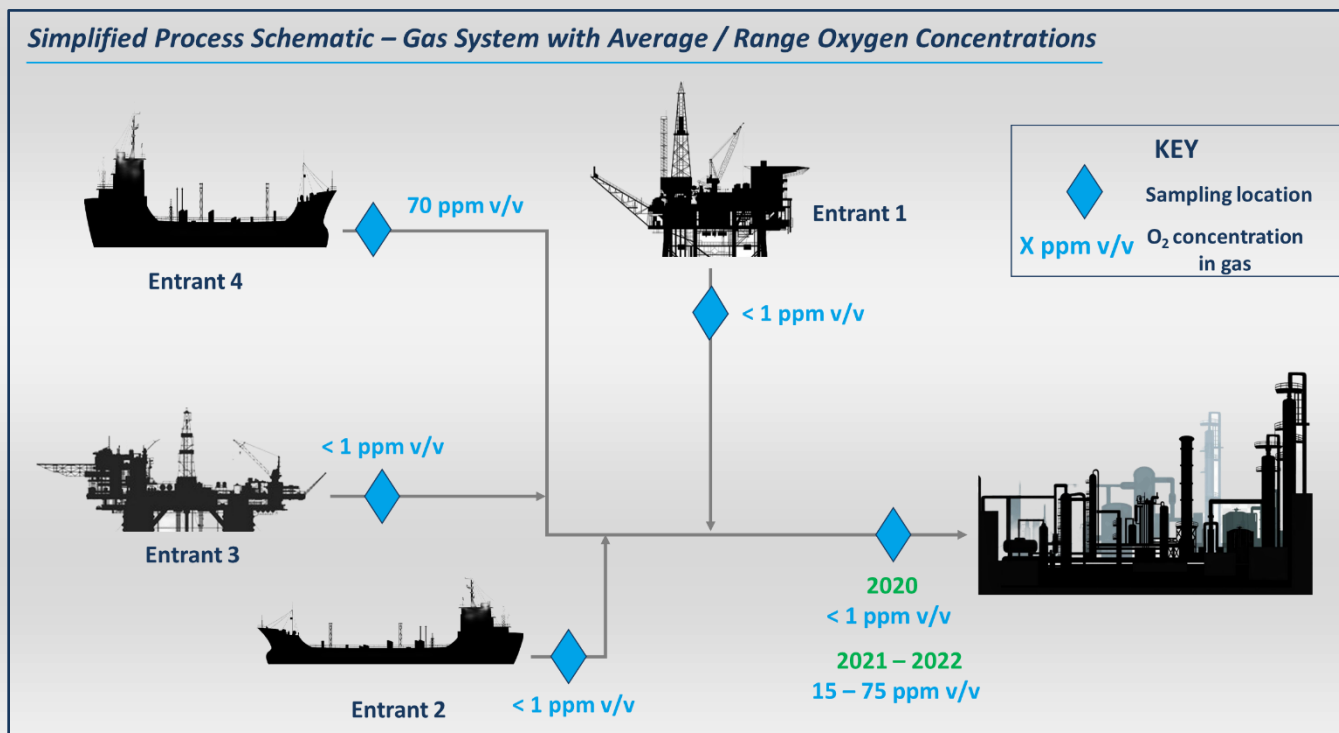


Figure 3: Schematic of the oxygen investigation at a processing system in Europe.

3.2 Case Study 2

As part of a pipeline compliance operation, after each new field had been brought online, an offshore operator was required to provide data for several contaminants over a number of different sampling periods to show the concentrations determined for the analytes of interest were (i) representative of normal production operating conditions and (ii) compliant with pipeline specification limits.

A total of twelve on-site visits were carried out during a period of three years and with the exception of the second survey, no oxygen was found in the export gas until survey ten. At the time of the second survey a new well was brought online and the positive oxygen concentration was attributed by the operations team to completions activities that may have introduced air into the system. As no oxygen was found in the export gas for the next seven surveys the positive concentrations found during the second visit were initially thought to be an outlier, however, positive oxygen concentrations were observed again during surveys 10 and 11 and 12.

