UNDERSTANDING CATALYSTS
A Handbook for the User

Part 1: Series Introduction, Misconceptions and Definition of a Catalyst

This is the first of a multi-part series aimed at helping you, the catalyst user, understand how catalysts are designed, produced and maintained.

There is probably not another piece of equipment you use daily that you know so little about other than the catalyst in your converter or combo. But you shouldn’t feel bad about that because not telling you how the catalyst is designed and manufactured has been the “Standard Operating Procedure” for years. Now though, with the ever-tightening regulatory situation, that has to change if you are to keep in compliance and keep moving gas.

In this series we’re going to discuss the choices and decisions that go into:
- Substrate design
- Washcoat composition
- Active components (ie: Precious Metals)
- Operating parameters and influences
- Challenges posed by the engine exhaust system

Our goal is that when the series concludes, you will be a more knowledgeable user of catalysts, and be more assured with asking questions of your catalyst supplier.

Let’s get started.

This “magic box” diagram illustrates what we’ve learned from you is a common perception of how a catalyst works:

While such a concept may work for Harry Potter, it is not reality and perhaps leads to the biggest myth or misconception of all about catalysts … that catalysts destroy pollution. But they do not. What we call pollution is a collection of molecules that contribute to the formation of smog and other undesirable conditions. Molecules are composed of atoms such as carbon (C), nitrogen (N), hydrogen (H) and oxygen (O). Therefore, pollutants in engine exhaust such as NOx (NO and NO2), carbon monoxide (CO), and hydrocarbons such as propane (C3H8), are just specific combinations of these atoms.

So what a catalyst really does is takes molecules apart and rearranges the atoms to form molecules that are better for the environment. For instance, here are a few of the chemical rearrangements that happen as the molecules pass through the catalyst.

You can see that the same atoms come out of the catalyst as went in, but they have been changed by the action of the catalyst.

Also notice that there are no additional atoms seen coming out of the catalyst that represent the atoms in the coating. By definition, a catalyst changes the rate of a chemical transformation while not being consumed by the chemical reaction. They do this by altering the amount of energy (in our case, heat) needed for the reaction.

In simpler terms, you can think of a catalyst as a chemical machine, one that manipulates atoms from one form to another, more quickly and at lower temperatures, than would naturally occur without being used up in doing the work.

ABOUT THE AUTHOR
John W. Robinson, Jr.
Catalytic Combustion Corporation
Vice President, Catalytic Group

Education
University of Oklahoma – B.S. Chemical Engineering

Experience
John has more than 20 years of experience in the catalyst industry. Previous to Catalytic Combustion Corporation, he was an applications engineer and product specialist for AlliedSignal Environmental Catalyst Company. He has also served as product manager for Degussa Chemical’s Stationary Emissions Control group.

His work history includes all facets of catalyst engineering from formulation development, substrate design, process modeling for sizing calculations, and deactivation studies for both traditional and new catalyst applications.

For your catalyst questions, contact:
johnrobinson@catalyticcombustion.com
Phone: 715-568-2882 Ext. 127
Fax: 715-568-2884

IN THE NEXT ISSUE …
“The bigger world of catalysts, and a brief history of engine catalysts.”

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The realization that in the presence of certain materials an enhanced chemical reaction would occur was discovered in the late 1700s and early 1800s by several European chemists. In 1835, Swedish chemist Jöns Berzelius used the term “catalysis,” a derivation of two Greek words, to describe an unknown force that promoted chemical reactions. Over the next century, a number of dedicated chemists and engineers made subsequent discoveries in the field of catalysis that have greatly improved our standard of living.

Engines and Catalysts
The use of catalytic converters on cars dates back just to the 1970s, but their earlier history is a story of the interplay between science and engineering, politics and bureaucracy, and health and economics.

The sequence of events began in 1947 when California created regional air pollution control districts over concerns about the health effects from the increasingly frequent smog days. In 1952, studies concluded automobile exhaust was the primary source, and using catalysts to control the emissions was identified as the technology of choice. Development didn’t come quick or easy, with too many details to recount in this series, but it is important to note the major hurdles that had to be addressed:

- Determination of what pollutants to control
- Determination of substrate type and format
- Comparison of the performance and durability of precious metals vs. base metals
- Temperature stability of the coating
- Resistance to poisoning and inhibition from lubrication oil and fuel contaminants

The effort culminated with the installation of the first catalytic converters on 1975 model-year cars. Initially they were just oxidation catalysts capable of controlling carbon monoxide (CO) and hydrocarbons, and required the use of an air pump under the hood to function. In 1978, the single greatest development occurred with the invention of the 3-way catalyst and the electronic air fuel ratio (AFR) control system, allowing the simultaneous conversion of nitrogen oxide (NOx), CO and hydrocarbons. Millions of cars later, we have now become so accustomed to the effectiveness of catalytic converters that we can tell from the smell alone when we’re driving behind a pre-catalytic converter model.

The highly sophisticated catalysts in our cars and trucks today are the result of 40 years of ongoing research, and the catalysts used on your industrial engines are their direct descendants.

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John W. Robinson Jr., V.P. Catalyst Group
jrobinson@catalyticcombustion.com
Phone: 715-568-2882 Ext. 127 • Fax: 715-568-2884

www.CatalyticCombustion.com

IN THE NEXT ISSUE …
“Building a catalyst, Part 1”
Part 3 – Building a Catalyst, Step 1 – Forming a Substrate

The structured monolith has emerged as the clear choice for the catalyst form used in industrial engines. Its three layers - substrate, washcoat and catalytically active materials - all play vital roles in the performance of the catalyst. Let's begin with the substrate.

Substrate
The substrate is more than just the framework that supports everything else so exhaust gases can come in contact with the catalytically active layer. The majority of substrates used for industrial engines are an Iron-Chrome-Aluminum alloy that has been rolled into a .002 inch thick foil strip. Foil is preferred for industrial engines, instead of the ceramic substrates typical in automobiles, because of the vibration, duty cycle changes and misfires it must endure.

Before substrate manufacturing begins, choices have to be made regarding the shape needed, the size of the cells (cell density), the cells longitudinal pattern and the inclusion of brazing materials or mechanical locks. Housings for round, rectangular, and other multi-sided shapes are in use and each shape has its pros and cons regarding installation and sealing effectiveness. Cell density is expressed as the number of cells per square inch, or cpsi. The most common cell densities are 200-400 cpsi, but they can range from 100-1,000 cpsi.

The longitudinal pattern of the substrate can be straight, herringbone (zig-zag), or angled from one face to the other. The combination of cell pattern and cell density provides a balance between maximizing the contact between the exhaust and the surface of the catalyst, which directly affects the performance of the catalyst while minimizing the backpressure on the engine.

The foil arrives on coils containing several thousand feet of foil already slit to the desired flow depth of the pattern. The cell structure is achieved by corrugating the foil with special gear forms, progressive die forming or a pleating process. Then the foil can either be formed into the substrate shape or it begins the coating process, depending upon the manufacturer's process. For this discussion, we will follow the first path and assume that a round element is being made.

