**DELTA F CORPORATION**

# APPLICATION NOTE NO. 103

THE DIFFERENCE DELTA F

# Oxygen Analysis in the Presence of Acid Gas

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## Introduction

Measurement of trace or percent oxygen in the presence of acid gases is among the more difficult applications required of on-line oxygen analyzers, because of the adverse effects that acid gases have on most oxygen-measuring cells. In 1975, Delta F corporation patented its STAB-EL™ electrolyte system which, for many applications, eliminates the necessity of removing acid gases prior to oxygen analysis.

## When should I consider the STAB-EL™ Option?

There are three situations for which you should consider the STAB-EL™ option:

### 1. Known Acid Gas Contamination

Consider the STAB-EL™ option if you know or suspect that your sample contains acidic gases such as:

| | |
|---|---|
| Carbon Dioxide | $CO_2$ |
| Nitrogen Oxides | $NO_x$ |
| Chlorine | $Cl_2$ |
| Hydrochloric Acid | HCl |
| Hydrogen Fluoride | HF |
| Sulfur Dioxide | $SO_2$ |
| Hydrogen Sulfide | $H_2S$ |
| Acetic Acid | $CH_3COOH$ |

These are the most common, but there are other halogens, [e.g. formic acid, (HCOOH)], and acid gas species which can compromise your analyzer's performance, and in some cases, permanently damage it. As a general rule, the STAB-EL™
system should be used whenever your sample contains a component that reacts with a strong base.

### 2. Temporary Upsets

Consider the STAB-EL™
option if there is any chance that your sample stream might momentarily contain an acid gas component.
Under normal conditions your process may be free from harmful substances, however, under an "upset" condition your process may release a burst of an acidic component.

An example of this might be found in semiconductor chemical vapor deposition (CVD) processing, where hydrogen fluoride (HF) is used to treat wafers. Normally, the HF is purged between each run, however, occasionally, the purge is incomplete and HF is vented to the oxygen analyzer. Under these conditions the STAB-EL™ system protects the analyzer from the harmful effect of the HF.

Another example of this might be when a sample conditioning element such as a scrubber fails or is overwhelmed, resulting in acid gas "breakthrough" and temporary contamination of your sample

stream.

3. **Trace Level Contamination**

Consider the STAB-EL™
option if there is any chance that your sample may have trace levels of acidic components. Users often overestimate the purity of their sample streams. for example, in the petrochemical industry, hydrocarbon sample streams often contain trace amounts of hydrogen sulfide ($H_2S$). These are frequently overlooked because of their low concentrations. Unfortunately, over time, these impurities can accumulate and lead to problems.

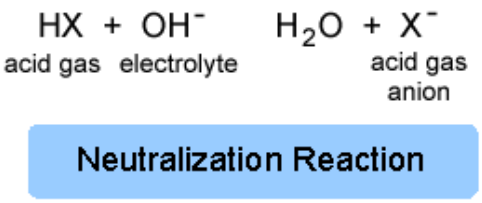
## Why are these acid gas components a problem?

All ambient temperature electrochemical oxygen analyzers contain an analysis cell which consists of a cathode (the reducing electrode), an anode (the oxidizing electrode) and an electrolyte. The cathode and anode must be specially fabricated to meet a stringent set of requirements. Likewise the electrolyte must be compatible with the oxidation and reduction processes occurring at the electrodes and it must provide a conductive path for the transport of ionic species between them.

Typically, a strongly alkaline solution (e.g. 1M KOH) is used as the electrolyte because its high pH facilitates the diffusion of hydroxyl ions and supports the reactions occurring at the electrodes.

Acidic components in your sample gas cause problems in two ways:

1. They diffuse into the cell and neutralize the alkaline electrolyte, reducing its pH:




This causes cell drift (calibration drift), slower response times, and reduced sensitivity. Sometimes these effects are subtle and go unnoticed for a while, raising the risk that your process is slowly slipping out of control.

In analyzers which use sealed (disposable) galvanic cells, this neutralization causes the cell to fail prematurely, leading to frequent and expensive cell replacement. In analyzers which use a replaceable electrolyte, such as those manufactured by Delta F, the effects of neutralization can be reversed by changing the electrolyte; while not difficult, this increases the need for routine maintenance.

2. Acidic components may permanently damage ("poison") the sensing electrodes. In the case of common galvanic-type sensors, the cathode electrode is made of silver which is readily oxidized by even trace levels of acid gases. The immediately wipes out sites at the cathode for $O_2$ reactions, thus producing false low readings.
   Once this happens, the only remedy is to replace the electrochemical cell.

## What are the benefits of using STAB-EL™

The patented Delta F STAB-EL™ system *protects your oxygen analyzer from the harmful effects of acid gases* and helps to insure that you will get the full value from your investment. There are many reasons why it makes good sense to order the STAB-EL™ option. Consider these:

- STAB-EL™ simplifies, and in most cases eliminates, the requirements for sample conditioning.
- STAB-EL™ counteracts the effect of acid gas neutralization, thus reducing process down time and minimizing maintenance efforts.
- STAB-EL™ protects you from expensive repairs arising from acid gas "poisoning".
- STAB-EL™ eliminates expensive process "scrappage" resulting from erroneous oxygen data.

