

### Introduction

Worldwide, natural gas is becoming an increasingly popular fuel due to its abundance and clean burning properties. There are many methods of extracting natural gas including offshore drilling, hydraulic fracturing (fracking), and traditional land based dry wells. In addition, natural gas is often a sub-component from crude oil extraction. No matter what source it is derived from, natural gas must go through processing and transportation before it can be used in household and industrial applications. In this paper we will explore the initial processing of natural gas and the critical effect that oxygen ( $O_2$ ) measurement plays in this process.

### Extraction

We know natural gas as methane ( $CH_4$ ) however the raw gas from the wellhead is actually a mixture of many components. These include the following:

Methane ( $CH_4$ )	70 – 90 %
Ethane ( $C_2H_6$ )	5 – 15 %
Propane & Butane	< 5%
( $CO_2$ ) ( $N_2$ ) ( $H_2S$ ) ( $O_2$ ) (He)	Balance

The additional hydrocarbon in the raw gas are referred to as Natural Gas Liquids (NGL's). Collection of the natural gas is done from multiple wellheads. The gas is funneled through feeder pipelines to production manifolds where it can go through multi-stage separation. Separation involves removal of NGL's, contaminating gases such as  $CO_2$  and Helium, and dehydration of any moisture present in the gas. The NGL gases such as propane and butane are valued and will be sold off as feedstock to petrochemical facilities.

### Corrosion Concerns

When the raw gas contains excess levels > 4ppm of hydrogen sulfide ( $H_2S$ ) then it is considered "Sour Gas".  $H_2S$  combined with oxygen and moisture greatly increases potential corrosion in the form of Sulfuric acid ( $H_2SO_4$ ). The corrosion is detrimental to the piping and valves leading up the separation plant.

Monitoring of oxygen is often done at the wellhead piping leading to production manifolds. If the gas field is a long distance from the separation plant then compressors are used to increase the gas flow. Compressors have a potential for leakage at the seals allowing the ingress of outside air. Once this air is mixed with the sour gas the potential for corrosion greatly increases. Downstream oxygen measurement provides the additional benefit leak detection when seals fail.

### Measurement Challenges

Measuring trace ppm oxygen (0 ~ 75 ppm) in natural gas pipelines is traditionally done by utilizing a electrochemical sensor referred to as a Clark Cell. A gas sample is extracted from the pipeline with either a portable or on-line analyzer mounted next to a slip stream. The sensor requires a sophisticated sample conditioning system to remove moisture, control the pressure and flow, and most importantly, remove  $H_2S$ . Moisture will interfere and clog the sample lines to the sensor requiring frequent maintenance of the system. Changes in pressure and flow will affect the readings of the membrane so the sample must be controlled.  $H_2S$  will quickly contaminate the sensor. If the  $H_2S$  level are high, the life of the sensor will be destroyed in a matter of hours.  $H_2S$  is one of the greatest challenges when using a membrane sensor