To make a round substrate the corrugated foil is combined with a layer of flat foil and is wound around a hub or mandrel. Winding is done under tension to keep the substrate flat and resist deformation from its own weight. Substrate size is limited by the catalyst manufacturer's downstream coating equipment, but elements as large as 72 inches have been produced.

Over the years many solutions to prevent the commonly seen sagging or “telescoping” failure mode have been implemented. Inserting rods through the foil across the diameter of the substrate, using retaining bars either laid across or placed flush with the faces of the substrate, and incorporating a “lock and key” pattern into the foil corrugation pattern have been tried with various degrees of success. By far the most robust method applies a brazing alloy or compound during the winding operation, which after being processed at high temperatures and vacuum levels approaching that of outer space, weld the layers together into a unified whole.

At this point our wound, brazed substrate is complete and ready for the coating process.

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John W. Robinson Jr., V.P. Catalyst Group 
jrobinson@catalyticcombustion.com
Phone: 715-568-2882 Ext. 127 • Fax: 715-568-2884

IN THE NEXT ISSUE...
“Building a Catalyst, Step 2 - The Wonderful World of Washcoat”
What is Washcoat and Why is it Important?

Simply put, the washcoat’s role is to provide more surface area on which to deposit the precious metals. Even though it takes many feet of foil to produce a substrate, overall it has fairly little surface area. Coating bare foil with precious metals would yield a catalyst that would have relatively poor activity, so it would take very large catalyst elements to reach high levels of control efficiency. Washcoating the foil changes the available surface area dramatically.

A washcoat is primarily composed of highly porous crystalline forms of aluminum oxide (aka: alumina) that have a massive surface area in a small amount of material. The surface area in a pound of Gamma Alumina spread out into a single flat layer would cover just shy of 1 million square feet. One cubic foot of catalyst will typically have 6-9 lbs of washcoat. Spreading the precious metals out over such a vast area yields the numerous active sites where the chemical reactions take place.

In addition to alumina, or other very porous compounds, other additives are blended into the washcoat to promote the chemical reactions, stabilize the crystalline structure for temperature stability or to give the catalyst the ability to absorb some amount of catalyst poisons without immediately losing its activity. One additive, cerium oxide, has the ability to “store” oxygen in its molecule and thus is a key step in NOx control by a 3-way catalyst.

The precious metals may be the glamorous portion of the catalyst, but the work put into developing and refining washcoats is constantly ongoing to improve both the efficiency and durability of the catalyst.

Applying Washcoat

Making washcoats involves blending alumina powder, rare earth oxides and other compounds together with water and acid to form a slurry. It is then milled to reduce the particle size to between 5-10 microns and finally has its pH and solids content adjusted to yield the viscosity and density needed for coating.

A substrate is prepared for coating by being heated to around 1,700°F and held there for several hours to oxidize its surface. The aluminum in the alloy migrates through the metal toward the foil’s outer surface where it reacts with oxygen from the air to form “whiskers” of aluminum oxide. This is not the same high surface area aluminum oxide found in the slurry but instead forms the basis for a chemical and mechanical bond with the washcoat.

When the oxidized substrate’s cells are filled with slurry, there is an electrostatic attraction between the foil and the solids in the slurry. Over several minutes this attraction forms a loose layer over the foil’s surface. After soaking, the substrate is air knifed to remove the excess slurry which leaves a thin film of washcoat behind. The washcoat is then dried and cured at 1,000°F where the washcoat becomes strongly bonded to the foil due to the chemical similarity of the washcoat’s alumina and the whiskers growing from the foil, as well as from a Velcro-like mechanical interaction between them.

Two or more washing cycles are needed to reach the catalyst’s desired amount of surface area. Trying to achieve it all in a single step can result in a poor washcoat that easily flakes off.

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jrobinson@catalyticcombustion.com
Phone: 715-568-2882 Ext. 127
Fax: 715-568-2884

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The development of catalytic converters for cars teaches us that the precious metals platinum, palladium and rhodium outperform other catalytically active elements in performance and durability, and offer a wide range of versatility for controlling engine exhaust pollutants.

Which ones to use?

For 3-way catalysts used in rich burn engines, rhodium is used for NOx control while platinum and palladium function for converting carbon monoxide (CO) and hydrocarbons. So a typical 3-way catalyst is composed of platinum or palladium, in combination with rhodium.

An oxidation catalyst for lean burn engines will often be a combination of platinum and palladium, since CO and hydrocarbons (including hazardous air pollutants (HAPs), i.e. formaldehyde) are what is required.

The choices made also take into account the susceptibility of the each metal to poisoning, and their interaction with the washcoat and its role in the chemical reaction.

What is the loading?

At the low end of the spectrum is having the minimum amount of metal needed to get the reaction going. On the opposite extreme is the point where adding more metal does not improve performance. In between lies the optimized loading that gives the conversion efficiencies required for an acceptable lifespan. Performance is also affected by the amounts of the metals in the coating relative to each other. A complete coating description will give you the total metal loading and the ratio between the metals.

What is your catalysts?

The loading and ratios can vary greatly from one catalyst manufacturer to another, and many don't share that information. Whether this is a good policy or not is for you to decide, but either way, it does have an impact on performance.

How these decisions affect you

Consider this example as how it all works: You have two catalysts of the same size, cell pattern and precious metal ratio installed in two identical engines. One catalyst has a loading of 25 g/ft³ and the other is at 50 g/ft³. Initially they both may reach the needed control efficiencies, but what happens as ash begins to build up on the catalyst's face or if cell openings get bent over?

During manufacturing, the precious metals were distributed into the pores of the washcoat and on its surface all along the walls of the cells, where they are found in the form of metal crystals containing a few atoms to several hundred atoms.

Thus a heavier loaded catalyst will have many more crystals along the walls of each cell than the more lightly loaded catalyst. As cells are blocked off, it retains a greater opportunity for the pollutants to be converted. This durability translates into the heavier loaded catalyst lasting longer before it requires either washing or replacing.

So how do you evaluate what you are getting? The best answer is to ask the catalyst vendor what the loading is. Given the volatility in the global precious metals market, lighter loadings or ratios using lower priced metals are strategies used to keep prices down but may not necessarily be the best solution for performance or longevity.

Price versus frequency of replacement, in conjunction with the expense of additional elements, plus the costs of labor time and lost production during the change out, must all be considered when evaluating catalyst purchases. So is making sure your engines comply with regulations, as fines and/or shut-downs can make a lower price an expensive alternative to quality.

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John W. Robinson Jr., V.P, Catalyst Group
jrobinson@catalyticcombustion.com
715-568-2882 Ext. 127 • Fax: 715-568-2884

IN THE NEXT ISSUE …
“The Mystery of Catalyst Sizing”

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So far in this series we have focused on building a catalyst. Now it’s time to discuss the process for sizing a catalyst for your engine. Remember that a catalyst works by rearranging the atoms in molecules to form less environmentally harmful compounds. Proper sizing of the catalyst determines the percentage of the incoming molecules that must be rearranged to meet the required performance level as set by your operating permit.

For any combination of catalyst formulation and substrate, the variables of temperature and space velocity are what the applications engineer can manipulate to achieve the needed control efficiency. Temperature provides the energy for the chemical reaction, and space velocity sets the amount of time that a molecule has to come in contact with the active sites of the coating as it passes through the catalyst cells. Let’s spend some time reviewing each of these variables and their effects on the performance of the catalyst, starting with temperature.

