

Segal's Law of Atmosphere Heat Treatment

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Many in the thermal processing industry can recite dew-point conversion tables with closed eyes. Others may have certain phase diagrams committed to memory. Perhaps a select few are even familiar with Adolf Fick and Walther Nernst -- pioneers in developing the Laws of Diffusion that we unknowingly, yet instinctively, rely upon.

However, the even older "Segal's Law" may be new to us all: "A man with a watch knows what time it is. A man with two watches is never sure."

This proverb is more relevant today than ever. Technology in all industries is developing faster than ever. So how can it be that equipped with nothing beyond an Alnor Model 7000 dew pointer, we knew exactly what our equipment's carbon potential was, and never questioned it?

Fast-forward twenty years and we are surrounded by improved dew point sensors, three-gas analyzers and a variety of other instrumentation. Yet we are less certain what the atmosphere truly is. How can this be? The overwhelming volume of information makes Segal's Law a reality for many. This article will help you regain that lost confidence by detailing such instrumentation's assumptions and its best use (maintenance, production, and secondary verification).

Dew-point Sensors

Dew-point sensors are simple in design, flowing an extracted sample across a dielectric ceramic cell that measures relative humidity. Changes in the sensor's capacitance, coupled with a measured temperature, result in a calculated dew-point.



Figure 1: Dew Point Capacitive Cell

Dew-point can be converted to an atmosphere's carbon potential (C_p) if the furnace temperature (T_R) is known. Conversion tables make several assumptions--notably fixed carbon monoxide (CO , of 20%) and hydrogen (H_2 , of 40%) concentrations consistent with stoichiometric endothermic atmospheres. With CO as the only carbon-carrying gas, a lower CO concentration results in lower C_p . Furnace gas compositions vary, causing such tables to be more a close estimate than a science. As such, dew points sensors are best used for troubleshooting or secondary verification purposes--not as the primary estimation of carbon potential.

A troubleshooting example could be establishing a "baseline dew point". To perform this test, close all additive gases and introduce endothermic gas to a furnace. Once the atmosphere has stabilized, measure dew-point at both the generator and furnace. In theory these measurements should be identical (though in practice the furnace is always greater since air leaks from cracked burner tubes, door seals, etc. are the only source altering the atmosphere). Maintaining such logs can help understand when such leaks worsen.

Measurement error is often introduced by poor sampling methods, with loose tube connections introducing air to the sample. Contamination (in the form of water or soot) is another concern and can damage the sensor. Fiber filters should be installed in line and replaced when the media becomes darkened. Sample valves should be opened before connecting tubing to allow water and soot to "blow out" before connecting the sensor.

A sensor exposed to moisture (resulting in an unusually high and unresponsive dew-point), can be "dried out" by sampling a (low pressure) dry nitrogen source -- this process may take 2-48 hrs depending on the amount of moisture. Dew point sensors should be factory-calibrated on a regular interval to maintain accuracy.

Carbon Probes

Carbon probes paired with some type of control instrument are referred to as a carbon control system. In understanding such systems, we must first understand the probe itself. Probes are constructed of a hollow, sealed zirconia (ceramic) tube inside a protective metal sheath. Reference air is pumped into the probe's interior--leading to an oxygen-rich atmosphere compared to the furnace's oxygen-less reducing atmosphere outside. The specialized ceramic allows oxygen ions to flow between the lower- and higher concentrations, generating a purely electromechanical millivolt output.

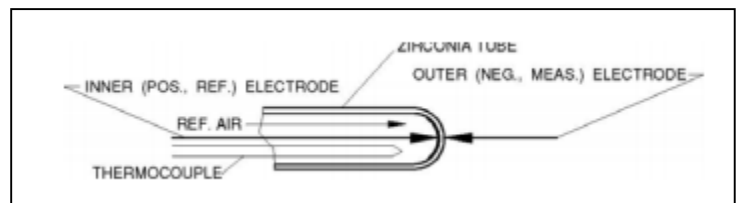


Figure 2: Probe Side View

In the above description it is important to notice the omission of the word carbon. Carbon probes do not measure carbon. These probes actually measure oxygen and calculate carbon based on the Nernst equation:

$$E = .02756 T_R \times \log_{10} \left(\frac{\% O_2 \text{ REF}}{\% O_2 \text{ FCE}} \right)$$

Figure 3: Nernst Equation

The Nernst equation demonstrates that the millivolt output is based on furnace temperature (T_R), oxygen concentration inside the probe ($\%O_2$ ref, or 20.95%), and oxygen concentration outside the probe ($\%O_2$ fce, often in parts per billion). Further, this equation is only applicable to heat treating when CO concentration is a known composition (approximately 20%).

