ACTION INSTRUMENTS
...the Industrial I/O Company

AP50 Carbon Probe
Benefits and Advantages

Feature and Selling Points

✓ **Compatibility**

✓ **Easy Serviceability**

✓ **Improved Warranty**

✓ **Competitive Pricing**

✓ **Small Sheath Size (Improved Burnoff Velocity)**

✓ **Unique Point Contact Anode**

✓ **Slip Cast Zirconia Substrate**

✓ **Cermet Sheath Coating (Minimize Soot / Maximize Life)**

✓ **Manufacturers Cross Reference**

Technical Information

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AP50 Carbon Probe Advantages

Introduction

The purpose of this paper is to describe the exciting features of our **NEW** AP50 Series Carbon Probes that may Double the Life of In-Situ Oxygen Probes. The introduction of the AP50 Series Carbon Probe represent the industries first "Third Generation" oxygen probe.

Compatibility

Total electrical and mechanical compatibility and interchangeability with most other commercially available probes.

Easy Serviceability

Very easy to install because of streamlined geometry - (non rotating 4" terminal head assembly common with most other probes).

Completely open access to signal connection terminals facilitate simple, quick cable hookup.

Probe is designed to be rebuilt after expiration of warranty period. Affordable refurbishment charges are approximately half of new probe replacement price.

Improved Warranty

Each probe is warranted for 12 months from date of installation.

Each new or refurbished probe is supplied with a 5-point certificate of test guaranteeing conformity to our rigid performance standards.

Free recertification service while probe is in initial warranty period.

Competitive Pricing

Lowest initial advertised purchase price in U.S.A.

Small Sheath Size (Burnoff)

Barber-Colman has identified probe burnoff as a vital link in applying oxygen probes successfully to all types of carbon control applications. We consciously made burnoff - specific design decisions to maximize the burnoff efficiency of the AP50 Probe. By reducing the sheath diameter and locating precisely sized access vent holes near the electrode tip, we have accomplished our objective. This has been substantiated by extensive field testing comparing our burnoff efficiencies with other probe suppliers.

Our smaller diameter sheath requires approximately 1/7 the volume of burnoff air and achieves much greater air velocity directed precisely at the Zirconia / anode interface.

Probe output should consistently fall below 200 mV after the burnoff procedure (in a 1700°F carburizing application). In side by side tests, we were unable to achieve a mV level approaching 200 mV with competitors' probes which have eight or more larger diameter access holes in the sheath tip area, even with burnoff air flow increased to volume twice that used in the AP50 Probe.

Tests indicated that in order to effectively burn off the electrode / Zirconia contact area, the oxidation reaction must be complete enough to drop the measured signal below 200 mV. If the signal does not drop below 200 mV during burnoff, then we suggest that adequate cleaning has not occurred and unreliable, inconsistent, sluggish and high resistance probe readings will result. Inaccurate, inconsistent probe output is the failure mechanism of approximately 80% of oxygen probes based on years of experience working with oxygen probes in heat treat applications. In many cases, these probes could be "salvaged" by proper and adequate burnoff.

Point Contact Anode

The alloy sheath is the outer electrode (anode) conductor. The design and assembly configuration the "measuring tip" of our AP50 Probe assures virtual point contact. This means lower resistance and faster response time and less chance of anode interface contamination (sooting). These features translate into improved probe performance, longer term reproducibility and accuracy. These design features are the subject of a recently issued U.S. patent.

Slip Cast Zirconia Substrate

The AP50 uses only slip cast, single piece, gas tight Zirconia tubes as our assembly electrolyte. The majority of other probe manufacturers use a CSIRO (Australia) developed two piece substrate. This assembly consists of an open length of alumina tubing which has a eutectically bonded plug of Zirconia in one end. Our experience is that these probes can develop leaks in the joint, causing slight measurement error. We have always contended that a minor error is always worse than a catastrophic failure because you do not always know it exists and it can be extremely difficult to troubleshoot. Our high performance, single piece Zirconia substrates are not subject to age induced or thermal cycling induced gas leaks. Barber-Colman is convinced that single piece integrity provides an improved measure of long term probe reliability.

AP50 Carbon Probe Advantages

Cermet Sheath Coating

Background

✓ 80% of "failed" Oxygen Probes returned while in warranty are faulty because of soot contamination.

✓ All makes of probes will become unreliable if successful, routine cleaning (burnoff) is not frequently accomplished.

✓ Soot is inherent in all hydrocarbon-based reducing atmosphere furnaces.

✓ Nickel bearing alloys in operating furnaces can provide a catalytic surface for the decomposition of natural gas (methane) into carbon and hydrogen. This carbon typically remains in solid state form as free soot and can cause serious control problems and premature component failures.

Our **NEW** AP50 Series Carbon Probes were designed specifically to address the problems listed above that are a plague to the automatic control of atmosphere furnaces.

Cermet Coating

Driven by a concern to improve probe performance, we have recently introduced the industries' first "third generation" oxygen probe.... the AP50 Carbon Probe. We are successfully applying cermet coating techniques to extend probe sheath life and reduce the catalysis effect with methane that is present with other probe alloy sheaths currently used. This design feature, along with the unique anode contact configuration is the subject of a recently awarded U.S. Patent.

Users operating equipment at elevated temperatures (1750°F) and carbon potential (1.25% C+) will experience the most significant gain in probe life expectancy. The cermet sheath treatment creates a tenacious, impenetrable layer to protect all exposed surfaces of the probe sheath from the process atmosphere; Reducing the surface nickel availability reduces soot formation and virtually eliminates high temperature corrosion (green rot).