Temperature Effects

As mentioned earlier, the energy required for the catalyst to initiate the reaction comes from the temperature of the exhaust. The performance can be dramatically affected by changes in exhaust temperature. EPA has set minimum catalyst temperatures for both rich burn and lean burn engines as a guide on what temperatures are needed, but the catalyst manufacturer should also provide the minimums for their products.

When a catalyst manufacturer recommends a minimum temperature, they look at data similar to what you see in the graph below. This is a light-off curve, and it shows the change in catalyst performance vs. temperature for a compound for a specific catalyst formulation, substrate cell pattern and space velocity (more on space velocity next month). Every compound has its own unique light-off curve for a given set of these parameters.

For the example compound shown in the graph, there are three regions to consider. Notice that below 250°F, the performance is minimal and the catalyst lacks sufficient energy for the reaction to begin. However, as the temperature increases between 250°F and 600°F, the efficiency goes from less than 5% to just over 90%. In this region the catalyst’s efficiency is limited by the rate of the chemical reaction itself and the amount of time that it takes the molecules to move from the gas stream into the pores of the washcoat to reach the precious metal sites. As you can see, small changes in temperature can result in large changes in performance. Above 600°F, the graph flattens out and reaches its maximum performance. In this region, the chemical reaction itself is nearly instantaneous, and the efficiency is limited solely by the ability of molecules to move from the flow through the cells to the surface of the coating, which has gotten faster as the temperature has increased. This final region is where we want the catalyst to operate.

However, temperature is constrained by the engine itself based on whether it is rich or lean burn, the heat content of the fuel, and whether or not it is turbocharged or naturally aspirated. What comes out of the exhaust connection on the engine is thus fixed at the highest temperature the catalyst could see. When deciding where to locate a catalyst it is critical to know the temperature of the exhaust where the housing will be installed, not just the temperature at the exhaust connection on the engine, especially for engines that normally have lower exhaust temperatures.

Have you ever seen a catalyst that works fine in summer, but struggles during winter? Assuming that the engine is running as expected and nothing else has damaged the catalyst, where do you think it is operating on its light-off curve? Check to see if the exhaust temperature at the catalyst inlet has cooled down below the manufacturer’s specification and if it has fallen too low. See if you can relocate the catalyst closer to the engine or insulate the exhaust piping to the catalyst housing.

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715-568-2882 Ext. 127 • Fax: 715-568-2884

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IN THE NEXT ISSUE …
“What the Heck is Space Velocity?”
Definition of Space Velocity

The term “Space Velocity” sounds like it should apply to satellites and rockets, right? Instead, it is a term used by catalyst engineers to describe the fractions of a second that it takes a segment of exhaust gas to pass from the catalyst’s inlet face to its outlet face, in a format that makes it easier to compare one catalyst to another.

Space velocity is defined as follows:

\[
\text{Space Velocity} = \frac{\text{Exhaust Flow (standard cubic feet/hour)}}{\text{Catalyst Volume (cubic feet)}}
\]

When you do the math, you end up with numbers that have units of measure with only hours in the denominator. For this reason, it is often called Gas Hourly Space Velocity or GHSV. For example:

\[
\text{Space Velocity} = \frac{4.650 \times 60}{1.46} = 108,904 \text{ hr}^{-1}
\]

To find the residence time in seconds you would take 3,600 seconds/hour and divide it by the GHSV value, which, for our example yields a residence time of 0.033 seconds. Now you can see that by using the larger GHSV numbers, even with the unusual units of measure, that the calculation yields make it easier to discuss catalysts than using seconds with three or four decimal places.

How Space Velocity is Used to Size a Catalyst

When a catalyst is developed for a given application, it is run through a series of trials to determine its operating limits. This involves passing a known amount of a compound through the catalyst over a range of temperatures at a specific space velocity, which yields the conversion efficiency of the catalyst for those conditions. The process is repeated at other space velocities and with other compounds to build a performance database for that catalyst. Figure 1 is a representative illustration of this data. Every compound will have its own unique set of curves for a given catalyst formulation and substrate combination.

Notice that space velocity and performance have an inverse relationship: as the space velocity increases, the performance of the catalyst decreases. This makes sense for a given catalyst volume because as the space velocity increases, the exhaust flow rate has to increase. Therefore, the amount of time that a compound has to move from the gas stream to the surface of the catalyst decreases.

When sizing a catalyst for an engine, an applications engineer will calculate the conversion efficiency for a compound based on the raw emissions from the engine and the limits of the operating permit. Engineers will then refer to their data to find the space velocity that yields that conversion efficiency for the temperature of the exhaust gas at the inlet face of the catalyst.

When evaluating an exhaust with several compounds that have different operating permit limits, engineers will normally select the space velocity for the compound that has either the highest performance requirements or is the hardest to convert for the sizing calculation. This means that the expected performance for the other compounds will end up being better than required.

Once they determine the space velocity required, they calculate the size of the catalyst using the exhaust flow rate and the equation above. Good practice dictates that a safety factor is used to allow for flow blockages inside the housing and to allow some loss of performance due to ashing or other deactivation mechanisms. Then you’ll arrive at the final size of the catalyst, which is then slightly larger than the calculation yields.
Now we turn to putting our completed catalyst into service, controlling emissions by properly sizing it for the efficiency level it must reach so that your engine is in compliance with your operating permit.

What Information is Needed

The applications engineer will need to know the engine model, its rated horsepower, fuel type, the exhaust flow rate, exhaust temperature, backpressure limitations, the uncontrolled emissions and the permit levels the catalyst has to achieve. For many engines, most of this information is available either from the engine manufacturer’s manuals or online, but not always, and generally not for engines made prior to the 1980s. If the engineer does not have data on your engine, you may be asked for the bore, stroke and number of pistons, the engine’s running speed, and the measured levels of NOx, CO, hydrocarbons and oxygen in the exhaust.

Where’s the Target?

Determining the catalyst’s Conversion Efficiency % (CE%) uses the raw emissions coming to the catalyst and the permit levels the engine has to achieve. It is calculated with the following equation:

$$ CE\% = 1 - \left( \frac{\text{Permit Limit}}{\text{Raw Emissions}} \right) \times 100\% $$

When doing this calculation, the units of measure for the raw emissions and permit level must be the same. As long as they are the same, you can do this calculation with g/bhp-hr, pounds/hour, tons/year or ppm.

How Big is that Catalyst in the Window?

Once the CE% for all the pollutants is known, the engineers will determine which catalyst formulation is required for the type of engine. Then they will review performance data for the substrate type and cell density they want to use to see what space velocities are needed to reach the CE% for each of the pollutants. Whichever pollutant requires the lowest space velocity to reach the CE% sets the value for that design.

Typically a safety factor is added to this space velocity to allow for blockages of the catalyst face inside the housing, ashing and other deactivation mechanisms. Doing so means that the initial performance will be greater than this and that the catalyst has a reasonable lifespan before needing to be washed or replaced. This effective space velocity is then used with the exhaust flow rate (in SCFM) to calculate the volume of catalyst required. A selection is then made from the available element diameters and depths to yield at least this amount of catalyst volume.

