

After extraction, raw natural gas must go through processing before it is suitable for industrial, commercial, and residential usage. Often the first stage of gas processing is known as "sweetening" where hydrogen sulfide (H₂S) and carbon dioxide (CO₂) are removed through exposure to chemicals known as amines. In this paper we will look at the negative affects of entrained oxygen on the amine sweetening process and explore the Barben 4401OXY Oxygen Analyzer as a measurement solution for this application. The second half of the paper will examine the use of Barben's Performance Series pH sensors in the amine regeneration process.

Overview

Purified natural gas, known as "pipeline quality" is typically 95% methane (CH₄); however, raw gas from the wellhead is actually a mixture of many components. These include the following:

Methane (CH ₄)	70 – 90 %
Ethane (C ₂ H ₆)	5 – 15 %
Propane & Butane	< 5%
(CO ₂) (N ₂) (H ₂ S) (O ₂) (He)	Balance

As a contaminant H₂S has multiple negative attributes. It is a well known toxin and lethal at high levels. If condensation is present in the pipeline, water will absorb H₂S to form sulfuric acid (H₂SO₄) resulting in pipeline corrosion. When H₂S levels exceed 4 ppm per 100 ft³

then the natural gas is considered "sour gas" and must be treated to meet US EPA standards [40CFR72.2].

Carbon Dioxide (CO₂), while not quite as undesirable as H₂S, can also cause similar acidic conditions in pipelines through the formation of carbonic acid (H₂CO₃). Excess CO₂ can also create problems in the cryogenic processing of liquid natural gas (LNG) since it has a melt point above that of CH₄. Pipeline companies will try to get < 2% by volume CO₂ in natural gas while LNG facilities will further remove CO₂ to < 50 ppm.

What Role Does Oxygen Play?

Amine sweetening is a frequently used method for removing H₂S and CO₂ from natural gas. Amines are nitrogen-based organic compounds. Most amines will have some selectivity toward one of the contaminant gases thus a blend is typically used to knock out both H₂S and CO₂. MDEA (Methyldiethanolamine) is the primary amine for absorption of H₂S while DEA (Diethanolamine) and MEA (Monoethanolamine) will remove CO₂.

Oxidation is the enemy of amines. The presence of oxygen will cause the amines to degrade into heat stable amine salts (HSAS) such as acetate, oxalate, glycolate, bicine, and formate. The formation of these salts creates multiple problems. The acid removal capabilities of the amine solution is now decreased due to the conversion to salts. Chemical usage must increase to reduce the