AP50 Probe Cross-Reference

Barber-Colman AP50	Barber-Colman AP1X	SSi	Marathon	Accucarb	T/C	Length	Coating
AP50-00120-001-1-00	AP10-00121-4X1-1-00	10000	F100040 or F100123		None	20+"	None
AP52-00120-001-1-00	AP12-00121-4X1-1-00	10001	F100042 or F100119		R	20+"	None
AP53-00120-001-1-00	AP13-00121-4X1-1-00	10008	F100041 or F100125		S	20+"	None
AP51-00120-001-1-00	AP11-00121-4X1-1-00	10009	F100043 or F100124		K	20+"	None
AP50-00111-001-1-00		10010			None	12"	None
AP52-00111-001-1-00		10011			R	12"	None
AP53-00111-001-1-00		10018			S	12"	None
AP51-00111-001-1-00		10019			K	12"	None
AP50-00130-001-1-00	AP10-00130-4X1-1-00	10020	F100045		None	<29"	None
AP52-00130-001-1-00	AP12-00130-4X1-1-00	10021	F100042		R	<29"	None
AP53-00130-001-1-00	AP13-00130-4X1-1-00	10028	F100041		S	<29"	None
AP51-00130-001-1-00	AP11-00130-4X1-1-00	10029	F100048		K	<29"	None
	AP10-00136-4X1-1-00		F100050		None	36"	None
	AP12-00136-4X1-1-00		F100052		R	36"	None
	AP13-00136-4X1-1-00		F100051		S	36"	None
	AP11-00136-4X1-1-00		F100053		K	36"	None
	AP10-00144-4X1-1-00		F100056		None	44"	None
	AP12-00144-4X1-1-00		F100057		R	44"	None
	AP13-00144-4X1-1-00		F100056		S	44"	None
	AP11-00144-4X1-1-00		F100058		K	44"	None

AP50 Probe Cross-Reference

Barber-Colman AP50	Barber-Colman AP1X	SSi	Marathon	Accucarb	T/C	Length	Coating
AP50-00120-101-1-00		10100			None	20+"	Ceramic
AP52-00120-101-1-00		10101			R	20+"	Ceramic
AP53-00120-101-1-00		10108			S	20+"	Ceramic
AP51-00120-101-1-00		10109			K	20+"	Ceramic
AP50-00111-101-1-00		10110			None	12"	Ceramic
AP52-00111-101-1-00		10111			R	12"	Ceramic
AP53-00111-101-1-00		10118			S	12"	Ceramic
AP51-00111-101-1-00		10119			K	12"	Ceramic
AP50-00130-101-1-00		10120			None	<29"	Ceramic
AP52-00130-101-1-00		10121			R	<29"	Ceramic
AP53-00130-101-1-00		10128			S	<29"	Ceramic
AP51-00130-101-1-00		10129			K	<29"	Ceramic
AP50-00120-201-1-00	AP10-00121-4X1-1-00	11000		AQ 604-0-C00-0-O	None	20+"	None
AP52-00120-201-1-00	AP12-00121-4X1-1-00	11001		AQ 604-R-C00-R-O	R	20+"	None
AP53-00120-201-1-00	AP13-00121-4X1-1-00	11008		AQ 604-S-C00-S-O	S	20+"	None
AP51-00120-201-1-00	AP11-00121-4X1-1-00	11009		AQ 604-K-C00-K-O	K	20+"	None
	AP10-00144-4X1-1-00				None	44"	None
	AP12-00144-4X1-1-00				R	44"	None
	AP13-00144-4X1-1-00				S	44"	None
	AP11-00144-4X1-1-00				K	44"	None

AP50 Probe Cross-Reference

Barber-Colman AP50	Barber-Colman AP1X	SSi	Marathon	Accucarb	T/C	Length	Coating
AP50-00111-201-1-00		11010			None	12"	None
AP52-00111-201-1-00		11011			R	12"	None
AP53-00111-201-1-00		11018			S	12"	None
AP51-00111-201-1-00		11019			K	12"	None
AP50-00130-201-1-00	AP10-00130-4X1-1-00	11020			None	<29"	None
AP52-00130-201-1-00	AP12-00130-4X1-1-00	11021			R	<29"	None
AP53-00130-201-1-00	AP13-00130-4X1-1-00	11028			S	<29"	None
AP51-00130-201-1-00	AP11-00130-4X1-1-00	11029			K	<29"	None
AP50-00120-301-1-00		11100			None	20+"	Ceramic
AP52-00120-301-1-00		11101			R	20+"	Ceramic
AP53-00120-301-1-00		11108			S	20+"	Ceramic
AP51-00120-301-1-00		11109			K	20+"	Ceramic
AP50-00111-301-1-00		11110			None	12"	Ceramic
AP52-00111-301-1-00		11111			R	12"	Ceramic
AP53-00111-301-1-00		11118			S	12"	Ceramic
AP51-00111-301-1-00		11119			K	12"	Ceramic
AP50-00130-301-1-00		11120			None	<29"	Ceramic
AP52-00130-301-1-00		11121			R	<29"	Ceramic
AP53-00130-301-1-00		11128			S	<29"	Ceramic
AP51-00130-301-1-00		11129			K	<29"	Ceramic

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Zirconia Sensor Theory
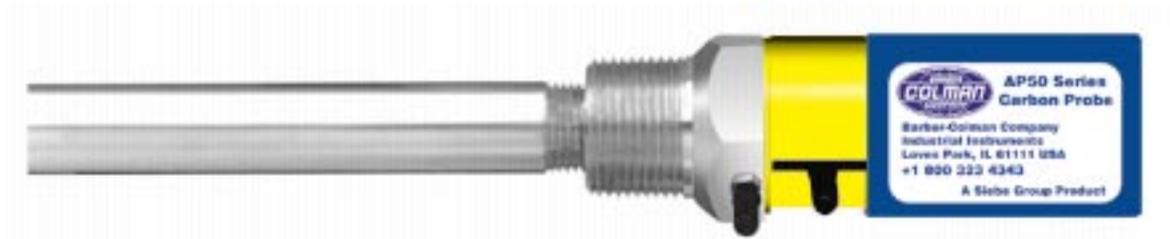
Barber-Colman
Carbon Probe

The zirconia carbon sensor is really an oxygen sensor. The primary mechanism for electrical current flow in many ceramic electrolytes is ionic conduction, in this case via oxygen ions. Typical construction, basic theory, opening equations and applications are covered in this document.

Technical Information

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Zirconia Sensor Theory

Introduction

The purpose of this paper is to describe the typical zirconia carbon sensor in general terms, and provide a thorough grounding in the mathematical equations governing its practical use.

