TROUBLESHOOTING GENERATED ATMOSPHERES

Proper atmosphere control is critical to success in heat treating, and is particularly important in carburizing. And regular maintenance of both gas generators and furnaces is absolutely necessary.

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The question is often asked, "What is an atmosphere?" The simple answer: A gas that can be introduced into a thermal processing furnace with the objective of providing:

• A surface protection environment for the workload

• A controlled oxidation environment for the workload

• The introduction of elements for surface modification

Protective furnace atmospheres for heat treating fall into five main categories: endothermic, blended gases, exothermic, elemental gases, vacuum, and air. Atmospheres can be generated or synthetic, or simply gases that are premixed/prestored.

Because of the growing demand for repeatable metallurgical results, great emphasis is being placed on obtaining consistent gas analyses in various metallurgical processes. To meet this objective, it is necessary to understand the basic reactions among the industrial gases used for metallurgical processing.

Gases used in heat treating

Depending upon the application, either individual gases or combinations of gases are chosen. The principal gases used in the heat treatment of steel are oxygen, nitrogen, carbon dioxide, hydrogen, water vapor, various hydrocarbons, ammonia, and argon. More information about each gas follows.

Oxygen: Perhaps the most freely available gas, oxygen is present in many generated gases, including endothermic gases. Oxygen will react readily with iron in steel to produce iron oxide, or scale. In addition, it will react with the carbon in the surface of the steel and cause surface decarburization. Note, however, that some processes take advantage of the presence of oxygen to create a controlled surface oxidation. This is done to provide a corrosion-resistant barrier on the surface of the steel.

Nitrogen: Nitrogen is usually present in an atmosphere as molecular nitrogen, which is passive to ferrite and used most successfully in annealing

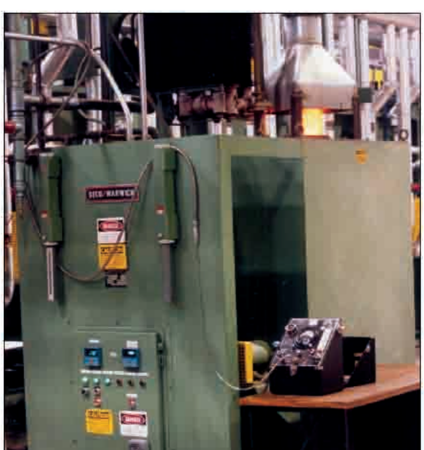

Fig. 1 — An endothermic gas generator, left, and two exothermic gas generators, right. Photos courtesy Seco/Warwick Corp., Meadville, Pa. (www.secowarwick.com).

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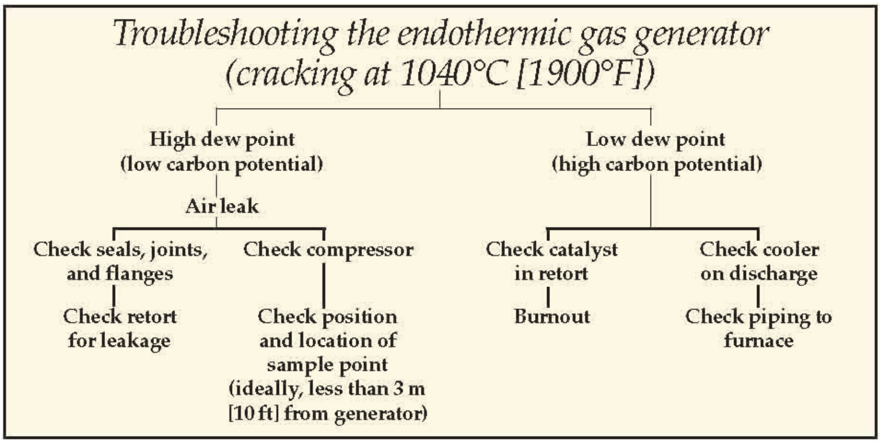

Fig. 2 — Flow chart gives basic guidelines for troubleshooting an endothermic gas generator to solve problems of high dew point (low carbon potential) or low dew point (high carbon potential). High dew points indicate that air is likely to be present.

of low-carbon steels. Clean, dry nitrogen is required for successful annealing. If the gas contains moisture, then surface oxidation and/or decarburization may result.