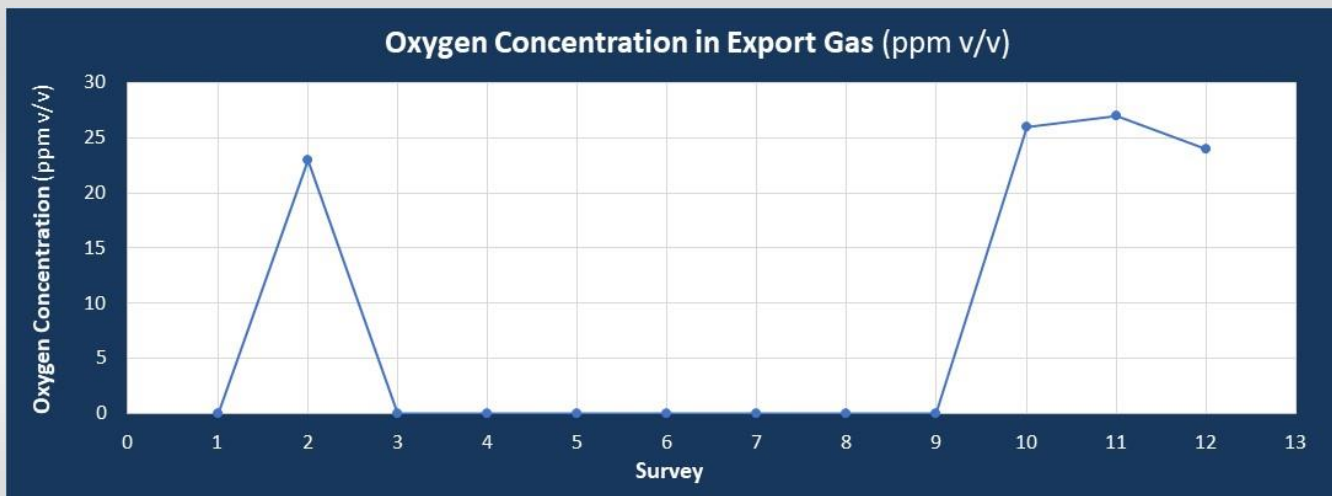


Figure 4: Oxygen concentration in the export gas.

A more detailed investigation of the process found that an FGR system had been installed but, up until survey 10 had been used only periodically and was almost certainly online during the second survey. Again, the consequence of the FGR system being in operation is that plant nitrogen, which was found to have percentage concentrations of oxygen, made up a significant volume of the FGR gas.

A more detailed investigation to evaluate the effects of intermittently running the FGR system was carried out during survey 11.