Commerial Sensors

The basic elements of all commercial carbon sensors are shown below.
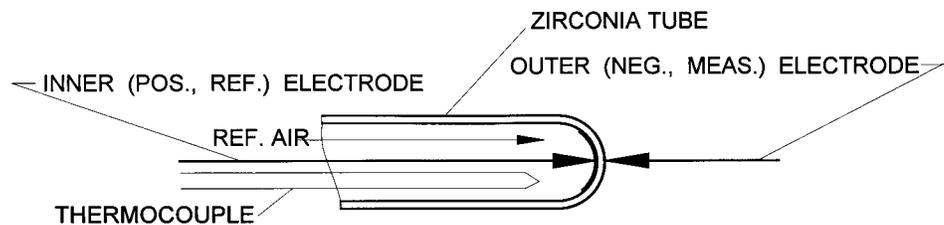
Figure 1

The tubular zirconia sensing element illustrated here is the preferred form for the Barber-Colman AP50 Carbon Probe. Slip cast and fired at exceptionally high temperatures to provide a dense, non-porous body, this component is not prone to develop the leakage paths that are common in probes using a cemented zirconia plug in a tubular alumina body.

The inner, reference electrode, is spring loaded to hold it in intimate contact with the inner zirconia surface. It consists of a specially formed extension of the lead wire that connects it to the probe terminal block. The inner reference components are especially resistant to the normally oxidizing reference atmosphere.

The outer, measuring electrode for most commercial probes is mechanically and electrically part of the alloy protective sheath, and the zirconia substrate is spring loaded to make intimate contact with this electrode. The Barber-Colman outer electrode, by virtue of premium quality, heat resistant alloy and a proprietary surface treatment, is designed to survive the rigors of the harsh furnace atmosphere.

While probe manufacturers use a variety of materials and geometries, all properly designed sensors will display precisely the same output when at equilibrium in a furnace atmosphere. Despite this fact, many control instrument manufacturers will provide different algorithms for probes from different manufacturers. This is primarily because manufacturers have derived their algorithms using different sources for data that are not in complete agreement.

Zirconia Sensor Theory

Principles of Operation

Pure zirconium oxide is a monoclinic crystalline material that transforms reversibly to a tetragonal form at 1832°F with a large change in volume. This makes it unsuitable for normal refractory use. If placed in solid solution, however, with 4% to 12% MgO, CaO or Y_2O_3, it is held in the stable isometric (cubic) form which has no transformation in the range of heat treating atmospheres. By virtue of the addition of these stabilizing oxides, oxygen ion vacancies are established in the crystal lattice. The mobility of O ions is greatly enhanced, and under certain conditions of temperature and composition, the conductivity is entirely due to oxygen ions. This condition coincides with the existence of the pure cubic crystalline phase, and is responsible for the oxygen sensing capability of stabilized zirconia which will be discussed later.

A minimum quantity of the stabilizing oxides will ensure the existence of the pure cubic crystalline phase of zirconia. When this amount is present, the zirconia is said to be fully stabilized. The commercially available zirconia for oxygen sensors will have somewhat less than this minimum amount, resulting in a "partially stabilized" electrolyte, having a better resistance to thermal fracture. The zirconia in Barber-Colman sensors contains about 6 mole % (10.5 weight %) of Y_2O_3. The cell construction of Figure 1 demonstrates a characteristic typical of electrolytes having unity transference numbers for an ionic species; there is an electromotive force displayed at its terminals that can be precisely related to the corresponding molecular concentration at the two surfaces. In the case of cubic zirconia, the cell e.m.f. is given by a form of the familiar Nernst equation,

$$E_C = 0.0275 T_R \log_{10}(p_0/p_1) \text{ millivolts} \qquad (1)$$

where T_R is the absolute temperature in degrees Rankine (= °F + 459.67), p_0 and p_1 are the oxygen concentrations at the inner and outer electrodes respectively, stated in any units (usually in atmospheres of partial pressure). Although there are applications where the oxygen present is the only critical parameter, the heat treater is concerned with two other variables he wishes to control; dew point and carbon potential. Fortunately, both parameters can be calculated directly from the oxygen measurement.

Zirconia Sensor Theory

Dew Point

This variable is utilized in control of endothermic generators that supply the basic environment to a heat treating furnace. This environment, commonly called endo or R_x gas, is created in the generator by combining air and a combustible such as natural gas or propane to provide a mixture of about 20% carbon monoxide, 40% hydrogen and 40% nitrogen.

The reversible reaction that expresses the separation into oxygen and hydrogen by water is:

$$H_2O \Leftrightarrow H_2 + 1/2\ O_2 \qquad (2)$$
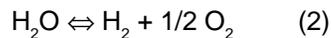
By applying the principals of the law of mass action we can write an expression that accurately describes the composition of the three components in a mixture at equilibrium:

$$K_W = PH_2 \times PO_2^{1/2} / PH_2O \qquad (3)$$

where K_W is the temperature dependent equilibrium constant for this reaction and PH_2, PO_2 and PH_2O are the partial pressures of the corresponding materials, usually stated in atmospheres. This equation dictates that a change of any of the variables causes the others to change as well in order that equilibrium be sustained and the equation remains satisfied. The equilibrium constant is precisely described by the following equation (from Wagman[2]):

$$\log_{10}K_W = 2.82 - 23000T_R \qquad (4)$$

The last relationship required to calculate the dew point from the measured variables is[3]:

$$\log_{10}PH_2O = 6.3979 - 4238.7 / (DP+460) \qquad (5)$$

where the dew point, DP, is reported in degrees Fahrenheit. Combining equations (2) through (5), we arrive at the Barber-Colman algorithm for dew point:

$$DP = 4238.7 / (9.55731 - \log_{10}PH_2 + (E_C - 1267.8) / 0.05512T_R - 460) \qquad (6)$$

It is important to note here that there are only three specified variables in this algorithm. E_C and T_R are measured directly by the sensor which <u>must</u> include a close coupled thermocouple for precise calculation. The third variable (PH_2) may be measured by other analytical means. More commonly, as in the case of endothermic generators, it is assumed to be approximately 0.4 atmospheres. Because its value will vary with the control set point, the gauge pressure at the sensor, and other factors such as peak shaving practices by the power company, it is commonly incorporated as part of a correction factor in the control instrument. This factor is set to a value that causes the computed value of dew point to agree with a manually measured value using a device such as the Alnor Dew pointer. The individual correction factor is very stable. Accordingly, heat treaters find that the frequency of manual dew point determination may be reduced significantly.