If atomic nitrogen is used, it will react with iron (and alloying elements) to form finely divided nitrides in the surface of the steel. Surface hardness will increase, and brittleness may result in some cases, particularly at sharp corners. (Cracking molecular nitrogen provides atomic nitrogen for a fraction of a second.)

Nitrogen is often considered a neutral atmosphere, but this is a misconception that neglects to consider how the gas behaves when heated. Nitrogen will prevent surface oxidation, but will not stop decarburization. To prevent decarburization, the carbon potential of the furnace atmosphere needs to be in equilibrium with the surface carbon potential of the steel.

Carbon dioxide: At austenitizing temperatures, carbon dioxide will react with the carbon in the steel surface to produce carbon monoxide:

$$(C) + CO_2 \rightarrow 2CO$$

This reaction will continue until there is no CO_2 available in the furnace atmosphere, or until the steel surface loses all its carbon. In other words, CO_2 is an oxidizing gas.

Hydrogen: Hydrogen is considered a reducing gas that will reduce iron oxide to iron, or copper oxide to copper. At temperatures above 705°C (1300°F), hydrogen will decarburize steel. Below 705°C (1300°F), decarburization is almost negligible. The presence of water vapor will increase the decarburizing effect because of its dissociation into hydrogen and oxygen. Hydrogen also will react with carbon in the steel surface to form methane:

$$(C) + 4H \rightarrow CH_4$$

Water vapor: If an endothermic gas generator is being operated, then the

Table 1 — Equilibrium dew point vs. percent carbon in austenite

Dew point, °F	Temperature, °F 1400°F	1500°F	1600°F	1700°F	1800°F	1900°F	2000°F	2100°F
–30								
–25	–	–	–	–	–	–	–	–
–20	–	–	–	–	–	–	1.535%	1.505%
–15	–	–	–	–	–	–	1.300%	1.20%
–10	–	–	–	–	–	1.455%	1.100%	0.925%
–5	–	–	–	–	1.235%	1.100%	0.85%	0.7%
0	–	–	–	1.65%	1.115%	0.900%	0.7%	0.575%
5	–	–	2.2%	1.35%	0.900%	0.725%	0.54%	0.45%
10	–	–	1.65%	1.05%	0.725%	0.575%	0.44%	0.345%
15	–	–	1.35%	0.875%	0.600%	0.45%	0.33%	0.275%
20	–	2.3%	1.10%	0.71%	0.475%	0.36%	0.27%	0.21%
25	–	1.75%	0.90%	0.585%	0.400%	0.28%	0.22%	0.175%
30	–	1.40%	0.775%	0.485%	0.31%	0.23%	0.18%	0.135%
35	2.6%	1.10%	0.63%	0.400%	0.25%	0.195%	0.15%	0.130%
40	2.0%	0.95%	0.55%	0.31%	0.215%	0.160%	0.12%	0.100%
45	1.6%	0.80%	0.46%	0.27%	0.170%	0.13%	0.1%	–
50	1.3%	0.65%	0.38%	0.225%	0.15%	0.11%	–	–
55	1.055%	0.54%	0.315%	0.19%	0.125%	–	–	–
60	0.85%	0.455%	0.26%	0.16%	0.105%	–	–	–
65	0.73%	0.39%	0.225%	0.135%	–	–	–	–
70	0.60%	0.33%	0.19%	–	–	–	–	–
75	0.57%	0.285%	0.165%	–	–	–	–	–
80	0.47%	0.24%	0.135%	–	–	–	–	–
85	0.40%	0.225%	0.115%	–	–	–	–	–
90	0.37%	0.200%	–	–	–	–	–	–
95	0.33%	–	–	–	–	–	–	–
100	–	–	–	–	–	–	–	–

Source: Pye Metallurgical Consulting Inc.

air that is being used to cause the endothermic reaction contains water vapor. Water vapor will oxidize the iron at the surface of the steel and also will combine with carbon in the surface to form carbon monoxide and hydrogen gases:

$$(Fe) + H_2O \rightarrow FeO + H_2$$

$$(C) + H_2O \rightarrow CO + H_2$$

This is why steam is often used as a bluing agent for steel motor laminations — if the temperature is held at around 370°C (700°F), a blue-colored surface oxide will form.