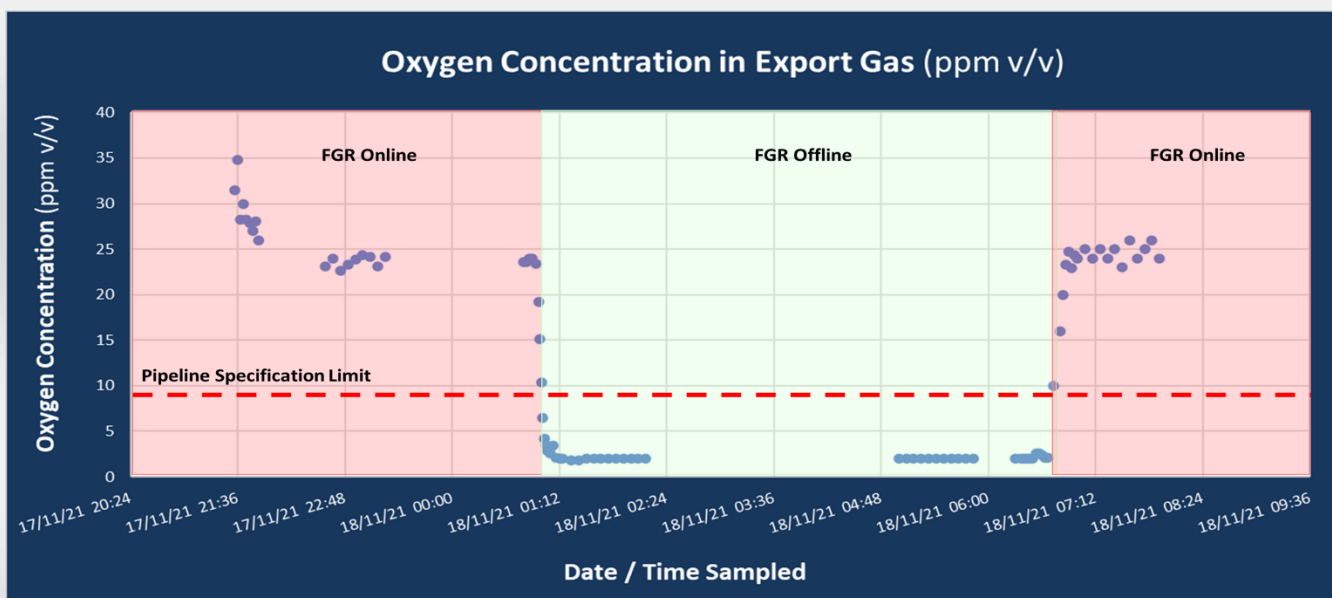


Figure 5: Oxygen concentration in export gas with FGR both online and offline.

As expected, when the FGR system was online the oxygen concentration in the export gas was found to be above the pipeline specification limit and when the FGR system was offline the oxygen concentration fell to below the specification limit; however, when the FGR was offline for the six hours during this study, the oxygen concentration in the export gas did not fall to below the reporting limit (< 1 ppm v/v). This was expected as a proportion of the export gas is reinjected for gas lift to aid production and therefore oxygen is introduced into the wellbore, which is then returned to the surface with the produced gas. If the FGR remained offline for a number of days, the oxygen concentration in the export

gas would be expected to fall to < 1 ppm v/v to reflect the innate concentrations in the natural gas produced from all contributing fields.

4 Consequences of Oxygen Ingress

The unintended introduction of oxygen into production primarily from FGR systems poses a serious risk to the steel infrastructure. The presence of oxygen is undesirable as it promotes several corrosion mechanisms:

- Oxygen in the presence of moisture can lead to Oxygen Absorption Corrosion (OAC) that will produce numerous iron oxides / iron hydroxides^[7].

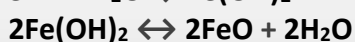
Anodic Reaction: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathodic Reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

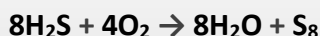
Iron (ii) can be further oxidised to iron (iii):

$4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$

The above reactions occur simultaneously and the following reactions can also occur, which are crucial to the formation of corrosion / rust products^[8].



- Dry corrosion of the steel with oxygen in the absence of moisture is unlikely as higher temperatures are required^[9].
- Oxygen in general has the ability to increase the corrosion rate of other contaminant mechanisms such as those initiated by H_2S and CO_2 ^[10].
- Oxygen can react with H_2S to form elemental sulphur, which increases the risk of under deposit localised corrosion^[11].



- Oxygen introduction into a sour system can also lead to a change in composition and morphology of the iron sulphide (FeS) layer, leading to the formation of an FeS scale that is less protective. This scale is more easily removed by the action of the flowing fluids/gases, which increases the risk of localised corrosion^[11].

In addition to the potential corrosion mechanisms influenced by oxygen, the secondary concern is the potential impact oxygen can have on gas treatment process. Oxygen is known to have adverse effects on process chemicals used in the industry. In systems where MDEA amines are utilised, oxygen can lead to the degradation of these chemicals resulting in unwanted byproducts^[12].



Figure 6: Pipeline with corrosion scale.

Studies have also shown that in certain conditions oxygen can lead to the degradation of glycols used in the dehydration of natural gas^[13].

Oxygen is also considered a transient poison in feeds to hydrogenation catalysts producing ethylene^[14]. In particular, if carbon monoxide is present in the feed gas this can be oxidised by oxygen to carbon dioxide resulting in an off-specification ethylene product. The hydrogenation of oxygen can also result in the unwanted generation of water that, over time, will slowly deactivate the catalyst.

5 Sampling and Analysis to Determine Trace Oxygen

As a consequence of the issues arising from the presence of oxygen, even at trace concentrations, it is common to find oxygen specifications at around 9.0 ppm v/v ($\mu\text{L/L}$)^[15] or lower imposed on pipelines and feedstocks to gas plants, refineries and petrochemical plants. As the requirement for zero routine flaring approaches, the potential for oxygen ingress will increase as operators modify their existing infrastructure to reduce or capture process gases that are normally sent to flare. Therefore, it is essential for operators to assess the oxygen concentration in (i) the plant nitrogen (ii) the LP flare gas and (iii) export gas to calculate the expected oxygen concentration in production gas prior to the modification of the production infrastructure to limit routine flaring. This data will be valuable in the forward planning of the design as it may instigate the need to provide a purer plant nitrogen or incorporate an oxygen removal system to eliminate oxygen from the plant nitrogen or LP flare gas.

