

Oxygen Removal in Natural Gas Systems

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ABSTRACT

The presence of oxygen and water in natural gas pipelines can result in corrosion and may lead to catastrophic leaks. In addition, some pipeline customers may use the gas as a chemical feedstock where the presence of oxygen poses problems. Though natural gas oxygen specifications vary from pipeline to pipeline, new contract specifications have trended downwards over recent years. When specified limits are exceeded, the installation of oxygen removal systems is required.

Various technologies are applicable for removal of oxygen from natural gas streams, using either hydrogen, H₂S or some of the heavier hydrocarbons (C₃+) to consume the oxygen in catalytic reactors or at solid scavengers. This paper reviews commercially available oxygen removal technologies as well as discusses alternate technologies that were found to be ineffective in economically removing oxygen from natural gas streams.

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Introduction

Oxygen contamination in natural gas can pose serious issues in gas plants, natural gas pipelines, gas gathering systems at production facilities and storage fields, and chemical process user facilities. In gas processing plants, oxygen can cause severe corrosion in piping system components resulting in safety hazards due to gas leaks, costly downtime and unplanned maintenance.

In gas processing, the presence of oxygen adversely affects glycol and mole sieve dehydration and amine treating units. Oxygen enhances degradation of glycol in dehydration systems where the degradation products can include acids, which increase corrosion, as well as aldehydes and polymers. In amine gas-treating systems, oxygen is known to react with the alkanolamines¹ to form heat stable salts, the presence of which reduces the overall amine available for acid gas removal and increases corrosion rates. When oxygen is present, replacement costs of amine treating chemicals increase and disposal of spent amine is a potential environmental concern.

Oxygen Contamination Causes

The gas produced in conventional natural gas and oil fields does not contain oxygen. When oxygen contamination is identified, the source is generally air ingress during gathering or processing. Some potential sources of oxygen from air ingress are:

- Inadequately controlled tank vapor recovery units (VRUs).
- Failure of tank blanketing systems or lack of a tank blanketing system
- Ingress through packing on compressors taking suction from low-pressure wells.
- Pipe & fitting leakage and leaking well casings in vacuum gathering systems.

Growth in worldwide energy demand has increased interest in some non-traditional natural gas sources. One such source is Coal Mine Methane (CMM), which is created by a geologic process known as coalification where methane and coal are formed together. In recent years, many coal mines have opted to recover and upgrade CMM gas and supply it to natural gas pipelines. In 2005, U.S. CMM pipeline sales had revenues of \$97 million². While natural gas that is recovered in advance of mining is nearly pure methane, gas recovered post mining is called “gob gas³”. Gob gas has been mixed with air and requires the application of gas upgrade technologies to remove oxygen and nitrogen.

Another non-conventional gas source is landfill gas created from the decomposition of organic waste. The growth in energy demand and the desire to reduce green-house gas emissions is driving the application of natural gas upgrading technology to high-Btu landfill gas projects⁴. Air ingress into landfill gas is a natural occurrence due to the low pressure of the collection system.

Eliminating Oxygen at Source

In many cases, eliminating oxygen at source is the cheapest way to deal with oxygen contaminated gas, and the best defense against oxygen contamination in conventional natural gas sources is good engineering and process operation practices.

VRU systems may be one of the most common sources of air entering natural gas streams. These systems are frequently designed with controls to prevent pulling a vacuum on storage tanks. However, such controls sometimes do not operate properly, are not located to allow consistent long-term operation, and/or do not contain enough redundancy to prevent the VRU from pulling a vacuum on some portion of the storage tanks or their vent piping. If controls are not operating properly, then the VRU compressor can pull a vacuum on the tank and air can be sucked into a tank or tank vent line through improperly sealed roof hatches, vacuum protection valves, and similar devices.

Even if VRU pressure sensing controls are working properly, air can still enter the system through working and breathing effects. The diurnal temperature change is large enough in some cases to cause vacuum breaker valves to allow air into the tank. A similar situation can occur when storage tank contents are loaded into trucks.

Leak detection involves measuring oxygen close enough to the source to determine which VRU-equipped tank battery or batteries are likely the source of the oxygen⁵. Correction generally involves putting VRU suction controls back into proper operation, possibly increasing set point pressure(s), relocating pressure sensing instruments/controls to points where they can properly or more reliably sense low pressures caused by the VRU compressor, adding redundant controls/alarms, sealing tank hatches and other air ingress points, and attempting to address working and breathing effects.

The industry also reports that a common source of air ingress is leakage through packing on the suction side of compressors that are pulling vacuum on production wells, as may be common in older oil and gas fields. Leak detection requires oxygen measurement close enough to the source to determine which compressor or compressors are likely the culprit(s), followed by oxygen measurement on suction and discharge of the suspect compressor to prove that it is a specific machine. Correction generally involves tightening packing and making sure lubricators are functioning. Another technique sometimes used is to maintain a slight positive pressure on the compressor distance piece by purging with an inert gas such as nitrogen.