Here’s an example of how, in general, the process would work for a three-way catalyst on a rich burn engine.

Example

Engine: XYZ

Exhaust Flow: 6,165 acfm at 965°F which calculates to 2,293 scfm (70°F reference temperature)

Design Safety Factor: 15%

<table>
<thead>
<tr>
<th>Raw Exhaust</th>
<th>Permit Level</th>
<th>CE%</th>
<th>GHSV Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx 11.4 g/bhp-hr</td>
<td>1 g/bhp-hr</td>
<td>91.2%</td>
<td>116,450 hr⁻¹</td>
</tr>
<tr>
<td>CO 10.5 g/bhp-hr</td>
<td>2 g/bhp-hr</td>
<td>81.0%</td>
<td>145,687 hr⁻¹</td>
</tr>
</tbody>
</table>

The 116,450 hr⁻¹ space velocity is the lowest figure, so it sets the value for this engine. Applying the safety factor gives the following:

Effective GHSV = 116,450 x (100%-15%) = 98,983 hr⁻¹

Therefore the catalyst volume would be:

$$ Volume = \frac{2,293 \text{ ft}^3}{\text{min} \times 60 \text{ min/hr} \times 98,983 \text{ hr}^{-1}} = 1.39 \text{ ft}^3 $$

For a single 3.5" thick element, a 29.6" diameter provides this volume, but because this is not a typical standard size, a 30.25" diameter x 3.5" element should be selected. Verification that the selected size and cell pattern does not exceed the available backpressure limitation is the final step in the process. If it does, then the process is repeated for a more open cell pattern and/or combination of cell pattern with flow depth and diameter.

For your catalyst questions, contact:

John W. Robinson Jr., V.P. Catalyst Group
jrobinson@catalyticcombustion.com
715-568-2882 Ext. 127 • Fax: 715-568-2884

www.CatalyticCombustion.com

IN THE NEXT ISSUE ... When is Hot too Hot?
Because a catalytic substance is not consumed by the chemical reaction in which it participates, a catalyst would never need replacing in a perfect world. In our world, however, ignition failures, backfires, coolant leaks, oil blow-by, load shifts and ricocheting turbo parts happen and they cause damage that afflicts the lifespan of the catalyst. Let’s now turn to how these events work on the catalyst.

Recall that the surface area of the washcoat is key to providing the locations where the precious metals are deposited so anything that reduces that surface area will decay the catalyst’s performance. When a catalyst is overheated, the crystal structure of the aluminum oxide in the washcoat changes from one that has a high surface area to one that is low in surface area.

Under normal operating conditions, the washcoat gradually undergoes this shift in crystal forms. This is called thermal aging, and several years can pass before enough surface area is lost for the catalyst to fall short of its operating targets. However, high temperature excursions can rapidly alter this timeline.

When the temperature on the catalyst’s surface approaches 1,400°F, even the best efforts at stabilizing the high surface area form of aluminum oxide in the washcoat fail. At this temperature, the life of a catalyst is shortened to a few hours, and the higher the excursion, the shorter the excursion time can be. Above 1,500°F, the surface area of the washcoat is ruined in seconds. Every time the temperature exceeds the maximum figure set by the catalyst manufacturer, it damages the catalyst. This damage is cumulative and irreversible.

How could this happen? Imagine what happens when a single cylinder misfires. The unburned air/fuel mixture is pushed into the exhaust and moves toward the catalyst. Once there, some of the fuel is converted by the catalyst and a little extra heat is liberated as a result of the reaction. If this happens once in a while, the slight increase in the temperature of the catalyst does little harm. But, what if it’s a dead hole or if there are more than one cylinder involved? Then you get into a situation where the extra heat drives the temperature of the catalyst beyond its limitations.

“But we have a high temperature shutdown system,” you say. True, but bear in mind that the materials of the converter housing will absorb some of the energy so that the exhaust gas temperature will lag behind the temperature on the catalyst’s surface. Location of the outlet thermocouple can further complicate the situation if it is located more than a scant few inches away from the outlet face of the element or if it is not situated into the exhaust flow.

If the increase is gradual, then the shutdown system has a good chance of catching it. On the other hand, if there is a sudden increase in fuel hitting the catalyst, the damage will be done before the system can respond. A catalyst housing that is glowing cherry red is a clear sign that something is badly wrong.

Preventing this from happening to your catalyst is achieved through minimizing misfires, keeping your shutdown system in good working order, locating the thermocouples as close to the outlet face of the catalyst as practical, and by routine checks to verify that the thermocouples are operating properly.

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jrobinson@catalyticcombustion.com
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www.CatalyticCombustion.com

IN THE NEXT ISSUE … Poisons and Masking Agents
Poisons and masking agents impede the catalyst's ability to perform the chemical conversion of the pollutant molecules from harmful forms into less harmful forms. However, the way they interfere is different, as is the remedy that you have to use when they are encountered.

**Poisons and Activity Inhibitors**

A catalyst poison is a substance that chemically reacts with either the precious metals or the compounds in the washcoat, and in doing so, fundamentally alters the catalyst. Inhibitors reduce the ability of the precious metal site to participate in the desired chemical reaction.

Heavy metals, such as lead, tin, zinc, iron or mercury, etc., can affect the catalyst by forming alloys with the precious metals or by being deposited next to the active precious metal site. These precious metal sites then become either completely inactive or have significantly reduced activity.

Silicones, organic phosphorus compounds and sulfur interact with the washcoat to degrade the performance of the catalyst. They do so by chemically reacting with compounds in the washcoat, such as the aluminum oxide. These reactions cause a physical change in the crystalline structure of the washcoat that can encapsulate the precious metal site or form a glass-like barrier. In either case, the precious metal can no longer be reached by the pollutants needing to be converted.

Catalysts have the ability to tolerate some poisoning. However, it is limited, and the performance of the catalyst can degrade extremely rapidly depending upon which poisons are present and their concentration in the exhaust stream.

**Masking**

Masking differs from poisoning in that it is solely a physical blockage of the active site rather than a chemical interaction. Masking agents are non-combustible materials, such as ash, dirt, corrosion debris from the exhaust piping or acoustical fiber matter from a high attenuation grade silencer installed before the catalyst. Masking agents tend to accumulate gradually so the performance of the catalyst will slowly degrade compared to what you see in a poisoning situation.

Masking agents reach the catalyst as particulate materials that, depending upon their size, can be deposited in the pores of the washcoat, fill the cells of the substrate or become trapped against the inlet face of the catalyst. Blockages result in an increase in the linear velocity of the exhaust through the remaining open cells, which increases the pressure drop across the catalyst. Monitoring the differential pressure of the element is the easiest method of detecting a masking situation. For this measurement to be useful, the engine needs to be operating under the same conditions that were used to determine the initial pressure drop of the new catalyst element.