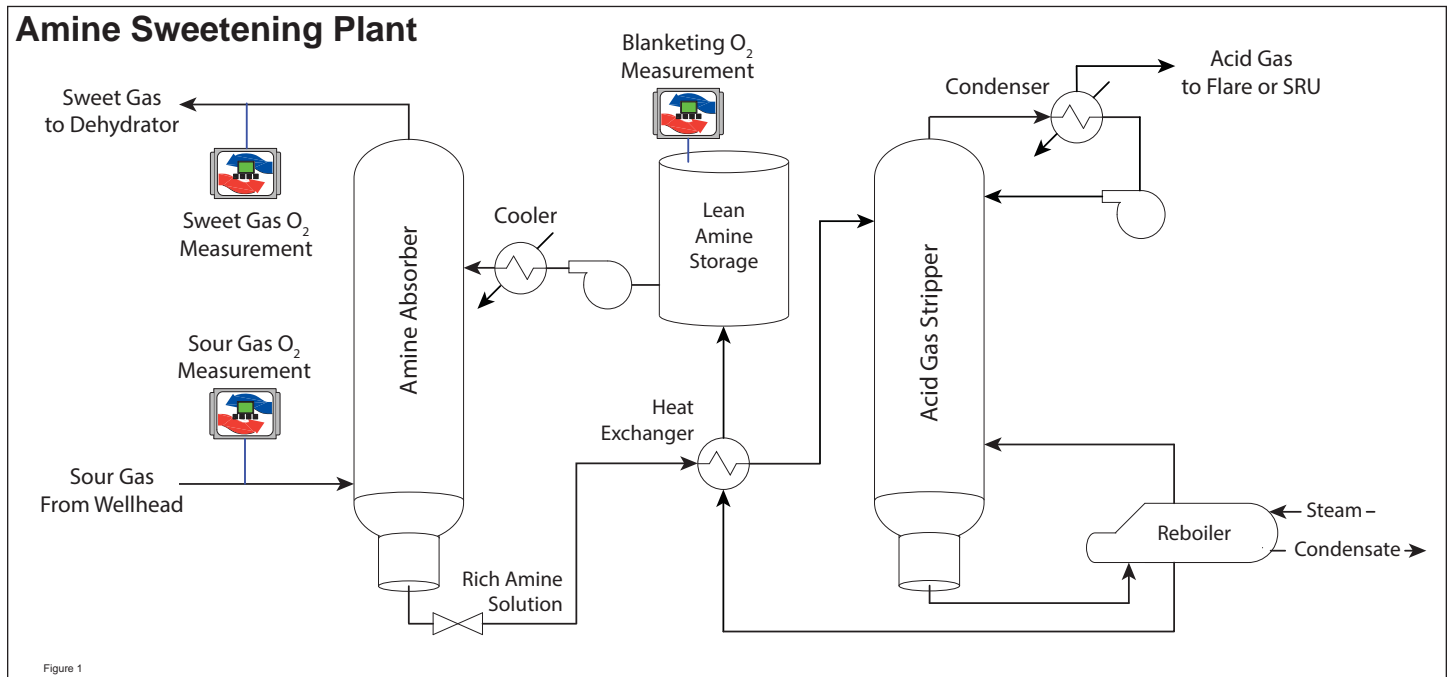


Figure 1

Application Note

Natural Gas Sweetening - pH & O₂

risk of contaminants passing through to the dehydrator. The second problem is the corrosive nature of the newly formed heat stable salts. Since moisture is present, the salts can dissolve in condensation. The result is acidic corrosion which will damage the absorber and related piping in the same way that H₂S and CO₂ would. If these salts precipitate in downstream piping they can create harmful build-up in pumps and valves while reducing the efficiency of heat exchangers. If all of this wasn't bad enough, heat stable amine salts promote excess foaming in absorber towers thus reducing contact area of the amines and inhibiting gas flow.

Even within the gas processing plant improper handling of the pure and lean amine solutions can cause oxygen degradation. All amine storage vessels should have some type of tank blanketing to prevent air ingress. Nitrogen is typically the inert gas used to pressurize the vessel so that outside air cannot enter. Reliable oxygen sensing is crucial in these applications as well.

Causes of Oxygen in the Natural Gas

Trace level oxygen may be found in the wet natural gas coming directly from the wellhead. More commonly, oxygen gets into the piping through leaks in the system. Common intrusion points include the following:

Separation / Water Knock-Out

- stuck separator dump valves

Vapor Recovery Unit

- poorly sealed or open tank hatch (thief hatch)
- leaking relief valves

Compressors

- leaking seals, worn piston packing

Piping

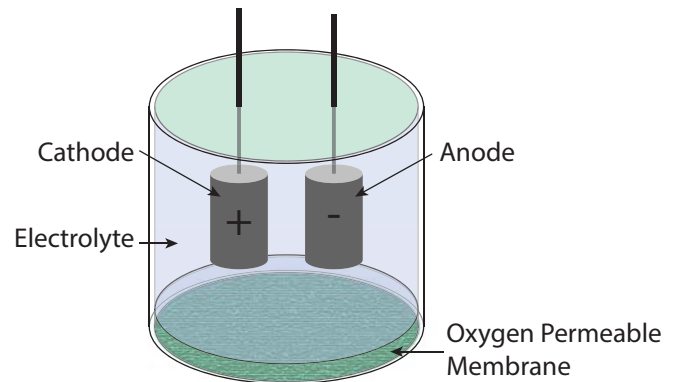
- Flanges, threaded connections, valves

The gas processing plant is at the mercy of the gathering wells and midstream suppliers. The sour gas pipeline into the plant is the final measurement point to catch oxygen contamination. Please request Barben Application Note "Sour_Nat_Gas_AN_RevA.pdf" for further information on upstream oxygen measurement.