Hydrocarbons: Hydrocarbon gases are rich in carbon and can be easily cracked. Those of particular importance to heat treaters include methane (CH_4), propane (C_3H_8), ethane (C_2H_6), and acetylene (C_2H_2).

These gases will produce carbon-rich atmospheres inside the furnace chamber. The chemical activity, which will take place at the surface of the steel, will depend upon having a surface temperature high enough to decompose the carbon-rich gas into nascent carbon. Great care must be taken to select a hydrocarbon that will minimize the risk of sooting.

Ammonia: Often used for one or both of its elemental gases, ammonia (NH_3) can be a source of nitrogen for nitriding, or a source of hydrogen for a reducing process. Ammonia can be generated, or supplied as a bottled or bulk storage gas.

Argon: Argon is a true inert gas and will not react with a metal surface. It's used most often in aerospace applications, where it provides a completely nonreactive atmosphere. Argon's major drawback is cost.

Endothermic gas generators

Endothermic-based atmospheres are manufactured in an endothermic gas generator. The generator is of simple furnace construction and its principle of operation is easy to understand. The generated gas is a mixture of a hydrocarbon gas and air in very specific ratios. Air, of course, will always contain moisture, so the hydrocarbon-air mixture is compressed and passed through a nickel-base alloy catalyst heated to approximately 1040°C (1900°F). Catalytic action decomposes the gas mixture and removes heavy carbon (soot). An example of an endothermic gas generator is shown in Fig. 1.

When the process gas exits the generator, it passes through a cooler where any remaining heavy carbon

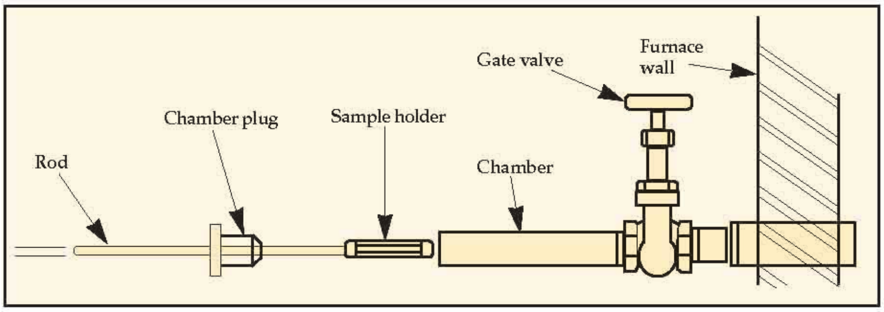

Fig. 3 — Apparatus for determining carbon potential by exposing shim stock to the furnace atmosphere and subsequently measuring its carbon content.

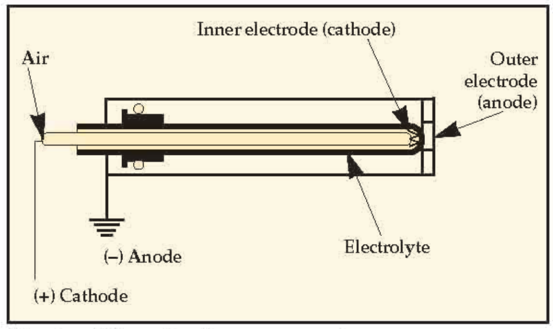

Fig. 4 — Schematic of an oxygen probe.

will condense out and be prevented from entering the process furnace. Decisions about blending the generated gas with the enriching gas are made at the furnace.

The gas produced by the generator has an approximate composition (in vol%) of 45.1 N_2, 19.6 CO, 0.3 CH_4, 0.4 CO_2, 34.6 H_2. This composition assumes an atmosphere temperature of 22°C (72°F) to produce a dew point of approximately 10°C (50°F). The carbon potential of the gas will be approximately 0.3% C, while the gas-to-air ratio should be approximately 2.8 volumes of air to 1 volume of gas. (The gas-to-air ratio will vary according to the "natural gas" source.)

Troubleshooting: If atmosphere problems arise at the furnace, it is prudent to check the performance of the endothermic gas generator. Troubleshooting may begin by following the sequence outlined in Fig. 2.