**Realities and Remedies**

When the EPA mandated catalytic converters for automobiles, it signaled the end of leaded gasoline because of its poisoning potential. Unfortunately, unlike the auto industry, industrial engines’ users cannot completely eliminate poisons and masking agents from the exhaust stream. Field gas can contain sulfur and lube oil, and engine coolants are formulated with known catalyst poisons. These include the anti-wear compounds in the oil, which contains zinc and phosphorus, while coolants have silicones. And while a catalyst manufacturer would want them totally eliminated, they cannot because of the vital role they play in these fluids doing their jobs.

Your role in limiting the affect of poisons and masking agents on the catalyst means following the recommendations for use of low ashing lube oils with the minimum amount of anti-wear compounds possible. It also means maintaining and operating the engine to minimize oil consumption and coolant leaks. Should you suspect a poisoning or masking condition is happening, it may be possible to prevent complete loss of the catalyst element if action is taken quickly. Contact your catalyst supplier to get their input on the situation.

It may be possible to recover a catalyst that has been affected by poisons or masking agents, and that topic will be covered in more detail in a later issue of this series.

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A Handbook for the User

Part 11 – Bypass Leakage

Compliance with engine emission rules will be difficult, if not impossible, if exhaust doesn’t come in contact with the catalyst. Bypass leakage of exhaust gasses render the catalyst incapable of converting enough pollutants to do the job, regardless of whose elements and housings are used.

How Leakage Affects the Performance of the Catalyst

Simply put, a bypass leak occurs when exhaust can flow through a pathway where no catalytic coating exists, or where the size of the opening is larger than that of the substrate’s cell pattern. When such a pathway is created by failure of a gasket, thermal expansion opening up a gap in the housing or a void forming in the substrate, among others, the upstream pressure of the exhaust will force flow through the bypass because it offers a lower resistance to the flow than does the catalyst element.

The portion of the exhaust that will flow through the bypass will increase until its pressure drop comes into balance with the portion of flow that is still passing through the cells of the catalyst. So as the size of the bypass pathways increases, you can reach a point where little or no exhaust is passing through the cells of the catalyst.

Normally the concentration of pollutants found after the catalyst is what was un-reacted by the catalyst. With a bypass, the concentration after the catalyst is a blend of the low concentration flow mixing with the high concentration bypass flow. The magnitude of the final concentration is dependent upon the initial concentration from the engine, the efficiency of the catalyst and the amount of leakage flow from all the pathways.

The graph in Figure 1 is an example of how little leakage it takes to dramatically affect the post catalyst concentration. In this example, missing just about 25% of the 1/8” gasketing around the element would result in enough bypass flow to fail a 1 g/bhp-hr permit level.

It is absolutely certain that as operating permits become tighter and tighter, the less bypass leakage that can be tolerated.

How to Limit Leakage

Limiting leakage is a relatively straightforward process. Use a gasket on the catalyst element in housing or combo units designed for one, and make sure it is the correct width and thickness. Never reuse an old gasket; it will be too rigid to conform to fill the gap between the sealing surfaces.

Inspect the catalyst sealing surfaces of the housing for warping, cracks or gouges that the gasketing cannot fill. Clean out any debris in the area where the catalyst sits. Repair or replace housings where the catalyst element cannot be sealed properly.

Check the catalyst element for loose foil that opens a void between layers. Look for gaps between the substrate and the inner surface of an outer band. Also make sure the element is still flat across its face and has its original round or square shape. Temporary fixes by adding gasketing or metal pieces to cover gaps might work for a while, but may not stop all the leakage. Big holes or missing foil simply require catalyst replacement.

Pay attention to performance. If a drastic change in the catalyst’s normal pressure drop is unexplainable, then the catalyst needs to be inspected as soon as possible. When an element’s performance changes suddenly or a new element just can’t seem to be dialed in, review the data with your catalyst supplier for expert assistance.

In the end, as the regulations continue to tighten up, all the effort to qualify and select a catalyst and housing for your engine will come to nothing if bypass leakage is occurring.

For your catalyst questions, contact:
John W. Robinson Jr., V.P. Catalyst Group • 715-568-2882 Ext. 127 • Fax: 715-568-2884 • jrobinson@catalyticcombustion.com

www.CatalyticCombustion.com  IN THE NEXT ISSUE ...It’s Washing Day
Over time, every catalyst will accumulate ash and other non-combustible debris in its cells and on its face, blocking the flow of exhaust. This decreases the overall performance of the catalyst and requires that the element be removed and cleaned or replaced with a new catalyst. Washing can offer a cost effective alternative to replacement if it is done correctly and if the limitations of the process are kept in mind.

Washing – The Right Way
Proper technique for catalyst washing uses a multi-step process to remove both non-combustible and organic debris from the catalyst. Because chemical solutions are used in the process, sending the element to a company that has the proper equipment, safety gear and know-how to handle and correctly dispose of used solutions will be easier than doing it yourself.

The initial step is to mechanically remove as much ash as possible using a vacuum or low pressure, oil-free compressed air. The element is then immersed and allowed to soak in a solution of de-ionized (DI) water and a base, typically sodium hydroxide at 3-10 weight %. This solution removes carbon soot and other lube oil or fuel derived organic deposits. The solution should be kept agitated so that flow through the cells is achieved. After soaking for 2-4 hours, the catalyst is removed and then thoroughly rinsed with DI water until the pH of the rinse solution is less than 8.

Next, the catalyst is soaked for 2-4 hours in an acidic solution (acetic acid sometimes along with oxalic acid), again at a 3-10 weight % level. This solution removes inorganic materials, such as rust and non-combustible dirt. After soaking, the element is then rinsed with DI water until the pH of the rinse water is between 5-7.

Finally, it is critical that the element be dry before being reinstalled in the housing. Oven drying is preferred, but if not possible, place the element in front of a fan and let air blow through the cells for 24-48 hours. When the element is dry, it should weigh less than it did before the washing process started. If not, it is still wet and needs further drying.

Washing – The Wrong Way
Do not take your catalyst to the local carwash and blast away at it. The pressure of the water from the wand can bend the foil over and permanently block cells and has enough force to strip the coating from the foil. The detergent may contain phosphorus, a severe catalyst poison, as well as chlorine and fluorine found in most municipal water supplies. Also, any dissolved solids in the water will be deposited into the washcoat where they will simply take the place of the exhaust debris you are trying to remove.

Putting a wet element back into the housing is a recipe for disaster. As the exhaust heats up the catalyst, the water in the pore structure of the washcoat will turn to steam where it tries to expand its volume by over 1,000 times. This creates tremendous pressure inside the pores and so the washcoat fractures. The now broken washcoat is blown out by the exhaust flow, and you are left with a dead catalyst.

Washing – The Limitations
Washing cannot restore the activity of a catalyst that has been poisoned, overheated or has been ignored for so long that the debris is packed too tightly into the washcoats’ pores to be removed. A general rule of thumb is that washing will bring a catalyst back to 95% of its original activity level the first time it is washed and less for each subsequent washing. Unfortunately, you cannot look at a cleaned element and tell if it will pass when reinstalled, and until recently, there has not been a good method of evaluating the activity level of these large engine catalysts, so you have had to rely on the “try it and see” approach. In the near future, you will see the introduction of a technique for determining whether an element is a candidate for washing or after washing if it responded well enough to warrant re-installation.