Measurement Challenges - Oxygen

Electrochemical cells (also known as galvanic cells, fuel cells, or Clark Cells) have been the traditional method of oxygen measurement. These sensors function similar to a battery using a cathode and a lead (Pb) anode in an electrolyte solution. An oxygen permeable membrane allows oxygen molecules to enter the cell where they react with the electrolyte creating a voltage response to the changing oxygen level (figure 2).

Electrochemical Clark Cell O₂ Sensor



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

Figure 2

This design is not without downsides. The two culprits of the natural gas processing plant, H₂S and CO₂, also create considerable problems with the electrochemical oxygen sensors. Both contaminant gases continuously penetrate the sensor membrane and react with the electrolyte causing poisoning of the oxygen sensor. When this occurs, frequent recalibration is required to correct for zero drift caused by the poisoning of the sensor. Eventually the sensor response will become erratic and replacement is required. An electrochemical sensor may require an upstream H₂S scrubber to function in these applications. The scrubber adds to the significant investment in maintenance time and spare parts needed to keep the sensor functional.

Other downsides of electrochemical oxygen sensors include error due to changing process conditions such as flow and pressure. Both flow rate and fluctuating pressure can affect permeability of the membrane thus creating error in the oxygen reading.

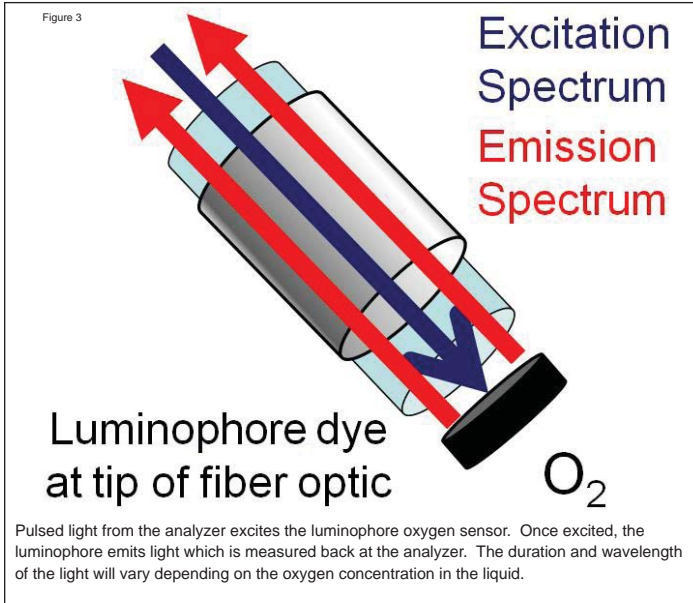
A Better Approach to Oxygen Measurement

Barben Analytical's 4401OXY Optical Oxygen Analyzer takes advantage of a different sensing technology to deal with the challenges of measurement in natural gas.

Fluorescence quenching technology provides trace part-per-million oxygen measurement with no risk of damage to the sensor in the application. An oxygen sensitive luminophore sensor provides the measurement technology for the 4401OXY. A blue light source is used to excite the luminophore sensor located in the process gas. Once excited, the luminophore emits light back at a specific