Carbon Potential

The carbon potential (%C) of a heat treating atmosphere is defined as "that value of carbon concentration achieved in a coupon of shim stock exposed to the atmosphere until it has reached equilibrium." The time required for this equilibration will vary with shim thickness and furnace temperature. Table 1 illustrates the approximate effects.

Shim Thickness			
TEMP	0.003"	0.005"	0.007"
1550	63	117	173
1600	50	91	136
1650	39	72	107
1700	32	58	86
1750	26	47	70

Table 1. Time to equilibrium (minutes)

Corresponding to the reaction (2) for dew point calculations is the following reversible reaction encountered in the furnace atmosphere:

$$CO \div C + 1/2\, O_2 \qquad (7)$$

The mass action equilibrium equation for this reaction is:

$$K_{CO} = a_C \times PO_2^{1/2} / PCO \qquad (8)$$

where K_{co} is the temperature dependent equilibrium constant, PO_2 and PCO are the partial pressures of oxygen and carbon monoxide and a_C is the carbon activity a concentration term similar to the partial pressure. As before, this equilibrium constant is a function of temperature (from Wagman et al)[2]:

$$K_{CO} = 4.5713 + 10638/T_R \qquad (9)$$

Finally, the carbon activity a_C has been experimentally related to %C (from Collin et al)[4]:

$$a_C = 1.07\, q\, (10^{3751/T})(C/(1-19.6C)) \qquad (10)$$

where q is a function of the alloy being treated, and is calculated as shown in Appendix A. Combining (1), (8), (9) and (10) and rearranging, we derive the Barber-Colman algorithm relating %C to the measured variables from the sensor:

$$\%C = 3.792\ e^Z / ((324.3q\ /\ PCO) + e^Z) \qquad (11)$$

where $\qquad Z = (E_C - 820.7) / 0.0239\ T_R$

Note: The value q/PCO is the correction factor (or a simple function of the correction factor) that is provided in most commercial controllers to make the calculated value of %C agree with shim stock tests.

Practical Considerations

Properly maintained, the zirconia sensor provides the valuable characteristic of repeatability to the heat treater. Periodic standardization using shim stock tests or dew point tests to establish the appropriate correction factors will ensure repeatability, and hence product quality assurance. Although the purist may frown at the use of such "fudge factors," the practical considerations overwhelmingly dictate their use. It may be found that the value of the correction factor will vary at the extremes of temperature and carbon potential. Appropriate values should be determined throughout the operating region and applied judiciously.

APPENDIX A - CALCULATION OF ALLOY FACTOR "q"

The value of q for carbon steels is close to 1.00. When alloying elements are incorporated in the steel, it is desirable to calculate an additive factor to adjust the value of q, using the formulae in the following table (from Neumann and Person)[5]:

To correct for	add this value to q (= 1.00)
Silicon	$0.15 \%Si + 0.33 \text{ o/o}Si^2$
Manganese	$0.0365 \%Mn$
Chromium	$-0.13 \%Cr + 0.0055 \%Cr^2$
Nickel	$0.03 \%Ni + 0.00365 \%Ni^2$
Molybdenum	$-0.025 \%Mo - 0.01 \text{ o/o}Mo^2$
Aluminum	$-0.03 \%Al - 0.02 \%Al^2$
Copper	$-0.016 \%Cu - 0.0014 \%Cu^2$
Vanadium	$-0.22 \%V + 0.01 \%V^2$

References

1. T. Lotze and T. Berry - SSi Super Systems
2. D.D. Wagman *et al.* J. Res. Burl Standards, 1945, 34, 143.
3. Metals Handbook 9th Ed., Vol. 4, 145.
4. R. Collin *et al.* J.I.S.I., Oct. 1972, 788.
5. F. Neumann and B. Person, Hart.-Techn. Mitt., 1968, 23, 296.

An Overview of Endothermic Generators
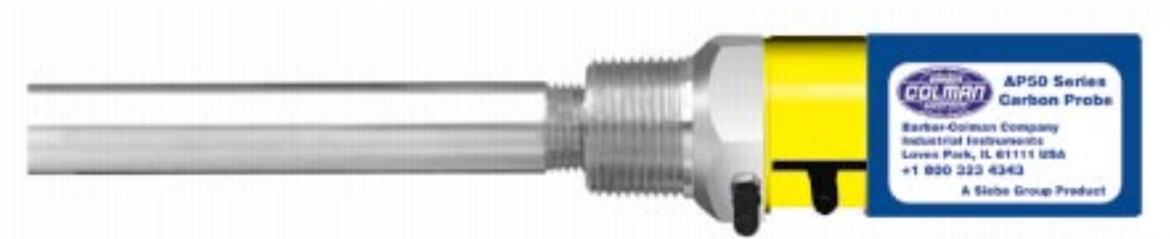
Barber-Colman
Carbon Probe

The endothermic generator creates an atmosphere to provide a positive pressure in a heat treating furnace, and a platform on which a carburizing or decarburizing environment can be formulated, by addition of enriching gas or dilution air. Generator maintenance scheduling, operation, and control are discussed.

Technical Information

Overview of Endo Generators

Introduction

Endothermic atmosphere, commonly called endo, carrier gas or Rx gas, is synthesized in the catalytic retort(s) of endo generators. This gas, combined with an additive gas such as natural gas, propane or air, is used in heat treating furnaces to modify the surface chemistry of work positioned in the furnace. Other carrier gases such as exothermic gas, dissociated ammonia and other nitrogen based atmospheres are found in many heat treating facilities, but endo is most common. Because endo can have a profound impact on the quality of processing, it is important to establish a preventive maintenance program for the generator and then follow the program religiously.

The most common source of endo is the reaction product of air and natural gas in ratios between about 2.5 to 1 to 5.5 to 1. Since the reaction is not spontaneous below ratios of 6 to 1, it is necessary to supply heat to the generator — hence the term endothermic, meaning heat absorbing. Typical endogas generators produce an atmosphere of approximately 20% carbon monoxide, 40% hydrogen and 40% nitrogen, and trace amounts of carbon dioxide and other gases originating in the natural gas or created by the reaction. The application of heat is not sufficient to create the desired products rapidly, so the reacting gases must be exposed to a catalytic agent to accelerate the reaction.

