UNDERSTANDING AND DETECTING O_2/H_2S/CO_2 IN NATURAL GAS

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INTRODUCTION

As the cost of maintenance of gas transmission lines and plant maintenance at gas gathering sites has increased, the detection and control of $O_{2,}$ H_2S, and CO, has become an important issue in cost controls and safety. Even though the actual costs related to the presence of these elements isn't known exactly, the cost per location is estimated to be in the millions of dollars annually. The corrosion-related cost to the transmission pipeline industries is estimated to be between $5 billion and $8 billion annually.

Obviously, all of these costs can't be attributed to of $O_{2,}$ H_2S, and CO„ but these three elements are a large contributing factor to these costs. In some gas high levels of CO, is present; therefore the removal of this element to meet the 4% contractual requirement is necessary thus contributing to the cost. In addition, CO, is an acid gas that contributes to the corrosion problem.

The safety of transmission lines has a far-reaching affect including life, property damage, and large monetary liabilities for the transmission companies involved. Early detection and preventing the corrosion of these transmission lines, which in turn, prevents pipeline explosions, is extremely important. These elements accelerate the corrosion on all carbon steel components including the pipeline systems and components in plants.

It is true that most of the carbon steel systems are protected with corrosion
inhibitors, but large quantities of oxygen cause the inhibitors to have a limited amount of protection. It has been determined that oxygen levels of 10 PPM or less will have very little affect on these inhibitors.

The identification of sources of oxygen and the recognition of hydrogen sulfide and carbon dioxide present in natural gas has become very important to corrosion prevention programs. The cost of this identification and elimination of the sources is far less than the cost of the repair and the liabilities of the corrosive affects if left unattended.

OXYGEN (O_2)

Oxygen normally is not a problem if drawn from naturally pressurized reservoirs, but as these reservoirs are depleted and pumping is required, oxygen can be drawn into the systems at the pump jacks. Oxygen can also occur at compressors, valves, tank batteries, vapor recovery units (VRU), leaking pipes, and a variety of other ways. Although the presence of oxygen in the transmission line has no immediate affect, it accelerates the rate of corrosion that results in costly inspections and maintenance or even worse, a pipeline explosion. The amount of oxygen that may cause this type of damage is very small, 20 parts per million and greater. The standard for oxygen has been lowered to 10 PPM. It has been determined that oxygen at this level and lower will not cause significant damage to the pipelines.

Oxygen contamination causes great damage to gas gathering systems and plants. As in pipelines, the presence of oxygen in the gas accelerates the corrosion process of all carbon steel components thus causing premature failure. In addition to the corrosion problem, the oxygen causes degradation to the Amine solution in the plants. The reaction of oxygen with Amine produces heat stable salts and organic acids that will accumulate in the Amine solution. This accumulation of salts and acids will cause corrosion in the Amine system to occur. The effectiveness of the Amine solution decreases as Amine is consumed by oxygen.

It has been determined that oxygen reacts with hydrogen sulfide in gas to form elemental sulfur. The catalyst for this reaction is the mol sieve bed. The formation of this sulfur will eventually plug off the sieve bed.

HYDROGEN SULFIDE (H_2S)

Hydrogen sulfide is naturally occurring and is very corrosive to carbon steel systems and very deadly if inhaled. To prevent the corrosion, corrosive inhibitors are used on carbon steel systems, but for safety reasons, the H_2S must be removed from the gas before the gas is transported to consumers or used for other purposes. Approximately 70% of the gas sweetening or removal of acid gases is performed in Amine based plants. This method is very effective, but for contract purposes and public safety, the maximum amount of H_2S permitted is normally around the 4ppm level; therefore the output of the Amine plant must be monitored to assure the chemicals are removing the H_2S. Similar applications occur when user install H_2S analyzers downstream of field scavenging systems. By monitoring the H_2S levels downstream of a scavenging system, users can more effectively determine the life span and efficiency of their removal material of choice.