Pipe and fitting leakage in vacuum gathering systems may also occasionally be a problem, especially in aging vacuum gathering systems. Detection and correction may be more complicated and/or expensive in the case of leaking fittings or piping, especially for underground systems.

Technologies Commercially Available for Oxygen Removal

The commercially available technologies for oxygen removal are catalytic oxidation and solid scavengers, but solid scavenger usage is limited or still under development. In catalytic oxidation, hydrogen or some of the heavier hydrocarbon compounds is used to consume the oxygen, but this paper does not consider the hydrogen oxidation schemes, as hydrogen is usually not available in natural gas plants.

Catalytic Oxidation

The catalytic removal of oxygen from a natural gas stream is achieved by passing the gas at an elevated temperature over a catalyst bed where the oxygen reacts with a portion of the natural gas to form CO₂ and water. Figure 1 depicts a generic catalytic oxygen removal system.

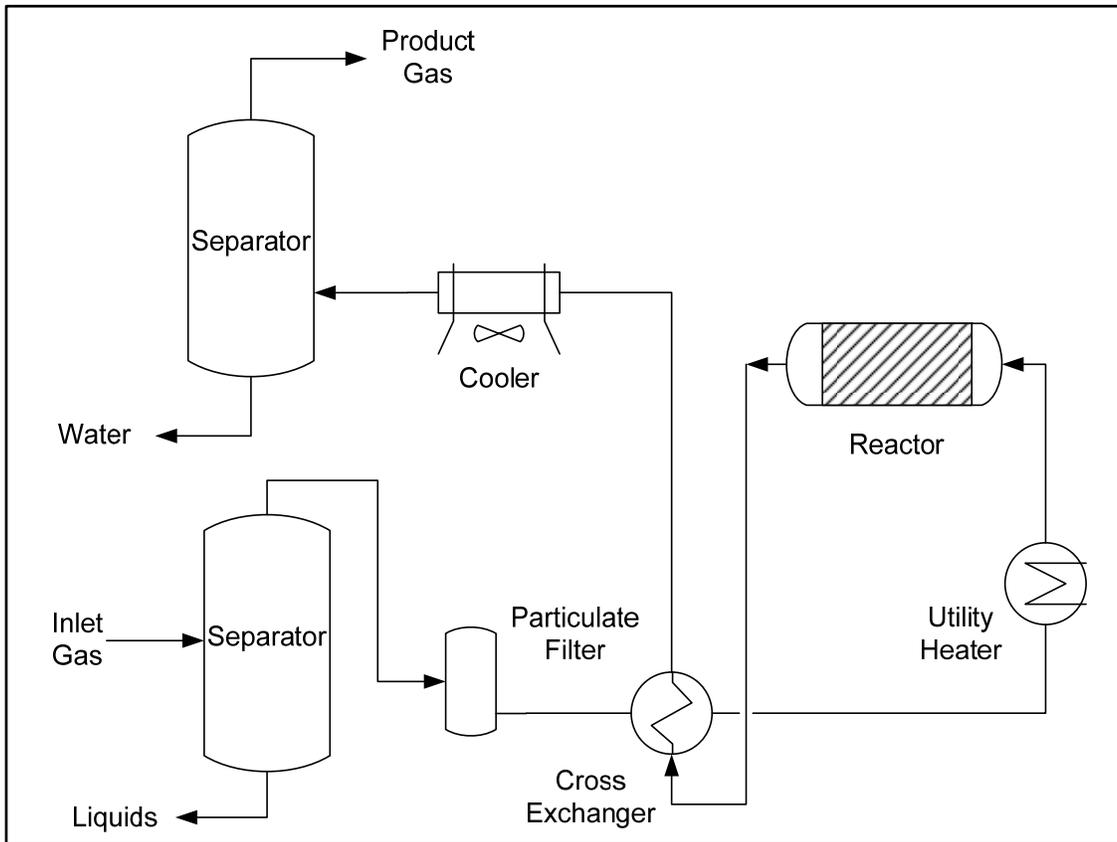


Figure 1– Catalytic Oxidation Unit

The gas stream enters an inlet separator to remove entrained liquids, followed by an inlet filter to remove particulate matter that may foul the solid catalyst bed. The gas stream is then pre-heated through cross exchange with the hot gas leaving the catalytic reactor. The reaction temperature is a function of the gas composition, gas oxygen content, treated gas oxygen specification and catalyst media. A minimum concentration of oxygen in the inlet gas is required in order to maintain the proper reaction temperature. If there is insufficient oxygen, additional heat may be added by a supplemental process heater. The gas stream then enters the reactor where the oxygen in the stream reacts with some of the hydrocarbons (usually the C₃+ fractions) in the natural gas stream and produces water and carbon dioxide. The hot gas stream is then cooled via cross exchange with the inlet gas stream and after-cooler heat exchangers. After cooling, the product gas enters an outlet separator where condensed water is removed from the treated gas. The outlet separator is optional and is required only if there is significant oxygen being removed from the gas. For typical cases where there is a low concentration of oxygen, water is made at low ppm levels and the after-cooler may not condense any water.