Proper functioning of the generator depends upon the performance of the nickel catalyst cubes, and it is necessary to keep them clean and clear of residual carbon. A simple burnout operation is required to ensure a clean generator that retains its ability to produce high-quality gas. To perform a burnout, turn off the process gas and reduce the generator cracking temperature to approximately 815°C (1500°F). The generator is then run with only the air compressor operating. The hot air inside the process retort will cause any residual carbon to ignite. The time needed to complete the burnout is generally between 1 and 4 hours, and depends upon the amount of carbon in the catalyst.

Table 1 shows the relationship among dew point, process temperature, and the carbon potential of the atmosphere being sampled either at the generator or the heat treating furnace (expressed as percent carbon in austenite).

Checking endo atmospheres

If it has been ascertained that the endothermic generator is functioning correctly, then the next step is to observe furnace atmosphere conditions. There are five methods of testing and controlling the furnace atmosphere:

- Shim analysis, by weight or by controlled burning
- Three- or four-gas analyzer
- Dew point
- Oxygen probe
- CO_2/infrared analyzer

The dew point method is the most common. This old but tried and tested method of atmosphere control typically is supported by one or two other methods of control, usually shim analysis (Fig. 3) and oxygen probe (Fig. 4).

Carbon potential, CP, in shim analysis can be determined using this formula:

$$CP = (W_f - W_o)/W_f \times 100\% + \%C_o,$$

where W_f = final shim weight, W_o = original shim weight, and C_o = original carbon content.

Clean parts: To ensure that no contamination is carried into the furnace with the parts, it is necessary to clean and/or degrease them to remove cutting fluids, cutting oils, and lapping compounds, which may contain chlorides, sulfides, silicones, and hydrocarbons. These contaminants can adversely affect the atmosphere in the furnace and at the work surface.

In addition, workpiece surfaces must be free and clear of oxides. Surface oxides will result in nonuniform case formation (if carburizing).

Air and water: If high dew points are being experienced in the furnace atmosphere, then it is likely that air is present. There are many ways that air can enter a furnace. First check that no door seal is broken or damaged. Then inspect any pneumatic cylinders that operate inner doors and elevators. If the furnace has an internal mechanical handling device, the drive housing mounted on the exterior of the furnace could be improperly sealed or the seal could be damaged. Yet another source of oxygen/air that is often overlooked and could contribute to high dew points is the atmosphere outside the furnace. High humidity will contribute to high furnace dew points.

A high level of water vapor in a furnace presents a serious risk of surface oxidation at process temperatures, per this reaction:

$$Fe + H_2O \longleftrightarrow FeO + H_2$$

Water vapor also will combine with carbon in the steel to form carbon monoxide and hydrogen:

$$(C) + H_2O \longleftrightarrow CO + H_2$$

Moisture in a furnace atmosphere also can lead to grain boundary oxidation, which can have a serious adverse effect on the surface of the steel, particularly if no machining will take place after heat treating.

The graph in Fig. 5 shows the effect of dew point and process temperature on the percent carbon within the heat treating furnace.

