



CATALYST

OPERATING

MANUAL

Honeycomb Monolith Catalysts
for
Nitric Acid Tail Gas Abatement

Table of Contents

INTRODUCTION	1
CATALYST DEFINITION	1
CATALYST DESCRIPTION	1
CATALYST THEORY	1
CATALYST PERFORMANCE CURVES	ERROR! BOOKMARK NOT DEFINED.
CATALYST LIMITATIONS	1
DESCRIPTION	2
PHYSICAL DESCRIPTION	2
GAS REQUIREMENT	2
FLOW DISTRIBUTION	2
SYSTEM OPERATION	3
SYSTEM STARTUP	3
MEASUREMENT TECHNIQUES	5
NOX MEASUREMENT	5
OXYGEN MEASUREMENT	5
HYDROCARBON MEASUREMENT	5
<i>Sampling location</i>	5
CATALYST CARBONIZING	6
THEORY OF CARBONIZING	6
RECOGNITION OF CARBONIZING	6
PREVENTIVE MEASURES	7
CATALYST AGING	8
WARNING SIGNS	8
REJUVENATION	8
MAINTENANCE	8
CATALYST CLEANING PROCEDURE	8

Introduction

Catalyst definition

Catalyst *n.*: a substance that alters the rate of chemical reaction and is itself unchanged by the process. Catalytic presence in the process stream will produce a higher rate of reactivity at lower temperature, and a higher rate of efficiency at lower temperatures than what could be achieved under noncatalytic conditions. As noted, the catalyst itself will not become involved in the reaction, therefore theoretically it will perform indefinitely. However, factors discussed later in the manual will have a strong effect on catalyst life and efficiency.

Catalyst description

The EnProSol, Inc. catalyst manufactured for the NO_x reduction application is a high surface area, precious metal catalyst, deposited on ceramic honeycomb support. The catalyst consists of six layers of a platinum/palladium coating, twelve layers of a platinum coating, and two layers of a platinum/rhodium coating. The layers are organized in a specific order to provide low light-off temperature and high temperature stability.

Catalyst theory

The EnProSol, Inc. catalyst for this application is designed to operate with natural gas or its components, e.g., butane or propane. When natural gas is introduced into the catalytic combustor the natural gas will react with O₂ and NO_x to form N₂, CO₂ and H₂O. NO_x reduction is a nonselective catalytic reduction and it will occur only under oxygen deficient conditions. The first rate reaction will be between O₂ and CH₄ creating CO and H₂O. Some CO₂ will be created at the first rate reaction. The second rate reaction will be between free carbon, CO and NO/NO₂. Therefore it is necessary to operate the reactor slightly fuel rich to create enough thermal inefficiency to create sufficient amounts of CO to react with the NO/NO_x combination. The first reaction will be a conversion of NO₂ to NO. This is fairly quick reaction and it will occur under oxygen rich conditions. Although, at the start there will be no immediate NO_x reduction, visible color will disappear. The complete reaction of the available oxygen and an operation slightly above stoichiometric is necessary to accomplish the degree of reduction necessary.

Catalyst limitations

The catalyst supplied by EnProSol, Inc. is designed for a nonselective catalytic operation with continuous air flow and maximum catalyst exit temperature of no higher than 1410°F (765°C).

Description

Physical Description

The EnProSol, Inc. NO_x abator catalyst provided consists of multiple layers of precious metal coated honeycomb ceramic substrate.

Substrate size: 150mm x 150mm square x variable depth

Cell density: 230-300 cpsi (cells per square inch)

Precious metal distribution:

Pd Inlet Layers: Typically 10% of total volume

Pt Middle Layers: Typically 60% of total volume

Pt/Rh Bottom Layers: Typically 30% of total volume

Gas requirement

The EnProSol, Inc. NO_x abator catalyst can be used with a variety of fuels, e.g., natural gas, butane, propane, purge gas and other hydrocarbons. Theoretically, the catalytic abator requires 1:1 Mole ratio of CH₄ vs. O₂ and NO_x. However, to maintain 1:1 ratio will require almost perfect gas mixing. Therefore, the recommended CH₄ to O₂ and NO_x ratio is 1.03 : 1 or no more than 1000 ppm of excess hydrocarbons.

Flow Distribution

It is imperative that the inlet gas flow to the abator be well mixed and evenly distributed across the catalyst surface.