Principal components of an endogas generator are:
1. A heating chamber to supply heat by combustion or electric heating elements, one or more cylindrical retorts (usually vertical) in the heating chamber with...
2. numerous small, porous ceramic pieces, impregnated with nickel as a catalyst for the reaction. Also included as part of the generator is...
3. a cooling heat exchanger to rapidly cool the reaction products to a temperature that will not allow the reaction to proceed further. One of the most critical parts of the system is...
4. the control system that maintains the reaction temperature and adjusts the gas/air ratio to provide the desired dew point.

Maintenance Schedule

Note: The maintenance schedule suggested in the following paragraphs has been assembled from numerous "industry standards" as well as from the application experience of Barber-Colman staff working with the equipment. Because of the make and design of your equipment, and your routine maintenance procedures, not all of these recommendations may apply.

Daily:

1. Visually examine all instrumentation to assure that operation is normal and without incident. Determine that control outputs are within the expected range of operation.
2. Check temperature of water discharged from heat exchanger.

Overview of Endo Generators

Weekly:

1. Regenerate (burn out) carbon in generator using air (preferred method), exothermic gas, or lean endothermic gas.
2. After regeneration and readjustment of generator to proper dew point, check the gas analysis (including CH_4 content) with an infrared analyzer if possible.
3. Clean the air filter.

Monthly:

1. Clean air-gas mixing valve (carburetor) thoroughly.
2. Check calibration of gas analysis and control equipment such as automatic dew point controllers, manual dew point indicators, CO/CO_2 analyzers and oxygen probe carbon potential control systems. The primary standard for carbon analyzers is shim stock tests. Alnor or equivalent dew point testing gives a reasonable indication of correct operation.
3. Inspect thermocouples and protection tubes and replace every 3 to 4 months.
4. Check natural gas pressure after the regulator to maintain balance to the carburetor.
5. Verify correct operation of Limitrols® (over temperature controls).

Semi-annually:

1. Replace heat exchanger with standby, clean and refurbish for next service.
2. Inspect catalyst in retort and fill to proper level or replace.
3. Inspect and clean all burners.
4. Clean endo delivery lines to furnaces.
5. Inspect cooling water thermostats solenoids.
6. Perform complete instrument calibration and service, including safety controls.
7. Have oxygen probe (carbon sensor) refurbished, inspected and certified.

Annually:

1. Check compressor blades.
2. Check motor and compressor bearings.

Additional Troubleshooting Considerations

Problems at the furnace can alter an otherwise correct endo atmosphere due to air or water incursion. Therefore both the atmosphere manifold and the furnace should be checked carefully when a problem is encountered before attempting any corrective changes in the generator atmosphere control system.

Air Maintenance

One of the major sources of difficulty, and hence a nagging maintenance problem, is poor quality air. Contaminants in the air can include dust or fumes from acid cleaning tanks and oil quenching systems. Airborne dust has been linked to failure of pumps and flowmeters, and poor electrical contact in relays. Combustible vapors can cause a carbon sensor to read low, resulting in over carburization.

In order to maintain a good air quality, it is necessary to establish a routine for cleaning filters. In some cases it may be necessary to install ductwork to bring outside, contaminant free air to the equipment. Dust-tight electrical housings are sometimes necessary to eliminate dust and fume problems.

Overview of Endo Generators

Cooler Maintenance

The design objective of coolers is to cool the generated atmosphere as quickly as possible to below about 260°F in order to stabilize the composition before being delivered to the furnace. Two problems impact on operation of the water cooled heat exchanger. First, dissolved and suspended solids in the water will deposit and coat the tube walls, thereby reducing the heat transfer rate. Further, dissolved oxygen in the water can promote oxidation of the tubes, resulting in premature failure.

Water cooled heat exchangers should be cleaned and pressure tested for leaks during catalyst replacement. Air cooled exchangers should be blown out with air or rodded as necessary also during catalyst replacement.

Gas Supply

For the successful operation of any gas generator, an adequate supply of gas of the proper composition is required at all times.

Dirt, scale and water vapor can cause plugging and failure of regulators and control valves. Flowmeters are especially susceptible to dirt build-up on the float and walls. Gummy deposits from a poor gas mixture can also cause sticking of valve parts and carburetors.

One of the most troublesome problems is the inconsistent analysis of the supply fuel. Propane-air additives to natural gas supplies ('peak shaving') alter effective generator ratios. Unsaturated hydrocarbons such as ethylene and propylene break down quickly into oily soot or coke. Unfortunately, there is little choice when using utility-supplied natural gas. In some instances, propane is selected to avoid these problems, but it is not always an economical solution.

Sulfur, both naturally occurring and as additive mercaptans, can cause poisoning of the nickel catalyst and an ultimate failure of the generator to crack gas properly.

It is therefore essential that the gas supply system be kept under close observation, and that all critical components of the system, such as those previously mentioned, be inspected and cleaned as required on a programmed basis. It may be advisable to inform your gas/utility supplier of your special concerns should they, at their discretion opt to alter your feedstock supply by "dosing" or "spiking" (i.e. peak shaving) your gas. We find, in many instances, that the gas utility companies will not advise you of this practice and are reluctant to discuss it.

Maintenance of the Combustion System

The maintenance of the combustion system of a gas fired endothermic generator is not different from other combustion systems; that is, it should be kept clean and adjusted. Most such systems are relatively simple.

Electrical Maintenance

A reliable, uniform supply of regulated power is necessary to operate relays and solenoid valves.

Electrical problems are usually easy to spot, since maintenance personnel are well trained and have sufficient test equipment and wiring diagrams for trouble shooting.

Thermocouples and Protection Tubes

In most atmosphere generators, we recommend the use of Type S thermocouples. Because of the relatively high temperatures maintained in atmosphere generators (1850°F to 1950°F), thermocouples should be inspected every three to four months, and replaced if found faulty.

Protection tubes and seal rings should be checked each time the thermocouples are replaced; a broken or leaking tube will greatly shorten the life of the thermocouple. If there is a substantial difference in indicated temperature between the control and overtemp instruments, it can very well be caused by deterioration of one of the protection tubes, causing early failure of the couple. If this should happen, check and replace as necessary. It is often standard practice to replace the protection tubes when the thermocouple is replaced.

