“Designing CO Oxidation Catalyst for Your Permit Requirement”

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Starting Point: Application Design
(system variables that affect emissions)

- **Information input**
  - engine name and model
  - fuel type(s) and sulfur content
  - water injected or evap cooling? (water quality)
  - HRSG or simple cycle (no. starts/stops/yr.)
  - Duct firing? Fuel type.
  - exhaust mass flow rate, catalyst operating temp,
  - % flow and temperature variation
  - Inlet emissions, (CO, VOC, NO/NO$_2$, SO$_2$)
  - performance requirements
    - (% reduction CO, VOC, NO-NO$_2$, SO$_2$-SO$_3$)
    - Start-up & shutdown performance included?
  - desired warranty period and service life
  - installation information;
    - NEW or REPLACEMENT
    - Gas Path Size
    - allowable pressure drop

It’s possible to “over specify”:
- low temperature
- very high performance
- very low pressure drop
- small gas path
- lot’s of starts & stops
- long warranty period
- “cheap”
Catalyst Design
(catalyst variables that affect emissions)

• substrate cell geometry and geometric surface area
• wash coat formulation & loading
• precious metal formulation
• precious metal loading
• method of applying precious metals
• gas hourly space velocity
Oxidation Catalyst Performance
Discrete Cell vs. Tortuous Path

Identical wash coats and precious metals were applied to both substrates.

Performance of discrete cell substrate geometry equal to or better than tortuous path.
Oxidation Performance for CO & VOC Families

At 700°F and a given cell density and formulation

- CO
- Formaldehyde
- Toluene
- Propane

Gas Hourly Space Velocity

Catalyst Performance Efficiency (%)
Low Catalyst Temps Impose Other Risks to Owner

• **BEWARE**: Below 600°F a number of contaminants are prone to accumulation
  – Even common masking agents (sulfur) could be problematic
  – If mixed with high temp cases, desorption is possible

• Of >240 installations the few that experienced high levels of contamination
  – All below 600°F
  – All accumulated enormous amounts of sulfur and phosphorous
Examples of Chemical Contamination

- ash & carbon nanoparticles
- sulfur masking
- Pt alloy formed with contaminant
- wash coat
- oxidized foil
- platinum

THE POWER OF CATALYSIS
## Selecting Precious Metals for Oxidation Catalyst

<table>
<thead>
<tr>
<th></th>
<th><strong>Platinum</strong></th>
<th><strong>Palladium</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO</strong></td>
<td>Best</td>
<td>Good when new</td>
</tr>
<tr>
<td><strong>VOCs</strong></td>
<td>Best</td>
<td>Good when new</td>
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<tr>
<td><strong>Light-off temp</strong></td>
<td>250-400°F</td>
<td>400-650°F</td>
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<tr>
<td><strong>Catalytic activity</strong></td>
<td>High</td>
<td>Moderate</td>
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<tr>
<td><strong>Thermal stability</strong></td>
<td>Good to 1200°F</td>
<td>Good to 1200°F</td>
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<tr>
<td><strong>Poison resistance</strong></td>
<td>High</td>
<td>Low</td>
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<tr>
<td><strong>Response to chemical washing</strong></td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td><strong>Durability</strong></td>
<td>High</td>
<td>Low to moderate</td>
</tr>
<tr>
<td><strong>Price per troy oz.</strong></td>
<td>$1560</td>
<td>$690</td>
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</table>
Oxidation Performance
Platinum vs. Palladium

Performance for a given GHSV, cell density and total PGM loading

Start-up emissions

Catalyst Operating Temp (F)
Performance as a Function of Precious Metal Loading

At a given temp, GHSV and cell density

more durable

more economical
Simultaneous Collateral Reactions

- **NO-NO$_2$ Oxidation**
  - Favors NO$_2$ at low temps; NO at high temps
  - Effects SCR reactions, NH$_3$ consumption
  - Destroys sulfur bound carbon nanoparticles

- **SO$_2$-SO$_3$ Oxidation**
  - Increases with temperature
  - Precursor to particulate matter
  - Ammonia slip reacts to form bi-sulfate particulate after SCR

- Catalyst formulations can suppress these
Overall Effect of Operating Temp on Catalyst Reactions

For a given GHSV, cell density & formulation

Catalyst Operating Temp (F)
Conversion Efficiency

CO DRE
VOC DRE
SO2-SO3
NO-NO2
Putting it all together…

How does HRSG temperature effect catalyst design and price?
Effect of HRSG Temperature Zone on Oxidation Catalyst Performance

• Hi CO performance
• Hi VOC performance
• Lowest catalyst volume
• Lo NO to NO₂ conversion
• Hi SO₂ to SO₃ conversion
• Lower Pt
• Lowest cost catalyst

~1000°F
Effect of HRSG Temperature Zone on Oxidation Catalyst Performance

- ~750°F
- Hi CO performance
- Good VOC performance
- Moderate catalyst volume
- Moderate NO to NO₂ conversion
- Moderate SO₂ to SO₃ conversion
- Economical Pt-loading
Effect of HRSG Temperature Zone on Oxidation Catalyst Performance