## What is STAB-EL™?

STAB-EL™ consists of three elements:

A. A custom electronic circuit designed to counteract the neutralization effect of acid gases.

B. Proprietary sensing electrodes formulated to resist the poisoning effect of many acid gases.

C. Special cell construction to prevent back diffusion of acidic anions.

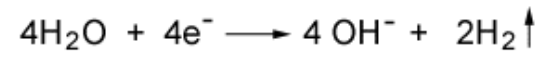
Together, these three elements provide optimum protection for your analyzer and your process.

## How does the STAB-EL™ System Work?

### A. The STAB-EL™ Circuit

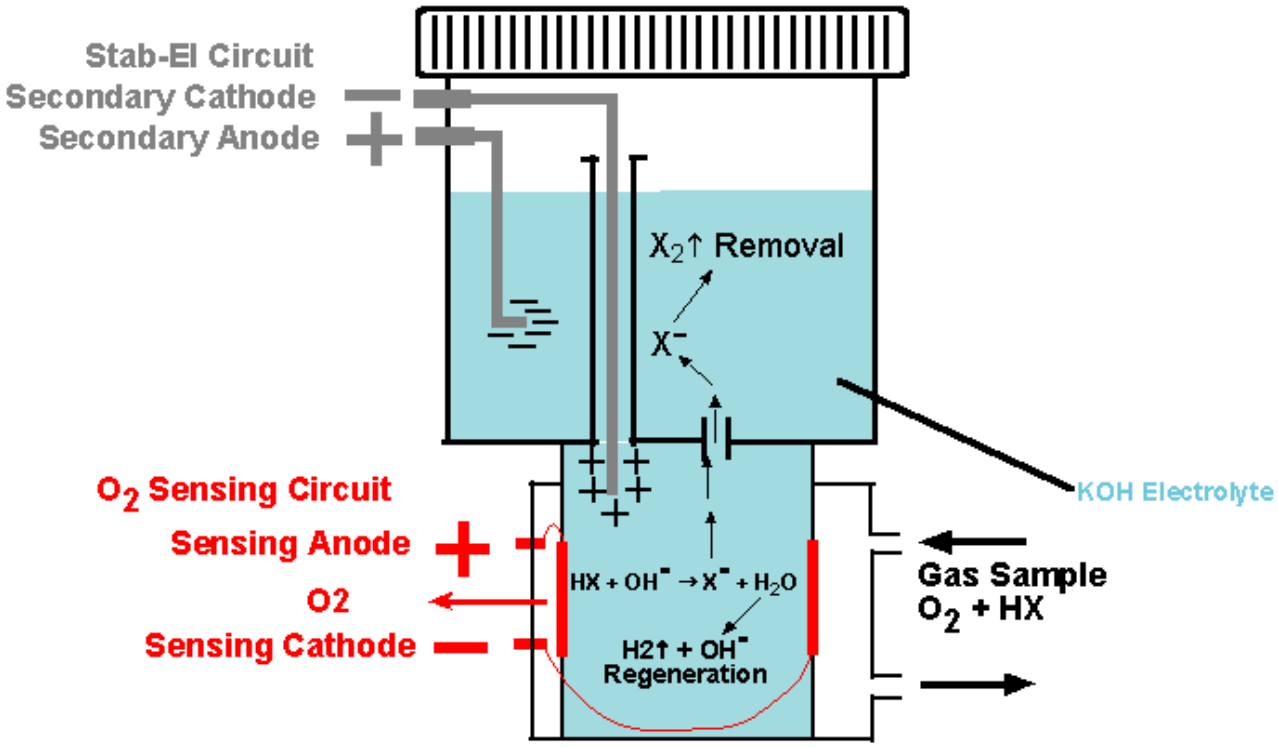
The STAB-EL™ circuit works in conjunction with the two secondary electrodes built into the Delta F oxygen cell. The electrodes consist of two metallic conductors, a cathode located in the electrolyte cavity where the sensing electrodes are housed, and an anode located in the electrolyte reservoir on top of the cell. The STAB-EL™ circuit applies a voltage across these electrodes inducing a negative charge on the cathode and a positive charge on the anode.

As the pH of the electrolyte in the sensing chamber decreases due to the neutralization reaction, water is electrochemically reduced at the secondary cathode to form hydroxyl ions:



Secondary Cathode Reaction

# Delta F Stab-El™ Sensor




The hydroxyl ions produced replace those neutralized by the acid gas. **This reaction maintains the high alkalinity of the electrolyte in the sensing chamber.**

Two other reactions are occurring simultaneously at the secondary anode located in the reservoir.