Maintenance of Temperature Controls

In addition to temperature controls, most atmosphere generators have an over temperature (high limit) instrument to shut the system down in the event of a runaway temperature.

Because of the great variety of recorders, recorder/controllers and controllers, it is difficult to discuss exact inspection, calibration and repair procedures, but general rules of thumb apply. Pens, ink and charts should be checked daily. This ensures a quick look at the instrument to determine if it is operating properly. Manufacturers recommendations for routine maintenance should be scheduled. Temperature calibration is usually fairly stable, but should be checked every six months, at the same time as the thermocouples.

The overtemperature instrument requires little service, but it does require a monthly check for proper function, and semi-annual calibration.

Installation of Catalyst

Catalyst specialists recommend a layer of untreated (no nickel) alumina substrate on the diffuser block extending 2" to 4" into the combustion chamber, to act as a buffer zone. This material can be recovered and reused when changing catalyst.

Slowly pour catalyst into the retort, avoiding dust that may have resulted from shipping. A good rule to follow is to fill the retort to a point just below the top of the combustion chamber. On most generators, this is about 8" below the top plate. Do not overfill. Catalyst in the cooler area above the combustion zone will create sooting due to a reversible reaction in this temperature transition zone. Replace the retort cover plate, using a new gasket.

Overview of Endo Generators

Breaking in New Catalyst

Heat the generator slowly to 1500°F and hold for one hour. This is intended to avoid too rapid expansion of the retort and refractory lining of the combustion chamber. Then raise to normal operating temperature and hold for two hours before attempting to crack gas.

The new catalyst can be broken in by operating at your normal air/gas ratio. Considerable moisture is formed at this point due to reaction with the air in the retort and the pores of the catalyst substrate. This moisture will normally collect at the cold end of the heat exchanger, and should be drained out at the petcocks in the cold gas manifold. Allow sufficient time to dry out the pipes before taking dew point readings and adjusting the ratio for dew point control.

Once the catalyst is broken in and reduced, it is not necessary to repeat this operation if "burnout" or reactivation is properly conducted.

Catalyst Maintenance

With any specific gas generator, the manufacturer provides recommendations regarding the catalyst — the kind used and its care. Maintenance of the catalyst is vital, and cannot be overemphasized.

The catalyst will last longer if a dew point above 35°F is maintained. Generally speaking, operation at lower dew points will cause a buildup of carbon which will appreciably shorten catalyst life. When the catalyst breaks down, it is difficult to achieve maximum gas flow. At that point, new catalyst must be charged. To avert such breakdown, carbon should be burned out of the catalyst bed every week. This is achieved by halting gas production, establishing a temperature of 1600°F, then establishing the recommended flow of air as indicated here:

Generator Size	Recommended Air Flow
500 CFH	25 CFH
750 CFH	35 CFH
1000 CFH	50 CFH
1500 CFH	75 CFH
Multiple Retorts	75 CFH/per retort

If carbon is present on the catalyst, a blue flame will appear at the generator burnoff can or pipe. As soon as the flame disappears, stop the air flow. This is important. Do not continue air flow after the flame disappears. This indicates that all carbon has been removed. If air is continued, the nickel catalyst will become oxidized, and then must be reduced by the procedure outlined for breaking in new catalyst.

The generator can be idled during weekends at 1500°F to 1600°F without cracking gas. The amount of time to burn off soot should not take more than a few minutes if the generator has been operated properly above 35°F. Operating generators at low dew points will require more time to burn off the carbon accumulation. It is important for good, efficient gas cracking to remove any carbon. It is also important to obtain the maximum catalyst life. The high refractory catalyst base resists disintegration by carbon, but even the best of catalysts will deteriorate with time in the presence of a heavy carbon deposit. Remember that any catalyst loses its

efficiency if the nickel is blanketed by a layer of carbon. Therefore, it is important to check your generator occasionally to see if it is being operated properly and to remove any carbon deposit.

If, after the catalyst reactivation, the dew point or CO_2 control cannot be achieved, the catalyst will require changing.

Application of Dew Point Controls

Numerous attempts have been made to apply automatic control to endo genera-tors. At best, many would agree that most of these systems have not performed consistently up to user expectations. Since the early 80's, however, oxygen probe based control systems have provided a more reliable and meaningful approach to automatic dew point control. Surprisingly, they have been shown to minimize the impact of peak shaving.

Two of the early attempts involve insertion of the probe directly into the top of the retort.... either vertically, or at an angle, so that the probe is located 2 to 3" above the surface of the catalyst bed. By this siting, the probe is exposed to the endogas flow at a temperature between 1550°F and 1750°F typically. While the primary objective of these techniques is to have "in situ" exposure, a number of operating and maintenance concerns have become evident.

Some of the most troubling features of the in situ mounting are:
1. High ambient temperatures on the top of the generator;
2. Difficult maintenance at this location;
3. Concerns related to mounting in a single retort of a multi-retort unit - what's happening in the other retort(s) ?
4. Shortened probe life because of the high temperature exposure; and
5. Shortened probe life because of soot buildup in the probe sheath.

Note: Burnoff is not an option in this location due to the pressure levels in the endo manifold and impact on the product by the burnoff air.

A third, more recent application using O_2 probes has shown the most promise compared to previously attempted methods. The overall system is shown in Figure 1, with a closeup view of the sensor installation in Figure 2. This method does not require accessing the probe into the retort or its exit piping. Instead, a small sample of cooled endogas from the generator exit manifold, or an individual retort in a multi-retort generator, is transported to the short probe which is fitted into a reheat well in the side wall of the generator heating chamber.