WARNING

Uneven flow will create "hot spots". The injected CH₄, unless thoroughly mixed, will linearize and create concentrated areas of reaction, resulting in excessive temperature rise. The excessive temperature increase can both deactivate the catalyst as well as physically destroy the substrate. This can occur without the operator ever recording or noticing anything unusual.

System Operation

System Startup

The EnProSol Inc. catalyst in this plant is designed to operate with purge gas, at an inlet temperature to the abator of no less than 480°F for purge gas and 900°F for natural gas.

Abator startup:

- 1 Insure that the plant is stable and there are no flow variations.
- 2 Check the inlet temperature to the abator. Confirm that the temperature is above the minimum requirement.
- 3 Check the outlet temperature to the abator. Confirm that the temperature is the same or above that of the inlet temperature.

WARNING

Although the inlet temperature to the abator is above the light-off point, the catalyst is a significant heat-sink, and the actual catalyst temperature will be lower than the inlet temperature. During the startup, allow enough time for the bed temperatures to equalize.

- 4 After confirming that the inlet and the outlet temperatures are above the light-off temperature, start injecting purge gas.
- 5 Start injection at 50% of required gas flow. Continuously monitor the exit temperature.
- 6 Confirm that the inlet O₂ concentration to the abator is within the required safety limits. At this point it should be within 10-15 % from the final operating concentration.
- 7 Confirm that the catalyst temperature rise agrees with the calculated temperature increase.
Calculate the temperature increase by:
Multiply % O₂ reduced by ~247°F
Multiply % NO_x reduced by ~157°F
Example: Inlet temperature = 900°F
 % O₂ reduced = 1.2
 % NO_x reduced = 0
 Outlet temperature = (1.2 x 257) + 900 = 1208°F
- 8 Continue to slowly inject the purge gas (10 % at a time) until you reach the desired NO_x concentration.

WARNING

There will be a short lag between the gas injection and the outlet temperature indication. The NO_x reduction will occur instantly.

- 9 Let the system stabilize. Trim the bleach air as necessary to remain within the temperature limits.
- 10 Measure excess hydrocarbon in the exhaust.

WARNING

To minimize carbon built-up on the catalyst and extend the catalyst life, the HC concentration throughout the life of the catalyst should not exceed 1000 ppm. This concentration should be closer to 300 ppm on the startup. With age the catalyst will require slightly more CH₄ and consequently the HC bypass will be greater.

- 11 If the plant is not equipped with an HC monitor, once the plant is stable perform the following:
 - 11.1 Calculate temperature increase based on O₂ and NO_x using the formula in item 7. Confirm that the actual and the theoretical increases are within range.
 - 11.2 Trim back the CH₄ injection (1-2% of total flow) in 15-20 minutes intervals until the NO_x begins to increase.
 - 11.3 Back-up to the last gas flow setting prior to the NO_x concentration change. This should bring the plant gas (CH₄) flow to the best fuel/NO_x ratio.

Measurement techniques

NOx measurement

There are several approaches to NOx measurement. They encompass everything from UV, chemical cells to chemiluminescence technologies. The preferred method by EnProSol, Inc. is a chemiluminescence method available from the large number of sources. It is particularly important to select a proper measurement method for the continuous monitoring of NOx in nitric acid plants. High level of NOx and residual CO and hydrocarbons can have both a detrimental effect on the analyzer as well as interference resulting in erroneous readings.

Oxygen measurement

As with the NOx measurement, oxygen measurement can be accomplished by a variety of measuring techniques. Although it is up to the individual customer to select the best possible method for their application EnProSol, Inc. recommends Zirconia based oxygen analyzers.

Hydrocarbon Measurement

Continuous excess hydrocarbon measurement is probably most critical parameter relative to catalyst life and performance. Excess hydrocarbons are necessary for the NOx reduction, but if not tightly controlled they will have an adverse effect on the catalyst. The section “Catalyst Carbonizing” further addresses this situation. Prototech recommends a quality flame ionization, total hydrocarbon analyzer.

Sampling location

It is imperative that the sample be taken at the proper location and that the sample is treated before analyzing. The sample should be extracted well after it is thoroughly mixed. There should be a length of a straight run of no less than 8 times the pipe diameter between the catalyst vessel and the sample point. The sample entering the analyzer must be dry and free of contaminants.