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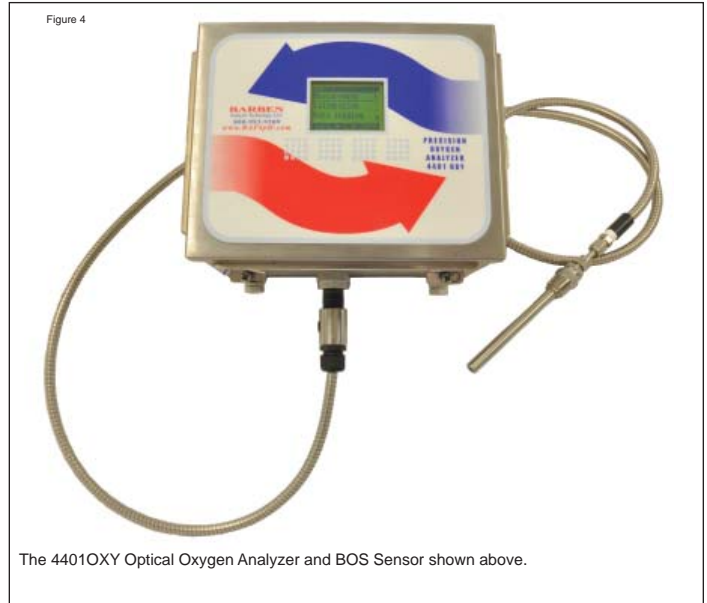
wavelength and intensity (figure 3). When oxygen is present, the emitted light is quenched, causing a time domain phase shift and reduced light intensity. The change in the luminophore output can be directly correlated to the partial pressure oxygen levels in both gas and liquid phases. Advantages of the optical sensor design include no interference due to moisture, H₂S, CO₂, and other contaminant gases. The oxygen measurement is independent of flow rate. The luminophore can withstand condensation and mild particulate build-up. The response time is extremely quick ($T_{90} < 6$ seconds) as is calibration time (3-5 minutes).

Because of these advantages, the 4401OXY Optical Oxygen Analyzer simplifies the sample system design. Contaminant gases do not need to be scrubbed prior to the measurement. The end result is increased reliability, better accuracy, and faster response in sour natural gas processing applications.

Installation

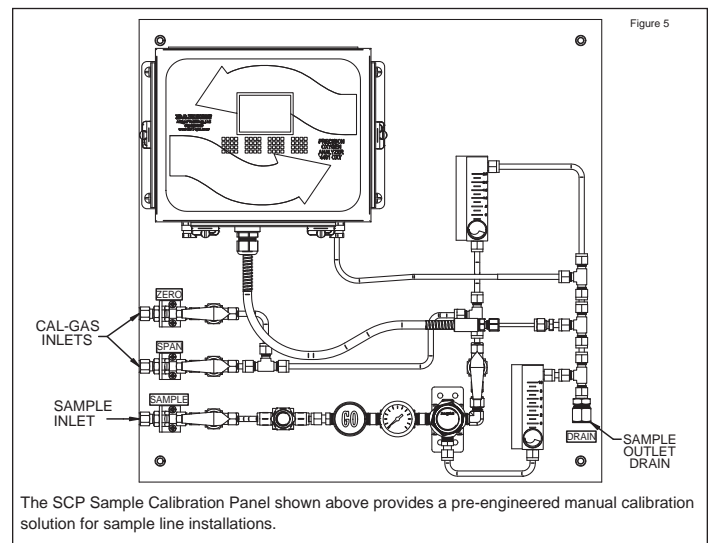
There are several options for installation of an Optical Oxygen Analyzer. A basic system includes the 4401OXY Analyzer and a BOS Optical Sensor. The 4401OXY Analyzer provides a local HMI interface and agency approval for non-incendive installations (Ex nA, Class I Division 2). The BOS Optical Sensor has several measurement range options depending on the amount of oxygen in the natural gas.

Sensor	Range
BOS1	0 - 4.2% O ₂
BOS3	0 - 300 PPM O ₂ (1000 PPM over-range)



The BOS sensor consists of an armored fiber optic cable connected to a 12mm probe with the luminophore sensing element on the tip. Barben Analytical offers the 12mm probe and mating flow cell in 316 stainless steel, Titanium Gr. 2, and Hastelloy C-276 for full material compatibility. Temperature compensation of the oxygen measurement is provided by an external PT1000 RTD for quick response.

Barben Analytical can also provide a pre-engineered sample calibration panel (figure 5). The SCP panel provides connections for calibration gases as well as flow meters, pressure regulators, and a fast loop for quick response. The BOS Oxygen Sensor and PT1000 RTD are pre-wired to the analyzer which is mounted directly to the panel. The SCP panel can save considerable engineering and design work in new installations.



Application Note

Natural Gas Sweetening - pH & O₂

Amine Regeneration - pH

As the rich amine solution leaves the absorber it will be pumped to the acid gas stripper for regeneration. The regeneration process uses steam heat from the reboiler to strip out the acid gas components (H₂S and CO₂) from the amines. The concentration of these acid gas components is referred to as the "Acid Gas Load". The acid gas load will directly impact the efficiency of the acid gas stripper.