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John W. Robinson Jr., V.P. Catalyst Group • 715-568-2882 Ext. 127 • Fax: 715-568-2884 • jrobinson@catalyticcombustion.com

www.CatalyticCombustion.com

IN THE NEXT ISSUE...Rules of the Road
Looking Back

A common question is, “Why do we have to control the emissions from our engines?” The answer lies in the history of the environmental movement and public outcry over pollution that culminated in the creation of the EPA in 1970 by Congress at the request of President Nixon. Despite the noise coming from both sides of the political debate, EPA’s mission is best summarized by this excerpt from the memo that recommended its formation to the president:

The enormous future needs for land, minerals, and energy require that the protection of our environment receive a powerful new impetus. In this, the nation will be on the “horns of a dilemma.” The economic progress which we have come to expect, or even demand, has almost invariably been at some cost to the environment.

Pesticides have increased the yield of our crops and made it possible for less land to produce more food. They have also polluted the streams and lakes. Automobiles have broadened our economic and social opportunities, even as they have dirtied the air and jammed our highways. Some means must be found by which our economic and social aspirations are balanced against the finite capacity of the environment to absorb society’s wastes.

Where We Are Today

Over the intervening years, EPA, in conjunction with the states and sometimes even smaller local administrative districts, have enacted rules aiming to reduce the emissions of pollutants that have demonstrated human health or other adverse environmental effects. Currently the sections of the Code of Federal Register (CFR) known as Quad J (40 CFR Part 60, Subpart JJJJ) and Quad Z (40 CFR Part 63, Subpart ZZZZ) set the maximum amounts that can be emitted from an engine.

The Quad J rules cover what are called Criteria Pollutants: NOx, CO and VOCs. The limits on engine emissions are determined based on the engines combustion type (rich or lean burn), horsepower, date of manufacture, fuel source and operating hours. Quad Z regulations derive from the Clean Air Acts requirement to control the emissions of Hazardous Air Pollutants (HAPs), such as formaldehyde, which are known or suspected to be carcinogens.

Likewise the Quad Z regulations have different emission limits depending upon the engines combustion type and horsepower, but additionally have different limits depending upon whether the site where the engine is located is classified as a Major Source of HAPs or an Area Source. A Major Source is defined as a location that has the potential to emit more than 10 tons/year of any single HAP or more than 25 tons/year of any combination of HAPs.

In order to address ozone levels that contribute to smog formation, certain states and other local administrative districts have enacted even stricter regulations. Southern California and the corridor from Dallas-Fort Worth (DFW) to Houston are two examples of this. For instance, while the Quad J limit for NOx emissions on a new rich burn engine is 1 g/bhp-hr, in the DFW region is 0.5 g/bhp-hr. For spark ignited, 4 stroke, Lean Burn engines located at a Major Source, EPA has given you the choice of demonstrating control of CO instead of formaldehyde. However, your state may have requirements to control formaldehyde to higher levels than required for CO.

It is up to you to stay informed with what your emissions limits are and how frequently you need to test your emissions to demonstrate compliance.

What Will Happen Tomorrow

The societal discussion or argument, rather, on the merits of pollution control vs. economic growth will continue. Overall, the trend in emissions limits since the 1970s has been for continual tightening of regulations no matter which party is in power in Washington. It is likely that this trend will continue and that everyone involved with industrial engines will have to keep working to meet the challenges that will come.
Ashing of a catalyst is an inescapable problem with industrial engines. However, certain choices pertaining to the catalyst can significantly influence the overall performance of the engine/catalyst system. Let's draw on what we've discussed in earlier parts of this series to see what they are.

**What is Ash?**

The particles that make up what we call ash are an agglomeration of the non-combustible portions of lube oil, wear metals from the engine, dirt that makes it through the intake air filters, and condensable hydrocarbon residue from lube oil and fuel gas. The amount of ash generated depends upon several variables, including the engine make and model, operating load, general health of the engine and the ash content of the lube oil. Studies have determined that a range of particle sizes is produced, but the mean size is approximately 35 nanometers and the concentration of particles can hit figures as high as 10 million particles per cubic centimeter in the exhaust flow. Ash particles are not neat spheres, but are an endless variety of jagged shapes.

**Cell Density**

Thankfully, not every particle that comes from the engine ends up being trapped by the catalyst. Otherwise, the effective lifespan would be very short indeed. The mechanism of cell plugging is complicated, and while it may seem intuitive that a higher cell density catalyst would plug faster, it may not and depends upon your specific situation. The time it takes different cell densities to reach a certain increase in pressure drop, compared to the elements' initial reading, is the information you will need to make this decision.

**Precious Metal Content**

Recall that precious metals are deposited along the length of the cell as discrete crystal sites. A catalyst with a lower level of precious metals will have fewer crystal sites available to facilitate the chemical reactions. A catalyst with a reduced precious metals content compared to another catalyst may well indeed have sufficient sites for the initial performance requirements when installed.

Now recall that the space velocity for a catalyst is the ratio of the flow rate to the available volume of catalyst and is selected to achieve the required conversion efficiency needed for the engine to be in compliance. As ashing plugs cells, the available volume decreases, so the space velocity has to increase in the remaining open cells. This leads to a gradual degradation in the effectiveness of the catalyst because time is insufficient for the pollutants to diffuse to the surface of the catalyst before the flow carries them out of the element.

However, you are hit with a double whammy when the catalyst has a reduced precious metals loading and becomes ashed up. Comparing catalysts with different levels of precious metals will reveal that the degree of performance degradation accelerates with reductions in the level of precious metals. Why? With fewer crystal sites available, as the space velocity in the remaining cells increases, you end up reducing the likelihood of a pollutant coming in contact with a site and being chemically converted. The graph seen here clearly illustrates the effect of precious metals content on the loss of performance as the percentage of the catalysts blocked by ash increases.

A lower precious metal loaded catalyst will offer an initial cost savings to you. Depending upon the engine's ashing characteristics, in the end it may cost you more when you factor in maintenance costs coupled with lost production from that engine. It is up to you to determine if the cost/benefit analysis works in your favor.

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John W. Robinson Jr., V.P. Catalyst Group • 715-568-2882 Ext. 127 • Fax: 715-568-2884 • jrobinson@catalyticcombustion.com

www.CatalyticCombustion.com

IN THE NEXT ISSUE...Oxygen: The Balancing Act
The common factor in the chemical reactions that a catalyst facilitates is the transfer of oxygen between molecules. Oxygen is either removed from or added to the pollutant molecules to form the more desirable exhaust components. This function is influenced by the total amount of oxygen present in the system, so keeping the right amount of oxygen present is vital to ensure the 3-Way catalyst can do its job in controlling the emissions from rich burn engines.

In-Cylinder Fuel Combustion Reactions

Figure 1 shows the change in an engine’s raw emissions as they relate to the air-to-fuel or Lambda setting. When run very rich to maximize horsepower, the raw exhaust contains much more CO than NOx. High CO levels are due to there not being enough oxygen to burn the fuel all the way to CO₂. At low Lambda settings the relatively cool in-cylinder temperatures combined with the low oxygen availability limits the amount of NOx formed.