CARBON DIOXIDE (CO_2)

Some gas contains too much CO, to meet established pipeline specifications; therefore the CO, must be removed or reduced to an acceptable level. CO, is an acid gas and therefore corrosive to carbon steel systems. Normally the CO, is measured on the inlet side and the outlet side of the sweetening plant. On the outlet side of the plant, the gas must not contain more than 3% C02 and in some cases as low as 1%; therefore it is very important to monitor the content in the gas stream. In several areas (West Texas, the Rocky Mountains, Eastern Kansas & Oklahoma), CO, Injection/Flooding is being used as the primary method for tertiary recovery projects, thus the monitoring and trending of CO, levels has become increasingly important.

DETECTION SYSTEMS

O, and H_2S systems are designed to detect small quantities of these elements in natural gas and provide either dry contact control and/or an output that may be used for alarming, tracking, or controlling. These units are designed to detect PPM (Parts Per Million) as low as 1 PPM through 10,000 PPM and 0% to 100%. If needed electrochemical cells can also be purchased to detect in the PPB (Parts Per Billion) range. The C02 units are primarily percentage units of 0%-100% for the inlet side of the gas sweetening plant and 0%-10% for the outlet side of the plant and custody transfer locations.

The output is an analog output (4-20 mA) or a voltage output of 1-5 VDC. These outputs are received by a PLC (Programmable Logic Controller), EFM (Electronic Flow Computer) or an RTU (Remote Terminal Unit) and then used for controlling, notifying, or are sent to a SCADA (Supervisory Control And Data Acquisition) system. This provides immediate access to the data that is being provided by the detection units, and allows operators the ability to instantaneously detect and trend the gas levels read by the on-line field analyzer.

OPERATIONAL OVERVIEW

The fundamental operation of the **O,** and H_2S detection units is basically the same with only a change in the detection cell configuration. The CO, detection system uses an infrared (IR) cell rather than an electrochemical cell.

The detection system for **O,** and H_2S is comprised of three basic components — cell holder, cell, and electronic circuit board. The cell holder contains the gas to be sampled and the cell. The cell provides the current output for the circuit board. The circuit board interprets the output of the cell and provides a control output and a digital reading of the gas being detected.

The design of the cell holder permits the gas to be sampled to enter at the top of the cell and exit at the bottom of the cell. The cell holder also has a set of contacts that contact the cell establishing a path for the current to the circuit board. There are several methods (cells) used for detection of the 0, – Electrochemical, Coulometric, and Paramagnetic. The most common used is electrochemical. H_2S commonly uses electrochemical cells.

<u>Electrochemical (Galvanic):</u> Oxygen or Hydrogen Sulfide reacts with the anode to produce a current that is linear with the amount of these two elements present in the sampled natural gas. This type of cell is called “consuming” cell.

<u>Coulometric:</u> The oxygen is ionized in the electrolyte solution contained in the cell. This method also produces a current linear to the amount of these two elements present in the gas being measured. These are called “non-consuming” cells.

<u>Paramagnetic:</u> These take advantage of the fact that oxygen is attracted to a magnetic field. These are normally used in laboratory environments because of the expense and they are relatively delicate, however they are resistant to the effects of acids gases.

<u>Lead Acetate Tape (H_2S):</u> **A** strip of film/tape concentrated with Lead Acetate ((Pb(OAc)2) is run through an optical sensor which acts as both the reference and measurement function. By using a stored voltage reading from the used tape and a new reading from an unused strip of tape the microprocessor proportionally measures the difference between the voltages and generates an H_2S reading on the LCD.

In this paper, the Electrochemical (galvanic) cell will be used for discussion. The cell consists of an anode, cathode, dispersing membrane, and an electrolyte. As the oxygen or hydrogen sulfide enters the cell through the dispersing membrane, a chemical reaction occurs producing a very low current that is transmitted to the electronic circuit board. This current is approximately 2.2 nA's per part of oxygen or hydrogen sulfide present and is linear to the amount of oxygen or hydrogen sulfide detected.

