Furnace atmospheres are critical to meet metallurgical specifications defined by control processes. The makeup of a furnace’s atmosphere in the heat treating process varies based upon the application. This paper will cover the different types of atmospheres, the sensors used to measure the atmosphere, and troubleshooting procedures for validation of the environment.

**Endothermic Atmosphere**

Typical endothermic gas generators supply an atmosphere using air and hydrocarbon gas which are mixed and passed over nickel bearing catalyst at about 1900°F (1038°C). Using methane (CH₄) mixed at an air-to-gas ratio of 2.77:1, a properly functioning generator will theoretically produce an endothermic gas consisting of 20% carbon monoxide (CO), 40% hydrogen (H₂), and 40% nitrogen (N₂). Using propane (C₃H₈) in lieu of CH₄ and an air-to-gas ratio of 7.16 to 1, the resulting endothermic gas composition will be approximately 24% CO, 32% H₂ and 44% N₂. The gas is then cooled to maintain the integrity of the gas composition. Correct cooling of the gas is critical to avoid CO from reversing into carbon (soot) and carbon dioxide (CO₂). This is the base atmosphere used in the carburizing process. A few assumptions must be made when determining carbon potential in the furnace with a supply of endothermic gas. Measuring this atmosphere can be accomplished in a number of ways; the focus of this article is use of oxygen sensors, dew point, and infrared measurement.

**Nitrogen Methanol**

When used in a furnace at the typical operating temperatures, methanol (a.k.a. methyl alcohol, CH₃OH) immediately dissociates into CO and H₂. When mixed in a ratio of 60% CH₃OH and 40% N₂, an endothermic equivalent atmosphere is formed in the furnace.

\[
\text{CH}_3\text{OH} \rightarrow 33\% \text{ CO} + 66\% \text{ H}_2
\]

19.8% CO + 39.6% H₂ + 40.6% N₂ = Endothermic Equivalent Gas

Methanol has a boiling point of 149°F (65°C). One gallon of CH₃OH vaporizes and dissociates into approximately 222 ft³ of H₂ and CO in standard conditions. To calculate the correct flow of CH₃OH and N₂ required (for a 20% CO atmosphere), multiply the total flow by 0.60 to get the dissociated CH₃OH flow and multiply by 0.40 to get the N₂ flow. To get the liquid CH₃OH flow required, divide the dissociated CH₃OH flow by 222. This will give the CH₃OH flow in gallons per hour (GPH).
For example, if you require 400 CFH of total flow into the furnace:

Dissociated Gaseous CH₃OH = 400*0.60 = 240 CFH

Liquid CH₃OH = 240/222 = 1.08 GPH

N₂ = 400*0.40 = 160 CFH

Assumptions are made when determining carbon potential. Using sensors and the base atmosphere in the furnace under equilibrium conditions, these assumptions must be consistent, known, and repeatable.

Exothermic Atmosphere

Exothermic gas is the byproduct of combustion, and is widely used in the Annealing process. Hydrocarbon gases such as natural gas, propane, or butane are burned in an exothermic gas generator with air to create a rich or lean mixture based on the air-to-gas ratio. Rich, medium, and lean mixtures are described in the chart. The mixtures do contain high moisture content.

<table>
<thead>
<tr>
<th></th>
<th>RICH EXOGAS</th>
<th>MEDIUM RICH EXOGAS</th>
<th>LEAN EXOGAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>11%</td>
<td>8%</td>
<td>5%</td>
</tr>
<tr>
<td>CO₂</td>
<td>5%</td>
<td>7%</td>
<td>9%</td>
</tr>
<tr>
<td>CH₄</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>H₂</td>
<td>14%</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Measuring an Endothermic Atmosphere in a Generator

The most common measurement of this atmosphere is confirmed by using a dew point measuring device or an oxygen sensor. Dew point is the temperature and pressure at which water vapor begins to condense into a liquid. The dew point measurement is accomplished by taking a sample of the atmosphere after the cooling section of the generator.