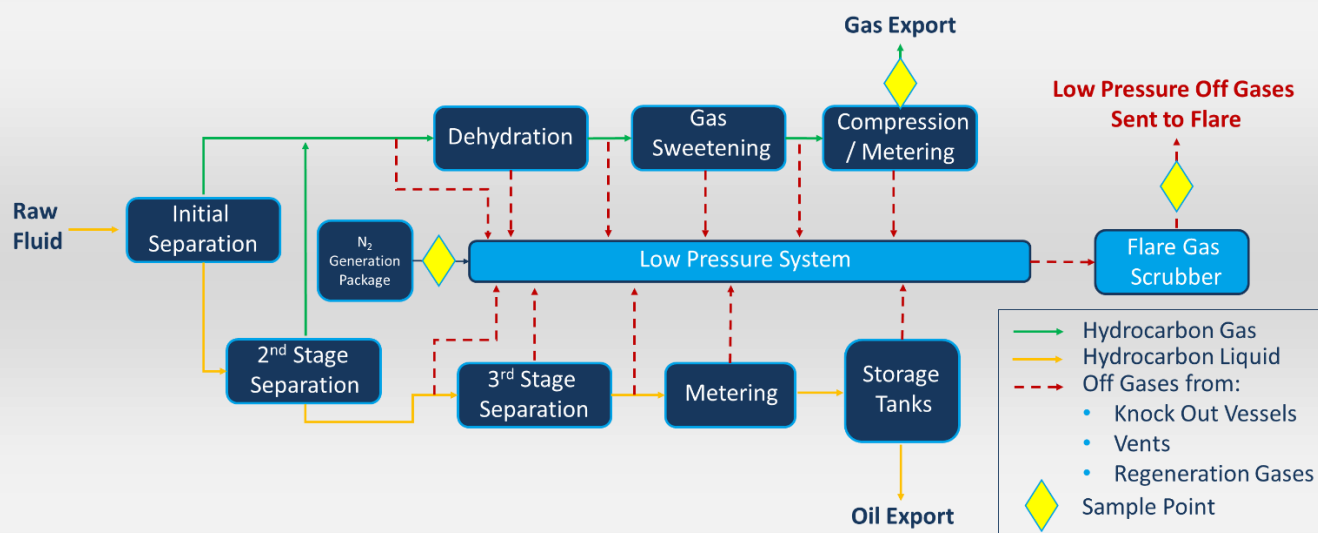


Figure 7: Typical process schematic with locations for oxygen monitoring

As oxygen presents a serious integrity risk coupled with stringent specification limits imposed by pipeline operators, it is of paramount importance that when monitoring oxygen concentrations sampling should be such that no contamination from air influences the results produced. Thus, as a QC check it is advised that the instrument calibration is checked using a matrix matched certified calibration standard at or around the specified concentration limit imposed by the pipeline operator before and after each period of monitoring.

Invariably, the potential for the introduction of air contamination becomes significant when collecting samples into cylinders for subsequent analysis off site; contamination of the sample with air may occur, either at the sampling point if sufficient flushing cannot be accommodated and/or in the laboratory

when the sample is introduced into the analytical instrument. For this reason, the preferred method for quantification of oxygen in production and process gas is to utilise an analytical technique that can be operated at-line. This allows an extended blanking time with an oxygen free inert gas to ensure that a background measurement below the reporting limit of the instrument is achieved prior to analysing live samples.

When using conventional, commercially available oxygen analysers to determine oxygen in accordance with ASTM D7607/D7607M-19, a lengthy equilibrium time requiring significant volumes of product gas is usually needed to be confident that no air contamination is introduced into the analytical instrument during; however, Qa³ have designed an at-line system that utilises a commercial analyser but incorporates some in-house design modifications to the sampling apparatus and analysis protocol in order to (i) prevent contamination from atmospheric oxygen (ii) reduce equilibrium time and (iii) achieve a reporting limit commensurate with *client requirements*. Typically, a limit of detection of 0.3 ppm v/v is achievable, however, due to the variation seen when blanking the instrument, the reporting limit for the at-line method is set at 1 ppm v/v.