First, hydroxyl ions are oxidized to from hydrogen ions:

$$2\ OH^- \longrightarrow O_2\uparrow + 4e^- + 2\ H^+$$

**Secondary Anode Background Reaction**

If no acid gas is present, the net reaction at the secondary cathode and anode is a mild electrolysis of

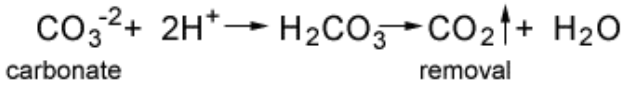
$$2\ H_2O \rightarrow 2\ H_2\uparrow + O_2\uparrow$$

**Secondary Electrodes Overall Reaction**

water:

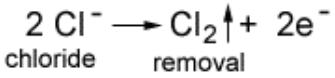
Second, if an acid gas is present, anions formed by the neutralization reaction are drawn to the anode where three possible reactions can occur.

1. If the acid gas is carbon dioxide, carbonate anions are formed during the neutralization reaction with the electrolyte. These migrate to the anode, where they concentrate. When the solubility level is exceeded, the carbonate ions decompose to water and carbon dioxide.




**Secondary Anode Effervescence**

2. If the cell is exposed to acid gases such as hydrochloric, etc., the anionic species formed during the neutralization reaction migrate to the secondary anode where they are oxidized and evolve as a gas:




**Secondary Anode Oxidation**

3. For acid gases containing sulfur, nitrogen or organic anions, such as hydrogen sulfide ($H_2S$), which neutralize to form anions that cannot be released by either effervescence or direct oxidation, a gradual accumulation results.
   In this case, the reservoir must be emptied and the electrolyte renewed on a periodic basis. In many cases, the optional Electrolyte Condition Indicator will signal when a change is necessary. Calibration is not affected by the renewal of the electrolyte.

## B. Acid Gas Resistant $O_2$ Sensing Electrodes

The inert carbon-bases sensing electrodes used in the Delta F oxygen cells are fabricated to have high conductivity, high oxygen permeability, high resistance to alkali and acids, and high surface area. Of particular importance are the characteristics of the cathode. When an acid gas is presented, unwanted reactions can occur which will oxidize or foul ordinary electrodes. The result is a decrease in sensor sensitivity and eventual failure of the electrochemical cell.

The proprietary electrodes used with the STAB-EL™ system were specially developed to eliminate the corrosive reactions with acid gases.

## C. Special Cell Construction

The electrolyte flow path in the STAB-EL™
cell prevents back diffusion of anionic species to the measuring cavity. Providing further protection is the fact that the electrolyte solution in the measuring cavity is of greater density than that of the reservoir. This difference in density, coupled with the cell construction, is effective in reducing back diffusion of the acidic components.

From this discussion you can see that the three component STAB-EL™ system effectively counteracts the harmful effects of acid gases.

- It provides a reliable means for regenerating the hydroxyl ions neutralized by the acid gas.
- It insures that the sensing electrodes are protected from acid gas corrosion.
- It prevents measurement interferences from acidic anions by restricting back diffusion.

## What are the limitations of STAB-EL™?

The STAB-EL™
system provides protection from varying amounts of acid gases, depending on the analyzer range. For instance, a 0-25% oxygen analyzer can be exposed continuously to samples containing up to 3% $CO_2$,

3000 ppm $SO_2$, 3000 ppm $NO_x$, 3000 ppm $H_2S$, 1500 ppm HC1, or 1500 ppm $Cl_2$. In cases where there is a temporary exposure to acid gases, the limits of the STAB-EL™ system can be much higher depending on concentrations and length of exposure.

However, there are applications where the acid gas components may exceed the upper limits of the STAB-EL™ system. In these circumstances, we recommend that you compliment the STAB-EL™ system with a gas scrubber to remove the bulk of the acid constituent.

Using the STAB-EL™ system together with the scrubber provides two advantages. First, your analyzer is now capable of continuous stable performance even if small amounts of acid gas are carried through to your analyzer.
Second, on those occasions when a momentary breakthrough occurs, allowing high concentrations of acid gas to enter the sample stream, your analyzer's STAB-EL™ system will keep the cell within normal operating range, avoiding catastrophic loss of performance or damage to the analyzer.

## Applications

Requirements for the STAB-EL™
system are frequently found in industries such as petrochemical, chemical, pharmaceutical, natural gas transmission, heat treating, semiconductor, and others. Accurate on-line measurement of oxygen levels in cement
kilns, solvent extraction centrifuges, glass-processing furnaces, heat treating furnace atmospheres, etc., requires that difficult operating requirements be met, such as withstanding the continuous effects of acid gas exposure on the measuring cell.

## Recognized For Quality

Delta F's Quality Management System has been certified to ISO-9001 by Lloyd's Register Quality Assurance Ltd.
This demonstrated compliance with an internationally accepted standard assures you of the highest quality in product design, manufacturing, and service.

Delta F Oxygen Analyzers can be ordered with a full scale range of 0-2 parts per billion (ppb) to as high as 0-25 percent. For specific product recommendations, contact Delta F Corporation, 4 Constitution Way, Woburn, MA 01801-1087, Tel. (781)935-4600, FAX (781)938-0531, e-mail marketing@delta-f.com.