Catalyst carbonizing

Theory of carbonizing

Nonselective catalytic reduction is conducted under hydrocarbon rich conditions. These highly reducing cycles will cause a solid fuel accumulation. Both hydrocarbons and carbon monoxide will deposit on the catalyst surface and start blocking active catalyst sites. This solid fuel accumulation and its subsequent ignition (depending on the carbon accumulation) may result in high excess temperature. Due to a great catalyst mass this temperature rise may not be detected by the bulk tail gas thermocouple. Most likely it will be localized and create hot spots. If this condition is not kept in check it will result in catalyst damage. Potential damage could extend beyond the catalyst to the catalyst basket, vessel and expander.

Recognition of Carbonizing

Carbon accumulation can be tracked by two significant ways.

You can monitor the carbon accumulation by monitoring the ratio of natural gas consumption per ton of acid produced and it against graph excess fuel ratio. This method requires a relatively long catalyst run and catalyst/fuel monitoring.

A more accurate and reliable method, especially on start up of new catalyst charge, is to monitor catalyst NO_x destruction capability. At the start, after setting proper natural gas to NO_x ratio, it is important to log gas usage vs. acid production. Over the next 30-45 days careful observation will reveal a slight but continuous NO_x increase under steady conditions. Over time the catalyst will adsorb carbon and become slightly inefficient. At this point the operator should perform several checks to determine if:

- Catalyst is carbonizing
- Catalyst is aging
- Process conditions have changed

- 1 Catalyst is carbonizing. If this condition is occurring, the operator should do the following:
 - At the rate of no more than 5% of total fuel gas flow, start reducing fuel gas input to the abator.
 - Closely monitor catalyst exhaust temperature.
 - Closely monitor NO_x and O₂ concentration.
 - Exhaust temperature should slowly start rising. Temperature rise will be directly proportional to the amount of hydrocarbons available and excess oxygen.
 - Continue reducing gas input to the abator until NO_x concentration starts rising.
 - At this point maintain the fuel rate for a period of 4-5 minutes.
 - Return to normal operation.

WARNING! You must monitor NO_x concentration so as not to exceed allowable limits.

- 2 Catalyst is aging. With time the catalyst will lose its effectiveness due to several factors. The most important factors in the catalyst aging process are excess temperature and contaminants from the process flow; i.e. dust, oil, loose insulation, sulfur in the natural gas, etc. When this condition develops the operator will notice that regardless of the amount of natural gas injected, and after performing the above described procedure, there will be no change in the NO_x reduction. Another indicator of this condition will be a need for higher light-off temperature at the start-up.
- 3 Process conditions have changed.

BEFORE ATTEMPTING CATALYST REBURN CHECK THE ACCURACY OF THE OPERATOR LOGS AND THE PROCESS CONDITIONS.

Preventive Measures

Although there is no known way of preventing carbon build up on catalyst, the length of the run between regeneration can be greatly extended by the careful monitoring of excess gas injected into the catalytic abator. At no time should excess natural gas exceed 15% of stoichiometric.

Catalyst life also will be greatly prolonged by reducing the amount of contaminants in the process. This may include a high degree of air filtration, corrosion monitoring, etc.

Catalyst Aging

Warning Signs

There are several indicators that an operator can use to determine the onset and the extent of catalyst aging.

With age the catalyst will require higher and higher light-off and operating temperatures to sustain gas burning and NO_x reduction. By carefully logging these changes the operator can establish the catalyst aging trend. This will be different for every installation.

Rejuvenation

To maintain the catalyst at its best performance the operator of this catalytic abator should follow the instructions under the Maintenance section.

Maintenance

Depending on the severity of operation the catalyst should be periodically cleaned.

Catalyst Cleaning Procedure

Field maintenance of the NSCR catalyst is limited to high temperature de-carbonization and dust removal. If the operator determines that the temperature rise has diminished from when the catalyst was fresh, it is recommended that he contact EnProSol, Inc. for guidance regarding its rejuvenation. It is possible for the operator to perform a couple of operations to try to reclaim some of the catalyst performance.

High temperature de-carbonization is to be accomplished according to the procedure in the section Recognizing Carbonization.

If the pressure drop across the catalyst has been increasing, then it will need to have accumulated dust removed. This procedure should be performed after the high temperature de-carbonization. The catalyst can be blown out using an air lance at not more than 80 psi. Do not use high pressure steam since this could result in a loss of precious metals from the surface of the catalyst.

If either or both of these procedures do not satisfactorily return the catalyst performance, then it will need to be chemically rejuvenated. Any changes in catalyst performance should be noted in the performance log.