There are a number of commercially available catalytic oxidation processes, some of which are described below:

PSB Industries - Deoxo

PSB Industries offers the Deoxo process for oxygen removal from natural gas streams that do not contain or have removed H₂S and other sulfur compounds upstream. The natural gas enters a coalescing pre-filter where aerosol mists and particulate matter are removed. The stream is first heated in the cross exchange and then, if the oxygen content in the gas results in too low a temperature rise in the catalytic reactor, heated by an electric pre-heater to 500 °F or higher. Depending on the volume of gas and available utilities, other types of heaters, e.g. direct-fired or a heat exchanger using heat medium fluid, might be more suitable than electric heating. The heated gas then enters the stainless steel vessel containing palladium catalyst where the oxygen reacts with hydrocarbons. Sulfur contaminants such as hydrogen sulfide, mercaptans and or other organic sulfides can lead to catalyst poisoning. If sulfur-containing contaminants are present in the stream, then they must be removed prior to the Deoxo, e.g., via a guard bed.

Newpoint Gas Services - X-O₂TM

Newpoint Gas Services offers X-O₂TM, which is a proprietary oxygen removal system. The X-O₂ system is similar to other catalytic oxidation processes; with the exception that it optionally includes high temperature air coolers upstream of the cross exchanger on the treated gas side. The purpose of the Hi-temp air coolers is to cool the gas leaving the reactor and thereby reduce the temperature rating of the cross exchanger. For systems that treat low concentrations of oxygen, the high temperature air coolers are not required because the reaction does not generate a large temperature rise. X-O₂TM catalyst is anticipated to last five to ten years. The proprietary X-O₂TM catalyst is tolerant of sulfur and chlorine components in the natural gas stream. H₂S in the gas stream is converted to SO₂ in the reactor, the levels of which should be considered with respect to downstream customer specifications. If the concentration of H₂S present in the natural gas stream will result in exceeding an SO₂ specification, an H₂S removal unit upstream is recommended.

Sud Chemie –Palladium Catalysts

Sud-Chemie markets several palladium-based catalysts for the purpose of oxygen removal from natural gas streams. The catalytic oxidation process utilizing the G-74D palladium catalyst is similar to other catalytic processes. The natural gas stream enters the reactor at 650 °F where the oxygen in the stream is catalytically converted. The selection of G74D catalyst is dependent on the heavy hydrocarbons (C₃+) in the stream. If minimum levels of heavy hydrocarbons are not present in the process stream, then Sud Chemie recommends the G-43A catalyst with the corresponding inlet temperature to the reactor of 900 °F. Contaminants such as sulfur and chloride compounds can poison the Sud Chemie catalysts.

Solid Scavengers

Chemical Products Industries - OxyTrapTM

Removal of some types of gas contaminants (e.g., H₂S) using a solid scavenger is common in the gas industry, however; oxygen removal is not common. One commercially available and patent pending solid scavenger is an offering of Chemical Products Industries called OxyTrap^{TM6}

OxyTrapTM is an iron-based oxidation catalyst that is activated with hydrogen sulfide or other organic sulfur compounds. The oxygen consumption occurs via the oxidation of ferrous sulfide to form ferric

sulfide, sulfur and sulfate species. At the minimum, a stoichiometric quantity of sulfur-bearing species in the natural gas stream (preferably H₂S) is required to regenerate ferric sulfide to ferrous sulfide. The by-products of the sulfur oxidation, which include both elemental sulfur and metallic sulfate, remain on the solid scavenger. The oxygen removal process will continue as the ferrous iron is regenerated. Eventually, the bed will deactivate as the active ferrous sulfide oxidation sites are blocked by the elemental sulfur, metallic sulfate and other by-products.

This removal method has been demonstrated in a pilot scale unit to reduce up to 1% O₂ to an outlet concentration of <1 ppm until the catalyst is deactivated. At present, an upper limit of O₂ has not been established. Assuming that excess H₂S is present, the life of the catalyst bed is dependent on the quantity of catalyst charge and the oxygen content of the natural gas stream.

The oxygen removal beds can be designed in a similar fashion as solid scavengers in H₂S removal service. A lead-lag system is preferred for operational flexibility as depicted in Figure 2; however, a single vessel will also work.