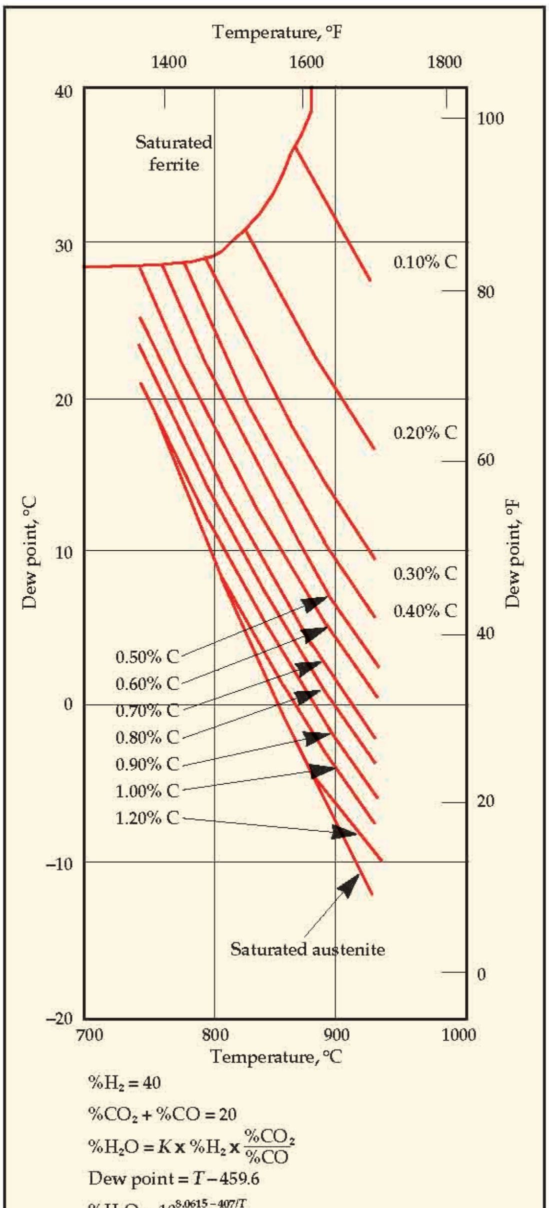

Fig. 5 — Dew point for equilibrium conditions with carbon steel of various carbon concentrations. Source: ASM Handbook, *Vol. 4,* Heat Treating, *ASM International, Materials Park, Ohio, 1991, p. 546.*

Carburizing atmospheres

To ensure a good carburized case, the carbon potential of the furnace atmosphere should be determined by the type of steel to be treated and the carburizing temperature.

Generally, an atmosphere carbon potential between the eutectoid line on the iron-carbon equilibrium diagram (~0.8% C) and a maximum of 1.2% C would be selected. If carbon potential control is not exercised, the carburized case can be adversely affected in many ways.

Examples of problems that can occur are retained austenite, grain boundary oxidation, intergranular cracking, surface cracking, low surface hardness, and carbide networking.

Enrichment gas: The carburizing furnace atmosphere consists of either:

- An endothermic carrier gas, plus a methane enrichment gas (city gas, for example)
- A nitrogen-methanol carrier gas, plus a methane enrichment gas

If it is determined that the carrier gas is being generated in a satisfactory manner and there are no problems with it in terms of dew point, then the quality of the methane enrichment gas should be checked. Major problems related to lack of control of the enrichment gas include sooting, low hardness, and grain boundary oxidation. Details follow.

Sooting: This problem is a direct result of too much carbon in the furnace atmosphere, which actually can be seen precipitating out of the atmosphere. This condition usually occurs at carbon potentials of about 1.6% C or greater. Sooting will cause furnace refractory brick to become overloaded with diffused carbon, which will lead to difficulties in atmosphere control. In addition, the surface of the steel being carburized will have a serious propensity for the formation of retained austenite.

Obvious remedies are to cut back on the enrichment gas flow or dilute the furnace atmosphere with air. Air dilution, however, increases the risk of forming grain boundary oxides and surface oxides.

If the furnace has been operated at high carbon potentials for long periods of time, it will be necessary to burn out the carbon from the refractories. Some modern furnaces feature built-in burnout systems. All the operator has to do is enter the program mode for burnout and the operation will be completed automatically.

With other furnaces, the standard procedure is to reduce the temperature to ~870°C (1600°F) and remove any atmosphere that might already be in the furnace chamber. The furnace's entry and exit doors are then opened and air is simply blown into the chamber. An external blower or a compressed air line can be used. Any carbon present in the refractory brick will subsequently ignite and burn. The temperature in the furnace will increase until all the of carbon is burned out. The process can be tracked using the furnace's temperature control instrument. Burnout generally takes 2 to 3 hours.

Low hardness: Having a carbon potential lower than the optimum can result in low hardness (insufficient carbon in the case). The cause could be an atmosphere dew point that's too low. If the carbon potential of the atmosphere is within specs and low hardness still results, the cause could be a slow (or slack) quench. Evidence of this would be excessive retained austenite or too much carbon in the surface of the steel.