The following variables will impact the acid gas load

- Changing upstream gas suppliers
- Oxygen
- Heat stable salts
- Amine degradation due to high temperature

The amine mixture used in gas processing plants is typical 30 to 70% water and is a weak base; typically 10 to 11pH dependent on which amine formulation is specified. Exposure to acid gases will cause the reading to drop quickly to approximately 5 to 6pH (amine type dependent). The change in pH then becomes an important indicator of acid gas load.

Understanding the acid gas load through pH measurement is an important control parameter. At the rich amine inlet to the stripper, pH measurement can be used to adjust the amine flow rate and reboiler temperature. Most noticeably, proper control of the reboiler temperature has multiple benefits:

- Optimized removal of acid gases
- Reduced amine degradation by avoiding elevated temperature

- Reduced amine carryover to the SRU
- Reduction in corrosion problems in the reboiler and stripper
- Reduced steam generation costs

At the outlet of the stripper pH measurement of the lean amine is also beneficial. The outlet pH will determine the efficiency of the stripper process, as well as control of additional of fresh amine makeup to the process. Typical outlet pH readings will be slightly basic at 7.5 to 8.5pH. Most facilities will rely on a differential pH reading between rich and lean amine measurements to get an overall understanding of acid gas removal effectiveness.

pH measurement challenges

Gas purification is a continuous process; however most facilities rely on once-a-day laboratory pH readings to adjust the stripping column controls. We believe this trend of lab pH checks is simply due to the historical difficulty of making a reliable on-line pH measurement on the rich and lean amine streams.

The rich amine stream has absorbed H₂S and CO₂. Of the two contaminants, H₂S is well known to shorten the life of pH sensors. The high mobility of H₂S allows it to quickly contaminate the electrolyte used within the reference half-cell of the pH sensor. The Ag/AgCl element within the reference half-cell is highly susceptible to H₂S attack. Under normal conditions the combination of AgCl and KCl electrolyte react to produce a stable reference voltage within the pH measurement circuit. H₂S in contact with the AgCl will cause a conversion to Ag₂S. This conversion will alter the reference voltage thus creating an unreliable pH