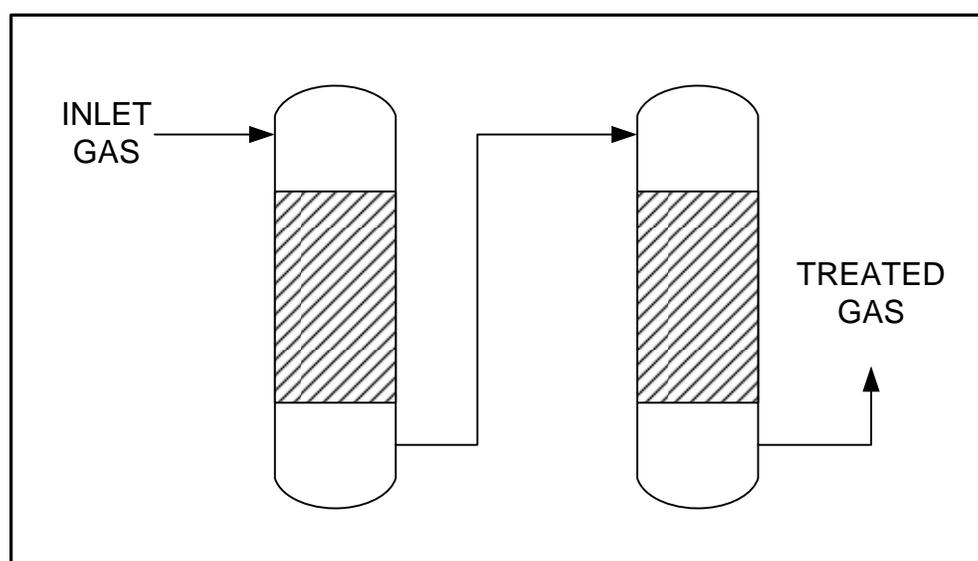
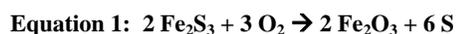


Figure 2 – Solid Scavenger Unit

Other Possible Solid Scavengers

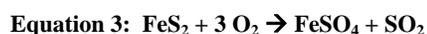
One patent⁷ discloses a method of oxygen removal from natural gas streams employing a solid bed of oxygen removal chemical such as Fe₂S₃ on wood chips. This technique claims use of the following reaction:



This process would be akin to using “spent” or ‘pre-sulfided” iron sponge. A major barrier to implementation of this process is the lack of publically available data on oxygen removal and the potential issue of handling the iron sulfide material due to its pyrophoric nature.

However, industry contacts reported some anecdotes of incidental oxygen removal when using iron sponge to remove H₂S in landfill gas applications. This observation is consistent with the occurrence of the reaction in Equation 1 and also consistent with iron sponge regeneration techniques⁸.

There are also other solid scavengers for oxygen removal that are used in guard beds on Claus units to protect the alumina catalyst in the second and third converters from oxygen contamination which can shorten the life span of the Claus catalyst. Axens IFP Group Technologies offers a solid scavenger that removes oxygen from the gas stream while being continuously regenerated in the presence of H₂S. This technique makes use of the following reactions:



The scavenger is installed as a small layer on top of the converter beds to protect the Claus catalyst from sulfation. No data or references were found for commercial use of this technology for oxygen removal from natural gas. Even if such a catalyst could be used to remove oxygen from natural gas, it would require some amount of H₂S in the natural gas and could affect the SO₂ content, which may approach end user specification limits.

Economic Analysis

The oxygen removal technologies described above were evaluated for two general cases (see Table 1). Cases A and B were used to evaluate catalytic oxidation methods. Case A is a 2.5 MMscfd stream of rich natural gas at 85 °F and 25 psig containing 1.5 % oxygen. Case B is a 25 MMscfd of natural gas at 95 °F and 750 psig containing 0.01 % oxygen. The desired outlet specifications for oxygen were 0.1 percent for Case A and 10.0 ppm for case B.

A modified Case B and a Case C were later created so that the solid oxygen scavenger could also be evaluated. Modified Case B is a 25 MMscfd stream of rich natural gas at 95 °F and 750 psig containing 0.01% (100 ppm) of oxygen and 0.01% H₂S. Case C is a 60 MMscfd stream of rich natural gas at 100 °F and 280 psig containing 0.01% (100 ppm) of oxygen and ~ 1% H₂S. The desired outlet specification for oxygen for both Case B (modified) Case C was 10 ppm. As previously stated, the solid scavenger technology has been demonstrated to remove up to 1% O₂ to an outlet concentration of <1 ppm.