At-line measurement accommodates quantification of oxygen in the gas even when sampled from dead leg sample points as the set-up allows a continuous flow of sample gas through the instrument sampling system to a safe vented area (normally low-pressure vent line). In addition, at-line measurement affords monitoring over an extended sampling period which (i) provides a better weighted average oxygen concentration and (ii) allows the data to be trended over an extended period to observe any changes to the oxygen concentration due to variation in day-to-day production conditions. This may include (i) actual changes to production rates and wells / fields online, (ii) the sources of and the flow rate of the LP flare gas and (iii) the volume and purity of the plant nitrogen being used. This data can be very useful when predicting both the minimum and maximum oxygen concentrations in the export gas when routine flaring is ceased.

6 Summary

A summary of the issue and how to check if an oxygen problem does or may exist?

- As the oil and gas industry strives towards its climate objective in reducing carbon emissions, many operators are now investing in FGR systems to limit the amount of routine flaring from their facilities; however, this comes with the unfortunate and frequently unconsidered potential for introducing undesirable oxygen into the exported natural gas.
- Historically, any plant nitrogen that has been used in process gases will typically be sent to flare via the low-pressure flare system. As such the design of the plant nitrogen and the process areas of use have not been considered critical in terms of product specification and corrosion risk as this is ultimately flared. Therefore, it is very common to find nitrogen purities in the range $\geq 95\%$, which means that without any remedial actions, low % concentrations of oxygen are invariably present in the plant nitrogen that will be reintroduced into export natural gas via FGR systems.
- There are numerous repercussions of introducing this oxygen to the exported production gas as (i) it may provide a product that is above the pipeline specification limit for oxygen with fiscal implications and (ii) oxygen poses a serious corrosion risk to the steel infrastructure via several mechanisms, which could prove to be extremely costly to mitigate. To put this into perspective the US spends approximately \$1.5 billion per year dealing with corrosion issues^[16].

- An assessment of the potential risk for oxygen introduction into the export gas should ideally be carried out prior to commissioning an FGR system. This requires analysis of the plant nitrogen, low-pressure flare gas and export gas to calculate accurately the expected oxygen concentration in the export once a flare gas recovery unit is brought online.
- If nitrogen is present in the FGR system, the oxygen concentration would be expected to be significantly higher than those seen in the production gas export system, perhaps in the 100's of ppm to low % concentration range. Thus, an assessment of the corrosion risk to the FGR and low-pressure systems should be sought.
- To minimise the risk of introducing air into the sample under test an at-line analytical instrument should be employed. In addition, blanking with an oxygen free gas and appropriate QC checks spanning each monitoring period should be incorporated into the procedure to provide an assessment of analyser performance and calibration integrity.
- QC checks should be carried out using a matrix matched certified standard with an oxygen concentration at or close to the specification limit set by the pipeline operator.
- Monitoring of export gas should be undertaken during normal stabilised production and preferably over multiple days to obtain a robust, representative data.

What if there is or will be positive concentrations of oxygen in the export gas?

- If it is found that the oxygen concentration in the export gas is or will be at a level that is either exceeding the pipeline specification or at a level that raises concerns of accelerated corrosion, then remedial action will be needed to be taken to limit the risk.
- As oxygen has the potential to cause corrosion via a number of mechanisms it would be prudent to consult a materials engineer to assess the potential rate of corrosion to the steel infrastructure that can be expected. It may highlight the additional need to quantify H₂S and moisture in the export gas to provide the data necessary for optimum modelling of the potential corrosion risk.
- The manufacturer of the plant nitrogen system should be consulted to see if, with modifications, a purer nitrogen can be produced. Typically membrane based systems will achieve nitrogen purities between 95.0 - 99.5%, whereas pressure swing adsorption systems can achieve purities up to 99.9%^[17]. Unfortunately, due to space restrictions, many offshore facilities may have limited capacity to modify existing plant nitrogen packages; however, the manufacturer may be able to suggest engineering solutions within the confines of the current plant design.
- In the absence of being able to further purify the plant nitrogen it may be necessary to incorporate an oxygen removal system to remove the oxygen^[18].

Offshore installations form part of a very dynamic system where production rates often vary and new wells may be brought into production. The volume of plant nitrogen and off-gases sent to LP flare also change on a frequent basis. For this reason, it is likely that the oxygen concentrations within the gases will fluctuate over time and should therefore continue to be monitored on a regular basis.

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