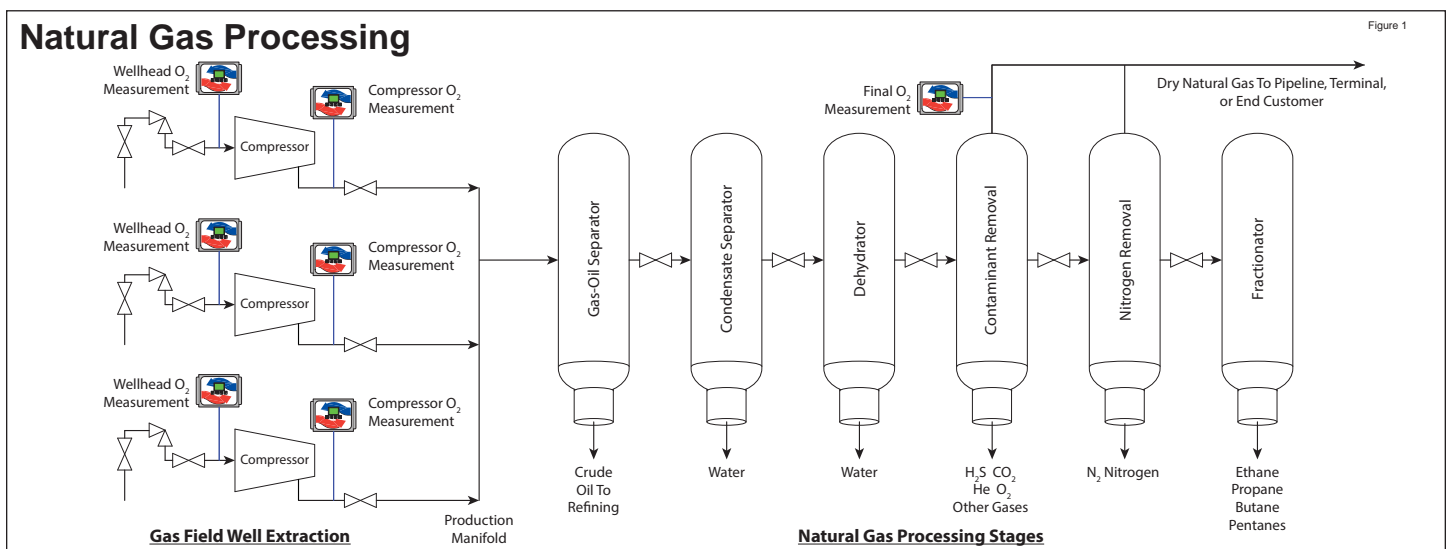


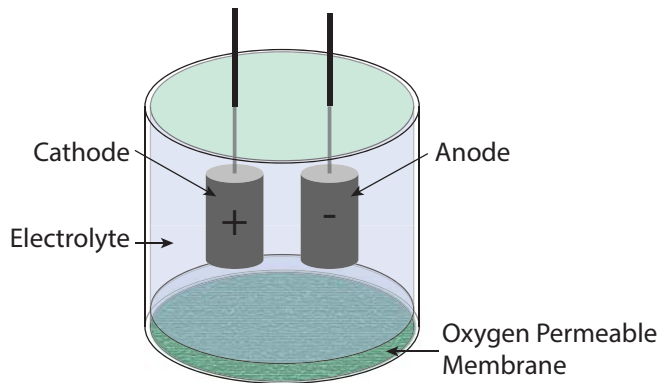
Figure 1

# Application Note

## Natural Gas Production

technology. The sample system will use an upstream H<sub>2</sub>S scrubber to prevent the gas from harming the sensor. If the sulfide concentrations are consistent then these scrubbers must be serviced weekly and sometimes daily to maintain reliable oxygen readings from the Clark Cell. Because these measurements are often made at remote wellhead sites the on-going maintenance and expense of the sample system can be problematic.

### Electrochemical Clark Cell O<sub>2</sub> Sensor



- Sensitive to flow and pressure changes
- Membrane sensitive to fouling, coating and attack
- Electrolyte poisoning

Figure 2

A secondary concern is sensor accuracy. All Clark Cell sensors generate output current similar to a battery. Since the Clark Cell output is based on oxygen concentration, high levels of oxygen will shorten sensor lifespan. The aforementioned contamination due to H<sub>2</sub>S will also influence the output giving a false readings. Both of these issues prevent an continuous, accurate measurement.

A final issue of electrochemical Clark Cell sensors is the requirement for periodic calibration using air (20.9% O<sub>2</sub>). Since natural gas measurements are < 100 ppm there is considerable lag time after calibration for the sensor to consume excess oxygen which permeated through the membrane during calibration. Often stabilization will not occur for 30 minutes or longer depending on the age of the cell. This wait time adds to loss of reading as well as using up valuable personnel time.

### Oxygen Measurement Solutions

Recent advancements in optical fluorescence quenching technology now allows a measurement at trace ppm levels of oxygen without the fear of damage to the sensor. An illustration of the measurement principle of these sensors can be seen in Figure 3.

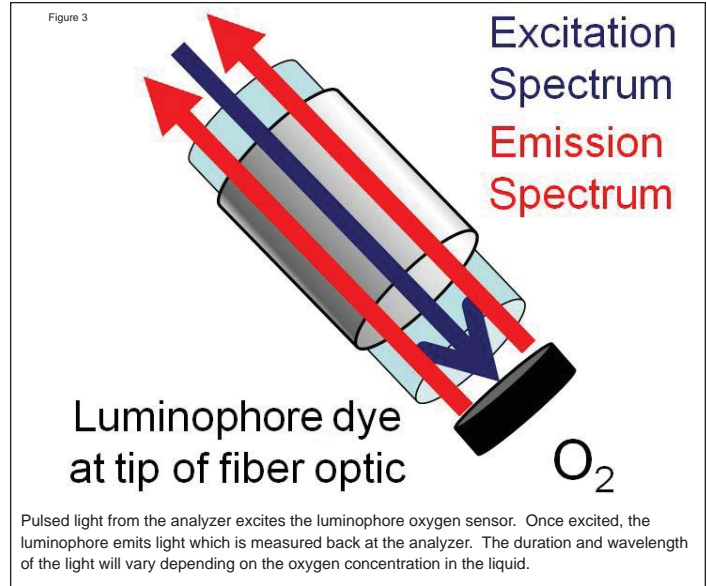


Figure 3  
Pulsed light from the analyzer excites the luminophore oxygen sensor. Once excited, the luminophore emits light which is measured back at the analyzer. The duration and wavelength of the light will vary depending on the oxygen concentration in the liquid.

Using an optical sensor (0 – 200 ppm) will allow accurate oxygen measurement without degradation due to over exposure of high oxygen or cross sensitivity at % level H<sub>2</sub>S or CO<sub>2</sub> concentrations. Expensive sample conditioning systems and their associated maintenance can be eliminated with optical sensors. Advantages over traditional measurements include greater accuracy, much faster response, simplified calibration, and virtually no maintenance.

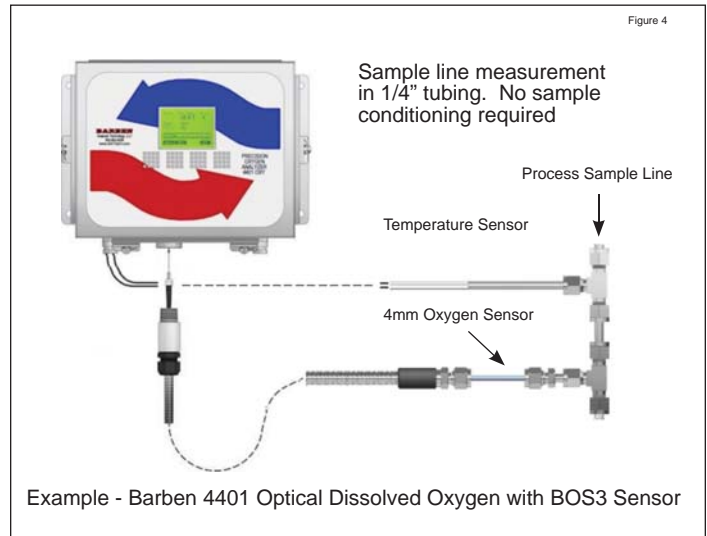


Figure 4  
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