Using an oxygen sensor to measure and control the dew point in an endothermic generator is done via a calculation in the dew point control instrument. This calculation uses the oxygen millivolts generated by the sensor, the hydrogen factor of the controlling instrument, and the temperature of the oxygen sensor. The temperature is required for the calculation but the dew point of the gas is not temperature dependent. Often oxygen sensors are installed at 1900°F (1038°C) although they will provide the same reading when operating at 1500°F (816°C). The generator gas exiting the retort is sent through a heat exchanger to freeze the composition. As long as the sensor is accurately measuring the oxygen millivolts of the gas, the temperature of the sensor can be as low as 1100°F (593°C). Changes in sensor location have occurred over the
years. Initially a sensor would be mounted on the top of a retort in an air cooled fabricated fixture to measure the oxygen. Then a ceramic reheat well mounted through the sidewall of the generator was used. Now a modified sheath with an integral reheat well makes the installation much easier. The sheath and the integral well are aluminized prior to assembly. (See Figure 1) The nickel in the RA330 sheath material does not react with the endothermic gas. This is especially important between 900°F and 1300°F (482°C and 704°C) where, over time, the endothermic reaction will reverse if nickel is available. This type of design has ability to run at lower temperatures, thus allowing many years of operation.

Lambda-style probes like those used in an automobile engine are used in generator applications, but do not provide the long-term stability of the zirconia technology and must be re-oxidized to avoid drift.

Dew point cells, like those used in portable units to verify the generator, can also be applied for continuous monitoring and control. A dew point cell must provide good filtration and avoid water contamination for long-term stability.

Measuring an Endothermic Atmosphere in a Furnace

Dew point, shim stock, and carbon sensors have traditionally been used to measure the endothermic atmosphere in a furnace. The carbon sensor is actually measuring the oxygen content in the furnace which is why the term oxygen and carbon probe are synonymous. An oxygen probe used in-situ for a furnace application has been the standard of the industry for years. Because of the durability, reaction time, and continuous measurement it is the most common form of control.

The oxygen probe will also react with the by-products of combustion if the furnace is gas fired and has a cracked radiant tube. The oxygen will dilute the atmosphere in the heat chamber when the furnace goes to high fire. As a result, the carbon controller will compensate by calling for more enriching gas to increase the carbon potential. This can often be identified on a chart or digital recorder with a saw tooth look to the carbon trend. Setting the control to low fire will eliminate the saw tooth effect and prove the leaky tube as the issue. The next step is to determine which tube is the problem.
When using an oxygen sensor in a carburizing atmosphere it may require air burnouts. The burnout frequency can be determined by the carburizing process in use.

<table>
<thead>
<tr>
<th>Atmosphere Type</th>
<th>Frequency of Sensor Burnout</th>
<th>Duration of Sensor Burnout</th>
<th>Flow of Burnout Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>24 Hours</td>
<td>90 Seconds</td>
<td>Minimum 10 CFH</td>
</tr>
<tr>
<td>High Carbon</td>
<td>8 to 12 Hours</td>
<td>90 Seconds</td>
<td>Minimum 10 CFH</td>
</tr>
</tbody>
</table>

A burnout consists of at least 10 CFH of air piped to the burn off fitting on the head of the probe. Pumped room air or filtered combustion air are most commonly used. It is important not to use compressed air due to the contamination of water and oil often present that can damage the oxygen probe. The carbon controller should control the frequency of the burnout and the duration. If this is not controlled by the carbon controller, excessive gas will be used while the burn off is taking place to compensate for the flow of air to the probe. Burnout flow and duration recommendations vary by manufacturer based on sheath diameter and tip design. It is good practice never to exceed 90 seconds to avoid overheating the tip of the probe. A consistent way to verify a correct burnout is to monitor the oxygen millivolts of the carbon controller during the burnout phase. If a proper burnout is taking place the oxygen millivolts will drop below 200 millivolts. This can also vary based upon the circulation in the furnace and the probe placement. If you are not able to reduce the millivolts based on the air supply available you can turn off the circulation fan. This will allow the concentration of air to passing across the tip not to be diluted. Take great care not to leave the fan off for more than 120 seconds.