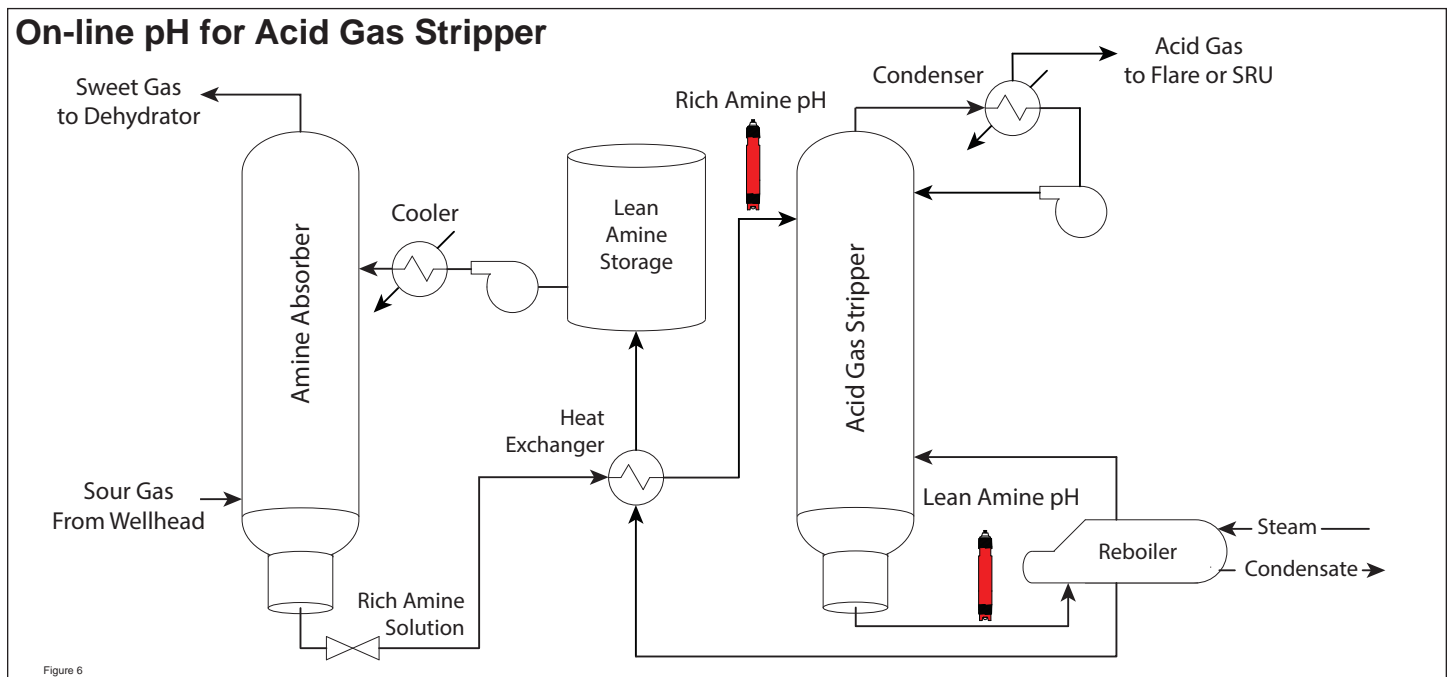


Figure 6

Application Note

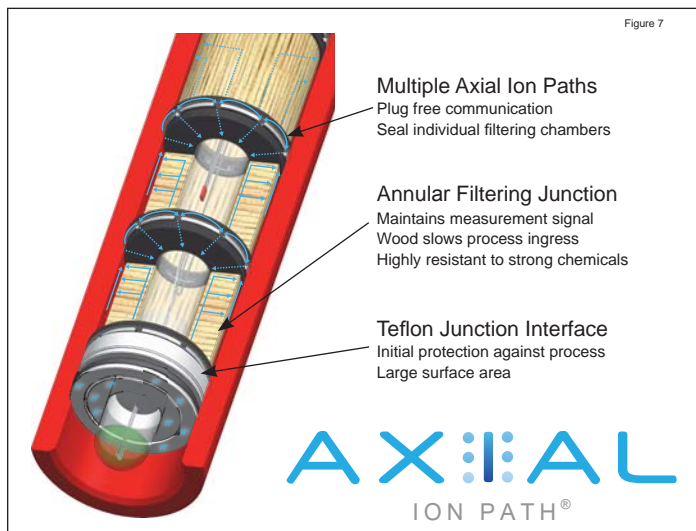
Natural Gas Sweetening - pH & O₂

measurement. During the initial phases of H₂S poisoning the pH error can be calibrated out. With ongoing poisoning from the process the pH sensor will become unstable and eventually must be replaced.

At the lean amine measurement, the H₂S concentration is greatly reduced thus poisoning of the pH sensor is slower; however elevated temperature of the amine becomes a factor in sensor life. Typical stripper outlet temperatures of 105 to 120°C (221 to 248°F) are common. These temperatures are above the limits of most commercially available pH sensors.

A Better pH Solution

Barben Performance Series pH sensors are specifically designed to meet the requirements of industrial pH applications. The Barben Axial Ion Path® reference technology helps to combat the degradation of the reference by filtering out H₂S so it cannot poison the sensor. Multiple Axial Ion Path® disks seal each filtering chamber to further prevent sulfide migration through the sensor while still maintaining a strong signal path. The large surface area Ag/AgCl takes much longer to poison and is encapsulated at the opposite end of the sensor from the process liquid to further avoid sulfide contamination.



For all amine regeneration pH applications we recommend the high temperature hemispherical glass measurement electrodes - type "R" or "CR". The glass electrode design allows reliable pH measurement up to 130°C (266°F) thus making it suitable for the lean amine measurement on the outlet of the stripper.