This cell requires the sample gas to be conditioned properly in order to preserve the integrity of the cell. The gas must be dry, at a pressure of 1-3 PSI, a flow rate of approximately 2 SCFH, and free of acid gases if the cell is an **O,** version. The cells will tolerate 95% non-condensing humidity, but no liquids. Liquids will clog the dispersing membrane.

The infrared cell used for CO, detection and is completely different to the chemical cells used for **O,** and H_2S. Using the infrared spectrum, the light is passed through two chambers, one using a reference gas such as nitrogen and the other cell containing the target gas, at different intervals. A chopper wheel is used to create the time intervals. As the light strikes the detectors at different intervals, an AC signal with a magnitude proportional to the difference in energy. This differential is linear to the volume of the target gas present in the natural gas stream.

The electronic circuit board filters the output of the cell and with the use of specific algorithms converts the current to either a digital or analog reading representing the amount of oxygen or hydrogen sulfide present in the natural gas. Normally the LCD reading is the average of several samples with specific or selectable time intervals between each sample. This averaging provides a stable output by averaging in any spikes that may occur in the levels of the oxygen and hydrogen sulfide detected in the natural gas.

The circuit board also produces an analog or dc output, consistent with the selected range of operation, to be used by various electronic instruments.
The electronics uses established algorithms (mathematical functions) to compensate for temperature changes in the gas thus producing a linear reading through the operating temperature range.

Most electronic boards provide some type of alarm(s) such as discrete to be used by another electronic instrument and/or dry contact alarms. Some of the instruments provide configurable alarms that permit the operator to use the alarms as high level or low-level alarms. All instruments are configurable to meet the specific requirements for the measuring environment. Some have more configurable options than others. All units used for detecting certain elements in natural gas require routine maintenance, especially to the gas conditioning systems. **A** typical conditioning system for **O,** is a water knockout (dryer), regulator, acid gas (H_2S) scrubbers, and a rotometer to control the rate of flow. If CO, is present in quantities of 1% or more, a special **O,** cell that is tolerant to CO, may be used instead of trying to eliminate this acid gas. Conditioning for the detection of H_2S is the same as **O,,** but without the acid gas scrubber.

Resetting the span of the unit should occur on a monthly basis. Factory published deterioration of cells is approximately 1% per month if the cell is operated under ideal conditions. The cell life is approximately one year under these ideal conditions.

CONCLUSION

Safety alone justifies the use of these types of detection units. The insurmountable cost of not preventing corrosion problems with early detection far outweighs the cost of the units. A good corrosion prevention program, supervised by the pipeline integrity management team should always include these detection units to enhance their awareness of and ability to control the levels of the aforementioned gases. The return on investment is excellent.