A possible side effect of extended burnout duration is the oxidation of the tip of the sensor. The problem can manifest itself with oxygen millivolts being elevated over time which will require a lower CO factor setting for the same calculation of carbon. Consideration should be made for the duration of the burnout based upon the carbon level in the furnace.
An NDIR three gas analyzer can be used to measure the atmosphere in a furnace or generator. The consistency of the endothermic gas produced at the generator significantly affects all downstream processes. In order for the atmosphere to be controlled consistently and accurately in the furnace with an in-situ sensor, it assumes the content of the endothermic gas. You should always view values between 18.8% and 20.5% for CO. The CO$_2$ should be between 0.20% and 0.40% with a preferred value of 0.24% CO$_2$. When using propane, CO$_2$ range would be 0.35% to 0.45% with a preferred value of 0.40%. If methane (CH$_4$) has a value of 0.50% or less, the generator is performing correctly. If the CH$_4$ is over 0.50% there may be a problem. It is advisable to burnout the generator as quickly as the facility can take the generator off line. If after burnout the CH$_4$ climbs back above 0.50% within a week or two then replace the catalyst. If the catalyst is depleted, uncracked CH$_4$ from 0.50% to 8.0% will be present. As a result a low dew point (CH$_4$ uncracked is very dry) and an increase in the air ratio will occur. The end result will be a wet gas with soot and water coming out of the generator. The furnace will try to compensate by adding more gas. Based on NDIR gas readings with CH$_4$ exceeding 0.50% it is recommended one performs a generator burn out. To perform a generator burn out stop the endothermic gas flow. Reduce the temperature of the generator to 1600°F - 1650°F (870°C - 900°C) then start flowing air up to 10% of the total endothermic flow. One should see a flame at the effluent. Once the available carbon is burned the flame will go out. The lower temperature protects the retort in case of a carbon deposit. If there is a carbon deposit present and the temperature is not reduced a localized area may increase dramatically in temperature and damage the retort.

**Measuring a Nitrogen Methanol Atmosphere in a Furnace.**

If measuring at the furnace using NDIR one should see between 14.0% and 28.0% CO. An ideal CO measurement is 20%. In addition, the CO$_2$, depending on carbon set point, will be from 0.10% to 0.80%. The CH$_4$ should be zero or as high as 8% depending on carbon set point. All testing should be done with a zero carbon set point and no CH$_4$ additions, if possible.

If the mixture is set incorrectly and a higher ratio of Methanol to Nitrogen is observed, the readings may show a CO level below 20%. The CO$_2$ may be 0.60% or higher, the level of CH$_4$ between 2% to 4%. The CH$_4$ is actually uncracked methanol. Lower the methanol flow and increase the N$_2$ until a 20% CO is observed and, CH$_4$, CO$_2$ readings are reduced. It is always good to figure out the gas mixtures with no CH$_4$ additions to start out.

Reasons for problems with Nitrogen Methanol might be flow mixture settings, plugging of the sparger, no sparger, or nitrogen bubbles in the supply line. This may be due to pressurizing the methanol liquid with N$_2$ or a low methanol tank that requires a refill. Another problem may be a furnace that is not tight allowing air to infiltrate.

If you are measuring an endothermic generator based atmosphere of a furnace, the trim gas can be turned off. This can be accomplished by setting a zero set point, or placing the atmosphere
controller in manual mode and setting the output to zero. The gas measured should be the same as the generator. Always start at the generator to get a base line. At the furnace the CO should be slightly lower. If the generator was 20% CO, at the furnace 19.5% CO would be common. A CO₂ of 0.40% at the generator should result in a 0.40% to 0.45% CO₂ at the furnace. A CH₄ measurement at the furnace with no gas addition should be 0.50% or less.

After proving the generator’s gas composition is accurate enter a carbon set point and observe the three gasses as they change. The CO will drop a little, the CO₂ will also go down, and the CH₄ will go up. The higher the temperature, the more CH₄ will be converted into 20% CO, 40% H₂, and 40% N₂. All of this depends upon the temperature of the furnace and how much air infiltration of the furnace exists. Final readings should not be recorded until the carbon percentage and temperature are stable.

When measuring these various protective atmospheres choosing the type of device needed may depend upon cost, longevity of operation, and the amount of information required to properly run a process. The oxygen probe has proven itself to be a dependable, consistent device repeatable in operation. Dew point measurement, while functionally the same over many years, has taken advantage of modern electronics to provide a more durable and easy-to-read display. NDIR has become the tool of choice for processes providing the most information available to help make a decision regarding changes to a process or the peace of mind that the process is within operating requirements.