500-550°F

- Risk of sulfur accumulation with decreased life
- Increase Pt for low-T lightoff and protection from masking & poisoning
- Good CO performance
- Lo VOC performance
- Larger catalyst volume
- High NO to NO₂ conversion
- Low SO₂ to SO₃ conversion
- Highest catalyst $$$

![Diagram](image.png)
# Effect of HRSG Temperature Zone on Catalyst System Price

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<tr>
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<th>550 F</th>
<th>790 F</th>
<th>1000 F</th>
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<tr>
<td><strong>Catalyst GHSV</strong>*</td>
<td>175,000</td>
<td>200,000</td>
<td>215,000</td>
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<tr>
<td><strong>Catalyst Volume</strong></td>
<td>310 ft³</td>
<td>270 ft³</td>
<td>250 ft³</td>
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<tr>
<td></td>
<td>most catalyst due to lower activity</td>
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<td>least catalyst due to high activity</td>
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<tr>
<td><strong>Platinum Loading</strong></td>
<td>~1.5X more Pt due to likely accumulation of contaminants</td>
<td>X</td>
<td>X</td>
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| **Frame Material** | carbon steel | carbon steel | stainless steel |

* Catalyst GHSV is approximate for illustration only, based upon a given cell density and formulation.
Effect of HRSG Temperature Zone on Catalyst System Price

Catalyst and frame prices are approximate for illustration only, based upon a given exhaust characteristic, catalyst design, gas path and Pt price.
Evaluate all operating cases (temp, flow, performance)

<table>
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<tr>
<th>PARAMETER</th>
<th>Units</th>
<th>DESIGN BASIS</th>
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<th>102</th>
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<td>GT Load</td>
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<td>50%</td>
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<td>EXHAUST CHARACTERISTICS FROM GT</td>
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<td>GT Flow with Tempering Air</td>
<td>lb/hr</td>
<td>647,792</td>
<td>666,129</td>
<td>629,703</td>
<td>522,225</td>
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<td>CO as ppmvd at 15% O2</td>
<td>%</td>
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<td>CO as ppmvd at 15% O2</td>
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<td>%</td>
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<td>VOC as ppmvd at 15% O2</td>
<td>%</td>
<td>8.41</td>
<td>3.00</td>
<td>8.42</td>
<td>8.40</td>
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<td>VOC as ppmvd at 15% O2</td>
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<td>VOC Destruction Required</td>
<td>%</td>
<td>76.2</td>
<td>33.4</td>
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<td>Required Pressure Drop</td>
<td>°H2O</td>
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<td>2.0</td>
<td>2.0</td>
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<td>Expected Pressure Drop</td>
<td>°H2O</td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

DETERMINE “GHSV” FOR EACH FLOW RATE AND TEMPERATURE TO ACHIEVE REQUIRED CO & VOC PERFORMANCE
Determine “GHSV” for each flow rate & temp to achieve CO & VOC performance
Convert GHSV into catalyst volume

• GHSV varies by
  – performance level
  – compound
  – temperature
  – formulation and loading of precious metals
  – formulation of wash coating

• catalyst volume (cubic feet) calculated by dividing volumetric gas flow rate (s-ft³/hr) by GHSV (1/hr)

\[
\frac{8,593,971 \text{ scfh}}{165,000 \text{ hr}^{-1}} = 52.1 \text{ ft}^3
\]
Calculate the required catalyst volume for each case.

\[
\frac{8,593,971 \text{ scfh}}{165,000 \text{ hr}^{-1}} = 52.1 \text{ ft}^3
\]

Identify case requiring highest catalyst volume.

"Design case"
Calculate catalyst depth

IDENTIFY CASE REQUIRING HIGHEST CATALYST VOLUME

CALCULATE CATALYST DEPTH
Remember…

- Catalyst performance dictates catalyst volume
  - (for a given cell density, Pt loading, wash coat, etc)
- Once catalyst volume is determined
  - Changing duct size results in thicker or thinner catalyst (to maintain volume)
    - Large frontal area and thin vs. small area and thick
- However, 100 ft$^3$ of catalyst in 100 modules costs less than 100 ft$^3$ in 120 modules
- There is a practical *minimum* thickness
Performance Over Time

Performance

Time (years)

SAFETY FACTOR

PERFORMANCE

WARRANTY
Origin of “Safety Factor”

• Emission performance over time is a function of system variables
  – type of combustion turbine
  – start-up profiles (no. starts/stops/yr.)
  – water injection & evap cooling
  – exhaust gas temperature
  – engine fuel composition – particularly Sulfur
  – seals, leakage and bypass
  – contaminants present in engine exhaust
  – effect of engine lube oil on catalyst

• Owners don’t report data over time for every combination
Thank you from EmeraChem