The reheat well can be inserted to a point in the refractory wall that establishes a probe operating temperature between 1350°F and 1550°F, preferably 1400°F. The thermal well provides a thermal shock barrier and a transition buffer between the sample and the combustion atmosphere. This arrangement also allows for a convenient burnoff of the sensor with absolutely no impact on the generated atmosphere quality. Troubleshooting is comfortably conducted at ground level without the extreme discomfort encountered when working with retort mounted
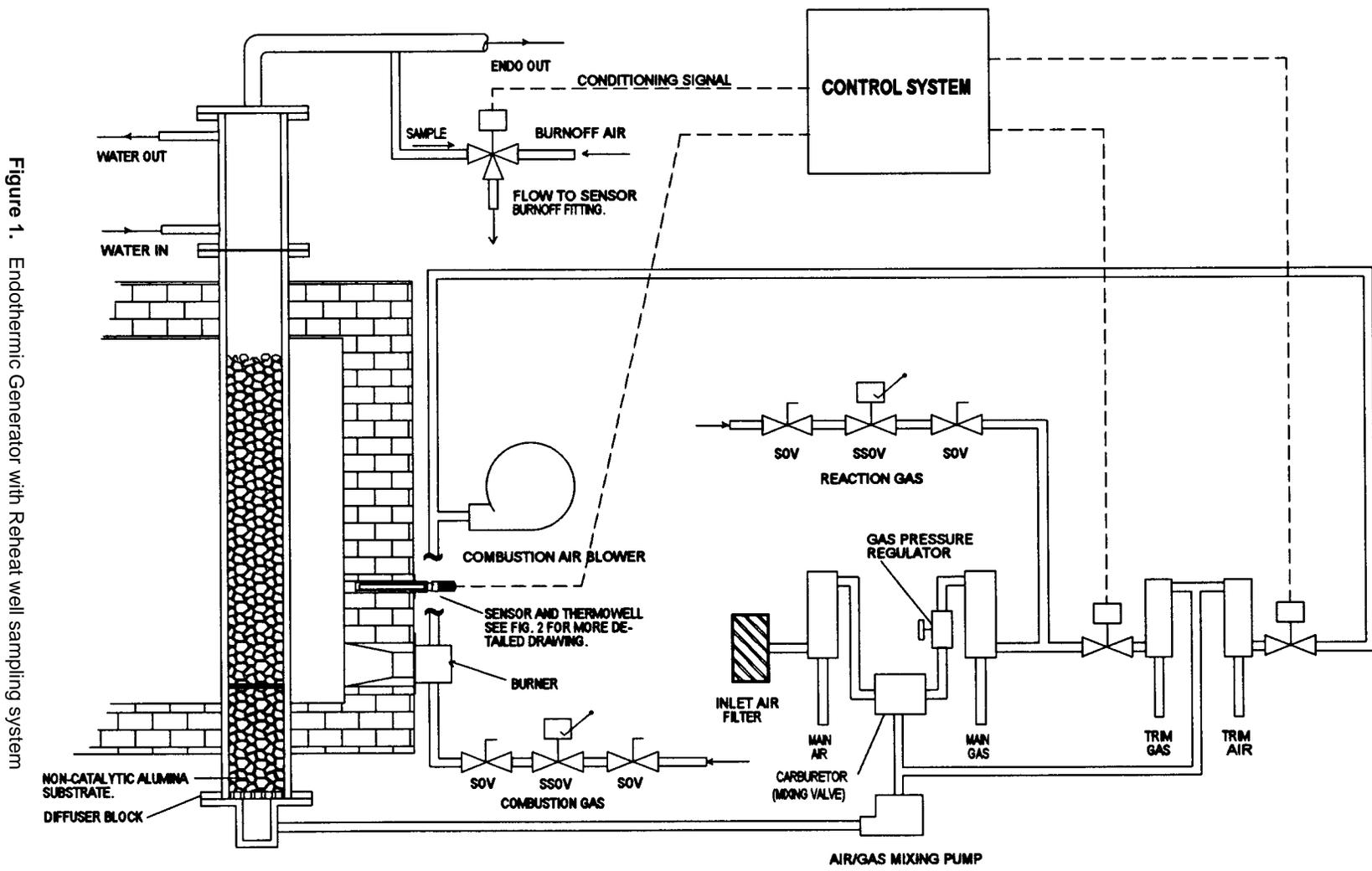
Figure 1. Endothermic Generator with Reheat well sampling system

probes. High probe temperature / short life expectancy concerns are eliminated. The proximity of endogas sampling ports for both the O_2 probe and conventional dew point devices (Alnor or equivalent) provide greater surety and confidence. There is a valid argument for concerns relating to sampling problems, equilibrium shifts and removal from the "in-situ" enviroment, but we believe the advantages of the reheat well / O_2 probe measuring system overwhelmingly outweigh the disadvantages.

Closing the loop for endo generator control is accomplished by connection to a state-of-the-art microprocessor analyzer/controller. This device should calculate and display dew point, control output, probe millivolt output and temperature. It should regulate the addition of enriching gas or dilution air for control. If you choose a programmable controller, you can write a "watchdog" program that will sound an alarm if the control output is nearing its maximum. An alarm display might state or infer, for example, that "you are adding over 90% of the maximum trim gas available - adjust your carburetor (mixing valve) to a richer ratio that allows control gas flow to approach zero." Because the problem has been immediately alarmed, corrective action can be taken to prevent serious malfunction. If programmability is not available, frequent (daily) visual inspection of the control output will determine if you are approaching the limit of control so that you may take steps to adjust the mixing valve.

Figure 2 shows the control components of Figure 1 and details of the combination reference air/probe burnoff system complete with timers, flowmeters and a sample filter to remove carbon particulates. A probe / well burnoff cycle is initiated on a regular basis, usually 12 to 24 hours. As the burnoff starts, a relay operates to disconnect power from the gas/air additive valves in order to maintain control while burnoff proceeds. After the burnoff period of 5 to 10 minutes is completed, power is restored to the additive valves and control operation is resumed. Because of the quick recovery of this system, virtually no deviation from set point can be noted.