Conversely, as the engine is leaned to improve fuel economy, more NOx is produced than CO. With more oxygen available, and the higher in-cylinder temperatures, less CO is produced, but more NOx is formed. This trend continues until the engine becomes lean enough that the additional air intake begins to cool the combustion temperature and NOx production decreases.

Catalyst Considerations

Figure 2 incorporates the conversion efficiency of a 3-Way catalyst, further illustrating how the balance of oxygen affects catalyst performance. When operating very rich, the NOx conversion is very high, but the CO conversion is non-existent to poor. That’s because the catalyst takes any remaining free oxygen in the exhaust, and the oxygen out of the NOx molecule, to use in the conversion of CO to CO₂ (and VOCs as well). However, the system is in total oxygen deficient, so the catalyst will show great performance on NOx, but poor performance on CO.

As Lambda increases, the situation improves. With more oxygen available, the CO conversion gets better as the NOx conversion remains high. But notice what happens just over Lambda = 0.99, the point of maximum catalyst effectiveness. Further leaning of the engine causes the NOx conversion to fall sharply due to the change from being oxygen deficient to having excessive oxygen. The portion of the catalyst's make-up that extracts and holds the oxygen for the reaction with CO and VOCs is highly effective at grabbing oxygen wherever it can. But as more free oxygen becomes available in the exhaust it will take the free oxygen from the exhaust rather than extract it from the NOx. So, as the system becomes leaner than the maximum conversion point, the NOx performance degrades rapidly.

These examples reveal how a 3-Way catalyst's high performance level is greatly dependent upon optimal oxygen balances. Your Air/Fuel Ratio controller and O₂ sensors are responsible for this critical role, so making sure that they are robust and properly adjusted is vital to keeping in compliance.
UNDERSTANDING CATALYSTS
A Handbook for the User

Part 16 - The Cell Density Games

Facilitating intimate contact between the surface of the catalyst and the pollutants needing to be converted is key in producing an effective catalyst. The structure of the element’s cells is how this is controlled and optimized for maximum performance.

Flow in the Cells
When exhaust gas enters a cell, a flow profile develops where the velocity is faster in the center of the cell and slower toward the walls. Friction with the walls of the cell forms a nearly stagnant boundary layer just over the surface of the wall. As illustrated in Figure 1, pollutant molecules have to diffuse through this boundary layer to reach the precious metal sites. In a properly designed catalyst, the amount of time it takes for diffusion to occur is the controlling step in the reaction pathway. Thus minimizing the thickness of the layer helps improve performance.

The science of fluid mechanics teaches that turbulent flow produces the smallest boundary layers. Techniques for keeping flow turbulent include cells with zigzag patterns, fins or protrusions into the cell path or by simply making the cells smaller by increasing the cell density. These techniques introduce disruptions that either re-mix the gas flow or otherwise keep the velocity of the gas through the cells high enough to remain turbulent for more of the depth of the element.

Performance Evaluations
Another aspect of changing a pattern’s cell density is that higher cell densities have more square inches of surface area per cubic inch of substrate volume. More surface area translates into a wider distribution of the precious metals, which yields more discrete sites for the chemical reaction. This means that for two elements of the same size, the one that has either the higher cell density or turbulence inducing geometry at the same cell density will have better conversion efficiency.

When sizing a catalyst, it is desirable to use the smallest catalyst practical that can exceed performance requirements. However, the techniques used to keep flow turbulent expend more of the exhaust gas’ momentum as it passes through the cell, resulting in a higher pressure drop. The engineer calculates the catalyst size required to meet the performance limits for a given combination of cell pattern/density and then evaluates the pressure drop for that selection. In doing so, a balance is struck between the engine’s available backpressure limit vs. the pressure drop across the catalyst, silencer and the rest of the exhaust piping. The process is repeated for other cell patterns and cell densities to find the optimum combination.

Sometimes the calculations show that for a given catalyst size and cell density, not all the pollutants would reach the required conversion efficiency. When this happens, the engineer will hold the catalyst size constant and increase the cell density until all the conversion efficiencies are achieved.

Performance Gains
A situation may arise where either an existing unit has to achieve lower emissions, or a package needs to be moved into an area with tighter emission limits than it can achieve with its existing catalyst housing. Rather than immediately conclude that a new larger housing is needed, instead consider if an increase in cell density will solve the problem. The graph in Figure 2 shows the changes in performance as a function of the cell density alone. Of course, the additional pressure drop that the change will bring also needs to be evaluated to confirm that the engine has the backpressure capacity to spare. This may not work for all instances, but when it does, changing out just the catalyst elements is certainly preferable to upsizing the housing or combo unit.

For your catalyst questions, contact:
John W. Robinson Jr, V.P. Catalyst Group  •  715-568-2882 Ext. 127  •  Fax: 715-568-2884  •  jrobinson@catalyticcombustion.com

www.CatalyticCombustion.com

IN THE NEXT ISSUE ... The Great Detective
Determining the cause when a catalyst’s performance declines rapidly is a necessary step for keeping subsequent catalysts operating as they should. The detective work involves attention to details and a methodical application of analytical techniques to identify the source of the problem.

**Phase 1**
Upon realizing that a catalyst’s performance has changed, it is vital to investigate the running condition of the engine to ensure that the exhaust flowing to the catalyst corresponds to the conditions for which the catalyst was sized. Are the amounts of pollutants in the raw exhaust correct for the engine? Is the oxygen content correct, and is the temperature at the catalyst’s inlet at or above the minimum set point?

You will want to verify that there isn’t a leak in the exhaust piping ahead of the catalyst that can draw in oxygen downstream of the oxygen sensor. Also, look over the exterior of the housing to see if it has become warped and allowed a bypass between the element and the housing to open.

Review the engine’s logs for unusual consumption rates for lube oil or coolant. Check for notations indicating spark plug or other ignition failures. Examine the recent load rate on the engine, paying attention to any notations on shutdowns due to high catalyst exit temperatures or back pressures.

The goal of the Phase 1 examination process is to identify any obvious items that would compromise the catalyst. An imbalance between the NOx and CO levels or the incorrect oxygen content can prevent a 3-way catalyst from functioning properly. Excessive lube oil or coolant use can deposit masking agents or poisons that cripple the catalyst. A sudden drop in the catalyst’s backpressure suggests that a bypass has opened.

After examining the system and repairing or replacing plugs and sensors as needed, it’s then necessary to recheck the performance of the catalyst. Now is the time to make adjustments to the engine while it is running to see what effect they have on the catalyst. Be sure to document the changes made and what the operating conditions are for the engine. Most importantly, determine the pre- and post-catalyst readings for each adjustment using a portable analyzer. Getting a pre-catalyst reading is critical information for the catalyst supplier to know how the catalyst is performing. Review your findings with your catalyst supplier for troubleshooting.

**Phase 2**
Now is the time to open the housing to look for bypasses in the gasketing and determine if the element is loose inside. Make note if the element has telescoped or warped. When an element telescopes, a significant portion of the coating breaks loose and blows away. Look at the outlet side of the element for indications that the foil has been too hot. Cells that looked like they’ve drooped, or foil that is brittle and breaks off easily, are telltale signs of too much heat.