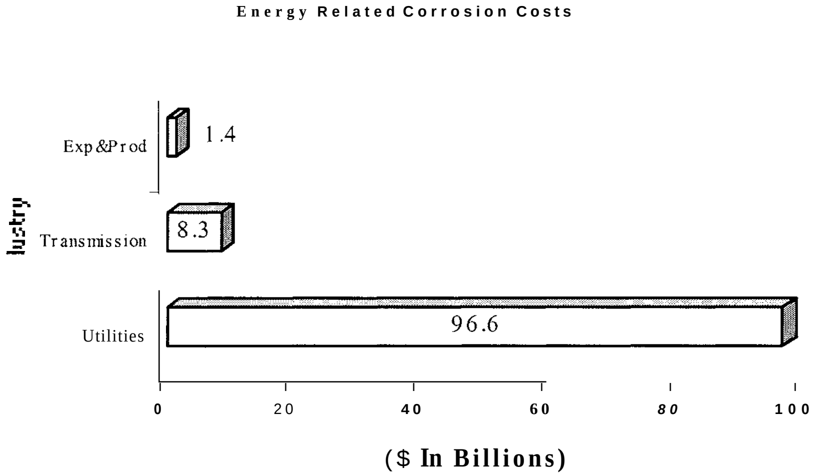

Figure 1

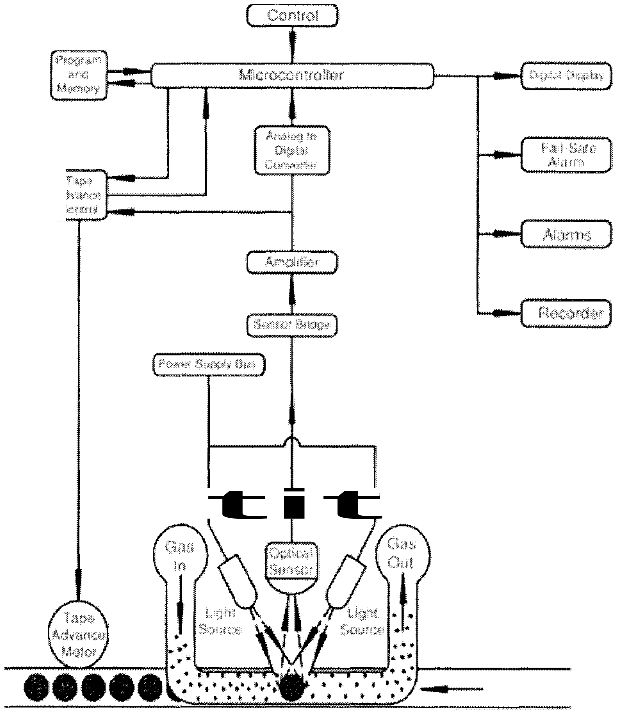

Figure 2

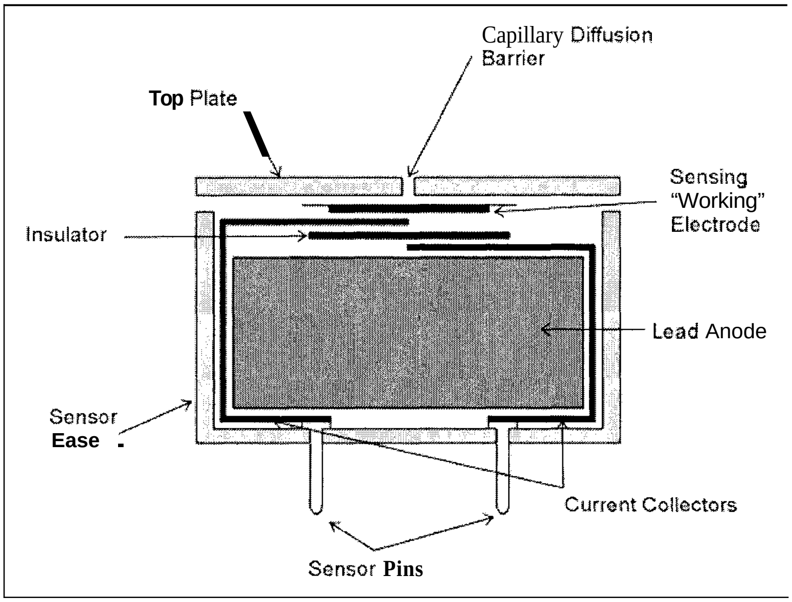

Figure 3

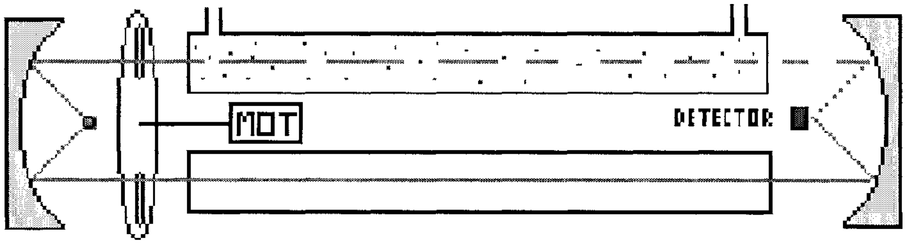

Figure 4