Table 1 - Stream Compositions for Economic Evaluations

Stream	Case A Mole%	Case B Mole%	Case B (modified) Mole%	Case C Mole %
Flow, MMSCFD	2.5	25	25	60
Temperature, °F	85	95	95	100
Pressure, psig	25	750	750	280
Nitrogen	6.15	0.50	0.50	0.50
Carbon Dioxide	0.50	0.75	0.75	1.00
Hydrogen Sulfide	0.01	0.00	0.01	1.00
Methane	64.84	89.09	89.08	87.89
Ethane	15.25	6.00	6.00	6.00
Propane	8.25	2.50	2.50	2.50
i-Butane	0.65	0.20	0.20	0.20
n-Butane	1.25	0.60	0.60	0.60
i-Pentane	0.35	0.10	0.10	0.10
n-Pentane	0.75	0.20	0.20	0.20
n-Hexane Plus	0.50	0.05	0.05	0.05
Oxygen	1.50	0.01	0.01	0.01
Total	100.00	100.00	100.00	100.00

A summary of the economic analysis for each the technology is provided in Table 2 and Table 3. The average capital and operating costs in Table 2 are for PSB Industries and Newpoint Gas Services systems and includes equipment and initial catalyst costs. The analysis assumes a straight-line depreciation over 5 years; a salvage value of 30% of the purchased equipment costs, and an on-stream time of 350 days/yr. Capital and operating costs were provided in vendor quotes and other cost estimating tools such as Preliminary Design and Quoting Service (PDQ\$).

Table 2 – Catalytic Oxidation Methods - Average Estimated Capital and Operating Costs

Case	Purchased Equipment Costs, \$MM	Installation Factor	Estimated Capital Costs, \$MM	Estimated Annual Operating Costs, \$MM	Annual 5-yr Straight Line Depreciation, \$MM	Estimated Operating Costs & Depreciation, \$/MMscf	Total Annual Cost, \$MM
A	1.1	1.5	1.7	0.004	0.16	4.42	0.16
B	2.3	1.5	3.4	0.247	0.32	28.22	0.56

Table 3 – Solid Scavenger Method – Estimated Capital and Operating Costs

Case	Purchased Equipment Costs, \$MM	Installation Factor	Estimated Capital Costs, \$MM	Estimated Annual Operating Costs, \$MM	Annual 5-yr Straight Line Depreciation, \$MM	Estimated Operating Costs & Depreciation, \$/MMscf	Total Annual Cost, \$MM
B (modified)	0.259	1.5	0.389	0.23	0.04	25.85	0.26
C	0.335	1.5	0.502	0.53	0.05	25.12	0.57

Though the gas stream Case B and Modified Case B are similar, the presence of H₂S in the Modified Case B allows for the possible application of the solid scavenger method, which eliminates the need for a utility heater, reactor and cross-exchangers, resulting in a much lower purchased equipment cost.

TECHNOLOGY SELECTION

Currently, only the catalytic oxidation technologies are known to be used in industrial applications. The solid scavenger technology, though yet to be installed in a full scale commercial application, offers substantial cost savings because it has the advantage of operating at ambient feed gas temperature and does not require process equipment beyond standard process vessels and piping. However, the solid scavenger technology requires that H₂S be present in the gas stream.

Within the catalytic oxidation technologies discussed in this paper, the first issue is whether H₂S or other sulfur compounds are present, since sulfur compounds may poison the PSB, Deoxo and the Sud Chemie catalysts. For cases where there are no sulfur compounds present or when the sulfur compounds can be removed economically upstream, it is best to work with the vendors to determine which technology is best suited for a particular application.

In addition, gas feeds with low oxygen contents will have smaller temperature rises across the catalyst bed, and may require an external utility heater to reach the required bed inlet temperatures. Operating concerns and issues regarding high gas temperatures should be discussed with the vendor. In evaluating the economics of the competing catalytic oxidation technologies, the total cost should be included. This can potentially include the cost of H₂S (or SO₂) removal, as well as the incremental cost to remove more CO₂ and H₂O when the end use of the treated gas requires that these be removed (e.g., natural gas used as chemical feedstock). These costs were not included in the economic evaluation performed for this paper.

Technologies Not Suitable for Oxygen Removal

Many gas processing technologies including liquid scavengers, solid adsorbents and membranes have been demonstrated successfully for the removal of contaminants such as hydrogen sulfide, carbon dioxide and nitrogen^{9,10,11,12}. These technologies are sometimes mentioned in industry circles as suitable for oxygen removal from natural gas; however, other than the oxygen removal methods mentioned previously, alternate technologies using liquid oxygen scavengers, solid adsorbents, and membranes were found to be uneconomic and had no commercial applications for oxygen removal from natural gas.

Liquid Scavengers

The use of chemical scavengers such as sulfites is common in the deoxygenation of liquids such as boiler feed water as well as in the mitigation of oxygen contamination in alkanolamine solutions used for gas treating. However, chemical scavengers are not commercially available for the purpose of oxygen removal from gas phase streams such as natural gas. A key issue preventing the use of liquid oxygen scavengers is the very low solubility of oxygen in aqueous solutions and poor mass transfer from the gas phase into the liquid scavenger.