The probe’s non-adjustable output begs the question: How can such a system be calibrated? The answer that a carbon probe cannot be calibrated. Here enters the second part of the carbon control system, the control instrument. Control instruments calculate C_P by measuring even more fixed variables: furnace temperature (T_R), probe millivolts (E), and CO concentration. While specific algorithms may vary, the equations quickly become complicated:

$$C_P = \frac{3.792 \cdot e^Z}{6486000 + e^Z} \quad \text{Where: } Z = \frac{E - 820.7}{0.0239 \cdot T_R}$$

$CO \cdot COF$

Figure 4: Example Carbon Potential Calculation

As an industry standard, “calibrations” are offered in the form of Adjustment Factors (COF). Theoretically this represents changes in CO, but in practice compensates for changes in both the probe and furnace. Such changes are slow in nature and should therefore be small and incremental. Exceptions may apply to deep case, high C_P processes in which in-situ adjustment produces better metallurgy. As an example, a 0.10% CO change can result in a 0.02% atmosphere change, a large impact on calculated C_P . As an industry idiom we must shift away from the term “calibration”, opting instead for “verification checks” -- adjusting COF based on metallurgical and other analyzed results.

When problems arise with probes it is often a result of improper furnace placement (perhaps areas with poor circulation or erroneous gas mixtures not representative of the work area), lack of reference air, soot buildup between the probe’s ceramic and metal sheath (resolved by proper probe burnoffs), a crack in the ceramic (reducing the oxygen differential between the inside and outside), or an aging probe that requires replacement. Though beyond the scope of this article, many documents are available online to isolate the root cause of a failing carbon control system.

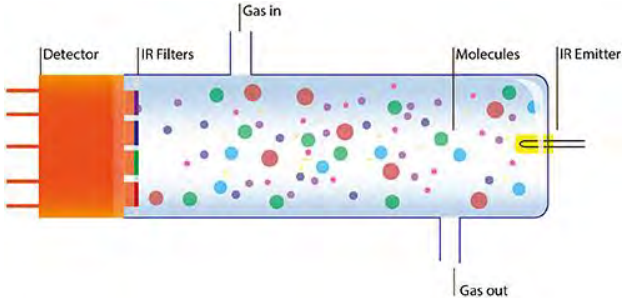
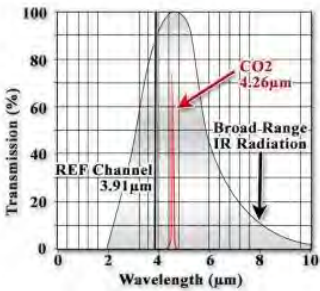
Carbon probes remain one of the oldest technologies in the industry and are still the center of production. Other instruments in our repertoire should be used to “dial in” to this system as it

proves the most stable over time, due to the low risk of sample contamination (compared to analyzers that extract samples), the robust design of the probe, and slower “calibration” drift.

Infrared 3-Gas Analyzers

Infrared gas analyzers (IGAs) operate like dew point sensors as they extract an atmosphere sample across a sensor, and they are also prone to the same contamination concerns. The dew point sensor’s single capacitive cell is replaced with several non-dispersive infrared cells--each uniquely configured for specific gas wavelengths. IGAs are extremely precise and sampling from ferrous ports may further react the gas, skewing the results. As such it is recommended to sample from a ceramic-lined port to avoid further reaction.