Remove the element and inspect its inlet face for ash buildup, and whether the ash is loose or has been driven hard into the cells. Is there a frosting-like layer built up on the face of the element? If so, cell blockage changes the effective space velocity of the catalyst and results in a poorer performance.

Does the foil seem loose, and are there any holes either in the field of the element or between the element and its outer band? These can be problematic when the element is hot, as thermal expansion of the foil can open up bypasses in loose areas and in gaps between the element and the band.

At this point in your detective process, if no obvious cause such as a coolant leak, set-point drift, substrate failure, etc., has been identified as responsible for the performance degradation, arrange to send the catalyst to your catalyst supplier for them to conduct an analysis of the catalyst coating.

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John W. Robinson Jr., V.P. Catalyst Group • 715-568-2882 Ext. 127 • Fax: 715-568-2884 • jrobinson@catalyticcombustion.com

www.CatalyticCombustion.com

**IN THE NEXT ISSUE ...The Great Detective, Part 2**
When a catalyst returns from the field because of a performance issue, the manufacturer has several items to investigate to identify a probable cause. How each manufacturer handles the task will vary, but here is one approach.

**Inspection**
Using the serial number for the element, the documents generated during the manufacturing process are retrieved and used as a reference to re-verify that the element was produced in accordance with the manufacturing specifications. The weight of the element is compared to the recorded weight to determine either how much ash has accumulated, or to see if there has been a loss of coating should the element be clean. A visual inspection will reveal signs of foil degradation due to gross overheating or damage caused by debris hitting the catalyst’s face.

**Coating Evaluation**
Portions of the foil are removed and examined under a microscope to reveal if the adhesion of the washcoat to the foil has failed, resulting in a loss of the coating. If bare foil is seen, then an assessment of the percentage loss is made, which is used to determine if it is sufficient to explain the field performance.

When overheating is suspected, a representative sample of the coating is removed, and a surface area analysis is conducted. The porosity of the washcoat does decrease over time during normal operation through a process called thermal aging. Operating a catalyst at temperatures in excess of the manufacturer's maximum limit accelerates the process dramatically, resulting in the precious metal sites becoming isolated from the exhaust flow. The test for surface area is called a BET analysis, named after the three inventors of the technique – Stephen Brunauer, Paul Emmett and Edward Teller. The technique itself measures the amount of a gas, commonly nitrogen, that is adsorbed by a solid. The amount adsorbed at a given pressure is related to the total surface area of the material. Washcoats often have surface area values in the range of 100-150 m²/gram of material or higher when new and 50-80 m²/gram at the end of their useful lives. A BET reading of less than this is a prime indicator that the catalyst was exposed to excessive temperatures.

When contamination of the coating is suspected, several techniques are available to identify it. A chemical analysis of the coating will reveal what chemical elements have been deposited on the catalyst. A sample of the washcoat can be removed from the foil, dissolved in acid and introduced to an Inductively Coupled Plasma (ICP) instrument that vaporizes the sample in an electric plasma and then detects the resulting ions of the individual chemical elements with a mass spectrometer. ICP analysis can detect very low levels of contamination but is susceptible to the presence of certain ions interfering with the detection of others.

Various X-ray techniques are available that not only can identify the individual chemical elements, but also can determine crystal structure and chemical properties of the coating. These techniques involve bombarding a section of the foil with X-rays and then collecting and analyzing either the reflected X-rays or other resulting emissions from the chemical elements caused by the bombardment. Detection levels by the X-ray techniques are not as low as ICP, but the preparation of the sample is easier.

The goal of the chemical analysis is to identify chemical elements that are not supposed to be on the catalyst and whether the quantities present are in excess of what is tolerable by the catalyst. Each manufacturer will have established the limits of permissible contamination and can be found in their warranty statements.

Unfortunately, elemental analysis is not like an episode of CSI or Star Trek where the results are perfectly clear in a just a few minutes. Careful evaluation and interpretation of the data is needed to draw the correct conclusions in order to identify potential sources of the contamination so corrective actions can be taken to protect the catalyst in the future.

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John W. Robinson Jr., V.P. Catalyst Group • 715-568-2882 Ext. 127 • Fax: 715-568-2884 • jrobinson@catalyticcombustion.com

www.CatalyticCombustion.com

IN THE NEXT ISSUE ...The Great Detective, Part 3
The ultimate evaluation of a field catalyst is to compare its ability to convert a reference compound under controlled, repeatable conditions to what it did when it was new. This is called an activity test. The changes between the new and used results can be very helpful in evaluating a field problem.

Traditional Test Method
The heart of a proper activity test lies in its ability to repeatably re-create the combination of flow rate, temperature and concentration so the catalyst can be evaluated under the same conditions every time. A test sample of the catalyst is removed from the element by cutting out a core using a hollow coring bit. The most common size extracted is a 1-inch diameter core that is the full flow depth of the element. It is extremely important during the coring process for the integrity of the core and its coating be maintained. The sample is then placed into a holder and installed into a reactor chamber for the test.

The laboratory reactor system precisely regulates the temperature of the sample. The flow to the sample can be either air that is passed through a series of filters to remove ambient background contamination or a completely synthetic mixture made up from cylinders of gas. The latter permits the creation of any combination of constituents, which can be very useful but is expensive to do. The test compound that will be reacted is metered into, and allowed to become well mixed with, the flow. Flow data is gathered and routed to the appropriate instruments, such as flame ionization detectors or gas chromatograph/mass spectrometers, to detect the compound at the concentrations expected.

The activity test itself can be configured in a number of different ways, and each manufacturer has its own philosophy regarding what conditions to use. However, it is usual for the conditions to be more challenging than what the catalyst is expected to see in service so that any degradation is readily apparent. This may take the form in a combination of a higher space velocity and lower temperature setting, or by using a difficult-to-convert compound. Sometimes a sweep across a range of temperature settings or space velocities is used, while at other times performance at a single point setting is sufficient.

Data Interpretation
The data is evaluated after test completion to see what it reveals. For instance, the sample catalyst’s conversion efficiency vs. temperature graph can be compared to that of a new catalyst. Characteristic changes in the shape of the curve due to masking, poisoning or overheating can be interpreted from these plots. The temperatures at which the sample achieved specific levels of conversion for a constant space velocity (i.e. 50%, 90% or 95%) are determined and compared with new catalyst figures to assess the degree of performance degradation.

Drawbacks and Pitfalls
The most obvious drawback of core sampling is that a piece of the element has to be extracted for the test, leaving a hole that has to be filled or covered to prevent leakage. Depending upon the size of the element, the hole can represent a significant portion of the overall catalyst volume. The vibration that occurs during the coring process can break loose the portion of the coating that fills in the corners of the cells. Additionally, the layers of foil in elements that are not brazed or welded together can shift relative to each other, which also can cause a loss of the coating. Any loss of coating will invalidate the test.

Testing of the entire element as a whole has not been practical, given the wide range of element sizes and configurations would require a test system that could generate an infinite matrix of flow and temperature conditions.

Activity tests for catalysts are routine for many industries, but for the reasons listed above, they have not been the routine for industrial engine catalysts. A new development in activity testing has the potential to change that situation, and it will be the final chapter in our detective story.