Preliminary estimates indicate that for a direct pipeline injection approach, the required injection rate is relatively high and cost prohibitive. Maintaining dispersion of the liquid scavenger in the pipeline for estimated required length of pipe (see Figure 3) would be an operational challenge. In addition, there would be the additional cost of liquid scavenger storage, injection and separation equipment.

**Direct Liquid Scavenger Injection
Reduction of Oxygen Concentration in Pipeline**

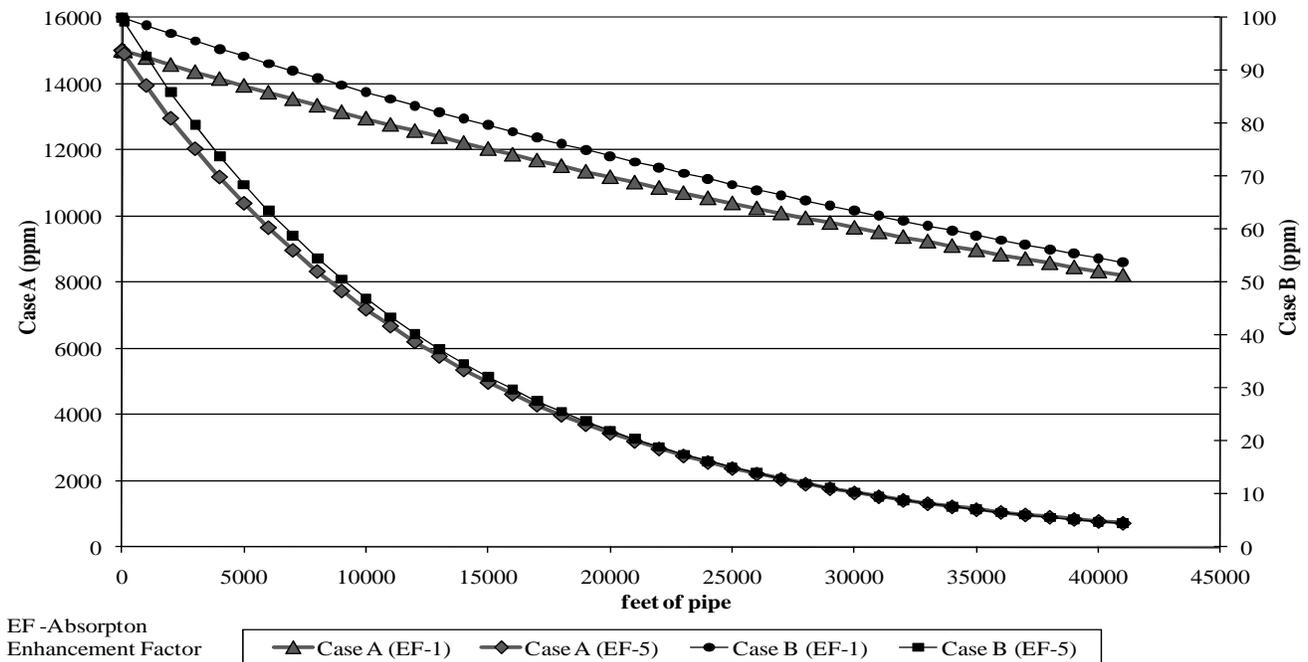


Figure 3 –Pipeline Liquid Scavenger Injection Estimates

As an alternate, the use of a bubble tower design (liquid-filled absorber with gas sparged through liquid) for scrubbing oxygen from a natural gas stream was investigated. The estimated calculation result indicated that this approach is also not economically feasible. Besides the relatively high circulation rates of liquid scavenger, preliminary calculations suggested that multiple towers in series would be required to reduce the oxygen in the natural gas to acceptable levels. Figure 4 shows the estimated reduction in oxygen concentration per foot of depth in a 15 ft diameter bubble tower for Case A and a 9 ft diameter bubble tower for Case B.