IGAs are complex in technology and what they measure, but simple in operation. IGAs estimate C_P by measuring CO, carbon dioxide (CO₂) and methane (CH₄)—with the user entering furnace temperature (T_R). Some IGAs include additional sensors to measure both oxygen (O₂) and H₂, further increasing the accuracy of the calculation.



Figures 5 & 6: Infrared Technology

Compared to these methods IGAs measure more and make fewer assumptions, thus they may seem better suited for both production and troubleshooting. In reality, most commercial heat treaters run such a variety of relatively short processes that use of IGAs result in potential “false alarms”. In such processes IGAs are best utilized as a support tool to a carbon control system, allowing the user to slowly adjust the COF. In certain deeper-case processes, constant COF adjustment may be ideal, resulting in more consistent metallurgy.

IGAs' most appropriate uses are troubleshooting and maintenance. Similar to the "baseline dew point" test, each furnace has unique IGA measurements across every temperature and C_P combination. Following a dew point test, open additive gasses. Once the atmosphere has stabilized, record the results along with furnace temperature, C_P and COF. Developing such a record history allows maintenance to understand the "norm" for a furnace, quickly distinguishing between a door seal and burner tube leak. Unfortunately lack of such records complicates future IGA troubleshooting.

Carbon Resistance Testing

Carbon Resistance Testing estimates C_P by measuring specific properties of a carburized ferrous material. The material is commonly a steel wire cut to a known length, coiled like a spring to reduce the overall size. Note that resistance naturally increases with length. Therefore, adjustments are required in the form of a length factor.

The coil is inserted into the furnace and processed for a pre-determined amount of time allowing the entire spring to obtain carbon equilibrium with the furnace. It is then extracted and cooled under atmosphere to retain metallurgical properties. Changes in the coil's resistance coupled with a measured temperature result in a calculated C_P .

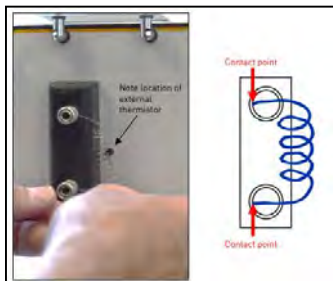


Figure 7: Carbon Resistance Coil

Measurement error is often a result of improper processing or failure to prepare the coil before measurement. Manufacturers establish strict guidelines for processing, with longer processing creating carbides, altering the resistance. Following extraction from the furnace, the sample must be carefully prepped to remove contamination (oils, soot, etc) from the coil's contact points. Contamination alters the surface's resistance, further skewing the results.

Carbon resistance testing's purpose is solely secondary verification — proving a carbon control system's accuracy. Carbon resistance testers can be either factory- or field-calibrated to maintain accuracy.

Shim Stock Analysis

Shim Stock Analysis is similar to Carbon Resistance Testing with a low carbon (~0.10% c) foil-like test coupon inside the furnace. Rather than measuring resistance, carbon is estimated by a weight method or direct chemical analysis. The weight method compares the original- and new weight of the coupon to estimate C_P . While simple to perform, this approach can be inaccurate.

$$\text{new \% carbon} = \frac{(\text{new weight} - \text{original weight}) * 100}{\text{new weight}} + \text{original \% carbon}$$

Figure 8: Weight Method Estimation

Chemical analysis uses a form of combustion to oxidize the coupon, measuring the infrared absorption and thermal changes to estimate C_P . This method, while extremely accurate, can be expensive and the results are often unknown until after completion of the process because many send samples to certified test laboratories. For all its disadvantages, chemical analysis remains the best option for carbon measurement and is recommended as often as feasible.

Summary

Carbon probes remain the most robust and economical solution for atmosphere control. Their results remain most consistent if COF is slowly adjusted using the results from a secondary method such as IGA, carbon resistance (daily/weekly) or shim-stock analysis (weekly/monthly). The results allow the user to adjust COF to reflect the furnace's true atmosphere. Dew-point sensors and IGAs are best suited as maintenance tools, with both requiring an established furnace baseline.

Perhaps if Segal had been alive today he would reword his law to state: "A heat-treater with an instrument knows his carbon potential. A heat-treater properly using more instruments understands his process."

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