It has become an unfortunate fact that oxygen probe control of generators has been so successful that routine manual dew point analysis becomes less and less frequent, in some cases abandoned altogether. This is a dangerous precedent. We strongly advise that dew point be checked at least once a shift, both to avoid catastrophic losses in the event of malfunction, and to maintain operator proficiency in operation of the dew pointer.
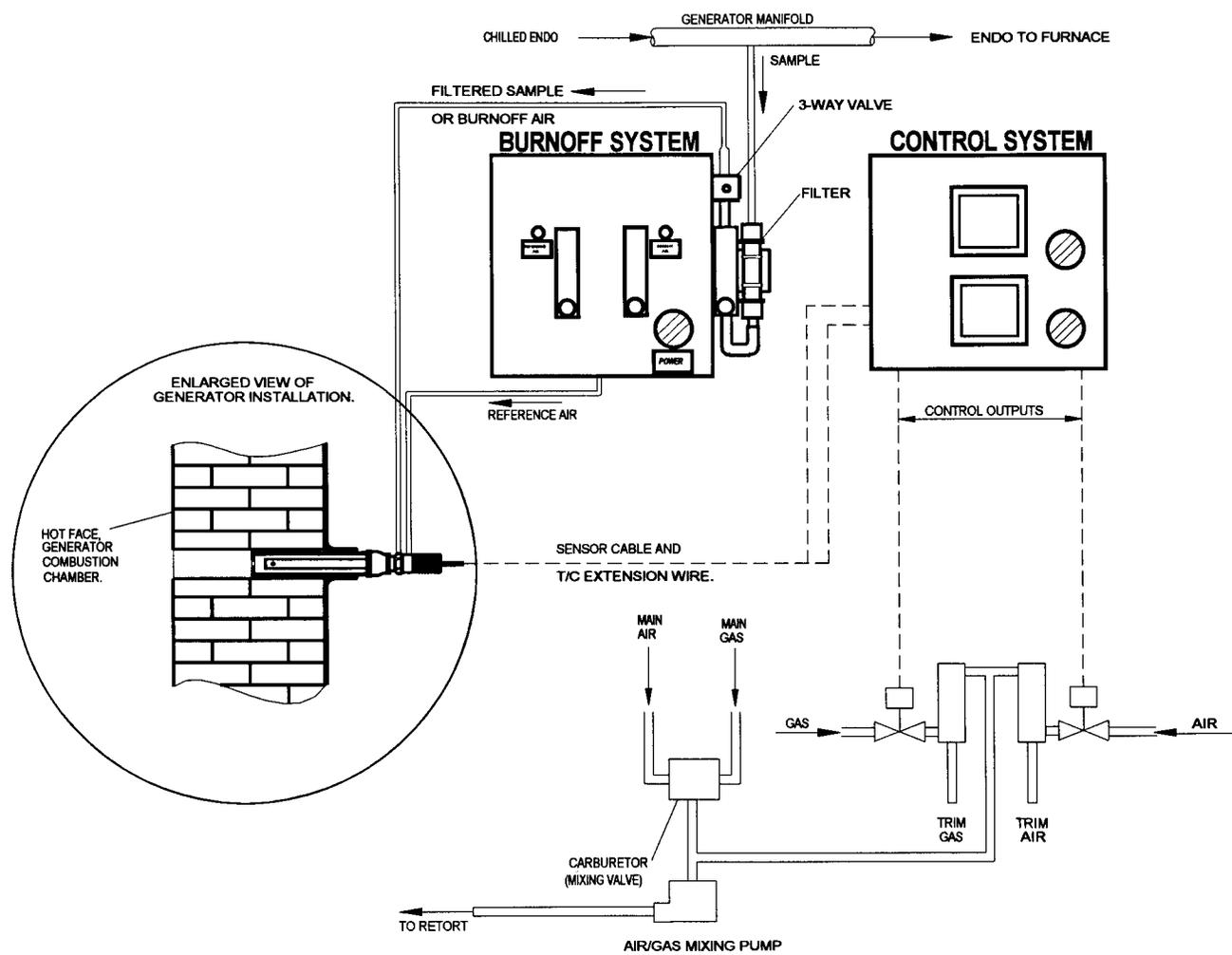
Figure 2. Endothermic Generator reheat well sampling, conditioning and control system

Dew point versus %C control?

A frequent question from owners of control instruments that do not provide the option of dew point control is, "why can't I control my generator using carbon potential?" To answer this question, let's first discuss the merits of using the oxygen probe signal to calculate and control an endo generator using dew point as the control variable. Any dew point reading displayed by the control instrument can be immediately verified by cross checking with a conventional dew point instrument, such as the Alnor. A similar verification when %C is the controlled variable could require several hours by a trained technician using shim stock analysis.... just not practical. Further, most heat treat personnel are familiar with the dew point scale for endo generators and are comfortable working with this control variable.

Finally, dew point is independent of atmosphere temperature. If we were to feed a 40°F dew point endo into three tight furnaces which were individually controlled at 1500°F, 1600°F and 1700°F, a manual dew pointer would show that each furnace atmosphere was exactly 40°F. But each would display carbon potentials of 0.85%, 0.59% and 0.40% respectively (see Table 1). To demonstrate why it is not practical to control a generator using %C as the controlled variable, consider the fact that most endo generators typically supply several furnaces. Because the flow from a generator can vary significantly, the probe temperature will correspondingly change. Refer again to Table 1. An instrument set to control at 0.6%C at a sensor temperature of 1600°F would provide 39°F dew point gas. A change of temperature to 1550°F at the same set point would deliver 45°F dew point gas. A probe temperature of 1650°F would result in a 34°F dew point. Therefore, *you cannot expect to control a generator using carbon potential as the control variable and expect the dew point to remain constant.*

TABLE 1- DEW POINT VS % CARBON, 20%C0, 40%H$_2$

%C	1500°F	1550°F	1600°F	1650°F	1700°F	1750°F	1800°F	1900°F	2000°F
0.30	73	66	60	54	48	43	38	30	22
0.35	68	61	55	49	44	39	34	26	18
0.40	64	57	51	45	40	35	31	22	15
0.45	60	54	48	42	37	32	27	19	11
0.50	57	50	44	39	34	29	24	16	9
0.55	54	47	42	36	31	26	22	14	6
0.60	51	45	39	34	28	24	19	11	4
0.65	48	42	37	31	26	21	17	9	2
0.70	46	40	34	29	24	19	15	7	0
0.75	44	38	32	27	22	17	13	5	-2
0.80	42	36	30	25	20	15	11	3	-4
0.85	40	34	28	23	18	14	9	2	-5
0.90	38	32	26	21	16	12	8	0	-7
0.95	36	30	25	20	15	10	6	-2	-8
1.00	34	28	23	18	13	9	5	-3	-10