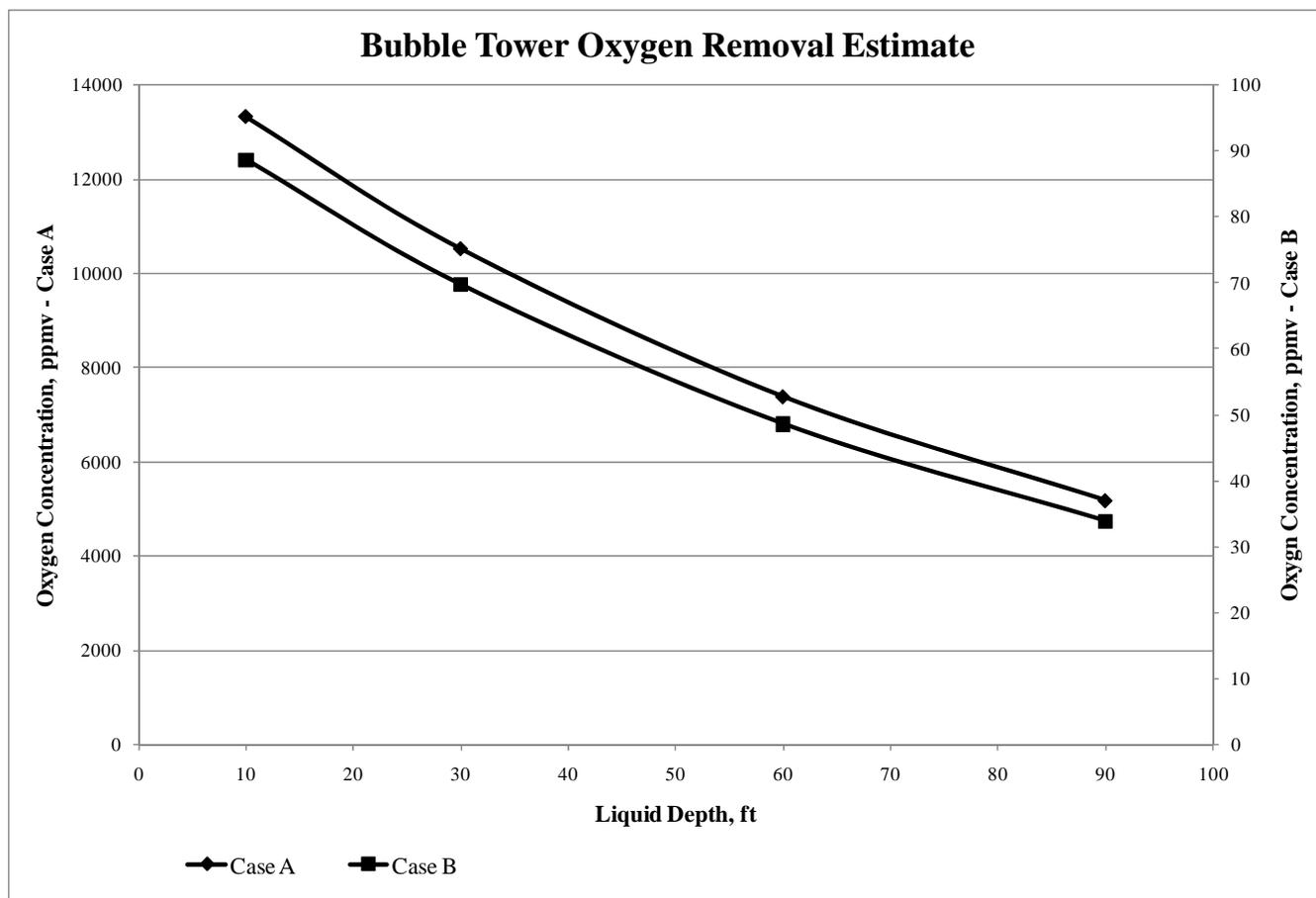


Figure 4 - Estimated Oxygen Removal for Bubble Tower

Physical solvents typically used in acid gas treating processes are another alternate, but are not effective in removal of oxygen from gas streams, due to the low solubility of oxygen in physical solvents. Table 4 shows a summary of solubility data for various gases in physical solvents relative to CO₂.¹³ The physical solvents listed are Dimethyl Ether of Polyethylene Glycol (DEPG), Propylene Carbonate (PC), N-Methyl-2-Pyrrolidone (NMP), and Methanol (MeOH).

Table 4 – Solubility of Gases in Physical Solvents Relative to CO₂

Gas Component	DEPG at 25 °C	PC at 25 °C	NMP at 25 °C	MeOH at -25 °C
Nitrogen	0.20	0.0084	-	0.012
Carbon Dioxide	1.0	1.0	1.00	1.0
Hydrogen Sulfide	8.82	3.29	10.2	7.06
Methane	0.066	0.038	0.072	0.051
Ethane	0.42	0.17	0.38	0.42
Propane	1.01	0.51	1.07	2.35
i-Butane	1.84	1.13	2.21	-
n-Butane	2.37	1.75	3.48	-
i-Pentane	4.47	3.50	-	-
n-Pentane	5.46	5.0	-	-
n-Hexane Plus	11.0	13.5	42.7	-
Oxygen	-	0.026	0.035	0.020

Solid Adsorbents

Solid adsorbents such as aluminum silicates, silica gels and activated carbons are often used in Pressure Swing Adsorption (PSA) units to separate one or more components from a mixture of gases. PSA technology takes advantage of the individual species' molecular characteristics and affinity for a particular adsorbent. The typical PSA process is a series of process steps that include a higher-pressure adsorption step, followed by depressurization and then a purge. The diagram in Figure 5 depicts this cycle.¹⁴ Depending on the impurity removal requirement, several PSA units in series may be needed.