Barben Analytical provides multiple options for pH sensor mounting. On-line pH measurements can be made directly on the process line with the 547 retractable "hot tap"

pH sensor. This design provides an isolation ball valve which allows the pH sensor to be removed from the process without shutting down the main pipeline. Removal of the sensor is required for cleaning, calibration, and eventual replacement (figure 8)

For sample line applications Barben Analytical recommends the 551 Quick Change pH sensor. This product uses a union nut to mount the sensor to the process. One inch MNPT Nut Lock fittings are available for mounting into tees or Barben can supply a flowcell for sample panel mounting (figure 9).

547 Retractable "Hot Tap" Sensors

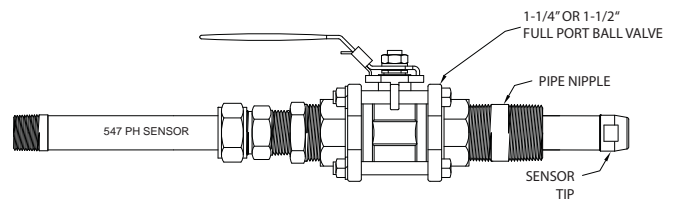


Figure 8

551 Quick Change Sensors

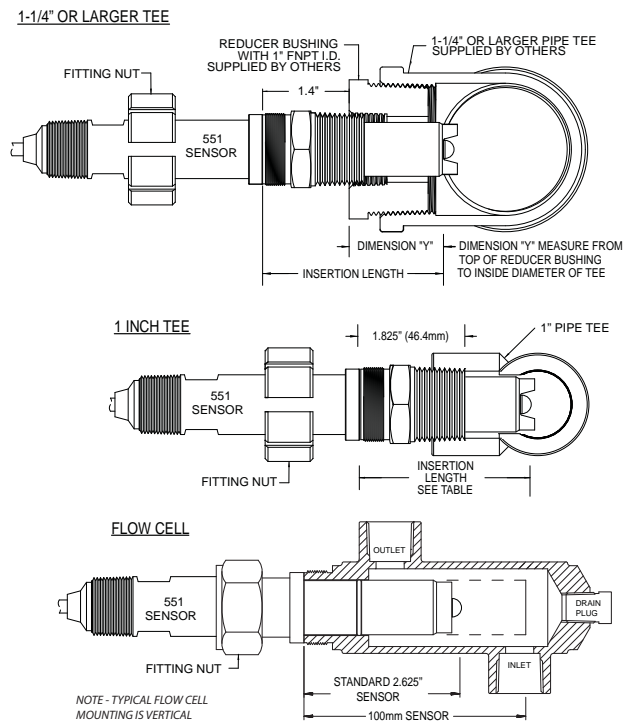


Figure 9

Barben pH sensors will easily connect to most modern pH analyzers in use today. Wiring diagrams for commonly available instruments can be found on www.BarbenAnalytical.com or via request from technical support.

Application Note

Natural Gas Sweetening - pH & O₂

Summary

Entrained oxygen in sour natural gas can create wide variety of problems for the amine sweetening process. Optical oxygen sensing technology from Barben Analytical provides many advantages over traditional electrochemical sensors. These include:

- Increased reliability
- Reduced maintenance
- Quicker calibration times
- Fewer spare parts
- Simplified sample systems

With the reliable oxygen measurement from the 4401OXY the gas processing plant can determine leak sources to reduce this problem. The end result is increased uptime for the plant and better pipeline quality sales gas for its customers.

For amine regeneration process pH plays an important role in determining the acid gas load in the rich amine solution. Barben Analytical Performance Series pH sensors provide an accurate, reliable method to measure amine pH levels continuously. Benefits include:

- Real-time pH measurement for changing processes
- Better control of stripper operations
- Higher accuracy pH measurements
- Less frequent cleaning and calibration than traditional pH sensors

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Natural Gas Sweetening - pH & O₂

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Contact Us

Barben Analytical is a leading supplier of analytical measurement technology targeting the industrial marketplace. It is a wholly owned subsidiary of Ametek.

Ametek has nearly 14,000 colleagues at over 120 manufacturing locations around the world. Supporting those operations are more than 80 sales and service locations across the United States and in more than 30 other countries around the world.

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