Solutions to this problem include checking the furnace atmosphere carbon potential and adjusting it as re-

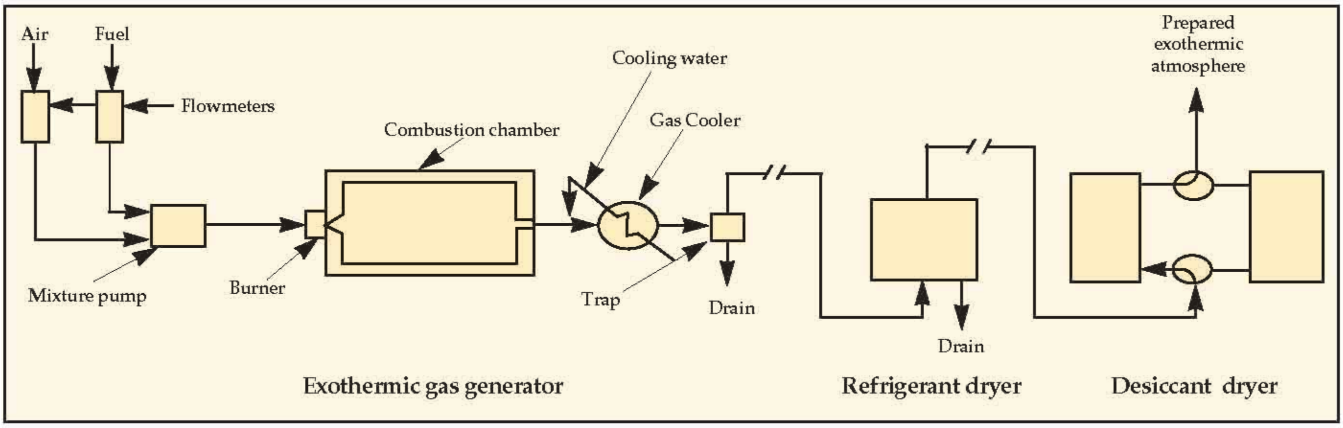

Fig. 6 — Flow diagram of an exothermic gas generator system. System components that require preventive maintenance include the refrigerant dryer. Source: ASM Handbook, *Vol. 4,* Heat Treating, *ASM International, Materials Park, Ohio, 1991, p. 549.*

quired, and making sure that the temperature of the quenchant is not too high.

Grain boundary oxides: Oxygen or moisture in the furnace atmosphere can cause grain boundary oxidation. To prevent this problem, check the furnace for potential air leaks, and measure the volume of dilution air being used and adjust accordingly. Close control of dilution air is necessary to reduce the risk of forming grain boundary oxides.

Atmosphere control: These are some of the potential problems that can result from inadequate furnace atmosphere control. Proper atmosphere control is critical to success in heat treating, and is particularly important in carburizing. Furnace operators must have an understanding of the process, how it's controlled, and the cause and effect relationships of taking corrective and noncorrective actions.

There are many aspects to the control of endothermically generated gas, as well as blended process gas, for both carburizing and hardening. The endothermic gas generator is relatively simple to both operate and maintain. Generator maintenance, however, is often overlooked; the burnout procedure in particular. If you ask a heat treater confronted with an atmosphere problem, "When did you last burn out the generator?," the answer is usually, "We don't need to." Or "What do you mean?" Burnout is an absolutely necessary maintenance procedure, and the recommended frequency is stated in the operation and maintenance manual supplied by the manufacturer. Also remember that burnout of the furnace is required to remove carbon from refractory brick, particularly when operating with high carbon potentials.

Exothermic gas generators

Exothermic gases have been used for many years as lower-cost prepared furnace atmospheres. There are two basic classes: rich and lean. The rich exothermic generator is a combustion chamber equipped with a burner and usually filled with a catalyst. The burner is supplied with a gas-air mixture having a closely controlled combustion gas-to-air ratio. Problems that occur with exothermic generators can usually be traced back to the air-gas mixing system, or to the gas cooler on the reacted-gas discharge side. Two exothermic gas generators are shown in Fig. 1.

In some instance, depending on the gas quality required, exothermically generated gas may pass through a refrigerant dryer (Fig. 6). The dryer will require preventive maintenance as called out in the operating and maintenance manual.

Prepare standard procedures

The need to troubleshoot furnace atmosphere problems can be dramatically reduced if standard operating procedures are written for both incoming material inspection and heat treating equipment operation.

Incoming material can cause considerable atmosphere problems if it has not been properly prepared and cleaned. Residual surface contaminants can cause, for example, corrosion or pitting, or an appearance problem. Oils, greases, lapping compounds, marker ink, paint, and cutting fluids should be completely removed by washing or degreasing.

Standard operating procedures for generators and furnaces also should include burnout procedures. Both the process and equipment operating procedures should be well understood by furnace operators/technicians. **HTP**

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