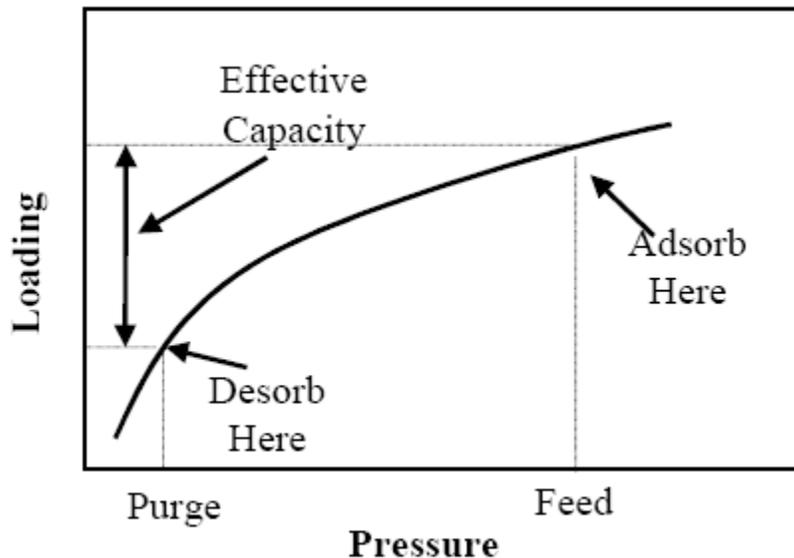


Figure 5 – Pressure Swing Adsorption Cycle

Some applications of the PSA technology use in industry are:

- 1) Removal of CO₂ in large-scale synthesis of H₂
- 2) Methane enrichment by removal of CO₂ from biogas
- 3) Production of high purity N₂ from compressed air

Per conversations with PSA vendors, it was thought at one time that, since an O₂ molecule is smaller than an N₂ molecule, adsorbents designed for N₂ rejection would remove O₂¹⁵ from a natural gas stream on an equal basis with N₂. However, it was found that N₂ is adsorbed preferentially to O₂, thus the O₂ removal rate is lower. Therefore, in order to remove the required amount of O₂, additional adsorption units are required. Each additional stage of adsorption results in additional natural gas losses, and the losses are large enough that none of the vendors contacted could recommend a PSA process configuration for O₂ removal.

Membranes

Membrane technology, which, among its many applications, is used to remove CO₂ from natural gas, was speculated by some industry contacts to also have application in the removal of oxygen from natural gas. Figure 6 is a diagram showing the relative transport of various gases through CO₂ removal membranes¹⁶.

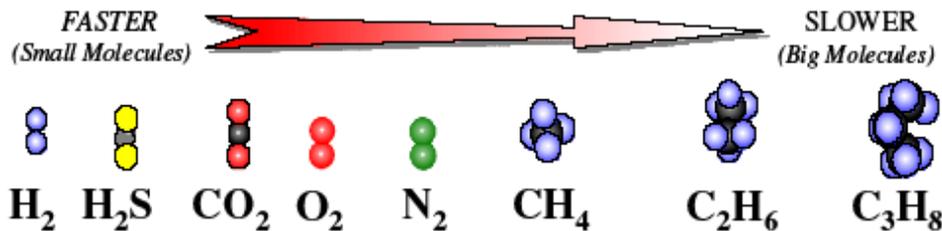


Figure 6 – Relative Transport of Gases through typical CO₂ removal Membranes

The rate at which each component permeates the membrane is a function of the membrane material and the component. Further investigation found that no membrane materials are commercially offered for the purpose of oxygen removal from natural gas.

Conclusions

There are currently two commercially available technologies for the removal of oxygen from natural gas streams: catalytic oxidation, which has offerings from several process equipment vendors and a patent-pending solid scavenging technology. A possibly simpler solution to eliminate oxygen from natural gas stream is to follow good engineering and operating practices and prevent the oxygen ingress in the first place.

Other technologies often have been hypothesized to be candidates for oxygen removal, including liquid scavengers, solid adsorbents and membranes. However, no commercial offerings of these technologies were found for oxygen removal from natural gas streams.

For additional details on the technologies, economics, and data provided by the vendors, readers are referred to the GPA research report, RR-201“Oxygen Removal in natural Gas Systems¹⁷”.

Acknowledgements

The authors would like to thank the many industry contacts that provided information on their experiences and ideas regarding removal of oxygen from natural gas streams.

This paper would not have been possible without the assistance and valuable information provided by many technology vendors, particularly the catalytic oxidation and solid scavenger vendors^{18,19,20,21}.

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